Synthesis, spectroscopic characterization and crystal and molecular structure of tetrakis(carbonyl)(tetraphenyldithioimidodiphosphinato)manganese(I), Mn(CO)₄[(SPPh₂)₂N]

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Abstract

$Mn(CO)_4[(SPPh_2)_2N]$ was prepared by allowing $[Mn(CO)_5]Br$ to react with $K[(SPPh_2)_2N]$, in THF. The compound was characterized by IR, mass and NMR (^1H, ^{13}C, ^{31}P) spectroscopy, and its crystal and molecular structure was determined by single-crystal X-ray diffraction. The lattice contains two independent, monomeric molecules, (1) and (1a). The metal atom has a distorted octahedral coordination geometry ($C_{ax}-Mn-C_{ax}$ 175.9(3)° in (1), 176.9(3)° in (1a)), with two carbonyl groups and the two sulfur atoms of the symmetric monometallic bidentate (mean P–S 2.021(2) Å in (1), 2.020(2) Å in (1a)) dithio ligand unit in equatorial positions (mean Mn–S 2.420(2), Mn–C$_{eq}$ 1.804(4), Mn–C$_{ax}$ 1.855(5) Å in (1), Mn–S 2.417(2), Mn–C$_{eq}$ 1.78(2), Mn–C$_{ax}$ 1.862(5) Å in (1a)). The main difference between the two independent molecules is the conformation of the inorganic MnS_2P_2N chelate ring.

Keywords: Manganese; Metal carbonyl; Dithioimidodiphosphinato ligand

1. Introduction

Metal derivatives containing anionic thiophosphorus ligands represent a research field of continuous interest owing either to their structural diversity or their particular uses (e.g. metal extractions, oil additives, biological activity, etc.). A large amount of work has been concerned with the investigation of inorganic and organometallic compounds of 1,1-dithiophosphorus ligands, i.e. phosphorodithioato, $(RO)_2PS_2^-$ (**a**), or phosphinodithioato, $R_2PS_2^-$ (**b**) [1,2], but there is relatively little knowledge of metal complexes of dithioimidodiphosphinato ligands (**c**), especially those containing organometallic moieties [3,4]. Such ligands are of par-

ticular interest due to the flexibility of the S–P–N–P–S backbone and their large S $\cdots$ S bite, which is larger than that of 1,1-dithio ligands (approx. 3.7–4.0 vs. approx. 3.0 Å).
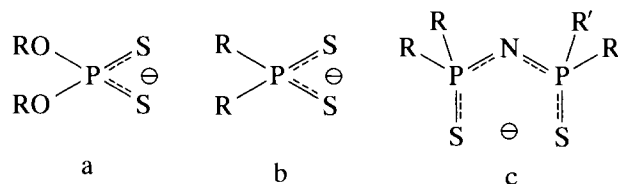

So far, manganese carbonyl derivatives of dithiophosphorus ligands have been only sparingly investigated. Early works described the syntheses and infrared spectra of complexes of the type: $Mn(CO)_4(S_2PR_2)$, $Mn(CO)_3(L)(S_2PR_2)$ (L = Py, PPh_3), and $[Mn(CO)_3(S_2PR_2)]_2$, for which structures containing monometallic bidentate (**d** and **e**) and bimetallic tridentate (**f**) phosphinodithioato groups have been proposed [5–10].

