Dicobalt–Hexacarbonyl Complexes of Acetylenic Phosphazenes[1]

Harry R. Allcock,* Robin A. Nissan, Paul J. Harris, and Robert R. Whittle

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received August 9, 1983

π-Complexes have been prepared between propynylcyclophosphazenes **4** and **6** and dicobalt hexacarbonyl. These complexes are models for phosphazene high polymers that bear pendent metalloacetylenic side units. The complexes **8** and **9** are catalysts for the cyclotrimerization of phenylacetylene or diphenylacetylene, for the cotrimerization of acetylenic cyclophosphazenes with phenylacetylene or diphenylacetylene, and for the self-trimerization of **4** or **6** to 1,2,4-tri(cyclophosphazenyl)benzenoid derivatives. Complexes of types **8** and **9** were studied by mass spectrometric, infrared, ^{1}H, ^{13}C, and ^{31}P NMR techniques and by X-ray diffraction methods. The spectroscopic data revealed the existence of strong electronic interactions between the acetylenic dicobalt carbonyl side unit and the phosphazene ring when the organometallic unit was linked to a 1,2-ynyl function (**9**) but not when the organometallic component was insulated from the ring by a methylene spacer group (**8**). The X-ray diffraction results showed that, for three typical complexes (**17**, **18**, and **19**), the organometallic unit induced distortions in the cyclophosphazene ring, the effect being greater when the metalloacetylenic unit was closest to the skeleton. Both steric and electronic influences appear to be responsible for these phenomena. Crystal structure data: $N_3P_3Cl_4(CH_3)[C_3H_3{\cdot}Co_2(CO)_6]$ (2-yne) (**17**), $a = 17.238$ (2) Å, $b = 7.470$ (7) Å, $c = 17.853$ (4) Å, $\beta = 99.92$ (1)°, $V = 2264$ (3) Å^3, $P2_1/c$ (No. 14, C^5_{2h}), $Z = 4$; $N_3P_3Cl_4(C_3H_5)[C_3H_3{\cdot}Co_2(CO)_6$ (2-yne) (**18**), $a = 8.038$ (3) Å, $b = 22.080$ (4) Å, $c = 13.064$ (3) Å, $\beta = 91.51$ (3)°, $V = 2418$ (2) Å^3, $P2_1/n$ (No. 14, C^5_{2h}), $Z = 4$; $N_3P_3Cl_4(CH_3)[(CH_3{\cdot}Co_2(CO)_6]$ (1-yne) (**19**), $a = 8.592$ (2) Å, $b = 14.58$ (1) Å, $c = 17.787$ (4) Å, $V = 2228$ (3) Å^3, $Pnma$ (No. 62, D^{16}_{2h}), $Z = 4$.

The synthesis of macromolecules that function as carriers for transition metals is a subject of widespread interest. Such complexes may function as macromolecular catalysts or electroactive materials.

In earlier papers we have described a synthesis technique in which new polymers are constructed by side group substitution reactions carried out on the reactive, linear macromolecular substrates, poly(dichlorophosphazene), $(NPCl_2)_n$, or its fluoro analogue, $(NPF_2)_n$.[2-4] For example, pendent phosphine or *nido*-carboranyl side groups have been linked to a polyphosphazene chain and have been used as binding sites for transition metals.[5,6]

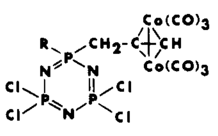
Our present objective is to explore routes that may allow the attachment of unsaturated alkyl groups to a high polymeric phosphazene chain and to use these unsaturated units for π-coordination to transition-metal units. A necessary step in the development of such synthetic routes is to examine prototype systems at the small molecule level,[7] since small molecules can be characterized with much greater ease than can macromolecules.

To this end we have examined the synthesis, reactions, and structure of a series of complexes formed between small molecule propynylcyclophosphazenes and dicobalt–carbonyl units. This system was chosen for the following reasons. Complexes formed by the reactions of alkynes with cobalt carbonyls have been investigated in detail.[8-15] Such species are catalysts for the trimerization of alkynes,[9] for carbonyl insertion reactions,[8] and for the reduction of acetylenes by pentaborane.[16] Moreover, dicobalt–hexacarbonyl units have been used as protecting groups for acetylenic structures.[12]

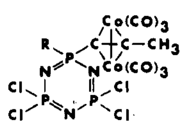
We have recently prepared two series of acetylenic cyclophosphazene trimers by the pathways shown in Scheme I.[17,18] The possibility existed that pendent acetylenic units in species such as **4** or **6** might function as π-donors for transition-metal units such as dicobalt–hexacarbonyl residues. Such complexes would be of value both as prototypes for the macromolecular polyphosphazene analogues and as possible initiators for the cyclooligomerization or polymerization of **4** or **6** through the acetylenic units to yield substituted benzenoid or polyacetylene derivatives with pendent cyclophosphazene units.

From a fundamental point of view it was also of interest, first, to establish whether the phosphazene skeleton or the propynyl groups would be the site for coordination of the metal and, second, to examine the influence of the organometallic unit on the bonding within the phosphazene skeleton. Such information is important for an extension of these principles to high polymeric analogues.

Specifically, in this paper we describe the synthesis, chemistry, and structure of a range of complexes derived from the reactions of dicobalt octacarbonyl with **4** and **6**, in which the side group R, geminal to the acetylenic unit, is CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, t-C_4H_9, and C_3H_5 (allyl). These compounds are different members of the two general structures shown in **8** and **9**.



8



9

---

(1) For a previous paper in this series see: Allcock, H. R.; Wagner, L. J.; Levin, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 1321.

(2) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.

(3) Evans, T. L.; Allcock, H. R. *J. Macromol. Sci., Chem.* **1981**, *A16*, 409.

(4) Allcock, H. R. *Makromol. Chem. Suppl.* **1981**, *4*, 3.

(5) Allcock, H. R.; Lavin, K. D.; Tollefson, N. M.; Evans, T. L. *Organometallics* **1983**, *2*, 267.

(6) Allcock, H. R.; Scopelianos, A. G.; Whittle, R. R.; Tollefson, N. M. *J. Am. Chem. Soc.* **1983**, *105*, 1316.

(7) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.

(8) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323.

(9) Hoogzand, C.; Hubel, W. "Organic Synthesis via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1968; Vol. 1, p 343.

(10) Greenfield, H.; Sternberg, H. W.; Friedel, R. A.; Wotiz, J. H.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1956**, *78*, 120.

(11) Hubel, W.; Hoogzand, C. *Chem. Ber.* **1960**, *93*, 103.

(12) Chalk, A. J.; Harrod, J. F. *Adv. Organomet. Chem.* **1968**, *6*, 119.

(13) Hillard, R. L.; Volhardt, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 4058.

(14) King, R. B.; Harmon, C. A. *Inorg. Chem.* **1976**, *15*, 879.

(15) Funk, R. L.; Volhardt, P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5245.

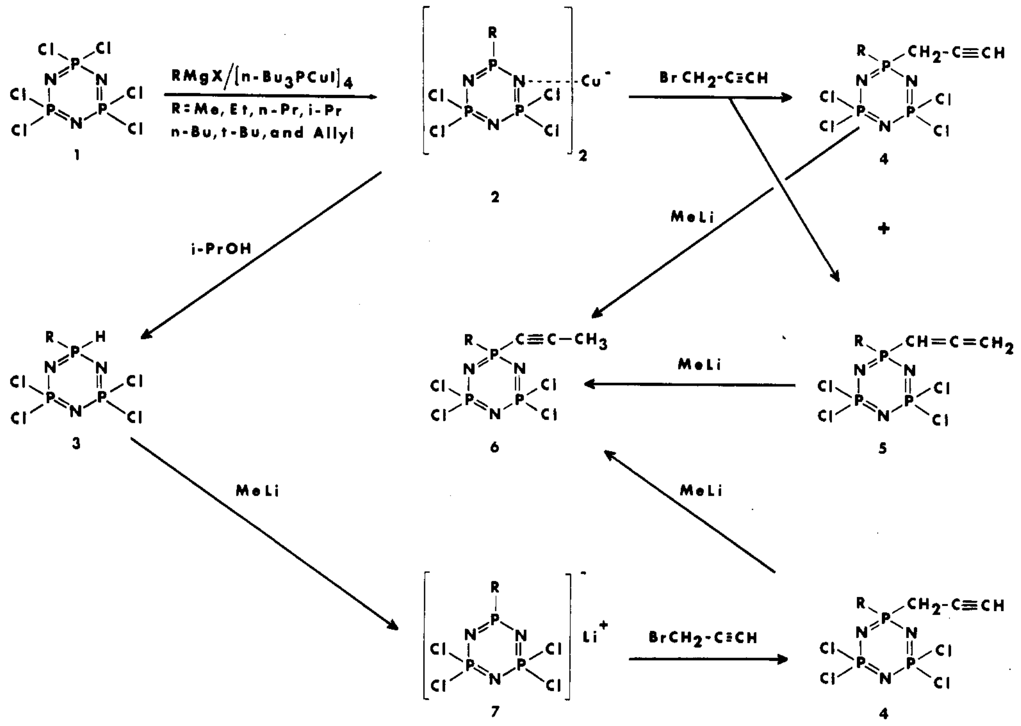
(16) Wilczynski, R.; Sneddon, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 2857.

