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Binuclear 1,2-Diphosphacyclopentadienyl Manganese(I) Complexes: Synthesis, Structure and Magnetic Properties

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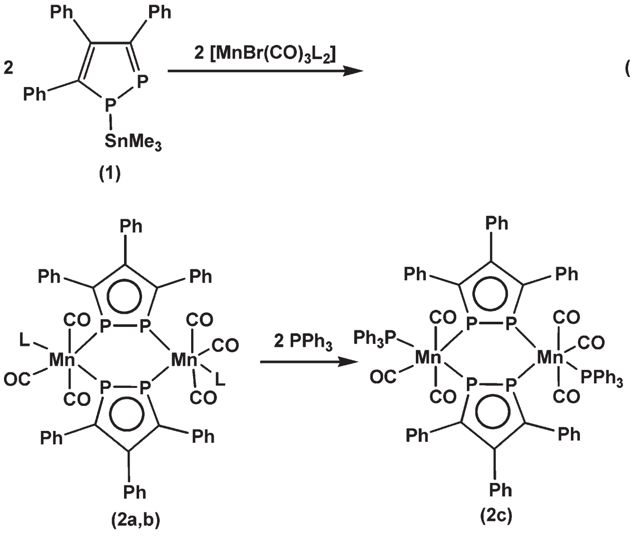
The reaction of $Mn(CO)_5Br$ with 1-trimethyltin-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene leads to formation of binuclear manganese(I) complexes with bridging 1,2-diphosphacyclopentadienyl ligands exhibiting magnetic properties apparently similar to Mn(II) compounds due to intramolecular redistribution of the electron density. Variation of peripheral ligands of binuclear complexes provides control over the magnitude of the magnetic moment, the contribution of the orbital magnetism, and the strength of the magnetic exchange.

Introduction

Electronic structure and magnetic properties of Mn-containing compounds continue to be a major research area because of the fascinating physical properties observed for these materials, such as single-molecule magnetism of multinuclear Mn complexes[1] or colossal magnetoresistance of manganese-based perovskite oxides.[2] These properties are closely related to the diversity of oxidation states and the effective magnetic exchange coupling between Mn ions provided by different short bridging ligands, such as O^{2-}, OH^-, CN^-, N_3^-, $RCOO^-$, $C_2O_4^{2-}$ and pyrazolate.[3] Surprisingly, only a few data on the magnetism of complexes containing Mn(I) ions is available, though in this oxidation state Mn is isoelectronic to Fe^{2+}, which is often found in a magnetic high-spin (HS) state. A rare example is a dimer complex of low-coordinated Mn(I) ions[4] with the open-shell configuration $4s^13d^5$, where the 4d-electrons built up a total HS state $S = 5/2$. We have supposed that a Mn(I) can be used for construction of molecular magnets by combination of Mn(I) ions with bridging ligands capable of charge transfer. In this respect the 1,2-diphospha-3,4,5-triphenylcyclopentadienide anion[5] should combine the ability to bridge metal atoms with the feasibility of charge transfer similar to pyrazolate.[6]

Results and Discussion

Complexes **2a**,**b** were prepared starting from the tin derivate **1** and Mn(I) bromide complexes (eq 1). It should be noted that formation of binuclear complexes is quite unexpected: similar reactions of the Sn derivate of 1,2,4-triphosphacyclopentadienide with $[Mn(CO)_5Br]$ resulted in 1,2,4-triphosphacymantrene only.[7]



(1)

L = CO (2a), MeCN (2b)

Acetonitrile ligands in **2b** can be further easily replaced by PPh_3 to form **2c** (eq 1).

