

A new ligating mode for the anions of the type $[\text{R}_2\text{P}(\text{S})\text{NP}(\text{S})\text{R}_2]^-$: study of the interaction of $[\text{K}\{\text{Me}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Me}_2\}]$ with the early transition halometalcarbonyl, $[\text{BrMn}(\text{CO})_5]$

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Abstract

The thermal reaction of $[\text{BrMn}(\text{CO})_5]$ with $[\text{K}\{\text{Me}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Me}_2\}]$ afforded the dinuclear complex $[\text{Mn}_2(\text{CO})_6\{\text{Me}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Me}_2-\mu-S,S'\}_2]$ (**1**). The single-crystal X-ray analysis of **1** shows that this complex is formed by three fused cycles: one four-membered ring and two six-membered rings. The latter show a pseudochair conformation with the Mn and N atoms at the apices. There are two molecules, **1** and **1a**, in the unit cell crystallographically independent with identical conformation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Bromopentacarbonylmanganese; Dichalcogenoimidodiphosphinate anions; Early transition metal; X-ray analysis

1. Introduction

The coordination chemistry of the $[\text{R}_2\text{P}(\text{S})\text{NP}(\text{S})\text{R}_2]^-$ ($\text{R} = \text{Ph}$ or Me) anions [1] has recently attracted a great deal of attention. This has resulted in a varied and rich chemistry [2,3]. Since the first reported complex with a transition metal, an Ni(II) complex [3p], the ligand $[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ has shown that its usual way of binding a metal center is through the sulfur atoms in a bidentate chelate fashion [2j,m,n,p-y]. The anion $[\text{Me}_2\text{P}(\text{S})\text{NP}(\text{S})\text{PMe}_2]^-$ presents a similar behavior [2c,i,l,o,3a,c,i-o]. Surprisingly the geometry around the Ni atom in both complexes, $[\text{Ni}\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2-S,S'\}_2]$ [2j,x,3a,l] and $[\text{Ni}\{\text{Me}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Me}_2-S,S'\}_2]$ [3a,k,l,n], is tetrahedral. Although many of the reported complexes of these anions are homoleptic tris and bis chelate [2j,n,q,x-z,3b,e,g-n,p], there is a growing number of imidodiphosphinato metal complexes with ancillary ligands [2d-f,k-n,p,s-w]. The contribution of transition metal organometallic complexes with imidodiphosphinato anions has been outstanding in this

last category, since they present, among other things, new ligating modes. For example, Smith and co-workers have recently reported the first organometallic complexes of the late transition-metals, ruthenium, rhodium, palladium and platinum, with σ/π -bonded hydrocarbon auxiliary ligands with a novel binding mode confirmed by X-ray crystallography analysis for the binuclear complex $[\{\text{Pd}-\eta^3-(\text{C}_3\text{H}_5)[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{Se})\text{Ph}_2-\text{Se}\}_2]$ [2e]. This complex possesses a central four-membered Pd_2Se_2 core and two pendant $\text{P}(\text{O})\text{Ph}_2$ moieties. Such a type of complex is not known for the anions $[\text{R}_2\text{P}(\text{S})\text{NP}(\text{S})\text{R}_2]^-$ ($\text{R} = \text{Ph}$ and $\text{R} = \text{Me}$). As far as we are concerned, the literature reports on the interaction of the $[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ anion with Mn have been limited to two structurally characterized complexes: the homoleptic Mn(II) complex $[\text{Mn}\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2-S,S'\}_2]$ with a tetrahedral geometry around the metal center [3h] and the Mn(I) complex $[\text{Mn}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2-S,S'\}_2]$, in which the six-membered inorganic metallacycle $\text{MnS}_2\text{P}_2\text{N}$ adopts two different ring conformations in the same unit cell [2m]. In both cases the bonding of the imidodithiodiphosphinato ligand to the manganese atom is achieved through the sulfur atoms. To our knowledge, the interaction of the $[\text{Me}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Me}_2]^-$ anion with manganese has not been reported.

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We report here the synthesis and characterization of a new manganese complex $[\text{Mn}_2(\text{CO})_6\{\text{Me}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Me}_2\text{-}\mu\text{-S,S'}\}_2]$ (**1**), with an unprecedented ligating mode for $[\text{Me}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Me}_2]^-$.

