

attributed the antiferroelectric character of phase II to a sinusoidal modulation of the electric moments of the NO_2^- ions along the a axis of the crystal. Hoshino and Motegi²⁴ deduced from X-ray diffraction data that the period of the sinusoidal modulation along the a axis drops from $\sim 10a_0$ to $\sim 8a_0$ in the narrow region of existence of phase II of NaNO_2 .

It is clear that the CHCl_3 solvates **1** and **2** each undergo two phase transitions within a narrow temperature range. For each complex there is a phase which exists in a narrow temperature region. The orientations of CHCl_3 molecules along each stack could come into play in characterizing this phase. In the low-temperature phase, the C-H vectors of the CHCl_3 molecules could

each be pointed in the same direction. In the high-temperature phase, the C-H vectors are reorienting rapidly. In the intermediate-temperature phase, which exists in a narrow temperature range, there could be a sinusoidal modulation of the orientation of C-H vectors.

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Supplementary Material Available: A table of molar heat capacities for compound **2** (3 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Massachusetts, Amherst, Massachusetts 01003

Reinvestigation of the Reaction of Triphenylphosphine with Tetracyanoethylene. Molecular Structure of *N*-(Heptacyanocyclopent-1-enyl)triphenylphosphoranimine

T. Mohan, Roberta O. Day, and Robert R. Holmes*

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The reaction of triphenylphosphine with tetracyanoethylene was reported to give the compound with the formula $\text{C}_{30}\text{H}_{15}\text{N}_8\text{P}$ on the basis of elemental analysis. The reaction was repeated and the composition confirmed by X-ray crystallography. However, the proposed phosphole ring structure containing pentacoordinated phosphorus was shown to be erroneous. Conclusive proof is provided from X-ray analysis that the product is a phosphoranimine containing the $\text{Ph}_3\text{P}=\text{N}$ unit.

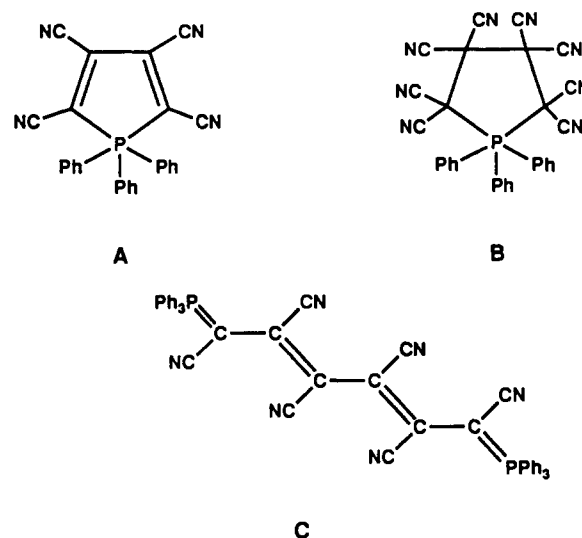
Introduction

Very little is known about the conformational requirements of five-membered rings in pentacoordinated phosphorus-carbon heterocycles compared to that known for the corresponding cyclic oxyphosphoranes.¹⁻³ This may be due to the unavailability of general feasible synthetic routes for such compounds, but more likely it is due to the decreased stability of these compounds brought about by a buildup of charge at phosphorus caused by the attachment of carbon ligands of reduced electronegativity.

Earlier, Reddy and Weiss⁴ had reported that the reaction of triphenylphosphine with dicyanoacetylene and tetracyanoethylene produced phosphoranes containing phosphole rings, formulated as A and B, respectively. Tebby et al.⁵ reinvestigated the former reaction and, on the basis of their data, concluded that the product formed was not a phosphole as represented by A but rather the acyclic derivative C, an alkene-1,6-diylidenediphosphorane. Their study⁵ suggested that the reaction leading to the product formulated as B⁴ also was suspect and prompted us to reinvestigate the reaction of Ph_3P with tetracyanoethylene. The results are the focus of this paper.

Experimental Section

All experiments were carried out in an atmosphere of dry nitrogen. Tetracyanoethylene and triphenylphosphine (Fluka) were used as such. Acetonitrile and methylene chloride were distilled by conventional methods before use.⁶



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An infrared spectrum was recorded on a Perkin-Elmer 783 spectrophotometer as a Nujol mull using NaCl windows. The $^{31}\text{P}(^1\text{H})$ NMR spectrum was recorded on a Varian XL-300 (121.5-MHz) spectrometer as a CDCl_3 solution using 85% H_3PO_4 as the external standard. Chemical shift values (δ in ppm) were assigned negative values when the signals were upfield relative to H_3PO_4 . The melting point was uncorrected.

