were connected with S_J 18/9 ball joints. An exit bubbler filled with Kel-F oil was connected to the last trap. The entire apparatus was situated in a well-ventilated walk-in hood behind a transparent safety shield.

A gas stream consisting of a mixture of helium (550 cc/min) and fluorine (30 cc/min) was passed through the system. Periodically, the gas stream was diverted and passed through an infrared gas cell by means of a tee and stopcock in the line between the two traps at −78°. The infrared spectra showed weak bands due to F_2NCN and CO_2. The solution became yellowish and then dark orange as the run progressed. During the fluorination, the infrared spectra of the product stream indicated a steadily increasing amount of CO_2 and a relatively constant F_2NCN concentration. After 1 hr, the gas stream was stopped, the fluorinated solution emptied, and the flask recharged with fresh reagents. Fluorination was continued for another hour. The water bath surrounding the reaction flask was held between 9 and 12° by adding ice.

Isolation of the material retained in the two −196° traps by vacuum line techniques yielded 14 mmoles of crude product. Infrared spectra of this product indicated that the composition was approximately 65% F_2NCN, 30% CO_2, and 5% other species. The molecular weight (gas density) of the mixture was 69. Preparative fractional codistillation was employed to isolate 7.5 mmoles of pure F_2NCN from the total crude product. Other species in the crude product, in addition to CO_2, were isolated by fractional codistillation and identified by infrared spectra: HCN, N_2F_4, HNF_2, HNCO, and N_2O.

Infrared Spectra.—The infrared data given in Table I were obtained with a Perkin-Elmer 521 grating infrared spectrophotometer. A Micro-Gas cell[17] was used, with a 10-cm path length and KBr windows. The cell was equipped with a Hoke 440 series stainless steel bellows valve and a stainless steel ball joint for connection to the vacuum line. Other spectra were obtained with a Perkin-Elmer Model 137B instrument.

Nmr Spectrum.—A Varian V4300B high-resolution nuclear magnetic resonance spectrometer operating at 56.4 Mc was used. Several different samples of F_2NCN were examined in *ca.* 10% solutions of $CFCl_3$ at 30°. The ϕ value given is the chemical shift in ppm relative to $CFCl_3$ as an internal standard.

Mass Spectrum.—The mass spectrum of F_2NCN was obtained with a Consolidated Electrodynamics instrument (Model 21-103) with the inlet at room temperature. Partial decomposition occurred with the inlet at 150°. An ionizing voltage of 70 v was used. The spectrum had the following characteristics (mass, ion, relative intensity): 31, CF, 100; 59, CN_2F, 88.7; 78, CN_2F_2, 81.3; 33, NF, 47.8; 26, CN, 24.5; 40, CN_2, 24.0; 14, N, 20.4; 52, NF_2, 12.6; 64, CNF_2, 3.9; 50, CF_2, 3.2.

Vapor Pressure.—Vapor pressures were measured on a freshly codistilled sample of F_2NCN with a simple U-tube Hg manometer. The manometer was isolated from the vacuum line with a Fisher Porter Co. needle valve (1.25 mm, Teflon plastic stem) giving a grease-free vapor space. Some observed pressures were: −93.5°, 98 mm; −78°, 282 mm; and −75°, 340 mm. Extrapolation of the log p_{mm} *vs.* $1/T$ plot resulted in a normal boiling point of −61 ± 1°. The straight-line relationship fits the equation $\log p_{\mathrm{mm}} = -1075/T + 7.97$. This equation gave a heat of vaporization of 4900 cal/mole and a Trouton's constant of 23.

Ultraviolet Spectrum of F_2NCN.—The gas phase spectrum obtained on a Cary Model 14 instrument showed a gradually increasing absorption toward the end of the measurable region in air. The absorbance at 262 $m\mu$ was calculated to be 1.0 at 760 mm in a 10-cm cell.

Rearrangement of F_2NCN to Difluorodiazirine.—A glass sample bulb, 10 cc in volume, was charged in a drybox with 1 g of CsF (American Potash and Chemical Corp.). The reactor was evacuated and warmed briefly with a heat gun. A 200-mm sample of F_2NCN was admitted and the mixture was allowed to stand for 75 min at 24°. After this period, the total pressure found in the reactor was 185 mm; less than 10 mm of the gas was not condensed at −196°. Infrared examination of the material condensed at −196° showed only difluorodiazirine.[14] Fractional codistillation of this product confirmed the presence of a single major component.