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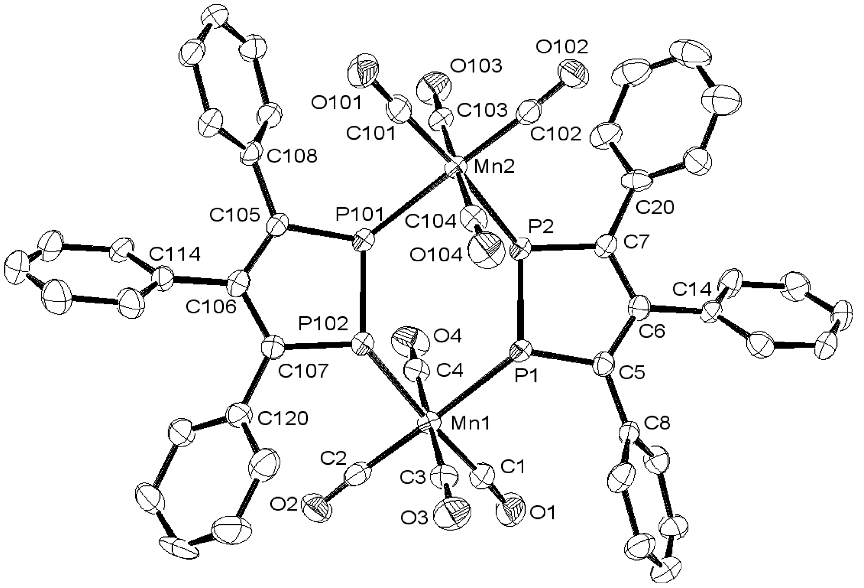

Figure 1. ORTEP view of bis(μ:η^1,η^1-1,2-diphospha-3,4,5-triphenylcyclopentadienyl)bis(manganesetetracarbonyl) (**2a**). Thermal ellipsoids are drawn at 50% probability. Selected bonds lengths (Å) and angles (deg): Mn(1)−P(102) 2.3655(12), Mn(1)−P(1) 2.3710(11), Mn(2)−P(101) 2.3758(11), Mn(2)−P(2) 2.3746(11), P(1)−P(2) 2.1103(13), P(101)−P(102) 2.1087(14), P(1)−C(5) 1.741(4), P(2)−C(7) 1.736(4), P(101)−C(105) 1.759(4), P(102)−C(107) 1.755(4), C(5)−C(6) 1.392(5), C(6)−C(7) 1.418(5), C(105)−C(106) 1.413(5), C(106)−C(107) 1.414(5); P(1)−Mn(1)−P(102) 84.64(4), P(2)−Mn(2)−P(101) 84.73(4), C(5)−P(1)−P(2) 94.78(13), P(2)−P(1)−Mn(1) 122.41(5), C(7)−P(2)−P(1) 94.39(12), C(105)−P(101)−P(102) 94.93(13), C(107)−P(102)−P(101) 94.81(13).

According to X-ray single-crystal diffraction, binuclear complex **2a** (Figure 1) has two Mn atoms doubly bridged by 3,4,5-triphenyl-1,2-diphosphacyclopentadienyl ligands in an μ:η^1,η^1-fashion. Only two examples of such coordination mode were described earlier for 1,2,4-triphosphacyclopentadienyl ligands with nickel and copper.[8] Each manganese atom has a slightly distorted octahedral environment. The geometry of the 3,4,5-triphenyl-1,2-diphosphacyclopentadienide ligand in the complex and in sodium salt[5b] is nearly the same, except for the slightly shorter P−C bonds in **2a**. All four Mn−P bonds in **2a** are equal within experimental error, and the average value is 2.372 Å, which is within the range 2.34−2.38 Å for the majority of Mn(I) complexes with trivalent phosphorus ligands[9] and is shorter than the P−Mn(II) bond, e.g., 2.430(1) Å, in manganese clusters.[1c]

The sum of the covalent radii of phosphorus and Mn in a low-spin state[10] is 2.46 Å and is significantly larger for Mn in a high-spin state (2.68 Å). The P−C bond lengths in complex **1a** vary from 1.736(4) to 1.759(4) Å and are shorter than the sum of the covalent radii P−C(sp^2), 1.80 Å. The P−P bonds are equal at 2.110(1) Å, which is between the P−P double bond (2.02−2.04 Å in coordination compounds)[11] and a single bond, which varies from 2.259 to 2.365 Å for P−P fragments bridging two Mn atoms.[12] The sums of angles at phosphorus atoms are around 340°, which are more typical for phosphorus in sp^3 hybridization. Together with the C−C intra-ring distances typical of aromatic C−C bonds, this indicates a significant delocalization of the π-electrons, though the phosphorus centers are both pyramidal. The formal oxidation states of both Mn ions calculated from the nominal charge of the ligands are +1.

