Reactions of 1,2-Diphosphetenes with Lithium and Lithium Alkyls

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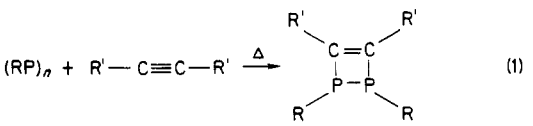
A structural comparison of the 1,2-diphenyl 3,4-R-substituted 1,2-diphosphetenes has been made for R = Ph and R = *t*-Bu. The replacement of Ph by *t*-Bu leads to a shortening of the P–P bond from 2.248 (1) to 2.214 (4) Å and to a lengthening of the endocyclic P–C bonds from 1.830 to 1.847 Å and of the P–Ph bonds from 1.814 to 1.848 Å. Accordingly, lithium in THF cleaves the P–P bond of the various 1,2-diphosphetenes studied (R, R = Ph, Ph; R, R = Ph, *t*-Bu; R, R = Me, *t*-Bu) except when R, R = *t*-Bu, *t*-Bu. In that case, a P–Ph bond cleavage takes place instead. Similarly, *n*-BuLi and *t*-BuLi cleave the P–P bond of 1,2,3,4-tetraphenyldiphosphetene in hexane whereas it is necessary to use the *t*-BuLi–TMEDA complex in hexane to observe a reaction with the 3,4-di-*tert*-butyl-substituted compound which leads to a splitting of the ring into an acetylenic and a diphosphine unit. Some chemistry has been performed with the potentially aromatic 2-phenyl-3,4-di-*tert*-butyl-1,2-diphospheten-1-yl anion. This anion is normally protonated and alkylated at the anionic phosphorus. The unsymmetrical diphosphetenes thus prepared show very low P···P coupling constants due to a balance between ^1J and ^3J couplings. A 1-(γ-chloropropyl)-1,2-diphosphetene has also been used as a precursor for a new seven-membered diphosphamacrocycle.

Since its discovery by Mahler in 1964,[2] five different syntheses of the 1,2-diphosphetene ring have been described in the literature. The first and simplest one relies on the direct reaction of cyclopolyphosphines with alkynes[2-4] (eq 1). The 1,2-diphosphetene is always accompanied by variable amounts of the corresponding 1,2,3-triphospholene, and the yields often are low. Somewhat related to this method are the photocleavage of a *P*-phenylphosphaalkene in the presence of tolan[5] (eq 2) and the ring contraction of the readily available 1,2,3-triphospholenes[4] (eq 3). In a different approach, while trying to prepare 1,4-diphosphabutadienes, Appel discovered that they readily cyclize to give 1,2-diphosphetenes[6,7] (eq 4). Finally, Becker has produced one particular 1,2-diphosphetene through the [2 + 2] head to head dimerization of a phosphaalkene[8] (eq 5).



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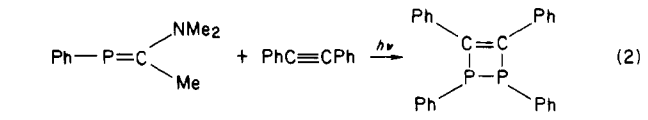

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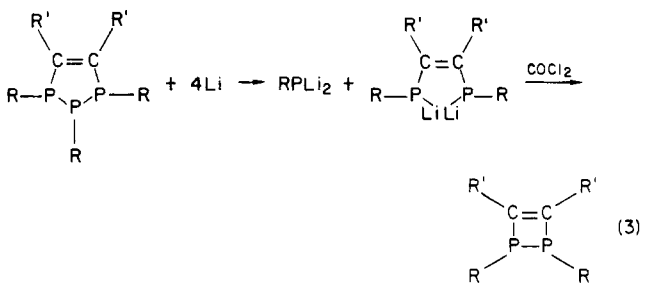

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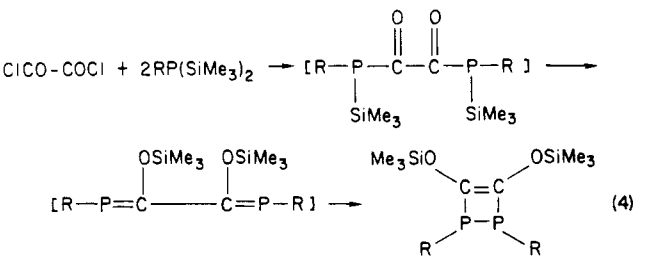

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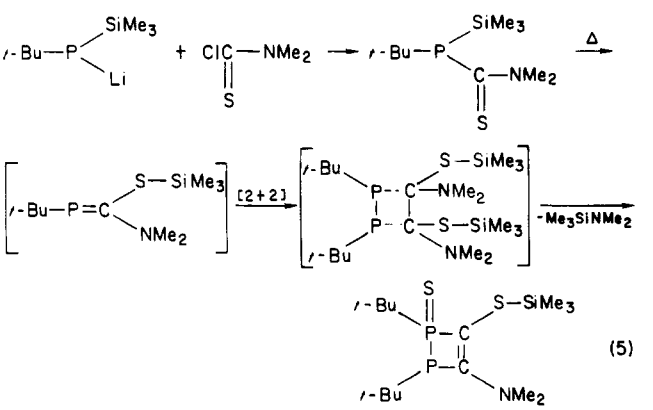

(5)

In spite of these numerous synthetic approaches, it can be stated that, broadly speaking, no original chemistry was performed with the 1,2-diphosphetene ring until our very recent discovery that it was possible to cleave preferentially one P–C exocyclic bond rather than the ring when 3,4-di-*tert*-butyl-1,2-diphenyldiphosphetene was allowed to react with lithium in THF. This unexpected finding prompted us to study in more detail the reactions of various 1,2-diphosphetenes with lithium and lithium alkyls.

Results and Discussion

Synthesis of New 1,2-Diphosphetenes. In order to give a broader basis to our study, we prepared some new

(1) (a) Laboratoire CNRS-SNPE. (b) Laboratoire de Chimie des Métaux de Transition.
(2) Mahler, W. *J. Am. Chem. Soc.* **1964**, *86*, 2306.
(3) Ecker, A.; Schmidt, U. *Chem. Ber.* **1973**, *106*, 1453.
(4) Charrier, C.; Guilhem, J.; Mathey, F. *J. Org. Chem.* **1981**, *46*, 3.
(5) Meriem, A.; Majoral, J. P.; Revel, M.; Navech, J. *Tetrahedron Lett.* **1983**, *24*, 1975.
(6) Appel, R.; Barth, V. *Tetrahedron Lett.* **1980**, 21, 1923.
(7) Appel, R.; Barth, V.; Knoch, F. *Chem. Ber.* **1983**, *116*, 938.
(8) Becker, G.; Becker, W.; Uhl, G. *Z. Anorg. Allg. Chem.* **1984**, *518*, 21.
(9) Charrier, C.; Mathey, F.; Robert, F.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 1707.

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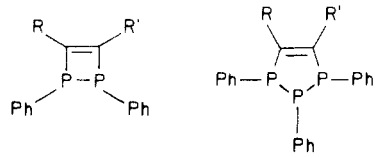
Table I. Synthesis of Some New Dissymetrical 1,2-Diphosphetenes and 1,2,3-Triphospholenes



R	R′	$(C_6H_5P)_5$ used, mmol	reactn conditns	1,2-diphosphetene no.	1,2-diphosphetene yield, %	1,2-diphosphetene mp or bp	1,2,3-triphospholene no.	1,2,3-triphospholene yield, %	1,2,3-triphospholene mp or bp
C_6H_5	CH_3	5	190 °C, 24 h	1	7	200 °C (0.02 torr)	5	37	mp 108 °C
C_6H_5	$Si(CH_3)_3$	4	160 °C, 48 h	2	15	220 °C (0.02 torr)	6	45	bp 250 °C (0.02 torr)
C_6H_5	$C(CH_3)_3$	4	190 °C, 24 h	3	40	148 °C	7	15	mp 93 °C
CH_3	$C(CH_3)_3$	4	190 °C, 24 h	4	34	95 °C	8	31	mp 105 °C
C_6H_5	H	4	160 °C, 24 h		0			0	

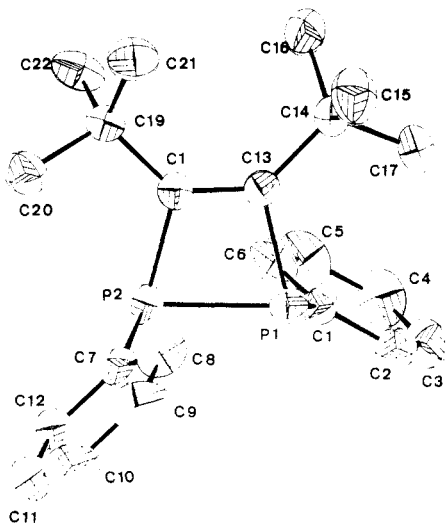
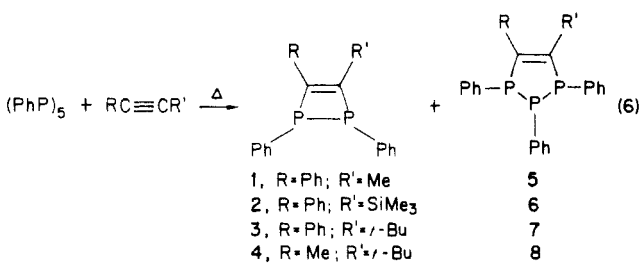


Figure 1. ORTEP view of $C_{19}H_{22}P_2$ with thermal ellipsoids at the 50% probability level (Johnson, C. K. ORTEP, Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965).

diphosphetenes by the reaction of pentaphenylcyclopentaphosphine with alkynes (eq 6). The results are



summarized in Table I. As in our preceding study,[4] we noted once again that the steric bulk of the C substituents favors the formation of 1,2-diphosphetenes. However, this is not the only factor since the trimethylsilyl group appears to be much less effective in that respect than the *tert*-butyl group. In these unsymmetrical species, we also noted for the first time one characteristic feature of the 1,2-diphosphetene ring, i.e., the very low NMR coupling between the two phosphorus atoms of ca. 70 Hz for **1**–**4**. These low values probably reflect the balance of a negative ^1J(P—P) coupling[10] with a positive ^3J(*P*—C=C—P) coupling. The absolute values of such ^3J couplings have been measured for a series of acyclic *cis*-diphosphinoalkenes[11] and sometimes are extremely high (up to 146 Hz in some cases). The

