

Reaction of β -Diketones with P_4S_{10} To Produce Novel Alkyl–Phosphorus–Sulfur Clusters

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One component of on-going investigations of β -diketonates and related bidentate anions as ligands for chemical vapor deposition of certain metals¹ requires the preparation of various β -dithione compounds.² Previous reports for transformation of ketone to thione functionality by treatment with P_4S_{10} indicated one potential route to the desired compositions.³ Unexpected products were observed from the reactions between selected β -diketone compounds and P_4S_{10} (Scheme 1) and are reported at this time.

The solid state structures of compounds **1** and **2** (Figures 1 and 2, respectively), as determined by single-crystal X-ray diffraction, reveal phosphorus pentasulfide structural units often found in inorganic compounds but rarely found in organic compounds. In these new molecules, the P_2S_5 group consists of two phosphorus atoms attached at C1, one sulfur atom (S5) bridging P1 to P2, one sulfur atom (S4) bridging P1 to C3, and one sulfur atom (S3) bridging P2 to C3. Terminal sulfur atoms (S1 and S2) are attached to each phosphorus atom, completing the P_2S_5 fragment, which bears a strong resemblance to one-half of the original P_4S_{10} skeleton.⁴ The carbon backbone is unchanged from that of the starting β -diketone. The P_2S_5 fragments observed for **1** and **2** are isostructural, each retaining both the relic hydrocarbon component of the organic reactant and the pseudo-adamantoid framework of the inorganic reactant.

A previous example of a structurally characterized organic compound containing the P_2S_5 moiety was reported by Fluck *et al.*⁵ (**3**) and is illustrated in Figure 3. The bicyclic compound **3** substantially differs from **1** and **2** in its regiochemistry. A crystal structure of another compound containing phosphorus in a similar environment has been reported by Roesky *et al.*, **4** (Figure 3).⁶ Compound **5**, reported by Grossmann *et al.*,⁷ was made by reacting 1,2-diphosphinylbenzene with elemental sulfur.

The chair angles between the planes P2–S5–P1, P1–P2–S3–S4, and S3–S4–C3 are 69.4 and 74.3° in **1** and 70.0 and 76.1° in **2**, compared to 73.8° in **3**,⁸ 56.5° in P_4S_{10} ,⁹ and 72.7

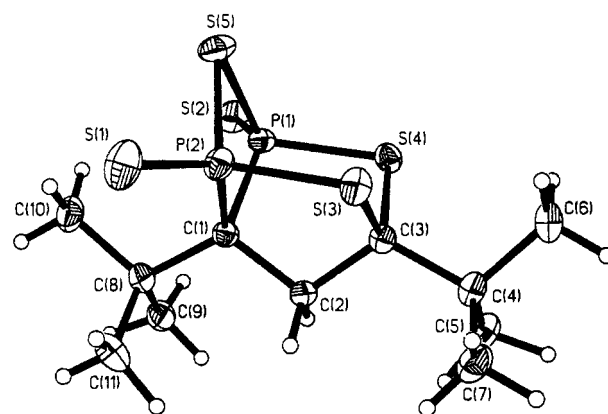


Figure 1. ORTEP representation of the solid state single-crystal X-ray diffraction structure of **1**, with 30% thermal ellipsoids for non-hydrogen atoms and arbitrary spheres for hydrogen atoms.

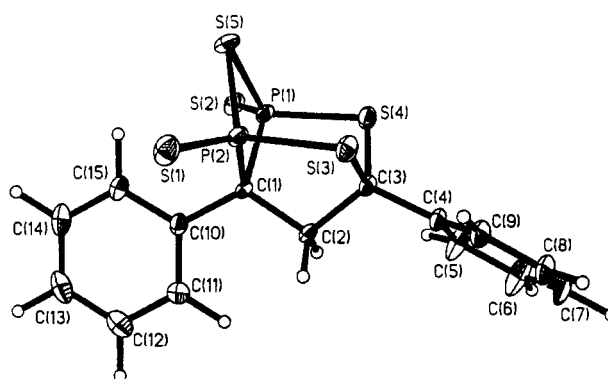


Figure 2. ORTEP representation of the solid state single-crystal X-ray diffraction structure of **2**, with 30% thermal ellipsoids for non-hydrogen atoms and arbitrary spheres for hydrogen atoms.

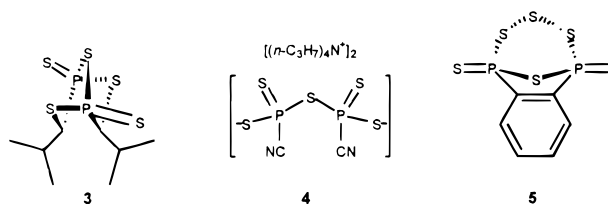
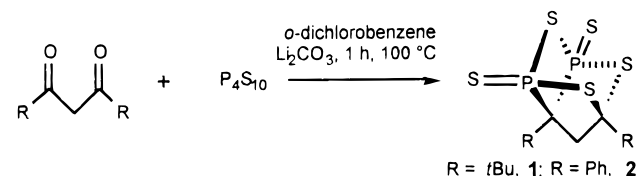


Figure 3. Phosphorus(V) containing compounds related to **1** and **2**.

