terminal C–O stretching bands also fall short of the number predicted on the basis of the above structure. The unexpected presence of at least three bridging C–O absorptions (in KBr) is easily explained in terms of the X-ray results, which show that there are two isomers of $Fe_3(CO)_{11}P(C_6H_5)_3$ present in the crystal.[8]

Because the bridging C–O absorptions in both $Fe_3(CO)_{12}$ and $Fe_3(CO)_{11}P(C_6H_5)_3$ are so much weaker in solution than in the solid state, it seemed possible that two or more isomeric forms of these compounds could be present in solution as has been found in the case of $Co_2(CO)_8$.[9] In the $Co_2(CO)_8$ studies, Noack observed that the position of the equilibrium between the C–O bridged and the nonbridged structure depended on the temperature of the solution. We conducted a similar study on $Fe_3(CO)_{12}$ in a thermostated infrared cell and found that on changing the temperature of the solution from 15 to 60° no new peaks appeared and the relative intensities of the carbonyl absorptions remained constant. The temperature variation did, however, change the intensities of all the absorptions, due to the expansion of the solvent. These results suggest that there is *not* an equilibrium between bridged and nonbridged species and that only one isomer is present in solution. Since the terminal C–O stretching spectrum of $Fe_3(CO)_{12}$ in solution[10] is greatly different from that of the known nonbridged metal carbonyl $Os_3(CO)_{12}$,[11] it appears that $Fe_3(CO)_{12}$ does not exist in solution as a nonbridged structure.

Acknowledgment.—We thank Professor Robert A. Jacobson and Donald J. Dahm for preliminary results of the X-ray investigation of $Fe_3(CO)_{11}P(C_6H_5)_3$.

(9) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963).

(10) K. Noack, *Helv. Chim. Acta*, **45**, 1847 (1962).

(11) D. K. Huggins, N. Flitcroft, and H. D. Kaesz, *Inorg. Chem.*, **4**, 166 (1965).

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Concerning the Ring Sizes of Cyclopolyphosphines

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Recent X-ray crystallographic studies have revealed that the cyclopolyphosphine system of general formula $(C_6H_5P)_n$ is surprisingly complex. Form A (mp 150°) involves five-membered phosphorus rings,[1] while the trigonal polymorph of form B (mp 190°) involves six-membered phosphorus rings.[2]

At least two polymeric forms of this material are also known. Perhaps the most interesting structural feature is that both forms A and B appear to be $(C_6H_5P)_4$ in solution,[3] thereby inferring a facile ring interconversion.

Very recently Kuchen and Grunewald[4] have presented gas chromatographic and molecular weight evidence for the presence of $(C_2H_5P)_5$ in what had heretofore been assumed pure $(C_2H_5P)_4$. The purpose of this communication is to report mass spectrographic and P^{31} nmr evidence which both supports Kuchen and Grunewald's conclusions[4] and suggests that other alkyl-substituted "cyclotetraphosphines" are similarly complex. We also report a new result for the reaction of $Ni(CO)_4$ with form A of $(C_6H_5P)_n$.

Experimental Section

The cyclopolyphosphines were prepared by literature methods.[5] The mass spectra were run on a CEC 21-102 instrument equipped with a heated inlet system operating at a temperature of 200°. The P^{31} nmr spectra were recorded[6] on a Varian DP-60 spectrometer at 24.3 Mc/sec. Infrared spectra were run on a Perkin-Elmer Model 521 spectrophotometer.

For the preparation of $(C_6H_5P)_5 \cdot Ni(CO)_3$ 0.3787 g of $(C_6H_5P)_n$ (form A) was treated with excess $Ni(CO)_4$ at 0° on a vacuum line. Carbon monoxide was readily evolved and the solution turned yellow. Evaporation of the excess $Ni(CO)_4$ left a yellow powder. *Anal.* Calcd for $(C_6H_5P)_5 \cdot Ni(CO)_3$: C, 58.02; H, 3.69; P, 22.68. Found: C, 57.85; H, 3.84; P, 22.65. An infrared spectrum (Nujol mull) showed peaks at 1995 (broad), 2040, and 2069 cm^{-1} in the carbonyl stretching region, together with the characteristic[7] monosubstituted benzene modes at 687, 730, 738, 997, and 1023 cm^{-1}.

