

Synthesis, Characterization, and Molecular Structure of Hexa(dialkylgerma)tetraphosphides^{1a,b}

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Received March 25, 1975

Abstract: The thermal condensation of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ and $(\text{C}_2\text{H}_5)_2\text{Ge}(\text{PH}_2)_2$ results in formation of $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$ (I) and $[(\text{C}_2\text{H}_5)_2\text{Ge}]_6\text{P}_4$ (II) respectively, in high yield. Chemical reaction and spectral (^1H NMR, ir, and mass) characterization data for the new compounds have been obtained. The crystal structure of I has been determined. The compound crystallizes in space group *I*23 with lattice constant 10.901 (3) Å, with one molecule per unit cell. Least-squares refinement of all nonhydrogen atoms resulted in a conventional *R* factor of 0.024. Compound I has tetrahedral symmetry, a structure in which the P atoms are at the four apices and the $(\text{CH}_3)_2\text{Ge}$ moieties are at the six edges of the tetrahedron. Intermediates in the $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ condensation, $[(\text{CH}_3)_2\text{GePH}_2]_2\text{PH}$ (III) and $[(\text{CH}_3)_2\text{GePH}_2]_3\text{P}$ (IV), have been isolated and characterized by ^1H NMR, ^{31}P NMR, and mass spectral analyses. A possible reaction path for the formation of I involving redistribution reactions on phosphorus is discussed. Preliminary studies of the O_2 -oxidation of I are described. Preparative and characterization data for the $(\text{C}_2\text{H}_5)_2\text{Ge}(\text{PH}_2)_2$ are reported.

Cage molecules whose structures are based on the P_4 -tetrahedral unit represent one of the most basic cage structural types.^{3,4} Well-characterized examples of P_4 cages which can be described as edge-substituted only, include the group 6A and group 5A moiety-substituted systems, P_4S_3 , P_4Se_3 , P_4O_6 , and $\text{P}_4(\text{NCH}_3)_6$.⁴ In a preliminary account,⁵ we reported the synthesis of hexa(dimethylgerma)tetraphosphide, $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$, the first example of a P_4 cage to contain germanium-moiety substitution, from the thermal condensation of dimethyl(bisphosphino)germane. In the report below, the complete details of the preparation, isolation, and mechanism of formation of $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$ and its ethyl analog, $[(\text{C}_2\text{H}_5)_2\text{Ge}]_6\text{P}_4$, are given. In addition the crystal structure of $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$ has been obtained and it provides confirmation of these as edge-substituted P_4 -structural types.

Experimental Section

Apparatus, Materials, and Techniques. All manipulations were carried out in a high-vacuum system or in N_2 -flushed polyethylene glove bags.⁶ Since the phosphines involved in this study may be highly toxic, care should be taken to handle them only under inert atmosphere or vacuum line conditions. Melting points were measured in sealed capillary tubes. Mass spectra were obtained on Varian MAT CH-5 and CH-7 spectrometers at 70 eV. Infrared spectra were obtained using Perkin-Elmer Model 337G and Beckman IR-12 spectrometers. Gaseous samples were contained in 10-cm cells equipped with KBr windows. Solid samples were examined as KBr pellets. Proton NMR data were obtained at 60 and 100 MHz with Varian A-60A and HA-100 spectrometers. Chemical shifts were measured relative to internal $(\text{CH}_3)_4\text{Si}$. Negative δ values indicate shifts downfield from $(\text{CH}_3)_4\text{Si}$. Phosphorus-31 NMR spectra were obtained at 40.5 MHz using the HA-100 equipped with standard ^{31}P probe accessories and a Varian C-1024 computer of average transients.

Bis(phosphino)dimethylgermane⁷ and $[(\text{CH}_3)_2\text{GeOP}(\text{O})\text{HO}]_2$ ⁸ were prepared and purified as described elsewhere. Hydrogen chloride (Matheson, anhydrous) was passed twice through a -160° trap before use. Chloroform (Baker, spectral grade) was freshly distilled from P_4O_{10} in vacuo before use. Bis(phosphino)diethylgermane was prepared and characterized during this study (see below). Diethylgermanium dichloride was obtained from Alfa Inorganics. Triglyme was double distilled from LiAlH_4 before use.

Reaction materials in the reactions below were identified by comparison of their physical and/or spectral properties with those reported in the literature or with spectra obtained of samples prepared independently in our laboratories.

Mass spectral analyses of reaction products often required that the theoretical isotopic distribution patterns⁹ for polygermanium

atom species containing two–six germanium atoms be known. Isotopic distribution patterns were computed essentially as reported by Dombek et al.¹⁰ The most intense peak in the envelopes for the atom clusters are (number of Ge atoms in parentheses): 146 (Ge_2), 218 (Ge_3), 290 (Ge_4), 364 (Ge_5), and 436 (Ge_6).

Bis(phosphino)diethylgermane. The $(\text{C}_2\text{H}_5)_2\text{Ge}(\text{PH}_2)_2$ was prepared according to the previously described^{7,11} general phosphination procedure by the reaction of $(\text{C}_2\text{H}_5)_2\text{GeCl}_2$ with $\text{LiAl}(\text{PH}_2)_4$ in triglyme. Repeated passage of reaction materials through a -15° trap into a -78° trap yielded pure $(\text{C}_2\text{H}_5)_2\text{Ge}(\text{PH}_2)_2$. Elemental analysis data for $(\text{C}_2\text{H}_5)_2\text{Ge}(\text{PH}_2)_2$ were obtained by conversion of a weighed sample to $(\text{C}_2\text{H}_5)_2\text{GeCl}_2$ and PH_3 by reaction with excess HCl. Anal. Calcd for $(\text{C}_2\text{H}_5)_2\text{Ge}(\text{PH}_2)_2 \cdot \text{PH}_3$: $(\text{C}_2\text{H}_5)_2\text{GeCl}_2$, 1.00:2.00:1.00. Found: 1.00:2.01:1.06.

