RESEARCH ARTICLE

Synthesis and characterization of manganese(II) complexes supported by cyclopentadienyl-phosphine ligands†

Gao-Xiang Wang,‡ Jianhao Yin,‡ Jiapeng Li,‡ Zhu-Bao Yin, Wen-Xiong Zhang [ID] * and Zhenfeng Xi [ID] *

A series of manganese(II) complexes supported by cyclopentadienyl-phosphine ligands have been synthesized and characterized. A reaction of potassium salts of a cyclopentadienyl-phosphine ligand (**LK**) with MnX_2 provided dimeric complexes $[LMn(\mu-X)]_2$ (X = Cl, **1a**; X = Br, **1b**) in high yields. The monomeric complex $[K(18\text{-crown-}6)][LMnCl_2]$ (**2**) was obtained with the addition of 18-crown-6. $[LMn(\mu-Cl)]_2$ (**1a**) served as a precursor to dimeric amido and methyl manganese(II) complexes including $[LMn(\mu-NH_2)]_2$ (**3**) and $[LMn(\mu-Me)]_2$ (**4**). Treatment of $[LMn(\mu-Cl)]_2$ (**1a**) with EtMgCl, PhMgBr or other reductants resulted in the formation of sandwich manganese(II) complex L_2Mn (**5**). Complexes **1a,b, 2−5** were characterized by a single-crystal X-ray structural analysis.

Introduction

Since the first organomanganese(II) complexes (PhMnI and Ph_2Mn) were reported in 1937,[1] synthesis and reactivity of organomanganese halides (RMnX), manganese diorganyls (R_2Mn) and organomanganates (R_3Mn^- and R_4Mn^{2-}) have been investigated for more than half a century.[2] In particular, the manganese alkyl,[3] aryl[4] and amide[5] derivatives have played an important role in the development of organomanganese chemistry.

As usual, ligands play a very important role in the structure and reaction of organomanganese compounds, which are often stabilized by a variety of ligands, such as the cyclopentadienyl group[6] and phosphines.[7] The cyclopentadienyl-phosphine ligand (Fig. 1), in which a multi-substituted cyclopentadienyl moiety and a phosphine moiety are linked by an alkyl or aryl group, is a potential chelating ligand.[8] Its cooperative coordination mode with transition metals forming so-called constrained geometry complexes (CGC) may result in resonance interactions between the lone pair on the phosphorus center and the cyclopentadienyl π system.[9,10]

We have developed a convenient method for the synthesis of multi-functional phosphine ligands.[11] With our continued interest in their application as a chelating and stabilizing ligand for novel transition-metal complexes,[12] we have now investigated their coordination behaviour with manganese. Herein, we report the synthesis and structural characterization of a series of well-defined manganese(II) complexes supported by cyclopentadienyl-phosphine ligands. The results demonstrated that the chelating and stabilizing effects of cyclopentadienyl-phosphine ligands enabled different structures and reactivities of manganese(II) complexes.

Results and discussion

Synthesis and characterization of $[LMn(\mu-X)]_2$ (X = Cl, 1a; X = Br, 1b) and $[K(18\text{-crown-}6)][LMnCl_2]$ (2)

Based on our previous work,[12] we successfully synthesized the potassium salt of a cyclopentadienyl-phosphine ligand (**LK**) as a yellow powder (Scheme 1). The reaction of **LK** and anhydrous
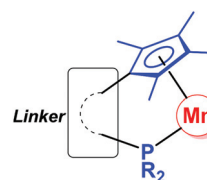
Beijing National Laboratory for Molecular Sciences, MOE Key Laboratory of Bioorganic Chemistry and Molecular Engineering, College of Chemistry, Peking University, Beijing 100871, China. E-mail: wx_zhang@pku.edu.cn, zfxi@pku.edu.cn
† Electronic supplementary information (ESI) available: Infrared spectroscopy for **1a,b, 2–5**. CCDC 1870180, 1870203, 1870204, 1870205, 1870206 and 1870207. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8qi01054d
‡ These authors contributed equally to this work.

