440 ($M^+ + 2$, 8), 438 (M^+, 8), 299 (26), 175 (92), 167 (33), 155 (87), 148 (96), 41 (100). Anal. ($C_{20}H_{23}BrO_6$) C, H.

γ-Lactone 13. A mixture of crude keto acid **6** (55 mg, 0.15 mmol) and triphenylphosphine (50 mg, 0.15 mmol) in 5 mL of carbon tetrachloride was first heated at 45 °C for 24 h and then at reflux for 6 h. Solvent was then removed in vacuo to give a foamy residue, which was dissolved in ether and saturated sodium bicarbonate. After the layers were separated, the organic fraction was dried ($MgSO_4$) and then concentrated to give an oil. This was chromatographed on a 20 × 20 × 0.1 cm silica gel plate with 25% ethyl acetate in hexane as solvent. γ-Lactone **13** was isolated (48 mg, 87%) as an oil which crystallized on storage. Recrystallization from methylene chloride–heptane gave white needles: mp 126–128 °C; NMR ($CDCl_3$) δ 0.82 (d, 3, $J = 7$ Hz); 0.96–1.70 (m, 7), 1.90–2.20 (m, 1), 2.53 (br s, 2), 2.51–3.20 (m, 3), 3.62 (s, 3), 6.00 (s, 2), 6.59 (d, 1, $J = 8$ Hz), 6.62 (br s, 1), 6.80 (d, 1, $J = 8$ Hz); IR ($CHCl_3$) 1785, 1740, 1515, 1500, 1455, 1260 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 360 (M^+, 7), 176 (20), 162 (9), 149 (32), 148 (100). Anal. ($C_{20}H_{24}O_6$) C, H.

2-Methoxy-5β-methyl-4α-(3,4-(methylenedioxy)phenyl-6-propylcyclohepta-2,6-dienone (15). A solution of the bromo γ-lactone **12** (439 mg, 1 mmol) and 0.5 N potassium hydroxide (16 mL) in tetrahydrofuran (10 mL) was stirred under an argon blanket for 1 h and then diluted with brine. The aqueous mixture was extracted thoroughly with ether; the ethereal solution was dried ($MgSO_4$) and evaporated in vacuo to give 271 mg of oily enol **14**: NMR ($CDCl_3$) δ 3.76 (d of d, 1, $J = 4$ Hz, 9 Hz); IR ($CHCl_3$) 3400, 1645, 1600 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 300 (M^+, 16), 135 (100).

The crude product was dissolved in 7 mL of dimethylformamide and to this was added excess silver(I) oxide (0.8 g) and methyl iodide (1 mL). The resulting suspension was stirred vigorously at room temperature for 20 h; insoluble materials were filtered and washed thoroughly with ethyl acetate and water. After the layers were partitioned, the organic phase was washed three times with water and then dried ($MgSO_4$). Removal of solvent gave a pale oil. Filtration through a short column of silica gel with 25% ethyl acetate in hexane gave dienone **15** (213 mg, 68% from **12**) as an oil which crystallized on storage. Recrystallization from ether–hexane gave an analytical sample: mp 75–77 °C; NMR (CCl_4) δ 0.69 (br t, 3, $J = 7$ Hz), 0.81–1.22 (m, 2), 1.33 (d, 3, $J = 7$ Hz), 1.84 (br t, 2, $J = 7$ Hz), 2.40–2.73 (m, 1), 3.62 (s, 3), 3.66 (d of d, 1, $J = 4$ Hz, 9 Hz; one set is underneath the methyl signal), 5.42 (d, 1, $J = 9$ Hz), 5.81 (br s, 1), 5.93 (s, 2), 6.64 (br s, 3); IR ($CHCl_3$) 1655, 1640, 1510, 1495, 1260 cm^{-1}; UV (95% EtOH) 255 nm (ϵ 11 900), 283 (6500) 315 (sh, 3100); mass spectrum (70 eV), m/e (relative intensity) 314 (M^+, 69), 300 (10), 299 (49), 271 (28), 175 (100). Anal. ($C_{19}H_{22}O_4$) C, H.

2-Methoxy-5-methyl-4-(3,4-(methylenedioxy)phenyl)-6-propyltropone (17). A mixture of the dienone **15** (43 mg, 0.137 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (37 mg, 0.16 mmol) in dry benzene (8 mL) was heated at reflux for 6 h under an atmosphere of nitrogen. After the mixture cooled, ether was added and the solution was washed successively with saturated sodium bicarbonate and brine and then dried ($MgSO_4$). Evaporation of the solvent gave an oil which was chromatographed on a 20 × 20 × 0.1 cm silica gel plate with 50% ethyl acetate in methylene chloride as solvent. Pure tropone **17** (33.9 mg, 80%) was isolated as an oily solid. Crystallization from ether–hexane–methylene chloride gave small plates: mp 148–50 °C; NMR ($CDCl_3$) δ 1.02 (br t, 3, $J = 7$ Hz), 1.46–1.80 (m, 2), 2.09 (s, 3), 2.62 (br t, $J = 7$ Hz), 3.84 (s, 3), 6.07 (s, 2), 6.58–6.73 (m, 3), 6.90 (d, 1, $J = 8$ Hz), 7.30 (s, 1); IR ($CHCl_3$) 1605, 1595, 1560, 1510, 1500, 1480, 1440, 1245, 1200 cm^{-1}; UV (95% EtOH) 248 nm (ϵ 35 000), 320 (sh, 10 600), 348 (11 600); mass spectrum (70 eV), m/e (relative intensity) 312 (M^+, 47), 285 (21), 284 (100). Anal. ($C_{19}H_{20}O_4$) C, H.

Acknowledgment. We thank the National Institutes of Health (GM 09868) and the Hoffmann-La Roche Foundation for financial support. High-resolution mass spectra were provided by the facility, supported by the National Institutes of Health (Grant RR 00317; principal investigator, Professor K. Biemann) from the Biotechnology Resources Branch, Division of Research Resources.