2. Experimental

All preparative work was carried out in an atmosphere of dry oxygen free nitrogen, using conventional Schlenk techniques. Solvents were carefully dried; tetrahydrofuran, ethyl ether and hexane were dried and deoxygenated by distillation from sodium benzophenone ketyl. $[\text{BrMn}(\text{CO})_5]$ [4] and $[\text{K}\{(\text{SPMe}_2)_2\text{N}\}]$ [1c,2o] were prepared according to the literature procedures. IR spectra were obtained in solution (4000–580 cm^{-1}) using a Nicolet FT-IR 55X spectrometer and in KBr disk (4000–200 cm^{-1}) using a Perkin–Elmer 283B spectrometer. ^1H - 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 TMS 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.

2.1. General procedure

2.1.1. Synthesis of

$[\text{Mn}_2(\text{CO})_6\{\text{Me}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Me}_2\text{-}\mu\text{-S,S'}\}_2]$ (**1**)

$[\text{K}\{(\text{SPMe}_2)_2\text{N}\}]$ (0.100 g; 0.418 mmol) was added to a solution of an equimolar amount of $[\text{BrMn}(\text{CO})_5]$ (0.115 g; 0.418 mmol) in 50 ml anhydrous THF. After 30 min under reflux an off-white precipitate was deposited. The changes in the reaction were monitored by IR spectroscopy in the characteristic region for carbonyl stretching vibrations. The reaction mixture was stirred under THF reflux for 3 h. The off-white powder (KBr) was filtered off leaving a yellow solution. Removal of the solvent under reduced pressure resulted in a yellow product (0.100 g; 70% yield) which crystallized from a 4:1 mixture of CH_2Cl_2 –hexane, m.p. 140° (dec.). Anal. Found: C, 24.1; H, 3.4; N, 3.9%. Calc. for $\text{C}_{14}\text{H}_{24}\text{Mn}_2\text{N}_2\text{O}_6\text{P}_4\text{S}_4$: C, 24.79; H, 3.57; N, 4.13%. IR (KBr, cm^{-1}): $\nu(\text{CO})$ 2080m, 1980s, 1960vs; $\nu_{\text{as}}(\text{P}_2\text{N})$ 1185s; $\nu_{\text{s}}(\text{PS})$ 524m, $\nu_{\text{as}}(\text{PS})$ 508m. ^1H -NMR (acetone- d_6 , 270 MHz, δ): 1.80 (m), 1.68 (m) [$^2J(\text{PCH}) + ^4J(\text{PNPCH}) = 12.6$ Hz]. $^{31}\text{P}\{^1\text{H}\}$ -NMR (acetone- d_6 , 109.25 MHz δ): 43.17 (d), 40.91 (d, [$^2J(\text{PP}) = 12.4$ Hz]). MS (m/e): 594, $[\text{M} - 3\text{CO}]^+$; 510, $\{\text{Mn}_2[(\text{SPMe}_2)_2\text{N}]_2\}^+$; 255, $[\text{Mn}(\text{SPMe}_2)_2\text{N}]^+$; 147, $[\text{MnP}_2\text{Me}_2]^+$; P_B 73, $[\text{CH}_2=\text{P}=\text{N}=\text{CH}_2]^+$.

2.2. Crystal data

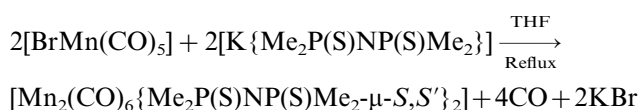
$\text{C}_{14}\text{H}_{24}\text{Mn}_2\text{N}_2\text{O}_6\text{P}_4\text{S}_4$, M 678.4, triclinic, $a = 10.531(2)$, $b = 10.998(2)$, $c = 13.433(2)$ Å; $\alpha = 75.71(2)$, $\beta = 74.53(2)$, $\gamma = 69.62(2)^\circ$; $V = 1385.1(3)$ Å³, $Z = 2$, $D_c = 1.626$ g cm^{-3} , $F(000) = 688$, space group $P-1$, $\text{Cu-K}\alpha$ radiation, $\lambda = 0.71037$ Å, crystal size $0.20 \times 0.14 \times 0.10$ mm³.