Scheme 1. Synthesis of **1** and **2**



and 65.4° in **5**.⁸ The dihedral angle between C1–C3–S5 and P1–P2–S3–S4 in **1** is 90.0° and in **2** is 89.2°. In **2** the C1–C3–S5 plane is 68.3° relative to the C3-bound phenyl ring and 1.7° relative to the C1 bound ring. The latter phenyl ring thus appears to be kept in registry with C1–C3–S5 by the influence of S1 and S2. The observed interatomic distances H15–S2

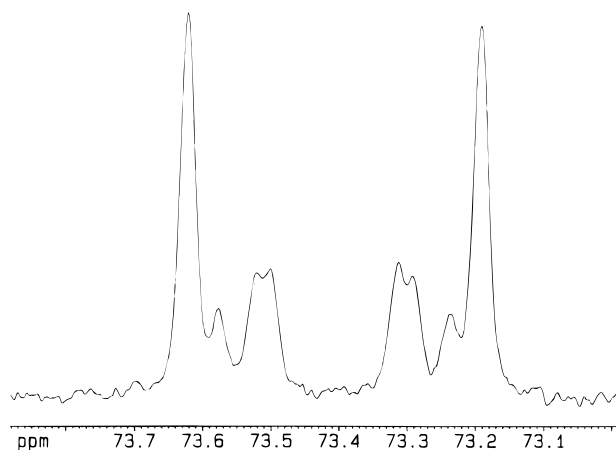
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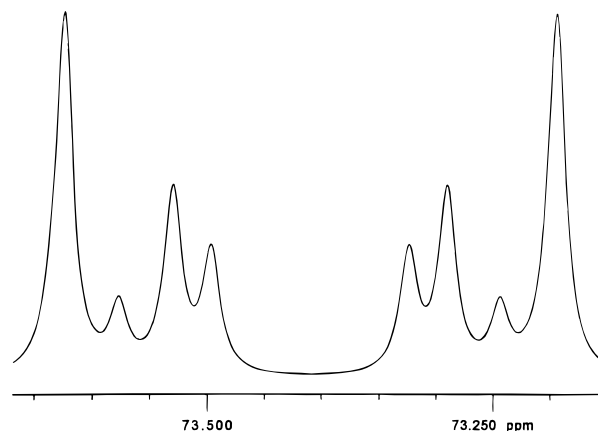
Table 1. Selected Interatomic Distances (Å) and Angles (deg) for P₄S₁₀, **1–5**

	P ₄ S ₁₀ ⁹	1	2	3 ⁵	4 ⁶	5 ⁷
P=S	1.950(15)	1.9280(8)	1.9206(14)	1.921(1)	1.937(2) 1.954(2)	1.9140(8)
(μ-S) P–S	2.08(1)	1.9310(8)	1.9068(16)	1.912(1)	1.943(2) 1.946(2)	1.9185(8)
P–S–C/P–S		2.1095(9)	2.1198(14)	2.117(1)	2.114(2)	2.1007(11)
		2.1031(8)	2.1169(15)	2.098(1)	2.128(2)	2.1036(7)
P–S–C/P–S		2.0865(8)	2.0857(14)	2.078(1)		
		2.0799(8)	2.0747(14)	2.093(1)		
S–C		1.866(2)	1.854(4)	1.837(3)		
		1.867(2)	1.863(4)	1.839(3)		
P–S–P	109.0(13)	80.34(3)	80.00(5)	86.5(1)	110.5(1)	93.99(3)
P–S–C		94.57(7)	93.98(12)	102.1(1)		
		94.50(7)	93.76(12)	100.2(1)		
S=P–S	109.2(15)	113.85(4)	114.21(7)	117.2(1)	103.4(1)	114.06(2)
		114.03(4)	116.43(6)	113.1(1)	114.2(1)	110.68(4)
		112.94(4)	116.33(7)	112.2(1)	115.5(1)	114.78(4)
		114.35(4)	117.75(6)	118.7(1)	102.0(1)	110.72(3)

**Figure 4.** Ambient-temperature ³¹P NMR (161.98 MHz) spectrum of **1** in CDCl₃.

(3.42 Å) and H15–S1 (3.56 Å) shorten to 2.33 and 2.38 Å, respectively, in a computer-constructed model with 90° rotation imposed on the phenyl ring. Selected interatomic distances and angles for **1** and **2** are given in Table 1 along with comparable data for P₄S₁₀, **3**, **4**, and **5**.

