

# A manganese carbonyl complex derived from the P,N-bonding ligand (2-aminophenyl)diphenylphosphine

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## Abstract

Thermal reaction of  $[\text{H}_3\text{Mn}_3(\text{CO})_{12}]$  with  $\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2$  gives good yields of  $[\text{Mn}_2(\text{CO})_6(\text{PPh}_2\text{C}_6\text{H}_4\text{NH})_2]$ , an X-ray single crystal structure determination of which reveals a P,N-chelating ligand with each of the NH groups, formed by deprotonation of the amine groups, bridging the two metal atoms.

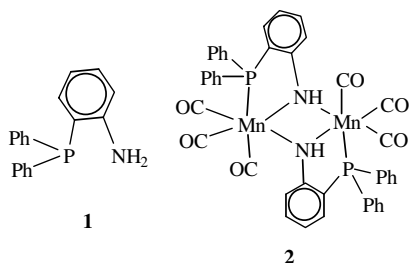
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## 1. Introduction

Many bidentate hemilabile ligands have been explored for their ability to combine a stabilising effect on the metal centre with the possibility of readily generating a vacant coordination site for catalysis [1–5]. The most common ligating atom combinations are P,O or P,N which exploit the mismatch in bonding tendencies between soft P and hard O or N. Recent summaries giving examples are available [6–8].

One readily prepared ligand which has had some application in organometallic chemistry is  $\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2$  (**1**), which not only includes a soft-hard P,N combination but also retains potentially reactive N–H bonds [9,10].



Metal carbonyl complexes derived from **1** have been reported for both mononuclear and cluster compounds [11–18]. However, there are as yet no reports that we are aware of where derivatives of manganese have been prepared with **1**. Our longer term interest stems from the possibility of controlling the reactivity of the Mn–C bond in cyclomanganated compounds with such ancillary ligands [19], but here we describe a novel complex (**2**) from initial explorations of the reactions of **1** with simpler manganese carbonyls.

## 2. Experimental

### 2.1. General

Reactions were carried out under a nitrogen atmosphere using Schlenk techniques and solvents that were distilled under nitrogen from appropriate drying agents before use. Electrospray mass spectra were recorded on a VG Platform II spectrometer, operated as detailed elsewhere [20,21]. Assignments were confirmed by simulation of the characteristic isotope patterns using the ISOTOPE program [22]. NMR spectra were obtained on a Bruker AC300 instrument operating under standard conditions. IR spectra were recorded on a Digilab Scimitar instrument.

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$\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2$ -2 and  $[\text{H}_3\text{Mn}_3(\text{CO})_{12}]$  were prepared by the literature methods [23,24].

## 2.2. Preparation of 2

$[\text{H}_3\text{Mn}_3(\text{CO})_{12}]$  (40 mg, 0.079 mmol) was dissolved in heptane (5 mL) in a Schlenk flask. (2-Aminophenyl)diphenylphosphine (45 mg, 0.16 mmol) was added to the flask and the temperature of the reaction mixture was gradually increased to between 80 and 90 °C over a period of 50 min. During this time a colour change from orange–red to orange–yellow was observed, with a yellow precipitate starting to form at 80 °C. After cooling to room temperature, the solvent was removed in vacuo and the residue was redissolved in a small amount of dichloromethane. A similar volume of diethyl ether was added and the mixture was placed in the freezer. After one week, yellow crystals of **2** were obtained (40 mg, 61%). M.p. 110–116 °C. *Anal.* Calc. for  $\text{C}_{42}\text{H}_{30}\text{N}_2\text{O}_6\text{P}_2\text{Mn}_2$  ( $M_r = 830$ ) requires C, 60.74; H, 3.65; N, 3.37. Found: C, 59.99; H, 3.62; N, 3.38%.  $\nu_{\text{CO}}$  ( $\text{CH}_2\text{Cl}_2$ ) 2002 (s), 1923(s), 1898(s); ESI-MS, (MeOH, added NaOMe [20,21]), positive ion  $m/z$  853  $[\text{M}+\text{Na}]^+$ , 825  $[\text{M}+\text{Na}-\text{CO}]^+$ , negative ion  $m/z$  801  $[\text{M}-\text{H}-\text{CO}]^-$ , 773  $[\text{M}-\text{H}-2\text{CO}]^-$ . NMR ( $\text{CDCl}_3$ ; 300 MHz):  $^1\text{H}$ :  $\delta$  7.0–8.5 (m); the NH signal was either too broad to be observed or was amongst the aryl proton signals and could not be assigned.  $^{13}\text{C}$ : owing to decomposition over the period of accumulation, the spectrum was poor and singlet signals were not resolved; doublet signals assigned to the ring carbons *ortho* and *para* to the amino group were at 111.0 ( $J = 7$  Hz) and 118.9 ppm ( $J = 11$  Hz), the remainder overlapping at 128–135 ppm.  $^{31}\text{P}$ : 65.4 ppm.

## 2.3. X-ray crystallography

X-ray intensity data were collected on a Siemens SMART CCD diffractometer using standard procedures and software. Multiscan absorption corrections were applied (SADABS [25]). Structures were solved by direct methods and developed and refined on  $F^2$  using the SHELX programmes [26] operating under WINGX [27,28]. Hydrogen atoms were included in calculated positions, except for the hydrogen attached to N(1), which was located as the highest peak in a penultimate difference map and was refined with an isotropic temperature factor.