Fig. 1 Cooperative coordination mode of organomanganese complexes bearing a cyclopentadienyl-phosphine ligand.
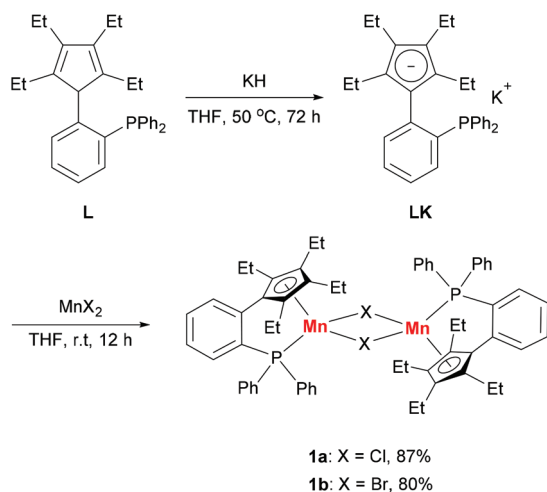
Scheme 1 Synthesis of dimeric manganese(II) halide complexes **1a** and **1b**.

1a: X = Cl, 87%
1b: X = Br, 80%

Scheme 2 Synthesis of monomeric manganese(II) halide complex **2**.

2: 96%

$MnCl_2/MnBr_2$ in THF at room temperature proceeded smoothly with the elimination of KX (X = Cl, Br). The dimeric complexes $[\text{LMn}(\mu\text{-Cl})]_2$ (**1a**) and $[\text{LMn}(\mu\text{-Br})]_2$ (**1b**) were obtained in 87% and 80% yields, respectively. **1a** and **1b** are sensitive to air and moisture and can be recrystallized from hexane/THF.

Solution magnetic measurements of **1a** and **1b** in C_6D_6 at room temperature gave effective magnetic moments of $6.7(1)\mu_B$ per dimer and $6.8(2)\mu_B$ per dimer, respectively, which are consistent with weakly antiferromagnetically coupled high-spin manganese(II) centers. The molecular structures of **1a** and **1b** were confirmed by X-ray crystallography. Both **1a** and **1b** are halogen-bridged dimers in the solid state. The ORTEP drawing of **1a** is shown in Fig. 2. In these two compounds, each manganese center is coordinated by the cyclopentadienyl ring, the phosphorus atom and the two bridging halogens. The structural parameters of **1a** are similar to those of **1b**, and only the bromine bridges in **1b** cause a major lengthening of the
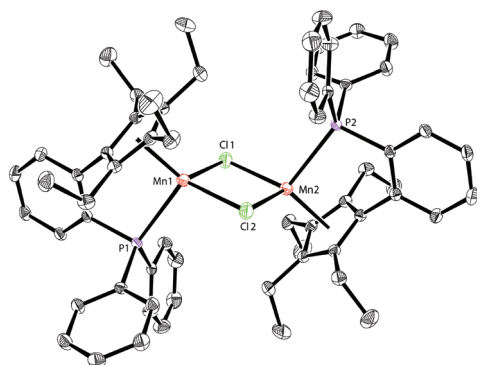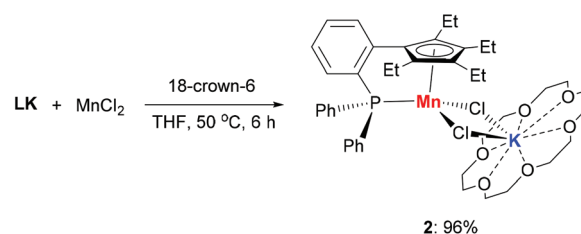
distances of the Mn_2X_2 ring. The distances between two manganese atoms are 3.287 Å and 3.580 Å for **1a** and **1b**, respectively, indicating that there are no Mn–Mn bonds (2.170–3.291 Å) in **1a** and **1b**.[13]