The 0° vapor tension of $(\text{C}_2\text{H}_5)_2\text{Ge}(\text{PH}_2)_2$ is <1 mm. Vapor tension vs. temperature and infrared spectral measurements were not attempted due to the thermal instability of the sample. The proton NMR spectrum (CHCl_3 solution) exhibits a broad singlet (area 10) at $\delta -1.06$ ppm and a doublet of complex multiplets (area 4) at $\delta -1.39$ ppm ($^1J_{\text{PH}} = 183$ Hz) attributable to the ethyl and phosphino protons, respectively. The PH_2 resonance is complex. A complete assignment of the coupling pattern was not attempted. The ^{31}P NMR spectrum (neat sample) exhibits a triplet ($J = 185$ Hz) of complex multiplets at $\delta 360 \pm 5$ ppm relative to P_4O_6 . The highest mass peak in the mass spectrum occurs at m/e 200 and is assigned to the $(\text{C}_2\text{H}_5)_2$ $^{76}\text{Ge}(\text{PH}_2)_2^+$ parent molecular ion.

Catalyzed Condensations. (A) Preparation of Hexa(dimethylgerma)tetraphosphide (I). Typically, 10–20 mmol of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ was condensed into a 500-ml reaction bulb equipped with a side arm so that the bulb could be sealed and later reopened. About 5 Torr of dry O_2 or 10–15 Torr of dry air was introduced into the reaction bulb, and the contents were allowed to warm to 0° for 30 min. The bulb was sealed-off and heated at 120 – 140° for 72–96 hr. After pyrolysis, the break-seal equipped side arm of the reaction bulb was attached to a horizontal sublimation tube (600 ml length, 10 mm o.d., Pyrex tubing). After removal of high-volatility materials, PH_3 , $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$, and traces of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$, the white solid which remained in the bulb was sublimed at 200° into the end of the sublimation tube. In the catalyzed reactions, only a trace of detectable residue remained in the bulb. The bulb was removed and a gradient-wound resistance wire-heated tube was placed around the sublimation tube and heated. Traces of a viscous liquid (fraction 1) sublimed slowly up the tube followed by the major fraction (fraction 2). An extremely small third fraction remained behind and was discarded.

Fraction 2 was pure $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$ (I), typically obtained in a 90–95% yield and in a molar ratio to the PH_3 formed of 1:8. The I decomposed slowly without melting at ca. 300°C in a sealed capillary. Anal.¹² Calcd for $\text{C}_{12}\text{H}_{36}\text{Ge}_6\text{P}_4$: C, 19.48; H, 4.90; P, 11.72. Found: C, 19.32; H, 4.77; P, 17.00. The ^1H NMR spectrum of I in

Table I. Infrared Absorption Maxima^{a,b}

Compound		Tentative assignment
$[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4^c$	$[(\text{C}_2\text{H}_5)_2\text{Ge}]_6\text{P}_4^c$	
3070 (w)		2960 (m) CH ₃ asym str ^{e,f}
3030 (w)		2895 (s) CH ₃ sym str ^{e,f}
		2260 (s) PH str ^{e,f}
		2010 (vw)
		1797 (vw)
	1450 (m)	
1400 (w)	1420 (w)	1405 (m) CH ₃ asym def ^e
	1375 (m)	
1234 (s)	1200 (m)	1220 (s) CH ₃ sym def ^e
1226 (s)		
		1055 (m) PH ₂ def ^g
	1020 (s)	
	970 (m)	
		830 (vs)
808 (vs)		800 (vs) PH ₂ wag ^g
	755 (s)	
735 (w)	675 (s)	
		635 (vw)
586 (s)	570 (s)	595 (vs)
566 (s)	545 (s)	570 (vs)
		Ge-C str ^h

^a Absorption maxima are in cm⁻¹ units. ^b Abbreviations in parentheses are: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; and sh, shoulder. ^c Samples in KBr pellets. ^d Sample as a thin liquid film between KBr disks. ^e See ref 12. ^f See ref 13 and 14. ^g E. R. Nixon, *J. Phys. Chem.*, **60**, 1054 (1958). ^h R. S. Tobias and S. Hutcheson, *J. Organomet. Chem.*, **6**, 535 (1966); M. P. Brown and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 4166 (1960).

CHCl₃ solvent (Figure 1A) consists of a broadened symmetrical multiplet at δ -0.45 ppm. The low solubility of $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$ precluded our obtaining the ³¹P NMR spectrum. Infrared spectral data are shown in Table I. The most intense peak in the ten most intense mass spectral envelopes occur at *m/e* (per cent abundance): 740 (100), 725 (67), 623 (22), 519 (14), 308 (14), 267 (12), 237 (12), 221 (22), 207 (13), and 119 (67).

Fraction 1 was repeatedly resublimed and shown by mass spectral analysis to consist of two germanium-phosphorus compounds whose parent molecular-ion envelopes are centered at *m/e* 302 and 432. Both species contain (CH₃)₂Ge moieties. The lower molecular weight material could not be obtained in pure form; however, it clearly contained two germanium atoms. Trace quantities of a higher-molecular weight material were obtained pure. The compound exhibits a series of mass spectral envelopes up to *m/e* 440, the most intense peak in each of the six most intense envelopes occurring at *m/e* (per cent abundance): 432 (15.2), 417 (12.6), 237 (6.5), 139 (14.8), 119 (100), and 89 (46.2). The distribution of peaks in the envelope centered at *m/e* 432 agrees with that expected for a three-germanium atom species.

(B) Preparation of Hexa(diethylgerma)tetrphosphide (II). After pretreatment with O₂ as described above, 1-2 mmol of $[(\text{C}_2\text{H}_5)_2\text{Ge}]_6\text{P}_4$ was heated in a 100-ml flask for 24 hr at 120°. Reaction materials were separated by the same sublimation techniques used above, however, three of four sublimations were needed in order to remove small quantities of incompletely condensed materials. The final crystalline product (yield typically ca. 75%) melts at 220-222°. Anal. Calcd for C₂₄H₆₀Ge₆P₄: C, 31.73; H, 6.66. Found: C, 32.01, H, 6.73. The ¹H NMR spectrum obtained in CHCl₃ solvent (Figure 1B) consists of an unsymmetrical resonance with three maxima at δ -1.12, -1.17, and -1.24 ppm. The compound undergoes about 25% decomposition when exposed to ambient air at 25° for 3 hr. The infrared spectral data are given in Table I. The most intense peak in each of the ten most-intense mass spectral envelopes occurs at *m/e* (per cent abundance): 908 (11), 879 (16), 778 (17), 749 (21), 295 (15), 237 (18), 207 (12), 161 (58), 133 (100), and 102 (27).

