Organophosphorus Compounds; 52.[1] Phosphatriafulvenes and Their Reactions with Electrophiles

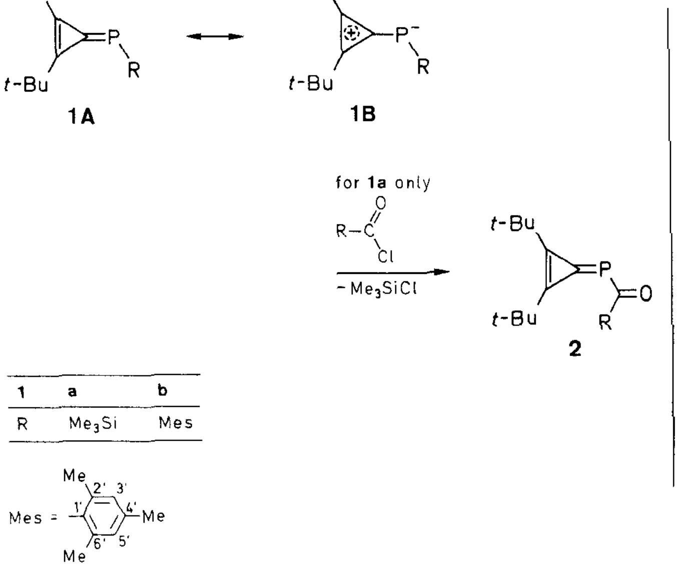
Eberhard Fuchs, Bernhard Breit, Uwe Bergsträßer, Jürgen Hoffmann, Heinrich Heydt, Manfred Regitz*
Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D-6750 Kaiserslautern, Germany

Dedicated to Professor H. J. Bestmann in recognition of his services to Synthesis during his term as Executive Editor

Electrophilic reagents attack the phosphatriafulvenes **1a** and **1b** exclusively at the phosphorus atom. Hence **1b** is methylated by methyl iodide to furnish the cyclopropenylium iodide **3** which, in turn, is converted to the triazine **6** by reaction with sodium azide. Ketenes **8** react with **1a** through subsequent P → O silyl shifts to give the vinylphosphatriafulvenes **10**. Isocyanates **13a** and **13b** behave analogously (→ **15**). In the reactions of **1a** with isothiocyanates **13c** and **13d**, in contrast, a P → N silyl shift is observed which leads to the formation of **16**. Acetylenedicarboxylates **17** undergo insertion into the P/Si bond of the silylated phosphatriafulvene **1a** (→ **19**). In the case of the reaction of the mesityl-substituted phosphatriafulvene **1b** with **17**, kinetically controlled formation of the dihydrooxophosphinines **20** takes place; at room temperature, the latter products undergo slow rearrangement to give the thermodynamically more stable isomers **21**.

In phosphaalkenes,[2] the phosphorus atom possesses a positive partial charge and the carbon atom a negative partial charge, this is in complete harmony with the Pauling electronegativities (2.1 and 2.5, respectively). Accordingly, the hydrogen atom of a protic nucleophile, HX, adds to the carbon and the X part to the phosphorus of the phosphaalkene.[3]

In contrast, the situation in the phosphatriafulvenes **1A** ↔ **1B**, recently synthesized for the first time by Peterson olefination, is completely reversed.[1,4]



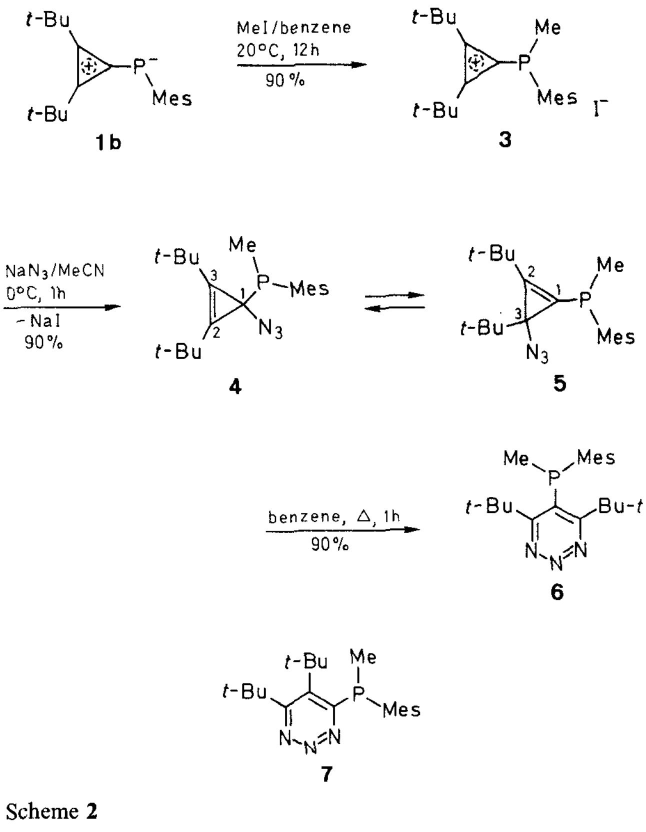
1	a	b
R	Me$_3$Si	Mes

Scheme 1

These compounds possess an inverse electron density in which, as shown by **1B**, the positive charge on the carbon atom is stabilized in the Hückel aromatic cyclopropenylium moiety and the phosphorus atom is compelled to accept an unnatural negative charge. This situation is reflected, among others, by the unusual high-field shifts of the ^{31}P-NMR resonances of **1a** and **1b** ($\delta = -74.1$ and -23.2, respectively, as compared to $\delta = +200-300$ for phosphaalkenes with normal electron densities).[5] It can thus be expected that nucleophiles will attack the three-membered ring of **1** and electrophiles the phosphorus atom. To date it was only known that **1a** reacted with acyl chlorides in the above manner via acylation of the phosphorus atom to furnish products **2**.[1] In the present work, we have shown that electrophilic reagents such as methyl iodide, ketenes, isocyanates, isothiocyanates, and acetylenedicarboxylates commence their reactions with **1a** and **1b** at the heteroatom.

Methylation of 1b (→ 3)

When the mesityl-substituted phosphatriafulvene **1b** is allowed to react with methyl iodide, it is smoothly methylated at phosphorus to furnish the phosphanylcyclopropenylium iodide **3**. An analogous reaction between cyclopropenone and for example, methyl trifluoromethanesulfonate has been reported previously.[6] In the ^{13}C-NMR spectrum of **3**, the signals of the cyclopropenylium carbon atoms are shifted to lower field as compared to those of **1b**[1] and are also split by coupling with phosphorus [$\delta = 180.7$ ($^2J_{C,P} = 6.7$ Hz, C-2/C-3), 184.3 ($^1J_{C,P} = 51.5$ Hz, C-1)].



Scheme 2

In accord with its constitution, compound **3** can be converted by way of iodide/azide exchange into the phosphanyl-1,2,3-triazine **6**.[7] Initially, a mixture of isomers, i.e., the covalently bonded azidocyclopropenes **4** and **5**, is formed; these isomers presumably coexist in a solvent-dependent equilibrium via the corresponding cyclopropenylium azide. The unsymmetrical isomer **5** predominates in the mixture [ratio **4**/**5** = 35:65 (C_6D_6), 7:93 ($CDCl_3$)]. Of course, it cannot be excluded that only one isomer exists in the crystalline state.

Irrespective of this, the subsequent reaction step is specific: when the mixture of **4** and **5** is heated in benzene, the triazine **6** is formed exclusively. Thus, the isomerization process can only start from **5** and involves attack of the terminal azide nitrogen at C-2 before opening of cyclopropene ring can occur. No evidence for the existence of the possible isomer **7** could be obtained by NMR spectroscopy although its formation from both **4** and **5** is feasible.

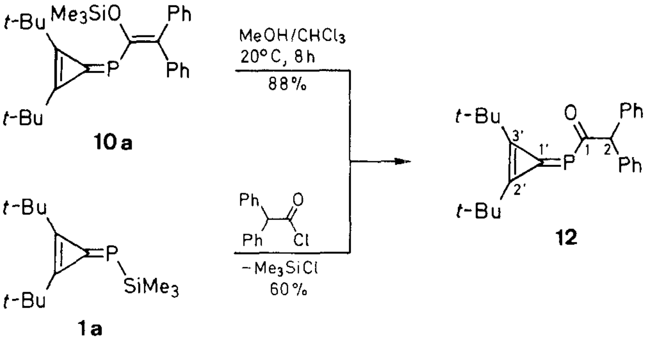
Differentiation between the two triazines **6** and **7** is simple since the former possesses a mirror plane of symmetry. This is responsible for the magnetic equivalence both of the carbon atoms C-4 and C-6 as well as of the two *tert*-butyl groups (see experimental section). The two ring carbon atoms, C-4/C-6, resonate at $\delta = 165.6$ and thus do not differ significantly from the corresponding signals of 4,5,6-tri-*tert*-butyl-1,2,3-triazine [**6**, *t*-Bu in place of P(Me)Mes at C-5; $\delta = 164.3$].[7]

Reactions of Ketenes with 1a (→ 10)

Ketenes have pronounced electrophilic character and thus it can be expected that **8a** and **8b** will react with the phosphatriafulvene **1a** to furnish the betaines **9a** and **9b**. However, the reactions do not stop at this stage but continue further giving rise to the formation of the siloxyvinylphosphatriafulvenes **10a** and **10b** in at least high selectivity by way of [1,3]silyl shifts to the oxygen atom originating from the ketene. Within the detection limits of ^1H- and ^{31}P-NMR spectroscopy, a P → C silyl shift, which would lead to the isomer **11**, could not be detected. Analogous insertion reactions of heterocumulenes into the P/Si bonds of silylated phosphanes have been reported.[8]