Table 1. Fit Parameters of the Static Magnetic Susceptibility

L	C, emu/K	θ, K	p_{eff}, μ_B per one Mn
(**2a**) CO	0.6	1	1.55
(**2b**) MeCN	1.21	17	2.20
(**2c**) PPh$_3$	1.79	18	2.67

The static magnetic susceptibility χ of the powder samples of **2a**−**c**, measured at temperatures between 2 and 300 K, follows closely the Curie−Weiss law (Figure S1, Supporting Information). Generally, the effective moment p_{eff} (Table 1) for all studied complexes is significantly smaller than that of Mn(I) in the high-spin state ($S = 2$, $g = 2$, $p_{\mathrm{eff}} = 4.9\ \mu_B$) and is rather close to the effective moment of Mn(II) in the low-spin state ($S = 1/2$, $g = 2$, $p_{\mathrm{eff}} = 1.73\ \mu_B$). Remarkably, p_{eff} of Mn continuously increases from **2a** to **2b** and further to **2c**. Since from the ESR data presented below the g-factor for all samples has the same value of $g \approx 2$, the growth of p_{eff} can be phenomenologically treated as an increase of an "effective" spin value from $S_{\mathrm{eff}} \approx 0.4$ to $S_{\mathrm{eff}} \approx 0.9$ when going from **2a** to **2c**. The observed systematic changes of p_{eff} give clear evidence of its dependence on the nature of the ligand at the manganese atom: complex **2a**, containing a strong π-acceptor such as CO, has the lowest p_{eff}, while the largest value of p_{eff} is found for complex **2c**, containing the good σ-donor PPh$_3$. Such a tendency gives strong indications that the redistribution of the electron density in the complex controlled by the ligand substitution affects the magnetic state of

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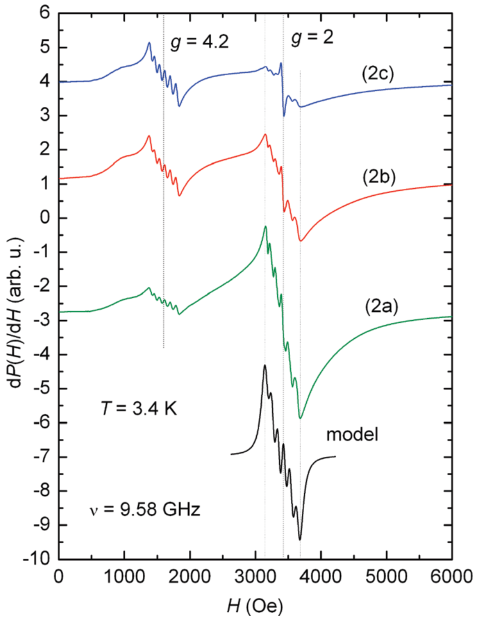

Figure 2. ESR spectra of powder samples of **2a**−**c** and a calculated spectrum (bottom) at ν = 9.56 GHz and T = 3.4 K.

the transition metal ions. Moreover, the decrease of the strength of the π-acceptor and increase of the σ-donor yields an enhancement of the antiferromagnetic interactions in the complexes, which is reflected in the increase of θ (Table 1). Thus the susceptibility data clearly suggest that in binuclear manganese complexes **2a**−**c** the metal-to-ligand charge transfer (MLCT) takes place with the formation of Mn(II) species, which causes antiferromagnetic interactions observed in a broad temperature range. Due to the long distance between both manganese atoms (5.200 Å), this interaction can be realized only through the 1,2-diphosphacyclopentadienide rings.

