was heated under reflux for approximately 5 h. The solution remained clear during this period. ^{31}P NMR spectroscopy indicated the presence of only unchanged starting material.

Attempted Reaction of $O_2S(t\text{-BuN})_2PCl$ (6) with Elemental Sulfur. A mixture of 2.63 g (0.96 mmol) of $O_2S(t\text{-BuN})_2PCl$ (6) and an excess of elemental sulfur was refluxed in benzene for approximately 5 h. When the mixture was allowed to stand overnight, yellow crystals of elemental sulfur deposited from the solution. NMR spectroscopic examination of the filtrate revealed only the presence of unchanged starting material.

Acknowledgment. The authors are grateful to the Office of Naval Research (Contract N00014-76-C-0577, Task No. NR 053-612), the Deutschen Forschungsgemeinschaft, dem Fonds der Chemischen Industrie, and Hoechst AG for generous financial support.

Registry No. **6**, 76037-02-0; **8**, 76037-03-1; **9**, 76037-04-2; **12**, 76037-05-3; **14**, 76037-06-4; **15**, 76037-10-0; $O_2S(t\text{-BuNH})_2$, 13952-67-5; PCl_3, 7719-12-2; SbF_3, 7783-56-4; Me_3SiNMe_2, 2083-91-2; $AgBF_4$, 14104-20-2; SbF_5, 7783-70-2; Fe_2CO_9, 15321-51-4.

Contribution from the Department of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania 16802

Synthesis and Molecular Structure of Two Cyclotriphosphazenes with Phosphorus–Iron Bonds

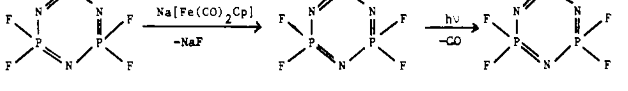
HARRY R. ALLCOCK,* PAUL P. GREIGGER, LINDA J. WAGNER, and MARGUERITE Y. BERNHEIM

Received March 6, 1980

Hexafluorocyclotriphosphazene (I), $(NPF_2)_3$, reacts with sodium dicarbonylcyclopentadienylferrate to form photolytically unstable 1,1-bis(dicarbonylcyclopentadienyliron)-3,3,5,5-tetrafluorocyclotriphosphazene (II). This compound decarbonylates to 1,1-[μ-carbonyl-bis(carbonylcyclopentadienyliron)(*Fe–Fe*)]-3,3,5,5-tetrafluorocyclotriphosphazene (III) on exposure to light. Compounds II and III are the first phosphazenes known that contain direct phosphorus–metal side group bonds. In addition, III is the first phosphazene with a three-membered spirocyclic ring at phosphorus. Compounds II and III are forerunners of a potentially important class of new compounds based on other transition-metal systems. Spectroscopic evidence and X-ray crystallographic analyses were used to confirm the two structures. Compound II crystallizes in a triclinic unit cell of $P\bar{1}$ symmetry with lattice constants of $a = 9.035\ (3)$ Å, $b = 14.287\ (15)$ Å, $c = 8.613\ (4)$ Å, $\alpha = 104.04\ (4)°$, $\beta = 110.44\ (1)°$, and $\gamma = 96.56\ (2)°$; $\rho_{calcd} = 1.9$ g/cm^3 for $Z = 2$. Least-squares refinement gave $R_1 = 0.056$ and $R_2 = 0.066$ for 3906 observed reflections with $I \geq 3\sigma(I)$. The distance between the iron atoms in II is 3.922 (1) Å, and the Fe–P–Fe angle is 119.12 (3)°. Compound III crystallizes in a triclinic unit cell of $P\bar{1}$ symmetry with lattice constants of $a = 9.116\ (14)$ Å, $b = 14.219\ (9)$ Å, $c = 7.735\ (17)$ Å, $\alpha = 90.48\ (3)°$, $\beta = 113.93\ (4)°$, and $\gamma = 92.83\ (2)°$; $\rho_{calcd} = 1.9$ g/cm^3 for $Z = 2$. Least-squares refinement gave $R_1 = 0.0498$ and $R_2 = 0.0524$ for 2634 observed reflections with $I \geq 3\sigma(I)$. The Fe–Fe bond distance in III is 2.593 (1) Å and the Fe–P–Fe bond angle is 72.77 (3)°. The N–P–N bond angles at the phosphorus that is bonded to the iron atoms are 109.18 (11) and 110.09 (16)° for compounds II and III, respectively. In both compounds, an alternation of longer and shorter bonds exists for the P–N bonds located at increasing distance from the iron atoms.

Halophosphazenes, both polymeric and cyclic, are known to react with a wide range of nucleophiles including alkoxides, aryl oxides, amines, and organolithium or Grignard reagents[1] to yield *organo*phosphazenes of the type $[NP(OR)_2]_{3,4,n}$, $[NP(NHR)_2]_{3,4,n}$, or $(NPR_2)_{3,4,n}$. However few examples of phosphazene–transition-metal compounds have been reported,[2-7] and in most of these cases the phosphazene component served as a coordination ligand for the transition metal.

In this paper, we extend the known reactions of halophosphazenes into a new and important area—the synthesis of the first compounds that contain a metal-to-phosphorus covalent bond. This has been accomplished by the interaction of halophosphazenes with transition-metal carbonyl anions. Here we report the interaction of one of the most nucleophilic transition-metal carbonyl anions,[8] $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$, with $(NPF_2)_3$ (I). This has led to the isolation of two cyclophosphazenes that possess iron–phosphorus covalent bonds. These compounds have the structures shown in II and III.



I II III

Species II and III are of interest because (a) they are the first members of a potentially large group of transition-metal-linked cyclophosphazenes, (b) such compounds are expected to provide new information about the bonding within the phosphazene ring, and (c) these cyclic derivatives are models for the synthesis of the related phosphazene high-polymer derivatives. Polyphosphazenes of this type may be important because of their potential value in the development of new polymeric electrical conductors and because of their potential utility in polymer-supported catalyst systems. Work on these applied aspects is under way.

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0020-1669/81/1320-0716$01.00/0

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (Ethyl Corp. or El Monte Chemical Co.), was purified by sublimation (60 °C, 0.01 torr) followed by two recrystallizations from hexane. $(NPF_2)_3$ was prepared from $(NPCl_2)_3$ and NaF.[9] Tetrahydrofuran (THF) (Fisher) was dried and distilled from sodium benzophenone ketyl before use. Hexane and methylene chloride (Fisher) were degassed before use. The sodium dispersion (40% in mineral oil) and $[Fe(CO)_2Cp]_2$ were obtained from Alfa. Basic alumina (Brockman Activity I, 80–200 mesh) was obtained from Fisher. All reactions were carried out under an atmosphere of dry nitrogen.

Equipment. ^1H and ^{19}F NMR spectra were recorded on a JEOL PS-100 FT NMR spectrometer. ^1H NMR spectra were also obtained on a Varian A-60A NMR spectrometer. High-resolution ^{31}P NMR spectra were recorded on a Bruker WP 200 spectrometer at 80 MHz. The ^{31}P chemical shifts are relative to aqueous 85% H_3PO_4, with positive shifts downfield from this reference. Infrared spectra were recorded on a Perkin-Elmer 580 grating spectrophotometer, either as a solution in CH_2Cl_2 (NaCl plates with 0.1-mm spacers) or as a solid (KBr disks). Electron-impact mass spectral results were obtained with an AEI MS 902 mass spectrometer. Chemical ionization mass spectral data were obtained with a Finnigan 3200 mass spectrometer. Chromatographic separations were carried out with the use of a Waters Associates Prep LC/System 500 liquid chromatograph. Microanalytical information was supplied by Galbraith Laboratories, Knoxville, Tenn.

Preparation of $Na[Fe(CO)_2Cp]$. $Na[Fe(CO)_2Cp]$ was prepared by the method of Reger et al.[10] using sodium dispersion as a reducing agent. In a typical reaction, $[Fe(CO)_2Cp]_2$ (3.1860 g, 9 mmol) and sodium (2.0 g as a 40% sodium dispersion in mineral oil) were placed in a 250-mL round-bottomed flask which was equipped with a heating mantle, a reflux condenser, a magnetic stirrer, and a nitrogen inlet. The reactants were subjected to reduced pressure for 1 h, and THF (130 mL) was then added. The reaction mixture was heated to reflux for 10 h, was cooled to 25 °C, and was then filtered into an addition funnel.