Crystallography. The X-ray crystallographic study was done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(\text{K}\alpha_1) = 0.70930 \text{ \AA}$, $\lambda(\text{K}\alpha_2) = 0.71359 \text{ \AA}$) at an ambient temperature of $23 \pm 2 \text{ }^\circ\text{C}$. Details of the experimental and computational procedures have been described previously.⁷

Synthesis of *N*-(Heptacyanocyclopent-1-enyl)triphenylphosphoranimine, $\text{Ph}_3\text{PNC}_5(\text{CN})_7$ (1**).** To a stirred suspension of tetracyanoethylene (1.95 g, 15.3 mmol) in CH_3CN (20 mL) at $0 \text{ }^\circ\text{C}$ (ice bath) was added in ca. 1 h triphenylphosphine (2.0 g, 7.6 mmol) dissolved in CH_3CN (30

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Table I. Crystallographic Data for $\text{Ph}_3\text{PNC}_5(\text{CN})_7$ (**1**)^a

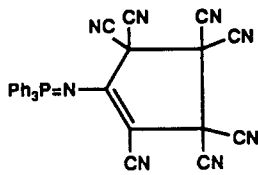
formula: $\text{C}_{30}\text{H}_{15}\text{N}_8\text{P}$	fw = 518.482
$a = 14.587$ (6) Å	space group: $P2_1/c$ (No. 14)
$b = 14.117$ (3) Å	$T = 23$ (2) °C
$c = 12.843$ (2) Å	$\lambda = 0.71073$ Å
$\beta = 99.74$ (2)°	$D_{\text{calc}} = 1.321$ g cm ⁻³
$V = 2607$ (2) Å ³	$\mu = 1.352$ cm ⁻¹
$Z = 4$	$R(F)^b = 0.035$
	$R_w(F)^b = 0.046$

^a4581 independent reflections measured (θ - 2θ scan mode; $2\theta_{\text{max}} = 50^\circ$; $+h, +k, \pm l$). Full-matrix least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_o/Lp/\sigma_F$, based on 3039 observed ($I \geq 3\sigma_I$) reflections. ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}$.

mL). The colorless reaction mixture slowly developed a pale buff color with more tetracyanoethylene going into solution. The reaction mixture was allowed to warm up to room temperature (ca. 25 °C) and stirred for an additional 12 h. The reaction was then stopped and filtered. The pale buff-colored precipitate was washed well with CH_3CN (4×1 mL) (2.32 g, 58.7%), crystallized using CH_2Cl_2 and CH_3CN mixtures (1:2, 15 mL), and identified as the colorless title compound: mp 165–166 °C (lit. 168.5–170 °C⁴). IR (4000–600 cm⁻¹): 3086 (w), 2262 (w), 2250 (w), 2204 (s), 1658 (w, sh), 1629 (s, sh), 1619 (s, sh), 1601 (vs), 1590 (vs), 1575 (vs), 1560 (vs, sh), 1553 (s, sh), 1548 (vs, sh), 1540 (s, sh), 1535 (m, sh), 1487 (s), 1462 (vs), 1445 (vs), 1440 (vs), 1390 (vs), 1370 (s, sh), 1360 (s), 1340 (m), 1315 (m), 1312 (m), 1191 (m), 1185 (m), 1165 (m), 1130 (m, sh), 1121 (vs), 1111 (vs), 1095 (m, sh), 1062 (s), 1017 (m), 1000 (s), 910 (vs), 829 (m), 815 (s), 791 (s), 762 (vs), 735 (vs, sh), 730 (vs), 695 (vs), 680 (s). ³¹P NMR (δ): 22.60.