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The dimeric structure **f** has been confirmed by X-ray diffraction for the rhenium analog, $[Re(CO)_3(S_2PEt_2)]_2$ [11].
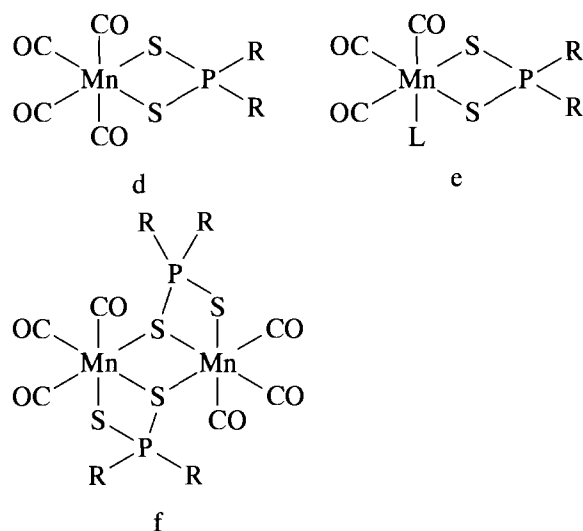
We report here on the synthesis, spectroscopic characterization and single-crystal structure of tetrakis-(carbonyl)(tetraphenyldithioimidodiphosphinato)manganese(I), $Mn(CO)_4[(SPPh_2)_2N]$, which is the first organomanganese derivative containing this type of ligand.

2. Results and discussion

The title compound was obtained according to Eq. (1) as yellow-orange crystals, partially soluble in THF, benzene, hexane or chloroform:

$$Mn(CO)_5Br + K[(SPPh_2)_2N]$$
$$\longrightarrow Mn(CO)_4[(SPPh_2)_2N] + CO + KBr \quad (1)$$
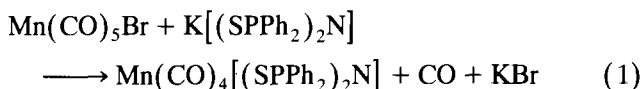
The infrared spectrum shows the expected four bands in the carbonyl stretching region (2088m, 2015s, 1988s,

and 1960s cm^{-1}, in *n*-hexane solution, and 2080m, 2000vs, 1993vs, 1960vs cm^{-1}, in KBr pellet), corresponding to non-degenerate $\nu(CO)$ vibrations $(2A_1 + B_1 + B_2)$ [12]. This behavior is characteristic of pseudooctahedral complexes with a carbonyl C_{2v} local symmetry, and is consistent with a monometallic bidentate coordination pattern of the dithio ligand, involving both sulfur atoms [6,7]. The infrared spectrum in KBr pellet shows medium intensity bands assigned to $\nu(PS)$ (600, 565 cm^{-1}) and $\nu_{as}(P_2N)$ (1210 cm^{-1}) stretching vibrations [13,14]. The latter is indicative of the coordination of the dithioimidodiphosphinato group in deprotonated form (cf. $\nu_{as}(P_2NH)$ approx. 930 cm^{-1} in $(SPPh_2)_2NH$) [13,14].

The ^{31}P NMR spectrum exhibits only one sharp resonance, suggesting the equivalence of phosphorus atoms in solution. In the aromatic region of the ^{13}C NMR spectrum the resonance of the *ipso* carbons appears as a doublet of doublets owing to phosphorus–

