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ORGANOPHOSPHORUS COMPOUNDS - 60[1]. REACTIONS OF PHOSPHATRIAFULVENES WITH NUCLEOPHILIC PARTNERS

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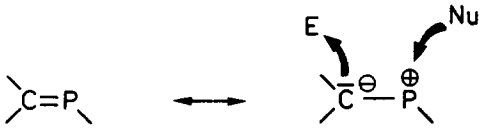
Abstract: The phosphatriafulvenes **1a,b** - phosphaalkenes with inverse electron density - react primarily at the three-membered ring with nucleophilic reagents. From their reactions with organolithium compounds **2a-c** and Grignard reagents **5a,b** the cyclopropenylphosphines **4a-f** are obtained after addition of chlorotrimethylsilane; of these products only **4a, d,** and **e** were isolated and characterized. Methanolysis of products **4a-f** yields the primary (**7a-d**) and secondary phosphines (**9a,b**) via cleavage of the P–Si bond. Compound **1b** reacts with the ynamines **10a,b** through cleavage of the three-membered ring to yield the 1-phospha-1,3,5-hexadienynes **11a** (X-ray structure) and **11b**. The same phosphatriafulvene reacts with the cyclobutadienes **17a,b** to furnish initially the 2-phosphabicyclohexenes **18a,b** which, on stirring in chloroform at room temperature, undergo [2 + 2] cycloreversion to give the open-chain isomers **20a,b**.

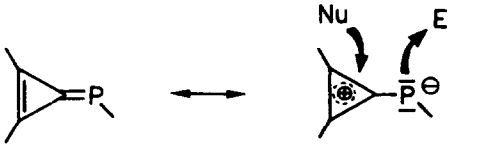
INTRODUCTION

Phosphaalkenes have recently become established as valuable building blocks in synthetic organo-element chemistry[2]. Their reactivity reflects the weakly polarized C/P double bond, for which Pauling electronegativities predict a partial negative charge at carbon and a partial positive charge at phosphorus. This qualitative description has been confirmed by semi-empirical and ab initio calculations[3,4]. In accord with these theoretical predictions, phosphaalkenes react preferentially with nucleophiles at phosphorus and, in contrast, with electrophiles at the carbon atom of the phosphaalkene unit (Formula A).

The synthesis of phosphatriafulvenes, i.e. phosphaalkenes in which the phosphaalkene carbon atom is incorporated in a Hückel aromatic cyclopropenylium system, however, provided the first opportunity to achieve an inverse electron density distribution at the C/P double bond[5,6]. The charge distribution ($\sigma + \pi$ as well as π) as

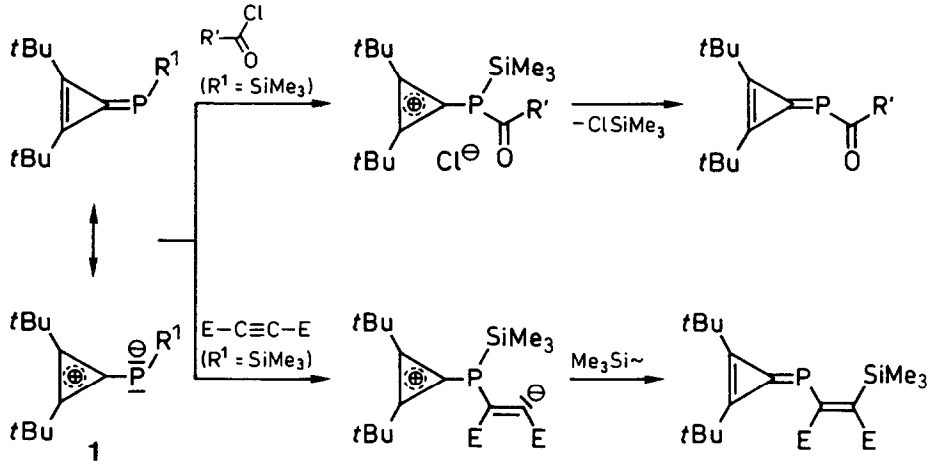


Formula **A**



Formula **B**

determined both by an ab initio calculation (Mulliken population analysis) provides unequivocal evidence for this situation which can be rationalized on the basis of a cross-conjugated π-bonding system[7]. Accordingly, nucleophiles should attack the carbocyclic three-membered ring whereas the exocyclic phosphorus atom should be the preferred site of attack for electrophiles (Formula B). The latter is indeed the case as has been demonstrated for the examples of the reactions of **1a** with acid chlorides (formation of *P*-acylphosphatriafulvenes after cleavage of chlorotrimethylsilane)[5] and with acetylenedicarboxylates (formation of *P*-vinylphosphatriafulvenes after trimethylsilyl shifts)[8] (Formula C).



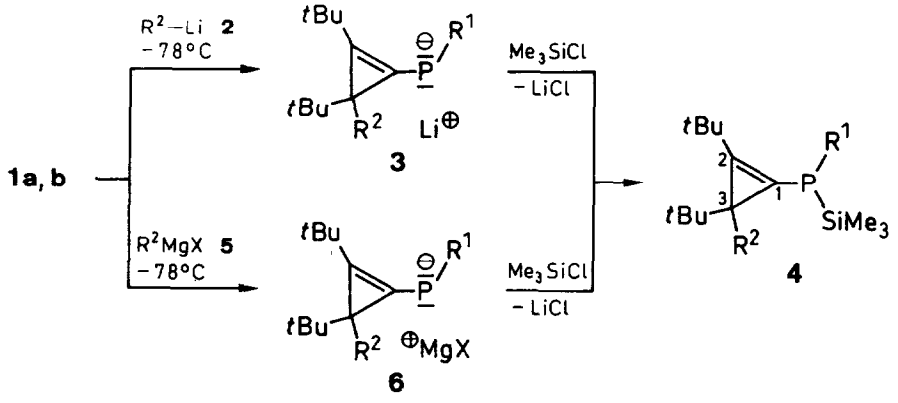
The present investigations are concerned with the question of whether nucleophiles really do attack the triafulvene three-membered ring. In addition to nucleophilic organometallic reagents, we also considered ynamines which are known to exhibit nucleophilic reactivity at the ß-C atoms[9] and kinetically stabilized antiaromatics (cyclobutadiene) which are also known to exhibit nucleophilic properties[10] as reaction partners for **1a,b**.