2.3. Structure determination

Suitable crystals of **1** were obtained from a 4:1 CH_2Cl_2 –hexane solution. Data were collected at 298 K on a Nicolet P3/F four-cycle diffractometer (Ni-filter) for 4138 reflections ($\theta/2\theta$ scan mode) of which 3446 were independent ($R_{\text{int}} = 5.50\%$) and 2626 ($F > 4.0\sigma(F)$) were used in the full-matrix least-squares refinement [5]. The structure was solved by direct methods. An empirical absorption correction was applied after isotropic refinement with the DIFABS program [6]. All nonhydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and their coordinates included in final cycles of refinement with fixed isotropic thermal parameters ($U = 0.08$ Å²). The final R values are $R = \Sigma|F_o - F_c|/\Sigma|F_o| = 6.60\%$ and $wR = [\Sigma w(|F_o - F_c|)^2/\Sigma|F_o|^2]^{1/2} = 8.52\%$ ($R = 8.14\%$ and $wR = 10.39$ for all data) with weights $w^{-1} = \sigma^2(F) + 0.0015F^2$ goodness-of-fit 1.49. The residual electron density from a final difference Fourier synthesis was in the range of 1.17, -0.45 e Å⁻³.

3. Results and discussion

The metathesis reaction of $[\text{BrMn}(\text{CO})_5]$ with $[\text{K}\{(\text{SPMe}_2)_2\text{N}\}]$ according to the following equation:



afforded an air-stable yellow crystalline powder which after spectroscopic analysis turned out to be $[\text{Mn}_2(\text{CO})_6\{\text{Me}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Me}_2\text{-}\mu\text{-S,S'}\}_2]$ (**1**). The IR spectrum of **1** shows three bands in the carbonyl stretching region (2085m, 1990s and 1952s cm^{-1} in THF). The dinuclear nature of complex **1** with two $-\text{Mn}(\text{CO})_3$ fragments might suggest a D_{3d} overall molecule symmetry accounting for two bands in the $\nu(\text{CO})$ IR spectrum region; however, the $[\text{Me}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Me}_2]$ moieties' unsymmetrical coordination prevents this situation giving rise to a carbonyl C_{3v} local symmetry corresponding to the $A_1 + E$ vibration modes where possibly the E band splits into two [7]. The IR spectrum in the KBr pellet shows bands at 2080 (m), 1980 (s), 1960 (vs) cm^{-1} corresponding to $\nu(\text{CO})$, and 1185 (s),

524 (m), 508 (s) cm^{-1} assigned to $\nu_{\text{as}}(\text{P}_2\text{N})$, $\nu_{\text{s}}(\text{PS})$ and $\nu_{\text{as}}(\text{PS})$, respectively [3a,e].

The $^1\text{H-NMR}$ spectrum shows two multiple signals, at 1.80 (m) and 1.68 (m) ppm, due to the methyl groups. Both methyl groups attached to each phosphorus atom are equivalent. The $^{31}\text{P}\{^1\text{H}\}$ spectrum exhibits two doublets with a $^2J(\text{PP})$ coupling constant of 12.4 Hz evidencing the nonequivalence of the phosphorus atoms in solution for each PNP fragment. No carbonyl signals were detected in the $^{13}\text{C-NMR}$ spectrum. This behavior may be a consequence of the broadening of the signals due to the coupling of the carbon-13 nucleus with the manganese-55 nucleus, which is subjected to a rapid quadrupole-induced relaxation [8], and/or a dynamic process of the carbonyl groups [9]; however, even at low temperatures (-80°C) no signals were observed. The mass spectrum shows the usual loss of the carbonyl groups [10] (Section 2).

The unit cell consists of two crystallographically independent molecules **1** and **1a** with very similar conformations. Selected bond distances for both molecules are listed in Table 1 and selected angles are shown in Table 2. Fig. 1 shows the structure of **1** with the atom numbering scheme. Since the conformations in **1** and **1a** are basically the same, only that of **1** will be discussed.

