Methods of Distinguishing between Cyano-stabilised Imino- and Methylene-phosphoranes. Crystal Structures of Adducts from Triphenylphosphine and Tetracyanoethylene (a Heptacyanocyclopentenyliminophosphorane) and from Triphenylphosphine and Dicyanoacetylene (a Hexacyanohexa-1,6-dienediphosphorane)

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Cyano-stabilised methylene- and imino-phosphoranes may be distinguished by the much faster rate of alkaline hydrolysis of the former and also by the position of the long-wavelength bands in their u.v. spectra, if the anion is delocalised over two or more multiple bonds. The adduct from triphenylphosphine and tetracyanoacetylene has been shown to be 2,3,3,4,4,5,5-heptacyanocyclopentenyliminotriphenylphosphorane. The molecular structure of this adduct (4) and also of (6), 1,2,3,4,5,6-hexacyanohexa-2,4-diene-1,6-diylidenebis(triphenylphosphorane), have been determined by X-ray crystallography.

We have previously determined the structure of a number of adducts derived from phosphines and electrophilic acetylenes.[1] Continuing our interest in this area we have studied the adduct from triphenylphosphine and tetracyanoethylene which was originally prepared by Reddy and Weiss.[2]
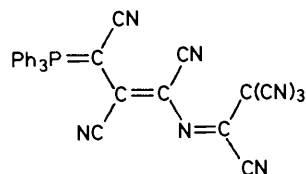
The adduct is derived from one molecule of triphenylphosphine and two molecules of tetracyanoethylene. It was originally assigned the five-co-ordinate structure (1) on the basis of its i.r. spectrum, its acid hydrolysis to butanetetracarboxylic acid, its assumed conversion to an iminoether, and the similarity of its [31]P n.m.r. chemical
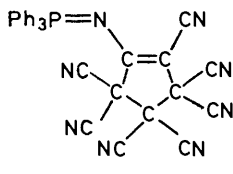

(1)

(2)

(3)

(4)
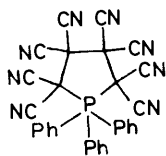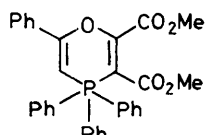
shift (δ_P 22 p.p.m.) † with that of the phosphorane (2), a structure which was later shown to be incorrect.[3] Hall and co-workers[4] used an optically active phosphine and found that the activity was retained in the adduct. These workers suggested the adduct was either the ylide (3) or the iminophosphorane (4), preferring the latter structure which was originally considered but dismissed by Reddy and Weiss.

† Positive chemical shifts, δ_P, are downfield of 85% phosphoric acid.

Little is known of the relative properties of stabilised imino- and methylene-phosphoranes and therefore a comparative study of model compounds was undertaken. Twenty-seven of these were prepared and their chemical and spectroscopic properties determined. In general, the methylenephosphoranes were more basic than their imino-analogues. However, when the anion was delocalised by two or more mesomerically electron-accepting groups, both types of compound resisted protonation. Zinc and acetic acid reduced both methylene and imino-phosphoranes but the products were difficult to identify. The [31]P n.m.r. chemical shifts were recorded and found to cover a similar range for both series. Protonation of the basic phosphoranes usually produced larger downfield shifts for the imino-compounds but the effect was not consistent. The i.r. spectra were recorded. All the compounds gave bands in both the ν(P=N) region (1 400—1 150 cm^{-1}) and the ν(P=C) region (900—800 cm^{-1}).[5]

U.v. spectroscopy provided the best physical method

TABLE 1

Long-wavelength u.v. absorption bands ($\lambda_{max.}$/nm) of weakly and strongly stabilised methylene- and imino-phosphoranes; $\varepsilon_{max.} \times 10^{-3}$ in parentheses

Iminophosphoranes	$\lambda_{max.}$	Methylenephosphoranes	$\lambda_{max.}$
Ph₃PNPh	305 (5.0)	Ph₃PCHPh	323
Ph₃PNC(CN)C(CN)₂	303 (13.4)	Ph₃PCHC(CN)C(CN)₂	417 (26.0)
Ph₃PNCN	304 (5.5)	Ph₃PCHCN	303 (1.8)
Adduct (4)	303 (5.74)	Ph₃PCPhC(CN)C(CN)₂	415) (15.6
Ph₃PNC(CN)CHCN	305 (14.3)	Ph₃PC(CN)C(CN)C(CN)₂	405) (19.0)

of distinguishing between the two types of compound. Table 1 shows that within the iminophosphorane series studied the long-wavelength band appears at the same

[1] N. E. Waite, D. W. Allen, and J. C. Tebby, *Phosphorus,* 1971, **1**, 139; M. A. Shaw and R. S. Ward, *Topics in Phosphorus Chem.,* 1975, **7**, 1.

[2] G. S. Reddy and C. D. Weiss, *J. Org. Chem.,* 1963, **28**, 1823.

[3] J. B. Hendrickson, C. D. Hall, R. Rees, and J. F. Templeton, *J. Org. Chem.,* 1965, **30**, 3312.

[4] M. P. Naan, R. L. Powell, and C. D. Hall, *J. Chem. Soc. (B),* 1971, 1683.

[5] L. C. Thomas, ' Interpretations of the Infrared Spectra of Organophosphorus Compounds,' Heydon, 1974, p. 87; W. Weigrabe, H. Bock, and W. Luttke, *Chem. Ber.,* 1966, **97**, 3737; W. Wiegrabe and H. Bock, *ibid.,* 1968, **101**, 1414; W. Luttke and K. Wilhelm, *Angew. Chem. Internat. Edn.,* 1965, **4**, 875.

position ($\lambda_{max.}$ 304 $\pm$ 1 nm) whereas for the methylene-phosphoranes the band is shifted to longer wavelength as the chromophore is extended.

