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A mixed-valence dimanganese complex synthesized from the $[Ph_2P(O)NP(O)Ph_2]^-$ anion with $[BrMn(CO)_5]$

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Abstract

The reaction of the $[Ph_2P(O)NP(O)Ph_2]^-$ anion with $[BrMn(CO)_5]$ in refluxed dichloromethane afforded the mixed-valence complex $[Mn_2(CO)_3\{Ph_2P(O)NP(O)Ph_2\text{-}\mu\text{-}O,O'\}_3]$ (**1**). The single-crystal X-ray analysis of **1** shows that its overall geometry can be regarded as confacial octahedral–trigonal prismatic. The six-membered MnO_2P_2N rings adopt a twisted-boat conformation. Although the distance between the metal centers, 3.160 Å, is rather short, we discard a formal bonding interaction since the fragment $-Mn(CO)_3$ fulfills the $18e^-$ rule with coordination to two oxygen atoms and a covalent interaction with a third oxygen atom. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The synthesis of the imidotetraphenyldiphosphinic acid, $(Ph_2PO)_2NH$ [1], triggered the study of the coordination chemistry of the corresponding $[Ph_2P(O)NP(O)Ph_2]^-$ anion. This anion has been coordinated to an extensive range of elements, from main-group metals [2], non-metals [3] to transition metals [4], including internal transition metals [5]. It has been shown that its usual way of bonding is through the oxygen atoms in a bidentate chelate fashion as shown in Scheme 1, to give homoleptic complexes (see for example Refs. [2d,e,4f,h,5b,c]); however, it has been proposed that a dimer is realized in the complex $\{[((C_6H_5)_2PO)_2N]_2Ni\}_n$, where the Ni(II) adopts a tetrahedral geometry (determined by the spin moment in the solid state and in solution) [4c]. This kind of complexation can be accounted for by a di-μ-oxo interaction, Ni_2O_2. Such a di-μ-oxo interaction has been crystallographically detected in the dimer $[Mn\{Ph_2P(O)NP(O)Ph_2\text{-}\mu\text{-}O,O'\}_2]_2$, where two of the imidophosphinate ligands are bonded to a metal center in a monometallic biconnective fashion, while the other two, responsible for the μ-*O* bridges, are bonded in a bimetallic triconnective mode [4g], see Scheme 2.

An interesting trait of the coordination chemistry of the $[Ph_2P(O)NP(O)Ph_2]^-$ ion is the scarcity of its organometallic complexes, although there have been reports on heteroleptic complexes, for example $[Sn\{Ph_2P(O)NP(O)Ph_2\text{-}O,O'\}_2I_2]$ [2f], $[MoO_2\{Ph_2P(O)NP(O)Ph_2\text{-}O,O'\}_2]$ [4b], $[ReOCl_2\{Ph_2P(O)NP(O)Ph_2\text{-}O,O'\}]$ [4e] (Scheme 3); these do not belong to the organometallic class.

In this regard, we are aware of only three main-group organometallic complexes with $[Ph_2P(O)NP(O)Ph_2]^-$: the tin complex $n\text{Bu}_2Sn[Ph_2P(O)NP(O)Ph_2\text{-}O,O']_2$ [2h] and the organoelement complexes $Ph_3Te[Ph_2P(O)NP(O)Ph_2\text{-}O,O']$ [3a] and $Ph_2SbCl_2[Ph_2P(O)NP(O)Ph_2\text{-}O,O']$ [3b], Scheme 4.

We have not been able to find in the literature any transition organometallic complex containing the $[Ph_2P(O)NP(O)Ph_2]^-$ ion. Some years ago, we reported on the reaction of $BrMn(CO)_5$ with the sodium salt of $[Ph_2P(O)NP(O)Ph_2]$. This reaction afforded the homoleptic Mn(III) complex $Mn[Ph_2P(O)NP(O)Ph_2\text{-}O,O']_3$, thus reinforcing the general notion that oxygen-donor ligands stabilize manganese(III) species [4h]. In an effort to gain more insight into the course of this reaction, we have been able to isolate a new

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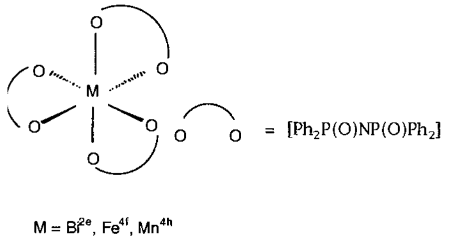
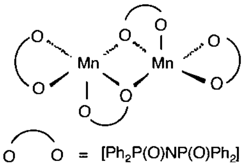
mixed-valence dimanganese complex synthesized from the $[Ph_2P(O)NP(O)Ph_2]^-$ anion with $[BrMn(CO)_5]$.