Registry No. **3**, 75522-10-0; **4**, 67271-93-6; **5**, 120-58-1; **6**, 75522-11-1; **7**, 75522-12-2; **8**, 75522-13-3; **11**, 75522-14-4; **12**, 75522-15-5; **13**, 75522-16-6; **14**, 75533-61-8; **15**, 75522-17-7; **17**, 75522-18-8; 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 84-58-2.

Synthetic, Structural, and Chemical Study of the 1,2-Diphosphetene Ring

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Received May 15, 1980

Synthesis of the diphosphetene ring by reaction of substituted acetylenes with cyclopolyphosphines was reinvestigated. In addition, a conversion of triphospholenes into diphosphetenes by lithium cleavage followed by ring closure with phosgene was devised. Thus, the two first alkyl-*C*-substituted diphosphetenes were obtained. The X-ray crystal structure of tetraphenyldiphosphetene is described. No cyclic delocalization takes place within the ring. The cyclic strain is probably minimized owing to a P—P bent bond and a predistorsion of the C=C double bond geometry by the bulky C substituents. Some reactions of tetraphenyldiphosphetene are also described including their ring cleavage by lithium and their complexation by iron carbonyls. At 150 °C, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ cleave the P—P bond to yield a phosphido-bridged $LFe_2(CO)_6$ complex through an intermediate complex of unknown structure. An excess of iron carbonyl then causes expulsion of the tolane subunit and gives a previously described phenylphosphinidene complex, $(PhP)_2[Fe(CO)_3]_3$.

Among the various carbon–phosphorus monocyclic compounds known up to now only a few possess a 6π-electron system capable of giving rise to a cyclic delocalization. Phospholes and phosphorins have been studied in depth mainly in view of their possible aromaticity. On the other hand, practically nothing is known about the chemistry of the 1,2-diphosphetene ring **1** in spite of its discovery in 1964.[2] In fact, only two such compounds are known where $R = R^1 = CF_3$ (**1a**)[2] and $R = R^1 = Ph$ (**1b**).[3] Besides this, a brief study has appeared on the metal

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[1] (a) Laboratoire CNRS-SNPE. (b) Institut de Chimie des Substances Naturelles.

[2] W. Mahler, *J. Am. Chem. Soc.*, **86**, 2306 (1964).

[3] A. Ecker and U. Schmidt, *Chem. Ber.*, **106**, 1453 (1973).

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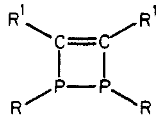
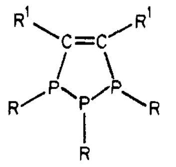


1a, R = R¹ = CF_3
b, R = R¹ = C_6H_5
c, R = C_6H_5; R¹ = C_2H_5
d, R = C_6H_5; R¹ = H
e, R = C_6H_5; R¹ = t-C_4H_9

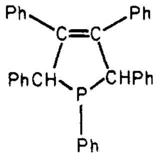


2a, R = R¹ = CF_3
b, R = R¹ = C_6H_5
c, R = C_6H_5; R¹ = C_2H_5
d, R = C_6H_5; R¹ = H
e, R = C_6H_5; R¹ = t-C_4H_9

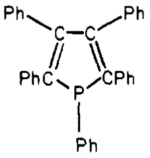
complexes of **1a**.[4] In view of this we decided to launch a thorough study of this ring. Special attention has been paid to possible electronic delocalization and to the consequences of cyclic strain.

Results and Discussion

Synthesis. According to Ecker and Schmidt,[3] the reaction of pentaphenylcyclopentaphosphine with tolane around 155–170 °C gave **1b** isolated as such in 11% maximum yield together with pentaphenyl-1,2,3-triphospholene (**2b**) isolated as its 1,3-disulfide in 5.5% yield and 1,2,3,4,5-pentaphenylphosphol-3-ene (**3**) isolated as its 1-oxide in ca. 0.5% yield.



3



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As a first step we have reinvestigated this reaction at various temperatures and for various ratios of $(PhP)_5$ and tolane. Our results were quite different from those of Ecker and Schmidt. Some of them are collected in Table I.

Our main product was always **2b** isolated as such in yields as high as 75%. The diphosphetene **1b** was isolated in 15% maximum yield and the only recovered byproduct was pentaphenylphosphole **4** which was fully characterized after isolation in ca. 2–3% yield. The phosphole was easily detected on a TLC sheet by its strong fluorescence under UV. In our opinion the 1,2,3,4,5-pentaphenylphosphol-3-ene 1-oxide isolated by Ecker and Schmidt did not result from the oxidation of the corresponding tervalent phospholene **3**, the formation of which would be very difficult to explain, but from the hydration of pentaphenylphosphole **4**. Indeed, such hydrations have been described previously in the literature.[5]

We then decided to check the scope of this synthesis of the diphosphetene ring by studying the reaction of $(PhP)_5$ with some alkyl-substituted acetylenes. At 170 °C for 48 h, the reaction of $(PhP)_5$ with $t\text{-BuC}{\equiv}\text{C-}t\text{-Bu}$ gave the expected diphosphetene **1e** in 30% yield (eq 1). The corresponding triphospholene **2e** was not detected. Obviously the steric bulk of the *tert*-butyl groups favored formation of the diphosphetene ring; this point will be discussed again in the next section. By contrast with 3-hexyne, the only fully characterized nonpolymeric product which was obtained was the triphospholene **2c**, and we were unable to identify the expected diphosphetene **1c**.

$$(PhP)_5 + R^1C{\equiv}CR^1 \xrightarrow{170\ ^\circ C} \mathbf{1} + \mathbf{2} \qquad (1)$$

$$R^1 = t\text{-Bu: } \mathbf{1e}, 30\%;\ \mathbf{2e}, 0\%$$

$$R^1 = \text{Et: } \mathbf{1c}, 0\%;\ \mathbf{2c}, 36\%$$

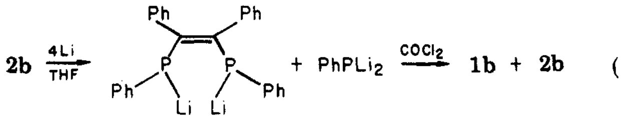
Table I. Reaction of Tolane with $(PhP)_5$

exptl conditions[a]	yield, % 1b	yield, % 2b
150 °C, 72 h	0	50
180 °C, 72 h	0	75
240 °C, 6 h	15	50
280 °C, 5 h	2	50

[a] After optimization, the molar ratio of tolane to $(PhP)_5$ was set at 1.20.