The rates of alkaline hydrolysis of most of the cyano-stabilised imino- and methylene-phosphoranes were determined by following the decrease in the intensity of the u.v. long-wavelength absorption, except for *N*-cyanoiminotriphenylphosphorane, where the broad nature of the band caused it to overlap that of triphenyl-phosphine oxide. In this case the hydrolysis was followed by the disappearance of the conjugated cyanide band in the i.r. spectrum. The rate constants and half-lives presented in Table 2 show that the iminophos-

TABLE 2

Rates of hydrolysis of selected cyano-stabilised imino- and methylene-phosphoranes using excess of 0.01M-NaOH at 20 °C

	Pseudo-first-order rate constant/s^{-1}	Half-life/s
Ph$_3$PNC(CN)C(CN)$_2$	0.0016	417
Ph$_3$PCHC(CN)C(CN)$_2$	0.22	3.2
Ph$_3$PNC(CN)CH(CN)	0.0037	186
Adduct (4)	0.0028	251
Ph$_3$PC(CN)C(CN)C(CN)$_2$	0.212	3.3
Ph$_3$PNCN	0.0046	150
Ph$_3$PCH(CN)	0.23	<3

phoranes were hydrolysed much more slowly than the methylenephosphoranes. The iminophosphoranes have half-lives >150 s, whereas the methylenephosphoranes have half-lives of *ca.* 3 s. The adduct from triphenyl-phosphine and tetracyanoethylene was hydrolysed by aqueous alkali with a half-life of 250 s. It was not protonated by perchloric acid and there was a band at $\lambda_{max.}$ 303 nm in its u.v. absorption spectrum. The lack of protonation of the adduct indicates that if it was a methylenephosphorane it would have an extended conjugated chromophore, such as that in structure (3),
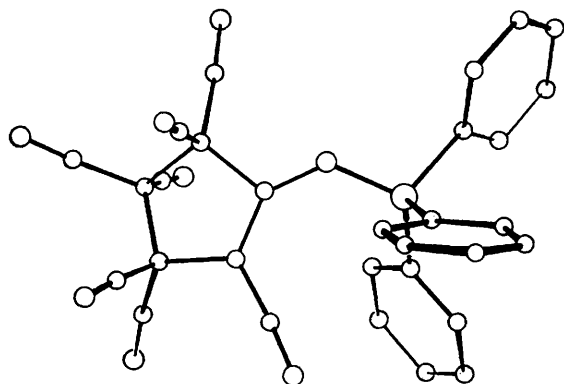

FIGURE 1   Perspective drawing of the triphenylphosphine–tetracyanoethylene adduct (4)

and would absorb above 400 nm. Thus the data indicates that the adduct is an imino- rather than a methylene-phosphorane.

X-Ray crystallographic analysis has established that the adduct has the cyclopentenyliminophosphorane

⁶ I. Kawamoto, T. Hata, Y. Kishida, and C. Tamura, *Tetrahedron Letters*, 1971, 2417; W. Dreissig, H. J. Hecht, and K. Plieth, *Z. Krist.*, 1973, **137**, 132.

structure (4); Figure 1 is a perspective drawing of the molecule. Tables 3 and 4 list bond lengths and angles,
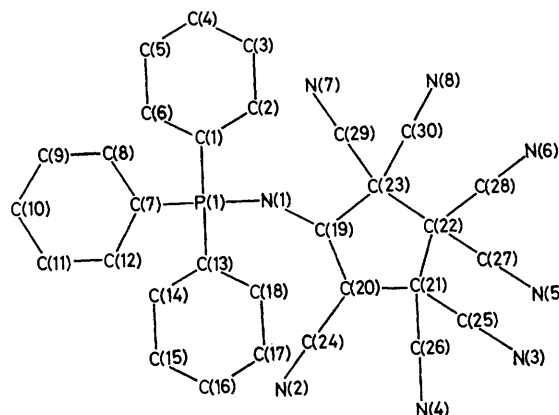

FIGURE 2   Crystallographic numbering system of the triphenylphosphine–tetracyanoethylene adduct (4)

and Table 5 a selection of torsion angles. Figure 2 shows the crystallographic numbering system.

TABLE 3

Bond lengths (Å) of adduct (4), with standard deviations in parentheses

P(1)–N(1)	1.615(2)	C(18)–C(13)	1.397(4)
P(1)–C(1)	1.792(2)	N(1)–C(19)	1.317(2)
P(1)–C(7)	1.789(2)	C(19)–C(20)	1.372(3)
P(1)–C(13)	1.793(2)	C(20)–C(21)	1.524(3)
C(1)–C(2)	1.388(3)	C(20)–C(24)	1.417(3)
C(2)–C(3)	1.389(4)	C(24)–N(2)	1.143(3)
C(3)–C(4)	1.377(4)	C(21)–C(22)	1.580(3)
C(4)–C(5)	1.386(4)	C(21)–C(25)	1.478(3)
C(5)–C(6)	1.381(4)	C(21)–C(26)	1.483(3)
C(6)–C(1)	1.396(3)	C(25)–N(3)	1.140(3)
C(7)–C(8)	1.389(3)	C(26)–N(4)	1.134(3)
C(8)–C(9)	1.393(3)	C(22)–C(23)	1.574(3)
C(9)–C(10)	1.379(3)	C(22)–C(27)	1.472(3)
C(10)–C(11)	1.377(3)	C(22)–C(28)	1.481(3)
C(11)–C(12)	1.392(3)	C(27)–N(5)	1.138(3)
C(12)–C(7)	1.389(3)	C(28)–N(6)	1.129(3)
C(13)–C(14)	1.390(3)	C(23)–C(19)	1.560(3)
C(14)–C(15)	1.397(4)	C(23)–C(29)	1.471(3)
C(15)–C(16)	1.372(5)	C(23)–C(30)	1.477(3)
C(16)–C(17)	1.384(5)	C(29)–N(7)	1.137(3)
C(17)–C(18)	1.389(4)	C(30)–N(8)	1.138(3)

This is the first crystallographic study of a cyano-stabilised iminophosphorane although two cyano-stabilised methylenephosphoranes have been previously examined.[6] The P–N bond length [1.615(2) Å] in the adduct (4) is typical of other stabilised iminophosphor-anes [7] and the anion delocalisation has the expected effect of lengthening the C(19)–C(20) and C(24)–N(2) multiple bonds and shortening the N(1)–C(19) and C(20)–C(24) single bonds. There is also a slight shorten-ing of the C(20)–C(21) bond 1.524(3) Å compared to the remaining saturated C–C bonds (mean 1.57 Å) in the cyclopentene ring. It is interesting to note that the phosphorus atom is only slightly distorted (7.1°) from the plane of the NC:CCN conjugated system which assists the delocalisation of the negative charge on nitrogen. The P–N–C bond angle (130°) is larger than in the less-stabilised iminophosphorane (5); [8] the contri-

⁷ T. S. Cameron and C. K. Prout, *J. Chem. Soc.* (*C*), 1969, 2285.
⁸ M. J. E. Hewlins, *J. Chem. Soc.* (*B*), 1971, 942.

bution of a second plane of d_π–p_π PN bonding has been discussed in terms of the P–N–C bond angle [9] although