RESULTS AND DISCUSSION

Reactions of 1a,b *with Organometallic Reagents*

When the phosphatriafulvenes **1a,b** are allowed to react with the organolithium reagents **2a-c** or the Grignard reagents **5a,b** in hexane/diethyl ether medium with subsequent addition of a 10% excess of chlorotrimethylsilane to the reaction mixture as trapping reagent, the cyclopropenyl(trimethylsilyl)phosphines **4a-f** are formed. These colorless to yellow oils are very sensitive towards hydrolysis and only the compounds **4a**, **d**, and **e** (yields: 51-90%) were isolated and purified by bulb-to-bulb distillation. The other products were subjected to methanolysis directly and phosphines containing PH units were obtained. Cyclopropenylphosphinides **3** or **6**,

primarily formed by nucleophilic attack of the organometallic compounds at C-2 or C-3 of **1a,b** are considered to be intermediates of the reaction. An ipso attack at C-1 of the triafulvene system is not observed or can be discounted on consideration of the spectroscopic data of **4**. Thus, the ^{1}H and ^{13}C NMR data immediately reveal that the molecule cannot possess C_v symmetry since the signals for the tert.-butyl groups have different chemical shifts (see Experimental Section). It is also readily seen from the ^{1}H and ^{13}C NMR spectra that the newly introduced substituent originating from the nucleophile must be at C-3 since in no case can coupling with the phosphorus at C-1 be detected. These first observations are sufficient to exclude the alternative structures which would be formed if the nucleophile were to attack at phosphorus or C-1. The ^{13}C NMR signals of the olefinic carbon atoms of the cyclopropene double bond are worthy of comment. Thus, we assign the signals between δ = 137.5 and 146.7 with $^{2}J_{C,P}$ couplings of 16.9 - 19.0 Hz to the carbon atom C-2 on account of the signal broadening due to the neighboring tert.-butyl group. In contrast, the signals for C-1 appear between δ = 103.7 and 113.3 with $^{1}J_{C,P}$ couplings of 42.2 - 54.5 Hz. When these values are compared with the data known from other acyclic alkenylphosphines[11], discrepancies in the chemical shifts as well as the $^{1}J_{C,P}$ and $^{2}J_{C,P}$ coupling constants become apparent: the signals for C-2 are in comparable regions and those for C-1 are shifted slightly to lower field, while the $^{1}J_{C,P}$ coupling constants are in the range of merely 7 - 8 Hz and the $^{2}J_{C,P}$ coupling constants are in the range 20 - 35 Hz. These differences must be attributed to the incorporation of the double bond in the strained cyclopropene ring. The ^{31}P NMR spectra of **4a** and **d** show signals at δ = –174.8 and –173.0, respectively, i.e. in the normal region for silylated phosphines; the presence of a mesityl group at phosphorus in **4e** results in the expected low-field shift to –99.8 ppm.

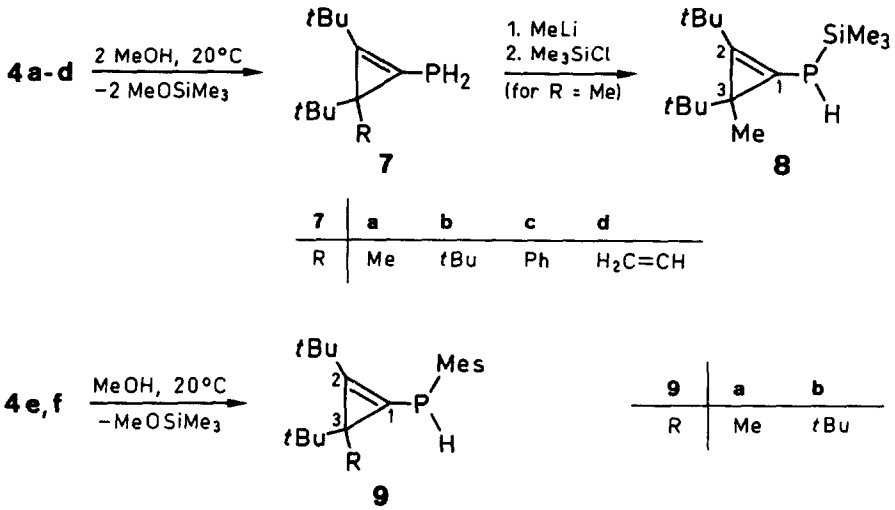


2	a	b	c
R^2	Me	*t*Bu	Ph

5	a	b
R^2	H_2C=CH	Ph

3, 4, 6	a	b	c	d	e	f
R^1	Me_3Si	Me_3Si	Me_3Si	Me_3Si	Mes	Mes
R^2	Me	*t*Bu	Ph	H_2C=CH	Me	*t*Bu

Since the two-step formation of **4** effectively constitutes a 1,4-addition to the phosphatriafulvene system, the question arises whether **4e** is formed as diastereomers since both C-2 or C-3, respectively, as well as the phosphorus atom in **4** can be considered as prochiral centers in this context. However, a doubling or broadening of the signals, which could be attributed to the existence of diastereomers, was not observed in any of the spectra. The variable temperature ^{31}P NMR spectra of **4e** down to 213 K exhibited only the sharp singlet at –99.8. It must therefore be assumed that the barrier to inversion at the $\lambda^3\sigma^3$ phosphorus atom is so low[12] that the isolation or even detection of diastereomers is not possible. In agreement with previous work, the presence of voluminous substituents at phosphorus could be responsible for the lowering of the barrier to inversion since they facilitate the flattening of the pyramidal phosphorus while concomitantly making rotation more difficult. When the steric requirements at phosphorus are reduced, the barrier to inversion increases appreciably and diastereomers can be observed (see **9a**).



