# Synthesis and X-ray crystal structure of complexes $Cp(CO)_2MnP(SR)_3$ (R = $Pr^i$, Ph)

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$Cp(CO)_2Mn \cdot THF$ reacts in THF with thiosters of phosphorus acid, $P(SR)_3$, to give new complexes $Cp(CO)_2MnP(SR)_3$ in which the manganese atom is coordinated to the phosphorus atom. The X-ray crystal structure of compounds with R = $Pr^i$ and Ph was established. The metal atom has a coordination enviroment of the three-legged "piano stool" type. The bond angles OC—Mn—CO and OC—Mn—P are 90.6—95.9(4)°. Bond distances are: Mn—P 2.188(2) and 2.171(2) E, P—S 2.097(3)—2.137(3) E.

**Key words**: manganese, dicarbonyl(cyclopentadienyl) complex; alkyl and aryl thiophosphites; Mn—P complex, crystal structure.

Previously we have shown[1,2] that in the reaction of $Cp(CO)_2Mn(THF)$ with the esters of phosphorus thioacids, $P(SR)_3$, the coordination of a 16-electron fragment $Cp(CO)_2Mn$ to both atoms of the ambident P—S system is possible. However, the stability of the forming products is dramatically different. Coordination of sulfur gives unstable complexes, identified in solution by IR spectroscopy,[1] which easily dissociate at the P—S bond to give free radicals $Cp(CO)_2MnSR$ (see Ref. 2). The latter were also obtained by other authors when the S—S bonds of disilfides were broken in the presence of $Cp(CO)_2Mn(THF)$ or by oxidation of mercaptans coordinated to the manganese ion.[3,4] Coordination with phosphorus gives rise to more stable complex compounds, $Cp(CO)_2MnP(SR)_3$. In the present work an X-ray study of two complexes of this type with R = $Pr^i$ (**1**) and Ph (**2**) was performed. These complexes were previously characterized by IR and NMR spectra.[1]

## Results and Discussion

Trithiophosphate complexes **1** and **2** are light-yellow crystalline compounds readily soluble in benzene and $CH_2Cl_2$. They are stable in the solid state and solutions.

X-Ray analysis showed that complexes **1** and **2** contain in their cells two crystallographically independent molecules (**A** and **B**), which have virtually identical valence geometry and only slightly different conformations.

The molecular structures of **1** and **2** are rather similar (Fig. 1, Tables 1 and 2). The Mn atoms in both molecules have a ligand environment of the "piano stool" type. Valent angles OC—Mn—CO and OC—Mn—P are in the same ranges (91—94°) as in cymantrene and related complexes of the $Cp(CO)_2Mn(P)$ type where (P) is a phosphine or phosphite ligand.[5] Consequently, the substitution of a trithiophosphite ligand for one of the CO groups in cymantrene involves no

**Table 1**. The main bond lengths (*d*) in complexes **1** and **2**

| Bond | *d*/ Å | | | |
|---|---|---|---|---|
| | **1A** | **1B** | **2A** | **2B** |
| Mn—P | 2.189(2) | 2.187(2) | 2.171(2) | 2.171(2) |
| Mn—C(1) | 1.792(10) | 1.790(9) | 1.759(9) | 1.747(9) |
| Mn—C(2) | 1.775(9) | 1.776(10) | 1.790(9) | 1.772(10) |
| Mn—C(3) | 2.133(10) | 2.143(10) | 2.129(10) | 2.151(10) |
| Mn—C(4) | 2.143(9) | 2.113(9) | 2.150(9) | 2.141(9) |
| Mn—C(5) | 2.143(10) | 2.146(10) | 2.122(10) | 2.153(10) |
| Mn—C(6) | 2.132(9) | 2.128(10) | 2.145(9) | 2.139(9) |
| Mn—C(7) | 2.132(9) | 2.143(9) | 2.159(9) | 2.135(9) |
| P—S(1) | 2.119(3) | 2.098(3) | 2.135(3) | 2.136(3) |
| P—S(2) | 2.121(3) | 2.114(3) | 2.125(9) | 2.137(3) |
| P—S(3) | 2.097(3) | 2.119(3) | 2.120(3) | 2.137(3) |
| C(1)—O(1) | 1.141(10) | 1.145(9) | 1.168(9) | 1.181(9) |
| C(2)—O(2) | 1.144(9) | 1.145(10) | 1.156(9) | 1.165(9) |
| S(1)—C(8) | 1.811(9) | 1.855(8) | 1.766(9) | 1.787(9) |
| S(2)—C(11) | 1.849(9) | 1.825(9) | — | — |
| S(2)—C(14) | — | — | 1.783(9) | 1.801(9) |
| S(3)—C(14) | 1.837(8) | 1.813(10) | — | — |
| S(3)—C(20) | — | — | 1.775(9) | 1.774 (9) |