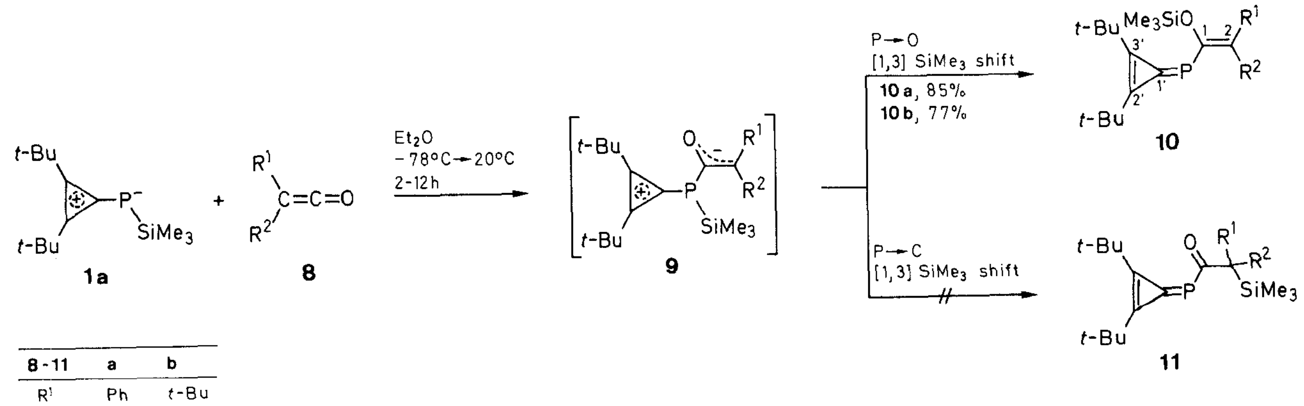
The fact that the CO group of the ketene is directly involved in the reaction is immediately apparent from the absence of carbonyl absorptions in the IR spectra of the reaction products **10a** and **10b**. The formation of a vinyl substituent on the phosphorus atom is unambiguously indicated by the presence in the ^{13}C-NMR spectra of the signals for two additional sp^2-hybridized carbon atoms which are respectively split by $^1J_{C,P}$ and $^2J_{C,P}$ couplings [**10a**: $\delta = 156.7$ ($^1J_{C,P} = 65.6$ Hz, C-1), 132.5 ($^2J_{C,P} = 4.6$ Hz, C-2); **10b**: $\delta = 175.3$ ($^1J_{C,P} = 70.3$ Hz, C-1), 113.5 ($^2J_{C,P}$ 11.4 Hz, C-2)].

In the case of **10b**, the occurrence of *cis*/*trans* isomers of the newly formed vinyl group is in principle possible but in fact does not occur. The configuration of the product can be unequivocally assigned in favor of the *Z*-isomer of **10b**: the signal in the ^{13}C-NMR spectrum for the nitrile carbon atom *cis* to phosphorus appears as a singlet whereas the signal of the tertiary carbon atom of the *tert*-butyl group *trans* to phosphorus is split by 24.8 Hz. Furthermore and in agreement with the above, no $^3J_{C,P}$ couplings are observed, for example, in cyclopropenes with inevitable *cis*-arrangements of P and C substituents at the double bond.[9]



Scheme 4

The constitution of **10a** can be also confirmed unambiguously by chemical means: on methanolysis the silyl group is eliminated and the primarily formed enol rearranges directly to the ketone form giving the known acylphosphatriafulvene **12**.[1] This product has also been prepared by the condensation of **1a** with diphenylacetyl chloride.[1] The silyl cleavage, **10a** → **12**, only proceeds smoothly in chloroform; this is presumably due to traces of acid in the solvent.



8-11	a	b
R1	Ph	t-Bu
R2	Ph	CN

Scheme 3

Insertion Reactions of Isocyanates and Isothiocyanates with 1a (→ 15 and 16)

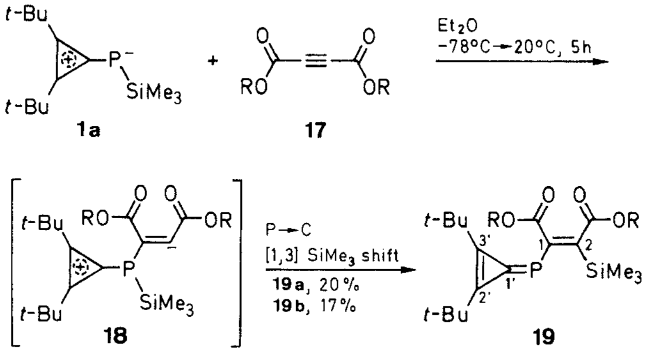
Following the successful insertion of ketenes into the P/Si bond of **1a**, it is reasonable to assume that comparable reactions with isocyanates and isothiocyanates will also take place. When **1a** is allowed to react with the heterocumulenes **13a–d**, pale yellow to yellow, crystalline 1 : 1 compounds are obtained, this time by way of the betaine intemediates **14**. In the cases of the isocyanates **13a** and **13b**, the imidoesters **15a** and **15b** are formed by way of P → O silyl shifts. With the isothiocyanates **13c** and **13d**, on the other hand, P → N silyl shifts are responsible for the products formed – the thioamides **16a** and **16b**.

The absence of carbonyl absorptions in the IR spectra of **15a** and **15b** provides initial, indirect evidence for the imidoester structures of these products. Together with the fact that, according to ^{13}C- and ^{31}P-NMR spectral analysis, the phosphatriafulvene system is retained intact (comparison with the spectra of other, structurally clarified members of the same substance class, see reference[1]), this practically rules out the formation of structural isomers. Further evidence is provided by the observation of signals exhibiting a splitting by the directly adjacent phosphorus atom for the newly formed imino carbon atoms (**15a**: $\delta = 164.6$, $^{1}J_{C,P} = 80.0$ Hz; **15b**: $\delta = 189.4$, broad[10]). Finally, a good agreement between the ^{13}C-NMR data of **15a** and **15b** and those of the insertion products obtained from isocyanates and trimethylsilylphosphanes is observed.[8a,11] The retention of the thiocarbonyl groups in the products **16a** and **16b** from reactions with isothiocyanates is apparent from their ^{13}C-NMR spectra which exhibit typical resonances at $\delta = 227.9$ and 229.2 with $^{1}J_{C,P}$ couplings of 79.6 Hz and 77.4 Hz, respectively [(Me$_3$Si)MeP–C(=S)–NPh(SiMe$_3$) was employed as reference substance; $\delta = 226.5$, $^{1}J_{C,P} = 47.5$ Hz].[12] The phosphatriafulvene skeleton is also retained intact in these systems (see Experimental Section).

In fact that the signals for the *tert*-butyl groups in the ^{1}H-NMR spectra as well as those of the ring carbon atoms C-2′/C-3′ (and also of the central C atoms of the *tert*-butyl groups bound to these ring C atoms) in the ^{13}C-NMR spectra are not separated at room temperature but rather appear as broadened signals provides unequivocal evidence for the occurrence of a coalescence phenomenon. It is reasonable to assume that this involves an *E*/*Z*-isomerization (degenerated, rotation or inversion) at the weakened P/C double bonds of **16a** and **16b**.[1] The phenomenon was not studied further in the present case.

Insertion Reactions of Acetylenedicarboxylates with 1a (→ 19)

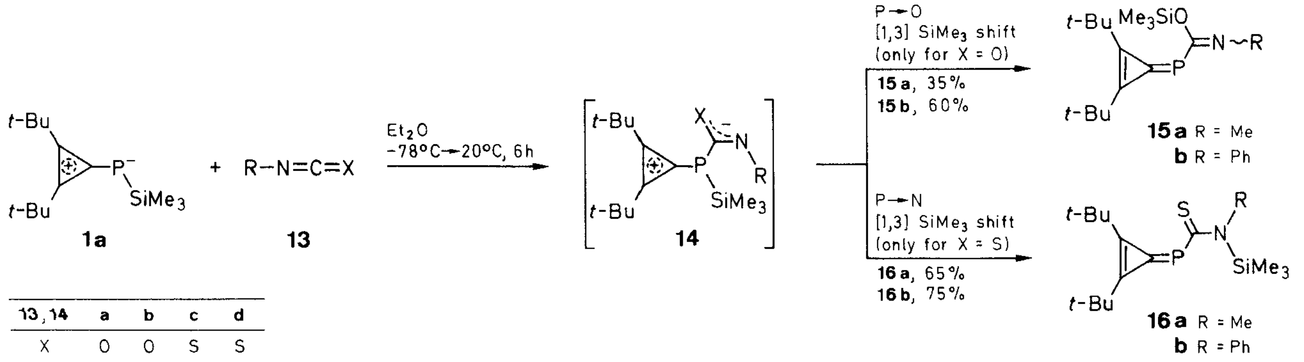
Electron-poor acetylenes such as **17a** and **17b** undergo insertion into the P/Si bond of **1a** with formation of **19a** and **19b**, in analogy with the previously discussed heterocumulenes. The orange to red colored crystalline products decompose very readily and can only be purified by filtration over silica gel and then only at the expense of large losses in yield.



17–19	a	b
R	Me	t-Bu

Scheme 6

The change at the PSiMe$_3$ increment of **1a** is already apparent from the ^{1}H-NMR spectra of **19a** and **19b**. The original $^{3}J_{H,P}$ coupling of 3.7 Hz[1] in the phosphatriafulvene disappears and is replaced by $^{5}J_{H,P}$ couplings of 0.7 and 0.6 Hz, respectively. As in the cases of **10**, **15**, and **16**, the characteristic ^{13}C- and ^{31}P-NMR resonances of the phosphatriafulvene moiety are retained. The fact that the CO groups are still present after incorporation of the acetylenedicarboxylate is seen from the appearance of two resonances for each product ($\delta = 169.9$, 171.2 and 169.4, 169.8, respectively) where