***Methanolysis of* 4a-f *to the Primary Cyclopropenylphosphines* 7a-d *and the Secondary Cyclopropenyl(mesityl)phosphines* 9a,b**

The silyl groups at phosphorus in **4a-d** can be cleaved by treatment with methanol at room temperature and the primary cyclopropenylphosphines **7a-d** are formed (yields: 13 - 87%). Thus, the methanolysis also contributes to the constitutional elucidation of compounds **4** since only silyl groups bonded to heteroatoms can be cleaved in such a ready manner. The spectroscopic data of **7a-d** correspond to a large extent to those of the starting materials (see Experimental Section). Of course, the signals for the silyl groups are absent and, instead, doublets with $^1J_{H,P}$ coupling constants of 202 - 204 Hz are observed in the ^1H NMR spectra between δ = 3.8 and 4.0 and can be immediately assigned to PH_2 moieties. The same coupling constants are observed in the triplet signals of the ^{31}P NMR spectra. With chemical shifts of –155.9 to –168.9, these are shifted slightly to lower field in comparison with **4**. When compounds **4e** and **f** are subjected to the methanolysis, the secondary cyclopropenylphosphines **9a** and **b** are formed in 85 and 48% yield, respectively. Again, the spectroscopic data re-

semble those of the starting materials **4**; the absence of the silyl group is apparent from the ^1H NMR spectra and new signals for the PH protons appear at δ = 5.4 or 5.6 with $^1J_{H,P}$ coupling constants of 227 and 230 Hz, respectively. The ^{31}P NMR signals appear as doublets with the same coupling constants at –106.3 or –99.3, respectively.

In the NMR spectra of **9a** it is seen that practically all signals are doubled, i.e. the product exists as a pair of diastereomers. Both ^1H and ^{31}P NMR spectra are indicative of an isomer ratio of 55:45. As already mentioned in the discussion of the properties of **4e**, the starting material for **9a**, the presence of sterically demanding substituents at phosphorus counteracts its chirality by lowering the barrier to inversion. However, on replacement of the bulky trimethysilyl group by hydrogen, the barrier to inversion is increased to such a degree that the formation of diastereomers becomes possible. A feasible reason for the non-observation of diastereomers in the case of **9b** is that the sterically demanding tert.-butyl group of the organolithium reagent **2b** attacks the cyclopropene carbon atom more selectively, leading finally to a higher diastereoselectivity which, under the employed work-up conditions, results in the isolation of only one diastereomer in 48% yield. In contrast, reagent **2a** with the sterically undemanding methyl group reacts without any diastereoselectivity.

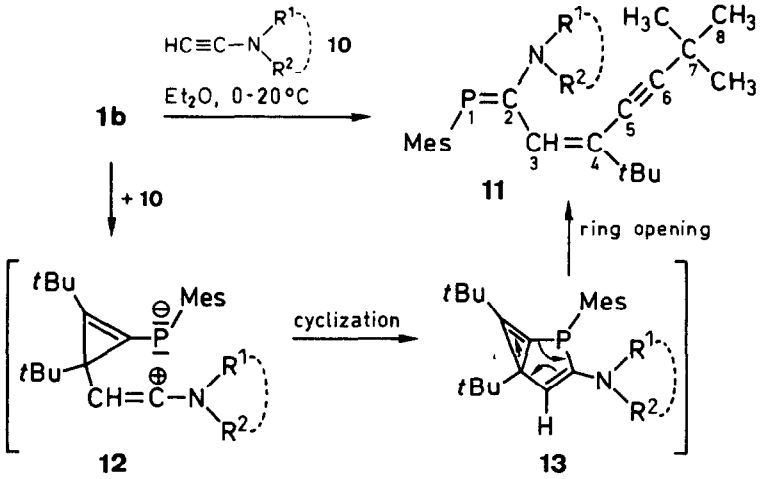
We have also addressed the question of whether secondary cyclopropenylphosphines with only *one* silyl group at phosphorus are also capable of forming diastereomers. For this purpose, the primary cyclopropylphosphine **7a** was metallated with methyllithium and the resultant cyclopropenylphosphide reacted with chlorotrimethylsilane to furnish the cyclopropenyl(trimethylsilyl)phosphine **8**. In the ^1H NMR spectrum of **8**, the signal for the silyl group at phosphorus appears at δ = 0.4 with a $^3J_{H,P}$ coupling constant of 4.8 Hz, the PH proton signal appears as two doublets at δ = 3.30 and 3.35 with $^1J_{H,P}$ coupling constants of 195 and 204 Hz, respectively, thus confirming the substitution at phosphorus. The further spectroscopic data are similar to those of **4a** and **7a** and require no further discussion. The occurrence of two doublets in the ^1H NMR spectrum for the PH proton provides first evidence that **8** exists as a pair of diastereomers (ratio 55:45). The coalescence temperature (363 K) was determined by variable temperature ^{31}P NMR spectroscopy. Slow exchange occurs up to 323 K (δ = –158.3 and –164.0) whereas rapid exchange takes place at 387 K (δ = –159.4). However, it is not yet known whether the rapid interconversion of the invertomers at higher temperature is due to inversion at phosphorus alone or to combined rotation and inversion processes[13].