Table II. Interatomic Distances (Å) and Angles (deg) for $C_{19}H_{22}P_2$

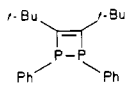
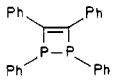
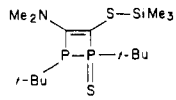
Bond Distances (Å)			
P(1)–P(2)	2.214 (4)	C(13)–C(18)	1.357 (5)
P(1)–C(1)	1.848 (4)	P(2)–C(7)	1.847 (4)
P(1)–C(13)	1.845 (4)	P(2)–C(18)	1.849 (3)
C(1)–C(2)	1.387 (5)	C(7)–C(8)	1.392 (6)
C(2)–C(3)	1.384 (6)	C(8)–C(9)	1.395 (6)
C(3)–C(4)	1.362 (7)	C(9)–C(10)	1.376 (8)
C(4)–C(5)	1.374 (7)	C(10)–C(11)	1.367 (8)
C(5)–C(6)	1.380 (6)	C(11)–C(12)	1.394 (7)
C(6)–C(1)	1.386 (5)	C(12)–C(7)	1.387 (6)
C(19)–C(14)	1.534 (5)	C(18)–C(19)	1.541 (5)
C(14)–C(15)	1.541 (6)	C(19)–C(20)	1.530 (5)
C(14)–C(16)	1.519 (6)	C(19)–C(21)	1.520 (6)
C(14)–C(17)	1.531 (6)	C(19)–C(22)	1.533 (6)
Bond Angles (deg)			
P(2)–P(1)–C(1)	104.6 (1)	P(1)–P(2)–C(7)	102.4 (1)
P(2)–P(1)–C(13)	76.1 (1)	P(1)–P(2)–C(18)	76.4 (1)
C(1)–P(1)–C(13)	103.7 (2)	C(7)–P(2)–C(18)	105.4 (2)
P(1)–C(1)–C(2)	117.3 (3)	P(2)–C(7)–C(8)	123.4 (3)
P(1)–C(1)–C(6)	123.7 (3)	P(2)–C(7)–C(12)	117.4 (3)
C(2)–C(1)–C(6)	118.8 (4)	C(8)–C(7)–C(12)	119.2 (4)
C(1)–C(2)–C(3)	120.2 (4)	C(7)–C(8)–C(9)	119.8 (5)
C(2)–C(3)–C(4)	120.8 (4)	C(8)–C(9)–C(10)	120.1 (5)
C(3)–C(4)–C(5)	119.3 (4)	C(9)–C(10)–C(11)	120.7 (5)
C(4)–C(5)–C(6)	120.9 (5)	C(10)–C(11)–C(12)	119.7 (5)
C(5)–C(6)–C(1)	120.0 (4)	C(11)–C(12)–C(7)	120.5 (5)
P(1)–C(13)–C(18)	103.2 (3)	P(2)–C(18)–C(13)	102.5 (2)
P(1)–C(13)–C(14)	121.7 (2)	P(2)–C(18)–C(19)	121.0 (2)
C(14)–C(13)–C(18)	134.9 (3)	C(13)–C(18)–C(19)	135.9 (3)
C(18)–C(14)–C(15)	109.8 (3)	C(18)–C(19)–C(20)	109.3 (3)
C(13)–C(14)–C(16)	112.1 (3)	C(18)–C(19)–C(21)	114.2 (3)
C(13)–C(14)–C(17)	110.5 (3)	C(18)–C(19)–C(22)	108.8 (3)
C(15)–C(14)–C(16)	111.1 (4)	C(20)–C(19)–C(21)	107.0 (4)
C(15)–C(14)–C(17)	105.9 (4)	C(20)–C(19)–C(22)	108.4 (4)
C(16)–C(14)–C(17)	107.3 (4)	C(21)–C(19)–C(22)	108.9 (4)

stereochemistry of these 1,2-diphosphetenes (**1**–**4**) at the phosphorus atoms is very probably trans since the reaction of $(PhP)_5$ with alkynes has been demonstrated by X-ray crystallography to give indeed *trans*-1,2-diphosphetenes in two cases [R = R′ = Ph[4]. R = R′ = *t*-Bu; this work]. Since the magnitude of the ^1J(P–P) coupling in diphosphines is known to be extremely sensitive to the lone pair–P–P–lone pair dihedral angle,[10] we can consider that the low P···P couplings recorded here are more precisely characteristic of *trans*-1,2-diphosphetenes. Thus, according to this criterion, all the 1,2-diphosphetenes described hereafter (**15**, **20**-**25**) very probably have the same trans stereochemistry.

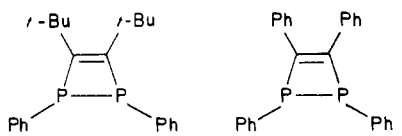
X-ray Crystal Structure Analysis of 3,4-Di-*tert*-butyl-1,2-diphenyl-1,2-diphosphetene. Since the formation of 1,2-diphosphetenes seemed to be highly dependent upon the substitution pattern of the ring, we decided to compare the structural features of 3,4-di(*tert*-butyl)-1,2-diphenyl-1,2-diphosphetene (**9**; the for-

(10) Albrand, J. P.; Robert, J. B.; Goldwhite, H. *Tetrahedron Lett.* **1976**, 949.
(11) Carty, A. J.; Johnson, D. K.; Jacobson, S. E. *J. Am. Chem. Soc.* **1979**, *101*, 5612.

Table III. Significant Bond Lengths (Å) and Angles (deg) for Some 1,2-Diphosphetenes

	P–P	P–C (mean) endo	P–C (mean) exo	C=C	∠P—P—C (mean) endo	∠P—P—C (mean) exo	∠P—C=C (mean)	ref
 9	2.214 (4)	1.847	1.848	1.357 (5)	76.2	103.5	102.8	this work
 10	2.248 (1)	1.830	1.814	1.358 (4)	74.7	107.0	102.1	4
	2.219 (1)	1.814	1.873	1.360 (5)	76.25	107.4	103.6	12

mation of which is highly favored) with those of 1,2,3,4-tetraphenyl-1,2-diphosphetene (**10**).[4] The structural data



9 10

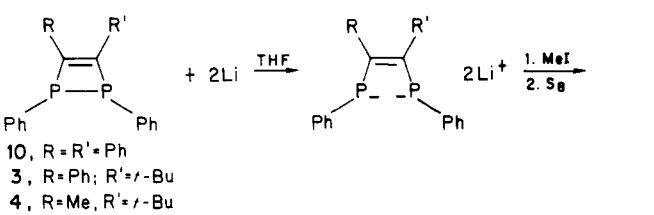
for compound **9** are collected in Table II. Comparison between the most significant structural features of compounds **9** and **10** is made in Table III. We have added the data for a 1,2-diphosphetene monosulfide studied independently by Becker.[12] Even though the P—C endo bonds are longer and the P—C=C bond angles slightly larger in **9** than in **10**, nevertheless the P—P bond is substantially shorter in the former case. This may be understood by considering the large change observed in the deviation from planarity of the ring. If the middle of the P–P edge is called M(1) and that of the C(13)–C(18) edge is called M(2), the dihedral angle of P(1)–M(1)–M(2)–C(13) is 10° in **9** while it is 19° in **10**. The higher deviation from planarity of **10** may be discussed in terms of delocalization along the PhC=CPh unit which needs a planar arrangement for better effectiveness. However, full planarity is not possible because of steric hindrance between the ortho hydrogens of both phenyl rings. Consequently, these phenyl rings turn as propeller blades to reduce this interaction but not too much to allow some π overlap. Since the two sp^2 carbons of the diphosphetene ring remain planar (sums of angles: 359.8° and 359.4°), this distorsion of the PhC=CPh fragment induces an additional distorsion of the diphosphetene ring.

On the basis of its synthesis, it is quite logical to consider the 1,2-diphosphetene ring as resulting from a combination of a trans diphosphene unit R—P=P—R and an acetylenic unit R′—C≡C—R′. From that point of view, it may be said that the diphosphene–acetylene interaction is looser in **9** than in **10**. Indeed, as already pointed out, the P–C endo bonds are much longer in **9** than in **10**. This may be due to electronic factors, but we feel that, since the diphosphene has a low-lying LUMO and good electron-acceptor properties,[13] its interaction with an electron-rich alkyne such as di-*tert*-butylacetylene is likely to be strong. Thus, we think that the explanation of these weaker bonds lies mainly in the steric repulsion between the two subunits.

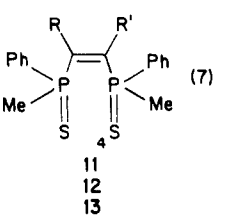
Finally, it is interesting to note that the P–Ph bonds are much weaker in **9** than in **10** although we have no obvious explanation for this.

Hereafter, we will see that all these structural features explain the different chemistry of **9** and **10**.

Reactions of 1,2-Diphosphetenes with Lithium and Lithium Alkyls. In view of our preliminary results,[9] we first compare the reactions of diphosphetenes **3**, **4**, **9**, and **10** with lithium in THF. The phosphorus anions thus formed were identified through their reactions with methyl iodide and sulfur (eq 7 and 8). The cleavage of the exo-

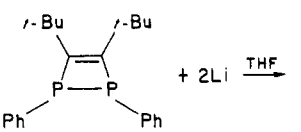


10, R = R′ = Ph
3, R = Ph; R′ = *t*-Bu
4, R = Me, R′ = *t*-Bu



(7)

11
12
13



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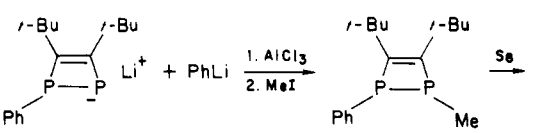
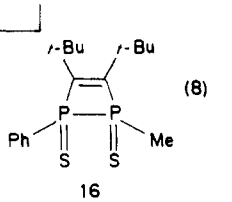


14 **15**



(8)

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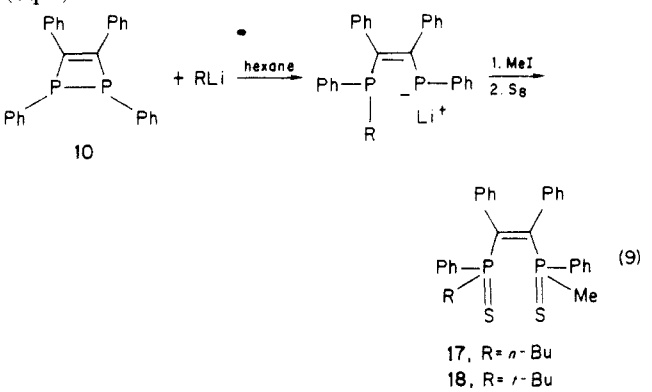
cyclic P–Ph bond takes place only when there are two bulky substituents on the ring carbons, as in **9**, but, as soon as one C substituent is not bulky enough, the "normal" P–P cleavage occurs instead, as in **3** and **4**. It is also interesting to note that, after the cleavage of the P–Ph bond of **9**, it is possible to destroy selectively phenyllithium

(12) Becker, G.; Becker, W.; Uhl, G. *Z. Anorg. Allg. Chem.* **1984**, *519*, 31.
(13) Lee, J. G.; Cowley, A. H.; Boggs, J. E. *Inorganica Chimica Acta* **1983**, *77*, L61.