2. Experimental

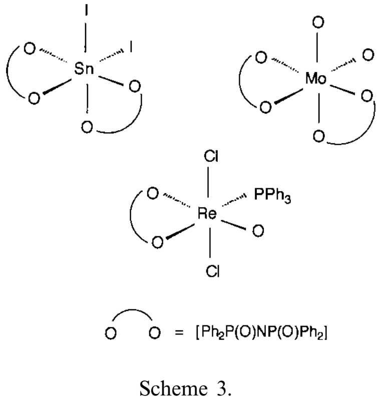
$[BrMn(CO)_5]$ [6] and $[Na\{(OPPh_2)_2N\}]$ [2f,4h] were prepared according to literature procedures. Unless otherwise stated all manipulations were carried out in an air open atmosphere. IR spectra were obtained in solution (4000–580 cm^{-1}) using a Nicolet FT-IR 5SX spectrometer and in KBr disk (4000–200 cm^{-1}) using a Perkin–Elmer 283B spectrometer. ^{1}H- and ^{31}P-NMR spectra were recorded in acetone-d_6 solutions using a JEOL 270-GSX instrument operating at 270 and 109.25 MHz, respectively. The chemical shifts are reported in ppm relative to Me_4Si and H_3PO_4 (85% aqueous solution), respectively. FAB(+) mass spectra were recorded using a JEOL SX-102A instrument. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The melting point was determined on a Fisher–Johns apparatus and is uncorrected.



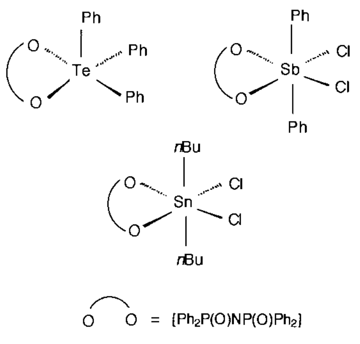
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

2.1. General procedure

2.1.1. Synthesis of $[Mn_2(CO)_3\{Ph_2P(O)NP(O)Ph_2\text{-}\mu\text{-}O,O'\}_3]$ (1)

$[Na\{(OPPh_2)_2N\}]$ (0.250 g; 0.567 mmol) was added to a solution of an equimolar amount of $[BrMn(CO)_5]$ (0.156 g; 0.567 mmol) in 70 ml of CH_2Cl_2. This suspension was heated until reflux temperature. At this temperature the reaction mixture was completely dissolved. Almost immediately a fine yellowish powder begins to form. The changes in the reaction were monitored by IR spectroscopy in the characteristic region for carbonyl stretching vibrations. The reaction mixture was allowed to react for 3.5 h. Longer reaction times showed no change in the ν(CO) pattern. The yellowish powder was filtered off remaining a bright yellow solution. The IR spectrum of the yellowish material in KBr pellet showed no recognizable functional groups. Removal of the solvent under reduced pressure resulted in a yellow product (0.195 g; 0.135 mmol; 71.3% yield) which crystallized from a 4:1 mixture of CH_2Cl_2–$CHCl_3$, m.p. 130 ° (dec.). Anal. Calc. for $C_{75}H_{60}Mn_2N_3O_9P_6\cdot CHCl_3$: C, 58.4, H, 3.94, N, 2.69. Found: C, 58.3, H, 4.1, N, 2.5%. IR (KBr, cm^{-1}): ν(CO) 1925vs, $\nu_{as}(P_2N)$ 1232m, ν(PO) 1129s, 1097m. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 140.7m, 135.3m. $^{31}P\{^1H\}$-NMR (CD_3OD, 121.423 MHz): δ 30.0s, 26.2s (3:1 relative intensity). MS; (m/e): 1358 $[M-3CO]^+$, 942 $\{Mn_2[(OPPh_2)_2N]_2\}^+$, 887 $\{Mn[(OPPh_2)_2N]_2\}^+$, B_p 471 $[Mn(OPPh_2)_2N]^+$.

2.2. Crystal data

$C_{75}H_{60}Mn_2N_3O_9P_6\cdot CHCl_3$, $M = 1562.39$, cubic, $a = 19.347(2)$ Å, $V = 7242(3)$ Å^3, $Z = 4$, $D_{calc} = 1.433$ g cm^{-3}, $F(000) = 3204$, space group $P2_13$, Mo–Kα radiation, $\lambda = 0.71037$ Å, crystal size $0.40 \times 0.32 \times 0.30$ mm^3.