Reactions of **1b** *with Ynamines to* **11a,b**

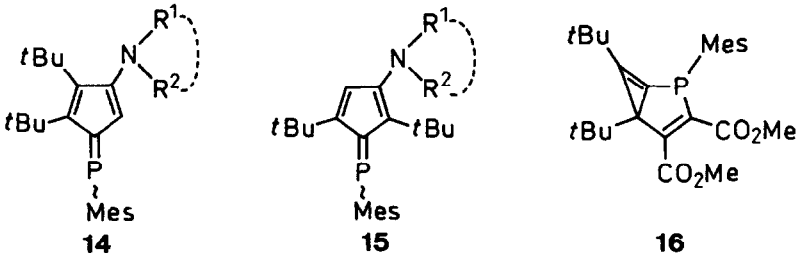
Ynamines are known to be suitable reaction partners for triafulvenes and heteroanalogous cyclopropenones[14,15]. In general, 2- or 3-aminocyclopentadiene derivatives result from such reactions. Hence, we have also investigated the reactions of phosphatriafulvenes with these reagents to determine whether the nucleophilic ß-carbon atom of the ynamine also attacks at C-2/C-3 of the phosphatriafulvene system and whether comparable reactions take place.

The first question can be answered affirmatively while, for the second question, it was found that phosphapentafulvenes of the type **14** or **15** were not formed, the products were rather the acyclic dienynes **11**. In the IR spectra, the characteristic alkyne triple bond vibrations were observed at 2200 and 2220 cm^{-1}; signals for the olefinic protons at δ = 5.90 and 6.05 were seen in the ^1H NMR spectra in accordance with the proposed structure. These signals are split into doublets with coupling constants of 4.8 and 6.6 Hz, respectively, due to $^3J_{H,P}$ couplings. The ^{13}C NMR spectra also provide characteristic values: the phosphaalkene carbon atoms produce signals at δ = 194.7 and 191.2, respectively, with $^1J_{C,P}$ coupling constants of 53.1 and 50.5 Hz. Assign-

ments of the alkyne carbon atom signals in the range δ = 77.7 - 105.8 without any coupling to the phosphorus atoms and the alkene carbon atom signals in the range δ = 128.4 - 132.1 with characteristic $^2J_{C,P}$ and $^3J_{C,P}$ couplings between 6.5 and 8.1 Hz were also not difficult. The ^{31}P NMR data of **11** demonstrate the presence of an electron-rich phosphaalkene double bond. The signals appear at δ = 89.2 and 98.8, i.e. in a region shifted by about 120-130 ppm to higher field as compared to normal phosphaalkenes[16].



10 - 13	a	b
R1, R2	$(CH_2)_2$ O $(CH_2)_2$	Me
		Ph



The structure of **11a** was finally confirmed by X-ray crystallography; *Figure 1* shows an molecule plot and *Table 1* lists selected structural parameters for this previously unknown bonding system.

The P–C2 bond length of 1.711(8) Å is relatively long in comparison to other phosphaalkenes[17]. Together with the shortened C2–N distance, this is an indication for conjugation of the amino substituent with the phosphaalkene double bond. The characteristic alternation in bond lengths for a conjugation can also be observed in the enyne moiety. Thus, the triple bond C5–C6 [1.228(9) Å] is lengthened while the single bonds C4–C5 [1.423(9) Å] and C6–C61 [1.449(10) Å] are shortened. The C3–C4 double bond [1.304(8) Å] is also

shortened. The skeletal atoms C2, C3, C4, C5, and C6 form a plane which is tilted by 70° with respect to the N, C2, P plane. Thus, no conjugation between the P/C double bond and the enyne system is possible and, accordingly, interactions with the amino substituent alone must be responsible for the stabilization of this energy-rich bond.

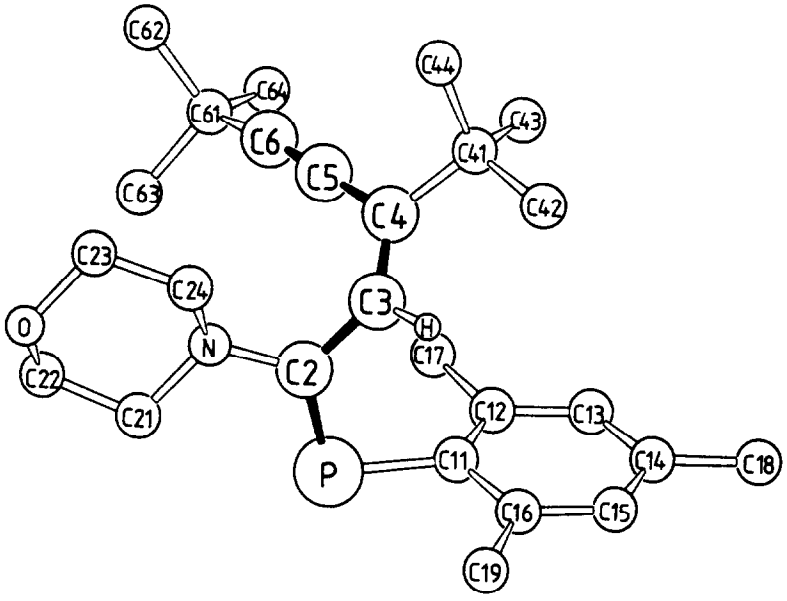


Figure 1. Molecule plot of *N*-[tert.-butyl-1-mesityl-7,7-dimethyl-1-phosphaocta-1,3-dien-5-yn-2-yl]morpholine (**11a**)

Table 1. Selected bond lengths [Å] and angles [°] for **11a**

Bond lenghts

P	— C2	1.711(8)	C4	— C5	1.423(4)	C2	— N	1.399(8)
C2	— C3	1.444(9)	C5	— C6	1.228(9)	C4	— C41	1.539(9)
C3	— C4	1.304(8)	P1	— C11	1.826(8)	C6	— C61	1.449(10)