The addition of 18-crown-6 to a mixture of **LK** and $MnCl_2$ afforded the monomeric complex **2** in 96% yield (Scheme 2). Complex **2** has a solution magnetic moment of $6.5(3)\mu_B$ in d^8-THF that showed a monomeric high-spin manganese(II) center. The molecular structure of complex **2** was confirmed by X-ray crystallography and the ORTEP drawing is shown in Fig. 3. The manganese centers of both **1a** and **2** are in the same coordination environment. In contrast to the dimeric complex **1a**, the Mn–P bond distance in complex **2** (2.726 Å) is longer than the that of dimer **1a** (2.607 Å) and slightly longer than the reported Mn–P bond distances.[14] The potassium atom in **2** is connected by two bridging chlorides and coordinated with six oxygen atoms in 18-crown-6.

Synthesis and characterization of organomanganese(II) derivatives: $[\text{LMn}(\mu\text{-NH}_2)]_2$ (3), $[\text{LMn}(\mu\text{-Me})]_2$ (4) and L_2Mn (5)

The substitution reactions of **1a** with nucleophiles were investigated to prepare organomanganese(II) derivatives (Scheme 3). Treatment of **1a** with excess $NaNH_2$ in THF at room temperature afforded the amido-bridged manganese(II) complex $[\text{LMn}(\mu\text{-NH}_2)]_2$ (**3**) in 86% yield. As far as we know, complex **3** is a rare example of manganese complexes with parent amido ($-NH_2$) ligands.[5b] The manganese(II) methyl complex

Fig. 2 Molecular structure of **1a** with thermal ellipsoids at 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn(1)−Cl(1): 2.3909(7), Mn(1)−Cl(2): 2.4603(7), Mn(1)−P(1): 2.6066(6), and Cl(1)−Mn(1)−Cl(2): 94.71(3).
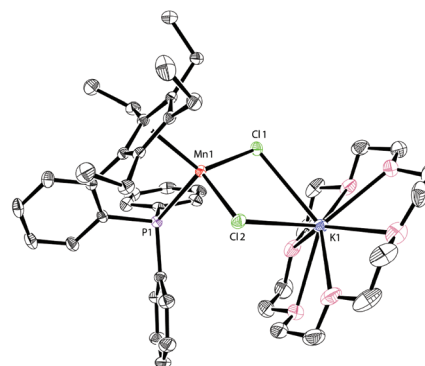

Fig. 3 Molecular structure of **2** with thermal ellipsoids at 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn(1)−Cl(1): 2.3997(6), Mn(1)−Cl(2): 2.3844(7), Mn(1)−P(1): 2.7264(6), K(1)−Cl(1): 3.1928(8), K(1)−Cl(2): 3.2865(8), Cl(1)−Mn(1)−Cl(2): 99.83(2), and Cl(1)−K(1)−Cl(2): 65.879(16).

Scheme 3 Synthesis of organomanganese(II) derivatives: amido-bridged complex **3**, methyl-bridged complex **4** and sandwich complex **5**.

Fig. 4 Molecular structure of **3** with thermal ellipsoids at 30% probability. Hydrogen atoms, except that on nitrogen atoms N1 and N2, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn(1)−N(1): 2.1299(19), Mn(1)−N(2): 2.096(2), Mn(1)−P(1): 2.6525(6), and N(1)−Mn(1)−N(2): 88.79(8).

The solid-state structure of **4** is depicted in Fig. 5. The Mn–P bond distance in complex **4** (2.706 Å) is also longer than that in **1a** (2.607 Å). The Mn–Mn distance of **4** (2.820 Å) is *ca.*

Fig. 5 Molecular structure of **4** with thermal ellipsoids at 30% probability. Hydrogen atoms, except that on carbon atoms C1 and C2, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn(1)−C(1): 2.2249(18), Mn(1)−C(2): 2.308(2), Mn(1)−P(1): 2.7056(6), and C(1)−Mn(1)−C(2): 104.24(7).