2.3. Structure determination

Suitable crystals of **1** were obtained from a CH_2Cl_2–$CHCl_3$ 4:1 solution. Data were collected at 298 K on a

Table 1
Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths			
Mn(1)–Mn(2)	3.160(1) [a]		
Mn(1)–O(1)	2.343(6)	O(2)–P(2)	1.517(7)
Mn(1)–O(2)	2.086(7)	C(25)–O(3)	1.125(14)
Mn(2)–O(1)	2.056(6)	P(1)–C(1)	1.809(9)
Mn(2)–C(25)	1.811(10)	P(1)–C(7)	1.815(10)
O(1)–P(1)	1.537(6)	P(2)–C(13)	1.808(10)
P(1)–N(1)	1.580(9)	P(2)–C(19)	1.802(12)
P(2)–N(1)	1.605(9)		
Bond angles			
O(2)–Mn(1)–O(2b)	91.2(2)	Mn(1)–O(1)–Mn(2)	91.6(2)
O(2)–Mn(1)–O(1)	85.2(2)	O(1)–Mn(2)–C(25)	94.8(4)
O(2)–Mn(1)–O(1b)	123.5(2)	O(1)–Mn(2)–C(25a)	174.6(4)
O(2)–Mn(1)–O(1a)	145.2(2)	O(1)–Mn(2)–C(25b)	98.5(4)
O(1)–Mn(1)–O(1a)	68.6(2)		
Torsion angles			
N(1)–P(1)–O(1)–Mn(1)	−38.8	N(1)–P(2)–O(2)–Mn(1)	−24.3
O(1)–P(1)–N(1)–P(2)	43.9	O(1)–Mn(1)–O(2)–P(2)	23.6
O(2)–P(2)–N(1)–P(1)	−14.8	O(2)–Mn(1)–O(1)–P(1)	9.9

[a] This distance is non-bonding (see text).

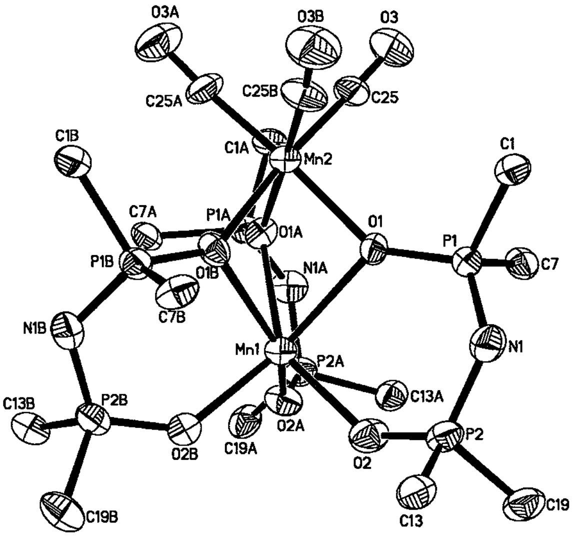


Fig. 1. Molecular structure of $[Mn_2(CO)_3\{Ph_2P(O)NP(O)Ph_2\text{-}\mu\text{-}O,O'\}_3]$ (**1**). Thermal ellipsoids are given at the 40% probability level. Only the *ipso* carbons of the phenyl groups are shown for clarity.

Siemens P4/PC diffractometer (Ni-filter) for 3145 reflections ($\theta/2\theta$ scan mode) of which 3011 were independent ($R_{int} = 2.17\%$) and 1845 ($F > 4.0\sigma(F)$) were used in the full-matrix least-squares refinement [7]. The structure was solved by direct methods. An empirical absorption correction was applied after isotropic refinement with the DIFABS program [8]. All non-hydrogen atoms were refined anisotropically. The structure has a rigorous C_3 symmetry axis. Hydrogen atom positions were calculated and their coordinates included in final cycles of refinement with fixed isotropic thermal parameters ($U = 0.08$ Å^2). The final R values are $R_1 = \Sigma|F_o - F_c|\Sigma|F_o| = 6.23\%$ and $wR_2 = [\Sigma w(|F_o - F_c|)^2/\Sigma|F_o|^2]^{1/2} = 6.72\%$ ($R_1 = 10.70\%$ and $wR_2 = 8.72\%$ for all data) with weights $w^{-1} = \sigma^2(F) + 0.0008F^2$; goodness-of-fit 1.29. The residual electron density from a final difference Fourier synthesis was in the range of 0.85, −0.87 e Å^{-3}.