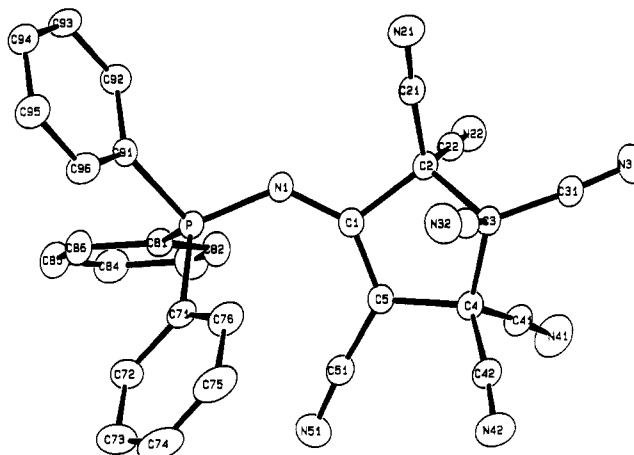
Results and Discussion

The reaction of triphenylphosphine with tetracyanoethylene produced a colorless compound whose melting point and ³¹P NMR chemical shift are similar to those reported by Reddy and Weiss.⁴ They had claimed that the compound was a phosphorane, formulated as **B**, containing a five-membered phosphorous-carbon ring skeleton on the basis of the ³¹P NMR chemical shift value of 22 ppm. Although a phosphorane having a ³¹P chemical shift value of 29.6 ppm has been reported for $(\text{CF}_2)_4\text{PF}_3$,⁸ in the present case the substituents on phosphorus are not sufficiently electronegative to cause such a pronounced downfield shift. Moreover, the chemical shift value of 22 ppm lies in the tetracoordinate region for phosphorus compounds, cf. Ph_3PO ,⁹ $[\text{Ph}_3\text{PNH}_2]\text{Cl}$,¹⁰ and $\text{Ph}_3\text{PN-S}_3\text{N}_3$.¹¹ On the basis of this chemical shift value, Weiss and Reddy⁴ discarded the possibility of the phosphoranimine structure which they themselves had proposed as a possibility. However, the X-ray structure of **1** reported here (Table I) provides conclusive evidence that the compound is the phosphoranimine.



1

X-ray Structure. The molecular geometry is shown in Figure 1. Tables II and III list selected atomic coordinates and selected bond lengths and angles, respectively, for **1**. It is evident that the compound is a phosphazene rather than a phosphorane. The P–N bond length of 1.618 (2) Å is in the range found for related phosphazenes and indicates double-bond character. Although over 600 phosphazenes are known,¹² comparison is made here only with

**Figure 1.** ORTEP plot of $\text{Ph}_3\text{PNC}_5(\text{CN})_7$ (**1**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.**Table II.** Selected Atomic Coordinates in Crystalline $\text{Ph}_3\text{PNC}_5(\text{CN})_7$ (**1**)^a

atom ^b	x	y	z	B_{equiv} , Å ²
P	0.22660 (4)	0.40135 (4)	0.84730 (4)	2.65 (1)
N1	0.3133 (1)	0.4739 (1)	0.8543 (1)	2.87 (3)
C1	0.3173 (1)	0.5597 (1)	0.8157 (2)	2.60 (4)
C2	0.4158 (1)	0.6056 (1)	0.8324 (2)	2.65 (4)
C3	0.4080 (1)	0.6737 (1)	0.7335 (2)	2.68 (4)
C4	0.3043 (1)	0.7104 (1)	0.7233 (2)	2.81 (4)
C5	0.2568 (1)	0.6258 (1)	0.7653 (2)	2.77 (4)
C51	0.1580 (2)	0.6272 (1)	0.7515 (2)	3.24 (4)
C71	0.1495 (2)	0.4032 (1)	0.7225 (2)	3.21 (4)
C81	0.1652 (1)	0.4232 (1)	0.9543 (2)	2.86 (4)
C91	0.2726 (1)	0.2836 (1)	0.8626 (2)	2.76 (4)

^aNumbers in parentheses are estimated standard deviations. ^bAtoms are labeled to agree with Figure 1. ^cEquivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Table III. Selected Distances (Å) and Angles (deg) for $\text{Ph}_3\text{PNC}_5(\text{CN})_7$ (**1**)^a

Distances			
P–N1	1.618 (2)	C2–C3	1.581 (3)
N1–C1	1.314 (3)	C3–C4	1.583 (3)
C1–C2	1.557 (3)	C4–C5	1.524 (3)
C1–C5	1.370 (3)	P–C71	1.795 (2)
P–C81	1.789 (2)	P–C91	1.791 (2)
Angles			
P–N1–C1	130.2 (1)	C1–C2–C3	101.7 (1)
N1–C1–C2	115.5 (2)	C2–C3–C4	101.7 (2)
N1–C1–C5	137.8 (2)	C3–C4–C5	101.6 (1)
C2–C1–C5	106.7 (2)	C1–C5–C4	113.9 (2)
C1–C5–C51	128.8 (2)	C4–C5–C51	117.2 (2)
N1–P–C71	113.98 (9)	C71–P–C81	111.3 (1)
N1–P–C81	109.64 (9)	C71–P–C91	106.16 (9)
N1–P–C91	107.81 (9)	C81–P–C91	107.6 (1)