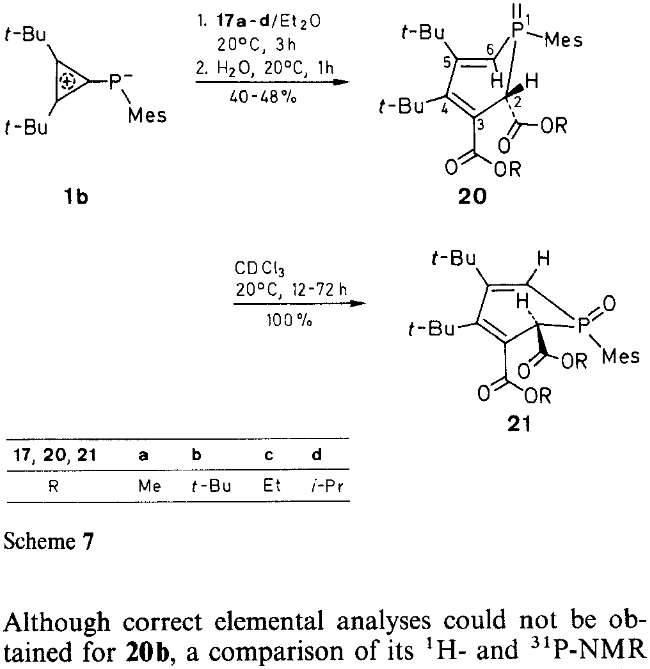
13, 14	a	b	c	d
X	O	O	S	S
R	Me	Ph	Me	Ph

Scheme 5

$^3J_{C,P}$ coupling constants of 10.3 and 7.9 Hz, respectively, are in opposition to a $^2J_{C,P}$ coupling of 0 Hz. The chemical shifts of the newly formed vinyl groups as well as the magnitudes of the splittings by the heteroatom are in accord with expectations and require no further comment. Once again, it seems reasonable for the reactions **1a** + **17a,b** → **19a,b** to assume an initial electrophilic attack according to **18** which must then be followed by a rapid P → C silyl shift. In the cases of both **19a** and **19b**, we propose the *cis* configuration (maleic acid derivatives) for the vinyl groups at phosphorus although this has not yet been proved directly. An insertion of dimethyl acetylenedicarboxylate into the C/Si bond of silylynamines giving rise to the same stereochemical consequences is known in the literature.[13] In addition, we have unequivocally demonstrated the maleic acid structure for the products of the insertion reactions of acetylenedicarboxylates into the P/Si bonds of 1-trimethylsilyl-1,2-dihydrodiphosphasiletes.[14]

1,2-Dihydro-1-phosphinine Oxides 20 and 21

An insertion reaction of electron-poor acetylenes with the silylated phosphatriafulvene, in analogy to that described above (**1a** + **17** → **19**), can be discounted from the start for the corresponding reactions of **1b**. ^{31}P-NMR monitoring of a preliminary experiment with dimethyl acetylenedicarboxylate (**17a**) showed, on completion, the formation of only a single product ($\delta = -11.1$). This compound is very unstable and undergoes uncontrollable decomposition on attempts to isolate it. However, when water is added as a trapping reagent, a 1 : 1 : 1 adduct of the three reaction partners can be obtained. As will be shown below, this adduct is assigned the structure **20a**. The acetylenedicarboxylates **17b–d** behave similarly and give rise to the products **20b–d**.



17, 20, 21	a	b	c	d
R	Me	*t*-Bu	Et	*i*-Pr

Scheme 7

Although correct elemental analyses could not be obtained for **20b**, a comparison of its ^{1}H- and ^{31}P-NMR data with those of the other 2*H*-1-phosphinine oxides (**20a,c,d**) removes any remaining doubts about its structure. In the following, the NMR data of compound **20a** only will be discussed in detail as a model for all four products.

In the ^{1}H-NMR spectrum of **20a** signals for two *tert*-butyl groups ($\delta = 1.09$, 1.25), two ester methyl groups ($\delta = 3.30$, 3.69), the hydrogen atoms of the mesityl moiety, and finally – in complete harmony with the proposed structure – two double doublets for the ring hydrogen atoms [$\delta = \; = 4.60$ ($^2J_{H,P} = 16.5$ Hz, $^4J_{H,H} = 1.2$ Hz, H-2) and $\delta = 6.45$ ($^2J_{H,P} = 28.3$ Hz, $^4J_{H,H} = 1.2$ Hz, H-6)] are observed.

The sp^3-hybridized carbon atom giving the signal at $\delta = 52.8$ in the ^{13}C-NMR spectrum is subject to coupling with a proton ($^1J_{C,H} = 131.5$ Hz) and a phosphorus atom ($^1J_{C,P} = 72.9$ Hz). In addition, signals for four sp^2-hybridized carbon atoms [$\delta = 123.3$ ($^1J_{C,P} = 106.9$ Hz, $^1J_{C,H} = 167.0$ Hz, C-6), 125.3 ($^2J_{C,P} = 8.8$ Hz, C-3), 162.5 ($^3J_{C,P} = 15.5$ Hz, C-4), and 168.1 ($^2J_{C,P} = 2.6$ Hz, C-5)] with the expected couplings to phosphorus and hydrogen can be seen.

The ^{31}P-NMR resonance at $\delta = +23.8$ is indicative of a $\lambda^5\sigma^4$-phosphorus atom; since the hydrogen atoms originating from the trapping reagent water are incorporated into the carbon skeleton of **20a**, the oxygen is most probably bonded to phosphorus. This assumption is further substantiated by the characteristic PO vibration in the IR spectrum ($\nu = 1250\,\text{cm}^{-1}$).

The final confirmation for the unusual structure of the product from the reaction **1b** + **17a** + H_2O is provided by an X-ray crystal structure analysis of **20c**. The RSPLOT (Figure 1) shows the twisted half-chair conformation of the dihydrophosphinine ring system. Selected bond lengths and bond angles are listed in the Table.

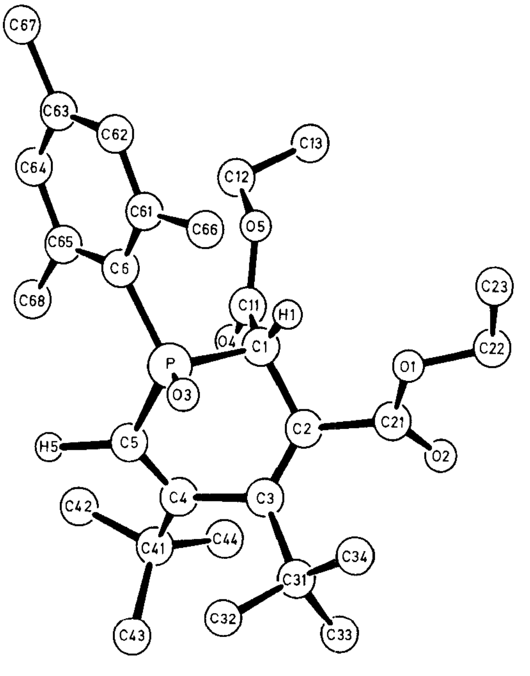


Figure 1. RSPLOT of Diethyl (1α,2β)-4,5-Di-*tert*-butyl-1-oxo-1-(2,4,6-trimethylphenyl)-1,2-dihydrophosphinine-2,3-dicarboxylate (**20c**)

Table. Selected bond lengths [Å] and bond angles [°] for compound **20c**.

Atoms	Atoms
P-O3 1.476(6)	P-C1 1.818(1)
C11-C1 1.493(1)	C2-C1 1.529(1)
P-C6 1.811(8)	C31-C3 1.581(1)
C4-C3 1.533(1)	P-C5 1.770(8)
C21-C2 1.506(1)	C3-C2 1.312(1)
C5-C4 1.334(1)	C41-C4 1.560(1)
C1-P-O3 114.6(4)	C5-P-C6 115.7(4)
C6-P-C1 102.8(4)	C2-C1-P 104.9(6)
C5-P-C1 97.4(4)	C4-C3-C2 117.5(7)
C11-C1-P 114.7(6)	C21-C2-C1 113.4(7)
C2-C1-C11 116.4(7)	C3-C2-C1 122.2(7)
C31-C3-C2 122.9(7)	C5-C4-C3 118.0(7)
C4-C3-C31 118.5(7)	C41-C4-C5 120.9(7)
C4-C5-P 118.0(6)	C3-C2-C21 124.0(7)
C6-P-O3 113.0(4)	C41-C4-C3 120.5(7)
C5-P-O3 112.1(4)	

The deviations from the least squares plan for the atoms C1, C2, C3, C4, and C5 amount to 0.084, −0.023, −0.147, 0.273, and −0.187 Å. The angle between this plane and the P-C1-C5 plane is 53.71°. The twisting angle of the double bonds C2/C3 and C4/C5 was determined as 48.97°, consequently the *s-cis*-1,3-butadiene system is no longer planar as a result of the presence of the two adjacent *tert*-butyl groups. This also has an influence on the bond lengths in the diene part of the molecule. The lengths of both double bonds [C2−C3 = 1.312(1) Å, C4−C5 = 1.334(1) Å] are in the range characteristic for isolated double bonds (average value: 1.33 Å)[15] because of the absence of conjugation effects. Similarly, the C3−C4 single bond length of 1.533(1) Å is also not significantly shortened (average value: 1.56 Å).[15]

The dihedral angles α(H−C−P=O) in the 2*H*-phosphinine oxide **20c** and the associated geminal P/H couplings are also worthy of comment (Figure 2).

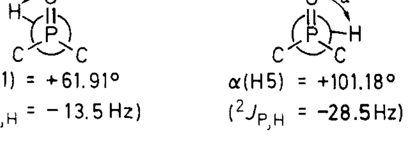


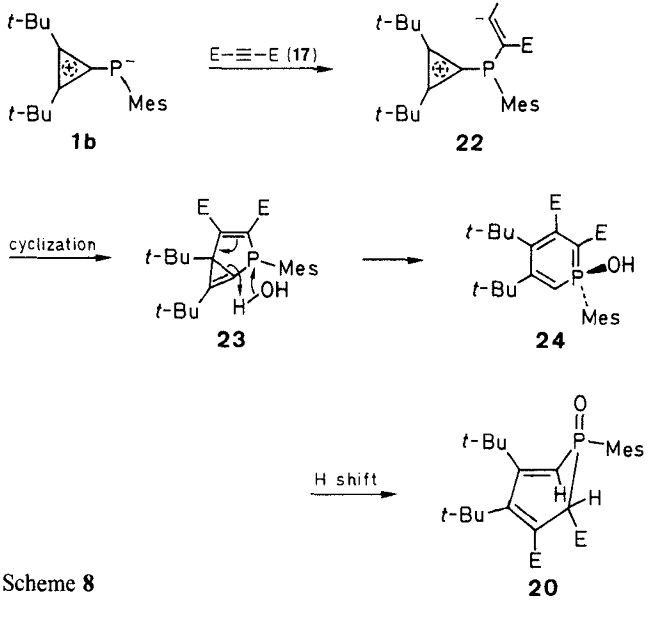
Figure 2. Dihedral Angles α(H−C−P=O) and geminal P/H couplings in the 2*H*-1-phosphinine oxide **20c**

The dihedral angle amounts to 61.91° for H1 and 101.18° for H5. In other, structurally confirmed, six-membered ring systems, the $^2J_{H,P}$ coupling constants were found to exhibit a strong dependence on the dihedral angle α; according to both theory and experiment these couplings have a negative sign[16] and this is also the case for **20c** (Figure 2). The $^2J_{H,P}$ coupling constant of −28.5 Hz for H5 is relatively large (for a dihedral angle of α = 101°, values between −6 and −18 Hz have been reported for structurally confirmed compounds).[16]

When the 1,2-dihydro-1-phosphinine oxides **20a** and **20c** are allowed to stand at room temperature in deuterochloroform for a few hours, quantitative conversion into the structurally related isomers **21a** and **21c** is observed; warming accelerates these transformations. The ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra of the new compounds **21a** and **21c** exhibit signals that are very similar to those of the starting materials **20a** and **20c**. The only differences are the $^2J_{H,P}$ coupling constants for the olefinic proton at C6 which are relatively small with 13.2 and 12.8 Hz, respectively. These observations allow us to consider the 1,2-dihydro-1-phosphinine oxides **20** as the kinetically controlled products of the reactions **1b** + **17** + H_2O and the isomers **21** as the thermodynamically controlled products.

