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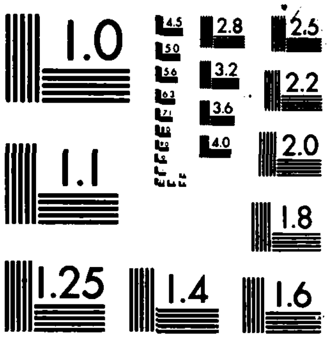

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Synthesis and Structure of Sulfur Derivatives of a (Methylene)phosphine

by

M. Caira, R.H. Neilson, W.H. Watson
P. Wisian-Neilson, Z.-M. Xie

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Chemistry Department
Fort Worth, TX 76129

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Thioxophosphorane

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The methylenephosphine $MesP{=}C(SiMe_3)_2$ (1, Mes=mesityl) is smoothly oxidized by elemental sulfur to the 3-membered ring system $MesP(=S)-S-C(SiMe_3)_2$ (3) which, upon treatment with n-Bu_3P, is converted to the 3-coordinate phosphorane $MesP(=S){=}C(SiMe_3)_2$ (2). The nearly isostructural nature of compounds 2 and 3 is confirmed by their X-ray crystallographic analyses.

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Synthesis and Structure of Sulfur Derivatives of a Methylenephosphine

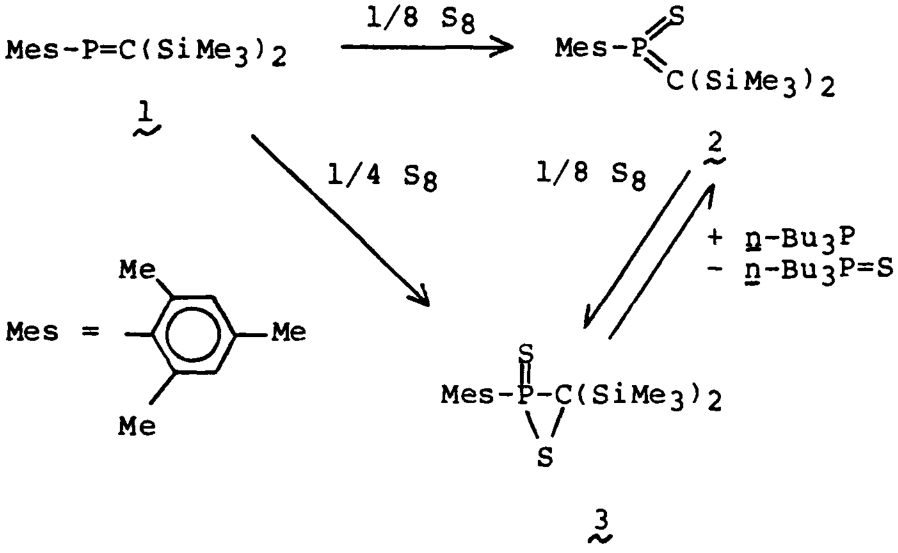
Mino Caira, Robert H. Neilson*, William H. Watson*,
Patty Wisian-Neilson, and Ze-Min Xie

Department of Chemistry, Texas Christian University
Fort Worth, Texas 76129 (USA)

Summary. The methylenephosphine $\mathrm{MesP{=}C(SiMe_3)_2}$ (1, Mes = mesityl) is smoothly oxidized by elemental sulfur to the 3-membered ring system $\mathrm{MesP(=S)\text{-}S\text{-}C(SiMe_3)_2}$ (3) which, upon treatment with n-$\mathrm{Bu_3P}$, is converted to the 3-coordinate phosphorane $\mathrm{MesP(=S){=}C(SiMe_3)_2}$ (2). The nearly isostructural nature of compounds 2 and 3 is confirmed by their X-ray crystallographic analyses.

There has been considerable interest recently in π-bonded phosphorus compounds such as the methylenephosphines and their related oxidation products.[1,2] We report here the synthesis and the crystal structure analyses of the products of the oxidation of mesityl[bis(trimethylsilyl)methylene]phosphine, 1,[3] by elemental sulfur.