(17) Harris, P. J.; Nissan, R. A.; Allcock, H. R. *J. Am. Chem. Soc.* **1981**, *103*, 2256.

(18) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.

0276-7333/84/2303-0432$01.50/0

Scheme I



Results and Discussion

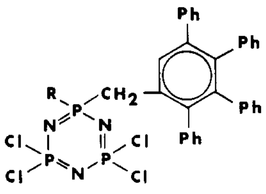
Syntheses. Alkynes 4 and 6 reacted cleanly with dicobalt octacarbonyl by decarbonylation to yield complexes 8 and 9. These red-orange products are air stable. Most of the 14 compounds synthesized are crystalline solids at 20 °C. Their characterization is discussed in later sections.

Influence of 8 and 9 on Acetylene Addition Reactions. In the following sections we will show that species 8 and 9 can function as catalysts for the cyclotrimerization of phenylacetylene or diphenylacetylene and can cotrimerize with diphenylacetylene and, to a lesser extent, with phenylacetylene. Finally, we will describe the cyclotrimerization of 4 (R = methyl or isopropyl) under the influence of 8 (R = methyl) to yield 1,2,4-phosphazenylbenzene derivatives.

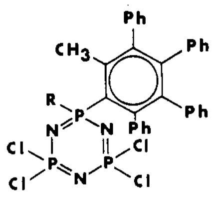
It is known from studies in other laboratories[9,19] that the trimerization of diphenylacetylene to hexaphenylbenzene takes place at 150 or 250 °C under the influence of cobalt catalysts. Species 8 and 9 (1 mol % concentration) induced the conversion of diphenylacetylene to hexaphenylbenzene in up to 20% yield at 150 or 200 °C. No other products were detected. In the absence of 8 or 9 diphenylacetylene underwent no reaction at these temperatures.

The influence of 8 or 9 on the addition reactions of phenylacetylene is less marked. At high concentrations of 8 or 9 (stoichiometric amounts) phenylacetylene was converted to 1,2,4-triphenylbenzene in over 80% yield at 150 °C. However, when only catalytic quantities of 8 or 9 were employed at 150 °C, the products $[(C_6H_5C{=}CH)_n, n \leq 6]$ were indistinguishable from those generated by free radical oligomerization reactions[20] in the absence of 8 or 9. No cyclization or linear oligomerization took place with phenylacetylene at 100 °C in the absence or presence of 1 mol % of 8 or 9.

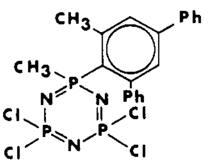
Cyclotrimerization and Cotrimerization Involving 8 or 9. The interaction of 1 equiv of 8 or 9 (R = methyl or isopropyl) with 2 equiv of diphenylacetylene at 150 °C in octane yielded hexaphenylbenzene (15%) and species 10 (12%) or 11 (14%) (see Experimental Section). Similarly, 8 or 9 (R = methyl) reacted with phenylacetylene to yield 1,2,4-triphenylbenzene (83%) and species 12 and 13 or 14 and 15 (<5% yields).



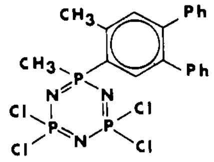
10a,b
a, R = CH_3
b, R = i-C_3H_7



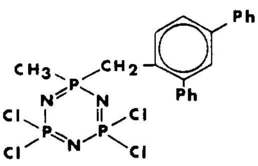
11a,b
a, R = CH_3
b, R = i-C_3H_7



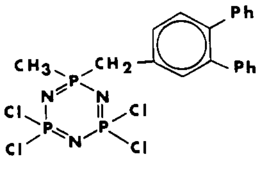
12



13



14



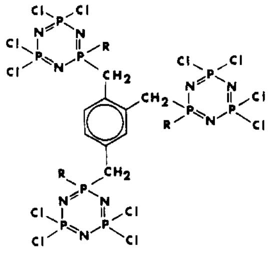
15

Compounds 4 (R = methyl or isopropyl) cyclotrimerized to yield 16 in the presence of 8 (R = methyl) at 150 °C. As discussed in Appendix I (supplementary material), the ^{31}P NMR spectra are compatible with structures 16. The

---

(19) Kruerke, U.; Hubel, W. *Chem. Ber.* **1961**, *94*, 2829.

(20) Chauser, M. G.; Rodionov, Yu. M.; Misin, V. M.; Cherkashin, M. I. *Russ. Chem. Rev.* (*Engl. Transl.*) **1976**, *45* (4). 348.



16a,b (R= CH_3 or i-C_3H_7)

^{31}P {^1H} NMR spectra are shown in Figures 1 and 2 (supplementary material). The 1,2,4-substituted structure of **16** is compatible with the stepwise mechanism for cyclotrimerization of acetylenes proposed elsewhere.[11]

However, no cyclotrimerization was detected when the "internal" acetylenic derivative **6** was treated with its organometallic analogue, **9**. No residual **6** could be detected after the reaction, and the products appeared to consist of a complex mixture of noncyclized and rearrangement products. The steric crowding inherent in **6** may inhibit cyclotrimerization.

The presence of P–Cl bonds in **4** and **6** and in complexes **8** and **9** is probably responsible for the eventual inhibition of catalysis by these complexes. The chlorophosphazene $(NPCl_2)_3$ (**1**) induces the decomposition of dicobalt acetylenic complexes such as **8** (R = CH_3). Replacement of the chlorine atoms in **4**, **6**, **8**, and **9** by organic side groups might avoid this problem.

Structure of 8 and 9. Spectroscopic Evidence. The spectroscopic evidence yielded preliminary structure proof and provided some information about the electronic interactions between the acetylenic/organometallic side units and the π-electrons of the phosphazene ring.

Characterization of **8** and **9** was accomplished by a combination of chemical ionization[21] or electron-impact[22] mass spectrometry, infrared spectroscopy,[23] and ^1H, ^{13}C, and ^{31}P NMR spectroscopy.[24] The results of X-ray diffraction studies are discussed in a later section.

The chemical ionization mass spectral data for all 14 complexes of types **8** and **9** showed parent 1+ ions, with the expected four-chlorine isotope pattern. Peaks associated with the loss of successive CO molecules were also detected. Similarly, peaks attributed to the parent ion minus two or three CO molecules were detected in the electron-impact mass spectra, although the parent ions were not evident.[25]

Solution-state infrared spectra for compounds **8** and **9** in hexane showed four or five CO-type bands between 2110 and 2000 cm^{-1} and a carbon–carbon stretching band at 1550 ± 20 cm^{-1}. These data are similar to those obtained from other (acetylene)dicobalt hexacarbonyl complexes.[26] The spectra of species **8** and **9** differed with respect to the position of the skeletal P–N stretching bands. The shift from 1200 cm^{-1} for **8** to 1150 cm^{-1} for **9** may reflect an increased electron withdrawal by the organometallic side group in **9**. Thus, the methylene spacer group in **8** insulates the organometallic residue from the π-system of the phosphazene ring. Additional evidence in favor of this conclusion is presented in the following sections.

The ^1H and ^{31}P NMR data for species **8** and **9** are summarized in Tables I and II (available as supplementary material). The proton NMR spectra were complex because of short- and long-range phosphorus–proton couplings. The spectra of the compounds where R = n-C_3H_7 or n-C_4H_9, for example, were characterized by broad peaks that could be resolved into individual lines only at high fields. Even then, it was not possible to measure all the coupling constants. The terminal acetylenic proton peak for **8** (R = C_3H_5) was very broad (~50 Hz at half-height). However, for three compounds (**8** where R = t-C_4H_9 and n-C_3H_7 or C_2H_5) a doublet structure was resolved with J_{PCCCH} = 2 and 3 Hz, respectively. The terminal acetylenic protons in **9** appeared as sharp doublets with J_{PCCCH} = 2 Hz (for R = t-C_4H_9 and C_3H_7). When the geminal group, R, was allyl, this four-bond coupling was not observed.