(C) Protolysis of Condensation Products. Protolysis of weighed quantities of I and II was effected by allowing the solids to react with excess gaseous HCl at 1 atm for 20-30 min at room temperature. Reaction products consisted only of a PH₃-HCl mixture

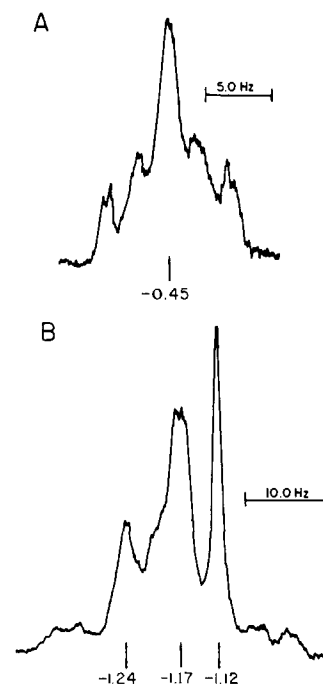


Figure 1. Proton NMR spectrum of: (A) $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$ in CHCl₃ at 60.0 MHz and (B) $[(\text{C}_2\text{H}_5)_2\text{Ge}]_6\text{P}_4$ in CHCl₃ at 100.0 MHz.

Table II. PH₃:(CH₃)₂GeCl₂ Mole Ratios

Exptl	Segment				
	1	2	3	4	5
1	1.48	1.39	0.95	0.84	0.70
2	1.40	1.31	1.10	0.91	0.75

(which was freed of HCl by complexation with (C₂H₅)₃N) and the dialkylgermanium dichloride. The (R₂Ge)₆P₄ consumed:R₂GeCl₂ formed:PH₃ formed mole ratios obtained were 1.00:5.97:3.95 and 1.00:5.88:3.88 for I and II, respectively. Substitution of DCl for HCl in the cleavage of I yielded pure PD₃ (>98%).

Analysis of Condensation Intermediates (A) Catalyzed Reactions. Samples of 1-3 mmol of O₂-treated (CH₃)₂Ge(PH₂)₂ were allowed to react at 150° for periods of 1-3 hr after which the reaction vessel was attached to a five-segment sublimation tube. The PH₃, unreacted (CH₃)₂Ge(PH₂)₂ and traces of (CH₃)₂Ge(PH₂)H and (CH₃)₂GeH₂ were removed. Low-volatility condensation products were sublimed slowly along the tube by heating it with a gradient-wound oven until material was evenly distributed over the length of the tube. Reaction of the material in each segment with HCl (as described above) resulted in PH₃:(CH₃)₂GeCl₂ mole ratios of products from the five segments for two typical experiments as shown in Table II. Segments 1-5 contained material in order of decreasing volatility. Only traces of material did not react with the HCl.

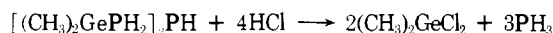
The mass spectra of material in each segment from a separate similarly conducted condensation were obtained. Components with highest-mass ion envelopes were observed at *m/e* (number of Ge atoms shown in parentheses) 638 (5), 536 (4), 432 (3), and 302 (2). Proton NMR spectra of the materials in each segment showed, in addition to traces of (CH₃)₂Ge(PH₂)₂, characteristic methylgermanium resonances around δ -0.65 ppm and phosphino resonances centered at δ -1.65 to -1.36 ppm which were too complex for unambiguous assignment to a particular condensation product.

(B) Uncatalyzed Reactions. Typically 1-3 mmol of (CH₃)₂Ge(PH₂)₂ were heated 1-3 hr at 110-120° as above, but without pretreatment with O₂. High-volatility products consisted of PH₃ and substantial amounts of (CH₃)₂Ge(PH₂)H and (CH₃)₂GeH₂. Sublimation of low-volatility condensation materials in a segmented tube, followed by mass spectral analysis of materials in each segment indicated that the mixture consisted of some (CH₃)₂Ge(PH₂)₂ (parent ion at *m/e* 170) and I (parent ion at *m/e*

740) along with four components whose highest-mass ion envelopes occurred at m/e (number of Ge atoms in parentheses) 638 (5), 536 (4), 432 (3) and 302 (2). The mixture contained considerably less I relative to other components than did the catalyzed mixtures. The ^1H NMR spectra of the mixtures of components showed a strong broad resonance in the δ -0.65 ppm region; however, the multiplets centered between δ -1.65 and -1.36 ppm (phosphino protons) were weak and in some cases absent. Reaction of the condensation products with HCl yields $(\text{CH}_3)_2\text{GeCl}_2$ and PH_3 as volatile products along with an intractable yellow solid. The solid shows three major mass spectral envelopes at m/e (per cent abundance) 448 (89), 372 (43), and 320 (100) and clearly did not contain germanium.

Isolation and Characterization of $[(\text{CH}_3)_2\text{Ge}(\text{PH}_2)]_2\text{PH}$ (III). Samples of III were prepared in a 100-ml reaction bulb which was attached to the vacuum line by a two U-tube side arm. To the second tube, an NMR tube, mass spectral capillary, or reaction tube could be attached, depending on what was to be done with the product. Typically, 1–5 mmol of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ was allowed to warm to room temperature for 12–14 hr after which the PH_3 and $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ which had formed were removed. The bulb was heated to 60 – 70° in order to distill the condensation products into the first U-trap. A slightly yellow liquid remained in the reaction bulb. Repeated distillation resulted in essentially pure III, sometimes contaminated with small amounts of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ (<5%). Typically, about 0.5 mmol of III was obtained from a 5-mmol reaction of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$.

Elemental analysis of $[(\text{CH}_3)_2\text{Ge}(\text{PH}_2)]_2\text{PH}$, accomplished by HCl cleavage, according to



yields a $(\text{CH}_3)_2\text{GeCl}_2:\text{PH}_3$ ratio: calcd, 2.00:3.00; found, 2.00:3.06.