Treatment of 1 with one equivalent of sulfur resulted in an inseparable mixture of the methylene(thioxo)phosphorane 2, the thiaphosphirane 3, and starting material 1. Addition of a second equivalent of sulfur afforded complete conversion of the mixture to 3. A pure sample of 2 was then obtained by the reaction of 3 with *n*-Bu_3P.



Compound 2 represents a stable analog to the proposed intermediate, $[(o\text{-}Me)_2C_6H_3]P(=S)=CPh_2$[2b] ($^{31}P$ δ 140.6)[4], in the oxidation of methylenephosphines by sulfur. Stable, non-crystalline analogs of both 2 and 3, $R_2N\text{-}P(=S)=CHR$ and $R_2N\text{-}\overline{P(=S)\text{-}S\text{-}C}HR$ ($R = Me_3Si$) have been prepared by Niecke and Wildbredt[2a] using a similar procedure. The crystal structures reported here are the first for the P-C-S three-membered ring system and one of the few[5] reported for three-coordinate P(V)compounds.

The molecular structures of 2 and 3 are shown in perspective views in Figures 1 and 2, respectively. They are, in fact, nearly isostructural[6,7] with twenty non-hydrogen atoms occupying very similar positions but with no electron density at the S(2) position in 2. In compound 2, the P=C(10) distance lies just below the lower limit of the range of P=C distances reported for methylenephosphines,[1] 1.68-1.72 Å. The sums of the valence angles subtended by atoms P and C(10) are 359.9° and 359.8°, respectively, confirming sp^2 hybridization at these centers. In contrast, atoms P and C(10) in 3 are pyramidallized, lying 0.42 and 0.36 Å, respectively, above the plane of their four bonded atoms (coplanar to within 0.04 Å) in the direction of S(2).

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References

1. Appel, R.; Knoll, F.; Ruppert, I. Angew. Chem. Int. Ed. Engl. 1981, 20, 731.

2. See for example: (a) Niecke, E.; Wildbredt, D.-A. J. Chem. Soc., Chem. Comm. 1981, 72. (b) Van der Knaap, T.A.; Klebach, T.C.; Lourens, R.; Vos, M.; Bickelhaupt, F. J. Am. Chem. Soc. 1983, 105, 4026. (c) Neilson, R.H. Inorg. Chem. 1981, 20, 1679.

3. Neilson, R.H.; Xie, Z.-M., manuscript in preparation.

4. Bickelhaupt, F., Reported at the International Conference on Phosphorus Chemistry, Nice, France, September, 1983.

5. (a) Pohl, S.; Krebs, B. Chem. Ber. 1977, 110, 3183.
(b) Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Hirotsu, K.; Higuchi, T. J. Chem. Soc., Chem. Commun. 1983, 862.

6. Crystal data for 2: a = 17.539(3), b = 13.393(2), c = 8.934(2)A, V = 2077.1(7) $Å^3$, orthorhombic, space group $Pn2_1a$ (standard setting $Pna2_1$), ρ_c = 1.089 gcm^{-3} for Z = 4, $\mu(CuK\alpha)$ = 3.02 mm^{-1}, F(000) = 736.0.

Crystal data for 3 : $a = 17.455(4)$, $b = 13.756(4)$, $c = 8.973(2)$Å, $V = 2154.5(9)$Å^3, orthorhombic, space group $Pn2_1a$, $\rho_c = 1.149$ gcm^{-3} for $Z = 4$, μ(CuKα) = 3.80 mm^{-1}, F(000) = 800.0.

