Novel Organometallic Derivatives of Thioesters of the Trivalent Phosphorus Acids: Synthesis and Structure

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Thioesters of the phosphorous acid containing cymantrenyl and ferrocenyl substituents at sulfur were obtained for the first time from the reaction of organometallic disulfides with white phosphorus. According to an X-ray diffraction study tricymantrenyl trithiophosphite adopts an unusual asymmetric *cis*, *gauche*, *trans* conformation along the P–S bonds with respect to the phosphorus lone electron pair. Tri-ferrocenyl trithiophosphate possesses a classical propeller-like structure in the solid state which is different from its oxygen analogue.

Introduction

The chemistry of the thioesters of the trivalent phosphorus acids is a topic of great current interest and has experienced significant advances in recent years.[1] Surprisingly, the synthesis and structure of organometallic thioesters of the trivalent phosphorus acids has not been previously reported. The synthesis of such compounds provides a promising approach to obtain novel bi- and polynuclear complexes of transition metals, the coordination ability of trithiophosphites being promoted by their conformational flexibility due to internal rotation around the P−S bonds.[2−6]

In this paper we report the method of synthesis and the structure of novel thioesters of the trivalent phosphorus acids containing cymantrenyl and ferrocenyl fragments at the sulfur atoms.

Results and Discussion

Syntheses

Three general methods for the preparation of the thioesters of the trivalent phosphorus acids are known. The first one[7] involves the phosphorylation of mercaptans by chlorides of the trivalent phosphorus acids. This reaction can proceed both in the presence or absence of the hydrogen chloride acceptors (R, R′ = alkyl or aryl):

$$\mathrm{RSH + R'_{3\text{-}n}PCl_n \longrightarrow R'_{3\text{-}n}P(SR)_n + HCl} \qquad (1)$$

Following this method we have synthesised *S*-cymantrenyldiphenylthiophosphinite, the first compound belonging to the class of organometallic thioesters of the trivalent phosphorus acids.[8] This compound was obtained from the reaction of cymantrenylmercaptan with diphenylchlorophosphane in boiling dichloromethane. However, it appears that this method has significant limitations and does not allow us to obtain organometallic thioesters of phosphorous or phosphoric acid, though oxygen analogues − triferrocenyl phosphite and the corresponding phosphate − were prepared by Max Herberhold and co-workers[9] by the interaction of ferrocenol with PCl_3.

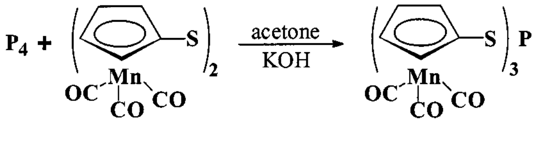
The second method[10] involves the phosphorylation of mercaptides of alkali metals by chlorides of the trivalent phosphorus acids:

$$\mathrm{RSNa + R'_{3\text{-}n}PCl_n \longrightarrow R'_{3\text{-}n}P(SR)_n + NaCl} \qquad (2)$$

The most simple and convenient way to obtain trithiophosphites[11] is by the treatment of dialkyl (diaryl) disulfides with white phosphorus, this reaction also being used[12] to synthesise triseleno- and tritellurophosphites:

$$\mathrm{6(RS)_2\ +\ P_4 \longrightarrow 4(RS)_3P} \qquad (3)$$

This reaction proceeds under mild conditions in aprotic solvents in the presence of a small amount of 15N KOH. In order to introduce a metal-containing thio-group at the phosphorus atom, for example cymantrenyl or ferrocenyl, the corresponding organometallic disulfides can be used as precursors to give tricymantrenyl and triferrocenyl trithiophosphites. Tricymantrenyl trithiophosphite was obtained in one step at room temperature in high yield by the reaction of white phosphorus with dicymantrenyl disulfide (**1**) in acetone solution.



1 **2**

Scheme 1. Synthesis of tricymantrenyl trithiophosphite

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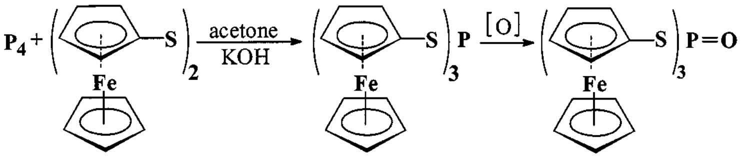

3 4

Scheme 2. Synthesis of triferrocenyl trithiophosphite and trithiophosphate

The identity of trithiophosphite **2** was unequivocally determined by ^{1}H, ^{31}P NMR and IR spectroscopy as well as by X-ray single crystal diffraction.