In fact by chromatography on silica gel we isolated a product which was eluted before **2c** (as expected for **1c**) but whose NMR spectrum showed ethylenic protons around 6 ppm exactly as if migration of the double bond had taken place from an endo- to an exocyclic position. We did not study this product further. However, at this point it was clear that the direct synthesis of the diphosphetene ring by reaction of cyclopolyphosphines with alkynes was of limited scope and seemed to be restricted to compounds substituted either by bulky or by electron-withdrawing R¹ groups.

Another synthesis of the diphosphetene ring was thus obviously needed. The triphospholene system was a logical starting point for that purpose since on the one hand it was generally by far the main product of the reaction of polyphosphines with alkynes and since on the other hand Baudler et al.[6] had shown that such species were also among the main products of the reaction of *cis*-1,2-dichloroalkenes with the dianions obtained by alkali metal cleavage of cyclopolyphosphines. Thus we decided to study the conversion of triphospholene **2b** into diphosphetene **1b**. We chose the following approach. The triphospholene **2b** was reacted with 4 equiv of lithium in THF at room temperature (eq 2). The resulting mixture was then reacted with a stoichiometric amount of phosgene. We thus obtained the expected diphosphetene **1b** contaminated with the starting triphospholene **2b**. The overall yield of **1b** was 25%.



(2)

We checked separately by TLC that the lithium cleavage was quantitative and that **2b** was re-formed during the final step. We then observed that when the lithium to magnesium exchange was performed by reacting $MgBr_2$ with the mixture of lithiophosphines before addition of phosgene, the re-formation of **2b** was minimized, and the diphosphetene yield reached 43%. Finally, by using the first procedure, we were able to obtain the unknown diphosphetene **1c** in 22% yield when starting from triphospholene **2c**. Then we attempted to prepare the first C-unsubstituted diphosphetene, **1d**. For that purpose we synthesized at first the corresponding unknown tri-

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(4) (a) A. H. Cowley and K. E. Hill, *Inorg. Chem.*, **12**, 1446 (1973). (b) While this manuscript was in the hands of the referees a new synthesis of the diphosphetene ring appeared in the literature; it relies upon the reaction of oxalyl chloride with bis(trimethylsilyl)phosphines; the yields are high but only diphosphetenes with R¹ = $OSiMe_3$ can be obtained: R. Appel and V. Barth, *Tetrahedron Lett.*, **21**, 1923 (1980).

(5) F. Mathey, *Tetrahedron*, **28**, 4171 (1972).

(6) M. Baudler and E. Tolls, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **33B**, 691 (1978).

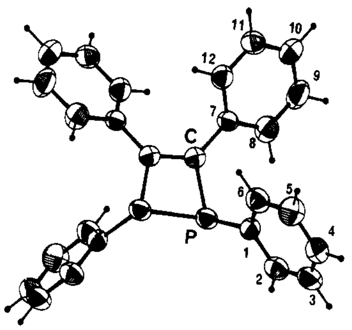


Figure 1. Structure of **1b**.

Table II. Final Atomic Coordinates ($\times 10^4$)[a]

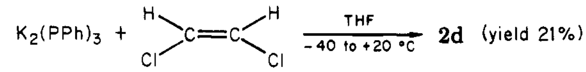
atom	x	y	z
P	3739.7 (1.0)	2605.6 (0.6)	7527.7 (0.6)
C	3173 (3)	2711 (2)	6438 (2)
C(1)	4077 (4)	3751 (2)	7909 (2)
C(2)	5021 (4)	3851 (3)	8592 (2)
C(3)	5319 (4)	4701 (3)	8920 (2)
C(4)	4678 (5)	5461 (3)	8586 (3)
C(5)	3745 (5)	5380 (3)	7910 (3)
C(6)	3439 (4)	4527 (2)	7570 (3)
C(7)	4040 (4)	3115 (2)	5761 (2)
C(8)	5581 (4)	3160 (3)	5798 (2)
C(9)	6395 (4)	3552 (3)	5165 (3)
C(10)	5688 (5)	3913 (3)	4482 (3)
C(11)	4161 (5)	3896 (3)	4438 (2)
C(12)	3355 (4)	3499 (3)	5067 (2)

[a] Estimated standard deviations in parentheses.

Table III. Bond Lengths (Å) with Esd's

P-C	1.830 (3)	C(4)-C(5)	1.376 (6)
P-C(1)	1.814 (4)	C(5)-C(6)	1.394 (5)
P-P	2.248 (1)	C(7)-C(8)	1.386 (5)
C-C(7)	1.464 (5)	C(7)-C(12)	1.393 (5)
C-C	1.358 (4)	C(8)-C(9)	1.378 (6)
C(1)-C(2)	1.394 (5)	C(9)-C(10)	1.373 (6)
C(1)-C(6)	1.387 (5)	C(10)-C(11)	1.373 (6)
C(2)-C(3)	1.381 (6)	C(11)-C(12)	1.372 (5)
C(3)-C(4)	1.365 (6)		

phospholene **2d** by using the method described by Baudler[6] for the analogous P-Me derivative (eq 3).



$$K_2(PPh)_3 + \mathrm{HClC{=}CClH} \xrightarrow[-40\ \text{to}\ +20\ ^\circ\mathrm{C}]{\text{THF}} \mathbf{2d}\ \text{(yield 21\%)} \qquad (3)$$

Unfortunately all our attempts to convert **2d** into **1d** by the procedure which was successfully used for the conversion of **2b** and **2c** into **1b** and **1c** failed. The only recovered product was always **2d** itself, suggesting a very low stability for **1d** (see the following section for a tentative explanation).