The ESR powder spectrum of each complex (**2**) consists of two structured signals, one centered about the field H corresponding to the g-factor value of ∼2.0 and the other centered about approximately half of that field value corresponding to the g-factor of ∼4.2 (see Figure 2). Each signal contains six partially resolved lines with a separation about ∼80 Oe, which is typical for low-spin Mn(II),[13] due to the hyperfine interaction $H_{\mathrm{HF}} = \boldsymbol{S}\cdot\boldsymbol{A}\cdot\boldsymbol{I}$ of the electron spin $\boldsymbol{S}$ with the nuclear spin $\boldsymbol{I}$ of Mn ($I^{\mathrm{Mn}} = 5/2$). The result of the simulation of such hyperfine split signal with the EasySpin toolbox for Matlab[14] (Figure 2, bottom spectrum) agrees reasonably well with the experimental one, yielding a tensor of the hyperfine interaction $\boldsymbol{A}[A_x; A_y; A_z] = [280; 280; 120]$ MHz $= [93; 93; 40] \times 10^{-4}$ cm^{-1}.

The occurrence of the half-field signal in the ESR spectrum of the studied complexes is remarkable. An isolated low-spin ($S = 1/2$) Mn^{2+} ion in the low-symmetry ligand coordination is characterized by a nearly isotropic g-factor close to a value of 2.[15] Thus only a single (hyperfine split) line due to the resonance transition $+1/2 \Leftrightarrow -1/2$ ($\Delta S^z = \pm 1$) within the Kramers spin doublet is expected at a "full" resonance field value $H_{\mathrm{res}} = h\nu/g\mu_{\mathrm{B}}|\Delta S^z|$.

However, a more complex ESR spectrum arises if the spins S_1 and S_2 of the two Mn ions in the complex are exchange coupled in a spin dimer. The relevant spin Hamiltonian $H = J\boldsymbol{S}_1\boldsymbol{S}_2 + \boldsymbol{S}_1\cdot\boldsymbol{D}\cdot\boldsymbol{S}_2 + g\mu_{\mathrm{B}}(\boldsymbol{S}_1 + \boldsymbol{S}_2)\boldsymbol{H}$ includes the isotropic and anisotropic exchange interaction, as well as the Zeeman interaction, first, second, and third terms, respectively.[16]

The energy scale on the order of ∼10 K for the isotropic Mn−Mn magnetic interaction J is suggested by the observed Curie−Weiss temperatures (Table 1). Since usually $|J| \gg |D|$, the strength of the anisotropic part of the magnetic exchange is likely to be comparable with the Zeeman interaction (∼0.5 K). In this regime the otherwise "pure" spin triplet states $|S^z{}_{\mathrm{tot}}> = |+1\rangle$, $|0\rangle$, and $|-1\rangle$ can be substantially mixed. Thus in addition to the allowed ESR transitions $\Delta S^z{}_{\mathrm{tot}} = \pm 1$ the formerly forbidden transitions $\Delta S^z{}_{\mathrm{tot}} = \pm 2$ may occur as well, yielding an intense half-field signal with the "doubled" effective g-factor $g_{\mathrm{eff}} = g|\Delta S^z| \approx 2g$. Interestingly, its intensity increases concomitantly with the increase of the Mn magnetic moment upon changing the ligand (Figure 2). Since the anisotropy of exchange arises due to relativistic spin−orbit coupling effects, one may conjecture that tuning the electron density in the complexes by the ligand substitution enhances the orbital contribution to the magnetism of the binuclear complex when passing from a strong π-acceptor in **2a** to a σ-donor one in **2c**.

Thus, we have for the first time demonstrated that bimetallic manganese(I) complexes with bridging 3,4,5-triphenyl-1,2-diphosphacyclopentadienyl ligands possess a magnetic behavior that might be attributed to the intramolecular charge transfer from the metal atoms to the diphosphacyclopentadienyl ring similar to the redistribution of electron density observed in complexes with noninnocent ligands.[17] Furthermore, we find that the fine-tuning of the electron density at the core of the molecular complex by variation of peripheral ligands provides control over the magnitude of the magnetic moment, the contribution of the orbital magnetism, and the strength of the intramolecular magnetic exchange realized through the 1,2-diphosphacyclopentadienyl ligand.