Results and Discussion

The presence of an intense peak corresponding to the species $(RP)_5^+$ in the mass spectrum of tetraethylcyclotetraphosphine (Table I) strongly suggests the presence of the pentamer, $(C_2H_5P)_5$, in this compound. This conclusion is strengthened by Kuchen and Grunewald's gas chromatographic and molecular weight experiments[4] on the same system. Analogous, but less intense, $(RP)_5^+$ peaks can also be detected in the mass spectra of the *n*-propyl and *n*-butyl homologs. Ions at m/e values even higher than those corresponding to $(RP)_5^+$ were found in the ethyl ($m/e = 393$) and *n*-propyl ($m/e = 389$) compounds. These presumably arise from species such as $(C_2H_5P)_5P_3^+$. No evidence for the presence of higher polymers was found in the mass spectra of $(CH_3P)_5$, $(CF_3P)_4$, or $(CF_3P)_5$.

On the basis of the present evidence we cannot reject the hypothesis that the higher polymers were produced by thermal rearrangement of the cyclotetraphosphines at the relatively high inlet temperatures (200°) necessary for their vaporization. However, comparable temperatures appear to have been employed by

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(1) J. J. Daly and L. Maier, *Nature*, **203**, 1167 (1964); J. J. Daly, *J. Chem. Soc.*, 6147 (1964).

(2) J. J. Daly and L. Maier, *Nature*, **208**, 383 (1965); J. J. Daly, *J. Chem. Soc.*, 4789 (1965).

(3) W. A. Henderson, M. Epstein, and F. S. Seichter, *J. Am. Chem. Soc.*, **85**, 2462 (1963). That form A is $(C_6H_5P)_4$ in solution has also been established by W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2296 (1958); F. Pass and H. Schindlbaur, *Monatsh. Chem.*, **90**, 148 (1959); and also in our own laboratories.

(4) W. Kuchen and W. Grunewald, *Chem. Ber.*, **98**, 480 (1965).

(5) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958); M. M. Rauhut and A. M. Semsel, *J. Org. Chem.*, **28**, 473 (1963); W. A. Henderson, M. Epstein, and F. S. Seichter, *J. Am. Chem. Soc.*, **85**, 2462 (1963).

(6) The authors are very grateful to Dr. Robert L. Carroll of Monsanto for the nmr data.

(7) D. H. Whiffen, *J. Chem. Soc.*, 1350 (1965).

TABLE I

MASS SPECTRA OF CYCLOPOLYPHOSPHINES[a]

m/e	Rel intensity	Assignment	m/e	Rel intensity	Assignment
	$(CH_3P)_5$			$(C_2H_5P)_n$	
230	53.6	$(CH_3P)_5^+$	393	2.3	$(C_2H_5P)_5P_3^+$
215	39.0	$(CH_3P)_4P^+$	300	61.2	$(C_2H_5P)_5^+$
184	4.5	$(CH_3P)_4^+$	271	100.0	$(C_2H_5P)_4P^+$
122	100.0	$(CH_3)_4P_2^+$	240	3.9	$(C_2H_5P)_4^+$
61	60.1	$(CH_3)_2P^+$	161	93.8	$C_2H_5PH^+$
	$(n\text{-}C_3H_7P)_n$			$(n\text{-}C_4H_9P)_n$	
389	3.7	$(C_3H_7P)_4P_3^+$	440	0.1	$(C_4H_9P)_5^+$
370	2.5	$(C_3H_7P)_5^+$	352	0.2	$(C_4H_9P)_4^+$
327	21.7	$(C_3H_7P)_4P^+$	264	9.5	$(C_4H_9P)_3^+$
296	1.4	$(C_3H_7P)_4^+$	48	87.8	$CH_3PH_2^+$ (?)
43	100.0	$(C_3H_7)^+$	41	100.0	$C_3H_5^+$ (?)
	$(CF_3P)_4$			$(CF_3P)_5$	
400	90.6	$(CF_3P)_4^+$	500	0.1	$(CF_3P)_5^+$
331	38.8	$(CF_3)_3P^+$	400	26.1	$(CF_3P)_4^+$
169	2.2	$(CF_3)_2P^+$	231	14.1	$(CF_3)_2P^+$
143	100.0	CF_3PPC^+	143	44.9	CF_3PPC^+
69	70.3	CF_3^+	69	100	CF_3^+

[a] Only includes peaks of high intensity and those germane to the discussion.

others[5] when distilling these compounds. Additional small peaks were also found in the P^{31} nmr spectra of the ethyl, n-propyl, and n-butyl compounds.[8] These may be due to impurities, of course, but the original compounds were found to yield satisfactory elemental analyses,[9] and, furthermore, the n-butyl compound gave the same P^{31} nmr spectrum regardless of whether it was prepared by Rauhut and Semsel's method[5] or by the magnesium coupling of $n\text{-}C_4H_9PCl_2$.