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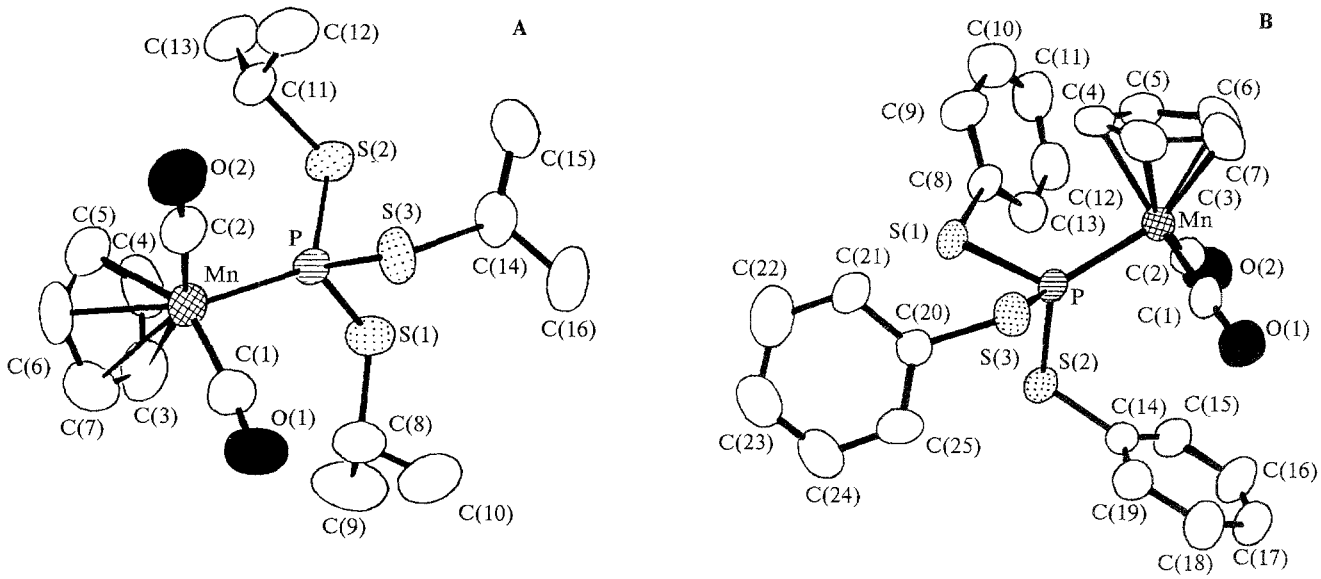


**Fig 1.** General view of comllexes **1A** and **2B** molecules.

significant distortions of the molecular structure. The relatively short Mn—P distances, which amount to 2.189(2) and 2.171(2) Å for compounds **1** and **2**, respectively are noteworthy. Analysis of the literature data revealed that the Mn—P distances in complexes $Cp(CO)_2Mn(P)$ depend on the donor-acceptor properties of the P atom. In the structure of $Cp(CO)_2MnPPr^i_2Me$, where phosphorus is bonded only to electron-donating alkyl groups, the Mn—P distance is 2.246 Å.[6] In complexes $Cp(CO)_2MnPPh_3$ and $MeC_5H_4(CO)_2MnPPh_3$, the Mn—P distances are slightly shorter, *viz.*, 2.236 and 2.232 Å, respectively[7,8] In compounds where phosphorus is connected with electron-withdrawing groups, the Mn—P distances are significantly shorter, amounting to 2.201 Å for the PPhHC(Ph)=CHPh ligand and 2.174 Å for $P(OMe)_3$.[9,10]