### 2.3.1. Structure of $[\text{Mn}_2(\text{CO})_6(\text{Ph}_2\text{PC}_6\text{H}_4\text{NH})_2] \cdot \text{CH}_2\text{Cl}_2$ ( $2 \cdot \text{CH}_2\text{Cl}_2$ )

Yellow crystals of **2** as the mono-solvate were obtained from  $\text{CH}_2\text{Cl}_2$ .

*Crystal data:*  $\text{C}_{42}\text{H}_{30}\text{N}_2\text{O}_6\text{P}_2\text{Mn}_2 \cdot \text{CH}_2\text{Cl}_2$ ,  $M = 1000.36$ , monoclinic, space group  $P2_1/n$ ,  $a = 10.8871(1)$ ,  $b = 14.7066(1)$ ,  $c = 14.1506(2)$  Å,  $\beta = 97.744(1)^\circ$ ,  $U = 2245.0(1)$  Å<sup>3</sup>,  $T = 190$  K,  $Z = 2$ ,  $D_{\text{calc}} = 1.48$  g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 0.921$  mm<sup>-1</sup>,  $F(000) 1016$ ; 12 596 reflections collected with  $2^\circ < \theta < 26^\circ$ , 4520 unique ( $R_{\text{int}} = 0.0433$ ) used after

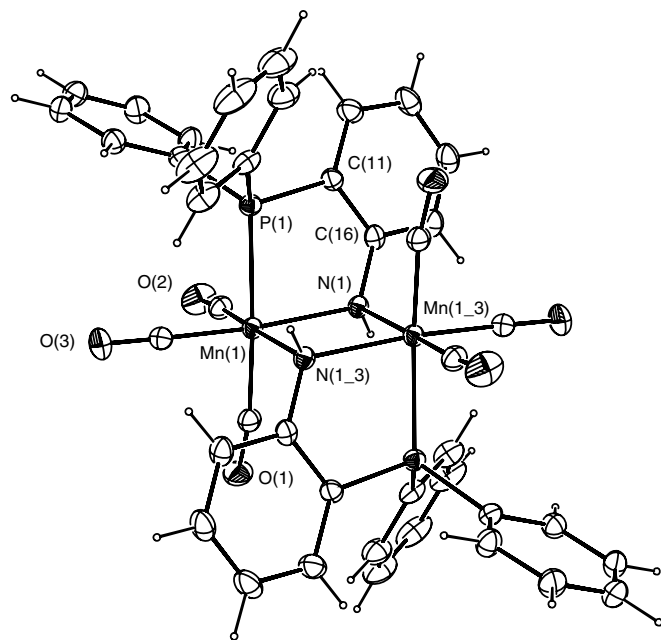


Fig. 1. The structure of the centrosymmetric dimer **2**. Bond parameters include bond lengths (Å): Mn–P 2.317(1), Mn–N(1) 2.084(3), Mn–N(1') 2.150(3), Mn...Mn 3.267(1); bond angles (°): Mn–P–C(11) 101.3(2), N(1)–Mn–N(1') 79.0(2), Mn–N(1)–Mn' 100.9(2), Mn–N(1)–C(16) 112.1(2).

correction for absorption ( $T_{\text{max,min}} = 0.7697, 0.7329$ ). Crystal dimensions  $0.36 \times 0.30 \times 0.30$  mm<sup>3</sup>. Refinement on  $F^2$  gave  $R_1$  0.0563 [ $I > 2\sigma(I)$ ] and  $wR_2 = 0.1580$  (all data), GoF = 1.027. The structure of **2** is illustrated in Fig. 1, with selected bond parameters summarised in the caption to the figure.

## 3. Results and discussion

### 3.1. Synthesis and properties of 2

We were unable to isolate any new compounds from the thermal reaction between the ligand **1** and  $\text{Mn}_2(\text{CO})_{10}$ , decomposition to insoluble brown residues taking place under conditions needed for reaction. However, the trinuclear species  $\text{H}_3\text{Mn}_3(\text{CO})_{12}$  underwent a smooth reaction at 80 °C with **1** to give good yields of a new species as yellow crystals. These were reasonably air-stable as a solid, but solutions tended to decompose giving a green product.  $^1\text{H}$  and  $^{13}\text{C}$  NMR of **2** gave little useful information, while  $^{31}\text{P}$  NMR gave a signal at  $\delta$  65.4, well-shifted from that of the free ligand at  $\delta$  –19.6. This indicated that a five-membered chelate ring had formed [29], though the shift of 75 ppm is unusually large [30]. The ESI mass spectrum suggested a mass of 830 from an  $[\text{M}+\text{Na}]^+$  ion at  $m/z$  853, corresponding to an empirical formula of  $[\text{Mn}_2(\text{CO})_6(\text{Ph}_2\text{PC}_6\text{H}_4\text{NH})_2]$ . To characterise the complex a single crystal X-ray determination was carried out. The structure is shown in Fig. 1. This shows a centrosymmetric molecule consisting of two  $\text{Mn}(\text{CO})_3$  units each coordinated to a phosphorus atom of a mono-deprotonated form of the

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