Preparation of II. In a typical reaction, a filtered solution of $Na[Fe(CO)_2Cp]$ (16 mmol) was added to a solution of $(NPF_2)_3$ (2.0 g, 8 mmol) in THF (100 mL) at 25 °C. The reaction mixture was stirred (in the absence of light) at 25 °C for 24 h. The reaction solvent was removed by the use of a rotary evaporator under a reduced pressure of nitrogen. The products were separated by column chromatography on a basic alumina column of dimensions 32 × 490 mm or by preparative high-pressure liquid chromatography with the use of silica gel columns. $[Fe(CO)_2Cp]_2$ was eluted with hexane as the eluant. Compound II eluted following a gradual increase in the concentration of methylene chloride in hexane until 100% methylene chloride was used. Purification of II was effected by recrystallization from a hexane–methylene chloride solvent mixture.

Preparation of III. Compound II was converted to compound III by exposure of II (in the solid state) to room light or by the irradiation of a hexane solution of II with light of wavelength 354 nm. Compound III was purified by recrystallization from a hexane–methylene chloride solvent mixture.

Single-Crystal X-ray Data Collection. Compound II was crystallized as pale yellow prismatic crystals from a hexane–methylene chloride solvent mixture. A crystal with dimensions ca. 0.20 × 0.23 × 0.40 mm was mounted along the longer axis and was used in the structure analysis. Once the yellow crystal was centered optically on the diffractomer, all the remaining measurements were carried out in the absence of light to prevent the conversion of II to III. Compound III crystallized as dark red parallelepipeds from hexane–methylene chloride. A suitable crystal with dimensions ca. 0.15 × 0.15 × 0.17 mm was cleaved from a larger crystal and was used in the X-ray analysis.

Individual crystals were mounted in a random orientation on an Enraf-Nonius CAD-IV diffractometer, and 25 reflections were located. For each crystal, a least-squares refinement of the 2θ values for these 25 reflections indicated triclinic lattices having the following dimensions. II: $a =: 9.035$ (3) Å, $b = 14.287$ (15) Å, $c = 8.613$ (4) Å, $\alpha = 104.04$ (4)°, $\beta = 110.44$ (1)°, $\gamma = 96.56$ (2)°, $V = 986.2$ (3) Å^3. III: $a = 9.116$ (14) Å, $b = 14.219$ (9) Å, $c = 7.735$ (17) Å, $\alpha = 90.48$ (3)°, $\beta = 113.93$ (4)°, $\gamma = 92.83$ (2)°, $V = 914.9$ (1) Å^3.

Both volumes are consistent with $Z = 2$ for a $\rho_{calcd} \simeq 1.9$ g/cm^3. An application of the zero-moment test of Howells, Phillips, and Rodgers[11] indicated a centrosymmetric cell for both crystals and therefore suggested space group No. 2, $P\bar{1}$.

A graphite-crystal incident-beam monochromator was used with Mo Kα radiation ($\lambda_{\alpha_1} = 0.709\,30$ Å) and data were collected at a takeoff angle of 2.80°. The crystal to incident-beam collimator distance was 48 mm, and the crystal to aperture distance was 17.3 cm. A $\theta/2\theta$ scan method was used with a variable scan rate ranging from 20°/min for the most intense reflections to 1°/min for weaker reflections. The angular scan width (ω) was variable and amounted to 0.6° before 2θ(Mo Kα_1) and $(0.6 + 0.347 \tan\theta)$° after 2θ(Mo Kα_2). Right and left backgrounds were each scanned for 25% of the total scan time. During the data collection, three standard reflections were monitored after every 4 h of actual X-ray exposure time and were used to place the data on a common scale. The change in intensities for the standards used for compound II over the entire data set varied ±4%, while the change in intensities for the standards for compound III was −30%.

For compound II, 6064 unique reflections were collected out to $2\theta = 70°$. Of these 6064 reflections sampled, 3906 were considered observed with $I \geq 3\sigma(I)$. (Here $\sigma(I) = [S^2(C + R^2B) + (\rho I)^2]^{1/2}$ and $I = S(C - RB)$, where S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, and $\rho = 0.05$.) A total of 9024 unique reflections were collected out to $2\theta = 50°$ for compound III. Of the 9024 reflections that were sampled, 2634 were considered observed with $I \geq 3\sigma(I)$. In both cases, the data were corrected for Lorentz and polarization factors[12] and were used in the refinement of the structures.

Structural Determination and Refinement. In this section of the paper, the structure solution for compound II will be explained in detail. The solution for III was similar, and corresponding values for III will be given in parentheses.

The atomic scattering factors used for all atoms were those of Cromer and Waber,[13] and these were corrected for anomalous dispersion[13] (both real and imaginary parts). The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma(F_o))^2$.

Starting positions for the two iron atoms and the three phosphorus atoms of II (for III, two iron atoms, three phosphorus atoms, and one fluorine) were obtained from a MULTAN E-map synthesis, where $E_{min} = 1.97$ (2.05). Refinement was carried out by the full-matrix least-squares method and yielded isotropic $R_1 = 0.327$ and $R_2 = 0.397$ ($R_1 = 0.300$ and $R_2 = 0.362$). Subsequent difference Fourier/least-squares refinements allowed the location of the remaining nonhydrogen atoms. Isotropic least-squares values at this stage were $R_1 = 0.106$ and $R_2 = 0.105$ ($R_1 = 0.153$ and $R_2 = 0.172$).

Anisotropic refinement converged to $R_1 = 0.057$ and $R_2 = 0.069$ ($R_1 = 0.055$ and $R_2 = 0.060$) with the esd of an observation of unit weight 3.317 (2.540). Hydrogen atoms were located at reasonable distances about the cyclopentadienyl carbons atoms. Refinement of the hydrogen positional parameters (isotropic B value at 1 more than the average value of ring carbon atoms) yielded final $R_1 = 0.056$ and $R_2 = 0.066$ ($R_1 = 0.0498$ and $R_2 = 0.0524$). (Convergence was considered complete when all the shifts were less than one-tenth their standard deviations.) Inclusion of the unobserved reflections had little effect on the bond distances and angles. The final difference maps were smooth, with maxima and minima of ±0.32 e/Å^3 (±0.39 e/Å^3). Here $R_1 = (\sum||F_o| - |F_c||)/(\sum|F_o|)$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum_i wF_o^2]^{1/2}$; $w = 1/(\sigma(F_o))^2$ and $\sigma(F_o^2) = [\sigma(I)^2 + (0.02F^2)^2]^{1/2}/(Lp)$ where $F_o^2 = F^2/(Lp)$.

The positional and thermal parameters from the final cycle of the full matrix least-squares refinement are given in Tables V and VI. Interatomic distances and bond angles with esd's are presented in Tables I and III. Selected least-squares planes and interplanar angles

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Table I. Distances and Angles in $[N_3P_3F_4(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$ (II)

Distances (Å)