The ^{31}P NMR spectra of **8** and **9** showed two resonances in every case. These corresponded to PRR′ (downfield resonance) and PCl_2 (upfield resonance). Intraring spin–spin couplings were detected in only a few cases (J_{PNP} = 3.0 Hz for **8**, where R = C_2H_5 or n-C_3H_7, and 4.9 Hz for **9**, where R = CH_3). In each case, a comparison of the spectra from species **8** and **9** (for the same cosubstituent group, R) showed that the "internal" acetylenic complex **9** induced upfield shifts in both the PRR′ and PCl_2 resonances. Again, this is consistent with strong electron withdrawal by the organometallic side group from the phosphazene ring. It is instructive to compare the ^{31}P NMR shifts of **4** and **6** before and after coordination to the metal carbonyl. The conversion of **4** to **8** brings about a very small (1–3 ppm) upfield shift in both the PRR′ and PCl_2 resonances. However, the conversion of **6** to **9** is accompanied by a dramatic (~25 ppm) downfield shift in the PRR′ resonance and a 2.5 ppm upfield shift in the PCl_2 resonance. Clearly, a strong interaction exists between the "internal" acetylenic units in **6** and **9** and the heterocyclic π-system of the ring.

The changes in the ^{13}C NMR spectra were less obvious (Table III, supplementary material). Consider the carbon atoms of the acetylenic unit to be designated as P–C_α–C_β–C_γ. For species containing an external acetylenic function (**4**), complexation to yield **8** resulted in a small (0.6 ± 0.5 ppm) upfield shift in C_α, an ~8 ppm downfield shift in the resonance of C_β, and a ~14 ppm downfield shift in C_γ. This is the expected behavior following coordination of a metal carbonyl to a conventional acetylene.[27-32] No influence by the phosphazene ring could be

---

(21) Chemical ionization mass spectra were recorded with a Finnegan 3200 spectrometer with methane or isobutane used as the ionizing gas.

(22) Electron-impact mass spectra were recorded on an AEI MS-902 mass spectrometer operating at 70-eV ionizing potential.

(23) Infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer. Solution (in hexane) and solid (KBr pellets) samples were used.

(24) ^{31}P NMR data were recorded on a JEOL JNM-PS-100 spectrometer operating at 40 MHz in the Fourier transform mode or on a Bruker WH-200 spectrometer operating at 81 MHz. ^1H and ^{13}C NMR data were recorded on a Bruker WH-200 spectrometer operating at 200 and 50 MHz, respectively. All samples were prepared in $CDCl_3$ solvent, or when peaks were obscured by the solvent, in benzene-d_6. Samples were filtered. Only small shift differences were noted in comparing spectra of identical compounds in the two solvents employed. ^{13}C and ^1H shifts are referenced to Me_4Si at 0 ppm, with a positive shift being downfield. ^{31}P shifts are referenced to external 85% phosphoric acid at 0 ppm, with a positive shift being downfield from the reference peak.

(25) Chivers, T. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 827.

(26) Iwashita, Y.; Ishikawa, A.; Kainosho, M. *Spectrochim. Acta, Part A* **1971**, *27A*, 271.

(27) Aime, S.; Milone, L.; Rossetti, R.; Stanghellini, P. L. *Inorg. Chim. Acta* **1977**, *22*, 135.

(28) Blizzard, A. C.; Santry, D. P. *J. Am. Chem. Soc.* **1968**, *90*, 5749.

(29) Nelson, J. H.; Jonassen, H. B. *Coord. Chem. Rev.* **1971**, *6*, 27.

(30) Greaves, E. O.; Lock, C. J. L.; Maitlis, P. M. *Can. J. Chem.* **1968**, *46*, 3879.

(31) Brown, D. A. *J. Chem. Phys.* **1960**, *33*, 1037.

(32) VanDam, H.; Stufkens, D. J.; Oskam, A.; Doran, M.; Hiller, I. H. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *21*, 47.

(33) "International Tables for X-Ray Crystallography"; 3rd ed.; Kynoch Press; Birmingham, England, 1969; Vol. 3.

(34) $R_1 = \sum ||F_o|| - ||F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

(35) Elder, R. C.; Florian, L. R.; Lake, R. E.; Yacynych, A. M. *Inorg. Chem.* **1973**, *12*, 2690.

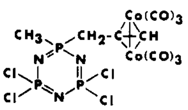
Table IV. Crystallographic Data for Compounds 17, 18, and 19

	17	18	19
color	red	red	red
size, mm	0.20 x 0.20 x 0.23	0.22 x 0.22 x 0.33	0.25 x 0.25 x 0.27
space group[a]	$P2_1/c$ (No. 14, C_{2h}^5)	$P2_1/n$ (No. 14, C_{2h}^5)	*Pnma* (No. 62, D_{2h}^{16})
cell constants			
a, Å	17.238 (2)	8.038 (3)	8.592 (2)
b, Å	7.470 (7)	22.080 (4)	14.58 (1)
c, Å	17.853 (4)	13.064 (3)	17.787 (4)
β, deg	99.91 (1)	91.51 (3)	
V, Å^3	2264 (3)	2418 (2)	2228 (3)
Z	4	4	4
d_{calcd}, g cm^{-3}	1.81	1.84	1.84
scan width, deg	0.55	0.60	0.65
scan rate, deg min^{-1}	1.0-5.0	1.0-5.0	1.0-5.0
drift correctn	0.969-1.046		
$2\theta_{\text{max}}$, deg	50.0	50.0	60.0
measd refl	4459	4700	3352
obsd refl ($I > 2\sigma(I)$)	2837	2911	1965
parameters	271	271	146
obsd refl/parameter[d]	10.5	10.7	13.5
p[g]	0.015	0.020	0.020
μ, cm^{-1}	22.30	21.83	22.67
R_1,[b] R_2[b]	0.048, 0.051	0.045, 0.047	0.039, 0.040
ESD[c]	2.920	2.277	1.837
highest peak,[e] e Å^{-3}	0.26	0.26	0.19
maximum s/e[f]	0.27	0.05	0.01
average s/e[f]	0.01	0.00	0.00

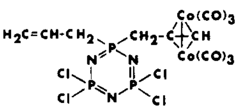
[a] See ref 33. [b] See ref 34. [c] Estimated standard deviation of an observation of unit weight. [d] Number of observed reflections for each parameter refined in the final cycles. [e] Largest peak remaining on a difference electron density map after convergence. [f] s/e is shift/error on the final cycle of refinement. [g] See ref 35.

discerned. Complexation of the dicobalt carbonyl unit to **6** brought about a 1.7 ± 0.5 ppm downfield shift for C_α, and small upfield or downfield shifts for C_β (0.5 ppm upfield when R was *i*-C_3H_7 to 1.5 ppm downfield when R was *t*-C_4H_9). The C_γ resonance was shifted 16.6 ± 0.8 ppm downfield following complexation, presumably a consequence of hybridization changes at C_β. However, the coupling constant J_{PC_α} was reduced dramatically following the conversion of **6** to **9** (from 213.1 to 137.7 Hz, where R = CH_3). This is compatible with the expected change from an sp-hybridized C_α atom to an atom with more sp^2 character.

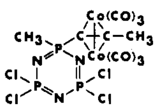
X-ray Structure Determination. Single-crystal X-ray structures were obtained for compounds **17**, **18**, and **19**.



17



18



19

The key questions kept in mind during these structural studies were the following: (a) Do these compounds have the molecular structure expected from the synthetic procedures used? (b) Does any evidence exist that the skeletal nitrogen atoms participate in binding the organometallic units? (c) What influence, if any, does the organometallic unit exert on the structure and bonding within the phosphazene ring and vice versa?

The space group and data collection information are summarized in Table IV. Observed and calculated structure factors are listed in Tables V, VI, and VII (supplementary material). Atomic positional parameters appear in Tables VIII, IX, and X (supplementary material). Bond distances and angles will be found in Tables XI, XII, and XIII (supplementary material), but the most important distances and angles are summarized in Figures 1, 2, and 3. Stereoviews are shown in Figures 6, 7, and 8. It should be noted that for **19** the plane of symmetry bisects the phosphazene ring and that P(1), N(2), C(1B),

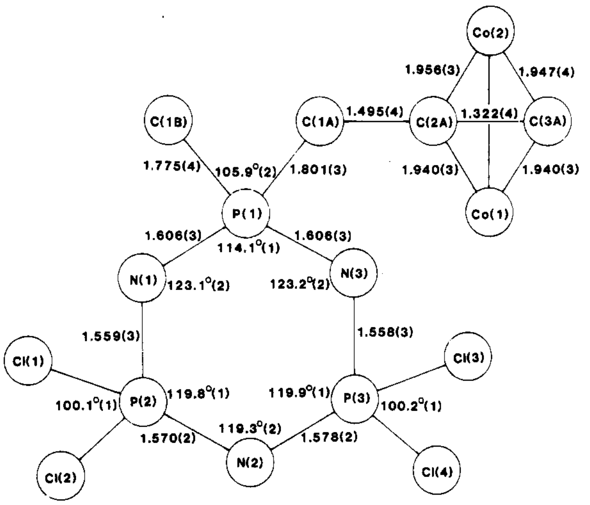


Figure 1. Selected structural features of compound 17.