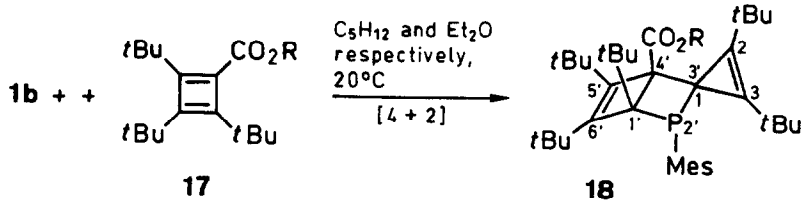
Bond angles

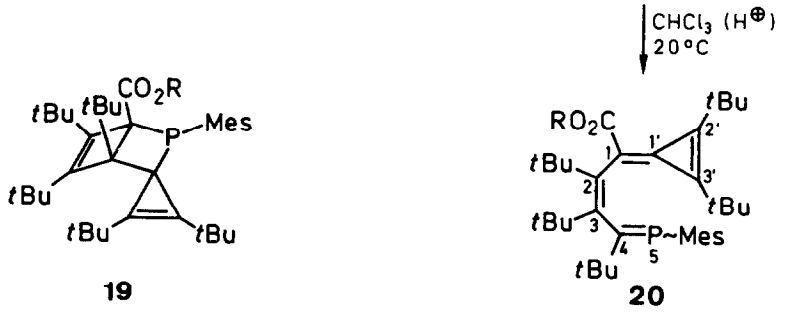
P	— C2	— C3	123.1(6)	N	— C2	— P	120.3(6)	C21	— N	— C24	112.8(6)
C2	— C3	— C4	129.6(7)	C3	— C4	— C41	125.0(6)	C22	— O	— C23	109.8(6)
C3	— C4	— C5	119.1(7)	C5	— C4	— C41	115.9(9)	C23	— C24	— N	110.3(7)
C4	— C5	— C6	176.5(8)	C5	— C6	— C61	170.8(9)	C24	— C23	— O	114.8(7)
C2	— P	— C11	100.3(4)	C2	— N	— C21	116.8(6)				

For a rationalization of the formation of **11**, we assume that the initial step is the nucleophilic attack of the ß-carbon atom of the ynamine at the cyclopropene part of the triafulvene system to form the intermediate **12**. The latter undergoes cyclization to **13** which, as an anti-Bredt bicyclic system, experiences ring opening to furnish the observed final product **11**. This putative mechanism corresponds to a large extent to the reactions of triafulvenes or cyclopropenones with ynamines[14,15]. It is interesting to note that the intermediate **16**, which is structurally related to **13**, can be generated by the reaction of the phosphatriafulvene with dimethyl acetylenedicarboxylate. But, under the action of water, **16** undergoes ring opening to furnish a phosphine oxide derivative[8].

Reactions of 1b *with Kinetically Stabilized Cyclobutadienes to* 18a,b *and* 20a,b

Kinetically stabilized cyclobutadienes such as tri-tert.-butylcyclobutadienecarboxylates react readily with cyclopropenones[18,19]. Triafulvene derivatives (e.g. **22** from the reaction with di-tert.-butylcyclopropenone) are obtained as final products from such reactions. These compounds are formed by way of cy





17-20	a	b
R	Me	*t*Bu

cloaddition of the C/O double bond to the less sterically hindered side of the cyclobutadiene and subsequent ring opening of the spiro-linked oxabicyclo[2.2.0]hexene (**21**; X = O, -R^1···R^2- represents the C atoms of the cyclopropene moiety). This prompts the question whether the analogous phosphatriafulvenes **1** also react comparably with kinetically stabilized cyclobutadienes.

When **1b** in pentane is allowed to react with the cyclobutadienes **17a,b** at room temperature, colorless crystalline products are isolated. According to their ^{31}P NMR spectra, these compounds do not contain P/C double bonds (no signals in the typical phosphaalkene region) so that the formation of triafulvenes analogous to those from the reactions with cyclopropenones can be discounted. The ^{31}P NMR spectra do, however, show signals at δ = 7.7 and 11.5 which are suggestive of $\lambda^3\sigma^3$ phosphorus atoms. In the ^{13}C NMR spectra, signals for three skeletal carbon atoms, two exhibiting $^1J_{C,P}$ couplings, are observed in the sp^3 region together with 4 olefinic carbon signals. These data suggest that the isolated compounds have the spiro-linked phosphabicyclo[2.2.0]hexene structures **18a,b**, i.e. the reactions have stopped at the stage of the primary cycloaddition. Other ^{13}C NMR signals are assigned as follows: δ = 69.7 or 71.1 with $^1J_{C,P}$ coupling constants of 24.2 or 24.9 Hz, respectively, to the spiro carbon atoms C-3'/C-1, δ = 68.0 or 69.7, broadened as a consequence of the directly adjacent tert.-butyl groups, with $^1J_{C,P}$ coupling constants of 21.1 or 20.2 Hz, respectively, to the carbon atom C-1', δ = 42.4 or 42.9 with $^2J_{C,P}$ coupling constants of 3.0 Hz to the bridgehead carbon atom C-4' bearing the ester carbonyl group, and those in the olefinic region between δ = 136.6 and 138.7 with $^2J_{C,P}$ coupling constants of 18 Hz to the olefinic carbon atoms of the cyclopropene unit. In contrast, the olefinic carbon atoms of the cyclobutene element are shifted to lower field and appear between δ = 150.8 and 156.6. The positions of these signals are typical for such bicyclohexene systems formed by cycloadditions of kinetically stabilized cyclobutadienes to suitable reaction partners - reactions proceeding with retention of the di-tert.-butyl substituted double bond and linkage of the heteroatom to a tert.-butyl substituted carbon atom of the cyclobutadiene[18,19,20].