3. Results and discussion

Some years ago we reported that the reaction of $[BrMn(CO)_5]$ with $[Na\{(OPPh_2)_2N\}]$ in boiling THF afforded the manganese(I) complex $Mn(CO)_4[Ph_2P(O)NP(O)Ph_2\text{-}O,O']$ as an air stable powder [4h]. Our attempts to crystallize this material in $CHCl_3$–hexane and CH_2Cl_2–hexane solutions resulted in the decomposition of the starting material and deposition of purple crystals of the manganese(III) complex $Mn[Ph_2P(O)NP(O)Ph_2\text{-}O,O']_3$. In an effort to study the course of these reactions we found that the change of solvent is of prime importance for the course of the reaction. The use of CH_2Cl_2 as solvent rendered the formation of complex **1** in good yield (see Section 2). After three days in an open atmosphere at room temperature, complex **1** underwent oxidation to the homoleptic manganese(III) complex $Mn[Ph_2P(O)NP(O)Ph_2\text{-}O,O']_3$.

The IR spectrum of **1** shows one broad band in the carbonyl stretching region (1925vs in KBr pellet). The $-Mn(CO)_3$ fragment of the dinuclear complex **1** gives rise to a carbonyl C_{3v} local symmetry corresponding to the $A_1 + E$ vibration modes where possibly both bands collapse into one due to the closeness in wavenumber. The IR spectrum in KBr pellet shows bands at 1129 versus $\nu_{as}(P_2N)$); 553s (ν_s(PO)); and 517m cm^{-1} (ν_{as}(PO)).

The NMR spectra showed broad signals in all the cases (^{31}P, ^1H and ^{13}C). This behavior may be due to the coupling of the ^{13}C nuclei with the manganese-55 nucleus, which is subjected to a rapid quadrupole-induced relaxation [9]; or to the paramagnetism of the Mn(II) ion for the ^{31}P, ^1H, and ^{13}C resonances. The ^{13}C-NMR spectrum shows two signals, one at 140.7m and the other at 135.3m ppm, arising from two different sets of phenyl groups. We were unable to detect any CO group ^{13}C-NMR signal. The $^{31}P\{^1H\}$-NMR spectrum exhibits two signals, 30.0 and 26.2 ppm evidencing the non-equivalence of the phosphorus atoms in solution for each OPNPO fragment. The mass spectrum shows the usual loss of the carbonyl groups [10] (see Section 2).

Selected bond distances and angles are listed in Table 1. Fig. 1 shows the structure of **1** with the atom numbering scheme.

The coordination to both metal centers causes the anion $[(OPPh_2)_2N]^-$ to adopt a *syn* conformation with a PNP angle of 124.4(6)° (in the acid $(OPPh_2)_2NH$ the molecule adopts a linear PNP disposition due to the prevalence of the $HOP(Ph_2)–N=P(Ph_2)O$ tautomer [11]). The three oxygen bridging interactions do not seem to introduce any appreciable distortion in this angle, since in the complex $Mn[Ph_2P(O)NP(O)Ph_2$-*O*,*O*′$]_3$ the PNP angles measure 124.6(6)° [4h]. These are standard values according to some reported PNP angles of the coordinated $[Ph_2P(O)NP(O)Ph_2]$ anion [2f,h,3,4b,d–f,h] (the largest reported PNP angle spans 137.9(5)° in the complex $[Ph_3Te\{Ph_2P(O)NP(O)Ph_2 - O,O'\}$ [3a] and the smallest angle amounts to 123.2(3)° in the complex $\{Ph_2P(O)NP(O)Ph_2$-*O*,*O*′$\}_2SnI_2$ [2f]). The OPNPO ligands in complex **1** are bonded in a bimetallic triconnective mode, hence there exist three different Mn–O bond distances, depending on the metal center, Mn(1) or Mn(2), with which each oxygen atom interacts. The bridging oxygen atoms, (O(1), O(1a) and O(1b)), present two different Mn–O bond distances: the short distance, 2.056(6) Å, arises from their interaction with the manganese atom of the $–Mn(CO)_3$ fragment, Mn(2); while the long distance, 2.343(6) Å, is a resultant of the interaction with the Mn(1) atom. This latter metal center is also coordinated to the oxygen atoms O(2), O(2a) and O(2b) at the other end of the inorganic backbones with a Mn–O bond distance of 2.086(7) Å. The P–O bond distances are equal within experimental error (1.527 Å), this also holds true for the P–N bond distances (1.593 Å). It is proposed a π delocalization in the OPNPO system since both P–O and P–N average bond distances in complex **1** range between a single P–O (1.60(2) Å in $Ph_2P(=S)OMe$ [12]) and a double P=O (1.487(2) Å in $Ph_3P(=O)$ [13]) bond distances. Similar P–N–P sequences with comparable bond lengths are commonly found in cyclic phosphazenes [14].