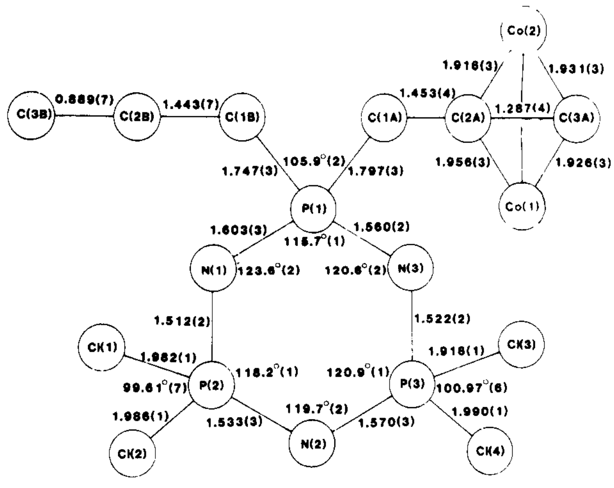


Figure 2. Selected structural features of compound 18.

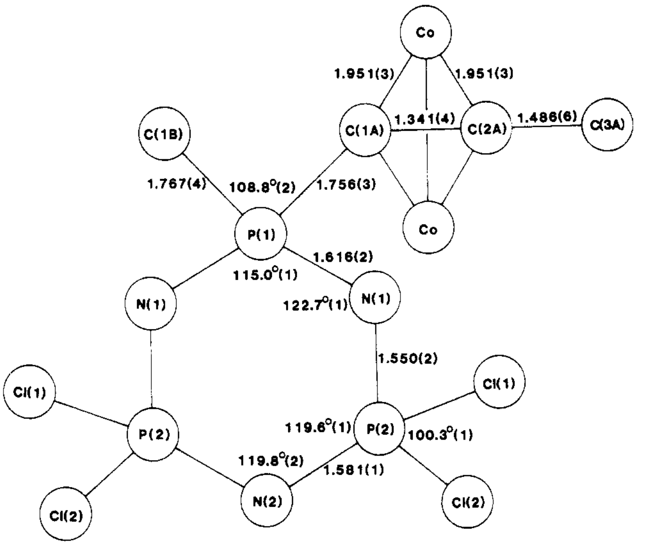


Figure 3. Selected structural features of compound **19**.

C(1A), C(2A), and C(3A) lie in the mirror plane. Root mean-square displacements are listed in Tables XIV, XV, and XVI (supplementary material).

The general structural features of **17**, **18**, and **19** were confirmed by the X-ray structure solution. In the following paragraphs the characteristics of (a) the phosphazene ring, (b) the dicobalt acetylenic organometallic unit, and (c) the geminal cosubstituent group, R, will be discussed in turn.

The cyclotriphosphazene rings in **17**, **18**, and **19** are planar but with the same curious distortion of ring symmetry seen in related compounds where organic or organometallic units are present on only one phosphorus atom.[36-41] Specifically, the phosphorus–nitrogen bond lengths closest to the organic units are longer than in $(NPCl_2)_3$, the two bonds adjacent to these are shorter than average, and those furthest from the organic units are of intermediate length (see Figures 1–3). This effect may reflect a distortion of the d_π–p_π orbital system as a consequence of an imbalance in the inductive and conjugative characteristics of the different substituents. However, no entirely satisfactory theoretical explanation is available. Equally plausible is the idea that the distortion is a result of steric repulsions between the organic and organometallic side groups. This would widen the C–P–C exocyclic bond angle (106–109°) compared to the Cl–P–Cl angle (100°) and alter the hybridization at P(1). Indeed, the N–P(1)–N ring angle is narrower than normal (~115°), as would be expected from a scissoring effect. In turn, this would result in a lengthening of the P(1)–N bond lengths. The P–C bond lengths in all three complexes are similar to those reported earlier for other alkylated phosphazenes,[36-40] and the P–Cl bond lengths are normal for chlorocyclophosphazenes.[38,39,41]

The structural features of the dicobalt–hexacarbonyl acetylenic units can be seen in Figures 1–3. In each case the dicobalt–hexacarbonyl unit is π-bonded to the appropriate acetylenic site, and the alkynyl groups are bent away from the dicobalt moiety to assume a cis orientation. The cobalt–cobalt bonding distances of 2.454 (1) for **17**, 2.437 (1) for **18**, and 2.494 (1) Å for **19** compare well with the average values (2.469 (3) Å) for 22 values given in the literature.[42-48] Similarly, the cobalt–acetylenic carbon bond distances, which average 1.941 (4) Å, and the cobalt–carbonyl carbon distances, which average 1.795 (5) Å, are compatible with the average literature values of 1.97 (1)[42-44,47,48] and 1.78 (1) Å,[42-47] respectively. The structural parameters for the propynyl groups are also normal.[42-48]

However, the allyl cosubstituent group in **18** presents an anomaly. Although the P–C_α bond length is normal and the C_α–C_β length is only slightly shorter than the literature value of 1.486 (9) Å,[49] the C_β–C_γ bond length of 0.889 (7) Å is unacceptably short compared to values reported elsewhere of 1.14 (3) to 1.46 (4) Å.[49-55] Moreover, the C–C–C angle of 171 (1)° is much wider than the reported values of 121 (1)° to 146 (2)°.[49,52-55] These anomalies are probably best explained by a side-to-side crystallographic disorder of the terminal carbon atom of the allylic group. This disorder was confirmed by the presence of residual electron density flanking this carbon atom and by the highly elongated thermal elipsoid associated with this atom. However, this disorder did not significantly affect the rest of the structure.

We conclude that π-bonding of metal carbonyls to propynyl phosphazenes is a facile process. It proceeds without interference from the skeletal nitrogen atoms. Acetylenic metal–carbonyl units adjacent to the phosphazene skeleton have a marked influence on both the structure (bond angles and bond lengths) of the phosphazene skeleton and on the distribution of electrons in the ring. These conclusions, together with the demonstration of catalytic activity by the organometallic moiety, provide an incentive for the synthesis of the analogous linear phosphazene macromolecular analogues.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (kindly provided by Ethyl Corp.) was purified by recrystallization from hexane and by vacuum sublimation. Grignard reagents were obtained from Aldrich or Alfa Ventron. Prop-2-ynyl bromide (Aldrich) was used without further purification. Dicobalt octacarbonyl (Alfa Ventron) was purified by sublimation. Tetrahydrofuran (THF) (Fisher) was dried over benzophenone ketyl and was distilled under an atmosphere of dry nitrogen directly into the reaction vessels. Hexane was dried over calcium hydride before use. Silica gel (60–200 mesh, activated) and alumina (neutral, Brockman activity 1) were obtained from Fisher. All manipulations involving organometallic reagents or air-sensitive intermediates were carried

---

[36] Marsh, W. C.; Trotter, J. *J. Chem. Soc. A* **1971**, 573.

[37] March, W. C.; Trotter, J. *J. Chem. Soc. A* **1971**, 569.

[38] Mani, N. V.; Ahmed, F. R.; Barnes, W. H. *Acta Crystallogr.* **1965**, *19*, 693.

[39] Ritchie, R. H.; Harris, P. J.; Allcock, H. R. *Inorg. Chem.* **1980**, *19*, 2483.

[40] Mani, N. V.; Ahmed, F. R.; Barnes, W. H. *Acta Crystallogr.* **1966**, *21*, 375.

[41] Allcock, H. R.; Scopelianos, A. G.; O'Brien, J. P.; Bernheim, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 350.

[42] Dellaca, R. J.; Penfold, B. R.; Robinson, B. H.; Robinson, W. T.; Spencer, J. L. *Inorg. Chem.* **1970**, *9*, 2197.

[43] Dellaca, R. J.; Penfold, B. R. *Inorg. Chem.* **1971**, *10*, 1269.

[44] Seyferth, D.; Spohn, R. J.; Churchill, M. R.; Gold, K.; Scholer, F. R. *J. Organomet. Chem.* **1970**, *23*, 237.

[45] Hota, N. K.; Patel, H. A.; Carty, A. J.; Mathew, M.; Palenik, G. J. *J. Organomet. Chem.* **1971**, *32*, C55.