7. Intensity data for 2 and 3 were collected at 293K from spherically-ground crystals (average radii 0.133, 0.125mm) mounted on a Syntex $P2_1$ automatic diffractometer employing CuK radiation. The space group was deduced from systematic absences and intensity statistics. The structure of 3 was determined by direct methods. Similarity in morphology, cell dimensions and the common space group indicated close correspondence between the two molecular structures and their crystal packing. For 2, the positions of P, S(1), Si(1) and Si(2) of 3 were accordingly used to phase difference Fourier syntheses from which the remaining atoms of 2 were located. Both structures were refined by blocked-matrix least-squares methods. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. H atoms were included at geometrically constrained positions (C-H 1.08Å) based on those found in difference maps, with fixed isotropic thermal parameters equal to those of their parent atoms. Final R factors were $R = 0.061$, $R_w = 0.064$ for 2 (1209 unique reflexions) and $R = 0.045$, $R_w = 0.047$ for 3 (1269 unique reflexions). Since the space group is polar and anomalous dispersion corrections were applied to the S,P and Si scattering factors, it was necessary to test the absolute polarities of the crystals chosen for analysis. Significance tests based on Hamilton's R-ratio indicated that the crystals of 2 and 3 chosen had opposite polarity. The deposited fractional coordinates reflect this difference. Enantiomers of 2 and 3 with the same chirality are illustrated in the Figures to emphasize the similarity between the molecular structures.

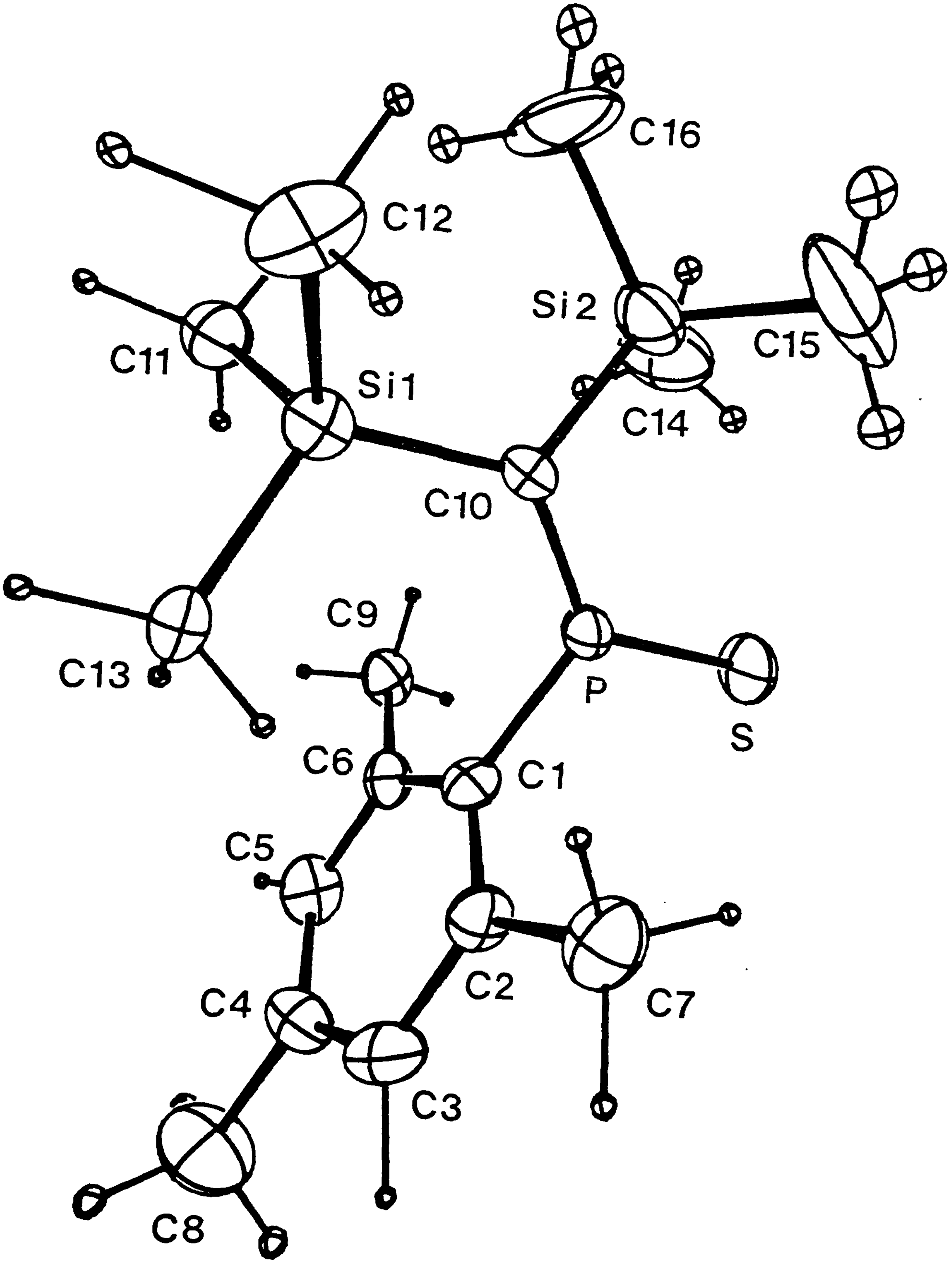
Table. NMR Spectroscopic Data [a,b]