Crystal Structure of 1,2,3,4-Tetraphenyl-1,2-diphosphetene (1b). Figure 1 shows the structure of the molecule. Figure 2 shows the packing in the unit cell. The final coordinates, bond lengths and angles are given in Tables II-IV. The molecular geometry of **1b** is governed by its C_2 symmetry. The cycle is not planar: if we name MPP and MCC the middle points of the bonds P—P and C═C, then the dihedral angle P-MPP-MCC-C is 19°. The lone pairs of the P atoms are pointing to both sides of the four-membered cycle. The conformation of the P-P subunit is more precisely illustrated in Figure 3 by a Newman projection along the P-P bond. The approximately semieclipsed conformation very similar to that of tetracyclohexylbiphosphine[7] is clearly unfavorable for an aromatization of the molecule. This lack of aromaticity is also supported by the following observations: the C═C bond length [1.358 (4) Å] does not differ significantly from that found in *cis*-stilbene [1.334 (15) Å];[8] the P-C (cycle) bond length [1.830 (3) Å] is very close to the sum of the covalent radii of phosphorus and carbon (1.84 Å) and is even longer than the P-Ph bond length [1.814 (4) Å]. These results are in good agreement with the conclusions that Cowley et al.[9] drew from a photoelectron spectroscopic study of **1a** as illustrated by the following quotation: "It is interesting that only one lone pair signal was obtained from **1a**. This could be due to orthogonality of the two phosphorus lone pair orbitals, combined with a negligible coupling to the C═C π MO". The other problem of interest is centered on the cyclic strain within the diphos-

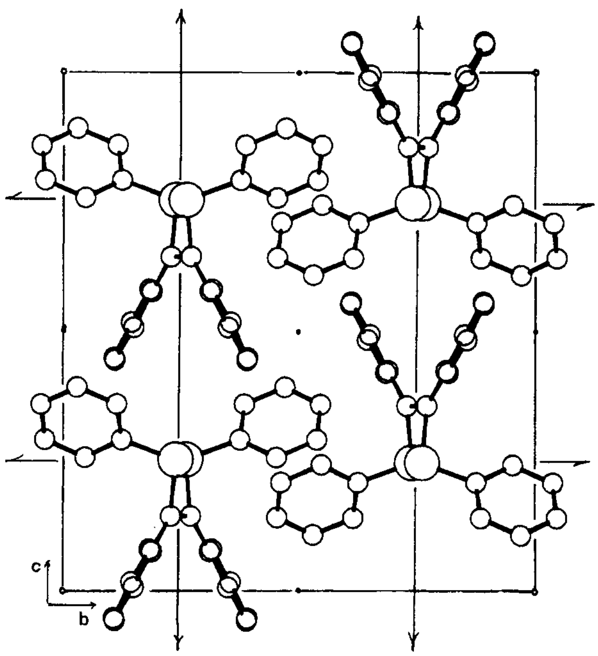


Figure 2. Packing in unit cell of **1b**.

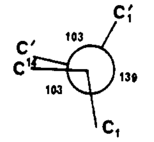


Figure 3. Newman projection along the P-P bond of **1b**.

Table IV. Interbond Angles (deg) with Esd's

C-P-C(1)	106.9 (1)	C(4)-C(5)-C(6)	120.4 (4)
C-P-P	74.7 (1)	C(1)-C(6)-C(5)	120.2 (4)
C(1)-P-P	107.0 (1)	C-C(7)-C(8)	121.3 (3)
P-C-C(7)	126.7 (2)	C-C(7)-C(12)	121.6 (3)
P-C-C	102.1 (2)	C(8)-C(7)-C(12)	117.1 (3)
C(7)-C-C	131.2 (3)	C(7)-C(8)-C(9)	121.2 (4)
P-C(1)-C(2)	117.7 (3)	C(8)-C(9)-C(10)	120.3 (4)
P-C(1)-C(6)	124.1 (3)	C(9)-C(10)-C(11)	119.7 (4)
C(2)-C(1)-C(6)	118.2 (3)	C(10)-C(11)-C(12)	119.8 (4)
C(1)-C(2)-C(3)	120.9 (4)	C(7)-C(12)-C(11)	121.8 (4)
C(2)-C(3)-C(4)	120.5 (4)		
C(3)-C(4)-C(5)	119.8 (4)		

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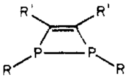
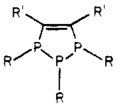
[7] Von R. Richter, J. Kaiser, J. Sieler, H. Hartung, and C. Peter, *Acta Crystallogr., Sect. B*, **B33**, 1887 (1977).

[8] M. Traetteberg and E. B. Frantsen, *J. Mol. Struct.*, **26**, 69 (1975).

[9] A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and M. C. Padolina, *J. Am. Chem. Soc.*, **96**, 3666 (1974). The lack of cyclic delocalization in diphosphetenes is also suggested by an ESR study of the anion radical of **1a**: T. C. Wallace, R. West, and A. H. Cowley, *Inorg. Chem.*, **13**, 182 (1974).