TABLE 4

Bond angles (°) of adduct (4), with standard deviations in parentheses

N(1)–P(1)–C(1)	109.7(1)	N(1)–C(19)–C(20)	137.8(2)
N(1)–P(1)–C(7)	107.6(1)	N(1)–C(19)–C(23)	115.6(2)
N(1)–P(1)–C(13)	114.1(1)	C(20)–C(19)–C(23)	106.6(2)
C(1)–P(1)–C(7)	107.6(1)	C(19)–C(20)–C(21)	113.9(1)
C(1)–P(1)–C(13)	111.3(1)	C(19)–C(20)–C(24)	128.9(2)
C(7)–P(1)–C(13)	106.2(1)	C(21)–C(20)–C(24)	117.1(2)
P(1)–C(1)–C(2)	119.2(2)	C(20)–C(21)–C(22)	101.3(2)
P(1)–C(1)–C(6)	120.4(2)	C(20)–C(21)–C(25)	110.5(2)
C(2)–C(1)–C(6)	120.0(2)	C(20)–C(21)–C(26)	113.5(2)
C(1)–C(2)–C(3)	119.7(2)	C(22)–C(21)–C(25)	113.3(2)
C(2)–C(3)–C(4)	119.9(3)	C(22)–C(21)–C(26)	112.1(2)
C(3)–C(4)–C(5)	120.1(3)	C(25)–C(21)–C(26)	106.4(2)
C(4)–C(5)–C(6)	120.3(2)	C(21)–C(22)–C(23)	102.2(2)
C(5)–C(6)–C(1)	119.6(2)	C(21)–C(22)–C(27)	115.2(2)
P(1)–C(7)–C(8)	120.9(2)	C(21)–C(22)–C(28)	108.8(2)
P(1)–C(7)–C(12)	119.4(2)	C(23)–C(22)–C(27)	111.7(2)
C(8)–C(7)–C(12)	119.7(2)	C(23)–C(22)–C(28)	106.8(2)
C(7)–C(8)–C(9)	119.8(2)	C(27)–C(22)–C(28)	111.5(2)
C(8)–C(9)–C(10)	120.3(2)	C(22)–C(23)–C(19)	101.6(1)
C(9)–C(10)–C(11)	120.1(2)	C(22)–C(23)–C(29)	112.7(2)
C(10)–C(11)–C(12)	120.2(2)	C(22)–C(23)–C(30)	111.2(2)
C(11)–C(12)–C(7)	119.9(2)	C(19)–C(23)–C(29)	115.5(2)
P(1)–C(13)–C(14)	121.3(2)	C(19)–C(23)–C(30)	107.7(2)
P(1)–C(13)–C(18)	118.3(2)	C(29)–C(32)–C(30)	108.0(2)
C(14)–C(13)–C(18)	120.3(2)	C(20)–C(24)–N(2)	174.7(2)
C(13)–C(14)–C(15)	119.4(3)	C(21)–C(25)–N(3)	174.0(3)
C(14)–C(15)–C(16)	120.1(3)	C(21)–C(25)–N(4)	175.8(3)
C(15)–C(16)–C(17)	120.9(3)	C(22)–C(28)–N(6)	175.4(2)
C(16)–C(17)–C(18)	119.8(3)	C(22)–C(27)–N(5)	174.4(2)
C(17)–C(18)–C(13)	119.5(3)	C(23)–C(30)–N(18)	117.9(2)
P(1)–N(1)–C(19)	130.0(1)	C(23)–C(29)–N(7)	175.4(2)

steric effects cannot be ignored in this case. The cyclopentane ring is close to planarity with the C(22) atom tilted 36° out of the plane.

isation of the anion and also delocalisation of the positive charge on phosphorus by back-bonding from nitrogen. This pathway also involves least rearrangement of the reactants. Reaction of phosphorus(III) atoms with electronegative atoms is well established [11] and triphenylphosphine has been shown to attack the nitrogen atoms of diazo compounds when a stabilised ion is produced.[12]

We have previously studied a similar cyano-stabilised adduct formed in the reaction of triphenylphosphine

TABLE 5

Selected torsion angles (°) of adduct (4)

N(1)–P(1)–C(1)–C(2)	21.2
C(18)–C(13)–P(1)–N(1)	35.3
N(1)–P(1)–C(7)–C(12)	61.4
P(1)–N(1)–C(19)–C(20)	7.1
P(1)–N(1)–C(19)–C(23)	–176.1
N(1)–C(19)–C(20)–C(24)	11.3
N(1)–C(19)–C(20)–C(21)	–171.5
C(23)–C(19)–C(20)–C(21)	11.5
C(19)–C(20)–C(21)–C(22)	12.7
C(23)–C(22)–C(21)–C(20)	–30.8
C(19)–C(23)–C(22)–C(21)	37.5
C(22)–C(23)–C(19)–N(1)	151.3
C(22)–C(23)–C(19)–C(20)	–30.9

and dicyanoacetylene. The adduct was assigned the 1,6-dimethylenephosphorane structure (6) on the basis of i.r., n.m.r., and mass spectral data.[13] It has a strong u.v. absorption at 485 nm (ε 21 800) which, from the foregoing study, is also in accordance with the methylenephosphorane structure (6). A crystallographic study was undertaken in order to confirm the structure and determine the stereochemistry of this novel structure.
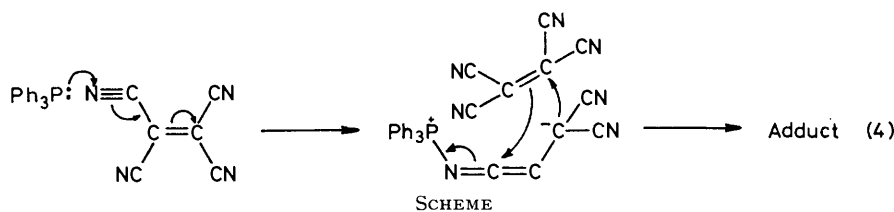
SCHEME

We consider that the adduct (4) is formed via the mechanism shown in the Scheme. Although there are

(5)   (6)
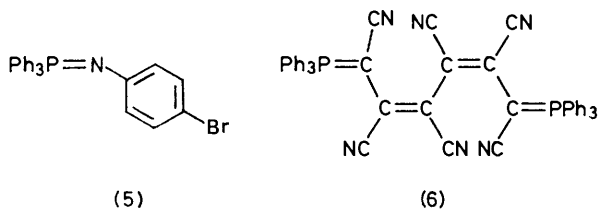
many examples of similar reactions proceeding by attack at the ethylenic carbon,[10] the attack at nitrogen gives an intermediate in which there is extensive delocal-

X-Ray crystallographic analysis has established that the triphenylphosphine–dicyanoacetylene adduct has the 1,6-dimethylenephosphorane structure (6); Figure 3 is a perspective drawing of the molecule looking down the y axis with, for clarity, only one atom of each phenyl ring shown. Tables 6 and 7 list bond lengths and angles and Table 8 contains a selection of torsion angles. Figure 4 shows the crystallographic numbering system.