Single-crystal X-ray structure studies have shown [2o] that in the $(\text{SPMe}_2)_2\text{NH}$ molecule the sulfur atoms display an *anti* disposition and the PNP system is bent ($133.2(2)^\circ$). In the present case the coordination to the metal center causes the anion $[(\text{SPMe}_2)_2\text{N}]^-$ to adopt a *syn* conformation with no change in the PNP angle,

Table 1
Selected bond lengths for **1** and **1a** (Å)

1			
Mn(1)–Mn(1a)	3.694 ^a		
Mn(1)–S(1)	2.438(3)	Mn(1)–S(2)	2.448(3)
Mn(1)–C(5)	1.791(14)	Mn(1)–C(6)	1.791(12)
Mn(1)–C(7)	1.817(11)	Mn(1)–S(2a)	2.437(3)
S(1)–P(1)	2.018(3)	S(2)–P(2)	2.062(3)
S(2)–Mn(1a)	2.437(3)	P(1)–C(2)	1.594(11)
P(1)–C(1)	1.796(14)	P(2)–C(3)	1.787(11)
P(2)–N(1)	1.558(9)	C(5)–O(5)	1.800(12)
P(2)–C(4)	1.790(17)	C(5)–O(5)	1.161(18)
C(6)–O(6)	1.126(16)	C(7)–O(7)	1.141(14)
1a			
Mn(2)–Mn(2a)	3.701 ^a		
Mn(2)–S(3)	2.434(4)	Mn(2)–S(4)	2.441(2)
Mn(2)–C(12)	1.791(14)	Mn(2)–C(13)	1.780(11)
Mn(2)–C(14)	1.774(9)	Mn(2)–S(4a)	2.431(2)
S(3)–P(3)	2.015(3)	S(4)–P(4)	2.059(4)
S(4)–Mn(2a)	2.431(2)	P(3)–C(8)	1.801(11)
P(3)–C(9)	1.791(14)	P(3)–N(2a)	1.592(8)
P(4)–N(2)	1.584(10)	P(4)–C(10)	1.791(10)
P(4)–C(11)	1.802(11)	N(2)–P(3a)	1.592(8)
C(12)–O(12)	1.164(17)	C(13)–O(13)	1.146(14)
C(14)–O(14)	1.166(12)		

^a These distances are nonbonding.

Table 2
Selected bond angles ($^\circ$) for **1** and **1a**

1			
Mn(1)–C–O(<i>mean</i>)	176.4(11)		
C(7)–Mn(1)–S(2a)	95.6(4)	C(7)–Mn(1)–C(6)	90.4(5)
S(2)–Mn(1)–S(2a)	81.7(1)	S(2)–Mn(1)–C(6)	96.8(5)
S(1)–Mn(1)–S(2a)	81.1(1)	S(1)–Mn(1)–C(6)	93.0(4)
C(5)–Mn(1)–S(2a)	95.0(4)	C(5)–Mn(1)–C(6)	86.8(6)
C(5)–Mn(1)–C(7)	91.7(5)	C(6)–Mn(1)–S(2a)	173.6(3)
C(7)–Mn(1)–S(2)	85.6(4)	C(7)–Mn(1)–S(1)	175.2(3)
S(2)–Mn(1)–S(1)	97.3(1)	C(5)–Mn(1)–S(2)	175.6(4)
S(1)–Mn(1)–C(5)	85.1(3)		
Mn(1)–S(2)–P(2)	110.3(2)	S(2)–P(2)–C(4)	108.2(4)
S(2)–P(2)–N(1)	119.1(3)	C(4)–P(2)–C(3)	106.0(7)
P(2)–N(1)–P(1)	133.0(6)	N(1)–P(2)–C(3)	111.6(6)
N(1)–P(1)–S(1)	116.8(3)	N(1)–P(2)–S(2)	119.1(3)
P(1)–S(1)–Mn(1)	113.3(1)	C(4)–P(2)–N(1)	106.2(6)
1a			
Mn(2)–C–O(<i>mean</i>)	176.3(11)		
C(12)–Mn(2)–S(4)	96.1(3)	C(12)–Mn(2)–C(13)	90.1(6)
S(4a)–Mn(2)–S(4)	81.1(1)	S(4a)–Mn(2)–C(13)	97.1(3)
S(3)–Mn(2)–S(4)	80.9(1)	S(3)–Mn(2)–C(13)	93.1(5)
C(14)–Mn(2)–S(4)	94.7(3)	C(14)–Mn(2)–C(13)	87.3(5)
C(14)–Mn(2)–C(12)	91.5(6)	C(13)–Mn(2)–S(4)	173.5(5)
C(12)–Mn(2)–S(4a)	86.2(3)	C(12)–Mn(2)–S(3)	175.0(3)
S(4a)–Mn(2)–S(3)	97.2(1)	C(14)–Mn(2)–S(4a)	175.0(4)
S(3)–Mn(2)–C(14)	84.8(5)		
Mn(2)–S(4a)–P(4a)	110.8(1)	S(4a)–P(4a)–C(10a)	106.9(4)
S(4a)–P(4a)–N(2a)	118.8(3)	C(10a)–P(4a)–C(11a)	105.1(5)
P(4a)–N(2a)–P(3)	131.0(6)	N(2a)–P(4a)–C(11a)	112.6(6)
N(2a)–P(3)–S(3)	116.5(4)	N(2a)–P(4a)–S(4a)	118.8(3)
P(3)–S(3)–Mn(2)	113.0(1)	C(10a)–P(4a)–N(2a)	107.3(6)