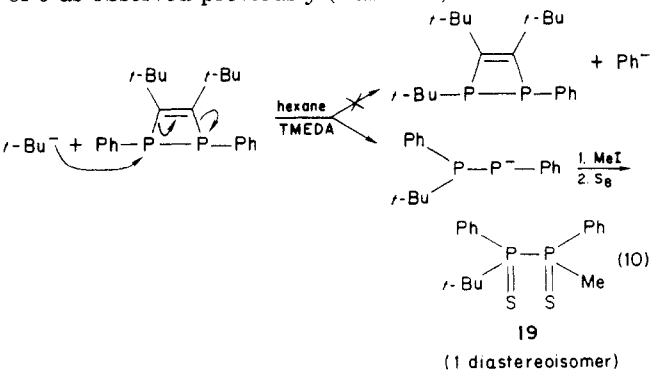
by adding a limited amount of anhydrous $AlCl_3$. This technique has already been used during the cleavage of the P–Ph bond of *P*-phenylphospholes (see, for example, ref 14) and underlines the low basicity and hence, probably, the aromaticity of the diphosphetenyl anion **14**. Finally, we have checked that the substituents at phosphorus play no role in the orientation of the cleavage (P–P vs. P–C). Indeed, lithium in THF selectively cleaves the P–Me bond of **15**. This preferential cleavage of the P–Me vs. the P–Ph bond seems rather surprising, and we have no obvious explanation for it. We have just checked that this result was not valid for all 1-alkyl-2-phenyl-3,4-di-*tert*-butyl-1,2-diphosphetenes. Indeed, simultaneous cleavage of the P–(*n*-Bu) and P–Ph bonds (ca. 1:1 ratio) is observed with the 1-*n*-butyl compound and lithium in THF.

As already pointed out,[9] there is a striking parallel between the relative strengths of the P–Ph and P–P bonds as monitored by the corresponding bond lengths (Table III) and the regioselectivity of the lithium cleavage. In the case of **9**, the driving force of the reaction is probably the aromaticity of the diphosphetenyl anion **14**. In the other cases, the ring strain overcomes this aromaticity and the ring cleavage takes place.

As an outgrown of this initial study, it was quite logical to study also the reactions of diphosphetenes with lithium alkyls. As expected, the reaction of either *n*-butyl- or *tert*-butyllithium with **10** causes cleavage of the P–P bond (eq 9).



In contrast, the reactivity of **9** was unpredictable. Both *n*-BuLi and *t*-BuLi in hexane and *n*-BuLi–TMEDA in hexane do not react with **9**. It is necessary to use *t*-BuLi–TMEDA in hexane at room temperature which gives a completely unexpected reaction (eq 10). The collapse of the ring is well correlated with the weak P–C endo bonds of **9** as observed previously (Table III).



The Chemistry of the 1,2-Diphosphetenyl Anion 14. We have mainly studied two characteristic reactions of the diphosphetenyl anion **14**, its hydrolysis and its alkylation.

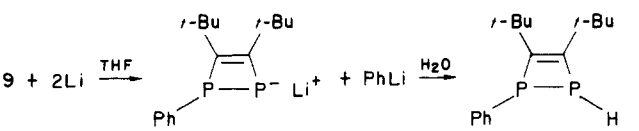
(14) Holand, S.; Mathey, F.; Fischer, J.; Mitschler, A. *Organometallics* **1983**, *2*, 1234.

Table IV. Atomic Coordinates and Isotropic Thermal Parameters[a]

atom	*x/a*	*y/b*	*z/c*	B_{eqv},[a] Å^2
P(1)	0.21427 (8)	0.1366 (1)	0.62469 (4)	3.89 (2)
P(2)	0.33543 (8)	0.2225 (1)	0.55351 (4)	3.97 (3)
C(1)	0.3016 (3)	0.1160 (5)	0.6946 (2)	4.03 (9)
C(2)	0.2690 (4)	−0.0030 (5)	0.7368 (2)	4.0 (1)
C(3)	0.3242 (4)	−0.0146 (7)	0.7926 (2)	6.2 (1)
C(4)	0.4109 (4)	0.0903 (8)	0.8070 (2)	6.9 (2)
C(5)	0.4457 (4)	0.2056 (8)	0.7647 (2)	7.1 (2)
C(6)	0.3915 (4)	0.2199 (6)	0.7089 (2)	5.8 (1)
C(7)	0.2768 (3)	0.1290 (5)	0.4832 (2)	4.4 (1)
C(8)	0.1610 (4)	0.1275 (5)	0.4694 (2)	5.6 (1)
C(9)	0.1235 (5)	0.0535 (7)	0.4154 (2)	7.2 (2)
C(10)	0.2010 (7)	−0.0169 (7)	0.3757 (2)	7.6 (2)
C(11)	0.3149 (6)	−0.0171 (7)	0.3889 (2)	7.2 (2)
C(12)	0.3533 (4)	0.0558 (5)	0.4429 (2)	5.5 (1)
C(13)	0.1867 (3)	0.3603 (4)	0.6195 (2)	3.56 (9)
C(14)	0.1049 (3)	0.4478 (5)	0.6638 (2)	4.5 (1)
C(15)	−0.0118 (4)	0.4729 (8)	0.6329 (3)	7.2 (2)
C(16)	0.1529 (5)	0.6107 (6)	0.6865 (2)	6.6 (1)
C(17)	0.0820 (5)	0.3401 (7)	0.7202 (2)	6.6 (1)
C(18)	0.2459 (3)	0.4059 (4)	0.5687 (2)	3.58 (9)
C(19)	0.2629 (3)	0.5668 (5)	0.5322 (2)	4.05 (9)
C(20)	0.3095 (5)	0.5255 (6)	0.4684 (2)	6.5 (1)
C(21)	0.1543 (4)	0.6661 (6)	0.5230 (2)	6.1 (1)
C(22)	0.3507 (4)	0.6744 (6)	0.5653 (2)	6.3 (1)

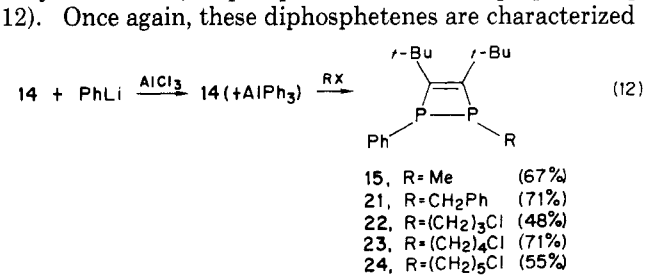
[a] $B_{eqv} = {}^1/_3\sum_i\sum_j B_{ij}a_i^*a_j^*\bar{a}_i\bar{a}_j$.

Hydrolysis of the crude mixture resulting from the reaction of **9** with lithium in THF gives directly the first known P–H containing 1,2-diphosphetene **20** (eq 11). Diphosphetene **20** is characterized by extremely low P–P coupling (29.3 Hz) and a ^1J(P–H) coupling constant (161 Hz) which lies at the lowest part of the range recorded for primary and secondary phosphines (155–235 Hz).[15] According to theoretical calculations,[16] this means that the s character of the P–H bond is high and thus, that the p character of either the P–P bond or the P lone pair is also high. We have already thoroughly discussed about the mechanisms through which the nonaromatic 1,2-diphosphetene ring achieves some stability and concluded that the P–P bond is bent[4] (and hence has considerable p character).



(11)

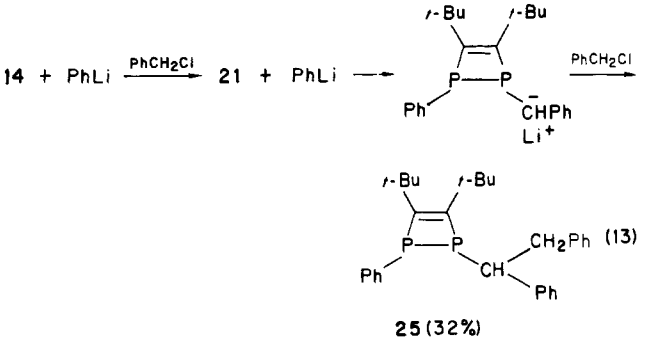
In order to get satisfactory results when alkylating **14** at phosphorus, it is first necessary to "neutralize" with $AlCl_3$ the phenyllithium which is produced during the cleavage of the P–Ph bond. With this technique, five new unsymmetrical 1,2-diphosphetenes have been prepared (eq 12). Once again, these diphosphetenes are characterized



(12)

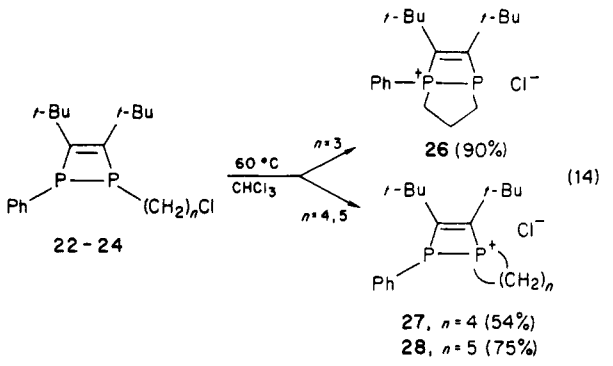
(15) Brazier, J. F.; Houalla, D.; Koenig, M.; Wolf, R. *Top. Phosphorus Chem.* **1976**, *8*, 99–192.
(16) Goetz, H.; Frenking, G.; Marschner, F. *Phosphorus Sulfur* **1978**, *4*, 309.

by a low P–P coupling, ca. 50 Hz. While studying the reaction of benzyl chloride with **14** without "neutralization" of PhLi, we fortuitously discovered that PhLi was able to metalate the benzyl group of **21** (eq 13). The first at-



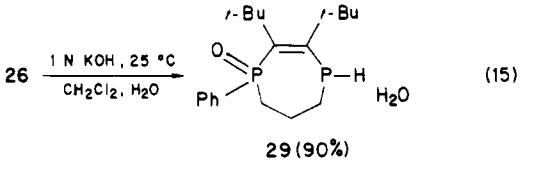
25 (32%)

tempted use of this new chemistry was the preparation of a range of original 1,4-diphosphamacrocycles. For that purpose, we studied the self-quaternization of 1-(ω-chloroalkyl)diphosphetenes **22–24** (eq 14) The structures



of **26–28** were established beyond doubt by studying their ^{13}C spectra while selectively decoupling the tervalent and the quaternary phosphorus atoms. In the case of **27** and **28**, both CH_2–P are strongly coupled with P^+ while in the case of **26**, one is strongly coupled with P^+ and the other with P.