The most important structural features are the cis-geometry about the β–γ carbon–carbon bonds C(20)–C(21), and the cisoid conformation of the molecule as a whole which originates from the stereochemistry about the C(21)–C(21)* bond. This central bond [1.476(5) Å] is not significantly longer than that normal for a conjugated system (1.46 Å), and the attached atoms are

[9] G. W. Adamson and J. C. J. Bart, Chem. Comm., 1969, 1036; A. W. Schlueter and R. A. Jacobsen, J. Chem. Soc. (A), 1968, 2317.
[10] L. Horner and K. Klupfel, Annalen, 1955, 591, 69; F. Ramirez, J. F. Pilot, and C. P. Smith, Tetrahedron, 1968, 24, 3735.
[11] H. Hoffmann and H. J. Diehr, Angew. Chem. Internat. Edn., 1964, 3, 737.

[12] B. H. Freeman, D. Lloyd, and M. C. Singer, Tetrahedron, 1974, 30, 211; A. W. Johnson, ' Ylid Chemistry,' Academic Press, 1966.
[13] M. A. Shaw, J. C. Tebby, R. S. Ward, and D. H. Williams, J. Chem. Soc. (C), 1968, 1609.

only 61° from a planar *cisoid* conformation. Although the suggested mechanism of formation of the diphosphorane (6) involves the *cis*-addition of dicyanoacetylene
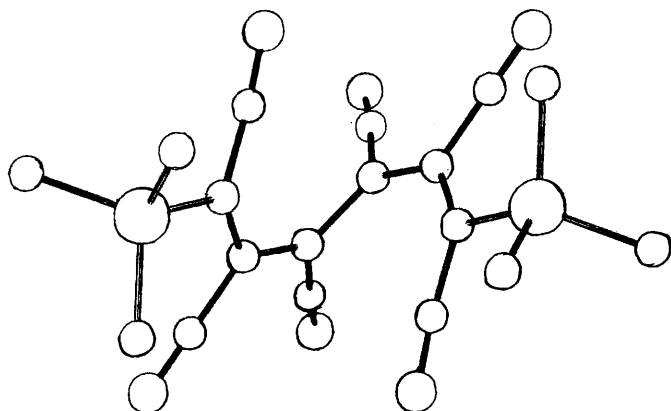

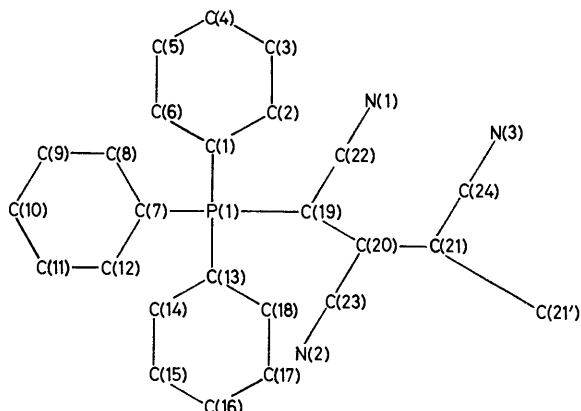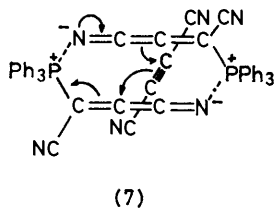FIGURE 3 Perspective drawing of the 1,6-dimethylenephosphorane (6)

FIGURE 4 Crystallographic numbering system of the 1,6-dimethylenephosphorane (6)

to a dimer of the 1 : 1 phosphine–acetylene intermediate,[13] as shown in (7), the stereochemistry is probably governed by other factors.

(7)

EXPERIMENTAL

Tetracyanoethylene (m.p. 200 °C, sealed tube) was purified by sublimation. I.r. spectra were recorded on a Perkin-Elmer 457 spectrometer, and u.v. spectra on a Perkin-Elmer 402 instrument. Proton n.m.r. spectra were measured on a JEOL MH 100 spectrometer.

2,3,3,4,4,5,5-*Heptacyanocyclopentenyliminotriphenyl-phosphorane* (4).—This was prepared from triphenylphosphine (5.8 g, 22 mmol) and tetracyanoethylene (5.2 g, 40 mmol) according to the method of Reddy and Weiss.[2] Recrystallisation gave buff crystals (8.8 g, 80%), m.p. 164—165 °C (lit.,[2] 168—170 °C) (Found: C, 69.4; H, 3.5; N, 21.4. $C_{30}H_{15}N_8P$ requires C, 69.5; H, 3.4; N, 21.6%);

$\nu_{max.}$ (KBr disc) 3 080w, 2 245w, 2 198s, 1 580s, 1 437s, 1 385s, 1 115s, 997s, 905s, 810s, 790s, 750s, 745s, and 728s cm⁻¹; $\lambda_{max.}$ (CH_2Cl_2) ($\varepsilon_{max.} \times 10^{-3}$), 238 (12.30), 268 (8.10), 277 (7.40), and 303 (5.74) nm.

Reduction of the Adduct (4).—The adduct (4) (5.2 g, 10 mmol) in chloroform (150 ml) was heated under reflux with

TABLE 6

Bond lengths (Å) of the 1,6-diphosphorane (6), with standard deviations in parentheses

P(1)–C(1)	1.802(3)	C(13)–C(14)	1.387(6)
P(1)–C(7)	1.805(4)	C(14)–C(15)	1.388(6)
P(1)–C(13)	1.779(4)	C(15)–C(16)	1.375(6)
P(1)–C(19)	1.761(4)	C(16)–C(17)	1.377(7)
C(1)–C(2)	1.376(5)	C(17)–C(18)	1.365(6)
C(2)–C(3)	1.376(6)	C(18)–C(13)	1.395(4)
C(3)–C(4)	1.354(8)	C(19)–C(20)	1.423(5)
C(4)–C(5)	1.357(7)	C(20)–C(21)	1.373(5)
C(5)–C(6)	1.375(6)	C(21)–C(21ᴵ) *	1.476(5)
C(6)–C(1)	1.384(6)	C(19)–C(22)	1.417(5)
C(7)–C(8)	1.388(5)	C(20)–C(23)	1.427(6)
C(8)–C(9)	1.385(7)	C(21)–C(24)	1.421(5)
C(9)–C(10)	1.384(9)	C(22)–N(1)	1.153(5)
C(10)–C(11)	1.358(8)	C(23)–N(2)	1.136(7)
C(11)–C(12)	1.398(8)	C(24)–N(3)	1.158(6)
C(12)–C(7)	1.384(6)		