$133.0(6)^\circ$. Both manganese–sulfur bonds, Mn(1)–S(1) 2.438(3) and Mn(1)–S(2) 2.448(2), as well as the nitrogen–phosphorus bonds, P(2)–N(1) 1.558(9), P(1)–N(1) 1.594(11) Å, in the $\text{MnS}_2\text{P}_2\text{N}$ system, are equal within experimental error. The phosphorus–sulfur bonds are different, P(2)–S(2) 2.062(3) and P(1)–S(1) 2.018(3) Å. The longest P–S bond length points at the participation of the S(2) atom in a bridge-bond [2o,3d]. Both P(2)–S(2) and P(1)–S(1) distances are intermediate between the P–S and P=S bond distances, and the P–N bond distances (average 1.576 Å) are shorter than the analogous bond distances in the free ligand (average 1.677 Å [2o]), but longer than the P=N bond distance, 1.529(2) Å [11], all this suggests that the $\text{S}_2\text{P}_2\text{N}$ system is delocalized as in most of the $[\text{R}_2\text{P}(\text{S})\text{NP}(\text{S})\text{R}_2]^-$, R = Ph, Me metal complexes reported so far. The structure of compound **1** consists of a tricyclic system entailing one four-membered ring fused with two six-membered-rings. The $\text{MnS}_2\text{P}_2\text{N}$ rings adopt a pseudochair conformation with the Mn and N atoms at the apical positions. The torsion angles Mn(1)–S(2)–P(2)–N(1) and Mn(1)–S(1)–P(1)–N(1) are 43.6 and 42.4 $^\circ$, respectively (in an ideal chair conformation these angles should be 60 $^\circ$). This distortion is caused by the bond lengths' differences in the $\text{MnS}_2\text{P}_2\text{N}$ ring. As a conse-

quence of these unequal bond lengths the methyl groups at the phosphorus atoms lie in pseudoaxial (or pseudoequatorial) positions, the shortest distance between two methyl carbons on different phosphorus atoms in the same ring is 3.803 Å. It has been proposed that at a distance of 3.629 Å there are interactions between hydrogen atoms associated with the CH₃(axial)–CH₃(axial) contact in the complex [Fe{Me₂P(S)NP(S)Me₂-μ-S,S'}₂], a reflection of this is the PNP angle 136.1(0.6)° [3i] (in the free ligand this angle spans 133.2(2)° [2o]). In the present case the value of the PNP angle, 133.0(6)°, together with the distance CH₃(pseudoax.)–CH₃(pseudoax.), 3.803 Å, for the [Mn₂(CO)₆{Me₂P(S)NP(S)Me₂-μ-S,S'}₂] complex point up the lack of 1,3-methyl interactions in the six-membered Mn₂S₂P₂N rings. The coordination geometry around the manganese atom is distorted octahedral with two carbonyl carbon atoms and two sulfur atoms, one bridging and one terminal sulfur atom, in the equatorial plane (deviation from the best plane C₂MnS₂: Mn(1) 0.0668, C(5) 0.0006, C(7) – 0.0006, S(1) – 0.0005, S(2) 0.0004 Å). The distortion in the octahedron is largely due to the strain imposed by the four-membered ring. The axial sites are occupied by one carbonyl carbon atom and one sulfur atom, the three CMnS angles are of similar magnitude 175.2(3), 175.6(4) and 173.6(3)°. The distances Mn–C(carbonyl group), average 1.799 Å, are as expected for SMn(CO) systems, where the S atom lies *trans* to a carbonyl group, for example in the heterocubane [MnSR(CO)₃]₄, R = furfuryl [12], the Mn–C(carbonyl group) average distance is 1.791(15)°. The four-membered ring is a rhomboid formed by the Mn₂S₂ system with SMnS and