The triafulvene system **20**, which is analogous to **22**, is obtained in quantitative yield when the spiro-linked bicyclic system **18** is stirred in chloroform solution at room temperature. The isomerization **18** ⇒ **20** also proceeds in benzene solution but more slowly (≥ 24 h as compared to 1-2 h). The triafulvenes **20a,b** are colorless, crystalline compounds in which the presence of the phosphaalkene structural unit is indicated by ^{31}P NMR signals at δ = 215.7 or 215.4, the typical low field region for $\lambda^3\sigma^2$ phosphorus. In addition, low field shifted signals at δ = 211.0 (broad) or 210.5 (with a $^1J_{C,P}$ coupling constant of 52.9 Hz) in the ^{13}C NMR spectra can be safely assigned to the carbon atoms of the phosphaalkene double bond. Signals for the further, structurally relevant skeletal carbon atoms are found only in the olefinic region (δ = 94.0 - 151.6) but not in the region for sp^3 hybridized carbon atoms (see Experimental Section). The signals for C-2 and C-3 are split into doublets with $^2J_{C,P}$ coupling constants of 5.8 and 7.5 Hz or $^3J_{C,P}$ coupling constants of 14.3 and 18.0 Hz, respectively. A direct comparison of the ^{13}C NMR chemical shifts of **20** with those of the known triafulvene **22** finally confirms the existence of the phosphorus analog of the triafulvene structure. In the IR spectrum, the shift of the ester carbonyl group vibration to shorter wave numbers (ν = 1650 cm^{-1}) indicates the increased single bond character of this structural element and, hence, the conjugation of the carbonyl group with the double bond of the triafulvene system.

The reactions of **1b** with the cyclobutadienes are particularly worthy of note in that it was thus possible for the first time to isolate the primary adducts from a cycloaddition reaction of a heteroanalogous triafulvene

system. The energetically unfavorable transition from a $\lambda^3\sigma^3$ phosphorus to a low-coordinated, energy-rich $\lambda^3\sigma^2$ phosphorus of a phosphaalkene is assumed to be responsible for the stability of the products.

EXPERIMENTAL SECTION

General Methods

All reactions were carried out under argon (purity > 99.998 %) in previously baked-out and evacuated apparatus. Melting points (uncorrected) were obtained with a Mettler FP 61 apparatus (heating rate 3°/min), and microanalyses 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 with a Varian MAT 311 spectrometer. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer. ^{1}H-NMR spectra were recorded on Varian EM 360, Varian EM 390, Bruker WP 200, and Bruker AM 400 spectrometers at 60 MHz, 90 MHz, 200 MHz, and 400 MHz, respectively. ^{13}C-NMR and ^{31}P-NMR spectra were measured on Bruker WP 200 and Bruker AM 400 spectrometers at 50.32 MHz respectively 100.64 MHz (^{13}C) and 80.8 MHz respectively 161.6 MHz (^{31}P). Chemical shifts for ^{1}H and ^{13}C are reported in parts per million (ppm) relative to tetramethylsilane as internal standard; the chemical shifts for ^{31}P are relative to external 85% orthophosphoric acid.

Materials

The solvents were dried by standard procedures and then distilled and stored under argon[21]. Phosphatriafulvenes **1a,b**[6], ynamines **10a**[22], **10b**[23], and cyclobutadienes **14a**[24, 25, 26], **14b**[25] were prepared by the published methods. Commercial reagents were purchased from Chemetal GmbH (n-butyllithium, 2.0 M solution in hexane) or Aldrich (methyllithium, 5% solution in diethyl ether, tert.-butyllithium, 1.7 M solution in pentane; phenyllithiun, 20% solution in cyclohexane/diethyl ether, 70:30; chlorotrimethylsilane).

Reactions of **1a** *and* **1b** *with Organolithium or Grignard Reagents; General Procedure:*

To the solution of **1a,b** in diethyl ether (equimolar amounts referred to the organolithium or Grignard reagent) is added dropwise with stirring at –78°C under an argon atmosphere a solution of the organometallic reagent [**1a:** 16.7 mL (15.4 mmol) **2a** in diethyl ether; 4.9 mL (8.1 mmol) **2b** in pentane; 4.0 mL (8.0 mmol) **2c** in cyclohexane / diethyl ether; 25 ml (25.0 mmol) **5a** in diethyl ether, **1b:** 4.3 mL (4.0 mmol) **2a** in diethyl ether; 1.9 mL (3.1 mmol) **2b** in pentane]. The mixture is allowed to warm to room temperature and stirred for 4 h (formation of a deep colored solution). Then, the mixture is cooled again to –78 °C and a solution of chlorotrimethylsilane in diethyl ether (10% excess) is added [**1a + 2a:** 2.0 mL (15.6 mmol); **1a + 2b:** 1.1 mL (8.2 mmol); **1a + 2c:** 1.0 ml (8.0 mmol); **1a + 5a:** 4.0 mL (32.0 mmol); **1b + 2a:** 0.52 mL (4.1 mmol) **1b + 2b:** 0.4 mL (3.1 mmol)]. The mixture is allowed to warm to room temperature and stirred for 15 h. The solvent is removed under vacuum, the residue is taken up in pentane, and insoluble material removed by centrifugation. The pentane solution is evaporated to give colorless to yellow oils which upon bulb-to-bulb distillation, afford **4a**, **4d** and **4e**. The crude **4b**, **4c** and **4f** are directly hydrolysed, resulting in the formation of **7b**, **7c**, and **9b**, respectively.