Experimental Section

All reactions and manipulations were carried out under dry, pure nitrogen in standard Schlenk apparatus. All solvents were distilled from sodium/benzophenone and stored under nitrogen before use. The NMR spectra were recorded on a Bruker MSL-400 (^{1}H 400 MHz, ^{31}P 121.7 MHz, ^{13}C 100.6 MHz). SiMe$_4$ was used as internal reference for ^{1}H and ^{13}C NMR chemical shifts, and 85% H_3PO_4 as external reference for ^{31}P. IR spectra were recorded on a Bruker Vector-22 in the range 4000−400 cm^{-1} at a resolution of 4 cm^{-1}. Static magnetic susceptibility has been measured with a superconducting quantum interference device (SQUID) magnetometer from Quantum Design. The ESR measurements have been performed with an X-Band (10 GHz) Bruker EMX spectrometer.

X-ray Single-Crystal Diffraction. The data set for **2a** was collected on a Bruker AXS Kappa APEX II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data collection was performed with APEX2,[18] data reduction with SAINT,[19] absorption correction with

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SADABS,[20] structure solution with SHELXS97,[21] and structure refinement by full-matrix least-squares against F^2 using SHELXL-97[22] and WinGX.[23] The picture was generated using ORTEP-3.[24] Crystal data for **2a**: formula $C_{50}H_{30}Mn_2O_8P_4\cdot 1.5\text{-}C_4H_8O$, $M = 1100.66$, $a = 9.2604(3)$ Å, $b = 19.1526(6)$ Å, $c = 15.0979(4)$ Å, $\beta = 99.859(2)°$, $V = 2638.2(1)$ Å^3, $\rho_{calc} = 1.386$ g cm^{-3}, $\mu = 0.656$ mm^{-1}, empirical absorption correction ($0.698 \leq T \leq 0.968$), $Z = 2$, monoclinic, space group $P2_1$ (No. 4), $T = 198$ K, ω and φ scans, 145 301 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.75$ Å^{-1}, 18 367 independent ($R_{int} = 0.089$) and 10 061 observed reflections [$I \geq 2\ \sigma(I)$], 617 refined parameters, $R = 0.052$, $wR^2 = 0.127$, max. residual electron density 1.20 (−0.43) e Å^{-3}. CCDC 734772 (**2b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1-Trimethyltin-3,4,5-triphenyl-1,2-diphosphacyclopentadiene (1). Solid Me_3SnCl (1.08 g, 5.4 mmol) was added at −78 °C to a suspension of sodium 1,2-diphospha-3,4,5-triphenylcyclopentadienide[5c] (1.9 g, 5.4 mmol) in 25 mL of toluene. The reaction mixture was stirred at RT for 6 h. The solvent was evaporated, and the residue was extracted with *n*-hexane (3 × 25 mL), filtered, and dried under vacuum to give 1.75 g (66%) of 1-trimethyltin-3,4,5-triphenyl-1,2-diphosphacyclopentadiene (**1**) as light yellow oil, which solidified on standing.

^{1}H NMR (C_6D_6): δ −0.005 (t, 9H, Me, $^2J_{Sn-H} = 26.9$ Hz), 6.89 (t, 3H, H_p, Ph, $^3J_{H-H} = 3.18$ Hz), 6.94−7.02 (m, 8H, Ph), 7.24 (d, 4H, H_o, Ph, $^3J_{H-H} = 6.36$ Hz). ^{31}P NMR (C_6D_6): δ 116.4 (s). ^{13}C NMR (C_6D_6): δ −5.7 (Me, $^1J_{Sn-C} = 324.4$ Hz), 127.30 (s, C_p, Ph), 127.57 (s, C_p, Ph), 128.76 (s, C_m, Ph), 128.86 (s, C_m, Ph), 130.28 (s, C_o, Ph), 132.20 (s, C_o, Ph), 140.04 (s, C_{ipso}, Ph), 142.92 (t, C_{ipso}, Ph, $^2J_{C-P} = 7.03$ Hz), 154.65 (t, C_2-C_p, $^2J_{C-P} = 4.96$ Hz), 181.06 (t, C_1-C_p, $^1J_{C-P} = 21.71$ Hz). ^{119}Sn NMR (C_6D_6) δ 50.8 (t, $^1J_{Sn-P} = 276$ Hz). Anal. Calcd for $C_{24}H_{24}P_2Sn$ (492.04): C 58.46; H 4.91; P 12.56. Found: C 58.35; H 4.81; P 13.01.