MnSMn internal angles of 81.7(1) and 98.3(1)°, respectively. The Mn–S bond distances are equal within experimental error, average 2.441(3) Å, and are a little longer than Σ_{cov} (Mn,S) = 2.41 Å [13] indicating the covalent nature of the Mn–S bond. The S··S bite in **1** is 3.195 Å. This bite distance is rather short compared with the distances reported for the complexed [Ph₂P(S)NP(S)Ph₂] anion [2j,m,r].

Several years ago we reported on the reaction of [K{Ph₂P(S)NP(S)Ph₂}] with [BrMn(CO)₅] to give the complex [Mn(CO)₄{Ph₂P(S)NP(S)Ph₂-S,S'}] under the same reaction conditions reported in the present paper [2m]. It is interesting to notice that the substitution of the methyl groups for the phenyl groups at the phosphorus atoms of the imidodithiodiphosphinate ligand leads to the dinuclear complex formation in the present case. Although it has been proposed that such coordination type could be realized by the [Ph₂P(S)NP(S)Ph₂][–] anion in the [Cu(I)L]_n (L = [Ph₂P(S)NP(S)Ph₂]) oligomers, it has been discarded due to the small angles around the sulfur atom [3c]. The M₂E₂ unit has been detected by X-ray crystallography analysis in two cases. (a) The case where M = Na and E₂ = O, S for the [Na{Ph₂P(O)NP(S)Ph₂-μ-O}] complex [14], where the bridging atom is oxygen, and (b) the case where M = K and E₂ = S, S; here both sulfur atoms form bridges to build up a ladder-like polymer chain with the ligand [Ph₂P(S)NP(S)Ph₂] [2r]. This kind of bridging interaction has not been previously reported for the [Me₂P(S)NP(S)Me₂][–] anion.

4. Conclusions

The complex reported in this paper adds to the list of the few complexes formed by an organometallic carbonyl fragment of the early transition metals with the imidodithiodiphosphinate ligands. The formation of this complex together with some previous studies shows that the substituents at the phosphorus atoms of the anions determine the nature of the resulting complex. In our case the substitution of methyl groups for phenyl groups in the SPNPS-backbone leads to the formation of a dinuclear complex, [Mn₂(CO)₆{Me₂P(S)NP(S)Me₂-μ-S,S'}₂], with bridging sulfur atoms instead of the expected mononuclear complex, [Mn(CO)₄{Me₂P(S)NP(S)Me₂-S,S'}], analogous to the [Mn(CO)₄{Ph₂P(S)NP(S)Ph₂-S,S'}] complex previously reported by us.

5. Supplementary material

Supplementary data (atomic coordinates, bond lengths and angles and thermal parameters) have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 155056. Copies of the data may be

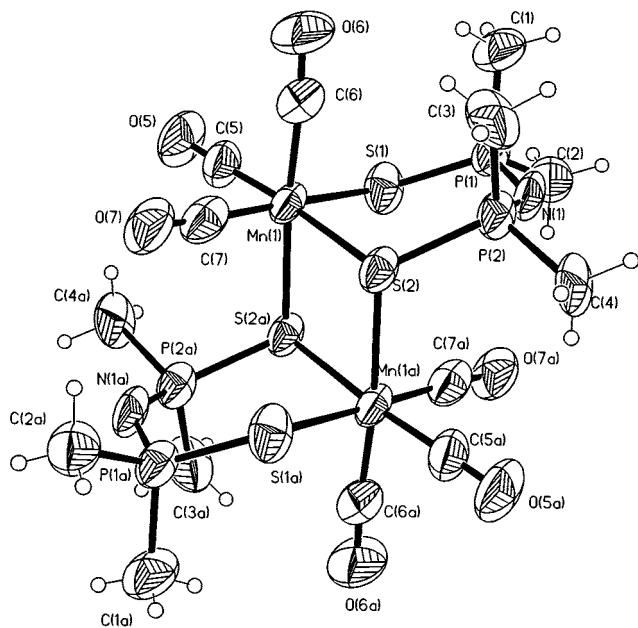


Fig. 1. Three-dimensional representation of the structure of **1**.

obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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