		^1H NMR		^{13}C NMR		^{31}P NMR
compd	signal	δ	J_{PH}	δ	J_{PC}	δ
2	Me_3Si	-0.22		2.11		190.9
		0.39		2.56		
	P-C			126.00	34.2	
	o-Me	2.23		22.50	7.3	
	p-Me	2.51	1.5	21.48		
3	Me_3Si	-0.26		0.14	3.1	2.6
		0.38		1.66	3.4	
	P-C			26.39	8.6	
	o-Me[c]	2.66	1.5	22.76	4.3	
		2.57	1.1	22.19	5.5	
	p-Me	2.20		21.15	1.2	

[a] Chemical shifts downfield from Me_4Si for ^1H and ^{13}C and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^1H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$. [b] Data for phenyl signals to be published.[3] [c] Non-equivalent o-Me groups due to hindered rotation about P-C(ring) bond.

Figure 1. Molecular structure of 2 : $\mathrm{Mes\text{-}P(=S)=C(SiMe_3)_2}$. Principal bond lengths (angstrom) and angles (degrees) are: P=S 1.925(4), P=C(10) 1.647(9), P-C(1) 1.80(1), Si(1)-C(10) 1.88(1), Si(2)-C(10) 1.89(1), S-P-C(1) 113.1(3), S-P-C(10) 127.8(4), C(1)-P-C(10) 119.0(5), P-C(10)-Si(1) 123.8(6), P-C(10)-Si(2) 115.8(6), Si(1)-C(10)-Si(2) 120.2(5). Thermal ellipsoids in both figures drawn at the 35% probability level.