Fe(1)···Fe(2)	3.922 (1)	C(1)R(2)-C(2)R(2)	1.403 (4)
Fe(1)-P(1)	2.272 (1)	C(2)R(2)-C(3)R(2)	1.382 (5)
Fe(2)-P(1)	2.277 (1)	C(3)R(2)-C(4)R(2)	1.404 (6)
Fe(1)-C(1)M(1)	1.732 (3)	C(4)R(2)-C(5)R(2)	1.375 (5)
Fe(1)-C(2)M(1)	1.748 (3)	C(5)R(2)-C(1)R(2)	1.418 (5)
Fe(2)-C(1)M(2)	1.738 (3)	C(1)R(1)-H(1)R(1)	0.868 (29)
Fe(2)-C(2)M(2)	1.750 (3)	C(2)R(1)-H(2)R(1)	1.436 (34)
C(1)M(1)-O(1)M(1)	1.160 (4)	C(3)R(1)-H(3)R(1)	0.862 (33)
C(2)M(1)-O(2)M(1)	1.141 (4)	C(4)R(1)-H(4)R(1)	0.889 (33)
C(1)M(2)-O(1)M(2)	1.156 (4)	C(5)R(1)-H(5)R(1)	0.914 (32)
C(2)M(2)-O(2)M(2)	1.142 (3)	C(1)R(2)-H(1)R(2)	0.938 (32)
Fe(1)-C(1)R(1)	2.101 (3)	C(2)R(2)-H(2)R(2)	0.828 (33)
Fe(1)-C(2)R(1)	2.126 (3)	C(3)R(2)-H(3)R(2)	0.646 (34)
Fe(1)-C(3)R(1)	2.108 (3)	C(4)R(2)-H(4)R(2)	0.730 (33)
Fe(1)-C(4)R(1)	2.086 (3)	C(5)R(2)-H(5)R(2)	0.860 (33)
Fe(1)-C(5)R(1)	2.097 (3)	P(1)-N(12)	1.666 (2)
Fe(2)-C(1)R(2)	2.101 (3)	P(1)-N(13)	1.665 (2)
Fe(2)-C(2)R(2)	2.121 (3)	P(2)-N(12)	1.533 (2)
Fe(2)-C(3)R(2)	2.095 (4)	P(2)-N(23)	1.563 (3)
Fe(2)-C(4)R(2)	2.106 (3)	P(3)-N(13)	1.527 (2)
Fe(2)-C(5)R(2)	2.104 (3)	P(3)-N(23)	1.576 (3)
C(1)R(1)-C(2)R(1)	1.399 (5)	P(2)-F(1)P(2)	1.539 (2)
C(2)R(1)-C(3)R(1)	1.401 (5)	P(2)-F(2)P(2)	1.533 (2)
C(3)R(1)-C(4)R(1)	1.425 (5)	P(3)-F(1)P(3)	1.538 (2)
C(4)R(1)-C(5)R(1)	1.385 (5)	P(3)-F(2)P(3)	1.533 (2)
C(5)R(1)-C(1)R(1)	1.392 (5)		

Angles (Deg)

Fe(1)-P(1)-Fe(2)	119.12 (3)
C(1)M(1)-Fe(1)-C(2)M(1)	94.67 (15)
C(1)M(2)-Fe(2)-C(2)M(2)	94.57 (15)
Fe(1)-C(1)M(1)-O(1)M(1)	177.05 (27)
Fe(1)-C(2)M(1)-O(2)M(1)	177.27 (33)
Fe(2)-C(1)M(2)-O(1)M(2)	177.08 (25)
Fe(2)-C(2)M(2)-O(2)M(2)	178.52 (29)
Fe(1)-P(1)-N(12)	106.64 (8)
Fe(2)-P(1)-N(13)	105.51 (8)
C(2)R(1)-C(1)R(1)-C(5)R(1)	109.61 (35)
C(1)R(1)-C(5)R(1)-C(4)R(1)	108.15 (34)
C(5)R(1)-C(4)R(1)-C(3)R(1)	107.30 (32)
C(4)R(1)-C(3)R(1)-C(2)R(1)	108.46 (32)
C(3)R(1)-C(2)R(1)-C(1)R(1)	106.46 (32)
H(1)R(1)-C(1)R(1)-C(5)R(1)	126.25 (2.02)
H(1)R(1)-C(1)R(1)-C(2)R(1)	124.13 (1.99)
H(2)R(1)-C(2)R(1)-C(1)R(1)	71.05 (1.36)
H(2)R(1)-C(2)R(1)-C(3)R(1)	65.22 (1.41)
H(3)R(1)-C(3)R(1)-C(4)R(1)	122.49 (2.39)
H(3)R(1)-C(3)R(1)-C(2)R(1)	128.84 (2.37)
H(4)R(1)-C(4)R(1)-C(5)R(1)	120.34 (2.19)
H(4)R(1)-C(4)R(1)-C(3)R(1)	131.77 (2.21)
H(5)R(1)-C(5)R(1)-C(1)R(1)	116.21 (2.15)
H(5)R(1)-C(5)R(1)-C(4)R(1)	134.77 (2.15)
C(2)R(2)-C(1)R(2)-C(5)R(2)	107.57 (30)
C(1)R(2)-C(5)R(2)-C(4)R(2)	107.79 (33)
C(5)R(2)-C(4)R(2)-C(3)R(2)	108.32 (32)
C(4)R(2)-C(3)R(2)-C(2)R(2)	108.55 (32)
C(3)R(2)-C(2)R(2)-C(1)R(2)	107.75 (32)
H(1)R(2)-C(1)R(2)-C(5)R(2)	121.31 (2.01)
H(1)R(2)-C(1)R(2)-C(2)R(2)	131.12 (2.02)
H(2)R(2)-C(2)R(2)-C(1)R(2)	125.10 (2.42)
H(2)R(2)-C(2)R(2)-C(3)R(2)	125.77 (2.44)
H(3)R(2)-C(3)R(2)-C(4)R(2)	129.55 (3.76)
H(3)R(2)-C(3)R(2)-C(2)R(2)	121.80 (3.75)
H(4)R(2)-C(4)R(2)-C(5)R(2)	139.82 (3.09)
H(4)R(2)-C(4)R(2)-C(3)R(2)	111.84 (3.09)
H(5)R(2)-C(5)R(2)-C(1)R(2)	122.07 (2.39)
H(5)R(2)-C(5)R(2)-C(4)R(2)	130.12 (2.38)
N(12)-P(1)-N(13)	109.18 (11)
N(12)-P(2)-N(23)	121.48 (13)
N(23)-P(3)-N(13)	121.34 (13)
P(1)-N(12)-P(2)	124.77 (14)
P(2)-N(23)-P(3)	117.90 (14)
P(3)-N(13)-P(1)	124.82 (14)
F(1)P(2)-P(2)-F(2)P(2)	95.54 (13)
F(1)P(3)-P(3)-F(2)P(3)	95.31 (13)
N(12)-P(2)-F(1)P(2)	111.14 (12)
N(23)-P(2)-F(2)P(2)	107.12 (13)
N(13)-P(3)-F(1)P(3)	111.17 (13)
N(23)-P(3)-F(2)P(3)	107.36 (13)

Table II. Least-Squares Planes for $[N_3P_3F_4(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$ (II)

A. Equations Defining Least-Squares Planes

plane I, through P(1), P(2), P(3), N(12), N(23), N(13)
$0.0908x + 0.6620y - 0.7439z - 3.3547 = 0$

plane II, through P(1), Fe(1), Fe(2)
$0.0569x - 0.6999y - 0.7120z - 5.3582 = 0$

plane III, through C(1)R(1), C(2)R(1), C(3)R(1), C(4)R(1), C(5)R(1)
$0.6562x - 0.7176y - 0.2334z - 0.7409 = 0$

plane IV, through C(1)R(2), C(2)R(2), C(3)R(2), C(4)R(2), C(5)R(2)
$-0.5195x - 0.7639y - 0.3828z - 5.4497 = 0$

B. Distances (Å) of Some Atoms from Plane I

P(1)	0.002 (1)	F(1)P(2)	−1.192 (3)
P(2)	−0.009 (1)	F(2)P(2)	1.081 (4)
P(3)	0.008 (1)	F(1)P(3)	1.192 (4)
N(12)	0.048 (4)	F(2)P(3)	−1.074 (3)
N(23)	0.012 (4)	Fe(1)	−1.943 (1)
N(13)	−0.081 (4)	Fe(2)	1.969 (1)

C. Distances (Å) of Some Atoms from Plane II

P(1)	0.000 (1)	O(2)M(1)	−0.411 (4)
Fe(1)	−0.000 (1)	C(1)M(2)	1.595 (5)
Fe(2)	0.000 (1)	O(1)M(2)	2.665 (4)
C(1)M(1)	−1.681 (5)	C(2)M(2)	0.565 (5)
O(1)M(1)	−2.815 (4)	O(2)M(2)	0.910 (4)
C(2)M(1)	−0.281 (5)		

D. Angles (Deg) between Normals to Planes

I and II	85.9	II and III	45.1
I and III	76.0	II and IV	39.0
I and IV	74.5	III and IV	72.7

are given in Tables II and IV. The observed and calculated structure factor amplitudes are available as supplementary material.