(2,3-Di-*tert*-butyl-3-methylcyclopropen-1-yl)bis(trimethylsilyl)phosphine (4a): Colorless oil; yield: 3.8 g (71%); bp 140 °C (0.005 mmHg). IR (film) ν = 2960, 2890, 2870, 1750, 1470, 1450, 1380, 1360, 1350, 1240, 1200, 1170, 1100, 970, 830, 750, 690, 620 cm^{-1}; ^{1}H NMR (C_6D_6): δ = 0.40 [d, $^3J_{H,P}$ = 4.8 Hz, 18H, $Si(CH_3)_3$], 1.20 [s, 9H, $C(CH_3)_3$], 1.35 [s, 9H, $C(CH_3)_3$], 1.38 s, (3H, CH_3); ^{13}C NMR (C_6D_6): δ = 1.7 [d, $^2J_{C,P}$ = 10.9 Hz, $Si(\underline{C}H_3)_3$], 22.5 (s, $\underline{C}H_3$), 29.3 [s, $C(\underline{C}H_3)_3$], 29.6 [s, $\underline{C}(CH_3)_3$], 30.0 [s, $C(\underline{C}H_3)_3$], 33.2 [d, $^3J_{C,P}$ = 12.8 Hz, $\underline{C}(CH_3)_3$], 36.2 (s, C-3), 109.1 (d, $^2J_{C,P}$ = 50.0 Hz, C-1), 146.7 (d, $^1J_{C,P}$ = 18.5 Hz, C-2); ^{31}P NMR (C_6D_6): δ = –174.8 (s); Anal. Calcd for $C_{18}H_{39}PSi_2$ (342.7): C, 63.09; H, 11.47. Found: C, 62.7; H, 11.3.

(2,3-Di-*tert*-butyl-3-ethenylcyclopropen-1-yl)bis(trimethylsilyl)phosphine (4d): Yellow oil; yield: 4.5 g (51%); bp 120 °C (0.005 mmHg); IR (film) ν = 3085, 2960, 2900, 860, 1755, 1620, 1470, 1460, 1400, 1390, 1360, 1250, 1210, 1160, 1040, 895, 840, 750, 695, 630 cm^{-1}; ^1H NMR (C_6D_6): δ = 0.5 [d,$^3J_{H,P}$ = 5.0 Hz, 9H, $Si(CH_3)_3$], 1.3 [s, 9H, $C(CH_3)_3$], 1.4 [s, 9H, $C(CH_3)_3$], 5.0 (m, 2H, CH_2), 6.7 (m, 1H, CH); ^{13}C NMR (C_6D_6): δ = 2.4 [d, $^2J_{C,P}$ = 13.3Hz, $Si(\underline{C}H_3)_3$], 29.7 [s, $C(\underline{C}H_3)_3$], 30.7 [s, $C(\underline{C}H_3)_3$], 33.2 [s, $\underline{C}(CH_3)_3$], 35.4 [s, $\underline{C}(CH_3)_3$], 40.7 (d, $^2J_{C,P}$ = 4.2Hz, C-3), 103.7 (d, $^1J_{C,P}$ = 54.5 Hz, C-1), 113.0 (s, $\underline{C}H_2$), 137.5 (d, $^2J_{C,P}$ = 16.9Hz, C-2), 145.5 (s, $\underline{C}H$); ^{31}P NMR (C_6D_6): δ = –173.0 (s); MS (70eV): *m/z* (%) = 354 (2, $M^{+\lambda}$), 297 (16, $M^{+\lambda}$ - C_4H_9), 281 (2), 224 (2), 208 (1), 177 (2), 150 (2), 120 (1), 73 (100), 57 (14), 41 (11); Anal. Calcd for $C_{19}H_{30}PSi_2$ (354.7): C, 64.34; H, 11.07. Found: C, 62.9; H, 10.7.

(2,3-Di-*tert*-butyl-3-methylcyclopropen-1-yl)mesityl(trimethylsilyl)phosphine (4e): Colorless oil, which solidified on standing at room temperature; yield: 1.4 g (90%); mp 68 °C (recrystallized from pentane); IR (KBr): ν = 2980, 2860, 1750, 1600, 1545, 1445, 1355, 1290, 1250, 1200, 1175, 850, 755, 700, 665, 630 cm^{-1}; ^1H NMR (C_6D_6): δ = 0.64 [d, $^3J_{H,P}$ = 6.0 Hz, 9H, $Si(CH_3)_3$], 1.37 [s, 9H, $C(CH_3)_3$], 1.41 [s, 9H, $C(CH_3)_3$], 1.70 (d, $^4J_{H,P}$ = 2.2 Hz, 3H, CH_3), 2.40 (s, 3H, 4′-CH_3-phenyl), 2.91, 2.98 (each s, each 3H, 2′,6′-CH_3-phenyl), 7.16, 7.17 (each d, $^4J_{H,P}$ = 2.4 and 2.3 Hz, respectively, each 1H, 3′,5′-H-phenyl); ^{13}C NMR (C_6D_6): δ = 1.4 [d, $^2J_{C,P}$ = 16.9 Hz, $Si(\underline{C}H_3)_3$], 21.1 (s, 4′-$\underline{C}H_3$-phenyl), 21.8 (s, $\underline{C}H_3$), 25.1, 25.2 (each d, $^3J_{C,P}$ = 11.7, and 19.7 Hz, respectively, 2′,6′-$\underline{C}H_3$-phenyl), 29.7 [s, $C(\underline{C}H_3)_3$], 30.0 [s, $C(\underline{C}H_3)_3$], 33.1 [s, $\underline{C}(CH_3)_3$], 36.5 (s, C-3), 38.5 [s, $\underline{C}(CH_3)_3$], 113.3 (d, $^1J_{C,P}$ = 42.2 Hz, C-1), 129.2, 129.2 (each s, C-3′, C-5′), 129.6 (d, $^1J_{C,P}$ = 13.3 Hz, C-1′), 138.5 (s, C-4′), 143.8, 144.5 (each d, $^2J_{C,P}$ = 7.1 and 10.4 Hz, respectively, C-2′, C-6′), 144.9 (d, $^2J_{C,P}$ = 19.0 Hz, C-2); ^{31}P NMR (C_6D_6): δ = –99.8 (s); Anal. Calcd for $C_{24}H_{41}PSi_2$ (388.7): C, 74.17; H, 10.63. Found: C, 73.8; H, 10.4.