[46] Sly, W. G. *J. Am. Chem. Soc.* **1959**, *81*, 18.

[47] Bailey, N. A.; Mason, R. *J. Chem. Soc. A* **1968**, 1293.

[48] Bird, P. H.; Fraser, A. R. *J. Chem. Soc., Chem. Commun.* **1970**, 681.

[49] Huffman, J. C.; Laurent, M. P.; Kochi, J. K. *Inorg. Chem.* **1977**, *16*. 2639.

[50] Drew, M. G. B.; Pu, L. S. *Acta Crystallogr., Sect. B* **1977**, *B33*, 1207.

[51] Brunelli, M.; Perego, G.; Lugli, G.; Mazzei, A. *J. Chem. Soc., Dalton Trans.* **1979**, 861.

[52] Halstead, G. W.; Baker, E. C.; Raymond, K. N. *J. Am. Chem. Soc.* **1975**, *97*, 3049.

[53] Schneider, M.; Weiss, E. *J. Organomet. Chem.* **1976**, *121*, 189.

[54] Mason, R.; Russel, P. R. *J. Chem. Soc., Chem. Commun.* **1965**, 97.

[55] Raper, G.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1972**, 265.

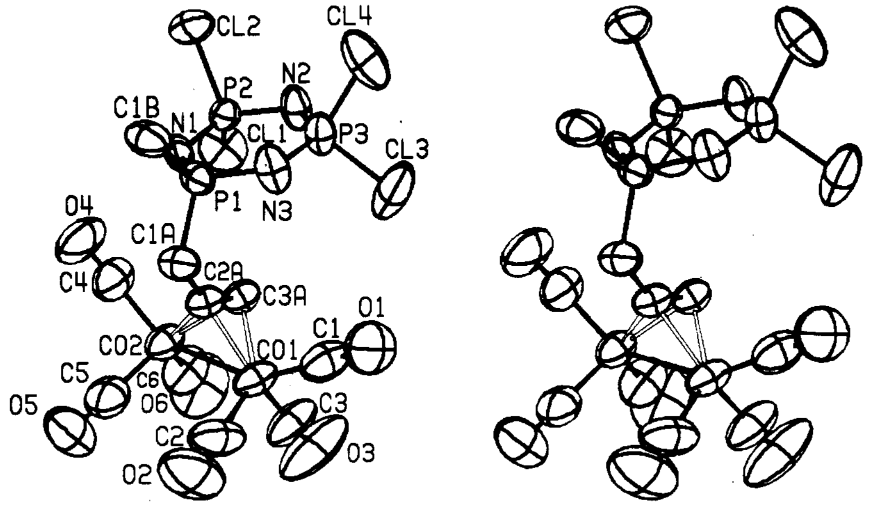


Figure 6. Stereo ORREP representation of compound **17**.

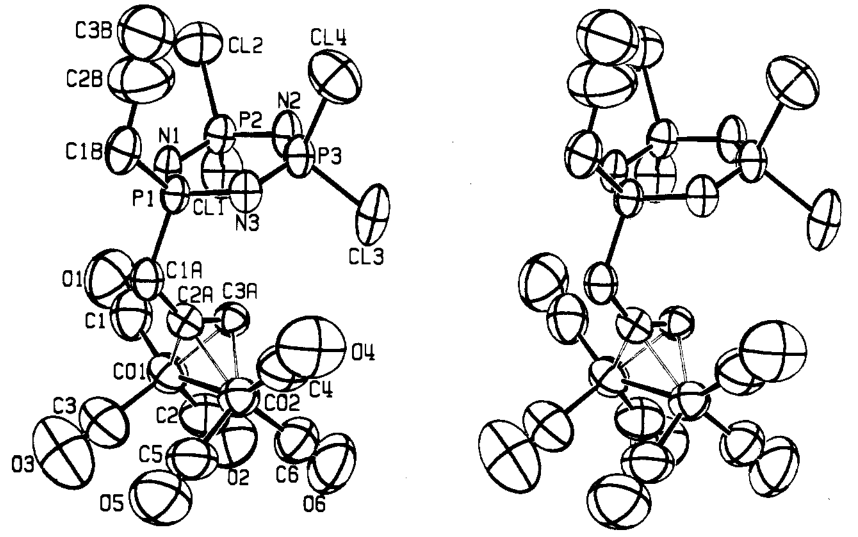


Figure 7. Stereo ORREP representation of compound **18**.

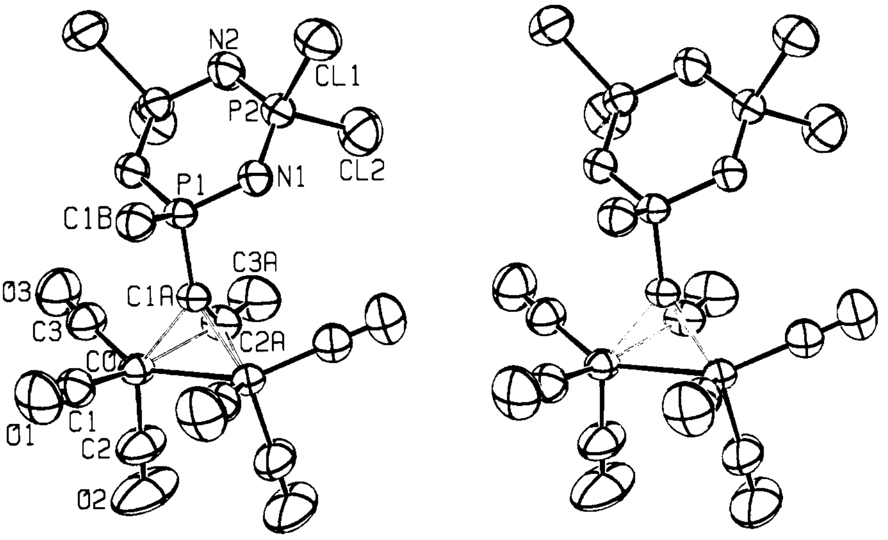


Figure 8. Stereo ORTEP representation of compound **19**.

out under an atmosphere of dry nitrogen.

Synthesis of 8 and 9. The acetylenic phosphazene precursors **4** and **6** were prepared via cuprio- or lithiophosphazene intermediates, as described elsewhere.[17,18] The reactions of the two precursors with dicobalt octacarbonyl were carried out by the use of the following typical procedure. 1-Methyl-1-(prop-2-ynyl)-tetrachlorocyclotriphosphazene (2 g, 0.006 mol) and dicobalt octacarbonyl (2.2 g, 0.006 mol) were allowed to react in hexane (50 mL) in a nitrogen-filled flask connected to a gas bubbler system. The reaction mixture was stirred until carbon monoxide evolution had ceased (generally within 30 min at 20–25 °C). The solvent was removed under vacuum, excess dicobalt octacarbonyl was sublimed from the residue, and the remaining material was chromatographed on silica gel with hexane and methylene chloride as eluents. A red compound (8, R = CH_3; 3 g, 80% yield) was obtained.

Trimerization of Diphenylacetylene. Diphenylacetylene (1 g, 5.6 mmol), $N_3P_3Cl_4(CH_3)(C_3H_3Co_2(CO)_6)$ (8 or 9) (50 mg, 0.08 mmol), and octane (1 mL) were degassed during three freeze-pump-thaw cycles, were sealed in a Pyrex glass tube, and were heated to 150 or 200 °C for 24 h. The contents of the tube were dissolved in methylene chloride and were filtered. Solvent was removed in vacuo, and the residues were extracted with hexane. In each case, 200 mg (20% yield) of a colorless microcrystalline material were obtained. This material was insoluble in hexane. It had a melting point of 428–430 °C and a mole weight of 534 (EIMS), $m/e + 1 = 535$ (CIMS). Infrared and ^1H NMR analyses were consistent with the structure of hexaphenylbenzene. The high-resolution EIMS for $C_{42}H_{30}$ was calculated to be 534.2347 and was found to be 534.2338. The hexane-soluble portion contained only diphenylacetylene starting material.

Attempted Trimerizations of Diphenylacetylene. Three tubes containing diphenylacetylene (1 g, 5.6 mmol), octane (1 mL), and $Co_4(CO)_{12}$ (35 mg, 0.06 mmol), $Co_2(CO)_8$ (35 mg, 0.12 mmol), or no added catalyst were degassed by three freeze-pump-thaw cycles, sealed in tubes, and heated to 200 °C for 24 h. The contents of the tubes were dissolved in methylene chloride and were filtered. Solvent was removed in vacuo, and the residues were crystallized from hexane to give recovered diphenylacetylene quantitatively. No appreciable hexane-insoluble material was formed in any of the reaction residues. Thus, under these reaction conditions, no trimerization of the diphenylacetylene occurred.