Samples of III for NMR spectral analysis were prepared as above and washed with CHCl_3 directly into an NMR tube. The ^1H NMR and ^{31}P NMR spectral parameters are given in Table III. Infrared spectral data are given in Table I. The 70-eV mass spectrum exhibited major envelopes at m/e (per cent abundance) 170 (3.8), 155 (3.2), 137 (35.4), 119 (16.7), 105 (20.8), 89 (100.0), and 74 (20.8). Weaker envelopes were seen also at higher m/e ; the highest-mass peak was centered at m/e 302. At lower ionizing voltages a small increase in the parent envelope relative intensity occurred.

The low thermal stability and volatility of III and the frequent presence of traces of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ precluded obtaining vapor pressure vs. temperature and melting point data.

Identification of $[(\text{CH}_3)_2\text{Ge}(\text{PH}_2)]_3\text{P}$ (IV). Samples containing IV were obtained by allowing $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ to react in a bulb to which an NMR or mass spectral analysis tube was attached. $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ (1–3 mmol) was allowed to stand at room temperature for 5–10 hr (catalyzed) or 30–48 hr (uncatalyzed), followed by removal in vacuo of high-volatility products. Typically, a condensation mixture would contain $[(\text{CH}_3)_2\text{Ge}(\text{PH}_2)]_2\text{PH}$ and $[(\text{CH}_3)_2\text{Ge}(\text{PH}_2)]_3\text{P}$ in about a 4:1 ratio along with some $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$. The NMR spectral parameters for IV, obtained from such a mixture, are given in Table III. The mass spectrum of a mixture containing IV exhibited only weak envelopes at greater than m/e 170. Weak envelopes of germanium-containing species up to m/e 432 were observed. Protolysis of these condensation mixtures by reaction with HCl yielded PH_3 and $(\text{CH}_3)_2\text{GeCl}_2$. In every case 95% or more of the material reacted with the HCl.

Examination of Condensation Catalysts. In separate experiments, the behavior of Hg, HgCl_2 , Hg_2Cl_2 , H_2O , H_3PO_4 , H_3PO_3 , and $[(\text{CH}_3)_2\text{GeOP}(\text{O})\text{HO}]_2$ as potential catalysts in the condensation of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ was examined. All experiments were done in carefully cleaned and dried 100-ml bulbs equipped with Fischer-Porter stopcocks. Under N_2 , the reaction vessel was charged with ca. 5 mg of the potential catalyst, the bulb was reattached to the vacuum line and charged with 1.5 mmol of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ and allowed to warm to room temperature. Phosphine was removed at 30-min intervals. Its rate of evolution served as an indicator of the extent of reaction when compared to the rate of PH_3 evolution observed previously in catalyst-free $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ condensations. The Hg, HgCl_2 , and Hg_2Cl_2 showed no measurable catalytic effect, H_2O and H_3PO_4 showed marked rate enhancements, typically about twice as fast, and H_3PO_3 and $[(\text{CH}_3)_2\text{GeOP}(\text{O})\text{HO}]_2$

Table III. NMR Spectral Parameters for $[(\text{CH}_3)_2\text{Ge}(\text{PH}_2)]_2\text{PH}$ and $[(\text{CH}_3)_2\text{Ge}(\text{PH}_2)]_3\text{P}$

Measurement	$[(\text{CH}_3)_2\text{Ge}(\text{PH}_2)]_2\text{P}''\text{H}$	$[(\text{CH}_3)_2\text{Ge}(\text{PH}_2)]_3\text{P}''$
^1H NMR Data ^{a,b,d}		
$\delta(\text{H}_2\text{C})$	-0.71 ± 0.05	-0.72 ± 0.05
$\delta(\text{HP}'')$	-1.41 ± 0.05	
$\delta(\text{H}_2\text{P}')$	-1.62 ± 0.05	-1.63 ± 0.05
$^1J(\text{HP}'')$	179 ± 2	
$^1J(\text{H}_2\text{P}')$	182 ± 2	180 ± 2
$^3J(\text{HCGeP}'')$	3.6 ± 0.2	3.6 ± 0.2
$^3J(\text{HCGeP}')$	3.6 ± 0.2	ca. 3.6 ± 0.2^e
$^3J(\text{HP}'\text{GeP}'')$	4.1 ± 0.2	4.0 ± 2
$^3J(\text{HP}''\text{GeP}')$	3.4 ± 0.2	
^{31}P NMR Data ^{c,d}		
$\delta(\text{P}'')$	310 ± 0.3	306 ± 0.3
$\delta(\text{P}')$	326 ± 0.3	325 ± 0.3
$^1J(\text{P}''\text{H})$	176 ± 3	
$^1J(\text{P}'\text{H})$	182 ± 2	180 ± 4

^a Obtained on 20–30% by volume solutions in CHCl_3 . ^b Chemical shifts in ppm downfield from internal $(\text{CH}_3)_4\text{Si}$. ^c Chemical shifts relative to external P_4O_6 . ^d Coupling constants in Hz. ^e Peak overlaps made precise measurement impossible.

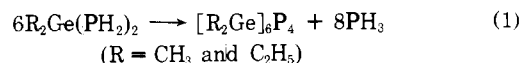
caused rate enhancements up to five times as fast. With H_3PO_3 or $[(\text{CH}_3)_2\text{GeOP}(\text{O})\text{HO}]_2$, crystalline $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$ (confirmed by mass spectrum) began to form on the walls of the reaction vessel after 10–12 hr.

Oxidation of Hexa(dialkylgerma)tetrachosphides. Dry O_2 was bubbled slowly through a suspension of 0.05 mmol of I in 2 ml of CHCl_3 until a colorless solution formed (ca. 5 min). Chloroform was removed in vacuo and the remaining viscous oil was separated using a gradient-heated horizontal sublimation tube. The predominant product was a glassy, highly hygroscopic solid which upon resublimation and mass spectral analysis appeared always to contain a trace of $[(\text{CH}_3)_2\text{GeOP}(\text{O})\text{HO}]_2$. The material was insufficiently soluble in aprotic solvents (diethyl ether, benzene, or CHCl_3) to allow NMR data to be obtained. The most intense peaks of the eight highest mass envelopes of the mass spectrum occur at m/e (per cent abundance): 498 (2.5), 483 (64.5), 469 (2.5), 453 (2.8), 432 (2.5), 419 (2.5), 380 (64.5), and 365 (100.0). Envelopes below m/e 365 were obscured by the $[(\text{CH}_3)_2\text{GeOP}(\text{O})\text{HO}]_2$ contaminant. The m/e 498 and m/e 483 envelopes were clearly attributable to three-germanium atom species.

