

# Preparation, properties, and reactions of metal-containing heterocycles XCIV<sup>1</sup>. Manganese-induced synthesis and crystal structure of 3,5-di(adamant-1-yl)-1-thia-2,4-diphosphole

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## Abstract

3,5-Di(adamant-1-yl)-1-thia-2,4-diphosphole (**2**) has been formed by insertion of  $\text{AdC}\equiv\text{P}$  into the  $>\text{P}\omega\text{S}$  bond of the ( $\eta^2$ -thiophosphinito)manganese complex  $(\text{OC})_4\text{Mn}(\eta^2\text{-S}\omega\text{PR}_2)$  (**1**) ( $\text{R} = \text{cyc-hex}$ ), followed by a [2 + 2] cycloaddition of the resulting intermediate  $(\text{OC})_4\text{MnPR}_2\text{-P}=\text{C}(\text{Ad})\text{-S}$  (**A**) with a second phosphalkyne and elimination of the  $(\text{OC})_4\text{MnPR}_2$  fragment **3**. The structure of **2** was determined by a single crystal X-ray diffraction analysis. Crystal data for **2**: space group  $P2_1/c$  with  $a = 14.324(2)$  Å,  $b = 11.900(1)$  Å,  $c = 11.800(1)$  Å,  $\beta = 100.31(1)^\circ$ ,  $V = 1978.9(4)$  Å<sup>3</sup>,  $Z = 4$ . The structure was refined to  $R = 0.0367$ ,  $wR = 0.0998$ .

**Keywords:** Manganese; Phosphaalkyne; Crystal structure; Group 7; Metallacycle; Phosphine

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## 1. Introduction

Investigations on the behavior of phosphacetylenes in the coordination sphere of transition metal complexes led to the knowledge that late transition metals ( $\text{M} = \text{Ni}, \text{Co}, \text{Rh}, \text{Fe}$ ) are capable of promoting the cyclodimerization to 1,3-diphosphacyclobutadienes [2]. In contrast to these results, early transition metals ( $\text{M} = \text{V}, \text{Zr}, \text{Hf}$ ) favor a cyclotrimerization or cyclotetramerization of that heteroalkyne [3]. Because of the similar covalent radii and comparable electronegativities of phosphorus and sulfur, the  $>\text{P}\omega\text{S}$  group in thiaphosphametallacyclopropanes surprisingly also behaves like a heteroalkyne [4]. Starting from the three-membered heterocycles  $[\text{M}]\text{-PR}_2\omega\text{S}$  ( $[\text{M}] = \text{Mn}(\text{CO})_4$  [5],  $\text{Co}(\text{CO})_2\text{PPh}_3$  [6]) with  $^t\text{BuC}\equiv\text{P}$  we recently obtained, in good yields, the 3,5-di(tert-butyl)-1-thia-2,4-diphosphole, provided that the substituent  $\text{R}$  at the phosphorus atom is sterically demanding [5,6]. To the best of our knowledge, only a few five-membered heterocycles of this type are mentioned in the literature. Some years ago the first thiadiphosphole with  $\text{SiMe}_3$  and  $\text{SSiMe}_3$  substituents was synthesized in good yields [7]. The occur-

rence of other derivatives of this heterocycle with  $\text{Ph}$  [8] and  $\text{OSiMe}_3$  [9] substituents was also mentioned, but they are formed only in side reactions in very low yields. In this investigation we want to demonstrate that the metal-mediated synthesis of thiadiphospholes, starting with phosphalkynes and thiophosphinito complexes, can be more generalized, even if the phosphacetylene carries a steric encumbering residue. Herein we describe the behavior of  $(\text{OC})_4\text{Mn}\omega\text{S}\omega\text{PR}_2$  ( $\text{R} = \text{cyc-hex}$ ) towards adamant-1-ylphosphaalkyne. In a smooth reaction 3,5-di(adamant-1-yl)-1-thia-2,4-diphosphole is accessible.