Table V. ^{31}P NMR Data[a] of Diphosphetenes and Triphospholenes

	R	R¹	no.	^{31}P	^1J(P-P)	ref
	CF_3	CF_3	1a	−40		2
	Ph	Ph	1b	−37.5		this work
	Ph	Et	1c	−32.2		this work
	Ph	*t*-Bu	1e	−51.4		this work
	CF_3	CF_3	2a	AB_2: ν_A −41 ν_B 55	220	2
	Ph	Ph	2b	ν_A −52.2 ν_B 47	250.6	this work
	Ph	Et	2c	ν_A −44.8 ν_B 41.5	242.5	this work
	Ph	H	2d	ν_A −25.2 ν_B 29.8	256.4	this work
	Me	H		ν_A −68.0 ν_B 11.3	236	6

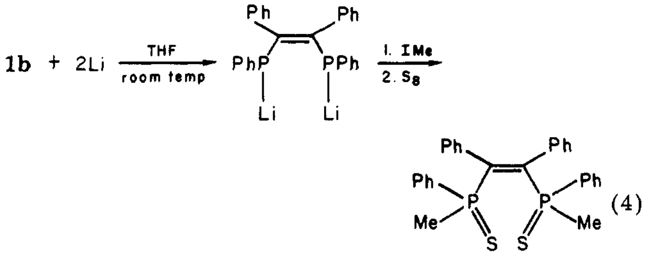
[a] In δ values; J values in hertz; 85% H_3PO_4 as external reference; positive values are for downfield shifts.

phetene ring. The geometry of the C=C double bond is strongly distorted as shown by the values of the Ph—C=C [131.2 (3)°] and P—C=C angles [102.1 (2)°]. In the same way the geometry of the P-P subunit is also distorted. The P-P bond length [2.248 (1) Å] is longer than usual for a biphosphine: Me_4P_2, 2.192 (9) Å;[10] $(C_6H_{11})_4P_2$, 2.215 (3) Å.[7] The bond angles around phosphorus also deviate from the normal values: in **1b**, P-P-C (cycle) = 74.7 (1)°, P-P-Ph = 107.0 (1)°; in gazeous Me_4P_2, P-P-C = 101.1 (7)°;[10] in crystalline $(C_6H_{11})_4P_2$,[7] P-P-C = 100.6 (3), 101.8 (3), 107.4 (3), and 108.0 (3)°. Clearly there is no significant distorsion of the P-P-Ph angle in **1b**, but, conversely, a drastic decrease of the P-P-C (cycle) angle is observed. From all these observations it appears that the diphosphetene ring is highly strained. At this point one question arises: if the four-membered cycle is very strained and if *no electronic stabilization (aromaticity)* operates within the ring, then why are diphosphetenes stable? We suggest two explanations: on comparison of the structure of *cis*-stilbene[8] with that of the PhC=CPh subunit in **1b**, it appears that practically no additional distorsion of the geometry of the double bond occurs when going from *cis*-stilbene to **1b**: PhC=C = 129.5 (7)° in *cis*-stilbene; Ph—C=C = 131.2 (3)° in **1b**. Thus it seems that C-substituents play a key role in the stability of the C_2P_2 cycle by "preforming" the needed C=C double bond geometry. Such an explanation is of no value for the Ph-P-P-Ph subunit. However, it must be remembered at this point that theoretical calculations have brought convincing evidence in favor of P-P bent bonds in the P_4 molecule.[11a] Phosphorus is able to minimize the strain by using its 3p orbitals. A similar explanation can be used for **1b**. If this is the case, then the s character of the lone pairs on the phosphorus atoms of **1b** is high, and some chemical consequences can be expected (for example a low basicity[11b]).

At the end of this section comment is made on the structure of triphospholenes **2b–d**. The ^{31}P NMR data (Table V) and especially the magnitudes of the $^1J(P\text{-}P)$ coupling constants imply the "all-trans" structure as already discussed in ref 6.

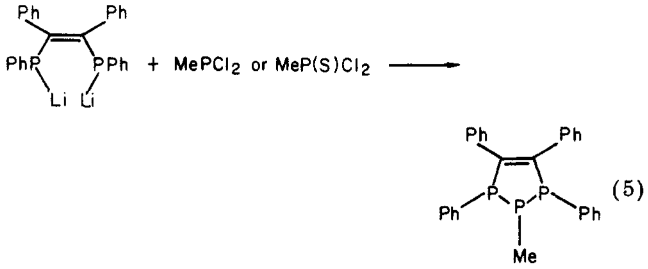
Chemical Reactivity. Ecker and Schmidt described only the reactions of **1b** with S_8 and H_2O_2.[3] We have completed their data by studying the reactions of **1b** with lithium and iron carbonyls.

Lithium in THF at room temperature cleaves the P-P bond of **1b**, but the reaction is more sluggish than with the corresponding triphospholene **2b** (eq. 4). By reaction of the dilithio compound thus obtained first with methyl iodide and then with sulfur, the two diastereoisomeric "cis" disulfides **5** were obtained in 89% combined yield.



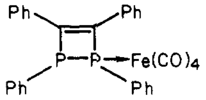
5

The dilithio compound also reacted with $MePCl_2$ or $MeP(S)Cl_2$ to give the corresponding triphospholene **6** in 35% yield (eq 5). The desulfuration which took place in the second case suggests that the central phosphorus of triphospholenes has a low nucleophilicity in the tervalent state. This suggestion is supported by the observation of Ecker and Schmidt[3] that reaction of **2b** with S_8 gives the 1,3-disulfide exclusively.



6

At room temperature **1b** reacted with $Fe(CO)_4{\cdot}THF$[12] to give a very unstable P→$Fe(CO)_4$ complex **7**, which was only characterized by its IR spectrum (cyclohexane): ν_{CO} 2050 (s), 1980 (s), 1950 cm^{-1} (vs). The spontaneous decomposition of **7** gave back **1b**, and thus we know that the



7

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[10] A. McAdam, B. Beagley, and T. G. Hewitt, *Trans. Faraday Soc.*, **66**, 2732 (1970).