Collection and Reduction of X-Ray Data. A single-crystal X-ray analysis of $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$ was carried out. The compound crystallizes in the cubic space group $I23$ with lattice constant 10.901 (3). There is one molecule in the asymmetric unit and the molecule must lie in special position with tetrahedral symmetry. Intensity data were collected by using a FACS-I diffractometer, at low temperature, using $\text{Mo K}\alpha$ radiation. A quarter of the sphere bounded by $2\theta = 65^\circ$ was collected. The positions of the heavy atoms were determined from the Patterson. Several attempts of difference Fouriers failed to locate the hydrogens of the methyl groups. A full-matrix refinement of the 142 reflections greater than 2.33σ converged to give conventional and weighted R values of 0.024 and 0.027, respectively. Observed structure factors are given in Table IV. Atomic coordinates and thermal parameters are given in Table V. Distances and angles between the atoms are given in Table VI.

Results and Discussion

Pyrolysis of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ and $(\text{C}_2\text{H}_5)_2\text{Ge}(\text{PH}_2)_2$, in the presence of traces of their oxidation product as catalysts, results in the formation of $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$ (I) and $[(\text{C}_2\text{H}_5)_2\text{Ge}]_6\text{P}_4$ (II), respectively, along with PH_3 according to



Optimum reaction conditions for the formation of I and II require the presence of catalysts and pyrolysis at 120 – 140° for periods of 72–96 hr. Typically, yields of I in excess of 95% were obtained. The II forms more slowly and less cleanly; however, yields of around 60% were obtained readily.

Table IV. Observed Structure Factors for $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$

<i>hkl</i>	F_o	<i>hkl</i>	F_o	<i>hkl</i>	F_o	<i>hkl</i>	F_o	<i>hkl</i>	F_o	<i>hkl</i>	F_o
110	175	543	66	761	78	941	80	10,10,6	55	13,30	72
200	125	550	178	733	106	943	89	11,21	87	13,41	83
211	123	552	41	735	66	950	88	11,32	95	13,43	50
220	113	554	95	772	120	952	40	11,43	41	13,50	92
222	362	600	99	774	47	954	119	11,52	61	13,54	61
310	70	611	42	776	89	970	59	11,61	67	13,74	47
321	108	620	70	800	248	981	80	11,63	75	13,83	50
330	75	622	236	811	91	985	61	11,65	48	13,85	59
332	163	631	110	820	53	990	110	11,70	51	13,90	64
400	136	633	91	822	77	994	72	11,72	89	13,94	69
411	92	640	72	833	50	998	70	11,76	71	14,00	59
420	96	642	72	840	119	10,00	62	11,10,3	56	14,22	72
422	96	644	76	842	51	10,10	56	11,10,7	52	14,44	51
421	104	651	56	844	192	10,20	45	11,11,2	72	14,62	64
440	353	653	39	851	62	10,22	144	12,0,0	82	15,21	57
442	79	660	60	853	73	10,33	75	12,2,2	56	15,32	64
444	141	662	189	855	97	10,40	72	12,40	117	15,63	56
510	108	664	43	860	61	10,44	46	12,44	64	16,00	65
521	42	666	128	862	57	10,53	46	12,51	52		
530	123	710	63	866	47	10,62	108	12,55	50		
532	83	721	119	871	42	10,66	102	12,62	48		
541	147	732	127	880	152	10,71	61	12,80	55		
		743	39	884	78	10,73	57	13,10	66		
		750	43	888	101	10,77	64				
		752	69	910	134	10,84	47				
		754	60	930	73	10,10,2	80				

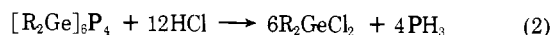
Table V. Atomic Coordinates and Thermal Parameters of the Heavy Atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C	0.3452 (11)	0.8984 (11)	0.8993 (11)	0.0033 (7)	0.0055 (12)	0.0042 (11)	0.0017 (17)	0.0018 (15)	-0.0036 (18)
P	0.3690 (1)	0.3690 (0)	0.3690 (9)	0.0021 (1)	0.0021 (0)	0.0021 (0)	-0.0010 (3)	-0.0010 (0)	-0.0010 (0)
Ge	0.2362 (1)	0.0000 (0)	0.0000 (0)	0.0013 (0)	0.0021 (1)	0.0024 (0)	0.0000 (0)	0.0000 (0)	0.0000 (0)

Table VI. Intramolecular Geometry

Bond angles, deg		Bond distances, Å	
Ge-P-Ge	103.29 (14)	C-Ge	1.9599 (137)
C-Ge-C	105.35 (68)	P-Ge	2.3217 (82)
C-Ge-P	107.26 (39)		
P-Ge-P	120.74 (19)		

Analytical and spectral data for I and II support their characterization as hexa(dialkylgerma)tetrphosphides. Hydrogen chloride cleavage of I and II occurs quantitatively to yield R_2GeCl_2 and PH_3 as



indicating the presence of Ge-P bonds and the absence of Ge-Ge and P-P bonds in the molecules. Mass spectral parent ion envelopes are observed at m/e 740 and 908, respectively. The fragmentation patterns for both compounds are quite similar as would be expected for structurally analogous compounds. The absence of infrared absorptions in the ca. 2290-cm^{-1} region indicates clearly the absence of P-H bonds in either I or II.^{13,14}

The structure of I, as established from the X-ray study is shown in Figure 2. Molecular parameters are given in Table VI. The four phosphorus atoms are located at the corners of a tetrahedron and the six dimethylgermanium moieties are at the tetrahedral edges. The structure is analogous to those of P_4O_6 and $\text{P}_4(\text{NCH}_3)_6$, known examples of phosphorus cage compounds of this structural type.^{3,4} The cage bond angles, Ge-P-Ge and P-Ge-P, are 103.29° and 120.74° , respectively, deviating somewhat from the tetrahedral bond angles of 109.5° . It is interesting to note that the deviation of these angles from tetrahedral is in the same direction, but to a lesser extent, than the O-P-O and P-O-P angles of 99° and 127.5° respectively, observed in P_4O_6 .¹⁵ The mea-