The hydrolysis of **26** gives the expected heterocycle **29** as a mixture of two isomers (eq 15). The P···P coupling has almost disappeared in **29** (8 Hz) while the ^1J(P–H) coupling constant is significantly higher (230 Hz) than in **20**.



29 (90%)

A generalization of this approach toward diphosphamacrocycles would require selective protection of the P-$(CH_2)_n$Cl phosphorus toward quaternization. To date, we have been unable to achieve such protection without deactivating the other phosphorus atom.

Experimental Section

All reactions were carried out under argon. Solvents and silica gel (70–230 mesh Merck) were used after being degassed with argon. NMR spectra were recorded on a Bruker WP 80 spectrometer at 80.13 MHz for ^1H, 32.435 MHz for ^{31}P, and 20.15 MHz for ^{13}C spectra. ^{31}P chemical shifts are externally referenced to 85% H_3PO_4; ^1H and ^{13}C chemical shifts are internally referenced to Me_4Si and are positive for downfield shifts in all cases.

General Procedure for the Synthesis of 1,2-Diphosphet-3-enes. A mixture of acetylenic compound (6–60 mmol) and pentaphenylcyclopentaphosphine[17] (2–20 mmol) (molar ratio 3:1) was heated in a sealed tube. The mixture of products thus obtained was distilled for **2** and **6** and chromatographed for **1**, **5–3**, **7** and **4**, **8** on silica gel (40 g of silica gel/g of product) with toluene–hexane (20:80). Solid diphosphetenes were crystallized in methanol and solid triphospholenes in hexane. For details, see Table I.

1,2,4-Triphenyl-3-methyl-1,2-diphosphet-3-ene (1): ^1H NMR ($CDCl_3$) δ 2.20 ($^3J_{HP_2}$ = 6.9, $^4J_{HP_1}$ = 1.5 Hz, CH_3); ^{31}P NMR ($CDCl_3$) δ −32.0 ($^1J_{PP}$ = 75.6 Hz, P_1), −28.8 (P_2); ^{13}C NMR ($CDCl_3$) δ 145.8 ($^1J_{CP}$ = 15.9, $^2J_{CP}$ = 6 Hz), 146.7 ($^1J_{CP}$ = 12.2, $^2J_{CP}$ = 5 Hz) (C_3 and C_4), 18.7 ($^2J_{CP}$ = 12.2, $^3J_{CP}$ = 3.7 Hz, CH_3); mass spectrum (200 °C) *m/e* 332.08798 (M, 100), calcd for $C_{21}H_{18}P_2$ 332.0877. Anal. Calcd for $C_{21}H_{18}P_2$: C, 75.90; H, 5.42. Found: C, 75.40; H, 5.34.

1,2,4-Triphenyl-3-(trimethylsilyl)-1,2-diphosphet-3-ene (2): ^1H NMR ($CDCl_3$) δ 0.27 ($^4J_{HP_2}$ = 0.9 Hz, CH_3); ^{31}P NMR ($CDCl_3$) δ −38.2 ($^1J_{PP}$ = 63.5 Hz, P_1), −10.0 (P_2); ^{13}C NMR ($CDCl_3$) δ 156.36 ($^1J_{CP}$ = 29.3, $^2J_{CP}$ = 15.8 Hz), 164.1 ($^1J_{CP}$ = 17.0, $^2J_{CP}$ = 8.5Hz) (C_3 and C_4), 0.12 (J_{CP} = 0 Hz, CH_3).

1,2,4-Triphenyl-3-*tert*-butyl-1,2-diphosphet-3-ene (3): ^1H NMR ($CDCl_3$) δ 1.03 (J_{HP} = 0 Hz, CH_3); ^{31}P NMR ($CDCl_3$) δ −33.1 ($^1J_{PP}$ = 66 Hz, P_1), −41.8 (P_2); ^{13}C NMR ($CDCl_3$) δ 148.0 ($^1J_{CP}$ = 22.0, $^2J_{CP}$ = 6.1 Hz), 161.45 ($^1J_{CP}$ = 21.9, $^2J_{CP}$ = 14.6 Hz) (C_3 and C_4), 38.9 ($^2J_{CP}$ = 11.0, $^3J_{CP}$ = 3.6 Hz, C(*t*-Bu)), 31.04 ($^3J_{CP}$ = 3.7 Hz, CH_3(*t*-Bu)); mass spectrum (200 °C), *m/e* (relative intensity) 374 (M, 100). Anal. Calcd for $C_{24}H_{24}P_2$: C, 77.00; H, 6.42. Found: C, 76.85; H, 6.55.

1,2-Diphenyl-3-*tert*-butyl-4-methyl-1,2-diphosphet-3-ene (4): ^1H NMR ($CDCl_3$) δ 1.15 (CH_3(*t*-Bu)), 2.05 (CH_3); ^{31}P NMR ($CDCl_3$) δ −35.9 ($^1J_{PP}$ = 64 Hz, P_1), −35.07 (P_2); ^{13}C NMR ($CDCl_3$) δ 144.0 and 159.06 (C_3 and C_4), 37.43 (C(*t*-Bu)), 29.8 (CH_3(*t*-Bu)), 19.84 (CH_3); mass spectrum (200 C°), *m/e* (relative intensity) 312 (M, 100). Anal. Calcd for $C_{19}H_{22}P_2$: C, 73.08; H, 7.05. Found: C, 72.81; H, 7.20.

1,2,3,5-Tetraphenyl-4-methyl-1,2,3-triphosphol-4-ene (5): ^1H NMR ($CDCl_3$) δ 1.97 ($^3J_{HP_3}$ = 11.2, $^4J_{HP_1}$ = 3 Hz, CH_3); ^{31}P NMR ($CDCl_3$) δ 47.45 ($^1J_{P_1P_2}$ = 242, $^2J_{P_1P_3}$ = 9.7 Hz, P_1), −44.90 ($^1J_{P_2P_3}$ = 242 Hz, P_2), 45.40 (P_3); ^{13}C NMR ($CDCl_3$) δ 144.10 ($^1J_{CP}$ = 23 Hz), 150.3 ($^1J_{CP}$ = 27 Hz) (C_4 and C_5), 19.10 ($^2J_{CP}$ = 29.3 Hz, CH_3); mass spectrum (200 °C), *m/e* (relative intensity) 440 (M, 100). Anal. Calcd for $C_{27}H_{23}P_3$: C, 73.64; H, 5.23. Found: C, 73.68; H, 5.27.

1,2,3,5-Tetraphenyl-4-(trimethylsilyl)-1,2,3-triphosphol-4-ene (6): ^1H NMR ($CDCl_3$) δ −0.18 ($^4J_{HP}$ = 1 Hz, CH_3); ^{31}P NMR ($CDCl_3$) δ 55.80 ($^1J_{P_1P_2}$ = 244, $^2J_{P_1P_3}$ = 9.8 Hz, P_1), −33.28 ($^1J_{P_2P_3}$ = 259 Hz, P_2), 69.65 (P_3); ^{13}C NMR ($CDCl_3$) δ 149.32 ($^1J_{CP}$ = 49 Hz), 168.85 ($^1J_{CP}$ = 34.1 Hz) (C_4 and C_5), 1.48 (J_{CP} = 6.1 Hz, CH_3); mass spectrum (200 °C), *m/e* (relative intensity) 498 (M, 53). Anal. Calcd for $C_{29}H_{29}P_3Si$: C, 69.88; H, 5.82. Found: C, 69.24; H, 5.73.

1,2,3,5-Tetraphenyl-4-*tert*-butyl-1,2,3-triphosphol-4-ene (7): ^1H NMR ($CDCl_3$) δ 1.06 ($^4J_{HP}$ = 1.2 Hz, CH_3); ^{31}P NMR ($CDCl_3$) δ 46.10 ($^1J_{P_1P_2}$ = 254, $^2J_{P_1P_3}$ = 7.3 Hz, P_1), −69.90 ($^1J_{P_2P_3}$ = 241.7 Hz, P_2), 62.35 (P_3); ^{13}C NMR ($CDCl_3$) δ 153.27 ($^1J_{CP}$ = 31.8 Hz), 154.30 ($^1J_{CP}$ = 29.3 Hz) (C_4 and C_5), 40.10 ($^2J_{CP}$ = 19.5 Hz, C-(*t*-Bu)), 32.85 ($^3J_{CP}$ = 8.5 Hz, CH_3); mass spectrum (200 °C), *m/e* (relative intensity) 482 (M, 100). Anal. Calcd for $C_{30}H_{29}P_3$: C, 74.69; H, 6.02; P, 19.29. Found: C, 74.94; H, 6.02; P, 19.73.

1,2,3-Triphenyl-4-*tert*-butyl-5-methyl-1,2,3-triphosphol-4-ene (8): ^1H NMR ($CDCl_3$) δ 1.34 ($^4J_{HP}$ = 1.2 Hz, CH_3(*t*-Bu)), 2.37 ($^3J_{HP}$ = 13.7, $^4J_{HP}$ = 2.2 Hz, CH_3); ^{31}P NMR ($CDCl_3$) δ 57.68 ($^1J_{P_1P_2}$ = 244, $^2J_{P_1P_3}$ = 5 Hz, P_1), −62.37 ($^1J_{P_2P_3}$ = 248.6 Hz, P_2), 49.28 (P_3); ^{13}C NMR ($CDCl_3$) δ 145.55 ($^1J_{CP}$ = 20.7 Hz), 155.67 ($^1J_{CP}$ = 31.7 Hz) (C_4 and C_5), 38.47 ($^2J_{CP}$ = 19.5, $^3J_{CP}$ = 2.5 Hz, C(*t*-Bu)), 31.6 ($^3J_{CP}$ = 9.8 Hz, CH_3(*t*-Bu)), 20.5 ($^2J_{CP}$ = 35.4, $^3J_{CP}$ = 2.4 Hz, CH_3); mass spectrum (200 °C), *m/e* (relative intensity)420 (M, 83). Anal. Calcd for $C_{25}H_{27}P_3$: C, 71.43; H, 6.43. Found: C, 70.64; H, 6.34.