[11] (a) See for example: M. F. Guest, I. H. Hillier, and V. R. Saunders, *J. Chem. Soc., Faraday Trans. 2*, **68**, 2070 (1972). (b) For a correlation of the basicity with the s character of the lone pair in P^{III} compounds, see H. Goetz, G. Frenking, and F. Marschner, *Phosphorus Sulfur*, 4, 309 (1978).

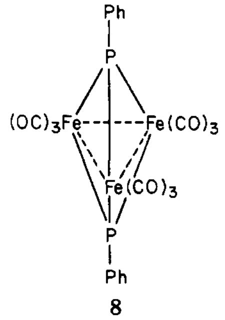
[12] F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 3438 (1974).

Table VI. Reaction of 1b with Iron Carbonyls

reagent	exptl conditions	product (yield, %)
$Fe_3(CO)_{12}$	90 °C, 1 h	**8** (5), **9** + **10** (60)
$Fe_3(CO)_{12}$	140 °C, 18 h	**8** (5), **9** (40)
$Fe_2(CO)_9$	80 °C, 5 h	**8** (5), **9** (3), **10** (75)
$Fe_2(CO)_9$	110 °C, 5 h	**8** (5), **9** (18), **10** (55)

diphosphetene ring is retained in **7**. By analogy with the corresponding complex of **1a**,[4] we assume that **7** is a mono complex. From the IR data it is obvious that the donor strength of **1b** is closer to that of Ph_3P[13] than to that of **1a**.[4]

The reaction of **1b** with Fe_2CO_9 or $Fe_3(CO)_{12}$ at higher temperature was much more interesting. Three complexes (**8**–**10**) were obtained (numbered according to decreasing R_f's in chromatography). Some experimental data are collected in Table VI. The following points are noteworthy: at 150 °C in xylene, **10** was converted into **9** in 75% yield; within 2 h at 150 °C in xylene, **9** reacted with $Fe_2(CO)_9$ to give **8** quantitatively; within 6 h at 150 °C in xylene, **10** reacted with $Fe_2(CO)_9$ to give **8** in only 50% yield together with **9** and **10**. These data indicate that **10** is the primary product around 80 °C whereas **8** is the final product around 150 °C if an excess of iron carbonyl is used. Complex **8** was easily identified since it has been previously described.[14] Its formula corresponds to the loss of the tolane subunit in **1b**. Its most characteristic feature is its very low field ^{31}P resonance: $\delta_{^{31}P}$ of **8** 316.3 (see ref 15).



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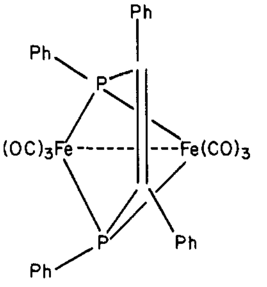

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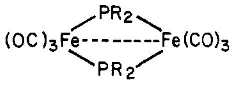
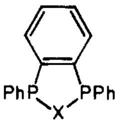


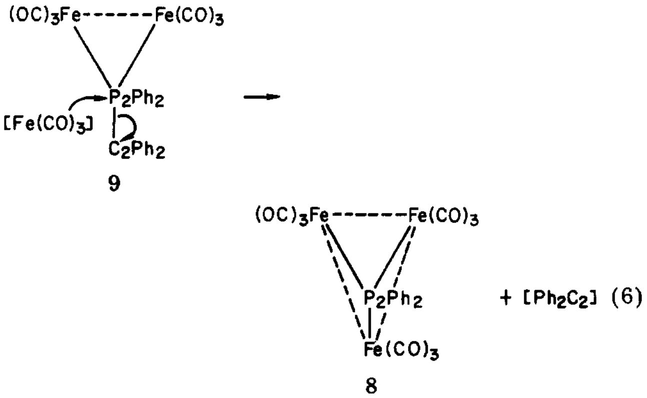
11

The structure of **9** was established beyond any doubt by elemental analysis and spectroscopy. Mass spectroscopy and elemental analysis indicate a $LFe_2(CO)_6$ formulation (L = **1b**). The cleavage of the P–P bond is shown by the close similarity of the IR and ^{31}P and ^{13}C NMR spectra to those of various authenticated phosphido-bridged complexes **11**: IR for **9** $\nu(CO)$ 2055 (m), 2015 (s), 1995 (s), 1970 (s), 1960 cm^{-1} (w) (cyclohexane); for **11** (PR_2 = P(Me)Ph sym)[16] $\nu(CO)$ 2055 (m), 2017 (s), 1996 (m), 1968 (m), 1960 cm^{-1} (w) (heptane); ^{13}C NMR for **9** $\delta(CO)$ 212.9 (C_6D_6); for **11** (PR_2 = PMe_2)[17] $\delta(CO)$ 212.7. A large downfield shift of the phosphorus resonance (105.8 ppm) was observed when converting **12** with X = PPh into **12** with X = $Fe_2(CO)_6$.[18] Thus, from the ^{31}P data of **2b** we calculate a ^{31}P shift of 152.8 ppm for **9**; the observed value is 152 ppm (C_6D_6).



12, X = PPh, $Fe_2(CO)_6$

The structure of **9** allows the easy visualization of its reaction with $Fe_2(CO)_9$ which leads to **8** by simple replacement of the Ph_2C_2 by a $Fe(CO)_3$ subunit (eq 6).



Unfortunately we have been unable to establish the structure of the primary complex **10**. The mass spectrum is very similar to that of **9**, but this indication is of no use since **10** is converted into **9** upon heating. The C, H, and P analysis seems to indicate a $LFe_2(CO)_6$ formulation, but the lower accuracy of the results cast some doubt upon this hypothesis. The ^{13}C NMR, ^{31}P NMR, and IR data are given in the Experimental Section but give no clue for our problem.

Investigations on the synthesis and chemistry of diphosphetenes are continuing.