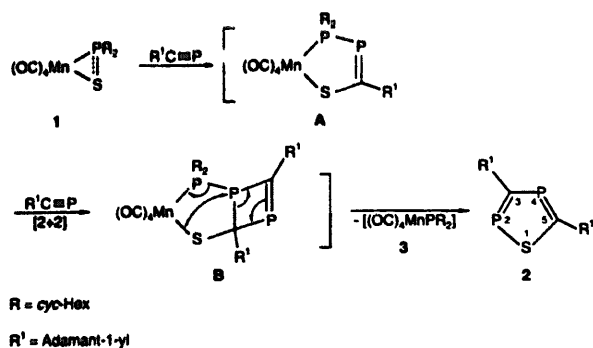
## 2. Results and discussion

Treatment of the ( $\eta^2$ -thiophosphinito)manganese complex **1** with adamant-1-ylphosphaalkyne in tetrahydrofuran at  $65^\circ\text{C}$  afforded, in good yields, the 3,5-di(adamant-1-yl)-1-thia-2,4-diphosphole (**2**) (Scheme 1). After purification with the aid of medium pressure liquid chromatography (MPLC), a colorless, stable solid was obtained which is soluble in all common organic solvents. The composition of **2** was confirmed by a field desorption mass spectrum displaying the molecular peak. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** one observes two

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<sup>1</sup> For Part XCIII, see Ref. [1].



Scheme 1.

characteristic doublets in the low field part. The size of the  $^2J(\text{PP})$  coupling indicates that there is no direct P–P interaction. Because of the electron withdrawing effect of sulfur, the low field signal is attributed to P2, the doublet at higher field is assigned to P4.

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum shows two significant low field doublets of doublets for the ring carbon atoms. Whereas the one with similar P–C coupling constants is ascribed to C3, the other with two different P–C coupling constants is attributed to C5.

To confirm the structure of the 1-thia-2,4-diphosphole **2** this heterocycle was characterized by an X-ray diffraction analysis. The ORTEP diagram with atom labeling is shown in Fig. 1. As expected, the five-membered ring is planar ( $\Sigma = 539.99^\circ$ ), with all bond lengths being shorter than those of the corresponding single bonds (Table 1). The P2–C1 and P1–C2 interatomic distances have the dimension of a P=C double bond [10] and are shorter than the P1–C1 interaction, which is between a single and a double bond. The distance

Table 1  
Selected interatomic distances (Å) and angles ( $^\circ$ ) for **2**

Selected bond lengths (Å)	
P(1)–C(1)	1.760(2)
P(1)–C(2)	1.715(2)
P(2)–C(1)	1.706(2)
P(2)–S	2.0650(7)
S–C(2)	1.721(2)
C(1)–C(11)	1.525(2)
C(2)–C(21)	1.524(2)
Selected bond angles ( $^\circ$ )	
C(2)–S–P(2)	101.33(6)
C(1)–P(2)–S	98.80(6)
P(2)–C(1)–P(1)	120.55(10)
C(2)–P(1)–C(1)	100.09(9)
P(1)–C(2)–S	119.22(10)

between P2 and S is slightly shorter than that of a single bond [11], the same applies to S–C2. The bond angles of P1 and C1 are comparable with those mentioned in Ref. [12].

Scheme 1 demonstrates a possible course of the reaction for the formation of **2**. In a first step the phosphalkyne is inserted into the P=S bond of the starting compound **1** [13]. The resulting intermediate **A** with a P–P contact is kinetically unstable and undergoes a [2 + 2] cycloaddition with a further phosphalkyne molecule to give the intermediate **B**. The latter decomposes with the elimination of the thiadiphosphole **2** [5,6]. The remaining metal complex fragment **3** obviously reacts with additional **1** to give the substitution product  $(\text{OC})_3(\text{HPR}_2)\text{Mn}(\eta^2\text{-S}\equiv\text{P}\text{R}_2)$  (**4**) (R = cyc-hex) (traces of water) and a sparingly soluble complex containing  $\text{Mn}(\text{CO})_4$  units (IR spectrum) which was not characterized (Scheme 2) [5]. If a more bulky