A similar method was used to obtain triferrocenyl trithiophosphite (**3**) from diferrocenyl disulfide and white phosphorus. Its structure was proved by ^{1}H and ^{31}P NMR spectroscopy.

Compound **3** did not form single crystals suitable for X-ray analysis, but was easily oxidized to give triferrocenyltrithiophosphate (**4**) which was studied by X-ray single crystal diffraction.

Structures

Tricymantrenyl trithiophosphite has nine axes of internal rotation: three P−S bonds, three C−S bonds and three Mn−cyclopentadienyl axes. Rotation around the P−S bonds results in a totally asymmetric structure with three cymantrenylthio-groups exhibiting different orientations towards the phosphorus lone electron pair: *cis* around the P−S3 bond (torsion angle −7.2°), *gauche* around the P−S2 bond (−31.0°) and *trans* (178.1°) around the P−S1 bond (Figure 1). The torsion angles around the S−C bonds vary within smaller limits with an almost orthogonal orientation of the P−S bonds with respect to the cyclopentadienyl planes and the largest deviation from the perpendicular arrangement of 16° for the *cis* cymantrenylthiogroup (S3−C31). As for the third set of axes, the rotational flexibility of the cymantrenyl substituents leads to large thermal displacement parameters of the carbonyl groups and their variable orientation respective to the cyclopentadienyl rings in the three cymantrenyl moieties.

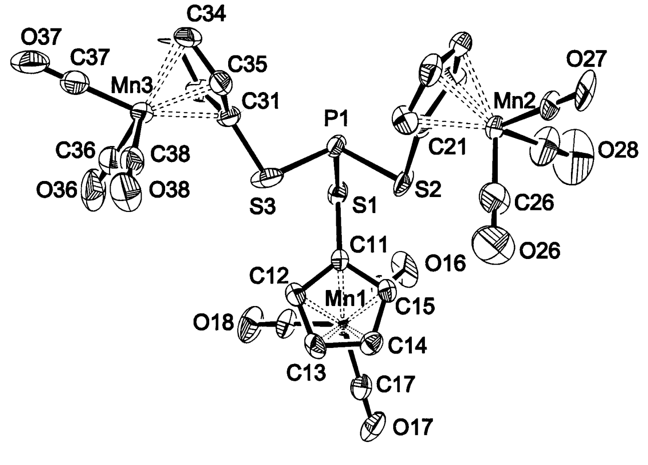

Figure 1. Molecular structure of compound **2** and atomic numbering

The carbonyl groups in the cymantrenyl substituents are staggered with respect to the C−S bonds and nearly eclipsed with respect to the C−H bonds, with torsion angles O=C···C−H of between 7 and 23°. The asymmetry of the structure accounts for an appreciable difference between the corresponding geometrical parameters in this molecule (Table 1). The P1−S1−C11 valence angle, 104.6(1)°, is 7° bigger than the angles at the two other sulfur atoms due to steric repulsion between the cyclopentadienyl ring (C11−C15) and the S2 and S3 atoms. Two short C−H···O intermolecular contacts, which meet the crystallographic criteria for weak hydrogen bonds are observed in the crystals of **2** with participation of the hydrogen atoms of the "trans"-cyclopentadienyl ring: C12−H12···O27′ (1 + *x*, 1/2 − *y*, −1/2 + *z*), C12−H12 0.88(3) Å, H12···O27′ 2.58 Å, ∠C12−H12−O27′ 158(2)°; C15−H15···O38″ (*x*, 1/2 − *y*, 1/2 + *z*), C15−H15 0.96(3) Å, H15···O38″ 2.59 Å, ∠ C15−H15−O38″ 153(2)°.