Results and Discussion

The Reaction of $(NPF_2)_3$ with Na[Fe(CO)$_2$Cp]. The reaction of $(NPF_2)_3$ with Na[Fe(CO)$_2$Cp] resulted in the isolation of two phosphazene–transition-metal compounds. The reaction with Na[Fe(CO)$_2$Cp] at 25 °C in THF gave a complex mixture of products, but chromatographic separation yielded a bright yellow product of structure II in 10% yield. The possibility exists that the remaining 90% of the products consisted of more highly substituted species or nongeminally substituted derivatives. However, no other pure products have yet been isolated from the reaction mixture or could be identified by spectroscopic techniques. When exposed to light, II released carbon monoxide to form the spirocyclic species III, a red, air-stable compound.[14]

In the following sections of this paper, the spectroscopic characteristics of compounds II and III are presented first, followed by a discussion of the structural features.

Spectroscopic Characteristics of II. The infrared spectrum of II (KBr disks) showed peaks that were consistent with the presence of terminal carbonyl absorbances at 2038 (sh), 2020 (s), and 1977 (br) cm^{-1}. Absorbances for P–N bonds were observed at 1240 and 1210 cm^{-1}. A C–H stretch was observed at 3120 (w) cm^{-1}. The ^{1}H NMR spectrum of II consisted of a singlet at 5.3 ppm (downfield from Me$_4$Si), attributed to the protons of the cyclopentadienyl rings. The high-resolution ^{31}P NMR spectrum of II permitted two types of phosphorus atoms to be identified. The PF$_2$ resonance appeared at −0.3 ppm as a major triplet, and J_{PF} = 891.4 Hz. Unresolved fine structure was also present from J_{FPNPF} and J_{PNP} coupling. The PFe$_2$ resonance appeared as a triplet at 158.4 ppm with J_{PNP} = 32.0 Hz. The electron-impact mass spectrum of II did not show the parent ion. Instead, the parent ion minus one carbonyl ligand was observed (*m/e* 537). However, the parent ion for

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[14] Greigger, P. P.; Allcock, H. R. *J. Am. Chem. Soc.* **1979**, *101*, 2492.

Table III. Distances and Angles in $[N_3P_3F_4(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3]$ (III)

Distances (A)

Fe(1)–Fe(2)	2.593 (1)	C(1)R(2)–C(2)R(2)	1.384 (7)
Fe(1)–P(1)	2.179 (1)	C(2)R(2)–C(3)R(2)	1.384 (7)
Fe(2)–P(1)	2.193 (1)	C(3)R(2)–C(4)R(2)	1.378 (6)
Fe(1)–C(1)B	1.928 (4)	C(4)R(2)–C(5)R(2)	1.392 (7)
Fe(2)–C(1)B	1.916 (4)	C(5)R(2)–C(1)R(2)	1.385 (7)
C(1)B–O(1)B	1.167 (4)	C(1)R(1)–H(1)R(1)	0.638 (43)
Fe(1)–C(2)M(1)	1.749 (5)	C(2)R(1)–H(2)R(1)	0.910 (38)
C(2)M(1)–O(2)M(1)	1.125 (5)	C(3)R(1)–H(3)R(1)	1.095 (39)
Fe(2)–C(2)M(2)	1.750 (4)	C(4)R(1)–H(4)R(1)	0.771 (41)
C(2)M(2)–O(2)M(2)	1.143 (4)	C(5)R(1)–H(5)R(1)	0.731 (43)
Fe(1)–C(1)R(1)	2.084 (5)	C(1)R(2)–H(1)R(2)	0.964 (38)
Fe(1)–C(2)R(1)	2.102 (5)	C(2)R(2)–H(2)R(2)	0.826 (39)
Fe(1)–C(3)R(1)	2.109 (4)	C(3)R(2)–H(3)R(2)	1.125 (36)
Fe(1)–C(4)R(1)	2.081 (5)	C(4)R(2)–H(4)R(2)	1.017 (38)
Fe(1)–C(5)R(1)	2.059 (6)	C(5)R(2)–H(5)R(2)	0.852 (37)
Fe(2)–C(1)R(2)	2.104 (5)	P(1)–N(12)	1.633 (3)
Fe(2)–C(2)R(2)	2.056 (5)	P(1)–N(13)	1.636 (3)
Fe(2)–C(3)R(2)	2.061 (5)	P(2)–N(12)	1.537 (3)
Fe(2)–C(4)R(2)	2.100 (4)	P(2)–N(23)	1.563 (3)
Fe(2)–C(5)R(2)	2.107 (4)	P(3)–N(13)	1.547 (3)
C(1)R(1)–C(2)R(1)	1.365 (8)	P(3)–N(23)	1.566 (3)
C(2)R(1)–C(3)R(1)	1.358 (7)	P(2)–F(1)P(2)	1.523 (3)
C(3)R(1)–C(4)R(1)	1.320 (9)	P(2)–F(2)P(2)	1.526 (2)
C(4)R(1)–C(5)R(1)	1.392 (10)	P(3)–F(1)P(3)	1.524 (2)
C(5)R(1)–C(1)R(1)	1.349 (10)	P(3)–F(2)P(3)	1.527 (2)

Angles (Deg)

Fe(1)–P(1)–Fe(2)	72.77 (3)
P(1)–Fe(1)–Fe(2)	53.87 (3)
P(1)–Fe(2)–Fe(1)	53.36 (3)
Fe(1)–C(1)B–Fe(2)	84.82 (16)
C(1)B–Fe(1)–Fe(2)	47.39 (12)
C(1)B–Fe(2)–Fe(1)	47.78 (12)
Fe(1)–C(1)B–O(1)B	137.37 (34)
Fe(2)–C(1)B–O(1)B	137.76 (35)
Fe(1)–C(2)M(1)–O(2)M(1)	178.22 (45)
Fe(2)–C(2)M(2)–O(2)M(2)	177.05 (36)
Fe(1)–P(1)–N(12)	115.94 (12)
Fe(2)–P(1)–N(13)	115.41 (12)
C(2)R(1)–C(1)R(1)–C(5)R(1)	107.56 (57)
C(1)R(1)–C(5)R(1)–C(4)R(1)	107.92 (62)
C(5)R(1)–C(4)R(1)–C(3)R(1)	107.20 (60)
C(4)R(1)–C(3)R(1)–C(2)R(1)	109.66 (58)
C(3)R(1)–C(2)R(1)–C(1)R(1)	107.64 (54)
H(1)R(1)–C(1)R(1)–C(5)R(1)	134.42 (5.36)
H(1)R(1)–C(1)R(1)–C(2)R(1)	118.02 (5.25)
H(2)R(1)–C(2)R(1)–C(1)R(1)	128.72 (2.66)
H(2)R(1)–C(2)R(1)–C(3)R(1)	123.00 (2.64)
H(3)R(1)–C(3)R(1)–C(4)R(1)	120.92 (2.16)
H(3)R(1)–C(3)R(1)–C(2)R(1)	129.30 (2.13)
H(4)R(1)–C(4)R(1)–C(5)R(1)	113.14 (3.91)
H(4)R(1)–C(4)R(1)–C(3)R(1)	139.56 (3.89)
H(5)R(1)–C(5)R(1)–C(1)R(1)	116.89 (3.89)
H(5)R(1)–C(5)R(1)–C(4)R(1)	133.84 (3.92)
C(2)R(2)–C(1)R(2)–C(5)R(2)	107.43 (48)
C(1)R(2)–C(5)R(2)–C(4)R(2)	108.29 (47)
C(5)R(2)–C(4)R(2)–C(3)R(2)	107.65 (46)
C(4)R(2)–C(3)R(2)–C(2)R(2)	108.18 (49)
C(3)R(2)–C(2)R(2)–C(1)R(2)	108.42 (47)
H(1)R(2)–C(1)R(2)–C(5)R(2)	120.60 (2.41)
H(1)R(2)–C(1)R(2)–C(2)R(2)	131.95 (2.40)
H(2)R(2)–C(2)R(2)–C(1)R(2)	123.94 (2.98)
H(2)R(2)–C(2)R(2)–C(3)R(2)	127.23 (3.01)
H(3)R(2)–C(3)R(2)–C(4)R(2)	118.61 (1.95)
H(3)R(2)–C(3)R(2)–C(2)R(2)	131.21 (1.96)
H(4)R(2)–C(4)R(2)–C(5)R(2)	127.03 (2.18)
H(4)R(2)–C(4)R(2)–C(3)R(2)	125.05 (2.18)
H(5)R(2)–C(5)R(2)–C(1)R(2)	125.48 (2.82)
H(5)R(2)–C(5)R(2)–C(4)R(2)	126.23 (2.81)
N(12)–P(1)–N(13)	110.09 (16)
N(12)–P(2)–N(23)	121.74 (17)
N(23)–P(3)–N(13)	120.34 (16)
P(1)–N(12)–P(2)	124.22 (20)
P(2)–N(23)–P(3)	117.33 (19)
P(3)–N(13)–P(1)	123.94 (19)
F(1)P(2)–P(2)–F(2)P(2)	95.69 (16)
F(1)P(3)–P(3)–F(2)P(3)	96.49 (14)
N(12)–P(2)–F(1)P(2)	110.07 (17)
N(23)–P(2)–F(2)P(2)	107.86 (17)
N(13)–P(3)–F(1)P(3)	109.74 (16)
N(23)–P(3)–F(2)P(3)	108.60 (16)