1,2-Diphenyl-3,4-di-*tert*-butyl-1,2-diphosphet-3-ene (9):[4] ^1H NMR ($CDCl_3$) δ 1.2 (J_{HP} = 0 Hz, CH_3); ^{31}P NMR ($CDCl_3$) δ

(17) Henderson, A.; Epstein, M., Jr.; Seichter, F. S. *J. Am. Chem. Soc.* **1963**, *85*, 2462.

−53.94; ^{13}C NMR ($CDCl_3$) δ 159.87 (C_3, C_4), 38.04 (C(*t*-Bu)), 31.56 (CH_3).

1,2,3,4-Tetraphenyl-1,2-diphosphet-3-ene (10):[4] ^{31}P NMR ($CDCl_3$) δ −37.30; ^{13}C NMR ($CDCl_3$) δ 146.43 (C_3, C_4).

1,2-Bis(phenylmethylthiophosphoryl)-1-*tert*-butyl-2-phenylethylene (*Z* Isomer) (12). Compound **12** was prepared from 1.0 g (2.67 mmol) of **3** as was **11** in ref 4 and purified by column chromatography on silica gel (60 g of silica gel/g of product) with hexane–ether (80:20). Recrystallization in absolute ethanol gave 24% yield of **12** (mp 110 °C): ^1H NMR ($CDCl_3$) δ 2.10 ($^2J_{HP}$ = 12.4 Hz, CH_3P), 1.16 ($^2J_{HP}$ = 10 Hz, CH_3P), 1.12 ($^4J_{HP}$ = 0 Hz, CH_3(*t*-Bu)); ^{31}P NMR ($CDCl_3$) δ 40.05 ($^3J_{PP}$ = 20.5 Hz), 41.90; mass spectrum (200 °C), *m/e* (relative intensity) 468 (M, 30). Anal. Calcd for $C_{26}H_{30}P_2S_2$: C, 66.67; H, 6.45; P, 13.22. Found: C, 66.82; H, 6.55; P, 13.00.

1,2-Bis(phenylmethylthiophosphoryl)-1-*tert*-butyl-2-methylethylene (*Z* Isomer) (13). Compound **13** was prepared from 1.0 g (3.2 mmol) of **4** as was **11** in ref 4. Two diastereoisomers were recovered after chromatography on silica gel (200 g of silica gel/g of product) with hexane–ether (70:30) (yield 77%). First diastereomer (ratio 25%): mp 161 °C; ^1H NMR ($CDCl_3$) δ 1.18 ($^4J_{HP}$ = 0 Hz, CH_3(*t*-Bu)), 2.02 ($^3J_{HP}$ = 16.9, $^4J_{HP}$ = 3.2 Hz, CH_3C=), 2.64 ($^2J_{HP}$ = 11.2 Hz, CH_3P), 2.82 ($^2J_{HP}$ = 11.9 Hz, CH_3P); ^{31}P NMR ($CDCl_3$) δ 36.0 ($^3J_{PP}$ = 29 Hz), 43.0; ^{13}C NMR ($CDCl_3$) δ 150.25 ($^1J_{CP}$ = 68.3, $^2J_{CP}$ = 6.1 Hz, C=), 156.67 ($^1J_{CP}$ = 64.6 Hz, C=), 32.05 ($^3J_{CP}$ = 4.8 Hz, CH_3(*t*-Bu)), 42.16 (J_{CP} = 14.6, J_{CP} = 11 Hz, C(*t*-Bu)), 24.6 (J_{CP} = 17.1, J_{CP} = 14.6 Hz, CH_3C:), 27.75 ($^1J_{CP}$ = 53.7 Hz, CH_3P), 32.47 ($^1J_{CP}$ = 57.4 Hz, CH_3P); mass spectrum (200 °C), *m/e* (relative intensity) 406 (M, 15). Anal. Calcd for $C_{21}H_{28}P_2S_2$: C, 61.58; H, 6.90; P, 15.27. Found: C, 62.17; H, 6.95; P, 15.13. Second diastereomer (ratio 75%): mp 158 °C; ^1H NMR ($CDCl_3$) δ 1.48 ($^4J_{HP}$ = 0 Hz, CH_3(*t*-Bu)), 2.36 ($^3J_{HP}$ = 16.4, $^4J_{HP}$ = 3.2 Hz, CH_3C:), 2.07 ($^2J_{HP}$ = 12.2 Hz, CH_3P), 2.11 ($^2J_{HP}$ = 12.6 Hz, CH_3P); ^{31}P NMR ($CDCl_3$) δ 37.2 ($^3J_{PP}$ = 27 Hz), 44.10; ^{13}C NMR ($CDCl_3$) δ 148.13 ($^1J_{CP}$ = 68.3, $^2J_{CP}$ = 7.3 Hz, C:), 153.64 ($^1J_{CP}$ = 64.7 Hz, C:), 32.59 ($^3J_{CP}$ = 4.9 Hz, CH_3(*t*-Bu)), 42.10 (J_{CP} = 13.4, J_{CP} = 11 Hz, C(*t*-Bu)), 24.23 (J_{CP} = 15.9, J_{CP} = 14.6 Hz, CH_3C:), 28.53 ($^1J_{CP}$ 57.4 Hz, CH_3P), 33.14 ($^1J_{CP}$ = 57.3 Hz, CH_3P); mass spectrum (200 °C), *m/e* (relative intensity) 406 (M, 25). Anal. Calcd for $C_{21}H_{28}P_2S_2$: C, 61.58; H, 6.90; P, 15.27. Found: C, 62.17; H, 7.2; P, 15.13.

(2-Phenyl-3,4-di-*tert*-butyl-1,2-diphosphetenyl)lithium (14). A mixture of 1 g (2.82 mmol) of **9** and 0.1 g (14.5 mmol) of lithium ribbon in 10 mL of dry THF was stirred at 20 °C. When the reaction was complete after 2 h, excess of lithium was removed. The black reddish solution was cooled to −30 °C, and 0.05 g (0.37 mmol) of $AlCl_3$ was added. The temperature then was raised slowly to 20 °C, and the solution was stirred for 1 h: ^{31}P NMR (THF) δ −18.45 ($^1J_{PP}$ = 80.6 Hz, P_1), −53.22 (P_2).

1-Methyl-2-phenyl-3,4-di-*tert*-butyl-1,2-diphosphet-3-ene (15). A solution of 0.397 g (2.8 mmol) of CH_3I in 2 mL of dry THF was added at room temperature to the previous solution of **14**. The solvent was evaporated, and the residue was chromatographed on silica gel (60 g of silica gel/g of product) with pentane–toluene (80:20). **15** was recovered in 67% yield (mp 45 °C): ^1H NMR ($CDCl_3$) δ 1.46 ($^2J_{HP}$ = 13.4, $^3J_{HP}$ = 5.4 Hz, CH_3P), 1.12 and 1.32 (CH_3(*t*-Bu)); ^{31}P NMR ($CDCl_3$) δ −59.90 ($^1J_{PP}$ = 44 Hz, P_1), −61.25 (P_2); ^{13}C NMR ($CDCl_3$) δ 155.7 ($^1J_{CP}$ = 13.4, $^2J_{CP}$ = 6.1 Hz), 160.6 ($^1J_{CP}$ = 13.4, $^2J_{CP}$ = 8.5 Hz) (C_3 and C_4), 31.5 and 31.3 (CH_3(*t*-Bu)), 37.8 and 37.2 (C(*t*-Bu)), 14.48 ($^1J_{CP}$ = 26.8 Hz, CH_3P). Anal. Calcd for $C_{17}H_{26}P_2$: C, 69.86; H, 8.90. Found: C, 70.35; H, 8.94.

1-Methyl-2-phenyl-3,4-di-*tert*-butyl-1,2-diphosphet-3-ene Disulfide (16). Compound **15** (0.55 g, 1.9 mmol) in 5 mL of dry THF was stirred with 0.13 g of sulfur and 0.01 g of LiI for 2 h at room temperature. The solvent was evaporated, and the residue was chromatographed on silica gel with pentane–ether (70:30): yield 60%; mp 143 °C; ^1H NMR ($CDCl_3$) δ 1.33 and 1.61 (CH_3(*t*-Bu)), 2.34 (CH_3P); ^{31}P NMR ($CDCl_3$) δ 56.29 ($^1J_{PP}$ = 41.8 Hz, P_1), 54.26 (P_2); ^{13}C NMR ($CDCl_3$) δ 157.45 and 157.70 (C_3 and C_4), 31.44 and 31.62 (CH_3(*t*-Bu)), 38.89 and 39.56 (C(*t*-Bu)), 22.15 (CH_3P). Anal. Calcd for $C_{17}H_{26}P_2S_2$: C, 57.36; H, 7.30; P, 17.38. Found: C, 57.86; H, 7.42; P, 16.90.

1-(Methylphenylthiophosphoryl)-2-(*n*-butylphenylthiophosphoryl)-1,2-diphenylethylene (*Z* Isomer) (17). A mixture of 0.59 g of **10** (1.5 mmol) in 20 mL of dry pentane and *n*-butyllithium (2.3 mL of a solution 1.3 M in pentane) was stirred 1 h at room temperature. Dry THF (5 mL) and, then, a solution of 0.42 g (3 mmol) of CH_3I in dry THF (3 mL) were added.

Sulfur (0.4 g) was added. The mixture was stirred overnight at room temperature. The solvent was evaporated, and the residue was chromatographed on silica gel (60 g of silica gel/g of product) with hexane–ether (70:30). Both diastereomers were recovered together in 64% yield (ratio 2:1): ^1H NMR ($CDCl_3$) δ 1.84 ($^2J_{HP}$ = 13.2 Hz, CH_3P (first diast), 1.78 ($^2J_{HP}$ = 12.7 Hz, CH_3P (second diast); ^{31}P NMR ($CDCl_3$) δ 36.49 ($^3J_{PP}$ = 10.3 Hz, P–CH_3), 42.48 (P-*n*-Bu) (first diast), 34.85 ($^3J_{PP}$ = 11.7 Hz, P–CH_3), 41.45 (P-*n*-Bu) (second diast); ^{13}C NMR ($CDCl_3$) δ 147.40 and 148.06 ($^1J_{CP}$ = 63, $^2J_{CP}$ = 8 Hz, C:), 26.78 ($^1J_{CP}$ = 59 Hz, CH_3P), 36.47 ($^1J_{CP}$ = 56 Hz, $CH_{2\alpha}$), 23.26 ($^2J_{CP}$ = 18 Hz, $CH_{2\beta}$), 24.05 ($^3J_{CP}$ 2.5 Hz, $CH_{2\gamma}$), 13.20 ($^4J_{CP}$ = 0 Hz, CH_3) (first diast), 148.12 and 147.88 ($^1J_{CP}$ = 63, $^2J_{CP}$ = 8 Hz, C:), 27.14 ($^1J_{CP}$ = 62 Hz, CH_3P), 35.56 ($^1J_{CP}$ = 57 Hz, $CH_{2\alpha}$), 23.26 ($^2J_{CP}$ = 18 Hz, $CH_{2\beta}$), 23.68 ($^3J_{CP}$ = 0 Hz, $CH_{2\gamma}$), 13.20 ($^4J_{CP}$ = 0 Hz, CH_3) (second diast); mass spectrum (100 °C), *m/e* (relative intensity) 530 (M, 35), 441 (M − *n*-BuS, 60), 421 (M − PhS, 100). Anal. Calcd for $C_{31}H_{32}P_2S_2$: C, 70.16; H, 6.07; P, 11.67. Found: C, 69.92; H, 5.98; P, 10.95.