**Table 2.** Bond angles (ω) in complexes **1** and **2**

| Angle | ω/deg | | | |
|---|---|---|---|---|
| | **1A** | **1B** | **2A** | **2B** |
| C(1)—Mn—C(2) | 92.4(4) | 93.3(4) | 94.4(4) | 95.9(4) |
| C(1)—Mn—P | 90.6(3) | 92.8(3) | 92.5(3) | 93.3(3) |
| C(2)—Mn—P | 93.2(3) | 92.0(3) | 94.6(3) | 91.6(3) |
| Mn—P—S(1) | 119.8(1) | 110.8(1) | 123.4(1) | 122.7(1) |
| Mn—P—S(2) | 121.3(1) | 120.3(1) | 123.7(1) | 120.9(1) |
| Mn—P—S(3) | 109.6(1) | 119.3(1) | 108.6(1) | 121.2(1) |
| Mn—C(1)—O(1) | 176.0(8) | 177.4(8) | 174.4(8) | 173.8(8) |
| Mn—C(2)—O(2) | 176.4(8) | 179.7(8) | 176.0(8) | 175.0(8) |
| S(1)—P—S(2) | 89.1(1) | 106.6(1) | 93.1(1) | 94.5(1) |
| S(1)—P—S(3) | 107.9(1) | 107.5(1) | 98.1(1) | 95.2(1) |
| S(2)—P—S(3) | 107.0(1) | 90.1(1) | 106.1(1) | 95.7(1) |
| P—S(1)—C(8) | 105.1(3) | 105.8(3) | 102.2(3) | 103.5(3) |
| P—S(2)—C(11) | 103.9(3) | 102.9(3) | — | — |
| P—S(2)—C(14) | — | — | 104.9(3) | 102.7(3) |
| P—S(3)—C(14) | 106.3(3) | 104.3(3) | — | — |
| P—S(3)—C(20) | — | — | 106.2(3) | 104.8(3) |

In closely related compounds containing either P—O or P—S bonds, *e.g.*, $[Cp(CO)_2MnPMe_2]_2X$ (X = O, S) and $[Cp(CO)_2MnPMe_2]_2S_2$, the lengths of the Mn—P bond are in the 2.178—2.200 Å interval.[11,12] This is close to the lengths of these bonds in **1** and **2** and is in good agreement with the σ-acceptor properties of the SR groups.[13] It should be noted that in **1** the Mn—P bond length is 0.017 Å longer than in **2** in agreement with the fact that the $Pr^i$ substituents have stronger donor properties than the Ph groups.

The Mn—C(Cp) distances in complexes **1** and **2** are virtually equal within the limits of the accuracy achieved (see Table 1) and are close to the sum of the covalent radii of Mn (1.38 Å [14]) and $C(sp^3)$ (0.77 E). The other bond lengths, including the P—S distances [2.119(3)—2.135(3) Å] are close to standard values.[15]

In compounds **1** and **2** phosphorus has a distorted tetrahedral environment: the Mn—P—S angles are sig-

**Table 3.** Crystallographic parameters of complexes **1** and **2**

| Parameter | $C_{16}H_{26}MnO_2PS_3$ | $C_{25}H_{20}MnO_2PS_3$ |
|---|---|---|
| | **1** | **2** |
| *a*/ Å | 6.911(2) | 16.199(1) |
| *b*/ Å | 18.280(5) | 26.706(4) |
| *c*/ Å | 33.100(2) | 11.356(2) |
| β/deg | — | 98.769(1) |
| V/ Å$^3$ | 4181.6 | 4853.7 |
| Group | $P2_12_12_1$ | $P2_1/c$ |
| Symmetry | Rhombic | Monocl. |
| *Z* | 8 | 8 |
| $d_{calc}$/g · cm$^{-3}$ | 1.37 | 1.46 |
| N ($F^2 \geq 3\sigma$) | 2190 | 4522 |
| μ/cm$^{-1}$ | 9.75 | 8.55 |
| *R* | 0.037 | 0.045 |
| $R_w$ | 0.046 | 0.069 |

**Table 4**. The coordinates of non-hydrogen atoms in the structure of **1** and their equivalent isotropic temperature factors, $B_{eq}$