The Raman spectra of several alkyl-substituted cyclopolyphosphines have been interpreted on the assumption that they are pure cyclotetraphosphines.[10] In this study the appearance of more than one Raman-active P–C stretching mode was attributed to either coupling effects or the presence of rotational isomers. In view of the foregoing it is also possible that the additional P–C stretches could arise from admixture of the cyclotetraphosphines with higher polymers. The interpretation of the Raman spectra[11] of forms A and B of $(C_6H_5P)_n$ in terms of different conformers of tetraphenylcyclotetraphosphine is at variance with the X-ray crystallographic data.[1,2]

Studies of the reaction of form A of $(C_6H_5P)_n$ with metal carbonyls indicate that the nature of the product is highly dependent upon reaction conditions. For instance, Ang and Shannon[12] isolated a compound of formula $(C_6H_5P)_4 \cdot Ni(CO)_3$ from the reaction of form A of $(C_6H_5P)_n$ with $Ni(CO)_4$ in diethyl ether at 15°, whereas we isolated $(C_6H_5P)_5 \cdot Ni(CO)_3$ under comparable conditions but in the absence of ether.

Until the conditions for the isolation of a particular cyclopolyphosphine have been determined it may be expedient to use $(CF_3P)_4$ and $(CF_3P)_5$ for spectroscopic studies, etc. These compounds do not appear to be complicated by the presence of higher polymers and the conditions for ring interconversion have been precisely determined.[13]

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[8] W. A. Henderson, *et al.*,[3] report P^{31} chemical shifts of −17, −13, and −14 ppm relative to 85% H_3PO_4 for $(C_2H_5P)_4$, $(n\text{-}C_3H_7P)_4$, and $(n\text{-}C_4H_9P)_4$, respectively. We found a broad singlet at −16 ppm in the ethyl compound, peaks at −53, −16, and −12 ppm in the n-propyl compound, and peaks at −13 and −17 ppm in the n-butyl compound.

[9] For instance, Calcd for $(C_2H_5P)_n$: C, 40.01; H, 8.39; P, 51.60. Found: C, 39.88, H, 8.42; P, 51.39.

[10] R. L. Amster, N. B. Colthup, and W. A. Henderson, *Spectrochim. Acta*, **19**, 1841 (1963).

[11] R. L. Amster, W. A. Henderson, and N. B. Colthup, *Can. J. Chem.*, **42**, 2577 (1964).

[12] H. G. Ang and J. S. Shannon, *Chem. Commun.*, 10 (1965).

[13] A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, **83**, 2388 (1961).

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A New Series of Organoboranes. VIII. The Reaction of Phosgene with the Dilithium Salts of *o*- and *m*-Carborane[1,2]

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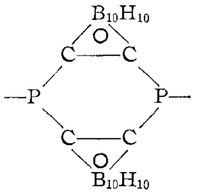
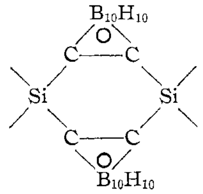
The ability of the carbon atoms of the *o*-carborane moiety to participate in the formation of a six-membered heterocyclic ring skeleton has recently been displayed with the examples of a diphospha-[3] and a disilacyclohexane[4] system





The simplest such ring system yet to be described is the cyclohexane-like skeleton composed of carbon atoms only, four of which are contributed from two carborane nuclei.

When phosgene was allowed to react with $o\text{-}B_{10}H_{10}C_2Li_2$ to generate the desired type of compound, $(o\text{-}B_{10}H_{10}C_2 \cdot CO)_2$ was obtained as a high-melting solid (mp 315°) in 50% yield. All chemical and instrumental analyses including molecular weight de-

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[1] Preceding communication: S. Papetti, B. B. Schaeffer, A. P. Gray, and T. L. Heying, Paper 33 in Symposium on Inorganic Polymers and Plastics, Division of Organic Coatings and Plastics Chemistry, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

[2] The nomenclature of the clovo boron–carbon hydrides is discussed by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963); the terms *o*- and *m*-carborane are used to designate 1,2- and 1,7-dicarbaclovododecaborane.

[3] R. P. Alexander and H. Schroeder, *Inorg. Chem.*, **2**, 1107 (1963).

[4] S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963).