1-(Methylphenylthiophosphoryl)-2-(*tert*-butylphenylthiophosphoryl)-1,2-diphenylethylene (*Z* Isomer) (18). Compound **18** was a mixture of two diastereomers (ratio 80:20). It was obtained from 0.59 g (1.5 mmol) of **10** and *tert*-butyllithium (2.3 mL of a solution 1.3 M in pentane) as was **17** in 35% yield: mp 189 °C; ^1H NMR ($CDCl_3$) δ 0.55 ($^3J_{HP}$ = 16.6 Hz, CH_3(*t*-Bu)), 1.18 ($^2J_{HP}$ = 12.7 Hz, CH_3P) (first diast), 0.74 ($^3J_{HP}$ = 15.6 Hz, CH_3(*t*-Bu)), 1.82 ($^2J_{HP}$ = 13.6 Hz, CH_3P) (second diast); ^{31}P NMR ($CDCl_3$) δ 36.70 ($^3J_{PP}$ = 9.2 Hz, P–CH_3), 55.84 (P-*t*-Bu) (first diast), 38.62 ($^3J_{PP}$ = 9.2 Hz, P–CH_3), 54.33 (P-*t*-Bu) (second diast); ^{13}C NMR ($CDCl_3$) δ 145.94 and 148.13 (C:), 28.90 ($^1J_{CP}$ = 69.9 Hz, CH_3P), 25.69 ($^2J_{CP}$ = 0 Hz, CH_3(*t*-Bu)), 39.07 ($^1J_{CP}$ = 51.3 Hz, C(*t*-Bu)) (first diast); mass spectrum (200 °C), *m/e* (relative intensity) 530 (M, 30) 473 (M − *t*-Bu, 70). Anal. Calcd for $C_{31}H_{32}P_2S_2$: C, 70.16; H, 6.07; P, 11.67. Found: C, 70.38; H, 6.14; P, 11.94.

1-(Methylphenyl)-2-(*tert*-butylphenyl)-1,2-diphosphine Disulfide (19). A mixture of 1.0 g of **9** (2.8 mmol) in 20 mL of dry hexane, 0.4 mL of TMEDA, and 2.3 mL of *tert*-butyllithium solution (1.3 M in pentane) was stirred for 1 h at room temperature. A solution of 0.42 g (3 mmol) of CH_3I in dry THF (3 mL) was added, and the mixture was stirred for 5 min. Sulfur (0.5 g) was added, and the mixture was stirred at room temperature overnight. The solvent was evaporated, and the residue was chromatographed on silica gel (60 g of silica gel/g of product) with hexane–ether (70:30). Compound **19** was recovered in 40% yield (mp 129 °C); ^1H NMR ($CDCl_3$) δ 1.97 (J_{HP} = 12.5, J_{HP} = 6.6 Hz, CH_3P), 1.20 ($^3J_{HP}$ = 18.3 Hz, CH_3(*t*-Bu)); ^{31}P NMR ($CDCl_3$) δ 31.20 ($^1J_{PP}$ = 63.5 Hz, P_1), 53.30 (P_2); ^{13}C NMR ($CDCl_3$) δ 19.99 ($^1J_{CP}$ = 53.0, $^2J_{CP}$ = 14.6 Hz, CH_3P), 26.47 ($^2J_{CP}$ = 7.3, $^3J_{CP}$ = 7.3 Hz, CH_3(*t*-Bu)), 41.95 ($^1J_{CP}$ = 35.4, $^2J_{CP}$ = 9.7 Hz, C(*t*-Bu)); mass spectrum (170 °C), *m/e* (relative intensity) 352 (M, 17), 295 (M − *t*-Bu, 100). Anal. Calcd for $C_{17}H_{22}P_2S_2$: C, 57.93; H, 6.25; P, 17.57. Found: C, 57.92; H, 6.19; P, 16.87.

2-Phenyl-3,4-di-*tert*-butyl-1,2-diphosphet-3-ene (20). The solution of **14** (2.8 mmol) was hydrolyzed. After extraction, compound **20** was distilled at 130 °C (0.01 torr) (42% yield): ^1H NMR ($CDCl_3$) δ 4.39 ($^1J_{HP}$ = 161 Hz, $^2J_{HP}$ = 5.3 Hz, H–P), 1.31 ($^4J_{HP}$ = 1 Hz, CH_3(*t*-Bu)), 1.11 ($^4J_{HP}$ = 0.8 Hz, CH_3(*t*-Bu)); ^{31}P NMR ($CDCl_3$) δ −116.0 ($^1J_{PP}$ = 29.3 Hz, P_1), −83.5 (P_2); ^{13}C NMR ($CDCl_3$) δ 155.7 (J_{CP} = 18.3, J_{CP} = 11.0 Hz), 158.9 (J_{CP} = 18.3, J_{CP} = 12.2 Hz) (C_3 and C_4), 31.4 ($^3J_{CP}$ = 5 Hz, CH_3(*t*-Bu)), 31.9 ($^3J_{CP}$ = 6 Hz, CH_3(*t*-Bu)), 37.9 ($^2J_{CP}$ = 12.0, $^3J_{CP}$ = 3.6 Hz, C(*t*-Bu)), 38.5 ($^2J_{CP}$ = 13, $^3J_{CP}$ = 3.6 Hz, C(*t*-Bu)); IR (Nujol) ν_{HP} 2220 cm^{-1}.

1-Benzyl-2-phenyl-3,4-di-*tert*-butyl-1,2-diphosphet-3-ene (21). The solution of **14** (2.8 mmol) was added to a solution of 0.35 g (2.8 mmol) of benzyl chloride in 5 mL of THF. The solvent was evaporated, and the residue was chromatographed on silica gel (40 g of silica gel/g of product). **21** was recovered in 71% yield as an oil: ^1H NMR ($CDCl_3$) δ 3.21 (CH_2), 1.35 ($^4J_{HP}$ = 0.9 Hz, CH_3(*t*-Bu)), 1.12 ($^4J_{HP}$ = 0.9 Hz, CH_3(*t*-Bu)); ^{31}P NMR ($CDCl_3$) δ −65.0 ($^1J_{PP}$ = 53.5 Hz, P_1), −42.57 (P_2); ^{13}C NMR ($CDCl_3$) δ 156.76 (J_{CP} = 20.7, J_{CP} = 12.2 Hz), 160.48 (J_{CP} = 19.5, J_{CP} = 17.1 Hz) (C_3 and C_4), 37.13 ($^1J_{CP}$ = 35.4, $^2J_{CP}$ = 6.1 Hz, CH_2), 31.38 ($^3J_{CP}$

= 6 Hz, CH_3(*t*-Bu)), 31.62 ($^3J_{CP}$ = 4.8 Hz, CH_3(*t*-Bu)), 37.62 ($^2J_{CP}$ = 13.4 Hz, C(*t*-Bu)), 37.74 ($^2J_{CP}$ = 17 Hz, C(*t*-Bu)); mass spectrum (200 °C) *m/e* 368.18227 (M, 100), calcd for $C_{23}H_{30}P_2$ 368.1823. Anal. Calcd for $C_{23}H_{30}P_2$: C, 74.96; H, 8.20; P, 16.81. Found: C, 74.58; H, 8.03; P, 16.80.

1-(3′-Chloropropyl)-2-phenyl-3,4-di-*tert*-butyl-1,2-diphosphet-3-ene (22). The solution of **14** (2.8 mmol) was added at −30 °C to a solution of 0.44 g (2.8 mmol) of 1-bromo-3-chloropropane in 5 mL of THF. After removal of the solvent, the residue was chromatographed on silica gel (40 g of silica gel/g of product). **22** was recovered in 48% yield as an oil: ^{1}H NMR ($CDCl_3$) δ 1.8–2.1 (CH_2 α and β), 3.54 (CH_2Cl), 1.12 ($^4J_{HP}$ = 0.9 Hz, CH_3(*t*-Bu)), 1.33 ($^4J_{HP}$ = 0.7 Hz, CH_3(*t*-Bu)); ^{31}P NMR ($CDCl_3$) δ −68.80 ($^1J_{PP}$ = 49 Hz, P_1), −47.25 (P_2); ^{13}C NMR ($CDCl_3$) δ 157.27 (J_{CP} = 19.5, J_{CP} = 12.2 Hz), 159.00 (J_{CP} = 18.3, J_{CP} = 14.6 Hz) (C_3 and C_4), 26.28 ($^1J_{CP}$ = 35.4, $^2J_{CP}$ = 6.1 Hz, $CH_{2\alpha}$), 30.05 (J_{CP} = 11, J_{CP} = 8.5 Hz, $CH_{2\beta}$), 45.73 ($^3J_{CP}$ = 7.3 Hz, CH_2Cl), 31.20 ($^3J_{CP}$ = 0 Hz, CH_3(*t*-Bu)), 31.50 ($^3J_{CP}$ = 0 Hz, CH_3(*t*-Bu)), 37.75 ($^2J_{CP}$ = 13.4, $^3J_{CP}$ = 3.7 Hz, C(*t*-Bu)). Anal. Calcd for $C_{19}H_{29}P_2Cl$: C, 64.31; H, 8.18. Found: C, 63.75; H, 8.15.