[**L**Mn(μ-Me)]$_2$ (**4**) was also prepared from the addition of methyl Grignard reagent MeMgCl to **1a** in THF at room temperature. By recrystallization from hexane/Et$_2$O several times, the methyl-bridged complex was isolated as a red solid in 84% yield. Magnetic measurements showed that **3** and **4** have effective magnetic moments of 6.2(1)μ_B per dimer and 5.9(3)μ_B per dimer at room temperature in C$_6$D$_6$, due to the antiferromagnetic interactions between the two manganese ions.

The reaction of **1a** with EtMgCl or PhMgBr in THF at room temperature produced a sandwich complex **5** in 46% yield rather than the expected ethyl or phenyl complexes.[15] However, the reactions between complex **1a** and other reductants, such as KHBEt$_3$, ^{n}BuLi and KC$_8$, did not yield the expected hydride complex or the other reduction product. Only complex **5** and a black precipitate were afforded. The sandwich complex **5** can also be prepared in 79% yield by the reaction of anhydrous MnCl$_2$ with two equivalents of **LK** in THF. The appearance of the sandwich complex **5** shows that the manganese center has a stronger coordination with the cyclopentadienyl moiety compared with the phosphine moiety. The solution magnetic susceptibility of complex **5** shows a magnetic moment of 5.4(2)μ_B at room temperature in d^8-THF.

The molecular structure of complex **3** was unambiguously confirmed by X-ray crystallography. The structure of **3** (Fig. 4) shows that it is dimerized through bridging two manganese centers by two amido groups. The Mn–P bond distance in complex **3** is 2.653 Å, which is longer than 2.607 Å in **1a**. The Mn$_2$N$_2$ core is almost a square with Mn–N bond distances of 2.123 Å and 2.096 Å and an N–Mn–N angle of 88.791°. The Mn–Mn distance in **3** is 3.019 Å, which is much shorter than the distances observed in **1a** and **1b**.
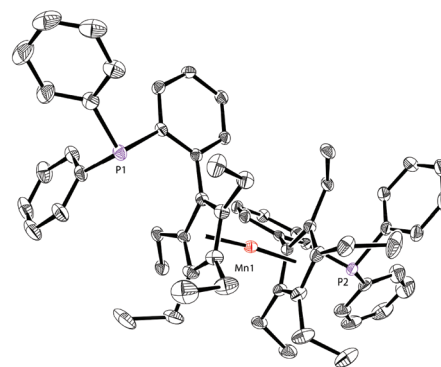

Fig. 6 Molecular structure of **5** with thermal ellipsoids at 30% probability. H atoms are omitted for clarity.

0.2 Å shorter than that of **3** (3.019 Å). This short Mn–Mn distance may indicate some interactions between the two metal atoms.[3f,g] The planar Mn_2C_2 core features the Mn–C bond distances (2.2249 Å and 2.308 Å) and the C–Mn–C angle (104.24°). These parameters are similar to those in other reported methyl-bridged dinuclear manganese(II) complexes.[3c,e–g]

The molecular structure of complex **5** was also identified by X-ray crystallography. As shown in Fig. 6, complex **5** shows a sandwich configuration. The manganese center is coordinated with the two penta-substituted cyclopentadienyl rings in two ligand molecules, leaving the phosphines uncoordinated.

Conclusions

In summary, we have synthesized a series of organomanganese complexes bearing the chelating and stabilizing cyclopentadienyl-phosphine ligand. Monomeric and dimeric manganese(II) halide complexes (**1a**, **1b** and **2**) were obtained by the reaction of a potassium salt of the cyclopentadienyl-phosphine ligand (**LK**) with MnX_2 (X = Cl, Br). The reaction of **1a** with $NaNH_2$ and MeMgCl afforded amido-bridged complex **3** and methyl-bridged complex **4**. In addition, we also investigated the formation of the sandwich complex **5**. The reaction chemistry of these complexes is under investigation. We hope that the present results in this paper can provide some useful information for the design of phosphines and cyclopentadienyl ligands in organomanganese chemistry.