* C(21ᴵ) is at 1 − x, y, 0.5 − z

TABLE 7

Bond angles (°) of the 1,6-diphosphorane (6), with standard deviations in parentheses

C(1)–C(1)–C(7)	106.3(2)	P(1)–C(13)–C(14)	121.2(3)
C(1)–P(1)–C(13)	110.3(2)	P(1)–C(13)–C(18)	118.6(3)
C(1)–P(1)–C(19)	111.3(2)	C(14)–C(13)–C(18)	120.3(4)
C(7)–P(1)–C(13)	109.6(2)	C(13)–C(14)–C(15)	119.7(3)
C(7)–P(1)–C(19)	110.9(2)	C(14)–C(15)–C(16)	119.0(4)
C(13)–P(1)–C(19)	108.4(2)	C(15)–C(16)–C(17)	121.4(5)
P(1)–C(1)–C(2)	119.7(3)	C(16)–C(17)–C(18)	120.1(4)
P(1)–C(1)–C(6)	120.5(3)	C(17)–C(18)–C(13)	119.5(4)
C(2)–C(1)–C(6)	119.8(3)	P(1)–C(19)–C(20)	126.6(3)
C(1)–C(2)–C(3)	118.8(4)	P(1)–C(19)–C(22)	113.4(3)
C(2)–C(3)–C(4)	121.5(5)	C(20)–C(19)–C(22)	118.3(3)
C(3)–C(4)–C(5)	119.4(4)	C(19)–C(20)–C(21)	125.6(3)
C(4)–C(5)–C(6)	120.7(5)	C(19)–C(20)–C(23)	119.5(3)
C(5)–C(6)–C(1)	119.7(4)	C(21)–C(20)–C(23)	114.9(3)
P(1)–C(7)–C(8)	120.7(3)	C(20)–C(21)–C(24)	121.2(3)
P(1)–C(7)–C(12)	119.4(3)	C(20)–C(21)–C(21ᴵ)	124.5(3)
C(8)–C(7)–C(12)	119.9(4)	C(24)–C(21)–C(21ᴵ)	114.3(3)
C(7)–C(8)–C(9)	119.9(5)	C(19)–C(22)–N(1)	176.0(3)
C(8)–C(9)–C(10)	119.9(5)	C(20)–C(23)–N(2)	176.3(4)
C(9)–C(10)–C(11)	120.4(5)	C(21)–C(24)–N(3)	174.7(5)
C(10)–C(11)–C(12)	120.5(6)		
C(10)–C(12)–C(7)	119.4(4)		

TABLE 8

Selected torsion angles (°) of the 1,6-diphosphorane (6)

C(2)–C(1)–P(1)–C(19)	− 158.1
C(8)–C(7)–P(1)–C(19)	− 118.8
C(14)–C(13)–P(1)–C(19)	− 124.0
C(1)–P(1)–C(19)–C(20)	− 91.4
C(7)–P(1)–C(19)–C(20)	150.5
C(13)–P(1)–C(19)–C(20)	30.1
P(1)–C(19)–C(20)–C(21)	− 171.8
C(19)–C(20)–C(21)–C(21ᴵ)	7.3
C(20)–C(21)–C(21ᴵ)–C(20ᴵ) *	61.0

* C(20ᴵ) is at 1 − x, y, 0.5 − z.

zinc powder (4 g) and acetic acid (5 ml) for 30 min. The reduced product precipitated from the filtered solution by addition of diethyl ether. Recrystallisation from aqueous alcohol gave N-[1-(2-aminomethyl)hexacyanocyclopentane]-aminotriphenylphosphonium acetate (4.0 g 70%), m.p. 278—280 °C (Found: C, 67.4; H, 4.35; N, 20.1. $C_{32}H_{25}$-N_8O_2P requires C, 67.7; H, 4.4; N, 19.7%); $\nu_{max.}$ (KBr disc) 3 500m, 3 350br,m, 3 050m, 2 980w, 2 250m, 1 740s,

1 670s, 1 580s, 1 445s, 1 125s, 950ms, 850m, 765m, and 750s cm⁻¹; $\tau(CF_3CO_2H)$ 2.2—2.5 (15 H, br,s), 4.6 (1 H, dd, $^3J_{PNCH}$ 15.0, $^3J_{HCCH}$ 7.0 Hz), 5.1 (1 H, m), 6.8 (3 H, s), and 7.7 (2 H, br,m).

N-*Tricyanovinyliminotriphenylphosphorane.*— Tetra-cyanoethylene (2.5 g, 20 mmol) in dry benzene (100 ml) was added dropwise to a stirred solution of iminotriphenyl-phosphorane [14] (5.4 g, 20 mmol) in dry benzene to give a buff-coloured solid (2.5 g). After Soxhlet extraction with benzene colourless crystals were obtained (1.5 g, 56%), m.p. 198—200 °C (lit.,[15] 192—194 °C) (Found: C, 72.6; H, 3.85; N, 14.45. Calc. for $C_{23}H_{15}N_4P$: C, 73.0; H, 3.95; N, 14.8%); $\nu_{max.}$ (KBr disc) 3 060w, 2 225s, 2 215s, 2 190m, 1 575br,m, 1 500br,m, 1 435s, 1 395s, 1 250s, 1 113s, 1 000m, 877s, 760ms, and 732s cm⁻¹; $\lambda_{max.}$ (CH$_2$Cl$_2$) ($\varepsilon_{max.}$ × 10⁻³), 233 (18.5), 268 (7.90), 276 (7.02), and 303 (13.40) nm.

Reduction of N-*Tricyanovinyliminotriphenylphosphorane.* —This was reduced as described for the adduct (4) and prepared as a colourless solid, m.p. 285—287 °C (Found: C, 69.85; H, 6.65; N, 12.65; $C_{23}H_{29}N_4O_2P$ requires C, 67.8; H, 6.46; N, 12.5%); $\nu_{max.}$ (KBr disc) 3 450br,m, 3 320m, 3 060w, 2 920w, 2 860w, 2 250w, 1 675s, 1 585s, 1 440s, 1 120s, 950ms, 845m, 760m, and 750s cm⁻¹; $\tau(CF_3CO_2H)$ 2.3—2.6 (15 H, br, s), 4.7 (1 H, br, dd, $^3J_{PNCH}$ *ca.* 15.0, $^3J_{HCCH}$ *ca.* 9.0 Hz), 5.15 (1 H, br,m), 6.85 (3 H, s), and 7.75 (4 H, br,m).