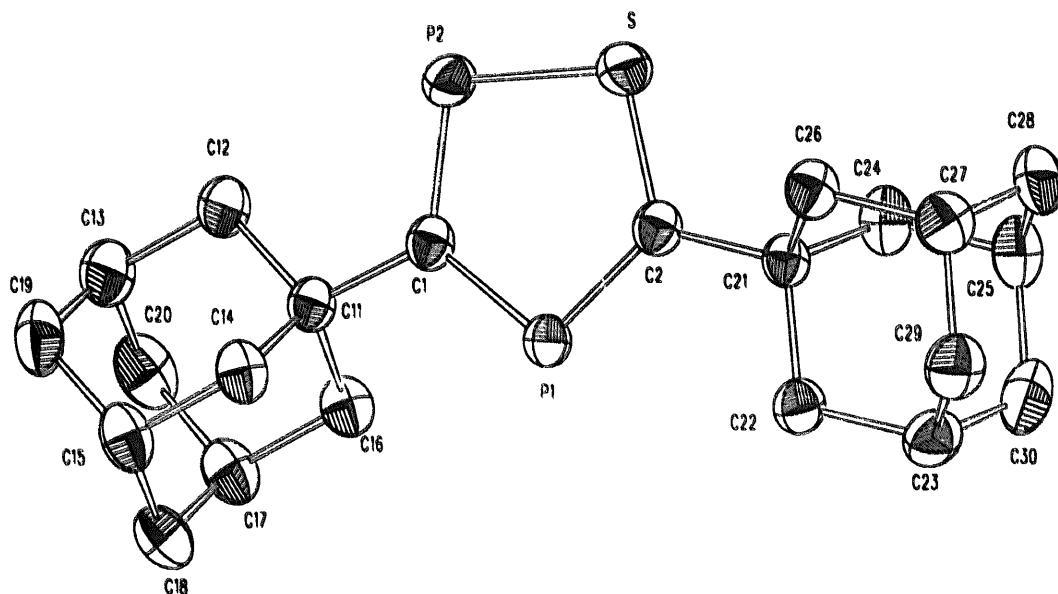
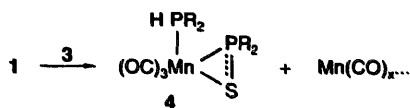


Fig. 1. ORTEP diagram of **2**. The atom numbering is different from that in Scheme 1.



Scheme 2.

organometallic fragment like the  $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}$  moiety instead of an  $\text{Mn}(\text{CO})_4$  residue is employed, the reaction is finished with the corresponding nickel-containing five-membered ring A. The structure of this heterocycle was recently determined by X-ray structural analysis [13].

The orientation of the inserted phosphalkyne is electronically and sterically controlled. In phosphacetylenes the phosphorus atom carries a positive and the carbon atom a negative partial charge [14]. In  $\eta^2$ -thiophosphinito metal complexes the sulfur and phosphorus atoms have a partially positive and negative charge respectively [4]. Starting from the intermediate B, a further [2 + 2] cycloaddition is not possible because of the steric demand of the substituent R at the phosphorus atom [5].

### 3. Experimental section

#### 3.1. Materials

All manipulations were performed under argon using vacuum-line and standard Schlenk techniques. Solvents were dried and deoxygenated by refluxing over the appropriate reagents prior to use and stored under argon. The IR spectrum was measured on a Bruker IFS 48 instrument. The FD mass spectrum was recorded on a Finnigan MAT 711A spectrometer modified by AMD (8 kV, 60°C). Elemental analyses were performed with a Carlo Erba 1106 analyser; the S analysis was carried out according to Dirschel and Erne [15] and Schöniger [16] and analysed as described by Wagner [17]. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were obtained on a Bruker WP 80 (external standard (coaxial insert) 1%  $\text{H}_3\text{PO}_4$  in acetone- $d_6$  for  $T \leq 273$  K) and a Bruker DRX 250 spectrometer operating at 32.39 and 101.25 MHz respectively;  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were measured with a Bruker DRX 250 at 250.13 MHz. Chemical shifts were recorded relative to partially deuterated solvent peaks which are reported relative to TMS. MPLC was carried out with a Knauer HPLC pump 64, UV/VIS filter photometer and Merck Lobar<sup>®</sup> Column B (310-25) LiChroprep<sup>®</sup> Si 60 (40-63).