Experimental

General methods

Unless otherwise mentioned, the synthesis of air and/or moisture sensitive compounds was carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen filled glovebox. Solvents were collected from an Mbraun SPS-800 Solvent Purification System. KH, ^{n}BuLi, $KHBEt_3$, KC_8, Grignard reagents, 18-crown-6, 3-hexyne, 2-bromobenzaldehyde, $MnCl_2$, and $MnBr_2$ were obtained from Strem, Aldrich, TCI, Alfa Aesar, Acros, J&K and others. ^1H and ^{31}P NMR spectra were recorded on a Bruker ARX500 spectrometer (FT, 400 MHz for ^1H; 202 MHz for ^{31}P) at room temperature. Ligand **L** can be synthesized based on the reported procedures.[12a] Elemental analysis was performed on a Vario EL elemental analyzer at the Analytical Center of Peking University. Infrared spectroscopy was performed on a Bruker Tensor 27 using a KBr cell. Solution magnetic susceptibility measurements were performed by the Evans method and experimental solutions contain a known amount of a TMSOTMS standard.[16]

Synthesis of LK. Ligand **L** (0.5 mmol) and KH (100 mg, 2.5 mmol) were added in THF (20 mL) under an atmosphere of nitrogen. The mixture was stirred at 50 °C for 72 h. The reaction was monitored by ^{31}P NMR. The resulting mixture was filtered through a Celite pad to remove excess KH and a dark red solution was obtained. After the solvent was evaporated under vacuum, the residue was washed with hexane (3 × 5 mL) to obtain a yellow powder (>95% yield). The yellow powder was used directly in subsequent reactions.

Synthesis of [LMn(μ-Cl)]$_2$ (1a). Under an atmosphere of nitrogen, a THF (5 mL) solution of **LK** (0.1 mmol) was added into the suspension of $MnCl_2$ (12.6 mg, 0.1 mmol) in THF (5 mL) at room temperature. The reaction mixture was stirred for 12 h and the solvent was evaporated under vacuum. After the addition of Et_2O (8 mL) to the orange residue, the solution were filtered through a Celite pad and the solvent was evaporated under vacuum, leaving the product as an orange powder, which was washed with hexane (2 × 3 mL) and dried under vacuum (45.9 mg, 87%). Single crystals of **1a** suitable for X-ray crystallography were obtained by recrystallization from hexane/THF. Magnetic susceptibility (C_6D_6, 296 K): μ_{eff} = 6.7(1)μ_B per dimer. Anal. Calcd (%). for $C_{62}H_{68}Cl_2Mn_2P_2$: C, 70.52; H, 6.49. Found: C, 70.46; H, 6.60.

Synthesis of [LMn(μ-Br)]$_2$ (1b). Following the procedure described for **1a**, under an atmosphere of nitrogen, adding a THF (5 mL) solution of **LK** (0.1 mmol) to a suspension of $MnBr_2$ (21.5 mg, 0.1 mmol) in THF (5 mL) at room temperature gave **1b** as a yellow powder (45.7 mg, 80%). Single crystals of **1b** suitable for X-ray crystallography were obtained by recrystallization from hexane/THF. Magnetic susceptibility (C_6D_6, 294 K): μ_{eff} = 6.8(2)μ_B per dimer. Anal. Calcd (%). for $C_{62}H_{68}Br_2Mn_2P_2$: C, 65.05; H, 5.99. Found: C, 66.44; H, 6.31.