Table 1
Important bond distances (Å) in $Mn(CO)_4[(SPPh_2)_2N]$

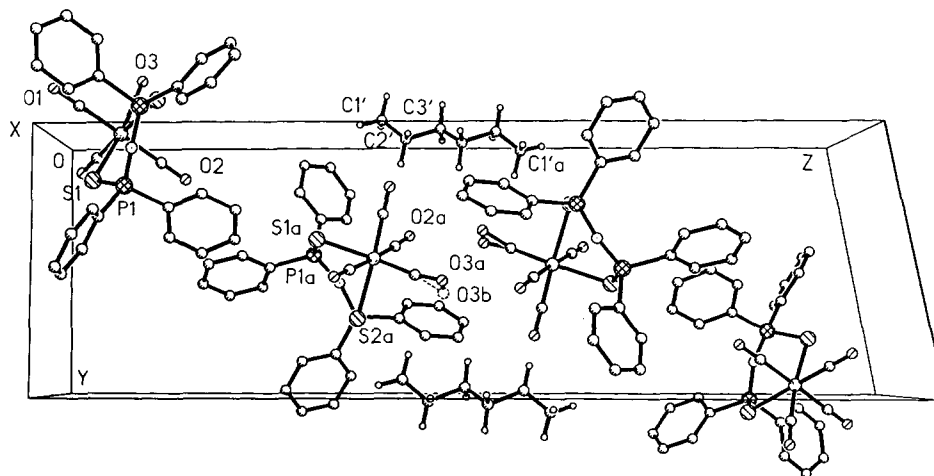| Molecule (1)		Molecule (1a)	
Mn(1)–S(1)	2.423(2)	Mn(1a)–S(1a)	2.412(2)
Mn(1)–S(2)	2.417(2)	Mn(1a)–S(2a)	2.421(2)
Mn(1)–C(1)	1.858(5)	Mn(1a)–C(1a)	1.865(7)
Mn(1)–C(2)	1.851(6)	Mn(1a)–C(2a)	1.858(7)
Mn(1)–C(3)	1.806(8)	Mn(1a)–C(3a)	1.765(7)
Mn(1)–C(4)	1.801(6)	Mn(1a)–C(4a)	1.786(6)
C(1)–O(1)	1.124(7)	C(1a)–O(1a)	1.133(9)
C(2)–O(2)	1.142(7)	C(2a)–O(2a)	1.135(8)
C(3)–O(3)	1.142(9)	C(3a)–O(3a) [a]	1.140(13)
C(4)–O(4)	1.137(7)	C(4a)–O(4a)	1.154(8)
P(1)–S(1)	2.023(2)	P(1a)–S(1a)	2.029(2)
P(2)–S(2)	2.018(2)	P(2a)–S(2a)	2.011(2)
P(1)–N(1)	1.586(3)	P(1a)–N(1a)	1.571(4)
P(2)–N(1)	1.581(4)	P(2a)–N(1a)	1.599(5)

[a] The terminal O(3a) is disordered: C(3a)–O(3b) 1.283(15).

Fig. 1. View of the cell unit of $Mn(CO)_4[(SPPh_2)_2N]$ (the *n*-hexane molecule is also included).

carbon couplings (^{1}J(PC) 71.8, ^{3}J(PC) 2.0 Hz), while the *ortho*, *meta* and *para* carbon signals exhibit a doublet (^{2}J(PC) 8.1 Hz), doublet (^{3}J(PC) 8.1 Hz), and singlet pattern, respectively. In the carbonyl region, two broad, singlet resonances ($\delta = 214.95$ and 209.54 ppm) are assigned to carbonyl carbon atoms. The broadening of the carbonyl signals can be attributted to coupling with the manganese nucleus, which is undergoing a moderately rapid quadrupole-induced relaxation [15].

Crystals of $Mn(CO)_4[(SPPh_2)_2N]$, suitable for the single-crystal X-ray diffraction investigation, were obtained from *n*-hexane. The unit cell contains two independent, monomeric molecules (abbreviated (1) and (1a) in the subsequent discussion) of the title compound, and, additionally, a molecule of *n*-hexane (solvent of recrystallization) for each four molecules of $Mn(CO)_4[(SPPh_2)_2N]$ (Fig. 1). Relevant bond distances (Table 1) and bond angles (Table 2) are given for the independent molecules (1) and (1a). Fig. 2 shows a three-dimensional representation of molecule (1), with the corresponding atom numbering scheme.

The dithioimidodiphosphinato ligand is symmetrically coordinated to Mn via both sulfur atoms, with equivalent Mn–S bond distances (av. 2.420(2) and 2.417(2) Å in (1) and (1a), respectively) indicative of their covalent nature (Σ_{cov}(Mn, S) = 2.41 Å) [16]. Moreover, in the SPNPS backbone the phosphorus–
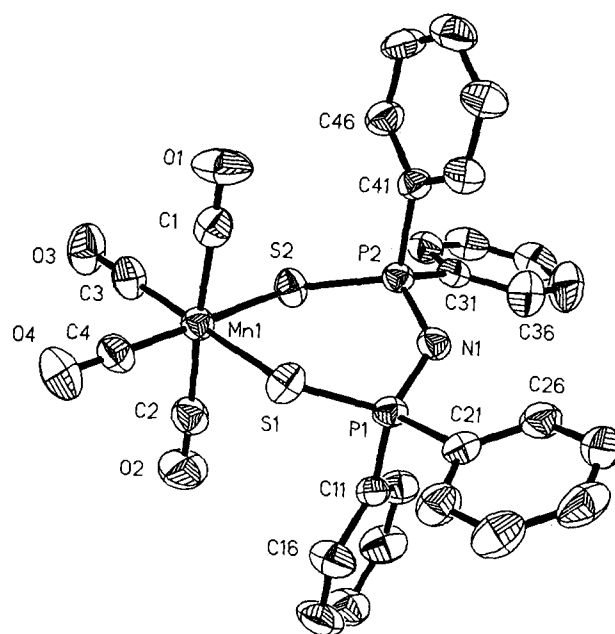

