maximum deviations from the appropriate least-squares planes are +0.249 Å for C(6), −0.217 Å for S(1), +0.344 Å for S(2), and −0.359 Å for C(7).

Summary. The structures presented here represent prototypes for MoO_2(tridentate) complexes in ligated and unligated (polymeric) forms. The polymeric structure of $[MoO_2(L-NO_2)]_n$ provides clear support for the claim of a similar chainlike arrangement in unligated MoO_2(salicylaldimato) complexes.[8] The infrared spectrum of unligated $MoO_2(L-NS_2)$, $MoO_2(L-NO_2)$, and the latter complexes[8] exhibits a broad IR band at ~800–850 cm^{-1}, which appears to be diagnostic of Mo═O···Mo bridges and is presumably the perturbed $\nu_{Mo=O}$ stretching frequency. The structure of $MoO_2(L-NS_2)\cdot$TMSO tends to substantiate earlier ligated formulations of MoO_2(tridentate)·D complexes.[7-10] The long Mo···O(TMSO) distance is a consequence of a neutral ligand and the trans effect of a Mo═O_t unit and leads to a higher degree of lability of ligands in this position. Research is continuing on complexes of the general type $MoO_{1,2}$(tridentate–NS_2), including those with labile binding sites and steric features that obviate formation of Mo(V)–O–Mo(V) complexes in the course of enzyme-related

$$\mathrm{Mo^{IV}O} \xrightleftharpoons{[O]} \mathrm{Mo^{VI}O_2}$$

oxo-transfer reactions.

Acknowledgment. This research was supported by NSF Grant CHE 81-06017. X-ray equipment used in this research was obtained by NSF Grant 80-00670.

Registry No. $MoO_2(L-NS_2)\cdot$TMSO, 85534-01-6; $[MoO_2(L-NO_2)]_n$, 85534-02-7; $MoO_2(acac)_2$, 17524-05-9.

Supplementary Material Available: Anisotropic temperature factors (Table S-I), calculated hydrogen atom coordinates (Table S-II), and calculated and observed structure factors (Table S-III) for $MoO_2(L-NS_2)\cdot$TMSO and $[MoO_2(L-NO_2)]_n$ (24 pages). Ordering information is given on any current masthead page.

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Molecular Structure of a Mixed-Ligand Chlorinated Sulfur-Containing Phosphorane[1]

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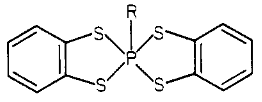
The synthesis and crystal structure of 5-phenyl-2,3-tetrachlorobenzo-7,8-(2′-methyl-5′,6′-benzo)-1,4-dioxa-6,9-dithia-5λ^5-phosphaspiro[4.4]nona-2,7-diene, $(Cl_4C_6O_2)(CH_3C_6H_3S_2)PPh$ (**7**), is reported. It crystallizes in the monoclinic space group *C*2/*c* (*Z* = 8) with *a* = 22.534 (8) Å, *b* = 8.710 (3) Å, *c* = 21.419 (7) Å, and *β* = 94.11 (3)°. The structure was refined to *R* = 0.072 and R_w = 0.083. The geometry around the phosphorus atom is rectangular pyramidal, being 93.0% (97.4% using unit vectors) displaced from the trigonal bipyramid toward the rectangular pyramid. Achievement of this structure is aided by the electron-delocalizing effect of the chlorine ring substituents, resulting in reduced bond electron-pair repulsions at phosphorus. It represents the least distorted rectangular-pyramidal phosphorane so far reported.

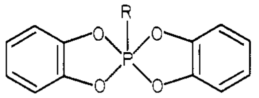
Introduction

Although only a few spirocyclic phosphorane structures that contain sulfur atoms bonded to phorphorus have been investigated,[2-5] it appears that thio-containing derivatives undergo considerable structural change with relatively small variations in ligand character, especially variations in the composition of the acyclic ligand.[2] For example, the spirocycle **1** is not



	R	% TP → RP
1	Ph	31
2	CH_3	79

far displaced from a trigonal bipyramid[2] (TP) (31% from the TP toward the rectangular pyramid (RP) along the Berry coordinate based on unit bond distances[6]) while **2**,[4] containing an acyclic methyl group in place of the phenyl group, is close to a rectangular pyramid (79% displaced from a TP[2]). The corresponding oxaphospholes, **3**[7] and **4**,[8] are 72% and 82%



	R	% TP → RP
3	Ph	72.0 (74.6)
4	CH_3	82.5 (85.0)

displaced toward the RP,[6] respectively, on the basis of actual bond distances in these derivatives (based on unit bond distances in parentheses). It has been commented[2] that the presence of the less electronegative sulfur atoms bonded to phosphorus causes enhanced bond electron-pair repulsions[9] between apical and basal bonds of a RP that tend to favor the TP.