Discussion of the Reaction Mechanism

It may be assumed, as proposed in the examples discussed previously, that the acetylenedicarboxylate **17** nucleophilically attacks the triafulvene phosphorus atom of **1b** to form a betaine (→ **22**) in the first step.



Scheme 8

Cyclization would then be responsible for the construction of the angularly strained heterobicyclic system **23**. This could also be the single species detected during the ^{31}P-NMR monitoring (δ = −11.1) of the reaction (see preceeding section). Cleavage of the three-membered ring system under the action of the trapping reagent water to give the λ^5-phosphinine **24** is followed by a proton shift to furnish the final product **20**.

All reactions were carried out under argon (purity > 99.998%) in previously baked-out and evacuated apparatus. The solvents used were dried by standard procedures and then distilled and stored under argon.[17] Melting points were determined on a Mettler FP 61 apparatus (heating rate 3°C/min). Microanalyses were obtained with a Perkin-Elmer Analyser 240 apparatus. Bulb-to-bulb distillations were performed in a Büchi GKR 50 apparatus, the temperatures given refer to the heating mantle. Mass spectra were obtained using a Varian MAT 311 spectrometer. IR spectra were recorded with a Perkin-Elmer 397 spectrophotometer. ^{1}H-NMR spectra were measured on Varian EM 360 (60 MHz), Varian EM 390 (90 MHz), Bruker WP 200 (200 MHz), and Bruker AM 400 (400 MHz) spectrometers with TMS as internal standard. ^{13}C-NMR spectra were measured on Bruker WP 200 (50.32 MHz) and Bruker AM 400 (100.64 MHz) spectrometers with TMS as internal standard. ^{31}P-NMR spectra were recorded on Bruker WP 200 (80.8 MHz) and Bruker AM 400 (161.6 MHz) spectrometers with 85% orthophosphoric acid as external standard.

Phosphanylcyclopropenylium Salts and Phosphanyltriazines from 1b:

2,3-Di-*tert*-butyl-1-[methyl(2,4,6-trimethylphenyl)phosphanyl]cyclopropenylium Iodide (3):

To a solution of **1b**[1] (1.2 g, 4.0 mmol) in benzene (20 mL) is added dropwise at 20 °C a solution of MeI (0.57 g, 0.25 mmol) in benzene (10 mL) and the mixture is stirred at this temperature for 12 h. Precipitated **3** is separated by centrifugation, washed with pentane, and dried to furnish yellow crystals; yield: 1.6 g (90%); mp 120 °C (dec).

$C_{21}H_{32}IP$ calc. C 56.63 H 7.24
(445.4) found 56.2 7.16

IR (KBr): ν = 2960 (CH), 2920 (CH), 1600, 1455, 1365, 1320, 1285, 1230, 1190, 1020, 875, 860, 845 cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = 1.4 [s, 18 H, $C(CH_3)_3$], 2.1 (d, 3 H, $^2J_{H,P}$ = 2.5 Hz, PCH_3), 2.3 (s, 3 H, 4-$C\underline{H}_3$-C_6H_2), 2.5 (s, 6 H, 2,6-di-$C\underline{H}_3$–C_6H_2), 6.9 (d, 2 H, $^4J_{H,P}$ = 3.9 Hz, C_6H_2).

^{13}C-NMR ($CDCl_3$): δ = 9.7 (d, $^1J_{C,P}$ = 8.7 Hz, PCH_3), 20.9 (s, 4-$\underline{C}H_3$–C_6H_2), 23.9 (d, $^3J_{C,P}$ = 15.2 Hz, 2,6-di-$\underline{C}H_3$–C_6H_2), 27.5 [s, $C(\underline{C}H_3)_3$], 34.9 [s, $\underline{C}(CH_3)_3$], 122.3 (d, $^4J_{C,P}$ = 4.8 Hz, C-4′), 129.9 (d, $^3J_{C,P}$ = 7.0 Hz, C-3′), 143.3 (s, C-2′), 144.2 (d, $^1J_{C,P}$ = 17.8 Hz, C-1′), 180.7 (d, $^2J_{C,P}$ = 6.7 Hz, C-2/C-3), 184.3 (d, $^1J_{C,P}$ = 51.5 Hz, C-1).

^{31}P-NMR ($CDCl_3$): δ = – 40.0 (s).

(1-Azido-2,3-di-*tert*-butyl-2-cyclopropenyl)methyl(2,4,6-trimethylphenyl)phosphane (4) and (3-Azido-2,3-di-*tert*-butyl-1-cyclopropenyl)methyl-(2,4,6-trimethylphenyl)phosphane (5):

NaN_3 (0.4 g, 6.1 mmol) is added to a solution of **3** (2.4 g, 5.5 mmol) in MeCN (20 mL) at 0 °C and the mixture is stirred at this temperature for 1 h. The solvent is then removed under vacuum, the residue is taken up in pentane, and insoluble material removed by centrifugation. The pentane solution is evaporated to give a colorless oil which slowly solidifies; yield: 1.8 g (90%), isomeric mixture of **4** and **5** (35:63 in C_6D_6; 7:93 in $CDCl_3$ by ^{1}H-NMR spectroscopy); mp 58 °C.

$C_{21}H_{32}N_3P$ calc. C 70.55 H 9.02 N 11.8
(357.5) found 70.9 8.96 11.5

IR (film): ν = 2960 (CH), 2100 (N_3), 1600, 1470, 1450, 1385, 1355, 1275, 1260, 1240, 1150, 1020, 910, 850 cm^{-1}.

^{1}H-NMR (C_6D_6): δ = 1.0, 1.1 [2 s, each 9 H, $C(CH_3)_3$], 1.6 (br d, 3 H, $^2J_{H,P}$ = 5.1 Hz, CH_3), 2.1 (s, 3 H, 4-$C\underline{H}_3$–C_6H_2), 2.6 (s, 6 H, 2,6-di-$C\underline{H}_3$–C_6H_2), 6.8 (d, 2 H, $^4J_{H,P}$ = 2.4 Hz, C_6H_2).

^{31}P-NMR ($CDCl_3$): δ = – 57.8 (s, isomer **4**), – 60.4 (s, isomer **5**).

4,6-Di-*tert*-butyl-5-[methyl(2,4,6-trimethylphenyl)phosphanyl]-1,2,3-triazine (6):

A solution of **4** and **5** (1.0 g, 2.8 mmol) in benzene (10 mL) is heated until the starting materials cannot be detected by ^{1}H-NMR spectroscopy (~ 1 h). Product **6** separates as a brown crystalline powder which is filtered off, washed several times with pentane, and dried to furnish colorless crystals; yield: 0.9 g (90%); mp 190 °C.

$C_{21}H_{32}N_3P$ calc. C 70.55 H 9.02 N 11.8
(357.5) found 70.50 8.97 11.6

IR (KBr): ν = 2960 (CH), 2900, 1600, 1470, 1440, 1400, 1380, 1360, 1285, 1210, 1180, 1130, 1050, 1015, 900, 855, 800, 750, 690 cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = 1.17 [s, 18 H, $C(CH_3)_3$], 1.45 (d, 3 H, $^2J_{H,P}$ = 6.9 Hz, PCH_3), 1.82 (br, 6 H, 2,6-di-$C\underline{H}_3$–C_6H_2), 2.14 (s, 3 H, 4-$C\underline{H}_3$–C_6H_2), 6.73 (d, 2 H, $^4J_{H,P}$ = 2.0 Hz, C_6H_2).

^{13}C-NMR ($CDCl_3$): δ = 18.9 (d, $^1J_{C,P}$ = 16.9 Hz, CH_3), 21.1 (s, 4-$\underline{C}H_3$–C_6H_2), 22.5 (d, $^3J_{C,P}$ = 15.3 Hz, 2,6-di-$\underline{C}H_3$-C_6H_2), 30.2 [d, $^4J_{C,P}$ = 6.2 Hz, $C(\underline{C}H_3)_3$], 39.7 [d, $^3J_{C,P}$ = 2.6 Hz, $\underline{C}(CH_3)_3$], 130.4 (s, C-3′), 134.7 (d, $^1J_{C,P}$ = 52.9 Hz, C-5), 134.9 (d, $^2J_{C,P}$ = 13.7 Hz, C-2′), 140.2 (s, C-4′), 142.8 (d, $^1J_{C,P}$ = 16.4 Hz, C-1′), 165.6 (s, C-4/C-6).

^{31}P-NMR ($CDCl_3$): δ = – 42.7 (s).

Reactions of 1a with Heterocumulenes

(2′,3′-Di-*tert*-butyl-2′-cyclopropenylidene)(2,2-diphenyl-1-trimethylsiloxyethenyl)phosphane (10a):

A solution of diphenylketene (**8a**[18]; 1.7 g, 9.0 mmol) in Et_2O (10 mL) is added dropwise to a solution of **1a** (2.3 g, 9.0 mmol) in Et_2O (20 mL) at – 78 °C. The mixture is stirred and allowed to warm to r.t. over 12 h. The solvent is then evaporated under vacuum, the residue is taken up in a small amount of pentane, and pale yellow crystals separate on cooling the solution to – 30 °C; yield: 3.4 g (85%); mp 106 °C.