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A Phosphine Derivative of Triiron Dodecacarbonyl

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Since the original formulation of triiron dodecacarbonyl in 1930,[1] the structure of this molecule has been investigated by a variety of techniques, but with limited success. Because of disorder in crystalline $Fe_3(CO)_{12}$,[2] the usual structural proof by X-ray methods was unfortunately not possible. Recently, however, Dahl and Blount,[3] on the basis of their X-ray investigation of $[HFe_3(CO)_{11}]^-$, suggested that the structure of $Fe_3(CO)_{12}$ consists of a triangular arrangement of the iron atoms. Two iron atoms, each bonding three terminal CO groups, are bridged by two CO groups, while the unique iron atom is bonded to four terminal CO groups. The postulated structure, however, depends on a close similarity between the molecular structures of $[HFe_3(CO)_{11}]^-$ and $Fe_3(CO)_{12}$. Such a similarity is suggested by Mössbauer studies of these compounds.[4]

In an attempt to resolve the structural problem, we have prepared a simple phosphine derivative of triiron dodecacarbonyl, $Fe_3(CO)_{11}P(C_6H_5)_3$, having properties very similar to those of its parent. Presumably, their molecular structures are also basically the same.

Experimental Section

Preparation of $Fe_3(CO)_{11}P(C_6H_5)_3$.—Approximately 50 g of $Fe_3(CO)_{12}$[5] and 25 g of $P(C_6H_5)_3$ dissolved in 500 ml of $CHCl_3$ were allowed to react at 45° for 45 min under nitrogen. After cooling to −72°, the solution was allowed to warm to room temperature under vacuum, during which time the $CHCl_3$ and $Fe(CO)_5$ distilled from the mixture. The solid residue was extracted with successively smaller portions (500, 250, 150, 100, and 100 ml) of CCl_4, leaving much of the $P(C_6H_5)_3$, $Fe_3(CO)_{12}$, $Fe(CO)_4P(C_6H_5)_3$, and $Fe(CO)_3[P(C_6H_5)_3]_2$ undissolved. The

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[17] Barnes Engineering Co., Instrument Division, Stamford, Conn.

[1] W. Hieber and E. Becker, *Chem. Ber.*, **63**, 1405 (1930).

[2] L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **26**, 1751 (1957).

[3] L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).

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[5] R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 193 (1963).

combined CCl_4 extracts were chromatographed under nitrogen on a 65-mm diameter column using 30 cm of dried and deaerated silica gel. The $Fe_3(CO)_{12}$ and $Fe(CO)_4P(C_6H_5)_3$ were eluted with CCl_4; the green band of $Fe_3(CO)_{11}P(C_6H_5)_3$ was eluted with $CHCl_3$ while the $Fe(CO)_3[P(C_6H_5)_3]_2$ remained at the top of the column. The $Fe_3(CO)_{11}P(C_6H_5)_3$ fraction was cooled to $-72°$ and the solvent allowed to distil off as the solution warmed to room temperature under vacuum. Often another chromatographic run under the same conditions was necessary to obtain the pure product. The yield of the green-black product was 1.5 g or 2%.

Anal. Calcd for $Fe_3(CO)_{11}P(C_6H_5)_3$: C, 47.2; H, 2.05; Fe, 22.7; P, 4.20; O, 23.8; mol wt, 738. Found: C, 47.8; H, 2.20; Fe, 22.8; P, 4.01; O, 23.7; mol wt, 757 (osmometer in benzene).

In the C–O stretching region of its infrared spectrum there were absorptions at 2088 (m), 2034 (s), 2013 (vs), ~1965 (w, sh), and 1825 (vw, br) cm^{-1} when taken in cyclohexane solvent (Figure 1). In a KBr pellet, the weak band in the C–O bridging region gained significantly in intensity and was resolved into three peaks. The absorptions occurred at 2086 (m), 2028 (s), 1995 (vs), 1949 (m), 1836 (w), 1815 (w), and 1795 (w) cm^{-1}.

$Fe_3(CO)_{11}P(C_6H_5)_3$ is soluble in common organic solvents in which it decomposes slowly when exposed to air or light. Evaporation of pentane solutions under nitrogen and in the absence of light yields dark green single crystals of the compound.

In solution, $Fe_3(CO)_{11}P(C_6H_5)_3$ reacts with additional $P(C_6H_5)_3$ to form only $Fe(CO)_4P(C_6H_5)_3$ and $Fe(CO)_3[P(C_6H_5)_3]_2$, as determined from the infrared spectra of the products.

Discussion

Triiron dodecacarbonyl is known[6] to react with $P(C_6H_5)_3$ to give $Fe(CO)_4P(C_6H_5)_3$ and $Fe(CO)_3[P(C_6H_5)_3]_2$. In the course of kinetic studies of this reaction, it became apparent that an intermediate was formed and that the steps of the reaction are better represented by the equations

$$Fe_3(CO)_{12} + P(C_6H_5)_3 \longrightarrow Fe_3(CO)_{11}P(C_6H_5)_3 + Fe(CO)_5 + Fe(CO)_4P(C_6H_5)_3 + Fe(CO)_3[P(C_6H_5)_3]_2 + CO \quad (1)$$

$$Fe_3(CO)_{11}P(C_6H_5)_3 + P(C_6H_5)_3 \longrightarrow Fe(CO)_4P(C_6H_5)_3 + Fe(CO)_3[P(C_6H_5)_3]_2 + CO \quad (2)$$