| Atoms | *x* | *y* | *z* | $B_{eq}$/ Å$^2$ | *x* | *y* | *z* | $B_{eq}$/ Å$^2$ |
|---|---|---|---|---|---|---|---|---|
| | | Molecule **A** | | | | Molecule **B** | | |
| Mn | 0.1157(2) | 0.90119(6) | 0.72752(3) | 3.10(2) | 0.2910(2) | 0.89776(6) | 0.51014(3) | 2.88(2) |
| S(1) | 0.0314(4) | 0.7375(1) | 0.78716(6) | 4.57(5) | 0.0080(3) | 1.0575(1) | 0.50111(7) | 4.22(5) |
| S(2) | 0.0597(3) | 0.7139(1) | 0.69842(6) | 3.88(4) | 0.4634(3) | 1.0860(1) | 0.53461(6) | 4.00(4) |
| S(3) | 0.3931(3) | 0.7413(1) | 0.73476(7) | 4.09(4) | 0.4229(4) | 1.0569(1) | 0.44590(6) | 4.59(5) |
| P | 0.1100(3) | 0.7824(1) | 0.73609(5) | 2.75(4) | 0.2905(3) | 1.01569(9) | 0.49900(5) | 2.65(3) |
| O(1) | 0.4187(8) | 0.9191(3) | 0.7887(2) | 5.2(1) | 0.0134(9) | 0.9076(4) | 0.5770(2) | 5.6(1) |
| O(2) | 0.3894(9) | 0.8959(4) | 0.6605(2) | 5.7(1) | −0.0098(9) | 0.8729(3) | 0.4497(2) | 5.2(1) |
| C(1) | 0.303(1) | 0.9097(4) | 0.7646(2) | 3.6(2) | 0.121(1) | 0.9054(4) | 0.5507(2) | 3.8(2) |
| C(2) | 0.285(1) | 0.8960(4) | 0.6872(2) | 4.0(2) | 0.108(1) | 0.8828(4) | 0.4734(2) | 3.3(2) |
| C(3) | −0.134(1) | 0.9385(5) | 0.7593(3) | 5.6(2) | 0.429(1) | 0.7979(4) | 0.4923(3) | 5.2(2) |
| C(4) | −0.193(1) | 0.9073(5) | 0.7225(3) | 5.9(2) | 0.538(1) | 0.8571(5) | 0.4799(3) | 5.1(2) |
| C(5) | −0.111(2) | 0.9478(5) | 0.6917(3) | 6.3(2) | 0.601(1) | 0.8964(4) | 0.5133(3) | 5.4(2) |
| C(6) | −0.004(2) | 1.0034(5) | 0.7092(3) | 5.9(2) | 0.525(1) | 0.8621(5) | 0.5470(3) | 5.6(2) |
| C(7) | −0.019(2) | 0.9979(5) | 0.7498(3) | 6.0(2) | 0.421(1) | 0.8004(5) | 0.5338(3) | 5.5(2) |
| C(8) | 0.051(2) | 0.7919(5) | 0.8295(2) | 5.9(2) | 0.031(1) | 1.1572(4) | 0.4921(3) | 4.6(2) |
| C(9) | −0.117(2) | 0.7964(7) | 0.8595(3) | 9.4(3) | −0.043(2) | 1.2002(5) | 0.5271(3) | 6.9(3) |
| C(10) | 0.222(3) | 0.7620(7) | 0.8507(4) | 11.7(4) | −0.074(2) | 1.1771(5) | 0.4539(2) | 6.8(3) |
| C(11) | −0.041(1) | 0.7570(4) | 0.6480(2) | 4.3(2) | 0.435(1) | 1.0483(4) | 0.5853(2) | 4.3(2) |
| C(12) | 0.131(2) | 0.7322(6) | 0.6251(3) | 6.1(3) | 0.281(2) | 1.0840(8) | 0.6097(3) | 9.2(4) |
| C(13) | −0.229(2) | 0.7404(6) | 0.6265(3) | 6.4(3) | 0.630(2) | 1.0552(7) | 0.6066(3) | 7.9(3) |
| C(14) | 0.372(1) | 0.6416(4) | 0.7403(2) | 4.1(2) | 0.348(2) | 0.9939(5) | 0.4066(2) | 6.4(3) |
| C(15) | 0.431(2) | 0.6055(5) | 0.7016(3) | 5.6(2) | 0.150(3) | 1.0155(6) | 0.3892(3) | 9.6(4) |
| C(16) | 0.489(2) | 0.6151(5) | 0.7750(3) | 6.8(3) | 0.496(3) | 0.9919(6) | 0.3743(3) | 11.2(5) |