$C_{28}H_{37}OPSi$ calc. C 74.97 H 8.31
(448.6) found 74.7 8.29

IR (KBr): ν = 2940 (CH), 1590, 1570, 1550, 1470, 1440, 1360, 1280, 1240, 1230, 1200, 1180, 1130, 1100, 955, 905, 855, 845, 770, 760, 740, 700, 670, 610 cm^{-1}.

^{1}H-NMR (C_6D_6): δ = 0.3 [s, 9 H, $Si(CH_3)_3$], 1.0, 1.3 [2 s, each 9 H, $C(CH_3)_3$], 7.5 (m, 10 H_{arom}).

^{13}C-NMR (C_6D_6): δ = 1.1 [d, $^4J_{C,P}$ = 2.9 Hz, $Si(CH_3)_3$], 27.5 [d, $^4J_{C,P}$ = 3.1 Hz, $C(\underline{C}H_3)_3$], 28.5 [s, $C(\underline{C}H_3)_3$], 32.7, 33.1 [2 s, $\underline{C}(CH_3)_3$], 125.9 (s, C_{arom}), 126.5 (s, C_{arom}), 127.7 (s, C_{arom}), 128.1 (s, C_{arom}), 130.6 (s, C_{arom}), 132.2 (d, $^4J_{C,P}$ = 4.6 Hz, C_{arom}), 132.5 (d, $^2J_{C,P}$ = 4.6 Hz, C-2) 142.1 (s, C_{arom}), 142.8 (d, $^3J_{C,P}$ = 3.1 Hz, C_{arom}), 156.2 (d, $^2J_{C,P}$ = 11.9 Hz, C-3′), 156.7 (d, $^1J_{C,P}$ = 65.5 Hz, C-1), 158.1 (d, $^2J_{C,P}$ = 26.1 Hz, C-2′), 165.6 (d, $^1J_{C,P}$ = 86.3 Hz, C-1′).

^{31}P-NMR ($CDCl_3$): δ = – 9.0 (s); (C_6D_6): δ = – 3.0 (s).

(2′,3′-Di-*tert*-butyl-2′-cyclopropenylidene)-[(*Z*)-2-cyano-3,3-dimethyl-1-trimethylsiloxy-1-butenyl]phosphane (10b):

A solution of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone[19] (1.9 g, 6.3 mmol) in toluene (50 mL) is heated at 85 °C for 1 h to generate a toluene solution of **8b**. This solution is cooled to – 78 °C and a solution of **1a** (3.0 g, 12 mmol) in Et_2O (20 mL) is added dropwise with stirring. The mixture is allowed to warm to r.t. over 2 h during which the solution takes on a deep-red color. The solvent is then evaporated under vacuum and the residue is recrystallized from pentane with cooling to – 30 °C to furnish orange-red, highly deliquescent crystals; yield: 1.8 g (77%).

$C_{21}H_{36}NOPSi$ calc. C 66.82 H 9.61 N 3.7
(377.5) found 66.5 9.54 4.1

IR (film): ν = 2960 (CH), 2860, 2200 (CN), 1530, 1470, 1455, 1390, 1300–1130 (br), 840, 710, 690 cm^{-1}.

^{1}H-NMR (C_6D_6): δ = 0.50 [s, 9 H, $Si(CH_3)_3$], 1.10, 1.35, 1.45 (3 s, each 9 H, $C(CH_3)_3$].

^{13}C-NMR (C_6D_6): δ = 1.7 [d, $^4J_{C,P}$ = 4.4 Hz, $Si(CH_3)_3$], 27.3, 28.5, 30.1 [3 s, $C(\underline{C}H_3)_3$], 32.8 [s, $\underline{C}(CH_3)_3$], 32.9 [d, $^3J_{C,P}$ = 24.8 Hz, $\underline{C}(CH_3)_3$], 34.0 [s, $\underline{C}(CH_3)_3$], 113.5 (d, $^2J_{C,P}$ = 11.4 Hz, C-2), 120.6 (s, CN), 157.8 (d, $^2J_{C,P}$ = 12.3 Hz, C-3′), 159.2 (d, $^2J_{C,P}$ = 26.4 Hz, C-2′), 167.9 (d, $^1J_{C,P}$ = 89.0 Hz, C-1′), 175.3 (d, $^1J_{C,P}$ = 70.3 Hz, C-1).

^{31}P-NMR (C_6D_6): δ = – 3.1 (s).

1-(2′,3′-Di-*tert*-butyl-2′-cyclopropenylidenephosphanyl)-2,2-diphenyl-1-ethanone (12) by Methanolysis of 10a:

A solution of **10a** (1.5 g, 3.3 mmol) in $CHCl_3$ (20 mL) is stirred with MeOH (1.0 mL) at r.t. for 8 h. The solvents are then evaporated under vacuum and the residue is crystallized from pentane with cooling to – 30 °C to furnish pale yellow crystals; yield: 1.1 g (88%); mp 119 °C. The product was identified by comparison of its IR and ^{1}H-NMR spectra with those of the compound obtained from **1a** and diphenylacetyl chloride.[1]

Reaction of 1a with Isocyanates 13a, b and Isothiocyanates 13c, d; General Procedure:

A solution of the respective heterocumulene (**13a**: 0.6 g, 10.5 mmol; **13b**; 1.25 g, 10.5 mmol; **13c**: 0.8 g, 11.0 mmol; **13d**: 1.42 g, 10.5 mmol) in Et_2O (10 mL) is added dropwise to a solution of **1a** (2.5 g, 10 mmol) in Et_2O (20 mL) at – 78 °C. The reaction mixture is allowed to warm to r.t. during 1 h and is then stirred for 5 h. The solvent is evaporated under vacuum and the residue recrystallized several times from pentane.

Trimethylsilyl (2′,3′-Di-tert-butyl-2′-cyclopropenylidenephosphanyl)-N-methylmethanimidate (**15a**): Pale yellow crystals[20] which decompose readily; yield: 1.0 g (35 %).

^1H-NMR (C_6D_6): $\delta = 0.3$ [s, 9 H, $Si(CH_3)_3$], 1.0, 1.1 (2 s, each 9 H, $C(CH_3)_3$], 3.0 (s, 3 H, NCH_3).

^{13}C-NMR (C_6D_6): $\delta = 0.7$ [s, $Si(CH_3)_3$], 27.5 [s, $C(\underline{C}H_3)_3$], 28.4 [d, $^4J_{C,P} = 8.3$ Hz, $C(\underline{C}H_3)_3$], 32.2 (d, $^3J_{C,P} = 29.1$ Hz, NCH_3), 32.9, 34.1 [2 s, $\underline{C}(CH_3)_3$], 159.9 (d, $^2J_{C,P} = 12.5$ Hz, C-3′), 161.9 (d, $^2J_{C,P} = 25.5$ Hz, C-2′), 164.6 (d, $^1J_{C,P} = 80.0$ Hz, C=N), 172.9 (d, $^1J_{C,P} = 82.0$ Hz, C-1′).

^{31}P-NMR (C_6D_6): $\delta = -8.7$ (s).

Trimethylsilyl (2′,3′-Di-tert-butyl-2′-cyclopropenylidenephosphanyl)-N-phenylmethanimidate (**15b**): Pale yellow crystals that decompose readily; yield: 2.35 g (60 %).

$C_{21}H_{32}NOPSi$	calc.	C 67.53	H 8.64	N 3.8
(373.5)	found[21]	65.9	8.41	3.8

^1H-NMR (C_6D_6): $\delta = 0.4$ [s, 9 H, $Si(CH_3)_3$], 0.9, 1.4 [2 s, each 9 H, $C(CH_3)_3$], 7.2 (m, 5 H_{arom}).

^{13}C-NMR ($CDCl_3$): $\delta = 0.5$ [s, $Si(CH_3)_3$], 27.9, 28.6 [2 s, $C(\underline{C}H_3)_3$], 33.1, 34.2 [2 s, $\underline{C}(CH_3)_3$], 126.9 (br s, C_{arom}), 129.0 (s, C_{arom}), 130.5 (br s, C_{arom}), 142.2 (br s, C_{arom}), 161.3 (br d, $^2J_{C,P} = 13.1$ Hz, C-3′), 162.0 (br, C-2′), 172.9 (br, C-1′), 189.4 (br, C=N).

^{31}P-NMR (C_6D_6): $\delta = -6.0$ (br).

(2′,3′-Di-tert-butyl-2′-cycloropenylidenephosphanyl)-N-methyl-N-trimethylsilylthiomethanamide (**16a**): Pale yellow, readily decomposing crystals; yield: 2.1 g (65 %).

$C_{16}H_{30}NPSSi$	calc.	C 58.70	H 9.23	N 4.3
(327.4)	found[21]	57.5	8.64	4.2

^1H-NMR (C_6D_6): $\delta = 0.5$ [s, 9 H, $Si(CH_3)_3$], 1.2 [br s, 18 H, $C(CH_3)_3$], 3.3 (s, 3 H, NCH_3).

^{13}C-NMR (C_6D_6): $\delta = 3.1$ [s, $Si(CH_3)_3$], 28.4 [br, $C(\underline{C}H_3)_3$], 33.6 [br, $\underline{C}(CH_3)_3$], 39.8 (d, $^3J_{C,P} = 30.8$ Hz, NCH_3), 160.0 (br, C-2′/C-3′), 169.0 (br, C-1′), 227.9 (d, $^1J_{C,P} = 79.6$ Hz, C=S).

^{31}P-NMR (C_6D_6): $\delta = +48.1$ (s).

(2′,3′-Di-tert-butyl-2′-cyclopropenylidenephosphanyl)-N-phenyl-N-trimetylsilylthiomethanamide (**16b**): Yellow crystals; yield: 3.07 g (75 %); mp 139 °C.

$C_{21}H_{32}NPSSi$	calc.	C 64.76	H 8.28	N 3.6
(389.5)	found	64.0	8.19	3.7

IR (KBr): $\nu = 2960$ (CH), 2880, 2860, 1590, 1470, 1450, 1360, 1280, 1255, 1230, 1180, 1140, 1060, 850, 700, 640 cm^{-1}.