In comparison with thiophosphites which do not contain a metal atom, tricymantrenyl trithiophosphite **2** has a rather unusual structure, although the geometry of its central inorganic part is very close to that of non metal containing derivatives, in particular triphenyl trithiophosphite.[13] In the crystal, a propeller-like conformation (C_3-symmetry) was observed for most of the phosphorus compounds containing three identical SR groups studied regardless of the phosphorus coordination number.[13−15] A *cis*-orientation of the SR group relative to the phosphorus lone electron pair is also unusual even in the liquid and gaseous phases, with a mixture of several conformers with *gauche* and *trans* orientations of the alkylthio or phenylthio groups relative to the phosphorus lone electron pair or phosphoryl (thiophosphoryl) bonds being found normally.[2−6] Thus, several factors might be responsible for the unusual structure of **2** in the crystalline phase: the bulkiness of the cymantrenyl groups, their irregularity caused by the respective rotation of the carbonyl moieties and cyclopentadienyl rings, the ability of the carbonyl groups to participate in intermolecular interactions with the C−H bonds. In a series of reviews[16−19] it was shown that such weak interactions can significantly influence the observed conformations of molecules and are responsible for their crystal packing.

In order to compare the structure of the cymantrenylthio fragment in trithiophosphite **2** and in disulfides, we have carried out an X-ray study of the dicymantrenyldisulfide **1**. Its molecular structure is shown in Figure 2. The orientation of the five-membered rings with respect to the carbonyl groups is identical for both cymantrenyl fragments in the molecule. Two cymantrenylthio groups are twisted around the central S−S bond by 103.3(1)° with the S−S bond being perpendicular to both cyclopentadienyl rings. The same perpendicular arrangement around the central S−S bond is observed in the chloro-substituted derivative of dicymantrenyl disulfide[20] and in bis[2-(1-dimethylaminoethyl)ferrocenyl]disulfide.[21] In general the structures of **1** and its chloro derivative are very similar and the values of the S−S and S−C bonds and valence angles at the sulfur atoms are the same within experimental error (Table 1). The substitution of one of the sulfur atoms in dicymantrenyl disulfide by phosphorus does not significantly effect the geometry of the cymantrenylthio moieties in **2**. The orientation of the S−P bonds relative to the cyclopentadienyl rings is perpendicular in trithiophosphite, as is the orientation of the S−S bond in **1**.

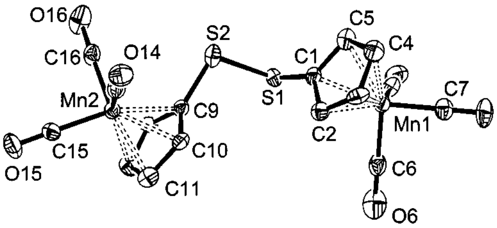

Figure 2. Molecular structure of compound **1** and atomic numbering

Table 1. Selected geometrical parameters[a]

Parameter	2	4
Bond lengths, Å		
P=O	–	1.453(6)
P1−S1	2.107(1)	2.077(3)
P1−S2	2.120(1)	2.080(4)
P1−S3	2.121(2)	2.090(4)
S1−C11	1.760(4)	1.76(1)
S2−C21	1.766(4)	1.781(9)
S3−C31	1.759(4)	1.75(1)
Bond angles, deg.		
S1−P1−S2	98.88(6)	100.6(1)
S1−P1−S3	103.38(7)	101.8(2)
S2−P1−S3	102.57(7)	102.3(2)
S1−P1−O1	–	117.1(3)
S2−P1−O1	–	117.3(3)
S3−P1−O1	–	115.3(3)
P1−S1−C11	104.6(1)	100.9(3)
P1−S2−C21	98.5(1)	103.0(3)
P1−S3−C31	98.3(1)	99.9(4)

[a] Selected parameters for compound **1**: Bond lengths S1−S2 2.066(1), S1−C1 1.764(3), S2−C9 1.757(3) Å; bond angles S2−S1−C1 102.1(1), S1−S2−C9 102.8(1)°.