Table IV. Least-Squares Planes for $[N_3P_3F_4(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3]$ (III)

A. Equations Defining Least-Squares Planes

plane I, through P(1), P(2), P(3), N(12), N(23), N(13)
$-0.7339x - 0.1179y - 0.6689z - 7.3257 = 0$

plane II, through Fe(1), P(1), P(2)
$0.4353x + 0.4510y - 0.7792z - 0.0258 = 0$

plane III, through C(1)R(1), C(2)R(1), C(3)R(1), C(4)R(1), C(5)R(1)
$0.9552x + 0.2177y - 0.2007z - 1.3752 = 0$

plane IV, through C(1)R(2), C(2)R(2), C(3)R(2), C(4)R(2), C(5)R(2)
$-0.2975x + 0.0683y - 0.9523z - 2.9579 = 0$

B. Distances (A) of Some Atoms from Plane I

P(1)	0.009 (1)	N(13)	−0.191 (4)
N(12)	0.055 (4)	F(1)P(2)	1.054 (4)
P(2)	−0.014 (2)	F(2)P(2)	−1.202 (4)
N(23)	0.013 (5)	F(1)P(3)	1.410 (3)
P(3)	0.017 (1)	F(2)P(3)	1.266 (3)

C. Distances (A) of Some Atoms from Plane II

Fe(1)	−0.000 (1)	N(13)	−1.339 (4)
P(1)	−0.000 (1)	C(1)B	−0.440 (5)
Fe(2)	−0.000 (1)	O(1)B	−0.774 (4)
N(12)	1.336 (4)	C(2)M(1)	−1.709 (6)
P(2)	1.319 (2)	O(2)M(1)	4.166 (5)
N(23)	0.007 (4)	C(2)M(2)	−1.705 (5)
P(3)	−1.319 (1)	O(2)M(2)	−2.818 (4)

D. Angles (Deg) between Normals to Planes

I and II	81.5	II and III	47.9
I and III	53.7	II and IV	50.0
I and IV	32.1	III and IV	85.5

II was seen in the chemical ionization mass spectrum, although some conversion of II to III occurred during the mass spectral analysis. Mass peaks were observed at *m/e* 566 (parent + 1) and 594 (parent + 29) when methane was used as the ionized gas. These data are compatible with structure II.

Spectroscopic Characteristics of III. The infrared spectrum of III showed peaks that were consistent with the presence of terminal carbonyl absorbances at 2019 (s) and 1984 (m, br) cm^{-1} and with a bridging carbonyl absorbance at 1805 (br) cm^{-1} (CH_2Cl_2 solution). Absorbances for P–N bonds were observed at 1260 and 1220 cm^{-1} (KBr disks). The electron-impact mass spectrum of III was identical with that of II and showed a parent peak at *m/e* 537 (molecular weight of III is 537) with the successive loss of three carbonyl groups (*m/e* −28) at *m/e* 509, 481, and 453. The elemental microanalysis was compatible with the structure shown for III.[15] The ^1H NMR spectrum of III consisted of a singlet at 4.9 ppm (downfield from Me_4Si), attributed to the protons of the cyclopentadienyl rings. The ^{19}F NMR spectrum of III was a doublet centered at 44.7 ppm (relative to C_6H_5F), with a P–F coupling constant of 897 Hz. From the interpretation of the ^{19}F NMR spectrum, it was concluded that all four fluorine atoms are equivalent and that they occupy a similar environment to those in $(NPF_2)_3$.[16] The high-resolution ^{31}P NMR spectrum of III revealed the presence of two types of phosphorus atoms. The spectrum of III resembled that of II. The PF_2 resonance appeared at 3.3 ppm as a major triplet with $J_{PF} = 918.0$ Hz. Unresolved fine structure was also present from J_{FPNPF} and J_{PNP}. The PFe_2 resonance appeared as an unresolved triplet at 272.3 ppm. The J_{PNP} value could not be determined. The NMR results were compatible with the conclusion that III is a geminally substituted derivative. The extremely low-field ^{31}P chemical shift positions for the PFe_2

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(15) Anal. Calcd for $N_3P_3F_4[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3]$ (III): C, 29.05; H, 1.86; N, 7.82; P, 17.32; F, 14.15. Found: C, 30.03; H, 2.24; N, 7.82; P, 17.32; F, 13.52.

(16) The ^{19}F NMR spectrum of $(NPF_2)_3$ is a doublet centered at 42.0 ppm relative to monofluorobenzene. The ^{19}F-decoupled ^{31}P NMR spectrum is a singlet at 9.4 ppm relative to H_3PO_4.