Fig. 2. Three dimensional representation of the monomeric structure of $Mn(CO)_4[(SPPh_2)_2N]$(molecule (1)).

sulfur and phosphorus–nitrogen bond distances are also equivalent (av. P–S and P–N: 2.021(2) and 1.584(4) Å in (1), 2.020(2) and 1.585(5) Å in (1a)). They are

Table 2
Important bond angles (°) in $Mn(CO)_4[(SPPh_2)_2N]$

Molecule (1)		Molecule (1a) [a]	
Mn(1)–C–O (*mean*)	178.3(5)	Mn(1a)–C–O (*mean*)	174.7(5)
Mn(1)–S(1)–P(1)	109.1(1)	Mn(1a)–S(1a)–P(1a)	106.9(1)
S(1)–P(1)–N(1)	117.9(2)	S(1a)–P(1a)–N(1a)	118.8(2)
P(1)–N(1)–P(2)	129.5(3)	P(1a)–N(1a)–P(2a)	132.9(3)
S(2)–P(2)–N(1)	118.9(2)	S(2a)–P(2a)–N(1a)	116.6(1)
Mn(1)–S(2)–P(2)	111.9(1)	Mn(1a)–S(2a)–P(2a)	103.1(1)
		axial–equatorial	
C(1)–Mn(1)–C(3)	90.7(3)	C(1a)–Mn(1a)–C(3a)	92.7(3)
C(1)–Mn(1)–C(4)	92.3(2)	C(1a)–Mn(1a)–C(4a)	92.1(3)
C(1)–Mn(1)–S(1)	85.2(2)	C(1a)–Mn(1a)–S(1a)	84.9(2)
C(1)–Mn(1)–S(2)	90.4(2)	C(1a)–Mn(1a)–S(2a)	82.9(2)
C(2)–Mn(1)–C(3)	92.0(3)	C(2a)–Mn(1a)–C(3a)	90.0(3)
C(2)–Mn(1)–C(4)	90.7(2)	C(2a)–Mn(1a)–C(4a)	86.4(3)
C(2)–Mn(1)–S(1)	92.4(2)	C(2a)–Mn(1a)–S(1a)	92.4(2)
C(2)–Mn(1)–S(2)	86.8(2)	C(2a)–Mn(1a)–S(2a)	98.6(2)
		equatorial–equatorial	
C(3)–Mn(1)–C(4)	90.6(3)	C(3a)–Mn(1a)–C(4a)	93.1(3)
C(4)–Mn(1)–S(1)	83.9(2)	C(4a)–Mn(1a)–S(1a)	89.0(2)
C(3)–Mn(1)–S(2)	85.2(2)	C(3a)–Mn(1a)–S(2a)	88.6(2)
S(1)–Mn(1)–S(2)	100.5(1)	S(1a)–Mn(1a)–S(2a)	89.2(1)
C(3)–Mn(1)–S(1)	173.0(2)	C(3a)–Mn(1a)–S(1a)	176.9(3)
C(4)–Mn(1)–S(2)	175.0(2)	C(4a)–Mn(1a)–S(2a)	174.8(2)
		axial–axial	
C(1)–Mn(1)–C(2)	175.9(3)	C(1a)–Mn(1a)–C(2a)	176.9(3)

[a] For the disordered oxygen atom: Mn(1a)–C(3a)–O(3b) 164.2(7).

longer and shorter, respectively, than the corresponding bonds in free $(S=PPh_2)_2NH$ (cf. P–S (double bond) 1.936(1), 1.950(1), P–N (single bond) av. 1.678(2) Å) [17]. Their magnitude is intermediate between single and double phosphorus–sulfur and phosphorus–nitrogen bond distances in the methyl ester, Me–S–$PPh_2=N–Ph_2P=S$ (P–S 2.069(3), P=S 1.956(3), P–N 1.610(4), P=N 1.568(4) Å) [18]. This suggests electron delocalization over the inorganic MnS_2P_2N ring.