In a further comparison of substituent effects, phosphoranes **5** and **6**, containing chlorinated rings, are nearly ideal rec-

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(1) (a) Pentacoordinated Molecules. 47. (b) Previous paper in this series: Day, R. O.; Schmidpeter, A.; Holmes, R. R. *Inorg. Chem.* **1982**, *21*, 3916.

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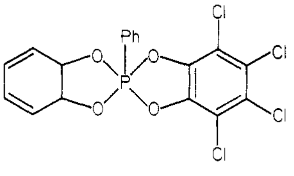
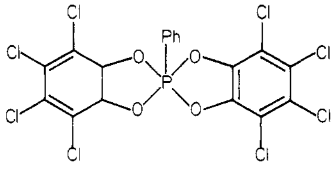


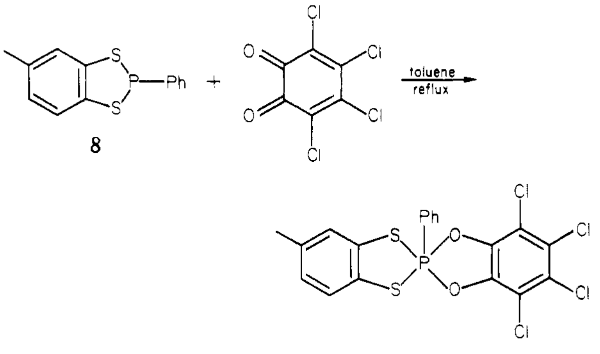
5 (% TP → RP: 94)



6 (% TP → RP: 94)

tangular pyramids[10] (based on unit bond distances). Here, the electron-withdrawing effect of the chlorine ring substituents tends to lessen electron-pair repulsion effects among the bonds attached to phosphorus and to equalize P–O bonding in the ring system.[10] Both of these effects have been cited[11,12] as factors favoring the rectangular-pyramidal geometry.

To ascertain the influence of the latter effect on a thio-containing cyclic phosphorane, we synthesized the mixed-ligand derivative **7** and have determined its crystal structure. It is synthesized by the oxidative-addition reaction of the phospholane **8** with *o*-chloranil in boiling toluene as shown in eq 1.



8

(1)

7

Experimental Section

Preparation of 5-Phenyl-2,3-tetrachlorobenzo-7,8-(2′-methyl-5′,6′-benzo)-1,4-dioxa-6,9-dithia-5λ^5-phosphaspiro[4.4]nona-2,7-diene (7). To a solution of 2-phenyl-2′-methyl-1,3,2-benzodithiaphospholane,[13] $(C_7H_6S_2)P(C_6H_5)$ (**8**) (1.5 g, 5.72 mmol), in toluene (25 mL) at room temperature was added *o*-chloranil (1.41 g, 5.73 mmol). When the reaction mixture was stirred at room temperature, an orange precipitate was thrown out of the solution. The resulting mixture was stirred at room temperature for $^1/_4$ h and then heated under reflux using an oil bath for $^1/_2$ h. A dark brown clear solution resulted. When the reaction mixture was cooled to room temperature, crystals deposited. The crude crystals were dissolved in boiling toluene, and the solution was filtered hot. When the filtrate was cooled to room temperature, crystals (yellow tint) of **7**, $(C_6Cl_4O_2)(C_7H_6S_2)P(C_6H_5)$, deposited; mp 147–162 °C dec (yield 2.7 g, 93.2%). Anal. Calcd for $C_{19}H_{11}S_2O_2Cl_4P$: C, 44.9; H, 2.18; Cl, 27.91. Found: C, 44.92; H, 1.88; Cl, 27.77.

The insolubility of phosphorane **7** in common organic solvents (C_6H_6, CH_2Cl_2, $CHCl_3$, CH_3COCH_3, CH_3CN) at room temperature precludes its ^1H and ^{13}P NMR measurements. **7** also was found to decompose during an attempt to dissolve it in $Me_2S{=}O$ at elevated temperatures (>100 °C). Crystals suitable for X-ray crystallography were grown from a solution of **7** in toluene.