Table V. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations for II

atom	x	y	z	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Fe(1)	0.24034 (7)	0.17873 (4)	0.93844 (7)	0.00994 (7)	0.00463 (3)	0.01154 (8)	0.00390 (8)	0.0085 (1)	0.00677 (7)
Fe(2)	0.18131 (7)	0.31481 (4)	0.58370 (7)	0.01035 (7)	0.00448 (3)	0.01260 (8)	0.00458 (8)	0.0113 (1)	0.00712 (7)
P(1)	0.0789 (1)	0.24556 (8)	0.7469 (1)	0.0077 (1)	0.00355 (5)	0.0105 (1)	0.0028 (1)	0.0083 (2)	0.0038 (1)
P(2)	−0.2563 (1)	0.15831 (10)	0.6062 (2)	0.0082 (1)	0.00496 (7)	0.0182 (2)	0.0021 (2)	0.0094 (3)	0.0039 (2)
P(3)	−0.1508 (1)	0.34055 (9)	0.8366 (2)	0.0119 (1)	0.00480 (6)	0.0195 (2)	0.0059 (2)	-0.0182 (2)	0.0054 (2)
F(1)P(2)	−0.3279 (3)	0.0672 (2)	0.6432 (4)	0.0173 (4)	0.0060 (2)	0.0412 (7)	0.0008 (5)	0.0327 (7)	0.0089 (6)
F(2)P(2)	−0.3771 (4)	0.1309 (3)	0.4170 (4)	0.0119 (5)	0.0116 (3)	0.0209 (6)	0.0048 (6)	−0.0030 (9)	0.0003 (7)
F(1)P(3)	−0.1932 (4)	0.4342 (2)	0.7904 (5)	0.0199 (5)	0.0057 (2)	0.0419 (8)	0.0106 (5)	0.0224 (10)	0.0126 (6)
F(2)P(3)	−0.1668 (4)	0.3698 (3)	1.0125 (4)	0.0236 (4)	0.0112 (3)	0.0251 (5)	0.0097 (6)	0.0365 (6)	0.0014 (6)
O(1)M(1)	0.4085 (6)	0.3720 (3)	1.1834 (5)	0.0254 (8)	0.0079 (3)	0.0185 (7)	−0.0030 (9)	0.0074 (13)	0.0014 (7)
O(2)M(1)	−0.0239 (4)	0.1615 (3)	1.0524 (4)	0.0201 (5)	0.0132 (3)	0.0284 (5)	0.0103 (7)	0.0333 (7)	0.0237 (6)
O(1)M(2)	0.2105 (5)	0.1271 (3)	0.3885 (5)	0.0380 (8)	0.0070 (2)	0.0180 (6)	0.0169 (7)	0.0302 (10)	0.0066 (6)
O(2)M(2)	−0.1494 (5)	0.2971 (3)	0.3540 (5)	0.0157 (6)	0.0117 (3)	0.0256 (7)	0.0080 (7)	0.0016 (12)	0.0193 (6)
N(12)	−0.0841 (4)	0.1567 (3)	0.6153 (4)	0.0089 (4)	0.0039 (2)	0.0130 (5)	0.0013 (5)	0.0082 (7)	0.0019 (5)
N(23)	−0.2958 (4)	0.2507 (3)	0.7114 (6)	0.0092 (4)	0.0051 (2)	0.0254 (7)	0.0029 (6)	0.0158 (9)	0.0026 (7)
N(13)	0.0238 (4)	0.3361 (3)	0.8618 (4)	0.0106 (4)	0.0039 (2)	0.0138 (5)	0.0026 (5)	0.0121 (7)	0.0008 (5)
C(1)M(1)	0.3411 (6)	0.2954 (4)	1.0817 (6)	0.0143 (7)	0.0061 (3)	0.0127 (7)	0.0026 (8)	0.007 (1)	0.0048 (7)
C(2)M(1)	0.0825 (6)	0.1702 (4)	1.0109 (5)	0.0159 (7)	0.0071 (3)	0.0151 (6)	0.0063 (8)	0.014 (1)	0.0114 (6)
C(1)M(2)	0.1995 (6)	0.2012 (3)	0.4701 (5)	0.0180 (7)	0.0058 (3)	0.0122 (6)	0.0073 (7)	0.016 (1)	0.0074 (6)
C(2)M(2)	−0.0192 (6)	0.3028 (4)	0.4444 (6)	0.0144 (7)	0.0060 (3)	0.0170 (7)	0.0054 (7)	0.011 (1)	0.0101 (6)
C(1)R(1)	0.2121 (7)	0.0244 (4)	0.8582 (7)	0.0219 (8)	0.0047 (3)	0.0285 (9)	0.0063 (8)	0.025 (1)	0.0111 (8)
C(2)R(1)	0.3404 (7)	0.0630 (4)	1.0209 (7)	0.0230 (9)	0.0067 (3)	0.0232 (8)	0.0131 (8)	0.017 (1)	0.0147 (7)
C(3)R(1)	0.4567 (6)	0.1271 (4)	1.0002 (8)	0.0128 (7)	0.0079 (3)	0.0240 (12)	0.0103 (8)	0.001 (2)	0.0038 (11)
C(4)R(1)	0.3969 (6)	0.1282 (4)	0.8243 (7)	0.0172 (6)	0.0074 (3)	0.0276 (8)	0.0129 (7)	0.030 (1)	0.0141 (8)
C(5)R(1)	0.2469 (6)	0.0635 (4)	0.7368 (6)	0.0185 (7)	0.0063 (3)	0.0188 (8)	0.0111 (7)	0.015 (1)	0.0092 (7)
C(1)R(2)	0.4196 (5)	0.3848 (4)	0.7584 (6)	0.0101 (6)	0.0065 (3)	0.0209 (8)	0.0013 (7)	0.011 (1)	0.0092 (7)
C(2)R(2)	0.3136 (6)	0.4385 (4)	0.8063 (6)	0.0137 (6)	0.0052 (3)	0.0203 (7)	0.0005 (7)	0.017 (1)	0.0072 (7)
C(3)R(2)	0.2285 (6)	0.4696 (4)	0.6676 (7)	0.0167 (7)	0.0058 (3)	0.0322 (10)	0.0079 (8)	0.022 (1)	0.0137 (8)
C(4)R(2)	0.2842 (7)	0.4386 (4)	0.5346 (6)	0.0217 (9)	0.0079 (3)	0.0250 (8)	0.0014 (9)	0.018 (1)	0.0183 (7)
C(5)R(2)	0.4006 (6)	0.3861 (4)	0.5885 (7)	0.0164 (6)	0.0071 (3)	0.0274 (8)	0.0032 (8)	0.029 (1)	0.0107 (8)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(1)R(1)	0.125 (5)	−0.018 (3)	0.837 (5)	3 (1)	H(1)R(2)	0.494 (6)	0.352 (3)	0.819 (6)	5
H(2)R(1)	0.285 (6)	0.143 (3)	0.962 (6)	5	H(2)R(2)	0.291 (6)	0.440 (3)	0.892 (6)	5
H(3)R(1)	0.546 (6)	0.165 (3)	1.078 (6)	5	H(3)R(2)	0.171 (6)	0.492 (3)	0.668 (6)	5
H(4)R(1)	0.443 (6)	0.155 (3)	0.765 (6)	5	H(4)R(2)	0.242 (6)	0.454 (3)	0.459 (6)	5
H(5)R(1)	0.165 (6)	0.050 (3)	0.632 (6)	5	H(5)R(2)	0.454 (6)	0.356 (3)	0.535 (6)	5

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta(1,1)h^2 + \beta(2,2)k^2 + \beta(3,3)l^2 + \beta(1,2)hk + \beta(1,3)hl + \beta(2,3)kl)]$.

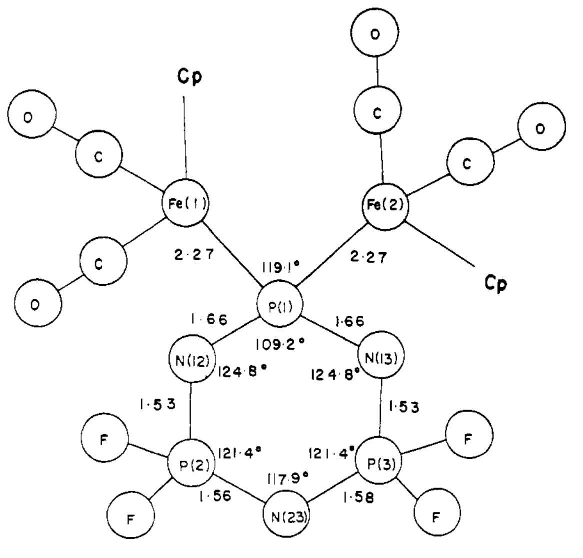

Figure 1. Representaton of the structure of II, showing specific bond angles and interatomic distances.

atoms in II and III are unusual.

General Structure of II. The X-ray crystal structure analysis of II revealed that the molecule consists of a fluorophosphazene ring in which two geminal Fe(η^5-C_5H_5)(CO)$_2$ units are attached to phosphorus via P–Fe bonds. The structural features for II are summarized in Tables I and II and in Figure 1. A stereoview is shown in Figure 2.

Coordination about the Iron Atoms in II. The two iron atoms are bound to the same phosphorus atom and are separated from each other by a distance of 3.922 Å. This suggests an absence of Fe–Fe bonding in II. The average Fe–P bond distance is 2.275 Å, and the Fe–P–Fe angle is 119.12°. The cyclopentadiene ligands are trans to each other with respect to the iron atoms. These rings are planar and are separated from the iron atoms by an average distance of 2.104 Å. The planes through the cyclopentadienyl carbon atoms are nearly perpendicular to each other with a dihedral angle of 85.9°. The dihedral angles between the planes of the cyclopentadiene rings and the phosphazene ring average to 75.2°. The average distance between an iron atom and a terminal carbonyl carbon atom is 1.742 Å. The carbonyl ligands are essentially collinear with the Fe–C bonds (average Fe–C–O angle 177.48°). The average C–O bond distance within the carbonyl ligands is 1.150 Å. The Fe–P–Fe plane and the plane of the phosphazene ring are roughly perpendicular to each other, having a dihedral angle of 85.9°.

Structure of the Phosphazene Ring in II. Three different P–N bond lengths were found in the skeletal ring of II. The two P–N bonds proximal to the two iron atoms were longer (1.666 Å) than the other P–N bonds. An alternation in longer and shorter bonds existed for the P–N bonds located at increasing distances from this phosphorus [P(1)]. Thus, P(1)–N(12) and P(1)–N(13) were 1.66 Å, P(2)–N(12) and P(3)–N(13) were 1.53 Å, and P(2)–N(23) and P(3)–N(23) were 1.56 and 1.58 Å, respectively. This pattern of variation in P–N bond lengths found in compound II has been observed in other cyclophosphazenes.[17-19] It has been attributed to the

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(17) Marsh, W. C.; Ranganathan, T. N.; Trotter, J.; Paddock, N. L. *J. Chem. Soc., Chem. Commun.* **1970**, 815.