Endocyclic interatomic angles C1–C2–C3 of 108.3 and 106.5° are observed for **1** and **2**, respectively. These may be compared to 121.5¹⁰ and 121.1°¹¹ for the parent diketones Htmhd and Hdppd, respectively, as well as 123.8°¹² and 125.3°¹³ for typical CuL₂ complexes (L = tmhd[−] and dppd[−], respectively). Likewise, substantial elongations are observed for C1–C2 and C2–C3, 1.52–1.53 Å (**1** and **2**), 1.38–1.46 Å (HL), and 1.39–1.40 Å (CuL₂). Minimal modification is observed for the exocyclic interatomic distances C3–C4 and C1–C8 (**1**) or C1–C10 (**2**), as compared to either HL or CuL₂. However, differences are observed in the C2–C3–C4 interatomic angles for these comparisons (**1**, **2**, 114.7–117.9°; HL, 120.9–126.6°; CuL₂, 121.0–122.3°). The opening up in HL may be explained by the lack of a cyclic lock-in for the internal rotation, whereas the tighter angles found in **1** and **2**, when

**Figure 5.** ³¹P NMR spectrum of **1**, as modeled with gnmr,¹⁵ using the coupling constants given in the text.**Table 2.** Comparison of ³¹P NMR Chemical Shifts for Selected Compounds

compound	³¹ P chemical shift (ppm)	reference
1	73.4	this work
2	73.4	this work
3	87.8	5
5	93.2	7
P ₄ S ₁₀	56.3	14

compared to CuL₂, result from the rigidity imposed by the bicyclic framework.

Due to the rigid structure of molecules **1** and **2**, the methylene protons on the C2 carbon atoms couple inequivalently with both phosphorus atoms, to give a complex splitting pattern in both the ¹H and ³¹P NMR spectra. The splitting pattern observed in the methylene proton signal of each compound is similar to the splitting pattern observed in the phosphorus signal of each compound. The observed coupling in both the ¹H and ³¹P spectra of **1** has been modeled as an H, H', P, P' spin system with high order coupling (Figures 4 and 5). Variable-temperature ³¹P NMR spectroscopy of **1** in *o*-dichlorobenzene revealed no modification of the ¹H–³¹P coupling pattern in the range of 300–423 K.

Treatment of **2** with an excess of PPh₃ in CDCl₃ selectively removed one terminal sulfur atom. The tentative product, C₁₅H₁₂P₂S₄ (**6**), was characterized by ³¹P{¹H} NMR spectroscopy [δ 110.33 (d, ²J(P,P) = 59.1 Hz), 88.00 (d, ²J(P,P) = 59.1 Hz)] and EI mass spectrometry (*M*⁺ = 382.1). The observation of two independent ³¹P NMR signals is representative of product asymmetry and thus suggests that a terminal, rather than bridging, sulfur was removed. Triphenylphosphine sulfide and

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(15) gnmr: Modeling software available from Cherwell Scientific.

excess triphenylphosphine were the only other phosphorus-containing species observed by ^{31}P NMR spectroscopy. Initial efforts at preparing a derivative of **1** by reacting with $\text{Hg}(\text{NO}_3)_2$ in 1:1 v/v acetonitrile/chloroform resulted in the observation of the ion $[\text{Hg}(\text{L})_2](\text{NO}_3)^+$ ($\text{L} = \mathbf{1}$) ($M^+ = 1014.7$) by FAB mass spectrometry. Additional investigations into the ligation potential of this new class of compounds is currently undergoing active exploration, and will be reported separately.

Experimental Section

1. To synthesize **1** (Scheme 1), a mixture of toluene (150 mL, freshly distilled from Na metal), 12.06 g (0.0271 mol) of P_4S_{10} (Aldrich, 99%), and 5.00 g (0.0271 mol) of 2,2,6,6-tetramethyl-3,5-heptanedione (Htmhd) (Lancaster, 99%) were heated at reflux while stirring for 1 h under a flow of pure, dry Ar. The toluene was removed at 100 °C under vacuum. The solid was extracted by refluxing with 150 mL of methylene chloride for 1 h. The extract was combined with 20 g of flash silica gel (J. T. Baker) and taken to dryness. The material was dry-loaded onto a column (14 cm \times 32 cm) of flash silica gel and eluted with hexane. Yield: 0.20 g (2.0%) of an air-stable, colorless solid, soluble in chlorinated hydrocarbon solvents and sparingly soluble in aliphatic hydrocarbon solvents.