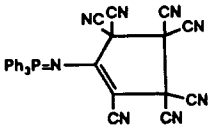
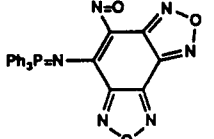
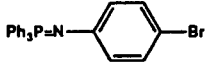
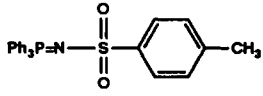
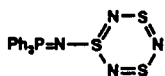
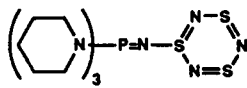
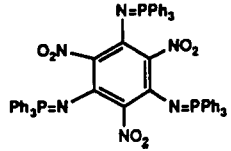
^aEstimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 1.

the acyclic monophosphazenes ($\text{R}_3\text{P}=\text{NR}'$). X-ray structural data on seven representative members of this class^{13–19} are listed in Table IV along with P=N bond lengths. A comparison of the phosphorus–nitrogen bond lengths of **1** (1.618 Å) reveals a range from 1.56 to 1.65 Å, thus placing the present value near the average

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Table IV. Comparison of P=N Bond Lengths (Å) in Acyclic Monophosphazenes

compd no.	compd	d(P=N)	ref
1		1.618 (2)	this work
2		1.630 (5)	13
3		1.567 (6)	14
4		1.579 (4)	15
5	Ph ₂ (F)P=N-CH ₃	1.641 (2)	16
6		1.645 (10)	17
7		1.595 (3)	18
8		1.558 (9)	19

value, close to that for a phosphorus–nitrogen double bond, 1.62 Å.²⁰

Although the bond between C1 and C5 is formally a double bond while the bond between C1 and N1 is formally a single bond, the relatively long length of the former (1.370 (3) Å compared to a tabulated C=C value of 1.33 Å²⁰) and short length of the latter (1.314 (3) Å compared to the tabulated C–N value of 1.51 Å²⁰) are consistent with a delocalized conjugated π system ex-

tending over the P–N1–C1–C5 network. The near coplanarity of atoms P, N1, C1, C2, and C5 (±0.030 (2) Å) is also consistent with this view.

The envelope conformation of the five-membered ring reflects the formal sp² hybridization at atoms C1 and C5. Atoms C1, C2, C4, and C5 are coplanar to within ±0.061 (2) Å, while the flap atom, C3, is displaced from this plane by a distance of 0.588 (2) Å.

The angle at N1 of 130.2 (1)° is larger than the expected 120°, as are the angles at C1 (N1–C1–C5 = 137.8 (2)°) and C5 (C1–C5–C51 = 128.8 (2)°). These enlarged angles most probably reflect a mitigation of the crowding between the cyano group bound to C5 and the phenyl group composed of atoms C71–C76. The largest of the “tetrahedral” angles at phosphorus (N1–P–C71 = 114.0 (1)°) also supports this view. Even in the presence of the above distortions there is a short contact (C51–C71 = 3.183 (3) Å). It is interesting to note that although there is an enlarged angle at both C1 and C5, the sum of the angles about both of these atoms is 360° within the limits of the error.

Infrared Data. The infrared spectrum shows a strong band at 1120 cm⁻¹, characteristic of the vibration due to the Ph–P stretch in a tetracoordinate geometry.¹⁰ In accord with the P=N bond being in conjugation with the electron-withdrawing C≡N groups, the P–N stretching frequency appears at 1390 cm⁻¹ as a very strong band, similar to that in Ph₃P=N–C₆H₄NO₂ (p).²¹ A strong band appearing at 2204 cm⁻¹ (C–N stretch) may be attributed to the cyano group which is in conjugation with the P=N²² system. In fact, this frequency is lowered compared to that in tetracyanoethylene (2260 and 2220 cm⁻¹).

Conclusion. The reinvestigation of the reaction of triphenylphosphine with tetracyanoethylene provided conclusive proof that the product is the phosphoranimine **1** and not the pentacoordinated phosphorane **B**. The novelty of forming the Ph₃P=N unit indicates its high stability relative to phosphole ring formation and suggests that additional interesting derivatives may be prepared from substituted cyanoolefins and cyanoacetylenes.

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE 88-19152) and the Army Research Office is gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, additional bond lengths and angles, and hydrogen atom parameters for **1** (Tables S1–S4, respectively) (8 pages); a listing of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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