Reaction of Phenylacetylene with 8 or 9. Phenylacetylene (1 g, 9.8 mmol), octane (1 mL), and either 8 or 9 (50 mg, 0.08 mmol) were degassed and sealed in glass tubes. The tubes were heated to 100 or 150 °C for 12 h. A marked increase in viscosity was noted in the contents of those tubes heated to 150 °C, and the contents were a darker red color. This red, viscous material was immiscible with octane. Extraction with methylene chloride (50 mL) yielded (on removal of solvent) a yellow solid that decomposed above 180 °C. CIMS showed peaks that could be attributed to $(C_8H_6)_n + 1$, where *n* varied from 2 to 6. Infrared analysis appeared compatible with the presence of 1,2,4-triphenylbenzene. However, the ^1H NMR spectra contained only broad resonances in the aromatic region (7–8 ppm). We conclude that the phenylacetylene in these tubes underwent a free radical oligomerization.[20] Control tubes containing only phenylacetylene and octane gave similar products at 150 °C. At 100 °C no reaction took place.

Stoichiometric Reactions of Complexes 8 and 9 (R = Methyl or Isopropyl) with Diphenylacetylene. These reactions were carried out in a similar manner to those described above, and the following is a description of a typical procedure for the case of 9 (R = isopropyl). Compound 9 (R = isopropyl; 90 mg, 0.14 mmol), diphenylacetylene (50 mg, 0.28 mmol), and octane (1 mL) were degassed, sealed in a Pyrex glass tube, and heated to 150 °C for 24 h. The contents of the tube were dissolved in methylene chloride and filtered, and solvent was removed in vacuo. The residues were extracted with hexane (2 × 25 mL) to yield, after removal of solvent, 30 mg of a mixture of diphenylacetylene and the hexasubstituted benzene (**11b**), 1-isopropyltetrachlorocyclotriphosphazenyl)-2-methyl-3,4,5,6-tetraphenylbenzene. Starting material was sublimed from the residues to leave the hexasubstituted benzene (15 mg, 0.02 mmol, 14% yield). Its structure was confirmed by CIMS ($m/e + 1 = 714$ base peak of a 4-Cl isotope pattern), ^{31}P NMR ($\nu(PRR')$ 40.3, $\nu(PCl_2)$ 15.6), and ^1H NMR (7.5–6.6 (20 ^1H), 2.7 (d, 3 ^1H, $J_{PCCCH} = 1.4$ Hz), 1.8 (m, 1 ^1H), 1.1 ppm (d, d, 6 ^1H $J_{PCCH} = 20.8$ Hz, $J_{HCCH} = 6.9$ Hz)). The high-resolution EIMS for $N_3P_3Cl_4C_{34}H_{30}$ was calculated to be 713.0407 and was found to be 713.0403. In addition, hexaphenylbenzene (15 mg, 30% yield, based on the starting material) remained after the original extraction with hexane. No phosphazene starting material or phosphazenylacetylene was recovered. The remainder of the product was insoluble in methylene chloride and was presumed to contain decomposed starting materials.

Similarly, from the reaction of 8 (R = methyl) with 2 equiv of diphenylacetylene, compound **10a** was isolated (20% yield based on starting material). Its structure was confirmed by EIMS (mole weight = 685 base peak of a 4-Cl isotope pattern), ^{31}P NMR ($\nu(PRR')$ 38.4, $\nu(PCl_2)$ 18.9), and ^1H NMR (7.7–6.8 (m's 21 ^1H), 3.3 (d, 2 ^1H, $J_{PCH} = 13.4$ Hz), 1.5 ppm (d, 3 ^1H, $J_{PCH} = 13.7$ Hz)). The high-resolution EIMS for $N_3P_3Cl_4C_{32}H_{26}$ was calculated to be 685.0094 and found to be 685.0112.

Compound **10b** (12% yield based on starting material) was isolated from the reaction of 9 (R = isopropyl) with 2 equiv of diphenylacetylene. EIMS gave a parent peak at 713 with a 4-Cl isotope pattern. ^{31}P NMR ($\nu(PRR')$ 49.8, $\nu(PCl_2)$ 19.4) and ^1H NMR (7.6–6.8 (m's, 21 ^1H), 3.2 ppm (d, 2 ^1H, $J_{PCH} = 11$ Hz), 1.8 (m, 1 ^1H), 1.1 ppm (d, d, 6 ^1H, $J_{PCCH} = 21$ Hz, $J_{HCCH} = 8$ Hz)) are consistent with the proposed structure of compound **10b**. The high-resolution EIMS for $N_3P_3Cl_4C_{34}H_{30}$ was calculated to be 713.0407 and was found to be 713.0352.

Finally, compound **11a** (23% based on starting material) was isolated from the reaction of 9 (R = methyl) with 2 equiv of diphenylacetylene. Its structure was once again confirmed by EIMS (mole weight = 685 base peak of a 4-Cl isotope pattern), ^{31}P NMR ($\nu(PRR')$ 37.0, $\nu(PCl_2)$ 18.9), and ^1H NMR (7.6–6.6 (m's, 20 ^1H), 2.7 (s, br, 3 ^1H), 1.7 (d, 3 ^1H, $J_{PCH} = 14.0$ Hz)). The high-resolution EIMS for $N_3P_3Cl_4C_{32}H_{26}$ was calculated to be 685.0094 and was found to be 685.0082.

Stoichiometric Reaction of Compound 9 (R = Methyl) with Phenylacetylene. Compound 9 (R = methyl, 350 mg, 0.6 mmol), phenylacetylene (120 mg, 1.2 mmol), and octane (1 mL) were degassed, sealed in a glass tube, and heated to 150 °C for 24 h. The contents were dissolved in methylene chloride and filtered, and solvent was removed. The residues were chromatographed on silica gel with 80/20 hexane/methylene chloride as the eluting solvent. A colorless solid, mp 120 °C (100 mg), was eluted first. The compound was identified from its IR, ^1H NMR, and mass spectra as 1,2,4-triphenylbenzene in 83% yield (based on phenylacetylene). High-resolution EIMS for $C_{24}H_{18}$ was calculated as 306.1408 and found to be 306.1381. In addition, further elution gave 10 mg of a red, solid material shown from ^{31}P NMR and CIMS data to be a mixture of three compounds. The major component was the dicobalt acetylene starting material 9: ^{31}P NMR 29.1 (t), 16.4 ppm (d, $J_{PNP} = 9.5$ Hz). Two additional sets of AB_2 patterns, 27.9 ppm(t), 15.7 ppm(d) $J_{PNP} = 10.8$ Hz, and 27.5 ppm(t), 16.9 ppm(d) $J_{PNP} = 8.0$ Hz were tentatively assigned as two of the possible tetra-substituted benzenes 12 and 13. EIMS and CIMS data confirmed this interpretation. High-resolution EIMS for $N_3P_3Cl_4C_{20}H_{18}$ was calculated to be 532.9468 and found to be 532.9456. These substituted benzenes were inseparable by standard chromatographic techniques. We attribute the low yields of these products to the greater reactivity of phenylacetylene toward trimerization.

Stoichiometric Reaction of Compound 8 with Phenylacetylene. Compound 8 (R = methyl, 600 mg, 1.0 mmol), phenylacetylene (200 mg, 2.0 mmol), and octane (1.5 mL) were degassed, sealed in a tube, and heated to 150 °C for 24 h. The contents were dissolved in methylene chloride and filtered, and solvent was removed. The residues were chromatographed on silica gel with 80/20 hexane/methylene chloride as the eluting solvent. A colorless solid (85 mg) was eluted first. This compound was again identified as 1,2,4-triphenylbenzene and, in this case, was formed in 43% yield from phenylacetylene. Further elution gave 30 mg of a brown material shown to be composed of two phosphazene-containing compounds tentatively assigned structures 14 and 15. ^{31}P NMR investigation of this mixture showed two PRR′ resonances at 38.0 and 37.7 ppm and their associated two PCl_2 resonances at 18.8 and 19.0 ppm, respectively. Surprisingly, no starting material (8) was detected. EIMS contained a parent peak at 533 with the expected 4-Cl isotope pattern, and the high-resolution EIMS for $N_3P_3Cl_4C_{20}H_{18}$ was calculated to be 532.9468 and found to be 532.9451.