The equations are not balanced because as the concentration of $P(C_6H_5)_3$ was increased the amount of product $Fe(CO)_4P(C_6H_5)_3$ decreased while that of $Fe(CO)_3[P(C_6H_5)_3]_2$ increased. This was true for both reactions 1 and 2. That $Fe_3(CO)_{12}$ reacts with $P(C_6H_5)_3$ by at least two pathways is evidenced by the formation of $Fe(CO)_5$ in reaction 1 but not in reaction 2. From the amounts of $Fe(CO)_5$ produced it was obvious that much of the $Fe_3(CO)_{12}$ reaction did not proceed through the $Fe_3(CO)_{11}P(C_6H_5)_3$ intermediate. The relatively small amount of formation of the intermediate according to eq 1 and its relatively rapid reaction according to eq 2 resulted in very low concentrations of the intermediate in solution. By quenching the reaction at the maximum concentration of $Fe_3(CO)_{11}P(C_6H_5)_3$, as determined from the intensity of the 2088 cm^{-1} absorption, it was possible to isolate the pure compound. Reaction mixtures of the phosphites, 4-methyl-3,6,7-trioxa-1-phosphabicyclo[2.2.2]octane [$P(OCH_2)_3CCH_3$], and 1-phospha-2,8,9-trioxaadamantane ($PO_3C_6H_9$),[7] with $Fe_3(CO)_{12}$ also showed an absorption at about 2092 cm^{-1} characteristic of the $Fe_3(CO)_{11}L$ intermediate.

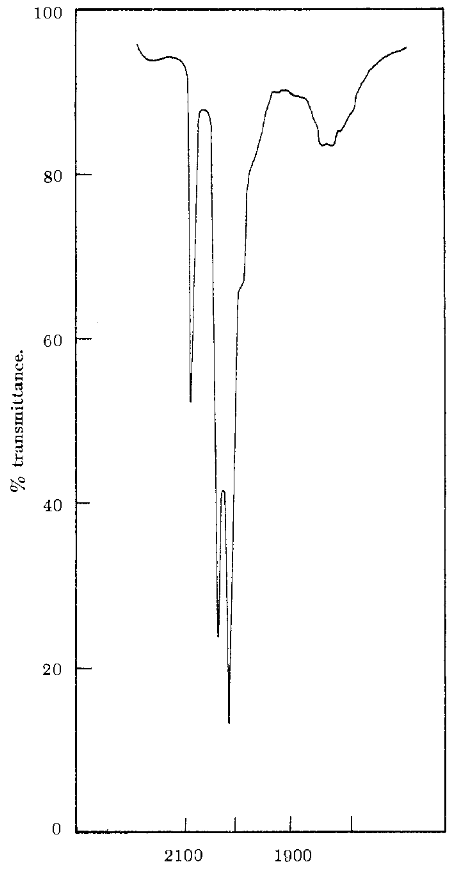

Figure 1.—Infrared spectrum of $Fe_3(CO)_{11}P(C_6H_5)_3$ in cyclohexane in the C–O stretching region.

If the structure of $Fe_3(CO)_{11}P(C_6H_5)_3$ were determined and used to infer the structure of $Fe_3(CO)_{12}$, it is important that strong similarities in the properties of these two substances exist. That the structures are closely related is suggested by the preparation of $Fe_3(CO)_{11}P(C_6H_5)_3$ directly from the parent molecule, $Fe_3(CO)_{12}$. In addition, both compounds are green-black in the solid state and give intensely colored green solutions. The solution spectra of both compounds in the C–O stretching region contain intense terminal C–O absorptions and weak absorptions in the C–O bridging region. In KBr pellets, the absorptions in the C–O bridging region increase in intensity substantially in both substances. All of this evidence strongly supports the contention that $Fe_3(CO)_{11}P(C_6H_5)_3$ and $Fe_3(CO)_{12}$ are structurally very similar.

Preliminary X-ray results[8] clearly indicate that $Fe_3(CO)_{11}P(C_6H_5)_3$ has a triangular structure with two bridging C–O groups. This is the structure proposed for $Fe_3(CO)_{12}$ by Dahl and Blount[3] on the basis of their X-ray investigations of $[HFe_3(CO)_{11}]^-$.

As noted previously,[3] the proposed structure of $Fe_3(CO)_{12}$ does not account for the paucity of observed terminal C–O stretching absorptions (only two), but is in agreement with the two observed C–O bridging absorptions. In $Fe_3(CO)_{11}P(C_6H_5)_3$, the four observed

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(7) J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *ibid.*, **4**, 83 (1965).

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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 $Fe_3(CO)_{11}P(C_6H_5)_3$.

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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).

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

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