However, the MnS_2P_2N ring is not planar, and its conformation is the main difference between molecules (**1**) and (**1a**) (Fig. 3). In (**1**) the phosphorus atoms are placed above and below the Mn(1)S(1)S(2) plane (deviations: P(1) 0.658, P(2) −0.661, N(1) −0.096 Å), while in (**1a**) both phosphorus atoms lie on the same side of the Mn(1a)S(1a)S(2a) plane (deviations: P(1a) −1.636, P(2a) −1.829, N(1a) −2.360 Å). The S ⋯ S 'bite' of the ligand is also different in the two molecules, i.e. S(1) ⋯ S(2) 3.722 Å, and S(1a) ⋯ S(2a) 3.392 Å, thus resulting in a larger S–Mn–S bond angle in (**1**) (100.5(1)°) than in (**1a**) (89.2(1)°). This behavior is consistent with the expected high flexibility of the SPNPS backbone.

The coordination geometry around manganese atom is distorted octahedral, with two carbonyl group carbons and the sulfur atoms in the equatorial plane (deviations from the best C_2MnS_2 plane: Mn(1) 0.012, S(1) −0.051, S(2) 0.045, C(3) −0.073, C(4) 0.067 Å in (**1**), and Mn(1a) −0.051, S(1a) −0.010, S(2a) 0.031, C(3a) −0.013, C(4a) 0.042 Å in (**1a**), respectively), and two carbonyl group carbons in the axial sites (C(1)–Mn(1)–C(2) 175.9(3)°, C(1a)–Mn(1a)–C(2a) 176.9(3)°). The distortion of the coordination polyhedron is reflected by the angles at Mn (Table 2). The axial Mn–C bond lengths are longer than the equatorial ones due to the *trans* effect of the sulfur atoms.

One may compare the molecular structure of the title compound with that described for the inorganic man-ganese(II) derivative, $Mn[(SPPh_2)_2N]_2$ [19,20]. This compound contains a slightly distorted tetrahedral MnS_4 core. The two MnS_2P_2N rings exhibit the same conformation as observed in molecule (**1**). The average bond distances within the inorganic rings (Mn–S 2.443(12), P–S 2.013(5) and P–N 1.588(6) Å) are of the same magnitude as have been found in $Mn(CO)_4[(SPPh_2)_2N]$. Differences may be noted in the corresponding bond angles. While the Mn–S–P, S–P–N and P–N–P–bond angles are basically of the same magnitude (100(3), 118.7(4) and 134(2)° in the inorganic complex), the S–Mn–S bond angles are significantly larger than in the organometallic compound (109.5(22)° vs. 100.5(10)° in (**1**) and 89.2(10)° in (**1a**)). This behavior emphasizes the high capacity of dithioimidodiphosphinato ligand to accomodate itself to the differing coordination geometry at the metal atom (tetrahedral vs. octahedral in this case) by modifying its S ⋯ S bite over a large range (3.392 Å in (**1a**), 3.722 in (**1**), and 4.048 Å in $Mn[(SPPh_2)_2N]_2$).