Trimerization of Acetylenic Phosphazenes 4 (R = Methyl or Isopropyl). Acetylenic phosphazene 4 (R = methyl; (0.25 g, 0.76 mmol), 8 (R = methyl; 5 mg, 0.008 mmol), and octane (1 mL) were degassed, sealed in a glass tube, and heated to 150 °C for 24 h. The contents of the tube comprised a clear solution with a blue-green precipitate. These products were extracted with methylene chloride and were filtered. A pale yellow solid (0.25 g) was obtained by removal of the solvent in vacuo. A ^{31}P NMR analysis revealed the presence of starting material [34.3 (t), 19.4 ppm (d, $J_{PNP} = 6$ Hz)], an additional set of peaks [three multiplets at 38.1, 37.5, and 36.7 ppm, 19.0 ppm (d, $J_{PNP} = 4.4$ Hz)], and a broad singlet at 18.6 ppm. Integration indicated that the singlet was twice the area of the doublet. Thus, it was assigned to two sets of PCl_2 units where J_{PNP} approaches 0. The colorless acetylenic phosphazene starting material was sublimed from the residue onto a cold finger at 110 °C (1 torr). The residue was the pale yellow substituted benzene **16a**, mp 282 °C (40 mg, 16% yield). EIMS yielded a parent peak at m/e 987 with a 12 Cl isotope pattern. A ^1H NMR spectrum contained peaks at 7.2 (3 ^1H (two multiplets in a 2/1 ratio)) and 3.1–3.5 ppm (three multiplets, 6 ^1H) and between 1.5 and 1.8 ppm (9 ^1H, three sets of doublets of triplets). High-resolution EIMS for $N_9P_9{}^{35}Cl_8{}^{37}Cl_4C_{12}H_{18}$ was calculated to be 994.5470 and was found to be 994.5570.

In a similar trimerization attempt, acetylenic phosphazene 4 (R = isopropyl; 0.6 g, 1.7 mmol), dicobalt acetylene 8 (R = methyl; 10 mg, 0.016 mmol), and octane (1 mL) were degassed and sealed in a tube and heated to 150 °C for 24 h. The contents of the tube consisted of a clear solution and a blue-green precipitate. These products were extracted with methylene chloride and filtered. Removal of the solvent gave 0.6 g of a pale yellow solid. This solid was analyzed by ^{31}P NMR spectroscopy and was found to contain starting material [45.2 (s) and 20.8 ppm (s, J_{PNP} = 0)] and another product which gave rise to multiplets at 49.8, 48.7, and 47.1 ppm and doublets at 19.3, 19.1, and 19.1 ppm (J_{PNP} = 4.5, 8.1, and 7.0 Hz), respectively. The acetylenic starting material (0.5 g) was sublimed from this mixture to leave a pale yellow solid, compound **16b**, mp 140 °C (87 mg, 15% yield): ^1H NMR 7.2 (3 ^1H, two multiplets in a 2/1 ratio), 3.1–3.4 (three multiplets, 6 ^1H), 2.0–2.2 (three broad multiplets, 3 ^1H), between 1.1 and 1.4 ppm (multiplets, 18 ^1H). EIMS showed a parent peak with a base m/e of 1071 and a 12-Cl isotope pattern. High-resolution EIMS for $N_9P_9{}^{35}Cl_{11}{}^{37}Cl_1C_{18}H_{30}$ was calculated to be 1072.6496 and found to be 1072.6612.

Attempted Trimerization of Acetylenic Phosphazene 6 (R = Methyl). Compound 6 (R = methyl; 1 g, 3.0 mmol), 9 (R = methyl; 20 mg, 0.03 mmol), and octane (1 mL) were degassed, sealed in a glass tube, and heated to 150 °C for 24 h. The tube contained a dark brown solution and a dark precipitate. The contents of the tube were extracted with methylene chloride and filtered. Solvent was removed in vacuo to leave a brown oil (0.3 g). The oil consisted of a small amount of acetylenic starting material plus several unidentified products. CIMS suggested that the acetylene had dimerized. No evidence was found for the presence of any substituted benzene products.

Crystallographic Data Collection and Reduction. Crystals were grown from a hexane solution by slow cooling near 0 °C. The observed densities are given in Table IV. Dark red crystals with the approximate dimensions shown in Table IV were mounted on glass fibers with the use of epoxy cement. The longest crystal dimension was in each case coincident with the glass fiber axis.

Our present crystallographic protocol will be described rather completely here and will not be repeated in detail in later papers. A given crystal was centered optically on an Enraf-Nonius four-circle CAD-4 automated diffractometer controlled by a PDP8 computer. A full rotation orientation photograph was taken by using the Polaroid cassette accessory. Twenty-five intense reflections were chosen and centered by using the manufacturer-supplied software.[56] The INDEX program was used to obtain an orientation matrix and unit cell parameters. Successive centerings and least-squares refinements of 2θ values found for the 25 precisely centered reflections gave the refined lattice constants listed in Table IV for each of the three crystals. Program TRACER was used to determine the validity of the unit cell chosen initially, and a transformation was applied in cases where the initial choice was found to be unsatisfactory. A small test data set (axial and zero layer reflections) was collected to determine the space group, and these are given in Table IV. They were confirmed by the successful refinement of the structures. The number of formula units per unit cell, Z (Table IV), was determined on the basis of the measured density of the dicobalt acetylene complexes.

Intensity data were collected at room temperature by using Mo K_α radiation (λ = 0.71073 Å) with a graphite single crystal monochromator (takeoff angle = 2.8°). A θ–2θ scan mode was used, with 2θ ranging from (A + 0.347 tan θ) below and above the calculated position of the $k\alpha_1$ and $k\alpha_2$ reflections. The A values used and the scan rate, which was varied automatically depending on the intensity of a reflection as determined by a preliminary brief scan, are also given in Table IV. Background counts were measured with the detector stationary and positioned at the beginning and end of the scan for each $^1/_4$ of the total scan time. Three standard reflections were measured every 80 min of X-ray irradiation time, and the same reflections were checked for centering automatically after every 200 reflections to check on the crystal orientation and stability. The total numbers of unique reflections measured, and their numbers with respect to the standard deviation in intensity (I) are indicated in Table IV for each of the crystals.

Linear absorption coefficients for Mo Kα radiation are given in Table IV. Psi scans indicated that the absorption problems were not severe, and no absorption corrections were applied. The integrated intensity, I, was calculated according to the expression $I = [SC - 2(B_1 + B_2)/B_R]T_R$, where SC is the count accumulated during the scan. B_1 and B_2 are the background counts at each end of the scan, B_R is the background time to scan time ratio, and T_R is the 2θ scan rate in degrees per minute. $\sigma(I)$ was calculated as follows: $\sigma(I) = T_R[SC + (B_1 + B_2)/B_R{}^2 + (\sigma I)^2]^{1/2}$. Values are indicated in Table IV.

In one case (**17**) the standard reflections were used to rescale the data automatically to correct for drift due to changes in temperature, centering, etc. during data collection. The ranges of random long-term drift are indicated in Table IV. The unique, normalized, integrated intensity set was processed to give $|F|$ and $|E|$ values. The polarization corrections were calculated on the basis that the incident beam is polarized to some extent by the monochromator assuming, for this purpose, the graphite crystal to be 50% perfect and 50% mosaic.

Structure Solution and Refinement. The position of the metal atoms in each case was determined from a sharpened, origin-removed Patterson map. The remaining non-hydrogen atoms were located with one or two Fourier syntheses. Hydrogen atoms were located at their calculated positions. In the case of methyl groups, a tetrahedral model was used wherein the hydrogen atoms were placed at positions giving the closest agreement with peaks found in difference Fourier maps (C–H = 0.97 Å). All hydrogen atoms were assigned isotropic temperature parameters[57] of B = 5.0 Å^2 or U = 0.0384 Å^2. The number of parameters varied in each case, including overall scale factor, positional parameters, and anisotropic thermal parameters,[57] are listed in Table IV. In the case of compounds **17** and **19**, positional parameters for hydrogen atoms were also varied, while for compound **18** the parameters for the hydrogen atoms were fixed. Neutral atom scattering factors were those given by Cromer and Mann[58] and by Stewart et al.[59] Real and imaginary anomalous dispersion corrections to the atomic scattering factors were included.[33] In the last cycle of least-squares refinement, the maximum parameter shift was less than 0.27 of a standard deviation. The final R values[34] are listed in Table IV. Final difference Fourier maps showed no peaks greater than 0.26 e Å^{-3} with the largest usually located ~1 Å from the metal atoms.

Acknowledgment. We thank the U.S. Army Research Office for the support of this work. We also acknowledge the assistance given by W. DeW. Horrocks and M. Y. Bernheim with respect to the X-ray work and R. Minard, G. Cunningham, and P. R. Suszko for the mass spectral analyses.

Registry No. 4 (R = Me), 77217-45-9; 4 (R = Et), 77217-46-0; 4 (R = *n*-Pr), 77217-47-1; 4 (R = *i*-Pr), 77217-49-3; 4 (R = *n*-Bu),

---

(56) Structure determination package was provided by Molecular Structure Corp.