Tetracyanoallylidenetriphenylphosphorane.—This was pre-pared by the method of Trippett,[16] m.p. 239—240 °C (lit.,[16] 239—240 °C); $\nu_{max.}$ (KBr disc) 3 050w, 2 230w, 2 210s, 2 195m, 2 182s, 1 463s, 1 435s, 1 364ms, 1 133m, 1 103s, 996mw, 810s, 752s, and 720s cm⁻¹; $\lambda_{max.}$ (CH$_2$Cl$_2$) ($\varepsilon_{max.}$ × 10⁻³) 230 (44.60), 268 (6.25), 276 (4.35), 401 (6.3), and 405 (19.0) nm.

Reduction of Tetracyanoallylidenetriphenylphosphorane.— This was reduced by the method described for the adduct (4). The product was a colourless solid, m.p. 262—265 °C (Found: C, 68.9; H, 6.75; N, 12.05. $C_{27}H_{33}N_4O_2P$ requires C, 68.1; H, 6.94; N, 11.78%); $\nu_{max.}$ (KBr disc) 3 315br,m, 3 295br,m, 3 040w, 3 000w, 2 930w, 2 220w, 1 680br,m, 1550br,s, 1 440s, 1 055s, 1 028s, 950s, 880w, and 750mw cm⁻¹; $\tau(CF_3CO_2H)$ 2.25—2.55 (15 H, br, s), 4.5 (1 H, br,m), 5.25 (1 H, br,m), 6.75 (3 H, s), and 7.65 (6 H, br,m).

N-*Cyanoiminotriphenylphosphorane.*—This was prepared from iminotriphenylphosphorane [14] and cyanogen bromide by the method of ref. 17 and recrystallised from benzene, m.p. 194—196 °C (lit.,[18] 195 °C).

2,3,3'-*Tricyanovinylbenzylidenetriphenylphosphorane.*— Benzylidenetriphenylphosphorane [19] (1.75 g, 5 mmol) in dry tetrahydrofuran (50 ml) was added dropwise to a solution of tetracyanoethylene (0.65 g, 5 mmol) in dry benzene (400 ml) with stirring. Recrystallisation of the precipitate from ethanol–light petroleum gave yellow crystals (1.9 g, 86%), m.p. 248—250 °C (Found: C, 79.4; H, 4.35; N, 9.40. $C_{30}H_{20}N_3P$ requires C, 79.5; H, 4.42; N, 9.28%); $\nu_{max.}$ (KBr disc) 3 060w, 2 238w, 2 200s, 2 180s, 1 587m, 1 500s, 1 474s, 1 440s, 1 360ms, 1 193w, 1 163w, 1 100s, 1 063m, 1 000ms, 903m, 815s, 750w, 745s, and 725s cm⁻¹; $\lambda_{max.}$ (CH$_2$Cl$_2$) ($\varepsilon_{max.}$ × 10⁻³) 236 (15.0), 265 (6.1), 269 (8.8), 297 (5.1), and 415 (15.6) nm.

2-*Cyanovinyliminotriphenylphosphorane.*— Methyltri-phenylphosphonium bromide [20] (4.5 g, 12 mmol) suspended in dry ether under nitrogen was treated with butyl-lithium (6 ml of 15% solution in hexane) (0.8 g, 15 mmol) with stirring. After 30 min cyanogen was added at room temperature until the yellow colour of methylenetriphenyl-phosphorane was removed. The buff-coloured precipitate was filtered off under nitrogen and dried *in vacuo* to give a hygroscopic buff-coloured powder, m.p. 210—214 °C (Found: C, 77.1; H, 4.85; N, 8.85. $C_{21}H_{17}N_2P$ requires C, 76.7; H, 5.18; N, 8.53%); $\nu_{max.}$ (KBr disc) 3 040w, 2 960w, 2 900w, 2 195s, 1 590w, 1 480m, 1 438s, 1 340s, 1 110s, 1 005m, 910ms, 760m, 745m, and 720s cm⁻¹.

Cyanomethyliminotriphenylphosphorane.— Chloroaceto-nitrile (0.75 g, 10 mmol) was added to a solution of imino-triphenylphosphorane [14] (2.8 g, 10 mmol) in dry tetrahydro-furan under nitrogen and the solution stirred for 1 h. The precipitated conjugate acid of compound (11) was collected, dried, and dissolved in dry acetonitrile. Butyl-lithium (5 ml of a 15% solution in hexane) (0.7 g, 12 mmol) was added with stirring under nitrogen. After 1 h the solution was filtered under nitrogen and the acetonitrile solvent removed by rotary evaporation to give the product as colourless crystals (2.2 g, 68%), m.p. 286—287 °C (sealed tube); $\nu_{max.}$ (KBr disc under nitrogen) 3 060w, 2 930w, 2 240w, 1 580m, 1 480m, 1 435s, 1 295s, 1 115s, 1 000ms, 850m, 845m, and 750s cm⁻¹; $\tau(CF_3CO_2D)$ 2.3—2.5 (15 H, m) and 5.1 (2 H, d, *J* 16.0 Hz). The compound was too unstable for us to obtain reproducible elemental analyses.

Alkaline Hydrolysis of Imino- and Methylene-phosphoranes. —A stock solution of each compound listed in Table 4 (1 × 10⁻³M in ethanol–water, 19 : 1) was prepared. The optical density of the long-wavelength absorption was calibrated directly with solutions of known concentration. Equal volumes of the stock solution and sodium hydroxide solution (0.01M in 95% ethanol) were mixed and the decrease in intensity of the long-wavelength absorption recorded by a driven chart at this fixed wavelength. The times taken for the absorption curve to reach the intensities of the successive half-concentrations were plotted against $\log_e$ of each con-centration. Linear plots were obtained and the half-lives were calculated from the slope (k) by use of the equation $k_{\frac{1}{2}} = 0.693/k$. The rate constant and half-lives are given in Table 4.

Alkaline Hydrolysis of N-*Cyanoiminotriphenylphos-phorane.*—Standard solutions were used to relate directly concentrations with the intensity of the i.r. absorption band at 2 180 cm⁻¹. The hydrolysis was performed in an infrasil cell and the decrease in intensity of the $\nu(CN)$ 2 180 cm⁻¹ band recorded by driven chart at this fixed wavelength. The rate constant and the half-life were calculated as already described.

X-*Ray Crystallographic Analysis of the Triphenylphos-phine–Tetracyanoethylene Adduct* (4).—Cell parameters were first determined from oscillation and Weissenberg photo-graphs and then by least squares from the setting angles of 14 reflections on a Hilger and Watts four-circle diffracto-meter.

[14] L. Birkofer and A. Ritter, *Angew. Chem. Internat. Edn.*, 1965, **4**, 417.