Experimental Section

All reactions were performed under an argon atmosphere. Silica gel and solvents were used after being degassed with argon. Molecular weights were measured on a AEI-MS-30 mass spectrometer at 70 eV. ^1H NMR spectra were recorded on a R24A Perkin-Elmer spectrometer. ^{31}P spectra were run on a WP 90 Bruker spectrometer; ^{31}P chemical shifts are externally referenced to 85% H_3PO_4 and are positive for downfield shifts. IR spectra were recorded on a Perkin-Elmer Model 297 spectrometer.

Reaction of Acetylenic Compounds with Pentaphenylcyclopentaphosphine. A mixture of acetylenic compound and pentaphenylcyclopentaphosphine (molar ratio 6:5) was heated in a sealed tube. The yellow oil thus obtained was chromatographed on a silica gel column (50 g of silica gel/g of product) prepared in benzene–hexane (1:4). Results are given in Table VII.

Reaction of $LiP(C_6H_5)P(C_6H_5)P(C_6H_5)Li$ with *cis*-Dichloroethylene. A 0.212-g sample of lithium and 5 g of $(C_6H_5P)_5$ were stirred for 5 h in 50 mL of THF. The mixture was cooled at −40 °C, and 1.55 g of *cis*-ClCH=CHCl was added dropwise. The mixture was stirred for 15 h at room temperature. The solvent was evaporated, and the residue was chromatographed through a silica gel column prepared in benzene–hexane (1:4). Two products were recovered.

1,4-Diphenyldihydro-1,4-diphosphorin: 0.06 g (2.5% yield); mp 82 °C; mol wt 268; ^1H NMR δ 7.1–7.7 (m, 10 H, phenyl), 6.3 (t, J_{PH} = 22 Hz, 4 H ethylenic); ^{31}P NMR δ -43.8. Anal. Calcd: C, 71.64; H, 5.26; P, 23.10. Found: C, 71.50; H, 5.06; P, 23.06.

1,2,3-Triphenyl-1,2,3-triphospholene (**2d**): 1.12 g (21% yield); mp 79 °C; mol wt 350. Anal. Calcd: C, 68.58; H, 4.89; P, 26.53. Found: C, 68.05; H, 4.59; P, 26.40.

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[13] A. Reckzeigel and M. Bigorgne, *J. Organomet. Chem.*, **3**, 341 (1965).

[14] P. M. Treichel, W. K. Dean, and W. M. Douglas, *Inorg. Chem.*, **11**, 1609 (1972).

[15] J. P. Lampin and F. Mathey, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **282**, 979 (1976).

[16] P. M. Treichel, W. M. Douglas, and W. K. Dean, *Inorg. Chem.*, **11**, 1615 (1972).

[17] R. D. Adams, F. A. Cotton, W. R. Cullen, D. L. Hunter, and L. Mihichuk, *Inorg. Chem.*, **14**, 1395 (1975).

[18] R. B. King and R. H. Reimann, *Inorg. Chem.*, **15**, 184 (1976).

Table VII

			diphosphetene				triphospholene			
acetylenic compd	temp, °C	*t*, h	yield, %	mp, °C	anal. found (calcd)	mass	yield, %	mp, °C	anal. found (calcd)	mass
$C_6H_5C{\equiv}CC_6H_5$	240	6	15 (**1b**)[a]	159	C, 78.91 (79.19) H, 4.97 (5.08) P, 15.63 (15.74)	394	50 (**2b**)	129	C, 76.62 (76.49) H, 4.74 (4.98) P, 18.50 (18.52)	502
$C_2H_5C{\equiv}CC_2H_5$	170	72	0 (**1c**)				37 (**2c**)	oil	C, 70.58 (70.93) H, 6.02 (6.15) P, 22.67 (22.90)	406
$(CH_3)_3CC{\equiv}CC(CH_3)_3$	170	48	30 (**1e**)	115.5	C, 74.74 (74.56) H, 8.07 (7.96) P, 17.45 (17.51)	354	0 (**2e**)			

[a] Also pentaphenylphosphole 4: mp 257 °C; mol wt 464; 2% yield.

Synthesis of Diphosphetenes from Triphospholenes. A 5-mmol sample of triphospholene in 100 mL of THF and 20 mmol of lithium were stirred together for 15 h. The mixture became reddish black with pentaphenyltriphospholene (**2b**) and red with 1,2,3-triphenyl-4,5-diethyl-1,2,3-triphospholene (**2c**). When the lithium had disappeared, 20 mmol of $MgBr_2$ was added. After 1 h, 10 mmol of phosgene in toluene (20%) was added dropwise at room temperature. The mixture was stirred again for 2 h, the solvents were evaporated, and the residue was chromatographed through a silica gel column prepared in benzene–hexane (1:4). 1,2,3,4-Tetraphenyl-1,2-diphosphetene (**1b**) was obtained by this method in 43% yield. On the other hand, without $MgBr_2$, 1,2-diphenyl-3,4-diethyl-1,2-diphosphetene (**1c**) was obtained in 22% yield as a colorless oil: mol wt 298; ^1H NMR δ 7.3 -7.6 (m, 10 H, phenyl), 2.3 (m, 4 H, methylene), 1.0 (t, 6 H, methyl, $^3J_{HH}$ = 7 Hz). Anal. Calcd: C, 72.41; H, 6.76; P, 20.83. Found: C, 72.30; H, 6.42; P, 20.57.

Attempts to Prepare 1,2-Diphenyl-1,2-diphosphetene. The reaction of 5 mmol of **2d** with 20 mmol of lithium in 100 mL of THF was not complete after 15 h. Only 50% of the lithium had reacted. With potassium, 75% of the metal had reacted. The reaction was complete when the sodium–naphthalene anion radical was used. A 0.145-g sample of sodium and 0.850 g of naphthalene in 70 mL of THF were stirred for 5 h, 1.5 mmol of **2d** was then added, the mixture was stirred again for 15 h, and 2 g of $MgBr_2$ was added. The dark red reaction medium immediately became yellow and transparent. $COCl_2$ (3 mmol) in toluene (20%) was then added at room temperature. The mixture was stirred for 1 h. The only main product recovered after chromatography was **2d** (~20%).