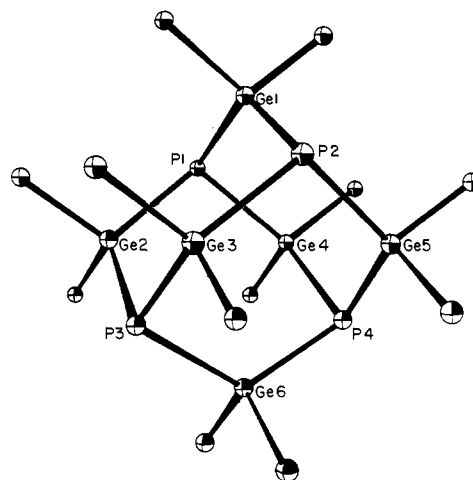


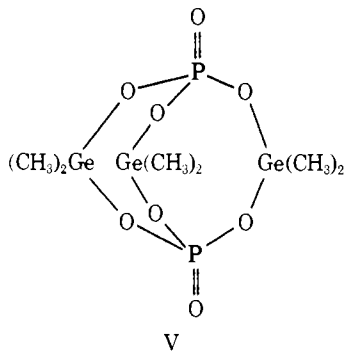
Figure 2. Structure of $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$. Carbon atoms are not labeled and hydrogen atoms are not shown for clarity.

surement of the phosphorus-germanium bond distance appears to be the first example of the measurement of this distance in a molecular system. The observed value of 2.317 \AA essentially equals the value of 2.32 \AA that is obtained by summing the accepted covalent single-bond radii for phosphorus and germanium,¹⁶ suggesting that the germanium-phosphorus bonds can be adequately described as single bonds with no significant degree of multiple bond character.

Compounds I and II appear to be the first structurally well-characterized examples of group 4A moiety substituted P_4 -cage molecular systems. Schumann¹⁷ has reported the preparation of compounds of formula $(\text{R}_2\text{Sn})_6\text{P}_4$, where $\text{R} = \text{CH}_3$, C_4H_9 , and C_6H_5 , from the trialkylamine promoted condensation of PH_3 with R_2SnCl_2 compounds. Al-

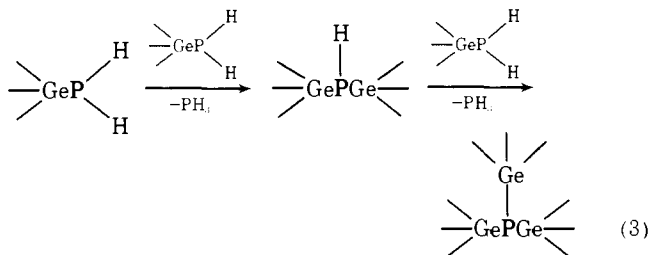
though conclusive structural data for these compounds are lacking, it seems quite likely that they are analogs of I and II.

Compound I is thermally stable in vacuo in excess of 300°C for several hours. Compound II is less stable, decomposing rapidly above 200°C. The lower stability of II is not surprising when the much higher steric repulsions that arise among ethyl groups in it are recognized. Both compounds undergo hydrolysis and oxidation in reactions with H₂O and O₂, respectively; however, II is generally more reactive than I. Both the hydrolysis and oxidation reactions yield complex mixtures of products. Hydrolysis results in cleavage of germanium-phosphorus bonds with the resultant formation of phosphine and germoxane products of the types [R₂GeO]_n (where n = 3, 4 and R = CH₃, C₂H₅), as has been observed with simple dialkyl(bisphosphino)germanes.¹⁸ Oxidation of III and IV yields complex mixtures of PH₃, germoxanes, phosphonygermoxanes, and phosphorus-oxygen materials, the latter apparently the result of oxidation of PH₃.¹⁹ From the oxidation of I, a small amount of material whose parent molecular ion occurs at *m/e* 498 was obtained. From the appearance of the parent ion envelope, the presence of three germanium atoms is established. Based on our earlier studies of phosphinogermane oxidations,²⁰ we conclude that this compound is hexamethylbicyclotriggermaphosphate, [(CH₃)₂Ge]₃O₈P₂ (V). No evidence for the formation of is-



olable species such as [(CH₃)₂Ge]₆P₄O₄, the apically substituted cage analog of P₄O₁₀^{3,4,19} or (CH₃N)₆P₄O₄^{3,4} was obtained.

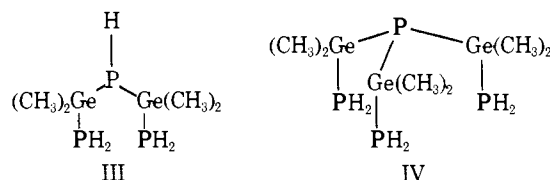
The condensation reactions which result ultimately in I and II from the R₂Ge(PH₂)₂ reactants can be classed generally as reactions in which the redistribution of groups on phosphorus occurs according to the general scheme



in which the final trisgermylphosphine product arises as a result of the redistribution of -H and >Ge- moieties on phosphorus. Analogous redistribution reactions for simple monophosphinosilanes^{21,22} and -germane²³ have been reported previously. Because the R₂Ge(PH₂)₂ compounds used in this study are difunctional, the possibility for more extensive condensation and the formation of cyclic germanium-phosphorus systems as a result of redistribution exists.

Under carefully controlled conditions of reaction and initial product separation, what appear to be the first two stable intermediates in the condensation reaction have been

isolated. The first intermediate, [(CH₃)₂GePH₂]₂PH (III), has been characterized by elemental analysis and, ¹H NMR, ³¹P NMR, and mass spectral analyses. The ir spectrum shows absorptions characteristic of phosphinogermanes, as shown in Table I. The position, peak multiplicities and relative areas of resonances in the ¹H and ³¹P NMR spectrum (Table III) support the structural assignment shown below. Thus, the elimination of phosphine from



between two molecules of (CH₃)₂Ge(PH₂)₂ results in III, a compound which contains one secondary and two primary germyl-substituted phosphino groups.