2. To synthesize **2**, a mixture of *o*-dichlorobenzene (175 mL), 14.87 g (0.0335 mol) of P_4S_{10} (Aldrich, 99%), 2.88 g (0.0390 mol) of Li_2CO_3 , and 5.00 g (0.0223 mol) of dibenzoylmethane (Hdppd) (Aldrich, 98%) were heated at 100 °C while stirring for 1 h under a flow of pure, dry Ar. The *o*-dichlorobenzene was removed at 100 °C under vacuum. The solid was extracted by refluxing 3 times with 300 mL portions of methylene chloride for 1 h each. The extract was combined with 20 g of flash silica gel and taken to dryness. The material was dry-loaded onto a column (2 cm \times 4 cm) of flash silica gel and initially eluted with hexane. Polarity was gradually increased with methylene chloride (final eluant, 100% methylene chloride) to elute the product. The crude product was recrystallized from acetonitrile, washed with 100 mL of hexane, and dried under vacuum at ambient temperature. Yield: 2.18 g (23.6%) of an air-stable, light yellow solid, soluble in chlorinated hydrocarbon solvents and sparingly soluble in aliphatic hydrocarbon solvents.

Physical Data for 1. Mp 194–198 °C. ^1H NMR (300.07 MHz, CDCl_3 , 25 °C, ref. CHCl_3 7.24 ppm): δ 3.06–2.82 (m, 2H, H2A, H2B), 1.68 (s, br, 9H, H9/10/11(A/B/C)), 1.32 (s, 9H, H5/6/7(A/B/C)). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CDCl_3 , 25 °C, ref. CDCl_3 77.00 ppm): δ 100.07 (t, $^1J(\text{P},\text{C}) = 27.7$ Hz, C1), 91.30 (s, C3), 52.44 (t, $^2J(\text{P},\text{C}) = 3.7$ Hz, C2), 40.33 (t, $^2J(\text{P},\text{C}) = 4.0$ Hz, C8), 38.46 (t, $^3J(\text{P},\text{C}) = 2.1$ Hz, C4), 28.47 (s, br, C9, C10, C11), 27.13 (s, C5, C6, C7). ^{31}P NMR (161.98 MHz, CDCl_3 , 25 °C; ref. 85% H_3PO_4 in sealed capillary, 0 ppm): 73.63–73.20 (m, P1, P2), modeled spectrum (gnmr) 73.4 (m, P1, P2, $^2J(\text{P1}, \text{P2}) = -6.5$ Hz, $^3J(\text{H1}, \text{P1}) = 15.4$ Hz, $^3J(\text{H1}, \text{P2}) = 54.2$ Hz, $^3J(\text{H2}, \text{P1}) = 54.2$ Hz, $^3J(\text{H2}, \text{P2}) = 15.4$ Hz, $^2J(\text{H1}, \text{H2}) = 6.5$ Hz). MS (EI 70 eV), m/z (%): 374.0 (8.6) [M^+], 342.0 (2.8) [$M^+ - \text{S}$], 309.0 (1.3) [$M^+ - \text{S}_2 + \text{H}$], 279.0 (0.3) [$M^+ - \text{S}_3 + \text{H}$], 246.1 (100.0) [$M^+ - \text{S}_4$], 231.0 (20.3) [$M^+ - \text{S}_4\text{CH}_3$], 214.1 (37.1) [$M^+ - \text{S}_5$], 199.1 (49.8) [$M^+ - \text{S}_5\text{CH}_3$], 183.1 (12.5) [$M^+ - \text{PS}_5$].

Physical Data for 2. Mp 175–178 °C. ^1H NMR (400.13 MHz, CDCl_3 , 25 °C; ref. CHCl_3 7.24 ppm): δ 7.82–7.39 (m, 10H, H5–H9, H11–H15), 3.85–3.69 (m, 2H, H2A, H2B). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CDCl_3 , 25 °C; ref. CDCl_3 , 77.00 ppm): δ 136.12–126.19 (8 signals, C4–C9, C10–C15), 93.97 (t, $^1J(\text{C},\text{P}) = 32.7$ Hz, C1), 81.08 (s, C3), 56.02 (t, $^2J(\text{C},\text{P}) = 1.9$ Hz, C2). ^{31}P NMR (161.98 MHz, CDCl_3 , 25 °C; ref. 85% H_3PO_4 in sealed capillary, 0 ppm): 73.99–73.60 (m, P1, P2); MS (CI, isobutane), m/z (%): 415.0 (2.5) [$M^+ + \text{H}$], 383.0 (5.0) [$M^+ + \text{H} - \text{S}$], 351.0 (0.2) [$M^+ + \text{H} - \text{S}_2$], 319.0 (3.1) [$M^+ + \text{H} - \text{S}_3$], 297.1 (10.4), 286.1 (3.1) [$M^+ - \text{S}_4$], 255.1 (100.0) [$M^+ + \text{H} - \text{S}_5$].

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for compounds **1** and **2** is available. Access information is given on any current masthead page.

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