3. Experimental details

3.1. Materials

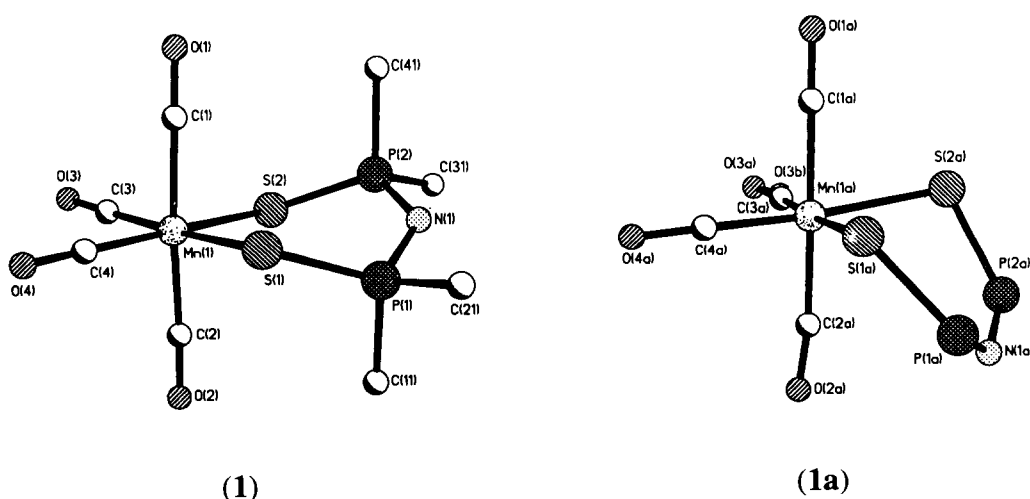(1)   (1a)

Fig. 3. Comparative view of the MnS_2P_2N ring conformation in molecule (**1**) and (**1a**) of $Mn(CO)_4[(SPPh_2)_2N]$ (for clarity, in (**1**) only *ipso*-carbons are shown, while in (**1a**) the phenyl groups attached to phosphorus are completely deleted).

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$)

	x	y	z	U(eq)
Mn(1)	9227(1)	367(1)	1013(1)	43(1)
S(1)	9862(2)	2165(1)	712(1)	51(1)
S(2)	11241(1)	−709(1)	1531(1)	50(1)
P(1)	11191(1)	2468(1)	1127(1)	40(1)
P(2)	13062(1)	−246(1)	1392(1)	39(1)
O(1)	11349(5)	−1157(4)	318(1)	90(2)
O(2)	7222(5)	1914(5)	1725(2)	90(2)
O(3)	8346(5)	−1840(4)	1258(1)	81(2)
O(4)	6600(5)	1581(4)	435(1)	77(2)
N(1)	12743(4)	1252(4)	1274(1)	44(2)
C(1)	10555(7)	−585(6)	581(2)	56(3)
C(2)	8017(6)	1339(6)	1455(2)	57(3)
C(3)	8687(6)	−981(6)	1172(2)	57(3)
C(4)	7622(6)	1115(5)	657(2)	53(2)
C(11)	10028(5)	3201(5)	1593(2)	42(2)
C(12)	10551(7)	2735(5)	2002(2)	57(3)
C(13)	9624(8)	3294(6)	2358(2)	71(3)
C(14)	8226(8)	4315(7)	2303(2)	79(4)
C(15)	7697(7)	4811(7)	1898(2)	79(3)
C(16)	8587(6)	4256(6)	1548(2)	67(3)
C(21)	11759(5)	3688(5)	845(2)	44(2)
C(22)	10707(7)	4797(5)	615(2)	63(3)
C(23)	11181(9)	5699(6)	402(2)	74(3)
C(24)	12701(9)	5518(7)	408(2)	75(4)
C(25)	13734(8)	4424(7)	633(2)	74(3)
C(26)	13266(6)	3521(5)	850(2)	59(3)
C(31)	14234(5)	−819(5)	1864(2)	43(2)
C(32)	14246(6)	−1859(5)	2142(2)	52(2)
C(33)	15198(7)	−2300(6)	2493(2)	63(3)
C(34)	16164(7)	−1723(7)	2557(2)	72(3)
C(35)	16160(8)	−689(8)	2285(2)	85(4)
C(36)	15189(7)	−233(7)	1937(2)	71(3)
C(41)	14320(5)	−1205(5)	972(1)	40(2)
C(42)	15007(6)	−650(5)	664(2)	53(2)
C(43)	16056(7)	−1371(7)	362(2)	66(3)
C(44)	16433(7)	−2675(7)	364(2)	66(3)
C(45)	15758(7)	−3273(6)	666(2)	72(3)
C(46)	14706(6)	−2544(5)	972(2)	57(3)
Mn(1A)	5386(1)	4909(1)	3918(1)	50(1)
S(1A)	5150(1)	4154(1)	3242(1)	52(1)
S(2A)	3625(2)	7129(1)	3669(1)	51(1)
P(1A)	2862(1)	4648(1)	3176(1)	38(1)
P(2A)	1589(1)	6999(1)	3653(1)	38(1)
O(1A)	7751(5)	5688(5)	3440(2)	93(3)
O(2A)	3188(5)	3920(4)	4383(1)	70(2)
O(3A)	5889(12)	5759(11)	4715(3)	81(3)
O(3B)	5313(15)	6217(13)	4724(4)	83(4)
O(4A)	7715(6)	2245(6)	4178(2)	102(3)
N(1A)	1640(4)	5703(4)	3466(1)	40(2)
C(1A)	6862(7)	5388(6)	3621(2)	65(3)
C(2A)	3943(6)	4361(5)	4195(2)	49(2)
C(3A)	5567(8)	5537(7)	4397(2)	76(4)
C(4A)	6812(7)	3286(8)	4067(2)	70(3)
C(11A)	2502(5)	3190(5)	3285(2)	43(2)
C(12A)	3294(8)	2110(6)	3053(2)	79(3)
C(13A)	2988(9)	992(6)	3129(3)	98(4)
C(14A)	1930(9)	971(7)	3448(3)	84(4)
C(15A)	1179(8)	2012(7)	3678(2)	79(3)
C(16A)	1449(6)	3130(5)	3600(2)	60(3)
C(21A)	2490(6)	5112(5)	2607(2)	42(2)
C(22A)	3654(7)	4697(6)	2293(2)	63(3)