^1H-NMR ($CDCl_3$): $\delta = 0.3$ [s, 9 H, $Si(CH_3)_3$], 1.4 [br, 18 H, $C(CH_3)_3$], 7.2 (m, 5 H_{arom}).

^{13}C-NMR (CD_2Cl_2): $\delta = 2.3$ [s, $Si(CH_3)_3$], 28.6 [br, $C(\underline{C}H_3)_3$]; 34.0 [br, $\underline{C}(CH_3)_3$], 127.6 (s, C_{arom}), 129.1 (s, C_{arom}), 129.2 (d, $^4J_{C,P} = 5.4$ Hz, C_{arom}), 146.6 (d, $^3J_{C,P} = 8.9$ Hz, C_{arom}), 165.0 (br, C-2′/C-3′), 171.5 (d, $^1J_{C,P} = 89.6$ Hz, C-1′), 229.2 (d, $^1J_{C,P} = 77.4$ Hz, C=S).

^{31}P-NMR (C_6D_6): $\delta = +51.5$ (s).

Reactions of 1a and 1b with Alkynes

Dimethyl 1-(2′,3′-Di-*tert*-butyl-2′-cyclopropenylidenephosphanyl)-2-(trimethylsilyl)maleate (19a); Typical Procedure:

A solution of dimethyl acetylenedicarboxylate (**17a**; 2.8 g, 20.0 mmol) in Et_2O (20 mL) is added dropwise to a solution of **1a** (5.0 g, 20.0 mmol) in Et_2O (50 mL) at – 78 °C. The mixture is allowed to warm to r.t. over about 1 h and is then stirred for 4 h. The solvent is evaporated under vacuum, the red, oily residue is taken up in pentane, the solution is rapidly filtered over silica gel (0.05–0.20 mm, column: 20 × 2 cm), and the column is subsequently washed with mixtures of Et_2O/pentane in ratios of 10:1 to 1:2. The fractions are monitored by ^{31}P-NMR spectroscopy and, if necessary, the purification steps are repeated but with considerable product loss. Red, highly deliquescent crystals are obtained; yield: 1.5 g (20 %).

MS (70 eV): m/z (%) = 396 ($M^{+\bullet}$, 10), 381 ($M^{+\bullet} - CH_3$, 16), 365 ($M^{+\bullet} - OCH_3$, 5), 340 (12), 325 (18), 247 (32), 233 (24), 212 (81), 197 (21), 150 (7), 141 (14), 111 (6), 105 (19), 83 (11), 73 (100), 57 (90), 41 (69).

IR (film): $\nu = 2960$ (CH), 2900 (CH), 2880 (CH), 1710 (C=O), 1480, 1460, 1430, 1370, 1210, 1130, 1060, 1010, 850, 770 cm^{-1}.

^1H-NMR (C_6D_6): $\delta = 0.6$ [d, 9 H, $^5J_{H,P} = 0.7$ Hz, $Si(CH_3)_3$], 1.1, 1.3 [2 s, each 9 H, $C(CH_3)_3$], 3.6, 3.7 (2 s, each 3 H, CO_2CH_3).

^{13}C-NMR (C_6D_6): $\delta = 0.1$ [d, $^4J_{C,P} = 6.3$ Hz, $Si(CH_3)_3$], 27.2, 28.2 [2 s, $C(\underline{C}H_3)_3$], 32.6, 32.7 [2 s, $\underline{C}(CH_3)_3$], 51.0, 51.4 (2 s, $CO_2\underline{C}H_3$), 149.7 (d, $^2J_{C,P} = 23.1$ Hz, C-2), 155.0 (d, $^1J_{C,P} = 64.9$ Hz, C-1), 156.2 (d, $^2J_{C,P} = 14.3$ Hz, C-3′), 157.7 (d, $^2J_{C,P} = 27.5$ Hz, C-2′), 165.8 (d, $^1J_{C,P} = 88.4$ Hz, C-1′), 169.9 (s, C=O), 171.2 (d, $^3J_{C,P} = 10.3$ Hz, C=O).

^{31}P-NMR (C_6D_6): $\delta = -11.0$ (s).

Di-*tert*-butyl (2′,3′-Di-*tert*-butyl-2′-cyclopropenylidenephosphanyl)-2-(trimethylsilyl)maleate (19b):

Prepared from **1a** (5.0 g, 20 mmol) and di-*tert*-butyl acetylenedicarboxylate (**17b**; 4.52 g, 20.0 mmol) in Et_2O as described above for **19a**. Orange, highly deliquescent crystals; yield: 1.63 g (17 %).

$C_{26}H_{45}O_4PSi$	calc.	C 64.96	H 9.40
(480.7)	found	65.6	9.12

IR (film): $\nu = 2970$ (CH), 2930 (CH), 2910 (CH), 2870 (CH), 1705 (C=O), 1475, 1460, 1390, 1365, 1240, 1165, 1065, 850 cm^{-1}.

^1H-NMR (C_6D_6): $\delta = 0.6$ [s, 9 H, $Si(CH_3)_3$], 1.1, 1.4, 1.6, 1.7 [4 s, each 9 H, $C(CH_3)_3$].

^{13}C-NMR (C_6D_6): $\delta = 0.7$ [d, $^4J_{C,P} = 5.1$ Hz, $Si(CH_3)_3$], 27.5, 28.3, 28.4, 28.8 [4 s, $C(\underline{C}H_3)_3$], 32.7 [s, $\underline{C}(CH_3)_3$] 32.8 [d, $^3J_{C,P} = 10.3$ Hz, $\underline{C}(CH_3)_3$], 80.3 [s, $CO_2\underline{C}(CH_3)_3$], 149.6 (d, $^2J_{C,P} = 15.2$ Hz, C-2), 154.3 (d, $^1J_{C,P} = 63.0$ Hz, C-1), 154.7 (d, $^2J_{C,P} = 13.5$ Hz, C-3′), 157.8 (d, $^2J_{C,P} = 27.1$ Hz, C-2′), 165.3 (d, $^1J_{C,P} = 89.5$ Hz, C-1′), 169.4 (s, C=O), 169.8 (d, $^3J_{C,P} = 7.9$ Hz, C=O).

^{31}P-NMR (C_6D_6): $\delta = -12.0$ (s).

Reactions of 1b with Acetylenedicarboxylates 17a–d

Dimethyl (1α,2β)-4,5-Di-*tert*-butyl-1-oxo-1-(2,4,6-trimethylphenyl)-1,2-dihydrophosphinine-2,3-dicarboxylate (20a); Typical Procedure:

A solution of **17a** (1.1 g, 7.7 mmol) in Et_2O (15 mL) is added dropwise to a solution of **1b** (2.3 g, 7.7 mmol) in Et_2O (20 mL) at 0 °C whereupon the solution takes on a deep red color. The mixture is stirred for 3 h at r.t. and then water (0.15 g, 7.7 mmol) in Et_2O (10 mL) is added dropwise. After 1 h, the solvent is evaporated under vacuum, the residue is treated twice with a small amount of pentane, and subsequent centrifugation of the pentane suspension furnishes the product as a pale yellow powder; yield: 1.4 g (40 %); mp 126 °C.

$C_{26}H_{37}O_5P$	calc.	C 67.81	H 8.10
(460.5)	found	67.5	8.29

MS (70 eV): m/z (%) = 460 ($M^{+\bullet}$, 10), 445 ($M^{+\bullet} - CH_3$, 37), 403 (20), 372 (10), 343 (12), 287 (10), 262 (43), 215 (52), 197 (52), 165 (27), 119 (69), 57 (100), 41 (71), 28 (28).

IR (KBr): $\nu = 3000$ (CH), 2980 (CH), 2930 (CH), 2880 (CH), 1730 (C=O), 1710 (C=O), 1610, 1570, 1540, 1440, 1420, 1370, 1310, 1250, 1220, 1200, 1170, 1150, 860, 850, 790, 785, 650 cm^{-1}.

^1H-NMR ($CDCl_3$): $\delta = 1.09$, 1.25 [2 s, each 9 H, $C(CH_3)_3$], 2.13 (s, 3 H, 4-$C\underline{H}_3-C_6H_2$), 2.44 (d, 6 H, $^4J_{H,P} = 0.5$ Hz, 2,6-di-$C\underline{H}_3$-C_6H_2), 3.30, 3.69 (2 s, each 3 H, CO_2CH_3), 4.60 (dd, 1 H, $^2J_{H,P} = 16.5$ Hz, $^4J_{H,H} = 1.2$ Hz, H-2), 6.46 (dd, 1 H, $^2J_{H,P} = 28.3$ Hz, $^4J_{H,H} = 1.2$ Hz, H-6), 6.74 (d, 2 H, $^4J_{H,P} = 3.8$ Hz, C_6H_2).

^{13}C-NMR ($CDCl_3$): $\delta = 21.3$ (s, 4-$\underline{C}H_3-C_6H_2$), 23.9 (d, $^3J_{C,P} = 4.5$ Hz, 2,6-di-$\underline{C}H_3-C_6H_2$), 31.7, 31.9 [2 s, $C(\underline{C}H_3)_3$], 39.0 [s, $\underline{C}(CH_3)_3$], 39.4 [d, $^3J_{C,P} = 11.4$ Hz, $\underline{C}(CH_3)_3$], 52.4, 52.7 (2 s,

$CO_2\underline{C}H_3$), 52.8 (dd, $^{1}J_{C,P}$ = 72.9 Hz, $^{1}J_{C,H}$ = 131.5 Hz, C-2), 123.3 (dd, $^{2}J_{C,P}$ = 106.9 Hz, $^{1}J_{C,H}$ = 167.0 Hz, C-6), 125.3 (d, $^{2}J_{C,P}$ = 8.8 Hz, C-3), 126.7 (d, $^{1}J_{C,P}$ = 107.3 Hz, C-1′), 130.7 (d, $^{3}J_{C,P}$ = 11.8 Hz, C-3′), 141.4 (s, C-4′), 141.6 (d, $^{2}J_{C,P}$ = 10.4 Hz, C-2′), 162.5 (d, $^{3}J_{C,P}$ = 15.5 Hz, C-4), 168.1 (d, $^{2}J_{C,P}$ = 2.6 Hz, C-5), 169.4 (s, C=O), 170.0 (d, $^{3}J_{C,P}$ = 4.5 Hz, C=O).