The six-membered MnO_2P_2N rings adopt a twisted-boat conformation (reflected by the torsion angles and the deviations from the Mn(1)–O(1)–O(2) plane shown in Table 1) with the Mn(1) and the N(1) atoms at the apices.

The overall complex **1** geometry can be regarded as confacial octahedral–trigonal prismatic. The $Mn[Ph_2P(O)NP(O)Ph_2]_3$ moiety's geometry is best described as a distorted trigonal prism with the largest O–Mn(1)–O angle of 145.2(2)° (this geometry could also be considered as a truncated prism with the O(2)–O(2a)–O(2b) triangular plane as the base; however, we prefer to describe it as a distorted trigonal prism since the sides of both triangles are not too dissimilar in magnitude: O(1)–O(1a), 2.639 Å and O(2)–O(2a), 2.980 Å). In the case of the $(\mu\text{-}O)_3Mn(CO)_3$ fragment the angles (C(25)–Mn(2)–O(1b), C(25a)–Mn(2)–O(1b), and C(25b)–Mn(2)–O(1a)) measure 174.6(4)°. In both metal centers the geometry distortions are due to the bridging interactions.

The O···O bite distance in **1** is 3.003 Å. This distance ranks intermediate among the reported OPNPO bite distances (among the longest distances reported are 3.646 Å in the complex $[Ph_3Te\{Ph_2P(O)NP(O)Ph_2$–*O*,*O*′$\}$ [3a] and 3.444 Å in K(18-crown-6)$[Ph_2P(O)NP(O)Ph_2$-*O*,*O*′$]\cdot H_2O$ [2i] and among the shortest distances is 2.85 Å in $Mn[Ph_2P(O)NP(O)Ph_2$-*O*,*O*′$]_3$, [4h]).

The Mn(1)–Mn(2) distance 3.160 Å is a rather short non-bonding distance. It has been reported a bonding distance of 3.126(2) Å between two metal centers in the complex $[Mn_3\text{-}\mu\text{-}(H)_3(CO)_{12}]$ [15]; however, we discard a formal bonding interaction between the Mn(1) and Mn(2) in the present complex since the fragment $–Mn(CO)_3$ fulfills the $18e^-$ rule with coordination to two oxygen atoms and a covalent interaction with a third oxygen atom.

4. Conclusions

The synthesis of the mixed-valence complex **1** from $[BrMn(CO)_5]$ and $[Na\{(OPPh_2)_2N\}]$ together with the fact that the Mn(III) complex $Mn[Ph_2P(O)NP(O)Ph_2$-*O*,*O*′$]_3$ can be obtained via aerial oxidation of complex **1** suggest that complex **1** is a reaction intermediate to $Mn[Ph_2P(O)NP(O)Ph_2$-*O*,*O*′$]_3$. It is therefore proposed that the oxidation from Mn(I) to Mn(III) takes place as shown in the next reaction scheme:

$$[BrMn(CO)_5] + NaL \rightarrow [Mn(CO)_4L] + CO + NaBr \tag{1}$$

$$2[Mn(CO)_4L] \overset{O_2}{\rightarrow} 1/2[MnL_2]_2 + MnO_2 + 8CO \tag{2}$$

$$[Mn(CO)_4L] + 1/2[MnL_2]_2 \rightarrow [Mn_2(CO)_3]L_3 + CO \tag{3}$$

$$[Mn_2(CO)_3L_3] \overset{O_2}{\rightarrow} [MnL_3] + MnO_2 + 3CO \tag{4}$$

$$L = [Ph_2P(O)NP(O)Ph_2]$$

where the oxidation process from Mn(I) to Mn(III) takes place in two steps, (2) and (4); while in the other (1) and (3), there is no change in the formal oxidation state of the Mn atoms. The mixed-valence complex herein reported is involved in the second oxidation step, Eq. (4); where the elimination of the $–Mn(CO)_3$ fragment from complex **1** affords the homoleptic Mn(III) complex $Mn[Ph_2P(O)NP(O)Ph_2$-*O*,*O*′$]_3$ formerly synthesized by us [4h]. Further studies are currently underway in order to have a better understanding of this oxidation process.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 160545 for compound **1**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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