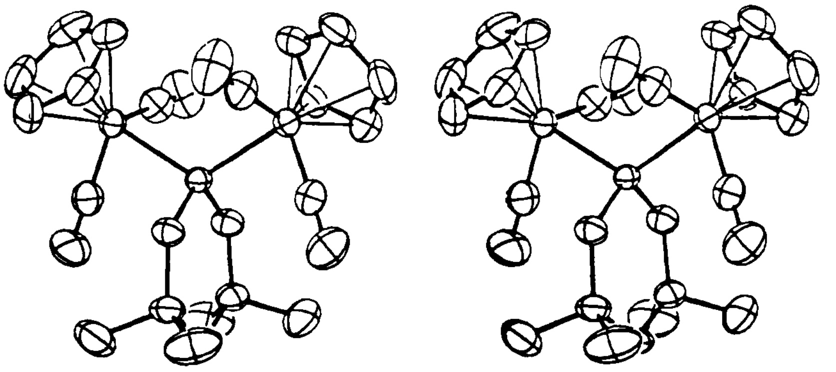

Figure 2. Stereoview showing the structure of II.

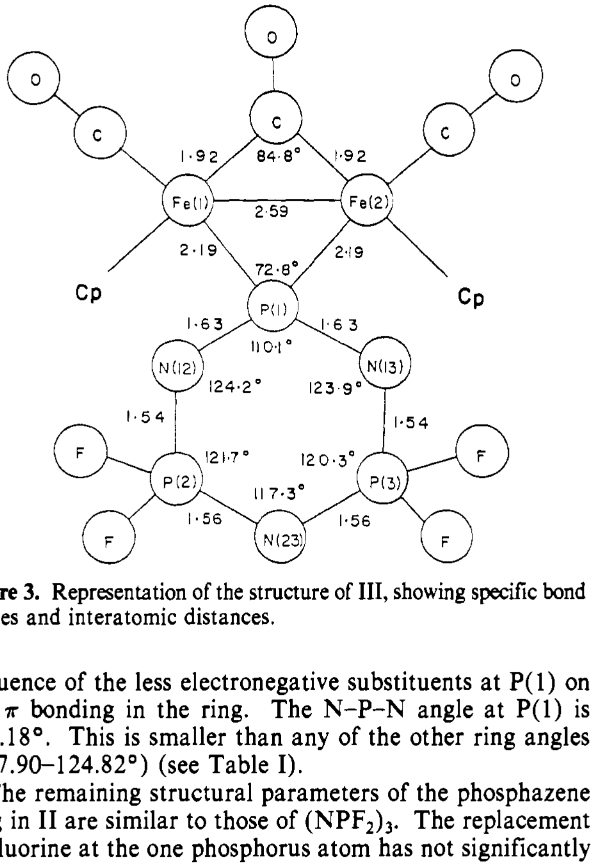

Figure 3. Representation of the structure of III, showing specific bond angles and interatomic distances.

influence of the less electronegative substituents at P(1) on the π bonding in the ring. The N–P–N angle at P(1) is 109.18°. This is smaller than any of the other ring angles (117.90–124.82°) (see Table I).

The remaining structural parameters of the phosphazene ring in II are similar to those of $(NPF_2)_3$. The replacement of fluorine at the one phosphorus atom has not significantly affected the structure of the remainder of the ring: the influence of the organometallic substituent is limited to the immediate environment of the phosphorus–iron bonds.

General Structure of III. The X- crystal structure analysis of III confirmed that III is a decarbonylation product from II. The presence of a bridging carbonyl group and an iron–iron bond were key features detected in III.

Coordination about the Iron Atoms in III. The Fe–Fe bond distance is 2.593 Å, similar to those observed in other systems that contain Fe–Fe bonds.[20-22] The two iron atoms are bound to the same phosphorus atom, with an average Fe–P distance of 2.186 Å. This bond length is very similar to those found in phosphido-bridged metal complexes:[21] for example, the Fe–P distance in $Fe_2(CO)_6[\mu\text{-}P(CF_3)_2]_2$ is 2.193 Å. The Fe–P–Fe angle in III is 72.77° and is similar to the Fe–P–Fe angle found in phosphido–metal complexes. This angle is very narrow and represents the smallest substituent–phosphorus–substituent angle found in any known phosphazene compound. This small angle is undoubtedly a direct result of the strength of the Fe–Fe bond.

The two cyclopentadiene ligands in III were cis to each other with respect to the metal–metal bond. However, we cannot rule out the possibility that trans III is also formed during the transformation from II but was not isolated by the separation techniques employed. The rings in III are planar and are separated from the iron atoms by an average distance of 2.086 Å. The planes through the cyclopentadienyl carbon atoms are nearly perpendicular to each other with a dihedral angle of 85.5°. The average distance from an iron atom to a carbonyl carbon atom is 1.750 Å, and the distance between the iron atoms and the bridging carbonyl carbon atom is 1.922 Å. The terminal metal–carbonyl structures are essentially linear (Fe–C–O angles 178.22 and 177.05°). The C–O distance of the bridging carbonyl (1.167 Å) is slightly longer than the average C–O distance of the terminal carbonyl ligands (1.134 Å). The Fe–C–Fe angle at the bridging carbonyl is 84.82°, a value similar to those observed in other iron carbonyl complexes.[21,22]

Structure of the Phosphazene Ring in III. The structural parameters of the phosphazene ring in III are very similar to those reported for II. Values for the appropriate bond distances and angles are given in Table III. It is perhaps surprising that the N–P(Fe_2)–N angles are similar in II and III (109.2 and 110.1°, respectively), while the Fe–P–Fe angles are so different (119.1° for II, 72.8° for III).

Conclusions. A number of transition-metal-containing phosphazene compounds have been reported previously.[2-7,23-26] These fall into three categories: (a) these compounds in which the metal is bound to the phosphazene by σ coordination with skeletal nitrogen[2-5,23,24] atoms, (b) species that may involve an attachment of the transition atom through the π electrons of the phosphazene skeleton[5,6,23,24] (the evidence for this mode of coordination is still tentative), and (c) compounds in which the transition atom is coordinated to a side-group structure.[7,25]

Compounds II and III are the first examples[14,26] of a fourth mode of attachment—direct covalent σ-bond linkage between

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(18) Marsh, W. C.; Trotter, J. *J. Chem. Soc. A* **1971**, 573.
(19) Marsh, W. C.; Trotter, J. *J. Chem. Soc. A* **1971**, 569.
(20) Mills, O. S. *Acta Crystallogr.* **1958**, *11*, 620.
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(26) A. Schmidpeter, K. Blanck, H. Hess, and H. Riffel (private communication to H.R.A.) have recently obtained evidence for the existence of a complex between platinum or palladium and the "tricoordinate" *phosphorus* atom of a cyclotriphosphazadiene. Presumably in this structure, the lone-pair electrons of the tricoordinate phosphorus function as a donor for the transition metal, and this structure also can be viewed as a phosphorus–metal covalent bond.