^{31}P-NMR (C_6D_6): $\delta = +23.8$ (s).

Di-*tert*-butyl (1α,2β)-4,5-Di-*tert*-butyl-1-oxo-1-(2,4,6-trimethylphenyl)-1,2-dihydrophosphinine-2,3-dicarboxylate (20b):

Prepared from **1b** (1.6 g, 5.3 mmol), **17b** (1.1 g, 5.3 mmol), and water (0.10 g, 5.3 mmol) in Et_2O (30 mL) as described for **20a**; colorless crystalline powder; yield: 1.2 g (42 %); mp 121 °C.[20]

IR (KBr): ν = 2975 (CH), 2920 (CH), 2880 (CH), 1710 (C=O), 1450, 1385, 1360, 1230, 1155, 1120, 1070, 850, 800, 770, 640 cm^{-1}.

^{1}H-NMR (CD_3CO_2D): δ = 1.23, 1.26, 1.41, 1.55 [4 s, each 9 H, $C(CH_3)_3$], 2.27 (br s, 3 H, 4-$C\underline{H}_3-C_6H_2$), 2.60 (br s, 6 H, 2,6-di-$C\underline{H}_3-C_6H_2$), 4.70 (d, 1 H, $^{2}J_{H,P}$ = 15.0 Hz, H-2), 6.56 (d, 1 H, $^{2}J_{H,P}$ = 30.0 Hz, H-6), 6.87 (d, 2 H, $^{4}J_{H,P}$ = 3.8 Hz, C_6H_2).

^{31}P-NMR ($CDCl_3$): $\delta = +31.6$ (s).

Diethyl (1α,2β)-4,5-Di-*tert*-butyl-1-oxo-1-(2,4,6-trimethylphenyl)-1,2- dihydrophosphinine-2,3-dicarboxylate (20c):

Prepared from **1b** (1.0 g, 3.4 mmol), **17c** (0.6 g, 3.4 mmol), and water (0.06 g, 3.4 mmol) in Et_2O (30 mL) as described for **20a**; colorless crystals; yield: 0.8 g (48 %); mp 95 °C.

$C_{28}H_{41}O_5P$	calc.	C 68.83	H 8.46
(488.6)	found	68.6	8.45

IR (KBr): ν: 2960 (CH), 2940 (CH), 1715 (C=O), 1700 (C=O), 1600, 1540, 1450, 1390, 1360, 1285, 1200, 1140, 1110, 1070, 1030, 945, 855, 825, 740, 640 cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = 0.86 (t, 3 H, $^{3}J_{H,H}$ = 6.9 Hz, $CO_2CH_2C\underline{H}_3$), 1.16 [s, 9 H, $C(CH_3)_3$], 1.26 (t, 3 H, $^{3}J_{H,H}$ = 6.9 Hz, $CO_2CH_2C\underline{H}_3$), 1.33 [s, 9 H, $C(CH_3)_3$], 2.2 [br s, 3 H, 4-$C\underline{H}_3$-C_6H_2), 2.56 (br s, 6 H, 2,6-di-$C\underline{H}_3$-C_6H_2), 3.8 (q, 2 H, $^{3}J_{H,H}$ = 6.9 Hz, $CO_2C\underline{H}_2CH_3$), 4.2 (q, 2 H, $^{3}J_{H,H}$ = 6.9 Hz, $CO_2C\underline{H}_2CH_3$), 4.7 (d, 1 H, $^{2}J_{P,H}$ = 13.5 Hz, H-2), 6.53 (d, 1 H, $^{2}J_{P,H}$ = 28.5 Hz, H-6), 6.75 (d, 2 H, $^{4}J_{P,H}$ = 3.9 Hz, C_6H_2).

^{13}C-NMR ($CDCl_3$): δ = 13.3, 13.8 (2 s, $CO_2CH_2\underline{C}H_3$), 20.7 (s, 4-$\underline{C}H_3$-C_6H_2), 23.5 (d, $^{3}J_{C,P}$ = 4.3 Hz, 2,6-di-$\underline{C}H_3$-C_6H_2), 31.2, 31.5 [2 s, $C(\underline{C}H_3)_3$], 38.5 [s, $\underline{C}(CH_3)_3$], 38.9 [d, $^{3}J_{C,P}$ = 12.0 Hz, $\underline{C}(CH_3)_3$], 52.5 (dd, $^{1}J_{P,C}$ = 72.7 Hz, $^{1}J_{C,H}$ = 131.2 Hz, C-2), 60.9, 61.2 (2 s, $CO_2\underline{C}H_2CH_3$), 122.6 (d, $^{1}J_{C,P}$ = 106.4 Hz, $^{1}J_{C,H}$ = 148.5 Hz, C-6), 125.3 (d, $^{2}J_{C,P}$ = 8.8 Hz, C-3), 126.5 (d, $^{1}J_{C,P}$ = 106.9 Hz, C-1′), 130.2 (d, $^{3}J_{C,P}$ = 11.4 Hz, C-3′), 140.7 (s, C-4′), 141.1 (d, $^{2}J_{C,P}$ = 10.4 Hz, C-2′), 161.6 (d, $^{3}J_{C,P}$ = 16.2 Hz, C-4), 167.1 (s, C-5), 169.0 (s, C=O), 169.1 (d, $^{3}J_{C,P}$ = 4.5 Hz, C=O).

^{31}P-NMR ($CDCl_3$): $\delta = +21.2$ (s).

Diisopropyl (1α,2β)-4,5-Di-*tert*-butyl-1-oxo-1-(2,4,6-trimethylphenyl)-1,2-dihydrophosphinine-2,3-dicarboxylate (20d):

Prepared from **1b** (0.9 g, 3.0 mmol), **17d** (0.7 g, 3.0 mmol), and water (0.05 g, 3.0 mmol) in Et_2O (30 mL) as described for **20a**; light yellow crystalline powder; yield: 0.6 g (41 %); mp 77 °C.

$C_{30}H_{45}O_5P$	calc.	C 69.75	H 8.78
(516.6)	found	69.1	8.75

IR (KBr): ν = 2970 (CH), 1715 (C=O), 1705 (C=O), 1600, 1450, 1370, 1280, 1130, 1100, 920, 850, 830, 800, 735, 728, 640 cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = 0.92, 1.05, 1.32, 1.37 [4 d, 12 H, $^{3}J_{H,H}$ = 6.1 Hz, $CH(C\underline{H}_3)_2$], 1.25, 1.43 (2 s, 18 H, $C(CH_3)_3$], 2.27 (br s, 3 H, 4-$C\underline{H}_3$-C_6H_2), 2.61 (br s, 6 H, 2,6-di-$C\underline{H}_3$-C_6H_2), 4.71, 5.15 [2 h, 2 H, $^{3}J_{H,H}$ = 6.1 Hz, $C\underline{H}(CH_3)_2$], 4.78 (d, 1 H, $^{2}J_{H,P}$ = 16.5 Hz, H-2), 6.60 (d, 1 H, $^{2}J_{H,P}$ = 28.3 Hz, H-6), 6.90 (d, 2 H, $^{4}J_{H,P}$ = 3.8 Hz, C_6H_2).

^{13}C-NMR ($CDCl_3$): δ = 15.3 (s, 4-$\underline{C}H_3-C_6H_2$), 21.3, 21.4, 21.6, 21.7 [4 s, $CH(\underline{C}H_3)_2$], 23.5 (d, $^{3}J_{C,P}$ = 4.7 Hz, 2,6-di-$\underline{C}H_3$-C_6H_2), 31.5, 31.8 [2 s, $C(CH_3)_3$], 38.7 [s, $\underline{C}(CH_3)_3$], 39.2 [d, $^{3}J_{C,P}$ = 11.8 Hz, $\underline{C}(CH_3)_3$], 53.1 (dd, $^{1}J_{C,P}$ = 74.3 Hz, $^{1}J_{C,H}$ = 131.09 Hz, C-2), 68.8, 69.2 [2 s, $\underline{C}H(CH_3)_2$], 122.9 (dd, $^{1}J_{C,P}$ = 107.0 Hz, $^{1}J_{H,H}$ = 167.2 Hz, C-6), 126.1 (d, $^{2}J_{C,P}$ = 8.5 Hz, C-3), 127.1 (d, $^{1}J_{C,P}$ = 107.5 Hz, C-1′), 130.5 (d, $^{3}J_{C,P}$ = 11.6 Hz, C-3′), 140.9 (s, C-4′), 141.4 (d, $^{2}J_{C,P}$ = 10.1 Hz, C-2′), 161.5 (d, $^{3}J_{C,P}$ = 16.7 Hz, C-4), 168.8 (s, C-5), 168.9 , 169.2 (2 s, C=O).

^{31}P-NMR ($CDCl_3$): $\delta = +18.8$ (s).

Isomerization of 20a,c to 21a,c; General Procedure:

A solution of **20a** (0.5 g, 1.1 mmol) or **20c** (0.5 g, 1.0 mmol) in $CDCl_3$ (3 mL) is stirred at r.t. until the starting material can no longer be detected by ^{1}H-NMR spectroscopy (12 or 72 h, respectively). Evaporation of the solvent under vacuum furnishes the analytically pure products **21a** or **21c**.

Dimethyl (1α,2α)-4,5-Di-tert-butyl-1-oxo-1-(2,4,6-trimethylphenyl)-1,2-dihydrophosphinine-2,3-dicarboxylate **(21a)**: Colorless crystalline powder; yield: 0.5 g (100 %); mp 140 °C.

$C_{26}H_{37}O_5P$	calc.	C 67.81	H 8.10
(460.5)	found	67.2	7.91

IR (KBr): ν = 3000 (CH), 2980 (CH), 1735 (C=O), 1715 (C=O, 1605, 1460, 1435, 1370, 1320, 1300, 1255, 1200, 860, 800, 630 cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = 0.80, 1.22 [2 s, each 9 H, $C(CH_3)_3$], 2.11 (s, 3 H, 4-$C\underline{H}_3-C_6H_2$), 2.54 (br s, 6 H, 2,6-di-$C\underline{H}_3-C_6H_2$), 3.56, 3.63 (2 s, each 3 H, CO_2CH_3), 4.76 (dd, 1 H, $^{2}J_{H,P}$ = 17.4 Hz, $^{4}J_{H,H}$ = 1.5 Hz, H-2), 6.18 (dd, 1 H, $^{2}J_{H,P}$ = 13.2 Hz, $^{4}J_{H,H}$ = 1.5 Hz, H-6), 6.72 (d, $^{4}J_{H,P}$ = 3.9 Hz, C_6H_2).