(57) Isotropic thermal parameters were of the form $\exp[-B(\sin^2\theta)/\lambda^2]$ and anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}{}^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

(58) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. B.* **1968**, *A24*. 321.

(59) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(60) For these two samples, ^{31}P NMR spectra were recorded on a Bruker WH-200 spectrometer operating at 81 MHz and on a Bruker WM-360 spectrometer operating at 145 MHz. Peak positions and coupling constants were assigned by comparison of the spectra at varied field strengths. No attempts were made to assign peaks to individual phosphorus nuclei.

77217-48-2; **4** (R = *t*-Bu), 77217-51-7; **4** (R = allyl), 77217-52-8; **6** (R = Me), 77217-53-9; **6** (R = Et), 77217-54-0; **6** (R = *n*-Pr), 77217-55-1; **6** (R = *i*-Pr), 77217-57-3; **6** (R = *n*-Bu), 77217-56-2; **6** (R = *t*-Bu), 77217-59-5; **6** (R = allyl), 77217-60-8; **8** (R = Et), 88131-26-4; **8** (R = *n*-Pr), 88156-67-6; **8** (R = *i*-Pr), 88131-27-5; **8** (R = *n*-Bu), 88131-28-6; **8** (R = *t*-Bu), 88131-29-7; **9** (R = Et), 88131-32-2; **9** (R = *n*-Pr), 88131-33-3; **9** (R = *i*-Pr), 88131-34-4; **9** (R = *n*-Bu), 88131-35-5; **9** (R = *t*-Bu), 88131-36-6; **9** (R = allyl), 88131-37-7; **10a**, 88131-38-8; **10b**, 88131-39-9; **11a**, 88131-40-2; **11b**, 88131-41-3; **12**, 88131-42-4; **13**, 88131-43-5; **14**, 88131-44-6; **15**, 88131-45-7; **16a**, 88131-46-8; **16b**, 88131-47-9; **17**, 88131-25-3; **18**, 88131-30-0; **19**, 88131-31-1; dicobalt octacarbonyl, 10210-68-1; diphenylacetylene, 501-65-5; hexaphenylbenzene, 992-04-1; phenylacetylene, 536-74-3; 1,2,4-triphenylbenzene, 1165-53-3.

Supplementary Material Available: Appendix I, analysis of the $^{31}P\{^1H\}$ NMR spectra of **16a,b**, tables of ^1H NMR data for complexes **8** and **9** (Table I), ^{31}P NMR data for complexes **8** and **9** (Table II), ^{13}C NMR data for complexes **8** and **9** (Table III), listings of structure factor amplitudes for compounds **17** (Table V), **18** (Table VI), and **19** (Table VII), tables of positional and thermal parameters for compounds **17** (Table VIII), **18** (Table IX), and **19** (Table X), tables of bond distances and angles for compounds **17** (Table XI), **18** (Table XII), and **19** (Table XIII), tables of root mean square amplitudes for compounds **17** (Table XIV), **18** (Table XV), and **19** (Table XVI), and figures of the ^1H decoupled ^{31}P NMR spectra of **16**, R = methyl (Figure 4), and **16**, R = isopropyl (Figure 5) (69 pages). Ordering information is given on any current masthead page.

Reaction of (Octaethylporphyrinato)cobalt Complexes with Diazoacetaldehyde. *N*-(Formylmethyl)- and *N*-(2-Hydroxyethyl)porphyrins

Jun-ichiro Setsune and David Dolphin*

Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

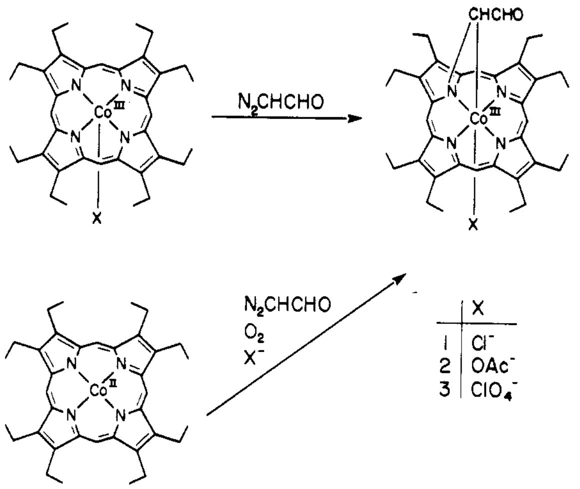
Received August 11, 1983

Reaction of divalent and trivalent cobalt complexes of octaethylporphyrin ($OEP{\cdot}H_2$) with diazoacetaldehyde gave *N,Co*-(formylmethylene)$OEPCo^{III}X$ ($X = Cl^-$, OAc^-, ClO_4^-) which were reduced electrochemically to afford *N*-(formylmethyl)OEP·H; *N*-(2,2-dimethoxyethyl)OEP·H and *N,N'*-(1,2-vinylidene)OEP were obtained from *N*-(formylmethyl)OEP·H under acidic conditions. $NaBH_4$ reduction of *N*-(formylmethyl)OEP·H gave *N*-(2-hydroxyethyl)OEP·H. These *N*-alkylporphyrins provide a firm basis for the characterization of some suicide metabolites of cytochrome P-450.

It has recently been reported that cytochrome P-450 monooxygenases are inactivated through the N-alkylation of the prosthetic heme during xenobiotic metabolism and the *N*-alkyl groups may be derived from olefins,[1] acetylenes,[2,3] and 1,4-dihydropyridine derivatives.[4,5] N-Substituted protoporphyrins IX were isolated, as the dimethyl esters, from inactivated cytochrome P-450 enzyme systems and analyzed spectroscopically. However, unequivocal identification of the N substituents has been frustrated due to the difficulties with which authentic materials are synthesized.

N-Alkylporphyrins are prepared by (i) alkylation of free base porphyrins with alkyl halides,[6,7] (ii) metal-to-nitrogen alkyl migration upon one-electron oxidation of (σ-alkyl)metal(III) porphyrins,[8-11] and (iii) protonolysis of a metal–carbon bond of unusual N,M(III)-bridged methylene complexes of metalloporphyrins.[12-14] The first method gives reasonably fair yields and selectivity for monoalkylation only when simple alkyl groups such as methyl and ethyl are introduced. Although the second and third methods have allowed N-alkylation to take place under milder reaction conditions, N-alkylation with functionalized alkyl groups is still difficult. There have been no reports on the synthesis of *N*-(2-hydroxyethyl)- or *N*-(formylmethyl)porphyrins which are produced when cytochrome P-450 monooxygenases are inactivated with ethylene or acetylene.[1,2]

Scheme I



---

[1] P. R. Ortiz de Montellano, H. S. Beilan, K. L. Kunze, and B. A. Mico, *J. Biol. Chem.* **256**, 4395 (1981).

[2] P. R. Ortiz de Montellano and K. L. Kunze, *Biochemistry*, **20**, 7266 (1981).

[3] P. R. Ortiz de Montellano, K. L. Kunze, H. S. Beilan, and Conrad Wheeler, *Biochemistry*, **21**, 1331 (1982).

[4] P. R. Ortiz de Montellano, H. S. Beilan, and K. L. Kunze, *Proc. Natl. Acad. Sci. U.S.A.*, **78**, 1490 (1981).

[5] K. L. Kunze and P. R. Ortiz de Montellano, *J. Am. Chem. Soc.* **103**, 4225 (1981).

[6] A. H. Jackson and G. R. Dearden, *Ann. N.Y. Acad. Sci.*, **206**, 151 (1973).

[7] D. K. Levallee and A. E. Gebala, *Inorg. Chem.* **13**, 2004 (1974).

[8] D. Dolphin, D. J. Halko, and E. Johnson, *Inorg. Chem.*, **20**, 4348 (1981).

[9] D. Mansuy, J.-P. Battioni, D. Dupre, and F. Sartori, *J. Am. Chem. Soc.*, **104**, 6159 (1982).

[10] H. J. Callot and F. Metz, *J. Chem. Soc., Chem. Commun.*, 947 (1982).

[11] P. R. Ortiz de Montellano, K. L. Kunze, and O. Augusto, *J. Am. Chem. Soc.*, **104**, 3545 (1982).

[12] M. Lange and D. Mansuy, *Tetrahedron Lett.*, **22**, 2561 (1981).

[13] A. W. Johnson, D. Ward, P. Batten, A. L. Hamilton, G. Shelton, and C. M. Elson, *J. Chem. Soc., Perkin Trans. 1*, 2076 (1975).

[14] H. J. Callot, *Tetrahedron Lett.* **20**, 3093 (1979).

0276-7333/84/2303-0440$01.50/0