Crystallography of 7. The X-ray crystallography study was done with an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.709\,30$ Å; $\lambda(K\alpha_2) = 0.713\,59$ Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[14]

A very small (0.08 × 0.15 x 0.35 mm) colorless crystal, cut from a polycrystalline mass of needles and mounted inside a sealed thin-walled glass capillary as a precaution against moisture sensitivity, was used for the X-ray studies.

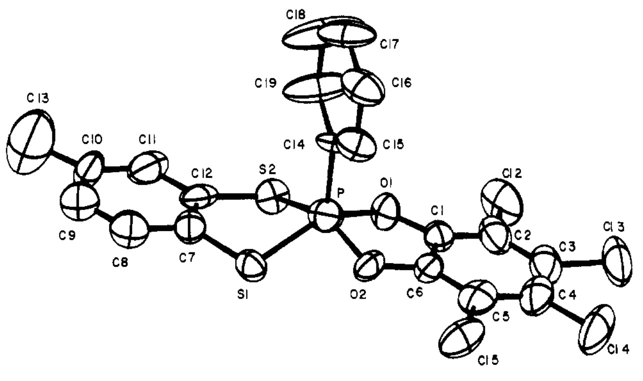


Figure 1. ORTEP plot of $(Cl_4C_6O_2)(MeC_6H_3S_2)PPh$ (**7**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for purposes of clarity.

Table I. Atomic Coordinates in Crystalline $(Cl_4C_6O_2)(MeC_6H_3S_2)PPh$ (**7**)[a]

atom type[b]	10^4x	10^4y	10^4z
P	5320 (1)	8187 (4)	712 (1)
S1	4415 (1)	7684 (4)	410 (2)
S2	5070 (2)	10002 (4)	1315 (2)
O1	5940 (3)	9309 (8)	685 (3)
O2	5438 (3)	7549 (9)	−18 (3)
Cl2	7123 (2)	10939 (5)	581 (2)
Cl3	7788 (2)	9649 (5)	−568 (2)
Cl4	7140 (2)	7262 (5)	−1473 (2)
Cl5	5838 (2)	6170 (4)	−1226 (2)
C1	6273 (5)	8914 (14)	207 (6)
C2	6818 (6)	9531 (15)	99 (6)
C3	7092 (6)	8968 (16)	−444 (7)
C4	6807 (6)	7933 (17)	−846 (7)
C5	6243 (6)	7398 (14)	−724 (6)
C6	5975 (5)	7904 (14)	−199 (5)
C7	4090 (5)	8285 (15)	1079 (6)
C8	3509 (6)	7768 (16)	1202 (7)
C9	3233 (7)	8292 (21)	1717 (8)
C10	3523 (7)	9309 (21)	2124 (7)
C11	4093 (6)	9863 (16)	2012 (6)
C12	4375 (5)	9346 (14)	1486 (5)
C13	3167 (10)	9743 (30)	2659 (11)
C14	5578 (4)	6591 (13)	1194 (5)
C15	5664 (6)	5197 (15)	925 (6)
C16	5874 (6)	3930 (15)	1303 (7)
C17	5980 (7)	4129 (17)	1913 (7)
C18	5887 (10)	5526 (19)	2180 (6)
C19	5686 (8)	6740 (16)	1815 (6)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 1.

Crystal Data: $C_{19}H_{11}O_2S_2PCl_4$; space group $C2/c$ (C^6_{2h}; No. 15),[15] from $2/m$ diffraction symmetry, extinctions, and successful solution and refinement; $a = 22.534$ (8) Å, $b = 8.710$ (3) Å, $c = 21.419$ (7) Å, $\beta = 94.11$ (3)°, $Z = 8$, and $\mu_{\mathrm{MoK}\alpha} = 0.834$ mm^{-1}; 2392 independent reflections ($+h,+k,\pm l$) measured by using the θ–2θ scan mode for $2° \leq 2\theta_{\mathrm{MoK}\alpha} \leq 43°$; no corrections made for absorption.

The structure was solved by using direct methods (MULTAN) and refined by full-matrix least squares.[16] The 28 independent non-hydrogen atoms were refined anisotropically while the 8 independent aromatic hydrogen atoms were included as fixed isotropic scatterers (calculated coordinates; C–H bond length updated to 0.98 Å). Methyl hydrogen atoms were not included in the refinement. The final

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(15) "International Tables for X-ray Crystallography"; Knoch Press: Birmingham, England, 1969; Vol. I, p 101.
(16) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oL_p/\sigma_I$. Mean atomic scattering factors were taken from ref 15, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for Cl and P were taken from the same source, pp 149–150.