Bis(μ,η^1:η^1-3,4,5-triphenyl-1,2-diphosphacyclopentadienyl)-bis(tetracarbonylmanganese) (2a). A mixture of [MnBr(CO)$_5$] (0.495 g, 1.8 mmol) and 1-trimethyltin-3,4,5-triphenyl-1,2-diphosphacyclopentadiene (**1**) (0.89 g, 1.8 mmol) in 50 mL of THF was stirred for 3 h at 65 °C. The solvent was reduced to 10 mL under vacuum and cooled to −10 °C to form red crystals, which were collected, washed with *n*-hexane (3 × 25 mL), and dried under vacuum to give 1.42 g (79.5%) of bis(μ,η^1:η^1-3,4,5-triphenyl-1,2-diphosphacyclopentadienyl)bis(tetracarbonylmanganese) (**2a**) as a red powder with a melting point of 138 °C (dec).

IR (*n*-hexane, cm^{-1}): 1986 (CO), 2004 (CO), 2014 (CO), 2051 (CO). Anal. Calcd for $C_{50}H_{30}Mn_2O_8P_4$ (991.97): C 60.50; H 3.05; P 12.48. Found: C 59.81; H 3.13; P 12.73.

Crystals suitable for X-ray analysis were obtained from a saturated solution of **2a** in THF at RT.

Bis(μ,η^1:η^1-3,4,5-triphenyl-1,2-diphosphacyclopentadienyl)-bis(tricarbonyl(acetonitrile)manganese) (2b) was obtained in a similar manner from [$Mn_2(CO)_6(MeCN)_2Br_2$][25] (0.39 g, 0.75 mmol) and 1-trimethyltin-3,4,5-triphenyl-1,2-diphosphacyclopentadiene (**1**) (0.74 g, 1.5 mmol). Yield: 0.43 g (56%), red powder, mp 92 °C (dec).

IR (*n*-hexane, cm^{-1}): 1918 (CO), 2001 (CO), 2048 (CO), 3124 (CN). Anal. Calcd for $C_{52}H_{36}Mn_2N_2O_6P_4$ (1018.62): C 61.31; H 3.56; N 2.75; P 12.16. Found: C 61.52; H3.27; N 2.16; P 12.54.

Bis(μ,η^1:η^1-3,4,5-triphenyl-1,2-diphosphacyclopentadienyl)-bis(tricarbonyl(triphenylphosphine)manganese) (2c). A mixture of bis(μ,η^1:η^1-3,4,5-triphenyl-1,2-diphosphacyclopentadienyl)-bis(tricarbonyl(acetonitrile)manganese) (**2b**) (0.81 g, 0.79 mmol) and triphenylphosphine (0.41 g, 1.58 mmol) in 50 mL of THF was stirred for 12 h at room temperature. The solvent was evaporated and the residue washed with *n*-hexane (2 × 25 mL) and dried under vacuum to give 1.1 g (95%) of **2c** as a red powder; mp 125 °C (dec).

IR (*n*-hexane, cm^{-1}): 1907 (CO), 1933 (CO), 2020 (CO). Anal. Calcd for $C_{84}H_{60}Mn_2O_6P_6$ (1461.09): C 69.05; H 4.14; P 12,72. Found: C 68.87; H 4.03; P 12.17.

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Supporting Information Available: Details of magnetic measurement and crystallographic information of **2a** are available free of charge via the Internet at http://pubs.acs.org or from the authors.

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