**Table 5**. The coordinates of non-hydrogen atoms in the structure of **2** and their equivalent isotropic temperature factors $B_{eq}$

| Atoms | *x* | *y* | *z* | $B_{eq}$/ Å$^2$ | *x* | *y* | *z* | $B_{eq}$/ Å$^2$ |
|---|---|---|---|---|---|---|---|---|
| | | Molecule **A** | | | | Molecule **B** | | |
| Mn | 0.51301(6) | 0.10738(4) | 0.80823(9) | 2.69(4) | 0.036(2) | 0.09273(6) | 0.41401(4) | 2.69(4) |
| S(1) | 0.52930(6) | 0.162(2) | 0.5045(1) | 3.3(1) | 0.1771(2) | 0.17404(8) | 0.6303(2) | 4(1) |
| S(2) | 0.6996(2) | 0.1402(1) | 0.659(2) | 3.34(7) | 0.15401(3) | 0.2095(2) | 0.36438(8) | 3.7(3) |
| S(3) | 0.56703(8) | 0.0457(2) | 0.5604(1) | 3.3(5) | 0.00732(9) | 0.22439(3) | 0.5165(2) | 4.1(2) |
| P | 0.5746(2) | 0.11504(9) | 0.65221(3) | 2.4(1) | 0.08651(6) | 0.1652(1) | 0.47414(7) | 2.8(1) |
| O(1) | 0.6158(1) | 0.02260(6) | 0.9049(2) | 5.77(4) | 0.181(2) | 0.0349(4) | 0.5209(2) | 5.4(3) |
| O(2) | 0.6106(4) | 0.186(2) | 0.9482(4) | 6.1(4) | −0.0621(7) | 0.0835(4) | 0.610(2) | 5.8(2) |
| C(1) | 0.5783(3) | 0.0576(8) | 0.8650(5) | 3.7(6) | 0.1237(6) | 0.0603(3) | 0.4826(8) | 4(1) |
| C(2) | 0.5749(1) | 0.1544(6) | 0.8925(3) | 3.9(5) | −0.0207(4) | 0.0884(1) | 0.5356(7) | 3.8(6) |
| C(3) | 0.4027(3) | 0.0655(7) | 0.7487(4) | 4.5(6) | −0.0008(7) | 0.1187(3) | 0.2342(1) | 3.4(6) |
| C(4) | 0.393(2) | 0.1126(5) | 0.6970(3) | 3.8(4) | 0.0566(5) | 0.0781(3) | 0.2354(6) | 3.4(2) |
| C(5) | 0.3998(8) | 0.1486(4) | 0.790(2) | 4.2(3) | 0.0190(6) | 0.035(2) | 0.2808(5) | 3.8(5) |
| C(6) | 0.4094(3) | 0.1222(8) | 0.9003(5) | 4.4(6) | −0.0603(7) | 0.0494(3) | 0.3110(8) | 4(1) |
| C(7) | 0.4110(1) | 0.0708(8) | 0.8760(4) | 5.0(6) | −0.0722(4) | 0.1018(2) | 0.2823(7) | 3.9(7) |
| C(8) | 0.4905(7) | 0.2141(5) | 0.5748(2) | 2.8(2) | 0.1374(3) | 0.1359(8) | 0.7383(4) | 3.4(7) |
| C(9) | 0.4081(5) | 0.2268(3) | 0.5354(7) | 4.6(2) | 0.175(2) | 0.0906(4) | 0.7682(2) | 4.4(3) |
| C(10) | 0.3742(4) | 0.269(2) | 0.5931(4) | 5.5(5) | 0.1441(7) | 0.0603(5) | 0.854(2) | 4.9(3) |
| C(11) | 0.4228(4) | 0.2940(9) | 0.6806(5) | 5.3(7) | 0.0792(7) | 0.0758(4) | 0.9054(8) | 5(1) |
| C(12) | 0.5068(1) | 0.282(1) | 0.7152(4) | 4.9(7) | 0.0426(5) | 0.1221(2) | 0.8774(7) | 6.3(8) |
| C(13) | 0.5406(8) | 0.2412(5) | 0.6616(1) | 4.0(4) | 0.0728(4) | 0.1533(8) | 0.7948(5) | 5.6(7) |
| C(14) | 0.7565(6) | 0.1099(3) | 0.7857(7) | 3.2(2) | 0.208(2) | 0.1630(6) | 0.2905(4) | 3.6(4) |
| C(15) | 0.7828(7) | 0.140(2) | 0.8851(5) | 4.4(6) | 0.1985(9) | 0.1652(5) | 0.169(2) | 4.2(4) |
| C(16) | 0.8303(5) | 0.117(1) | 0.9856(7) | 5.4(6) | 0.2382(6) | 0.1298(6) | 0.1067(7) | 6(1) |
| C(17) | 0.8518(4) | 0.0664(2) | 0.9830(8) | 4.8(7) | 0.2862(1) | 0.0926(7) | 0.1680(3) | 6.2(5) |
| C(18) | 0.8242(3) | 0.0377(8) | 0.8823(5) | 4.8(7) | 0.2951(7) | 0.0905(3) | 0.2937(2) | 5.8(4) |
| C(19) | 0.776(2) | 0.0594(6) | 0.7795(4) | 4.4(5) | 0.2566(6) | 0.1265(4) | 0.3546(9) | 4.3(3) |
| C(20) | 0.5970(8) | 0.058(2) | 0.4192(5) | 2.8(6) | −0.0870(9) | 0.2164(6) | 0.416(2) | 3.3(4) |
| C(21) | 0.5355(4) | 0.069(1) | 0.3217(8) | 3.6(7) | −0.0940(8) | 0.2330(4) | 0.296(1) | 4(1) |
| C(22) | 0.5582(1) | 0.077(1) | 0.2102(3) | 5.1(6) | −0.1698(4) | 0.2266(1) | 0.2206(8) | 5.0(8) |
| C(23) | 0.6437(6) | 0.0732(3) | 0.1953(7) | 6.2(3) | −0.2362(2) | 0.2052(7) | 0.2614(3) | 5.1(6) |
| C(24) | 0.703(2) | 0.0621(5) | 0.2911(3) | 5.2(4) | −0.2300(5) | 0.1887(3) | 0.3811(6) | 5.1(2) |
| C(25) | 0.682(1) | 0.0540(6) | 0.405(2) | 4.2(3) | −0.1554(5) | 0.195(2) | 0.4568(6) | 3.9(6) |