1-(4′-Chlorobutyl)-2-phenyl-3,4-di-*tert*-butyl-1,2-diphosphet-3-ene (23): same procedure as for **22** from the solution **14** (2.8 mmol) and 0.48 g (2.8 mmol) of 1-bromo-4-chlorobutane (71% yield); ^{1}H NMR ($CDCl_3$) δ 1.6-2 (CH_2 α,β, and γ), 3.50 (CH_2Cl), 1.12 ($^4J_{HP}$ = 0.9 Hz, CH_3(*t*-Bu)), 1.33 ($^4J_{HP}$ = 0.7 Hz, CH_3(*t*-Bu)); ^{31}P NMR ($CDCl_3$) δ −68.25 ($^1J_{PP}$ = 49 Hz, P_1), −45.5 (P_2); ^{13}C NMR ($CDCl_3$) δ 156.8 (J_{CP} = 19.5, J_{CP} = 11 Hz), 159.25 (J_{CP} = 18.3, J_{CP} = 14.6 Hz) (C_3 and C_4), 28.2 ($^1J_{CP}$ = 34.0, $^2J_{CP}$ = 6 Hz, $CH_{2\alpha}$), 24.17 (J_{CP} = 9.8, J_{CP} = 8.5 Hz, $CH_{2\beta}$), 33.80 ($^3J_{CP}$ = 7.3 Hz, $CH_{2\gamma}$), 44.28 ($^4J_{CP}$ = 0 Hz, CH_2Cl), 31.14 ($^3J_{CP}$ = 0 Hz, CH_3(*t*-Bu)), 31.44 ($^3J_{CP}$ = 0 Hz, CH_3(*t*-Bu)), 37.60 ($^2J_{CP}$ = 12, $^3J_{CP}$ = 2.4 Hz, C(*t*-Bu)). Anal. Calcd for $C_{20}H_{31}P_2Cl$: C, 65.13; H, 8.42; P, 16.82. Found: C, 65.60; H, 8.40; P, 16.80.

1-(5′-Chloropentyl)-2-phenyl-3,4-di-*tert*-butyl-1,2-diphosphet-3-ene (24): same procedure as for **22** from the solution **14** (2.8 mmol) and 0.52 g (2.8 mmol) of 1-bromo-5-chloropentane (55% yield): ^{1}H NMR ($CDCl_3$) δ 1.6–2.2 (CH_2 α, β, γ, and δ), 3.50 (CH_2Cl), 1.12 ($^4J_{HP}$ = 1 Hz, CH_3(*t*-Bu)), 1.33 ($^4J_{HP}$ = 0.7 Hz, CH_3(*t*-Bu)); ^{31}P NMR ($CDCl_3$) δ −67.70 ($^1J_{PP}$ = 49 Hz, P_1), −44.75 (P_2); ^{13}C NMR ($CDCl_3$) δ 156.75 (J_{CP} = 19.7, J_{CP} = 11 Hz), 159.72 (J_{CP} = 18.3, J_{CP} = 13.4 Hz) (C_3 and C_4), 29.10 ($^1J_{CP}$ = 33.0, $^2J_{CP}$ = 4.9 Hz, $CH_{2\alpha}$), 26.29 (J_{CP} = 9.8, J_{CP} = 8.5 Hz, $CH_{2\beta}$), 28.50 ($^3J_{CP}$ = 7.3 Hz, $CH_{2\gamma}$), 32.29 ($^4J_{CP}$ = 0 Hz, $CH_{2\delta}$), 44.77 ($^5J_{CP}$ = 0 Hz, CH_2Cl), 31.31 ($^3J_{CP}$ = 0 Hz, CH_3(*t*-Bu)), 31.62 ($^3J_{CP}$ = 0 Hz, CH_3(*t*-Bu)), 37.7 ($^2J_{CP}$ = 13.4 Hz, $^3J_{CP}$ = 2.4 Hz, C(*t*-Bu)). Anal. Calcd for $C_{21}H_{33}P_2Cl$: C, 65.88; H, 8.63; P, 16.21. Found: C, 65.56; H, 8.61; P, 16.20.

1-(1′,2′-Diphenylethyl)-2-phenyl-3,4-di-*tert*-butyl-1,2-diphosphet-3-ene (25). A mixture of 1 g (2.8 mmol) of **9** and 0.1 g of lithium ribbon in 10 mL of dry THF was stirred at room temperature for 2 h. Excess of lithium was removed. A solution of 0.5 g (4 mmol) of benzyl chloride in 5 mL of THF was added. After removal of the solvent and chromatography, compound **25** was recovered in 32% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 3.38 (CH_2 and CH), 1.18 ($^4J_{HP}$ = 0.7 Hz, CH_3(*t*-Bu)), 1.40 ($^4J_{CP}$ = 0 Hz, CH_3(*t*-Bu)); ^{31}P NMR ($CDCl_3$) δ −75.55 ($^1J_{PP}$ = 61 Hz, P_1), −25.81 (P_2); ^{13}C NMR ($CDCl_3$) δ 158.97 (J_{CP} = 20.7, J_{CP} = 11 Hz), 159.88 (J_{CP} = 23.2, J_{CP} = 17.1 Hz) (C_3 and C_4), 47.34 ($^1J_{CP}$ = 40.3, $^2J_{CP}$ = 2.5 Hz, CH), 37.92 ($^2J_{CP}$ = 12 Hz, CH_2), 31.5 ($^3J_{CP}$ = 6.1 Hz, CH_3(*t*-Bu)), 37.92 ($^2J_{CP}$ = 17 Hz, C(*t*-Bu)); mass spectrum (200 °C) *m/e* 458.22869 (M, 100), calcd for $C_{30}H_{36}P_2$ 458.2287

1-Phenyl-6,7-di-*tert*-butyl-1-phosphonia-5-phosphabicyclo[3.2.0]-6-heptene Chloride (26). Compound **22** was heated in chloroform at 60 °C for 48 h. The chloroform was evaporated, and the phosphonium salt was recrystallized from toluene (90% yield): mp 134.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.8–2 (CH_2), 1.22 ($^4J_{HP}$ = 0 Hz, CH_3(*t*-Bu)), 1.41 ($^4J_{HP}$ = 1 Hz, CH_3(*t*-Bu)); ^{31}P NMR ($CDCl_3$) δ 22.0 ($^1J_{PP}$ = 75.7 Hz, P_1), −41.75 (P_5); ^{13}C NMR ($CDCl_3$) δ 145.34 ($^1J_{CP_1}$ = 50.0, $^2J_{CP_5}$ = 12.2 Hz, C_7), 174.90 ($^1J_{CP_5}$ = 22.0, $^2J_{CP_1}$ = 6.1 Hz, C_6), 25.5 ($^1J_{CP_5}$ = 37.9, $^2J_{CP_1}$ = 0 Hz, C_4), 22.96 ($^2J_{CP_5}$ = 6.1, $^2J_{CP_1}$ = 1 Hz, C_3), 20.41 ($^1J_{CP_1}$ = 34.2, $^2J_{CP_5}$ = 0 Hz, C_2), 30.53 ($^3J_{CP_5}$ = 7 Hz, CH_3(*t*-Bu)), 30.89 ($^3J_{CP_1}$ = 6 Hz, CH_3(*t*-Bu)), 37.86 (J_{CP_1} = 4, J_{CP_5} = 0 Hz, C(*t*-Bu)), 38.89 (J_{CP_1} = 29.3, J_{CP_5} = 14.6 Hz, C(*t*-Bu)); mass spectrum (160 °C), *m/e* (relative intensity) 319 (M, 10). Anal. Calcd for $C_{19}H_{29}P_2Cl$: C, 64.32; H, 8.18; P, 17.49. Found: C, 63.41; H, 8.23; P, 17.72.

1-Phenyl-2,3-di-*tert*-butyl-1-phospha-4-phosphoniaspiro[3.4]-2-octene Chloride (27). Compound **23** was heated in chloroform at 60 °C for 48 h. The chloroform was evaporated, and the phosphonium salt was recrystallized from toluene (54% yield): mp 230 °C; ^{1}H NMR ($CDCl_3$) δ 1.8–2.7 (CH_2), 1.28 and 1.45 (CH_3(*t*-Bu)); ^{31}P NMR ($CDCl_3$), δ 35.55 ($^1J_{PP}$ = 110 Hz, P_4), −23.07 (P_1); ^{13}C NMR ($CDCl_3$) δ 179.08 ($^1J_{CP_1}$ = 17.1, $^2J_{CP_4}$ = 13.4 Hz, C_2), 150.25 ($^1J_{CP_4}$ = 40.3, $^2J_{CP_1}$ = 14.7 Hz, C_3), 21.57 ($^1J_{CP_4}$ = 31.7, $^2J_{CP_1}$ = 0 Hz, C_5), 24.29 ($^2J_{CP_4}$ = 6.1 Hz), 25.56 ($^2J_{CP_4}$ = 3.6 Hz) (C_6 and C_7), 23.99 ($^1J_{CP_4}$ = 29.3, $^2J_{CP_1}$ = 4.9 Hz, C_8), 29.99 (J_{CP_1} = 7.3 Hz, CH_3(*t*-Bu)), 30.77 (J_{CP_4} = 6.1 Hz, CH_3(*t*-Bu)), 38.59 ($^2J_{CP_4}$ = 29.3, $^3J_{CP_1}$ = 13.4 Hz, C(*t*-Bu)), 37.26 ($^2J_{CP_1}$ = 2.4, $^3J_{CP_4}$ = 6.1 Hz, C(*t*-Bu)). Anal. Calcd for $C_{20}H_{31}P_2Cl$: C, 65.12; H, 8.47; P, 16.79. Found: C, 64.79; H, 8.80; P, 16.53.

1-Phenyl-2,3-di-*tert*-butyl-1-phospha-4-phosphoniaspiro[3.5]-2-nonene Chloride (28): same procedure as for **27** from **24** (75% yield): mp 91 °C; ^{1}H NMR ($CDCl_3$) δ 1.5–3.5 (CH_2), 1.36 ($^4J_{HP}$ = 1.2 Hz, CH_3(*t*-Bu)), 1.52 ($^4J_{HP}$ = 0 Hz, CH_3(*t*-Bu)); ^{31}P NMR ($CDCl_3$) δ 6.1 ($^1J_{P_1P_4}$ = 83 Hz, P_4), −35.5 (P_1); ^{13}C NMR ($CDCl_3$) δ 174.72 ($^1J_{CP_1}$ = 13.5, $^2J_{CP_4}$ = 9.8 Hz, C_2), 155.21 ($^1J_{CP_4}$ = 45.1, $^2J_{CP_1}$ = 13.4 Hz, C_3), 20.17 ($^1J_{CP_4}$ = 26.8, $^2J_{CP_1}$ = 0 Hz, C_5), 21.81 (J_{CP_4} = 7.3 Hz), 22.96 (J_{CP_4} = 6.1 Hz), 23.32 (J_{CP_4} = 6.1 Hz) (C_6, C_7, and C_8), 24.17 ($^1J_{CP_4}$ = 24.4, $^2J_{CP_1}$ = 7.3 Hz, C_9) 30.59 ($^3J_{CP_1}$ = 8.5, $^4J_{CP_4}$ = 0 Hz, CH_3(*t*-Bu)), 31.88 ($^3J_{CP_1}$ = 7.3, $^4J_{CP_4}$ = 0 Hz, CH_3(*t*-Bu)), 39.13 ($^2J_{CP_4}$ = 28.0, $^3J_{CP_1}$ = 14.6 Hz, C(*t*-Bu)), 38.59 ($^2J_{CP_1}$ = 7.3, $^3J_{CP_4}$ = 0 Hz, C(*t*-Bu)); mass spectrum (160 °C), *m/e* (relative intensity) 347 (M, 18). Anal. Calcd for $C_{21}H_{33}P_2Cl$: C, 65.88; H, 8.63; P, 16.21. Found: C, 65.77; H, 8.50; P, 16.33.