Chemical Reactivity of Tetraphenyldiphosphetene. Reaction of Diphosphetene with Lithium. A 2.36-g sample of diphosphetene **1b** (6 mmol) and 0.084 g of lithium (12 mmol) in 100 mL of THF were stirred at room temperature for 15 h. ICH_3 (1.7 g, 12 mmol) in 20 mL of THF was added dropwise to the reddish black solution. The mixture was stirred for 2 h, and 0.4 g of sulfur was added. The solution was stirred overnight. The solvent was evaporated, and the residue was chromatographed through a silica gel column prepared in hexane. The excess sulfur was thus recovered; the column was then washed with ether–hexane (2:1), and 2.6 g of two solid diastereoisomers of $(C_6H_5)(CH_3)P(S)C(C_6H_5){=}C(C_6H_5)P(S)(C_6H_5)CH_3)$ (**5**, 89% yield) was recovered: mol wt 488; ^1H NMR δ 6.5–8 (m, 20 H, phenyl), 1.8 (d, J_{PH} = 13 Hz, 6 H, methyl, first diastereomer), 1.7 (d, J_{PH} = 13 Hz, 6 H, methyl, second diastereomer). Anal. Calcd: C, 68.83; H, 5.36. Found: C, 68.79; H, 5.10.

A 0.234-g sample of CH_3PCl_2 (2 mmol) in 5 mL of THF was added at -20 °C to a solution of 2 mmol of the dilithio compound prepared with 0.790 g of **1b** and 0.028 g of lithium in 50 mL of THF. The mixture was stirred for 3 h and warmed from -20 °C to room temperature. The solvent was removed, and the residue was chromatographed with benzene–hexane (1:4) to give 0.310 g (35% yield) of 1,3,4,5-tetraphenyl-2-methyl-1,2,3-triphospholene (**6**): mol wt 440; ^1H NMR δ 6.6–7.8 (m, 20 H, phenyl), 1.45 (dt, 3 H, methyl, $^2J_{PH}$ = 6.5 Hz, $^3J_{PH}$ = 16 Hz). Anal. Calcd: C, 73.63; H, 5.23. Found: C, 73.2; H, 4.9.

The same reaction was performed with 0.3 g of $CH_3P(S)Cl_2$, and 0.180 g (20% yield) of **6** was recovered.

Reaction of Diphosphetene with $Fe(CO)_4$·THF. $Fe(CO)_4$·THF was prepared as in ref 12 from $Fe_2(CO)_9$ (1 g) in THF (100 mL) under a CO atmosphere. Diphosphetene **1b** (200 mg) was then added, and the mixture was stirred at room temperature (3 h). The solvent was removed, and the residue was chromatographed through a silica gel column prepared in benzene–hexane (1:4). Complex **7** was recovered (0.2 g, 71% yield). It was unstable and gave back diphosphetene **1b** after some hours at room temperature.

Reaction of Diphosphetene with $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. A 0.394-g (1 mmol) sample of **1b** and 1.2 mmol of iron carbonyl in 50 mL of xylene were heated together. The solvent was evaporated, and the residue was chromatographed through a silica gel column prepared in benzene–hexane (1:4). Three complexes were recovered. Their ratios were dependent on experimental conditions (see Table VI).

Complex **8**: $(C_6H_5P)_2Fe_3(CO)_9$; mp 135 °C; mol wt 636; ^{31}P NMR 316.3.

Complex **9**: $(C_6H_5)_2P_2C_2(C_6H_5)_2Fe_2(CO)_6$; mp 206 °C (after recrystallization in pentane); mol wt 674; IR (cyclohexane) $\nu_{(CO)}$ 2055 (m), 2015 (s), 1995 (s), 1970 (s), 1960 cm^{-1} (w); ^{31}P NMR δ 152. Anal. Calcd: C, 57.01; H, 2.99; Fe, 16.62; P, 9.20. Found: C, 57.07; H, 3.07; Fe, 16.72; P, 9.18.

Complex **10**: $(C_6H_5)_2P_2C_2(C_6H_5)_2Fe_2(CO)_n$; mp 139.5 °C (after recrystallization in pentane); IR (cyclohexane) $\nu_{(CO)}$ 2060 (m), 2050 (s), 1980 (s), 1960 (vs), 1947 cm^{-1} (s); ^{31}P NMR δ 107. Anal. Calcd (for n = 6): C, 57.01; H, 2.99; P, 9.20. Found: C, 57.06; H, 3.12; P, 9.50.

Registry No. 1a, 2375-86-2; **1b**, 42451-95-6; **1c**, 75600-53-2; **1e**, 75600-54-3; **2a**, 2546-25-0; **2b**, 75600-55-4; **2c**, 75600-56-5; **2d**, 75600-57-6; **2e**, 75600-58-7; **4**, 1181-62-0; **5** (isomer 1), 75600-59-8; **5** (isomer 2), 75625-41-1; **6**, 75600-60-1; **7**, 75625-86-4; **8**, 38903-71-8; **9**, 75625-87-5; **11** (PR_2 = P(Me)Ph), 75684-20-7; **11** (Pr_2 = PMe_2), 14871-43-3; *cis*-dichloroethylene, 156-59-2; 1,4-diphenyldihydro-1,4-diphosphorin, 75600-61-2; tolane, 501-65-5; 3-hexyne, 928-49-4; 2,2,5,5-tetramethyl-3-hexyne, 17530-24-4; $Li(C_6H_5)P(C_6H_5)P(C_6H_5)Li$, 22961-05-3; $Fe(CO)_4THF$, 52268-67-4; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8.

Supplementary Material Available: Observed and calculated structure factors (F_o and F_c) (6 pages). Ordering information is given on any current masthead page.