[15] R. Partos and K. Ratts, *J. Amer. Chem. Soc.*, 1966, **89**, 4996; N. Zhmurova and R. S. Yurchenko, *Zhur. obshchei. Khim.*, 1968, **38**, 592.

[16] S. Trippett, *J. Chem. Soc.*, 1962, 4733.

[17] A. Schmidpeter and D. Ebeling, *Chem. Ber.*, 1968, **101**, 2602.

[18] M. E. Hermes and F. D. Marsh, *J. Amer. Chem. Soc.*, 1964, **86**, 4506.

[19] S. O. Grim, A. W. Yankowsky, S. A. Bruno, W. J. Bailey, E. F. Davidoff, and T. J. Marks, *J. Chem. and Eng. Data*, 1970, **15**, 497.

[20] V. Mark, C. Dungan, M. Crutchfield, and J. Van Wazer, *Topics in Phosphorus Chem.*, 1967, **5**, 227.

TABLE 9

Fractional co-ordinates ($\times 10^4$) of the adduct (4), with standard deviations in parentheses

Atom	x/a	y/b	z/c
P(1)	7 267(0)	4 013(0)	3 473(0)
C(1)	6 651(1)	4 232(1)	4 545(2)
C(2)	6 741(2)	5 102(2)	5 054(2)
C(3)	6 283(2)	5 265(2)	5 904(2)
C(4)	5 742(2)	4 566(2)	6 239(2)
C(5)	5 647(2)	3 698(2)	5 728(2)
C(6)	6 106(2)	3 522(2)	4 890(2)
C(7)	7 727(1)	2 836(1)	3 626(2)
C(8)	7 514(2)	2 169(2)	2 826(2)
C(9)	7 887(2)	1 260(2)	2 962(2)
C(10)	8 462(2)	1 019(2)	3 890(2)
C(11)	8 670(2)	1 676(2)	4 687(2)
C(12)	8 307(2)	2 589(2)	4 559(2)
C(13)	6 498(2)	4 031(1)	2 227(2)
C(14)	5 556(2)	3 840(2)	2 157(2)
C(15)	4 996(2)	3 787(2)	1 163(3)
C(16)	5 376(2)	3 927(2)	267(2)
C(17)	6 313(2)	4 125(2)	330(2)
C(18)	6 881(2)	4 174(2)	1 312(2)
C(19)	8 173(1)	5 595(1)	3 155(2)
C(20)	7 567(1)	6 257(1)	2 651(2)
C(21)	8 042(1)	7 104(1)	2 232(2)
C(22)	9 076(1)	6 736(1)	2 336(2)
C(23)	9 157(1)	6 058(1)	3 322(2)
C(24)	6 584(2)	6 271(2)	2 512(2)
C(25)	7 612(2)	7 316(2)	1 131(2)
C(26)	7 977(2)	7 986(1)	2 844(2)
C(27)	9 795(1)	7 479(1)	2 488(2)
C(28)	9 154(1)	6 132(1)	1 412(2)
C(29)	9 941(2)	5 394(2)	3 387(2)
C(30)	9 271(1)	6 604(2)	4 317(2)
N(1)	8 134(1)	4 735(1)	3 545(1)
N(2)	5 794(1)	6 355(2)	2 386(2)
N(3)	7 205(2)	7 477(2)	311(2)
N(4)	7 870(2)	8 660(2)	3 289(2)
N(5)	10 371(2)	8 025(2)	2 686(2)
N(6)	9 199(2)	5 622(2)	744(2)
N(7)	10 586(2)	4 931(2)	3 455(2)
N(8)	9 329(2)	7 020(2)	5 084(2)

TABLE 10

Fractional co-ordinates ($\times 10^4$) of the 1,6-diphosphorane (6), with standard deviations in parentheses

Atom	x/a	y/b	z/c
P(1)	3 397(1)	4 779(1)	1 839(1)
C(1)	2 520(2)	4 507(3)	1 122(2)
C(2)	2 074(3)	5 354(3)	764(2)
C(3)	1 394(3)	5 129(5)	234(3)
C(4)	1 163(3)	4 100(5)	50(3)
C(5)	1 611(3)	3 267(4)	395(3)
C(6)	2 289(3)	3 460(4)	936(2)
C(7)	3 840(2)	5 958(3)	1 543(2)
C(8)	3 958(3)	6 892(3)	1 971(2)
C(9)	4 299(3)	7 789(4)	1 735(3)
C(10)	4 545(3)	7 740(4)	1 086(3)
C(11)	4 406(3)	6 842(5)	653(3)
C(12)	4 045(3)	5 938(4)	873(2)
C(13)	3 159(3)	5 055(3)	2 694(2)
C(14)	2 387(2)	5 075(3)	2 742(2)
C(15)	2 222(3)	5 261(4)	3 423(2)
C(16)	2 831(3)	5 456(4)	4 034(2)
C(17)	3 598(3)	5 443(4)	3 987(2)
C(18)	3 768(2)	5 237(3)	3 324(2)
C(19)	4 044(2)	3 670(3)	1 970(2)
C(20)	4 075(2)	2 801(3)	2 478(2)
C(21)	4 641(2)	2 012(3)	2 636(2)
C(22)	4 423(2)	3 538(3)	1 389(2)
C(23)	3 474(2)	2 698(3)	2 864(2)
C(24)	4 552(2)	1 082(3)	3 055(2)
N(1)	4 690(2)	3 444(3)	887(2)
N(2)	2 993(2)	2 558(3)	3 161(3)
N(3)	4 528(2)	289(3)	3 380(3)

Crystal data. $C_{30}H_{15}N_8P$, $M = 518.5$. Monoclinic, $a = 14.594(3)$, $b = 14.112(2)$, $c = 12.833(3)$ Å, $\beta = 99.63(2)°$,

$U = 2 605.7$ Å^3, $D_c = 1.322$ g cm^{-3}, $Z = 4$, $D_m = 1.33$ g cm^{-3}, $F(000) = 1 064$. Space group $P2_1/c$ from systematic absences. Cu-K_α radiation (nickel filter), $\lambda = 1.5418$ Å; μ(Cu-K_α) = 12.24 cm^{-1}.