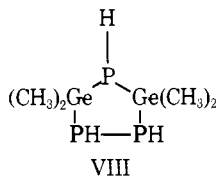
The second condensation intermediate, [(CH₃)₂GePH₂]₃P (IV), could not be separated from III; however, from the ¹H and ³¹P NMR spectra (Table III) of the mixtures the structural characterization of IV as a molecule containing one tertiary and three primary germyl-substituted phosphino groups is unambiguous. Intermediates of molecular weight higher than IV could not be obtained sufficiently concentrated in condensation samples to allow their NMR spectral characterization.

The results of the protolysis of catalyzed condensation fractions of successively lower volatility are shown in Table II. In all cases, essentially quantitative formation of (CH₃)₂GeCl₂ and PH₃ occurs indicating the absence of substantial quantities of P-P or Ge-Ge bonded materials in the condensation mixture. In addition, the successive fractions show steadily decreasing PH₃:(CH₃)₂GeCl₂ ratios, supporting the thesis that condensation occurs via the general elimination of PH₃ through redistribution of groups on phosphorus.

A plausible mechanistic scheme for the formation of I from (CH₃)₂Ge(PH₂)₂ via a series of stepwise redistribution on phosphorus reactions is shown in Figure 3. Condensation of two (CH₃)₂Ge(PH₂)₂ molecules with the elimination of PH₃ yields the first intermediate, III. Further addition of a phosphinogermyl moiety to III at the secondary phosphorus (P'') through redistribution at that phosphorus and the elimination of PH₃ would yield IV. In Figure 3, the symbols a and e refer to the addition of a phosphinogermyl unit and elimination of a PH₃ molecule, respectively. It is noteworthy that condensation via IV appears to proceed exclusively; no detectable quantity of VII, the condensation product expected to form as a result of redistribution occurring at the primary phosphorus (P') of III, could be isolated. Apparently the rate of redistribution of moieties on a phosphorus center in these compounds increases with increasing germyl-group substitution to the extent that redistributions on less-highly substituted phosphorus centers are no longer competitive.

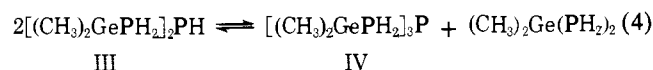
From the mass spectral examination of the fractions obtained from partially condensed mixtures, clear evidence for species containing two, three, four, and five germanium atoms as reaction intermediates between (CH₃)₂Ge(PH₂)₂ and I was obtained. These data, along with the protolysis PH₃:(CH₃)₂GeCl₂ ratios described above, support the presence of species containing four and five Ge atoms such as V and VI in the condensation series. However, in all cases, the highest mass molecular ions of the intermediate condensation materials occur at *m/e* ratios below those expected for the parent molecular ions. Species III-VI in the series shown would have parent molecular ions at *m/e* 304 (III),

438 (IV), 538 (V), and 640 (VI) instead of at the observed m/e values of 302, 432, 536, and 638, respectively. Even decreasing the ionizing voltage did not result in appearance of the expected molecular ions. It appears that in the mass spectrometer, elimination of hydrogen from the highly phosphinated intermediates such as III, to form species as VIII, occurs upon electron impact or more likely due to

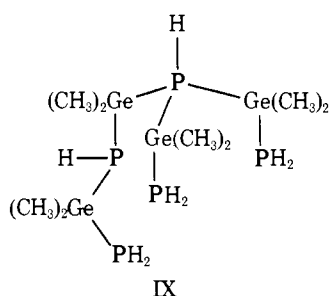


thermolysis in the heated source before ionization. Support for the latter argument comes from separate studies,²⁴ where it has been shown that pyrolysis of III results in the formation of VIII in high yield.

The reaction sequence proposed in Figure 3 implies that the buildup of molecules occurs via the successive addition of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ units to intermediate condensation materials. However, the possibility that the formation of successively higher-molecular weight products, e.g., of IV from III, occurs by complex redistribution equilibria of the type shown in eq 4 cannot at this time be ruled out



Also in the $\text{IV} \rightarrow \text{V}$, $\text{V} \rightarrow \text{VI}$, or $\text{V} \rightarrow \text{I}$ processes, the elimination of two molecules of PH_3 between species is implied. No evidence was obtained for species resulting from the elimination of one PH_3 molecule, as for example IX between IV and V. Species such as IX may be too unstable to



be isolated by our techniques or, more likely, the second PH_3 molecule is eliminated so rapidly that detectable concentrations are never built up in the condensation reaction.

The role and composition of catalysts in the bis(phosphino)dialkylgermane condensation reactions is a question of basic concern. It is interesting to note that in the presence of water, Drake and Riddle observed the rapid redistribution of GeH_3 - and H - groups on the phosphorus of GeH_3PH_2 to yield ultimately $(\text{GeH}_3)_3\text{P}$ and PH_3 .²³ However, in our experiments, water alone showed only a small catalytic effect.

The procedure of producing reaction catalysts by exposing the $\text{R}_2\text{Ge}(\text{PH}_2)_2$ compounds to O_2 (or air) undoubtedly yields a variety of reaction materials, many of which may function as catalysts in the condensation.²⁵ It has been reported previously that O_2 oxidation of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ yields $[(\text{CH}_3)_2\text{GeOP}(\text{O})\text{HO}]_2$, PH_3 -oxidation products, and considerable amounts of intractable residues.²⁰ In studies of the role of potential catalysts described herein, we find that phosphonoxy materials, phosphorous and phosphoric acids, and $[(\text{CH}_3)_2\text{GeOP}(\text{O})\text{HO}]_2$ function as catalysts. However, hexamethylcyclotrigermoxane or octamethylcyclotetragermoxane, $[(\text{CH}_3)_2\text{GeO}]_3$ or 4, the principal products of $\text{R}_2\text{Ge}(\text{PH}_2)_2$ hydrolysis¹⁸ did not. It appears

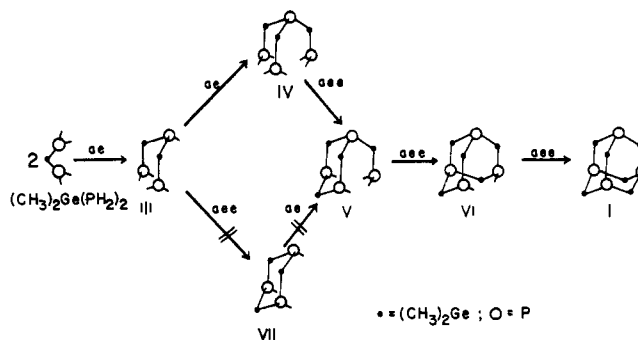


Figure 3. Proposed mechanistic scheme for the formation of $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$ (I) from $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$. The a and e refer to addition and elimination processes, respectively.