nificantly increased and equal 119.3—123.7(1)°; only the Mn—P—S(1) angle in molecule **1B** and the Mn—P—S(3) angle in molecules **1A** and **2A** are close to the ideal tetrhedral value of 109.5°. On the contrary, all of the S—P—S angles in both complexes are smaller than the "ideal" tetrahedral value and are within 89.1—107.9(1)°. At the same time their mean value (99.2°) is somewhat larger than thr S—P—S angle in non-coordinated triphenyl thiophoshphite (97.45°).[16]

## Experimental

**Dicarbonyl(cyclopentadienyl)manganese trithioisopropylphosphine (1).** The reaction of $Cp(CO)_2Mn(THF)$, generated photochemically from cymantrene (0.3 g) in THF (70 mL), with 0.9 equiv. of $P(S\text{-}Pr^i)_3$ (stirred in an inert atmosphere for 12 h, without UV-irradiation) results in a dark red solution. The reaction mass was filtered and the solvent was removed from the filtrate to leave a dark red viscous liquid. The latter was heated up to 50 °C under a vacuum (~ 0.1 Torr) in order to remove the unreacted starting compounds. In this way cymantrene and $P(SPr^i)_3$ were distilled off (as shown by TLC on Silufol), together with the paramagnetic free radical complex, $[Cp(CO)_2MnSPr^i]^{\cdot}$, which was identified by its ESR and mass spectra. The former consists of six broad peaks with *g*-factor 2.0321 and $a_{Mn}$ SOE, *cf.* Refs. 2,3; the latter displays the $M^+$ peak at *m/z* 251. The solid residue after sublimation and drying in a vacuum contained mainly complex **1**, which was purified by recrystallization from hexane-benzene (10:1). It is a light yellow crystalline compound, readily soluble in benzene and sparingly soluble in hexane. Yield 0.25 g (40 %), m.p. 133—134 °C. Found (%): C, 44.48; H, 6.11; P, 7.18; S, 22.48. $C_{16}H_{26}MnO_2PS_3$. Calculated (%): C, 44.44; H, 6.07; P, 7.18; S, 22.26. IR spectrum (hexane) $\nu/cm^{-1}$: 1898/1904, 1953/1959 ν(CO). The presence of four bands in the IR spectrum is caused by the existence of conformers in the solution.[1] Synthesis of complex **2** was described previously.[1]

**X-Ray study of compounds 1 and 2** was carried out on an automatic four-circle diffractometer Enraf-Nonius CAD-4 (λMo-Kα-irradiation, graphite monochromator, ω-scanning for **1** and ω/2θ-scanning for **2**, $\theta \leq 25°$. The data of the structural experiment and structure refinement are given in Table 3. Structures were deciphered by the heavy-atom method and refined in the anisotropic approach. All of the H atoms are placed to the calculated positions; their contribution to the amplitude structure was accounted for at the final stages of the refinement using fixed positional and isotropic temperature parameters ($B_{eq}$ = 5 $E^2$). Calculations were made on a PC using the SDP PLUS programs. The atomic coordinates are given in Tables 4 and 5.

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