1-Phenyl-2,3-di-*tert*-butyl-1,4-diphosphep-3-ene Oxide (29). A mixture of 0.64 g of compound **26** (2 mmol) in 5 mL of CH_2Cl_2 and 1 mL of KOH solution (1 N in H_2O) was stirred 1 h. After extraction and evaporation of the solvent, **29** was recovered in 90% yield (mixture of two isomers 1:1). ^{1}H NMR ($CDCl_3$): δ 4.87 ($^1J_{HP_4}$ = 244 Hz, HP), first isomer; δ 4.03 ($^1J_{HP_4}$ = 228 Hz, HP), second isomer; δ 1.15, 1.44, 1.46, and 1.49 (J_{HP} = 0 Hz, CH_3(*t*-Bu), both isomers. ^{31}P NMR ($CDCl_3$): δ 41.19 ($^3J_{PP}$ = 8 Hz, P_1), −38.18 ($^1J_{P_4H}$ = 244 Hz, P_4), first isomer; δ 52.41 ($^3J_{PP}$ = 0 Hz, P_1), −41.52 ($^1J_{P_4H}$ = 228 Hz, P_4), second isomer. ^{13}C NMR ($CDCl_3$): δ 154.97 ($^1J_{CP_1}$ = 97.6 Hz), 151.70 ($^1J_{CP_1}$ = 96.5 Hz) (C_2), 168.18 (J_{CP} = 29.3, J_{CP} = 9.7 Hz), 161.51 (J_{CP} = 25.6, J_{CP} = 11 Hz) (C_3), 24.29 (J_{CP} = 15.8 Hz), 24.62 (J_{CP} = 17 Hz), 24.59 (J_{CP} = 8 Hz), 25.93 (J_{CP} = 6 Hz) (C_5 and C_6), 38.95 ($^1J_{CP_1}$ = 71 Hz), 41.00 ($^1J_{CP_1}$ = 73 Hz) (C_7), 33.56 (J_{CP} = 5 Hz), 33.08 (J_{CP} = 6 Hz), 31.68 (J_{CP} = 11 Hz) (CH_3(*t*-Bu)), 41.01 (J_{CP} = 12.2 Hz), 42.22 (J_{CP} = 15.7 Hz) (C(*t*-Bu)). Anal. Calcd for $C_{19}H_{32}P_2O_2$: C, 64.40; H, 9.03. Found: C, 63.70; H, 8.17.

X-ray Data Collection and Processing. A transparent crystal shaped as a parallelepiped of 0.2 × 0.35 × 0.6 mm^3 was used for data collection. The space group determined by Laue and precession photographs is monoclinic $p2_1/c$. Lattice constants are a = 11.724 (5) Å, b = 8.103 (3) Å c = 21.828 (9) Å, β = 89.79 (5)°, V = 2073.6 Å^3, Z = 4, and D_{calcd} = 1.14 g·cm^{-3}. A total of 2661 independent reflections were collected at room temperature on a laboratory-made diffractometer with Mo Kα-radiation (λ = 0.710 69 Å) in the θ–2θ scan mode up to $2\theta_{max}$ = 46°. The scan rate was 1.5° min^{-1}, and the scan width was $\Delta\theta$ = 1.10 + 0.345 tan θ in Bragg angle. A graphite monochromator was set in front of the counter. The intensities were collected. A total of 471 reflections with $I \leq 3\sigma(I)$ were omitted from further calculations. The intensities were not corrected for absorption (μ = 1.17 cm^{-1}).

The structure was solved by using Patterson and successive Fourier maps. Full-matrix least squares and geometrical calculations were carried out with SHELX76. All atoms but hydrogen were refined with anisotropic temperature factors. The hydrogen coordinates were refined from calculated positions keeping constant the C–H distance (1.08 Å), and their overall isotropic temperature factor was refined to 8.5 Å^2. The secondary extinction coefficient was taken into account. The final conventional R factors are R = 0.05 and R_w = 0.06 with $w = 1.19/(\sigma^2(F) + 0.001F^2)$.

Registry No. **1**, 99511-44-1; **2**, 99511-45-2; **3**, 99511-46-3; **4**, 99511-47-4; **5**, 99511-48-5; **6**, 99511-49-6; **7**, 99511-50-9; **8**, 99531-54-1; **9**, 75600-54-3; **10**, 42451-95-6; **12**, 99511-52-1; **13** (isomer 1), 99511-51-0; **13** (isomer 2), 99511-60-1; **14**, 96693-31-1; **15**, 99511-53-2; **16**, 99511-54-3; **17** (isomer 1), 99511-55-4; **17** (isomer

2), 99511-67-8; **18** (isomer 1), 99511-56-5; **18** (isomer 2), 99511-68-9; **19**, 99511-57-6; **20**, 96693-32-2; **21**, 96693-33-3; **22**, 99511-58-7; **23**, 99511-59-8; **24**, 99511-61-2; **25**, 99511-62-3; **26**, 99511-63-4; **27**, 99511-64-5; **28**, 99511-65-6; **29** (isomer 1), 99511-66-7; **29** (isomer 2), 99511-69-0; $(PhP)_5$, 3376-52-1; PhC≡CMe, 673-32-5; PhC≡CSiMe$_3$, 2170-06-1; PhC≡CBu-*t*, 4250-82-2; MeC≡CBu-*t*, 999-78-0; PhC≡CH, 536-74-3; benzyl chloride, 100-44-7; 1-bromo-3-chloropropane, 109-70-6; 1-bromo-4-chlorobutane, 6940-78-9; 1-bromo-5-chloropentane, 54512-75-3.

Supplementary Material Available: Tables of hydrogen atoms coordinates (Table V), temperature factors (Table VI), distances from mean least-squares plane P_1, P_2, C_{13}, C_{14} (Table VII), and observed and calculated structure factors (Table VIII) (14 pages). Ordering information is given on any current masthead page.

Synthesis of a (Chloromethyl)cobalt(III) Carbonyl Complex, $Co(\eta^5\text{-}C_5Me_5)(CO)(CH_2Cl)Cl$, from Dichloromethane by a Photoassisted, Oxidative-Addition Reaction with $Co(\eta^5\text{-}C_5Me_5)(CO)_2$

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Presented herein are the preparation and structural characterization of $Co(\eta^5\text{-}C_5Me_5)(CO)(CH_2Cl)Cl$ which represents the first example of an isolable dichloromethane oxidative-addition product from a non-porphyrin cobalt(I) species. This (chloromethyl)cobalt(III) compound was prepared in ca. 60% yield by the photolytic reaction of $Co(\eta^5\text{-}C_5Me_5)(CO)_2$ with CH_2Cl_2 in diisopropyl ether. Its composition was deduced from IR, ^1H and ^{13}C NMR, and mass spectral analysis and confirmed from an X-ray crystallographic study. The molecular configuration expectedly conforms to the well-known three-leg piano-stool geometry with normal Co–CH_2Cl and Co–CO bond lengths of 1.991 (8) and 1.775 (10) Å, respectively. Of interest is that the ring carbon atoms of the pentamethylcyclopentadienyl ring exhibit a small but systematic distortion from a regular pentagonal geometry toward an "allyl–ene" geometry; the resulting C–C bond length pattern and slight ring puckering are virtually identical with those found in both $Co(\eta^5\text{-}C_5Me_5)(CO)_2$ and $Rh(\eta^5\text{-}C_5Me_5)(CO)_2$. The physical–chemical properties of this red, reasonably air-stable crystalline compound are reported together with its possible role as precursor for the synthesis of a variety of organocobalt compounds. $Co(\eta^5\text{-}C_5Me_5)(CO)(CH_2Cl)Cl$: M_r = 307.17; triclinic; $P\bar{1}$; a = 7.973 (4) Å, b = 13.860 (7) Å, c = 6.767 (3) Å, α = 95.70 (2)°, β = 110.43 (2)°, γ = 81.06 (2)°, V = 691.46 at T = 295 K; d_{calcd} = 1.47 g/cm^3 for Z = 2. The crystal structure was solved via direct methods followed by successive Fourier syntheses and anisotropically refined by least squares (RAELS) to R_1 = 4.05% for 907 independent diffractometry data with $|F_o| > 2.5\sigma(F_o)$.

Introduction

Metal–carbon bond formation by oxidative addition of organic halides to transition-metal complexes has played a central role in many organic reactions.[1] Studies of electrophilic alkylations of low-valent cobalt complexes have attracted considerable interest, due in part to the desire to find low-cost alternatives to rhodium-based catalytic processes. While many products have been isolated from oxidative-addition reactions of iodo- and diiodoalkanes with nucleophilic cyclopentadienylcobalt(I) complexes,[2-6] relatively few species have been reported from oxidative-addition reactions of chloro- and dichloroalkanes. In particular, the synthesis of stable (chloromethyl)cobalt(III) complexes from dichloromethane reactions has been heretofore accomplished only in reactions of CH_2Cl_2 with reduced vitamin B_{12} and reduced cobalamin model compounds.[7]

In an effort to prepare (chloromethyl)cobalt(III) complexes, Hofmann and Werner[8] found that the low-temperature reaction (−50 °C) of chloroiodomethane and $Co(\eta^5\text{-}C_5H_5)(PMe_3)(CO)$ gives a mixture of $Co(\eta^5\text{-}C_5H_5)(PMe_3)(CH_2Cl)I$ and $Co(\eta^5\text{-}C_5H_5)(PMe_3)(Cl)I$ which can be separated via solubility differences. Although stable in the solid state upon being crystallized at −78 °C, the former (chloromethyl)cobalt(III) complex eliminates CH_2 in solution above −30 °C to form the latter complex. Hofmann and Werner[8] also found that the addition of an equimolar quantity of a two-electron donor (where L =

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