Table 3 (continued)

	x	y	z	U(eq)
C(23A)	3284(9)	5018(7)	1862(2)	74(3)
C(24A)	1793(9)	5744(6)	1749(2)	70(3)
C(25A)	653(8)	6167(6)	2054(2)	70(3)
C(26A)	990(6)	5828(5)	2486(2)	56(3)
C(31A)	724(5)	7081(5)	4191(2)	45(2)
C(32A)	−268(6)	6483(5)	4307(2)	59(3)
C(33A)	−907(7)	6543(7)	4717(2)	75(3)
C(34A)	−592(8)	7189(8)	5007(2)	90(4)
C(35A)	371(9)	7809(8)	4902(2)	97(4)
C(36A)	1042(7)	7756(6)	4486(2)	71(3)
C(41A)	314(5)	8474(4)	3351(2)	42(2)
C(42A)	733(7)	8757(5)	2931(2)	58(3)
C(43A)	−229(8)	9887(6)	2697(2)	68(3)
C(44A)	−1564(8)	10736(6)	2869(2)	67(3)
C(45A)	−2002(7)	10465(6)	3272(2)	81(3)
C(46A)	−1064(7)	9330(6)	3518(2)	68(3)
C(1′)	5246(27)	−592(24)	4148(8)	309(11)
C(2′)	5344(23)	189(21)	4429(7)	256(8)
C(3′)	4691(23)	−308(20)	4879(7)	249(8)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.2. Synthesis of $Mn(CO)_4[(SPPh_2)_2N]$