that catalytic behavior is not due to germoxane functionality but rather the result of oxyphosphorus, oxyhydridophosphorus, or acidic hydrogens in the systems.²⁶

Condensation reactions, carried out in the absence of the above-described catalytic conditions, result in the formation of small amounts of products other than Ge-P bond containing products described above. The character of the products is not yet well understood; however, mass spectral evidence and protolysis reactions of the condensation mixtures suggests that compounds containing P-P bonds are formed. Protolysis is incomplete, yielding material containing only P and H, reminiscent of P_nH_{n+2} species.²⁷ Further studies on the role and nature of catalysts in the phosphino-germane condensation reactions are in progress and will be reported later.

Acknowledgment. We wish to thank Mr. David Fox for assistance in calculating germanium-isotope mass spectral patterns.

References and Notes

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was described as mercury catalyzed. Our present studies indicate that traces of phosphinogermane oxidation products are in fact the catalyst instead of mercury.

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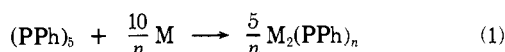
Structure and Dynamics of Catenated Phosphorus(III) Dianions

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Contribution No. 2731 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. Received April 9, 1975

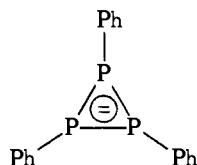
Abstract: ^{31}P NMR is used to study the structure of $\text{M}_2(\text{PPh})_n$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{and Cs}; n = 3 \text{ and } 4$) species in tetrahydrofuran. Analysis of phosphorus-phosphorus coupling constants at low temperatures shows that, for $n = 4$, the sodium and potassium compounds involve chelation of the metal ion by the phosphorus chain ("intimate ion pairing"), while the lithium compound has an acyclic structure. Exchange processes are evident in all three compounds at higher temperatures; for $\text{M} = \text{Na}$ and K , the coupling constants indicate equilibration to acyclic structures. The compound $\text{K}_2(\text{PPh})_3$, which is said to be a salt of the delocalized cyclic dianion $(\text{PPh})_3^{2-}$, is found to exhibit concentration-dependent ^{31}P NMR spectra. This is attributed to "ion pairing" equilibria. Addition of a crown ether dramatically alters the phosphorus chemical shifts of $\text{K}_2(\text{PPh})_3$ but leaves the coupling constants unchanged. It is concluded that $(\text{PPh})_3^{2-}$ is in reality acyclic, with only two phosphorus-phosphorus bonds.

The synthesis and characterization of polyphosphine dianion "salts", $\text{M}_2(\text{PR})_n$, is due almost exclusively to Issleib and coworkers.¹⁻¹⁰ When $\text{R} = \text{C}_6\text{H}_5(\text{Ph})$, the preparation involves reaction 1.



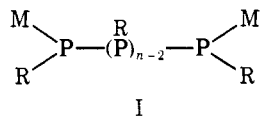
Here M is an alkali metal and $n = 1-4$. The resultant phosphide compounds are extremely potent nucleophiles. They form cyclic condensation products with both alkyl^{4,5,11,12} and aryl¹³ dihalides. With monohalogenated reagents, the expected straight-chain species may be generated. However, if the final phosphorus chain length exceeds two, the primary product decomposes to the biphosphine, $(\text{PPhR})_2$, and the cyclopolyphosphine, $(\text{PPh})_5$. Reactions with transition metal complexes are also known.^{6,14}

Earlier work^{3,4,7-10,13} suggests that the species $\text{M}_2(\text{PR})_n$ are acyclic. The compound $\text{K}_2(\text{PPh})_3$ represents the only exception. The ^{31}P NMR singlet observed for this compound has been interpreted⁶ in terms of a cyclic structure with two electrons delocalized in a π orbital. On the other

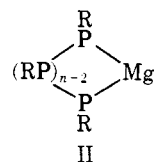


hand, electrochemical experiments have been interpreted¹⁵ as indicating that $\text{K}_2(\text{PPh})_3$ does not produce a cyclic dianion in solution; the NMR result is attributed to an unspecified "rapid exchange".

These alkali metal compounds are conventionally written as I, implying a truly open chain structure with one metal



associated with each chain terminus. The nature of the $\text{M}-\text{P}$ bond is generally unspecified but "univalent" bonding is an implicit *assumption*. In the several instances where a magnesium salt was isolated,⁷ cyclic structures (II) were written, consistent with the "divalency" of magnesium.



We now find that the phosphorus NMR spectra of $\text{M}_2(\text{PPh})_n$ species are not consistent with simple straight-chain structures (I). The spectra exhibit complex cation and temperature dependencies. However, the long range coupling which exists in catenated phosphorus compounds serves as a somewhat unique structural probe which provides an insight into the solution geometry of $\text{M}_2(\text{PPh})_n$ species.

Experimental Section

Phosphorus NMR spectra (Fourier transform) were recorded at 40.5 MHz as previously described.¹⁶ Chemical shifts are reported with respect to 85% H_3PO_4 , downfield chemical shifts being *positive*. Proton spectra were recorded at 220 MHz. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Iterative spectral calculations utilized the program LAOCN3.¹⁷ For the AA'BB' spectra, eight possible line assignments were typically made with iteration carried out on each. Typical root mean square errors for the best solution are 0.5 Hz, which is less than the error introduced by digitization. The parameters in Table I are therefore uniquely determined by the data.

Materials. Pentaphenylcyclopentaphosphine, $(\text{PPh})_5$, was prepared and characterized as described previously.¹⁸ All alkali and alkaline earth metals used were reagent grade and were rinsed well in the reaction solvent prior to use in order to remove any mineral oil. Other compounds were reagent grade and were used without further purification. Tetrahydrofuran (THF) was dried over Na/K alloy and distilled under N_2 prior to use. All reactions were carried out under prepurified N_2 which had been deoxygenated by activat-