Synthesis of [K(18-crown-6)][LMnCl$_2$] (2). Under an atmosphere of nitrogen, a THF (5 mL) solution of **LK** (0.1 mmol) was added into a suspension of $MnCl_2$ (12.6 mg, 0.1 mmol) in THF (5 mL) at room temperature for 12 h. After 18-crown-6 (26.4 mg, 0.1 mmol) was added, the mixture was stirred for 2 h. The solution was filtered through a Celite pad, and the solvent was evaporated under vacuum. The residue was washed with hexane (2 × 3 mL) and dried under vacuum to obtain **2** as an orange solid (83.2 mg, 96%). Single crystals of **2** suitable for X-ray crystallography were obtained by recrystallization from hexane/Et_2O. Magnetic susceptibility (d^8-THF, 294 K): μ_{eff} = 6.5(3)μ_B. Anal. Calcd (%). for $C_{43}H_{58}Cl_2KMnO_6P$: C, 59.58; H, 6.74. Found: C, 58.89; H, 6.85.

Synthesis of [LMn(μ-NH$_2$)]$_2$ (3). Under an atmosphere of nitrogen, a suspension of $NaNH_2$ (15.6 mg, 0.4 mmol) in THF (5 mL) was added into a solution of **1a** (52.8 mg, 0.1 mmol) in THF (5 mL) at room temperature. The resultant brown mixture was stirred for 6 h and the dark solution was filtered through a Celite pad. An orange filtrate was obtained and then the solvent was evaporated. The residue was washed with hexane (3 mL) and dried under vacuum to give **3** as an orange solid (43.7 mg, 86%). Single crystals of **3** suitable for X-ray crystallography were obtained by recrystallization from hexane/Et_2O. Magnetic susceptibility (C_6D_6, 294 K): μ_{eff} = 6.2(1)μ_B per dimer. Anal. Calcd (%). for $C_{62}H_{72}Mn_2N_2P_2$: C, 73.22; H, 7.14; N, 2.75. Found: C, 72.39; H, 7.04; N, 1.63.

Synthesis of [LMn(μ-Me)]$_2$ (4). Under an atmosphere of nitrogen, a solution of MeMgCl in THF (37 μL, 3 N in THF) was added into a solution of **1a** (52.8 mg, 0.1 mmol) in THF (10 mL) at room temperature. The resultant dark red mixture

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was stirred for 6 h and the solvent was evaporated under vacuum. After the addition of Et_2O (8 mL) to the red residue, the solution was filtered through a Celite pad and the solvent was evaporated to dryness. The residue was washed with hexane (3 mL) and dried under vacuum to obtain **4** as a red solid (42.6 mg, 84%). Single crystals of **4** suitable for X-ray crystallography were obtained by recrystallization from hexane/Et_2O. Magnetic susceptibility (C_6D_6, 296 K): μ_{eff} = 5.9(3)μ_B per dimer. Anal. Calcd (%). for $C_{64}H_{74}Mn_2P_2$: C, 75.73; H, 7.53. Found: C, 74.66; H, 7.40.

Synthesis of L₂Mn (5). Under an atmosphere of nitrogen, a THF (5 mL) solution of **LK** (0.2 mmol) was added into a suspension of $MnCl_2$ (12.6 mg, 0.1 mmol) in THF (5 mL) at room temperature. The reaction mixture was stirred overnight and the solvent was evaporated under vacuum. After the addition of Et_2O (10 mL) to the orange residue, the solution was filtered through a Celite pad and the solvent was evaporated under vacuum, leaving the product as a red solid, which was washed with hexane (2 × 3 mL) and dried under vacuum (36.8 mg, 79%). Single crystals of **5** suitable for X-ray crystallography were obtained by recrystallization from hexane/Et_2O. Magnetic susceptibility (d^8-THF, 296 K): μ_{eff} = 5.4(2)μ_B. Anal. Calcd (%). for $C_{62}H_{68}MnP$: C, 80.06; H, 7.37. Found: C, 80.13; H, 7.50.

X-ray crystallography

Data collection for **1a,b, 2–5** was performed at 180 K on a Rigaku diffractometer, using monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved using the SHELXTL or Olex program.[17] Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compounds **1a, b, 2–5** are summarized in the ESI.† Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1870180 (**1a**), 1870203 (**1b**), 1870204 (**2**), 1870205 (**3**), 1870206 (**4**) and 1870207 (**5**).†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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