Figure 2. Molecular structure of 3 : $\mathrm{Mes\text{-}P(=S)\text{-}S\text{-}C(SiMe_3)_2}$. Principal bond lengths (angstrom) and angles (degrees) are: P=S(1) 1.932(3), P-S(2) 2.049(3), P-C(10) 1.795(7), P-C(1) 1.793(7), S(2)-C(10) 1.918(8), Si(1)-C(10) 1.920(8), Si(2)-C(10) 1.918(7), S(1)-P-C(1) 112.7(2), S(1)-P-C(10) 123.2(3), C(1)-P-C(10) 116.3(3), P-C(10)-Si(1) 123.4(4), P-C(10)-Si(2) 115.8(4), Si(1)-C(10)-Si(2) 117.1(4), S(1)-P-S(2) 121.6(1), S(2)-P-C(1) 113.7(3), S(2)-P-C(10) 59.4(2), P-S(2)-C(10) 53.7(2), P-C(10)-S(2) 66.9(3), S(2)-C(10)-Si(1) 106.4(3), S(2)-C(10)-Si(2) 114.4(4).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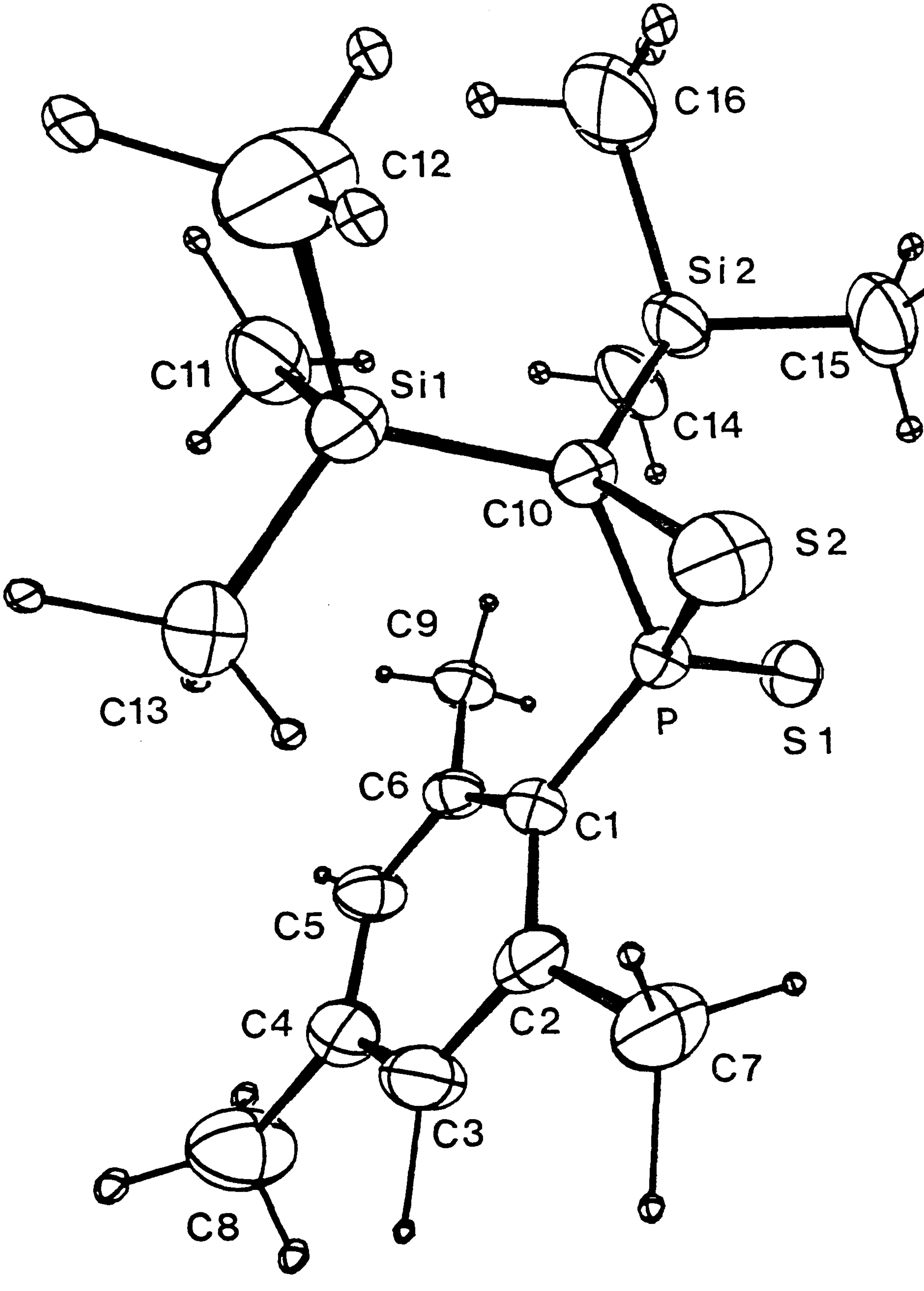
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