An X-ray study of triferrocenyl trithiophosphate (Figure 3) showed that this molecule, in contrast to tricymantrenyl trithiophosphite, adopts a classical propeller-like conformation with *gauche* orientations of all three ferrocenylthio groups relative to the P=O bond. Three C−S−P=O torsion angles in this molecule are equal to −54.2, −45.9, and −46.5°. The respective orientation of the ferrocenyl moieties and the P−S bonds is slightly different. It is perpendicular around the C1−S1 and C11−S2 bonds and slightly skewed around the C21−S3 bond with ∠ P−S3−C21−C22 = 75.6°. An almost symmetrical conformation results in equal (within experimental error) P−S, O=PS and PSC bond angles in the molecule (Table 1). The ferrocenyl substituents have the symmetrical structure of ferrocene with planar and nearly parallel cyclopentadienyl rings. The dihedral angles between the rings in the ferrocene moieties are 0.9 (Fc^1), 0.7 (Fc^2) and 2.5° (Fc^3). The angles δ at iron between the two cyclopentadienyl ring centers are 178.9 (Fc^1), 178.0 (Fc^2) and 178.7° (Fc^3). The geometry of the ferrocenyl substituents in **4** is the same as in its oxygen analogue triferrocenyl phosphate,[9] although the conformations of the two molecules are totally different. Unlike the thio derivative, triferrocenyl phosphate adopts an asymmetrical conformation in the crystal with *cis*, *gauche* and *trans* (∠O=P−O−C = −27.8, −73.4, 178.7°) orientations of the ferrocenyloxo groups with respect to the P=O bond. The dihedral angles between the P−O bonds and the cyclopentadienyl rings are also different, being equal to 40.2, −77.3 and −2.7° for the three ferrocenyl substituents. Thus, the organometallic thioester and ester of phosphoric acid have completely different structures. One of the reasons for this difference is the presence of several intermolecular C−H···O short contacts observed in the crystal of the oxygen derivative

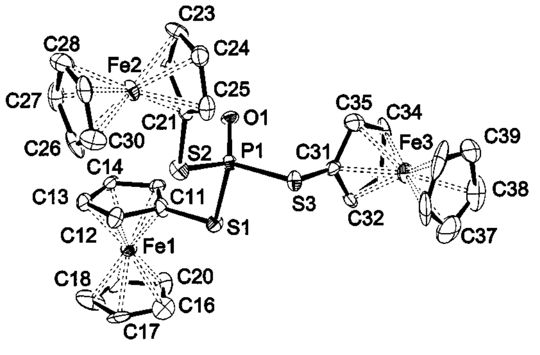

Figure 3. Molecular structure of compound **4** and atomic numbering

Experimental Section

All syntheses were performed using standard Schlenk techniques under an argon atmosphere using pre-dried solvents saturated with argon. The initial organometallic disulfides were obtained following refs.[22][23] IR spectra were measured on an UR-20 spectrometer. ^{1}H and ^{31}P NMR spectra were recorded on the NMR-FT spectrometers MSL-400 and WM-250 (Bruker) with deuteriated solvents (C_6D_6, $CDCl_3$).

Tricymantrenyl Trithiophosphite (2): To a solution of dicymantrenyl disulfide (0.75 g, 1.6 mmol) in acetone (30 mL) were added white phosphorus (0.037 g, 0.28 mmol) and KOH (0.02 mL 15N KOH). The reaction mixture was stirred at ambient temperature for one hour. The solvent was then evaporated and the residue was recrystallized twice from a mixture of benzene/hexane (1:1) to give yellow-green crystals of **2** (0.7 g, 90%), m.p. 125°C. – ^{1}H NMR(C_6D_6): $\delta = 4.21$ (m, 2 H_α), 4.56 (m, 2 H_β). – ^{31}P ($CDCl_3$): $\delta = 128$. – IR (hexane): $\nu_{C=O} = 1945, 2025$ cm^{-1}. – $C_{24}H_{12}Mn_3O_9PS_3$ (736.34): calcd. C 39.15, H 1.64, P 4.21, S 13.06; found C 38.94, H 1.62, P 4.00, S 13.25.

Triferrocenyl Trithiophosphite (3): To a solution of diferrocenyldisulfide (1.1 g, 2.5 mmol) in acetone (30 mL) were added white phosphorus (0.052 g, 0.4 mmol) and 0.2 mL 15N KOH. The reaction mixture was stirred at room temperature for one hour. The solvent was then evaporated and the residue was recrystallized twice from a mixture of benzene/hexane (1:1) to give dark-orange crystals of **3** (0.93 g, 81%), m.p. 200−203°C. − ^{1}H NMR(C_6D_6): $\delta = 4.35$ (m, 2 H_α), 4.52 (m, 2 H_β), 4.50 (s, 5 H). − ^{31}P ($CDCl_3$): $\delta = 131$. − $C_{30}H_{27}Fe_3PS_3$ (760.37): C 52.82, H 3.99, P 4.54, S 14.09; found C 52.74, H 3.95, P 4.25, S 14.15.