Table VI. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations for III

atom	x	y	z	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Fe(1)	0.96008 (8)	0.20969 (5)	0.7337 (1)	0.01061 (9)	0.00395 (4)	0.0150 (1)	0.0017 (1)	0.0118 (2)	−0.0014 (1)
Fe(2)	0.65226 (8)	0.18685 (5)	0.5385 (1)	0.01100 (9)	0.00299 (3)	0.0149 (1)	−0.0006 (1)	0.0121 (2)	−0.0007 (1)
P(1)	0.7819 (1)	0.30941 (9)	0.7196 (2)	0.0125 (2)	0.00269 (6)	0.0157 (2)	0.0000 (2)	0.0163 (3)	−0.0011 (2)
P(2)	0.7620 (2)	0.50504 (10)	0.6901 (2)	0.0139 (2)	0.00279 (7)	0.0230 (3)	−0.0009 (2)	0.0163 (4)	0.0008 (2)
P(3)	0.6798 (2)	0.42029 (10)	0.9477 (2)	0.0128 (2)	0.00328 (7)	0.0189 (3)	−0.0003 (2)	0.0172 (3)	−0.0037 (2)
F(1)P(3)	0.7503 (4)	0.4403 (2)	0.1606 (4)	0.0224 (5)	0.0053 (2)	0.0199 (6)	0.0005 (5)	0.0213 (8)	−0.0065 (6)
F(2)P(3)	0.5048 (3)	0.4063 (2)	0.9216 (5)	0.0128 (4)	0.0060 (2)	0.0341 (7)	0.0003 (5)	0.0266 (7)	−0.0025 (6)
F(1)P(2)	0.6531 (4)	0.5596 (2)	0.5224 (5)	0.0240 (6)	0.0050 (2)	0.0285 (8)	0.0069 (6)	0.0195 (11)	0.0096 (6)
F(2)P(2)	0.9093 (4)	0.5730 (2)	0.7419 (5)	0.0199 (5)	0.0043 (2)	0.0401 (9)	−0.0080 (5)	0.0281 (10)	−0.0022 (7)
O(1B)	0.8318 (5)	0.0192 (3)	0.6050 (6)	0.0215 (6)	0.0030 (2)	0.0373 (10)	0.0037 (6)	0.026 (1)	−0.0006 (8)
O(2)M(1)	0.9814 (6)	0.1524 (4)	0.0982 (6)	0.0377 (10)	0.0124 (4)	0.0197 (9)	0.0144 (11)	0.027 (1)	0.0124 (10)
O(2)M(2)	0.5472 (5)	0.1185 (3)	0.8231 (5)	0.0232 (6)	0.0067 (3)	0.0258 (8)	−0.0046 (7)	0.031 (1)	0.0019 (8)
N(12)	0.7929 (5)	0.4093 (3)	0.6216 (6)	0.0168 (6)	0.0033 (2)	0.0186 (8)	−0.0004 (6)	0.0209 (10)	0.0007 (7)
N(23)	0.6994 (5)	0.5132 (3)	0.8499 (6)	0.0170 (6)	0.0031 (2)	0.0247 (9)	0.0022 (6)	0.0228 (11)	−0.0012 (8)
N(13)	0.7422 (5)	0.3275 (3)	0.9049 (5)	0.0144 (6)	0.0033 (2)	0.0181 (8)	0.0013 (6)	0.0198 (9)	0.0006 (7)
C(1B)	0.8195 (6)	0.0998 (4)	0.6207 (7)	0.0146 (7)	0.0040 (3)	0.019 (1)	0.0012 (8)	0.018 (1)	−0.0014 (9)
C(2)M(1)	0.9708 (7)	0.1754 (5)	0.9551 (8)	0.0169 (9)	0.0068 (4)	0.021 (1)	0.0057 (10)	0.016 (2)	0.0011 (12)
C(2)M(2)	0.5906 (6)	0.1475 (4)	0.7137 (7)	0.0139 (7)	0.0033 (3)	0.021 (1)	−0.0016 (8)	0.017 (1)	−0.0016 (9)
C(1)R(1)	0.1226 (7)	0.3137 (5)	0.7170 (10)	0.0177 (8)	0.0072 (4)	0.051 (2)	−0.0092 (10)	0.042 (2)	−0.0142 (14)
C(2)R(1)	0.0438 (7)	0.2713 (5)	0.5422 (8)	0.0164 (8)	0.0078 (4)	0.025 (1)	−0.0027 (10)	0.023 (1)	0.0078 (12)
C(3)R(1)	0.0783 (7)	0.1791 (5)	0.5571 (8)	0.0223 (8)	0.0066 (4)	0.037 (1)	−0.0036 (10)	0.044 (1)	−0.0089 (12)
C(4)R(1)	0.1726 (7)	0.1622 (6)	0.7342 (11)	0.0193 (9)	0.0107 (5)	0.058 (2)	0.0164 (11)	0.043 (2)	0.0198 (18)
C(5)R(1)	0.2022 (8)	0.2471 (7)	0.8370 (10)	0.0121 (10)	0.0190 (9)	0.021 (2)	−0.0032 (16)	0.005 (2)	−0.0028 (20)
C(1)R(2)	0.5731 (8)	0.1248 (4)	0.2656 (8)	0.0283 (13)	0.0056 (4)	0.016 (1)	0.0063 (11)	0.011 (2)	−0.0040 (11)
C(2)R(2)	0.4494 (8)	0.1261 (5)	0.3257 (9)	0.0200 (11)	0.0071 (4)	0.022 (2)	−0.0111 (11)	−0.000 (2)	0.0016 (14)
C(3)R(2)	0.4244 (7)	0.2190 (5)	0.3554 (9)	0.0146 (9)	0.0084 (5)	0.022 (1)	0.0003 (11)	0.009 (2)	0.0024 (14)
C(4)R(2)	0.5329 (7)	0.2758 (4)	0.3155 (8)	0.0198 (11)	0.0048 (3)	0.016 (1)	0.0021 (10)	0.003 (2)	0.0005 (11)
C(5)R(2)	0.6264 (7)	0.2174 (5)	0.2619 (7)	0.0167 (9)	0.0079 (4)	0.012 (1)	−0.0011 (11)	0.008 (2)	0.0035 (12)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(1)R(1)	0.116 (5)	0.358 (3)	0.726 (6)	4.0000	H(1)R(2)	0.623 (5)	0.074 (3)	0.232 (6)	4.0000
H(2)R(1)	−0.010 (5)	0.298 (3)	0.429 (6)	4.0000	H(2)R(2)	0.394 (5)	0.079 (3)	0.329 (6)	4.0000
H(3)R(1)	0.034 (5)	0.122 (3)	0.449 (6)	4.0000	H(3)R(2)	0.339 (5)	0.253 (3)	0.405 (6)	4.0000
H(4)R(1)	0.211 (5)	0.120 (3)	0.796 (6)	4.0000	H(4)R(2)	0.548 (5)	0.347 (3)	0.335 (6)	4.0000
H(5)R(1)	0.236 (5)	0.260 (3)	−0.062 (6)	4.0000	H(5)R(2)	0.704 (5)	0.235 (3)	0.233 (6)	4.0000

[a] The form of the anisotropic thermal parameters is $\exp[-(\beta(1,1)h^2 + \beta(2,2)k^2 + \beta(3,3)l^2 + \beta(1,2)hk + \beta(1,3)hl + \beta(2,3)kl)]$.

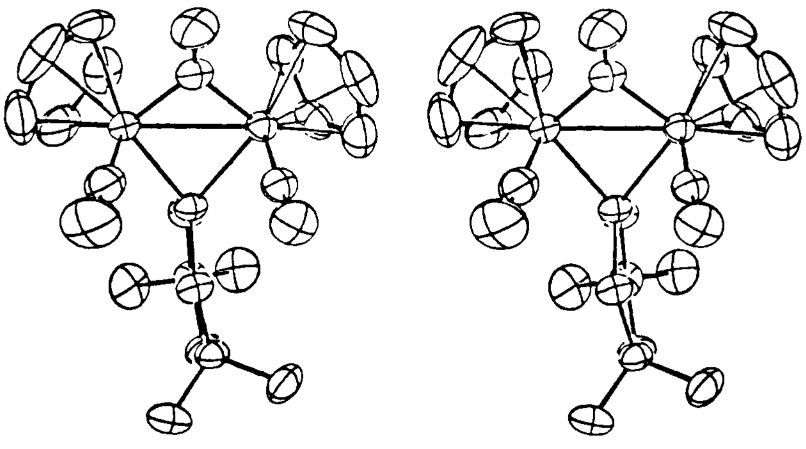

Figure 4. Stereoview showing the structure of III.

a transition metal and a skeletal phosphorus atom of the phosphazene. These compounds are of interest for a number of additional reasons. Compound III is the first example of a phosphazene that contains a three-membered side-group ring system at phosphorus. More important, compounds II and III allow structural comparisons to be made with other species that contain phosphorus–metal and metal–metal bonds in a manner that may provide much needed information about the electronic structure of phosphazene rings and chains. Moreover, the prospect exists that high polymeric species analogous to II or III may show unusual electrical properties. The broader implications of the existence of metals as side-group structures in phosphazenes should become clearer as other transition-metal analogues are studied. We are currently exploring the scope of this field.

Acknowledgment. We thank the U.S. Army Research Office for the support of this work. We also thank Dr. P. J. Harris for the NMR data and advice on the synthetic techniques and W. T. Ferrar for assistance with the synthetic and separation procedures.

Registry No. I, 15599-91-4; II, 75896-11-6; III, 70538-16-8; Na[Fe(CO)$_2$Cp], 12152-20-4.

Supplementary Material Available: Listings of the observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.