A stoichiometric amount of K[(SPPh$_2$)$_2$N] (0.888 g, 1.82 mmol) was added to a solution of [Mn(CO)$_5$]Br (0.508 g, 1.85 mmol) in 70 ml anhydrous THF. After approx. 30 minutes a yellowish precipitate was deposited and changes in the IR region characteristic for carbonyl stretching vibrations were observed. The reaction mixture was stirred at room temperature for 3 h, and then the resulted KBr was filtered off. The removal of the solvent from the clear filtrate resulted in a yellowish oily product, which was subsequently dissolved in *n*-hexane. Yellow-orange crystals of the title compound were deposited on cooling (0.85 g, yield 74%). M.p. 216–18 °C (dec.). Anal. Calc. for C$_{28}$H$_{20}$MnNO$_4$P$_2$S$_2$.0.25C$_6$H$_{14}$: C, 52.75; H, 3.14; N, 2.20; Found: C, 52.60; H, 3.50; N, 2.06%. IR (KBr): ν(PS) 600m, 565m, ν_{as}(P$_2$N) 1210m, ν(CO) 2080m, 2000vs, 1993vs, 1960vs cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): 7.89dm (8H-*ortho*, P–C$_6$H$_5$, ^{3}J(HH) 7.8, ^{3}J(PH) 13.5 Hz), 7.39m (12H-*meta + para*, P–C$_6$H$_5$). ^{13}C NMR (DMSO-d$_6$, 75.4 MHz): 214.95s, br (CO$_{eq}$), 209.54s, br (CO$_{ax}$), 136.66dd (C$_i$, ^{1}J(PC) 71.8, ^{3}J(PC) 2.0 Hz), 131.49s (C$_p$), 130.13d (C$_o$, ^{2}J(PC) 8.1 Hz), 128.43d (C$_m$, ^{3}J(PC) 8.1 Hz). ^{31}P NMR (DMSO-d$_6$, 121.4 MHz): 49.4. MS (m/e, (%)): 616 (2), M + H$^+$; 615 (1), M$^+$; 588 (6), [M + H, −CO]$^+$; 503 (100), [M−4CO]$^+$; 448 (0.2), (SPPh$_2$)$_2$N$^+$; 217 (2), SPPh$_2^+$; 154 (19), Ph$_2^+$.

3.3. Crystal structure determination of $Mn(CO)_4$-$[(SPPh_2)_2N]$

3.3.1. Crystal data

C$_{28}$H$_{20}$MnNO$_4$P$_2$S$_2$.0.25 C$_6$H$_{14}$, *M* 635.49, triclinic, *a* = 9.526(5), *b* = 11.201(5), *c* = 31.230(6) Å,

$\alpha = 84.21(3)$, $\beta = 85.84(3)$, $\gamma = 64.88(3)°$, $V = 2999.2(15)$ Å^3, $Z = 4$, $D_c = 1.410$ g cm^{-3}, $F(000) = 1304$, space group $P\text{--}1$, Cu Kα radiation, $\lambda = 1.54178$ Å, μ(Cu Kα) 6.182 mm^{-1}, crystal size 0.60 × 0.44 × 0.36 mm.

3.3.2. Structure determination

Suitable crystals of the title compound were obtained from n-hexane solution. Data were collected at 298 K on a Nicolet P3/F four-cycle diffractometer (Ni-filter) for 6355 reflections ($2\theta/\theta$ mode) of which 6199 were independent ($R_{int} = 8.64\%$) and 5728 ($F > 4.0\sigma(F)$) were used in the full-matrix least squares refinement [23]. The structure was solved by direct methods. An empirical absorption correction was applied after isotropic refinement with the DIFABS program [24]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and their coordinates included in final cycles of refinement with fixed isotropic thermal parameters ($U = 0.06$ Å^2). The terminal oxygen atom bounded to C(3a) was thermally disordered, and refined in two positions with site occupation factors of 0.5474 for O(3a) and 0.4526 for O(3b).

The final R values are $R = \Sigma|F_o - F_c|/\Sigma|F_o| = 4.57\%$ and $wR = [\Sigma w(|F_o - F_c|)^2/\Sigma|F_o|^2]^{1/2} = 6.14\%$ ($R = 5.02\%$ and $wR = 7.41\%$ for all data) with weights $w^{-1} = \sigma^2(F) + 0.0005F^2$; goodness-of-fit 1.47. The residual electron density from a final difference Fourier synthesis was in the range of 0.82, -0.34 eÅ^3. Refined values for the atomic coordinates are given in Table 3.

Acknowledgements

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