Triferrocenyl Trithiophosphate (4): A solution of triferrocenyltrithiophosphite (2.1 g, 3 mmol) in benzene (20 mL) was boiled with the constant bubbling of air through it during one hour. The solvent was evaporated and the residue was recrystallized from a mixture of benzene/hexane (2:1) to give dark-orange crystals of **4** (1.77 g, 85%), m.p. 230°C. − ^{1}H NMR(C_6D_6): $\delta = 4.3$ (m, 2 H_α), 4.45 (m, 2 H_β), 4.52 (s, 5 H). − ^{31}P ($CDCl_3$): $\delta = 47.7$. − $C_{30}H_{27}Fe_3OPS_3$ (776.37): C 51.60, H 3.89, P 4.44, S 13.77; found C 51.67, H 3.87, P 4.31, S 14.25.

X-ray Structure Determination: The X-ray diffraction data were collected on a CAD4 Enraf−Nonius automatic diffractometer with the graphite monochromated Mo K_α radiation ($\lambda = 0.71073$ Å) in the ω-scan mode.

Crystal Data for 1: $C_{16}H_8Mn_2O_6S_2$, formula weight 470.24, (yellow prism, crystal dimensions 0.1 × 0.2 × 0.3 mm), space group $P2_1/n$, $a = 6.495(1)$, $b = 12.141(2)$, $c = 22.509(2)$ Å, $\beta = 93.27(2)°$, $V = 1772.1(4)$ Å^3 at 20°C, $Z = 4$, $\rho = 1.76$ (g·cm^{-3}), $\mu = 16.24$ cm^{-1}, total number of reflections measured 6041, number of observed reflections with $I > 3\sigma(I)$ 2714, number of variables 267, final $R/R_w = 0.032/0.030$.

Crystal Data for 2: $C_{24}H_{12}Mn_3O_9PS_3$, formula weight 736.34, (crystal dimensions 0.4 × 0.25 × 0.2 mm), space group $P2_1/c$, $a = 10.519(3)$, $b = 21.598(6)$, $c = 12.788(2)$ Å, $\beta = 98.32(1)°$, $V = 2875(1)$ Å^3 at 20°C, $Z = 4$, $\rho = 1.70$ (g·cm^{-3}), $\mu = 15.58$ cm^{-1}, total number of reflections measured 9262, number of observed reflections with $I > 3\sigma(I)$ 3520, number of variables 409, final $R/R_w = 0.038/0.044$.

Crystal Data for 4: $C_{30}H_{27}Fe_3OPS_3 \cdot C_6H_6$, formula weight 776.37, (crystal dimensions 0.4 × 0.1 × 0.04 mm), space group $C2/c$, $a = 25.353(3)$, $b = 10.873(3)$, $c = 23.147(4)$ Å, $\beta = 103.04(1)°$, $V = 6212(2)$ Å^3 at 20°C, $Z = 8$, $\rho = 1.66$ (g·cm^{-3}), $\mu = 16.58$ cm^{-1}, total number of reflections measured 14329, number of observed reflections with $I > 3\sigma(I)$ 3669, number of variables 363, final $R/R_w = 0.058/0.057$. The stability of the crystals and the experimental conditions was checked every two hours by measuring three control reflections, while the orientation was monitored every 200 reflections by centering two standards. No significant decay was observed. Corrections for Lorentz and polarization effects were applied. An empirical absorption correction based on ψ-scans was applied for all crystals. The structures were solved by direct methods and difference Fourier syntheses using the MolEN package.[24] All non-hydrogen atoms were refined anisotropically, H-atoms, located in ΔF maps, were refined isotropically for **1** and **2**; for **4** H-atoms were placed into calculated positions and included into structure factor calculations with fixed positional and thermal parameters. It should be noted that crystals of **4** are stabilized by solvate benzene molecules, in which four carbon atoms are disordered.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 130650−130652 (**1, 2, 4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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