TABLE 11

[31]P n.m.r. chemical shifts data for alkyl- and amino-phosphonium salts, methylene- and imino-phosphoranes

$Ph_3\overset{+}{P}CH_3Br^-$	22.7 [a]
Ph_3PCH_2	20.3 [c]
$Ph_3\overset{+}{P}CH_2Ph\ Br^-$ [d]	23.5
Ph_3PCHPh	7.1 [f]
$Ph_3\overset{+}{P}CH_2COPh\ Cl^-$ [g]	26.5
$Ph_3PCHCOPh$ [i]	21.0
$Ph_3\overset{+}{P}CH_2CO_2Et\ Cl^-$ [j]	21.5
Ph_3PCHCO_2Et [j]	18.0
$Ph_3\overset{+}{P}CH_2CN\ Cl^-$ [g]	24.5
Ph_3PCHCN [g]	22.5
$Ph_3PCHC(CN)C(CN)_2$ [l]	23.5
$Ph_3\overset{+}{P}CH(CN)_2\ Cl^-$ [n]	29.0
$Ph_3PC(CN)_2$ [n]	27.2
$Ph_3PC(CN)COCO_2Me$ [p]	24.5
$Ph_3PC(Ph)C(CN):C(CN)_2$ [p]	22.0
$Ph_3\overset{+}{P}NH_2\ Cl^-$ [b]	36.0
Ph_3PNH [b]	-2.0
$Ph_3\overset{+}{P}NHPh\ Cl^-$ [e]	34.0
Ph_3PNPh [e]	2.0
$Ph_3\overset{+}{P}NHCOPh\ Cl^-$ [h]	25.5
$Ph_3PNCOPh$ [h]	21.5
$Ph_3\overset{+}{P}NHCO_2Et\ Cl^-$ [k]	23.0
Ph_3PNCO_2Et [k]	20.0
$Ph_3\overset{+}{P}NHCN\ Br^-$	38.0
Ph_3PNCN (9)	27.0
$Ph_3PNC(CN):C(CN)_2$ [m]	24.5
$Ph_3PNC(CN):CH(CN)$ [o]	21.0
$Ph_3PNC(CN):CH_2$	14.0
$Ph_3\overset{+}{P}NHCH_2CN\ Cl^-$	36.0
Ph_3PNCH_2CN	23.0

[a] Ref. 19. [b] Ref. 13. [c] S. O. Grim, W. McFarlane, and T. J. Marks, *Chem. Comm.*, 1967, 1191; T A. Albright and E. E. Schweizer, *J. Org. Chem.*, 1976, 41, 1168. [d] F. Ramirez, O. P. Madan, and C. P. Smith, *Tetrahedron*, 1966, 22, 567. [e] W. Wiegrabe and H. Bock, *Chem. Ber.*, 1968, 7, 661. [f] Ref. 18. [g] S. Trippett and D. Walker, *J. Chem. Soc.*, 1959, 3874. [h] H. H. Wassermann and R. C. Koch, *Chem. Ind.*, 1956, 1014. [i] G. Aksnes, *Acta. Chem. Scand.*, 1961, 15, 692. [j] G. Aksnes, *ibid.*, 1961, 15, 438. [k] H. R. Kricheldorf, *Synthesis*, 1972, 12, 695. [l] E. Zbiral, *Monatsh.*, 1965, 96, 1967. [m] Ref. 14. [n] L. Horner and H. Oediger, *Chem. Ber.*, 1958, 91, 37. [o] E. Ciganek, *J. Org. Chem.*, 1970, 35, 3631. [p] E. Ciganek, *J. Org. Chem.*, 1970, 35, 1725.

Reflections were measured out to $\theta \leqslant 75°$ by the ω—2θ scan mode. 4 223 planes having a net count $\geqslant 3\sigma$ were deemed observed. Lorentz polarisation but not absorption corrections were made. The structure was solved routinely by direct methods by use of MULTAN [21] and was refined without difficulty by block-diagonal least-squares. In the later stages a weighting scheme of the form $w = 1$ for $F_0 < A$ and $w = (A/F_0)^2$ when $F_0 > A$, the value of A was 20.0. Hydrogen atoms were included in calculated positions but were not refined. At convergence the conventional R was 4.7%.

Table 9 shows the fractional co-ordinates of the atoms. With the exception of MULTAN all calculations were made

[21] G. Germain, P. Main, and M. M. Wolfson, *Acta Cryst.*, 1971, A27, 368.

by use of the ' X-Ray '70 ' program system.[22] Observed and calculated structure factors and thermal parameters for both compounds [(4) and (6)] are available in Supplementary Publication No. SUP 22217 (28 pp., 1 microfiche).*

X-*Ray Crystallographic Analysis of the Dimethylene-phosphorane* (6).—Cell parameters were determined as before from the setting angles of 23 reflections.

Crystal data. $C_{48}H_{30}N_6P_2$, $M = 752.7$. Monoclinic, $a = 17.628(2)$, $b = 12.365(2)$, $c = 18.616(3)$ Å, $\beta = 104.57(2)°$, $U = 3\,927.2$ Å^3, $D_c = 1\,273$ g cm^{-3}, $Z = 4$, $D_m = 1.26$ g cm^{-3}, $F(000) = 1\,560$. Space group Cs/c from systematic absences. Mo-K_α radiation (graphite monochromator) $\lambda = 0.710\,69$ Å; $\mu(\text{Mo-}K_\alpha) = 1.14$ cm^{-1}.

The preliminary photographs had shown that the crystal was not single, but no better sample was obtainable and it proved possible to collect data from one of the component crystals with no obvious interference from the other components. Reflections were scanned (ω—2θ mode) out to $\theta \leqslant 25°$. 3 485 observable reflections were measured of which 2 041 having a net count $>3\sigma$ were deemed observed. Lorentz polarisation but not absorption corrections were applied.

* For details of Supplementary Publications see *J.C.S. Perkin I*, 1977, Index issue.

The structure was solved by use of the centrosymmetric direct methods program SHELX, which revealed the molecule lying on the two-fold axis at $x = 0.5$, $z = 0.25$. Refinement proceeded normally. In the final stages hydrogen atoms were included in calculated positions with U 0.05. The final weighting scheme was of the form $\omega = 1/(1 + [(F - B)/A]^2)$ with $B = A = 25.0$. The refinement with non-hydrogen atoms treated anisotropically was in three blocks, and the final R value was 6.1%. The perspective drawing was obtained by use of the PLUTO program.[23] Table 10 displays the fractional co-ordinates of the atoms.

For both structures intramolecular contacts were greater than the sum of van der Waals radii.

[31]P *N.m.r. Analysis.*—The spectra of the alkyl- and amino-phosphonium salts and their corresponding methylene- and imino-phosphoranes (usually in chloroform solution) were determined on a Perkin-Elmer R10 spectrometer operating at 24.6 MHz. The ^{31}P chemical shifts are given in Table 11.

[22] 1970 Revision of ' X-Ray 67,' eds. J. M. Stewart, F. A. Kundall, and J. C. Baldwin, University of Maryland Technical Report TR 6758, 1967.
[23] Cambridge Data Centre Program ' PLUTO,' W. D. S. Motherwell, personal communication.