^{13}C-NMR ($CDCl_3$): δ = 20.6 (s, 4-$\underline{C}H_3-C_6H_2$), 22.8 (d, $^{3}J_{C,P}$ = 6.3 Hz, 2,6-di-$\underline{C}H_3-C_6H_2$), 31.1, 31.5 [2 s, $C(\underline{C}H_3)_3$], 37.8 [s, $\underline{C}(CH_3)_3$], 39.0 [d, $^{3}J_{C,P}$ = 11.2 Hz, $\underline{C}(CH_3)_3$], 48.9 (dd, $^{1}J_{C,P}$ = 70.0 Hz, $^{1}J_{C,H}$ = 131.0 Hz, C-2), 51.7, 52.3 (2 s, 2 $CO_2\underline{C}H_3$), 122.8 (s, C-3), 123.4 (dd, $^{1}J_{C,P}$ = 101.2 Hz, $^{1}J_{C,H}$ = 160.9 Hz, C-6), 126.2 (d, $^{1}J_{C,P}$ = 102.6 Hz, C-1′), 129.8 (d, $^{3}J_{C,P}$ = 11.6 Hz, C-3′), 141.2 (s, C-4′), 141.6 (d, $^{2}J_{C,P}$ = 10.9 Hz, C-2′), 161.2 (d, $^{3}J_{C,P}$ = 17.1 Hz, C-4), 166.2 (s, C-5), 166.7 (s, C=O), 169.4 (d, $^{3}J_{C,P}$ = 6.2 Hz, C=O).

^{31}P-NMR ($CDCl_3$): $\delta = +18.8$ (s).

Diethyl (1α,2α)-4,5-Di-tert-butyl-1-oxo-1-(2,4,6-trimethylphenyl)-1,2-dihydrophosphinine-2,3-dicarboxylate **(21c)**: Colorless crystalline powder; yield: 0.5 g (100 %); mp 123 °C.

$C_{28}H_{41}O_5P$	calc.	C 68.83	H 8.46
(488.6)	found	69.0	8.45

IR (KBr): ν = 2960 (CH), 1720 (C=O), 1600, 1450, 1390, 1365, 1285, 1180, 1060, 1030, 930, 855, 825, 740, 650, 625 cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = 0.7, 1.1 [2 s, each 9 H, $C(CH_3)_3$], 1.0 (br t, 6 H, $CO_2CH_2C\underline{H}_3$), 2.0 (br s, 3 H, 4-$C\underline{H}_3-C_6H_2$), 2.4 (br s, 6 H, 2,6-di-$C\underline{H}_3-C_6H_2$), 3.8–4.1 (m, 4 H, $CO_2C\underline{H}_2CH_3$), 4.6 (d, 1 H, $^{2}J_{H,P}$ = 18 Hz, H-2), 6.0 (d, 1 H, $^{2}J_{H,P}$ = 12.8 Hz, H-6), 6.6 (d, 2 H, $^{4}J_{H,P}$ = 3.8 Hz, C_6H_2).

^{13}C-NMR ($CDCl_3$): δ = 13.0, 13.4 (2 s, $CO_2CH_2\underline{C}H_3$), 20.2 (s, 4-$\underline{C}H_3-C_6H_2$), 22.4 (d, $^{3}J_{C,P}$ = 5.6 Hz, 2,6-di-$\underline{C}H_3-C_6H_2$), 30.8, 31.0 [2 s, $C(\underline{C}H_3)_3$], 37.4 [s, $\underline{C}(CH_3)_3$], 38.5 [d, $^{3}J_{C,P}$ = 11.2 Hz, $\underline{C}(CH_3)_3$], 48.6 (dd, $^{1}J_{C,P}$ =71.3 Hz, $^{1}J_{C,H}$ = 130.8 Hz, C-2), 60.6, 60.8 (2 s, $CO_2\underline{C}H_2CH_3$), 123.0 (d, $^{2}J_{C,P}$ = 5.8 Hz, C-3), 123.1 (dd, $^{1}J_{C,P}$ = 106.6 Hz, $^{1}J_{C,H}$ = 162.6 Hz, C-6), 126.0 (d, $^{1}J_{C,P}$ = 107.3 Hz, C-1′), 129.3 (d, $^{3}J_{C,P}$ = 11.3 Hz, C-3′), 140.6 (s, C-4′), 141.1 (d, $^{2}J_{C,P}$ = 10.7 Hz, C-2′), 160.0 (d, $^{3}J_{C,P}$ = 16.5 Hz, C-4), 165.6 (s, C-5), 168.4, 168.5 (2 s, C=O).

^{31}P-NMR ($CDCl_3$): $\delta = +25.7$ (s).

X-Ray Crystal Structure Analysis of 20c

Crystal Data: $C_{28}H_{41}O_5P$, M_r = 488.6; triclinic; space group $P\bar{1}$; a = 11.600(6), b = 13.793(18), c = 9.791(11) Å, α = 107.18(10), β = 104.89(6), γ = 66.64(5)°, V = 1356.4 Å^3; Z = 2; $D_{calc.}$ = 1.196 g cm^{-3}, μ = 0.13 mm^{-1}.

Data Collection: The data collection was performed using an automatic four circle diffractometer (Enraf Nonius CAD 4). Crystal dimensions: 0.3 × 0.25 × 0.3 mm. The measurements were made in the range $2 < \Theta < 23°$, Mo K_α (graphite monochromator), h −12 → 12, k −15 → 15, l0 → 10, a total of 4029 reflections of which 3767 were independent reflections.

Structure Solution and Refinement: The structure was solved using direct methods (SHELXS-86)[22] and refined with a full matrix least squares method (SHELX-76)[23]. The hydrogen atoms H1 and H5 were calculated geometrically; all other hydrogen atoms were not taken into consideration. The anisotropic refinement [only heavy atoms, the hydrogen atoms H1 and H5 with a fixed temperature factor ($0.05\ \text{Å}^2$)] with 2991 reflections [$I > 2\sigma(I)$] converged at $R = 0.113$ and $R_w = 0.128$. The difference Fourier synthesis on the basis of the final structural model showed a maximum of $0.55\ \text{eÅ}^{-3}$ and a minimum of $-0.39\ \text{eÅ}^{-3}$.[24]

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(1) Part 51 see: Fuchs, E.; Breit, B.; Heydt, H.; Schoeller, W.; Busch, T.; Krüger, C.; Betz, P.; Regitz, M. *Chem. Ber.* **1991**, *124*, in press.
(2) Review: Appel, R., in: *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Regitz, M.; Scherer, O.J. (eds.), Thieme, Stuttgart, New York 1990, p. 157ff.
(3) See ref.[2], p. 161.
(4) Preliminary communication: Fuchs, E.P.O.; Heydt, H.; Regitz, M.; Schoeller, W.W.; Busch, T. *Tetrahedron Lett.* **1989**, *30*, 5111.
(5) See Karaghiosoff, K., in ref.[2], p. 463ff.
(6) Schubert, H.; Stang, P.J. *J. Org. Chem.* **1984**, *49*, 5087.
Stang, P.J.; Maas, G.; Smith, D.L.; McClosky, J.A. *J. Am. Chem. Soc.* **1981**, *103*, 4837.
(7) Curci, R.; Luccini, V.; Modena, G.; Kocienski, P.J.; Ciabattoni, J. *J. Org. Chem.* **1970**, *38*, 3149.
(8) See, for example:
(a) Becker, G.; Mundt, O. *Z. Anorg. Allg. Chem.* **1979**, *459*, 87.
(b) Becker, G.; Gresser, G.; Uhl, W. *Z. Anorg. Allg. Chem.* **1980**, *463*, 144.
(9) This is valid, for example, for 2,3-di-*tert*-butyl-3-methyl-1-[bis(trimethylsilyl)phosphanyl]cyclopropene: Fuchs, E. *Dissertation*, University of Kaiserslautern, 1989.
(10) It is possible that this is in the region of a rapid *syn/anti*-isomerization at the C=N double bond.
(11) Appel, R.; Poppe, M. *Angew. Chem.* **1989**, *101*, 70; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 53.
(12) Becker, G.; Massa, W.; Schmidt, R.E.; Uhl, G. *Z. Anorg. Allg. Chem.* **1985**, *520*, 139.
(13) Himbert, G. *J. Chem. Res. (S)* **1978**, 104; *J. Chem. Res. (M)* **1978**, 1445.
For analogous reactions with stannylated ynamines, see: Himbert, G. *J. Chem. Res. (S)* **1979**, 88; *J. Chem. Res. (M)* **1979**, 1201.
(14) Starting material:
Haber, S.; Boese, R.; Regitz, M. *Angew. Chem.* **1990**, *102*, 1523; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1436.
Isomerization reactions:
Haber, S. *Dissertation*, University of Kaiserslautern, 1991.
(15) Allen, F.H.; Kennard, O.; Watson, D.G. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1.
(16) Verkade, J.G.; Quin, L.D., in: *Methods in Stereochemical Analysis*, Vol. 8, Marchand, A.P. (ed.), VCH Publishers, Deerfield Beach/Florida 1987.
(17) Perrin, D.D.; Armarego, W.L.F.; Perrin, D.R. *Purification of Laboratory Chemicals*, 2nd Ed., Pergamon Press, Oxford 1980.
(18) Smith, L.J.; Hoehn, H.H. *Org. Synth., Coll. Vol. III*, **1955**, p. 356.
(19) Moore, H.W.; Weyler, W. *J. Am. Chem. Soc.* **1970**, *92*, 4132.
(20) In spite of concordant NMR data, satisfactory elemental analyses could not be obtained.
(21) Combustion was difficult.
(22) Sheldrick, G.M. *Fortran-77 Program for the Solution of Crystal Structures from Diffraction* Data, Institute for Organic Chemistry, University of Göttingen.
(23) Sheldrick, G. *M. Program for Crystal Structure Determination*, see ref.[22]
(24) Further details of the crystal structure determination can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany, upon citation of the deposition number CSD-55 470, the names of the authors, and the journal reference.