The starting complex  $(\text{OC})_4\text{Mn-S}\overline{\text{P}}\text{R}_2$  (R = cyc-hex) (**1**) [18] and  $\text{AdC}\equiv\text{P}$  [19] were synthesized as previously described.

#### 3.2. 3,5-Di(adamant-1-yl)-1-thia-2,4-diphosphole (**2**)

$\text{AdC}\equiv\text{P}$  (580 mg, 3.25 mmol) was added to a solution of **1** (520 mg, 1.31 mmol) in 50 ml of tetrahydrofu-

ran. The solution was stirred and refluxed for 6 h. After removing the solvent under vacuum the residue was redissolved in n-hexane (20 ml), the insoluble material was filtered off (P4) and the filtrate chromatographed by a short silica gel column. The main purification resulted from MPLC with a silica gel column (2. fraction). The solvent was removed and the residue dried under vacuum to yield 80 mg (31.4%) of **2**; m.p. 192–195°C. Anal. Found: C, 67.53; H, 7.84; S, 8.24.  $\text{C}_{22}\text{H}_{30}\text{P}_2\text{S}$  Calc.: C, 68.02; H, 7.78; S, 8.25%. IR (KBr):  $\nu(\text{P-S})$  525 (w)  $\text{cm}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR (101.25 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  247.95 (d,  $^2J(\text{PP})$  48.9 Hz, P4), 261.71 (d,  $^2J(\text{PP})$  48.9 Hz, P2).  $^1\text{H}$  NMR (250.13 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  1.75–2.19 (m, 30H,  $\text{C}_{10}\text{H}_{15}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (250.13 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  222.01 (dd,  $^1J(\text{PC})$  69.0,  $^1J(\text{PC})$  77.5 Hz, C3), 209.91 (dd,  $^1J(\text{PC})$  65.5,  $^2J(\text{PC})$  4.3 Hz, C5), 44.02 (dd,  $^2J(\text{PC})$  5.7,  $^3J(\text{PC})$  15.7 Hz, *ipso*-C of  $\text{C}_{10}\text{H}_{15}$ ), 43.30 (dd,  $^2J(\text{PC})$  17.1,  $^2J(\text{PC})$  17.8 Hz, *ipso*-C of  $\text{C}_{10}\text{H}_{15}$ ), 29.25–29.43 (m,  $\text{C}_{10}\text{H}_{15}$ ), 36.33 (s,  $\text{C}_{10}\text{H}_{15}$ ), 47.30–48.63 (m,  $\text{C}_{10}\text{H}_{15}$ ). MS (FD)  $m/z$  388.1 [ $\text{M}^+$ ].

#### 3.3. Tricarbonyldicyclohexylphosphine( $\eta^2$ -dicyclohexylthiophosphinito)manganese (**4**)

$\text{AdC}\equiv\text{P}$  (580 mg, 3.25 mmol) was added to a solution of **1** (520 mg, 1.31 mmol) in 50 ml of tetrahydrofuran. The solution was stirred and refluxed for 6 h. After removing the solvent under vacuum the residue was redissolved in ethyl acetate/petrol ether (60/90°C)

Table 2  
Crystal data and collection parameters for **2**

Formula	$\text{C}_{22}\text{H}_{30}\text{P}_2\text{S}$
<i>F</i> <sub>0</sub>	388.46
Crystal size (mm <sup>3</sup> )	0.20 × 0.20 × 0.20
Crystal system	monoclinic
Space group	$P2_1/c$
<i>a</i> (Å)	14.324(2)
<i>b</i> (Å)	11.900(1)
<i>c</i> (Å)	11.800(1)
$\beta$ (°)	100.31(1)
<i>V</i> (Å <sup>3</sup> )	1978.9(4)
<i>Z</i>	4
Calc. density (mg m <sup>-3</sup> )	1.304
<i>h</i> , <i>k</i> , <i>l</i> range	±16, -13 → 0, -1 → 13
<i>T</i> (K)	208(2)
<i>F</i> (000)	832
Wavelength (Cu K $\alpha$ ) (Å)	1.54184
Reflections collected	3881
Independent reflections	3357
Reflections observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	3149
No. of parameters	347
Goodness of fit	1.076
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0367
<i>wR</i> <sub>2</sub> <sup>b</sup>	0.0998

<sup>a</sup>  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ .

<sup>b</sup>  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \{ \sum [w(F_o^2)^2] \} \}^{0.5}$ .

Table 3  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **2**

Atom	x	y	z	$U_{eq}$
P(1)	2365(1)	4397(1)	-61(1)	32(1)
P(2)	3048(1)	6661(1)	-710(1)	39(1)
S	2251(1)	6795(1)	579(1)	41(1)
C(1)	2996(1)	5238(2)	-893(1)	30(1)
C(2)	1977(1)	5410(2)	779(1)	31(1)
C(11)	3512(1)	4669(2)	-1762(1)	30(1)
C(12)	4092(2)	5510(2)	-2346(2)	40(1)
C(13)	4617(2)	4903(2)	-3195(2)	48(1)
C(14)	2797(1)	4081(2)	-2711(2)	35(1)
C(15)	3321(1)	3480(2)	-3560(2)	40(1)
C(16)	4198(1)	3769(2)	-1142(2)	34(1)
C(17)	4722(1)	3174(2)	-2000(2)	39(1)
C(18)	3994(1)	2603(2)	-2921(2)	42(1)
C(19)	3896(2)	4330(2)	-4125(2)	49(1)
C(20)	5292(1)	4029(2)	-2550(2)	48(1)
C(21)	1432(1)	5147(2)	1745(1)	29(1)
C(22)	1220(1)	3879(2)	1788(2)	35(1)
C(23)	692(2)	3621(2)	2789(2)	42(1)
C(24)	2030(1)	5496(2)	2908(2)	39(1)
C(25)	1495(2)	5239(2)	3899(2)	45(1)
C(26)	481(1)	5788(2)	1578(2)	34(1)
C(27)	-50(1)	5517(2)	2571(2)	39(1)
C(28)	561(2)	5888(2)	3699(2)	46(1)
C(29)	-244(1)	4260(2)	2594(2)	44(1)
C(30)	1309(2)	3981(2)	3917(2)	50(1)

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

(1:3) (20 ml), the insoluble material was filtered off (P4) and the filtrate was chromatographed by short silica gel column. The main purification resulted from MPLC with ethyl acetate/petrol ether (60/90°C) (1:3) by a silica gel column (3. fraction). IR (n-hexane):  $\nu(\text{C}=\text{O})$  2015 (m), 1925 (vs), 1907 (s)  $\text{cm}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR (32.39 MHz, THF, 243 K):  $\delta$  53.15 (s,  $\text{HP}(\text{C}_6\text{H}_{11})_2$ ), 95.25 (s,  $\text{P}(\text{C}_6\text{H}_{11})_2=\text{S}$ ). MS (FD) $m/z$  566.3 [ $\text{M}^+$ ].

### 3.4. Structure determination of **2**

Crystal data and details of data collection are summarized in Table 2. The atomic coordinates and equivalent isotropic displacement parameters for **2** are given in Table 3. Single crystals were obtained by adding a few drops of n-hexane to a concentrated THF solution of **2**. The crystal was mounted on a glass fiber and transferred to an Enraf Nonius CAD4 diffractometer (graphite-monochromated Cu  $K\alpha$  radiation).

The lattice constants were determined with 25 precisely centered high-angle reflections and refined by full-matrix least-squares methods. The data collected with  $\Omega$ -scans at  $-65^\circ$  between  $\theta = 5.3$  and  $65$  resulted in 3881 intensity values. 3149 reflections with  $I >$

$2\sigma(I)$  have been used for the structure determination. The structure was solved by direct methods [20] and refined by full-matrix least-squares [21]. Refinement of the model with anisotropic temperature parameters and the hydrogen atoms calculated on ideal positions led to the final  $R$  value of 0.036.

### 4. Supplementary material available

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 404700, the names of the authors and the journal citation.

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