Table II. Selected Bond Lengths (Å) and Angles (deg) in Crystalline $(Cl_4C_6O_2)(MeC_6H_3S_2)PPh$ (7)[a]

P-O1	1.709 (7)	S1-C7	1.736 (13)
P-O2	1.698 (8)	S2-C12	1.731 (13)
P-C14	1.802 (10)	O1-C1	1.357 (12)
P-S1	2.141 (4)	O2-C6	1.333 (12)
P-S2	2.143 (4)		
O1-P-O2	88.5 (4)	S1-P-S2	92.7 (2)
O1-P-S1	150.5 (3)	S1-P-C14	106.0 (4)
O1-P-S2	81.3 (3)	S2-P-C14	108.1 (4)
O1-P-C14	103.3 (5)	P-S2-C12	99.5 (5)
O2-P-S1	82.1 (3)	P-S1-C7	97.9 (5)
O2-P-S2	149.5 (3)	P-O1-C1	112.2 (7)
O2-P-C14	102.2 (5)	P-O2-C6	113.4 (7)

[a] See footnotes *a* and *b* of Table I.

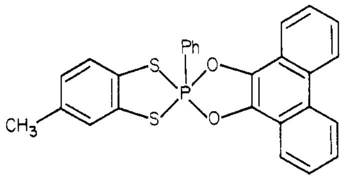
agreement factors[17] were $R = 0.072$ and $R_w = 0.083$ for the 1354 relfections having $I \geq 2\sigma_I$.

Results and Discussion

The atom-labeling scheme and the molecular geometry of 7 are shown in Figure 1. Atomic coordinates for non-hydrogen atoms are given in Table I. Important bond lengths and angles are given in Table II. Anisotropic thermal parameters, fixed parameters for hydrogen atoms, and remaining bond lengths and angles are provided as supplementary material.

The geometry about the phosphorus atom for 7 is essentially that of a rectangular pyramid with the chalcogen atoms occupying the four basal positions. The atoms S1, S2, O1, and O2 are coplanar to within ±0.007 Å, with the phosphorus atom displaced 0.491 Å out of this plane in the direction of the apical atom (C14).

In terms of the Berry coordinate,[18] the geometry is displaced an average of 93.0% (97.4% by using unit vectors[6]) from a trigonal bipyramid having S1 and O1 in axial positions toward the aforementioned rectangular pyramid, where C14 is the pivotal atom in the pseudorotational process. However, if one chooses S2 and O2 for axial positions of the reference trigonal bipyramid, no significant difference exists in the structural displacement since there is no significant difference in bond lengths and angles at phosphorus to indicate "residual" TP character. The structure is the least distorted rectangular-pyramidal phosphorane thus far reported. The bond parameters are very close to those in the related phenanthro derivatives **9**.[2] As a consequence, the structural displacement toward the rectangular pyramid is similar. It seems that the electron-delocalizing effect of the phenanthrene ring system is comparable to that of the fully chlorinated "catechol" ring.



9 (% TP → RP: 97)

It is noteworthy that no example of a rectangular pyramid for five-membered cyclic phosphoranes exists unless two rings are present; the rings contain unsaturation and like atoms are present in any one ring bound to phosphorus.[3]

Although the present study regarding sulfur insertion in place of oxygen does not make a direct comparison with the structural change encountered between the oxaphosphole **3** and its chlorinated derivatives, **5** and **6**, it is clear that the nearly ideal RP structure found for **7** is consistent with the view[2] that larger structural changes manifest themselves with thio-containing spirocyclic phosphoranes relative to their oxygenated counterparts, which have similar changes in ligand constitution.

In line with reduced bond pair repulsion favoring a RP,[11,12] we recently reported[19] the first rectangular-pyramidal structure for a pentacoordinated arsenic compound (**10**). This is the arsorane derivative of 3 and shows two molecules per unit cell, displaced 99% and 95% toward the RP (based on unit vectors).

Acknowledgment. The support of this research by the National Institutes of Health (Grant GM21466) and the NSF (Grant CHE8205411) is gratefully acknowledged. We also thank the University of Massachusetts Computing Center for generous allocation of computer time.

Registry No. **7**, 85421-73-4; **8**, 67826-80-6; *o*-chloranil, 2435-53-2.

Supplementary Material Available: Compilations of observed and calculated structure factor amplitudes, anisotropic thermal parameters (Table A), parameters for hydrogen atoms (Table B), and additional bond lengths and angles (Table C) for 7 (11 pages). Ordering information is given on any current masthead page.

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(17) $R = \sum||F_o| - |F_c||/\sum|F_o|$, and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

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