Methanolysis of* 4a - f; *Synthesis of Primary Cyclopropenylphosphines* 7a - d *and Secondary Cyclopropenylphosphines* 9a,b; *General Procedure:

To a solution of silylphosphines **4a - f** in 20 mL diethyl ether is added 1.5 mL methanol and the mixture is stirred for 8 h at room temperature. Then the solution is evaporated to give an oil which is subjected to bulb-to-bulb distillation.

(2,3-Di-*tert*-butyl-3-methylcyclopropen-1-yl)phosphine (7a): 4a (3.2 g, 9.3 mmol) gives 1.5 g (87%) **7a** as an extremely air-sensitive, colorless oil, bp 120 °C (0.005 mmHg); IR (film): ν =. 2960, 2900, 2860, 2290, 1760, 1475, 1460, 1370, 1360, 1250, 1110, 1075, 830 cm^{-1}; ^1H NMR (C_6D_6): δ = 1.05 [s, 9.H, $C(CH_3)_3$], 1.20 [s, 9H, $C(CH_3)_3$], 1.22 (d, 3H, $^4J_{H,P}$ = 0.6 Hz, CH_3), 3.8 (d, $^1J_{H,P}$ = 203 Hz, PH_2); ^{13}C NMR (C_6D_6): δ = 19.9 (s, $\underline{C}H_3$), 29.1 [s, $C(\underline{C}H_3)_3$], 29.3 [s, $C(\underline{C}H_3)_3$], 33.5 [s, $\underline{C}(CH_3)_3$], 36.0 [s, $C(CH_3)_3$], 37.0 (s, C-3), 106.9 (d, $^2J_{C,P}$ = 33.2 Hz, C-2), 150.0 (s, C-1); ^{31}P NMR (C_6D_6): δ = –166.8 (t, $^1J_{H,P}$ = 203Hz; MS (70 eV): *m/z* (%) = 198 (3, M^+), 183 (5, $M^+ - CH_3$), 141 [100, $M^+ - C(CH_3)_3$], 108 (13), 84 (6), 81 (15), 57 (99), 41 (61); Anal. Calcd for $C_{12}H_{23}P$ (198.3): C, 72.68; H, 11.69. Found: C, 71.1; H, 11.1.

(2,3,3-Tri-*tert*-butylcyclopropen-1-yl)phosphine (7b): Reaction of **1a** (2.0 g, 7.9 mmol) with **2b** (4.7 mL, 8.1 mmol) and chlorotrimethylsilane (1.1 mL, 8.2 mmol) followed by direct methanolysis of crude **4b** gives 0.9 g (48%) of **7b** as a colorless oil which crystallizes partially at room temperature; bp 120 °C (0.005 mmHg); IR (film): ν = 2940, 2860, 2270, 1865, 1470, 1450, 1380, 1360, 1245, 1210, 1065, 955, 825, 690 cm^{-1}; ^1H NMR (C_6D_6): δ = 1.2 [s, 18H, $C(CH_3)_3$], 1.3 [s, 9H, $C(CH_3)_3$], 4.0 (d, $^1J_{H,P}$ = 202 Hz, 2H, PH_2); ^{13}C NMR (C_6D_6): δ = 30.2 [s, $C(\underline{C}H_3)_3$], 32.6 [s, $C(\underline{C}H_3)_3$], 32.6 [s, $\underline{C}(CH_3)_3$], 39.3 [s, $\underline{C}(CH_3)_3$], 48.5 (s, C-3), 106.3 (d, $^2J_{C,P}$ = 34.2 Hz, C-2), 148.9 (s, C-1); ^{31}P NMR (C_6D_6): δ = –155.9 (t, $^1J_{H,P}$ = 202Hz); MS (70 eV): *m/z* (%) = 183 [70, $M^+ - C(CH_3)_3$], 150 (9), 81 (13), 57 (100), 41 (55); Anal. Calcd for $C_{15}H_{29}P$ (240.4): C, 74.95; H, 12.16. Found: C, 73.7; H, 12.0.

(2,3-Di-*tert*-butyl-3-phenylcyclopropen-1-yl)phosphine (7c): Reaction of **1a** (2.0 g, 7.9 mmol) and **2c** (4.0 mL, 8.0 mmol) with chlorotrimethylsilane (1.0 mL, 8.0 mmol) followed by direct methanolysis of crude **4c** gives 0.3 g (13%) of **7c** as a pale yellow oil; bp 120 °C (0.005 mmHg) ; IR (film): ν = 3080, 3060, 3020, 2960, 2900, 2860, 1775, 1590, 1475, 1460, 1250, 1070, 845, 770, 755, 740, 710, 640 cm^{-1}; ^1H NMR (C_6D_6): δ = 1.0

[s, 9H, $C(CH_3)_3$], , 1.1 [s, 9H, $C(CH_3)_3$], 3.9 (d, $^1J_{H,P}$ = 204 Hz, 2H, PH_2), 7.3 (m, 5H, H-phenyl); ^{13}C NMR (C_6D_6): δ = 29.4 [s, $C(\underline{C}H_3)_3$], 29.9 [s, $C(\underline{C}H_3)_3$], 33.0 [s, $\underline{C}(CH_3)_3$], 36.0 [s, $\underline{C}(CH_3)_3$], 45.5 (s, C-3), 105.3 (d, $^2J_{C,P}$ = 35.5 Hz, C-2), 125 - 130 (s, broad, C-2′, C-3′, C-4′, C-5′, C-6′), 146.5 (s, C-1); ^{31}P NMR (C_6D_6): δ = –159.4 (t, $^1J_{H,P}$ = 204 Hz); a correct elemental analysis could not be obtained because **7c** is extremely air-sensitive.

Compound **7c** is also accessible by reaction of **1a** with Gignard reagent **5b** and subsequent methanolysis.

(2,3-Di-*tert*-butyl-3-ethenylcyclopropen-1-yl)phosphine (7d): Methanolysis of **4d** (2.5 g, 7.0 mmol) gives 0.8 g (60%) **7d** as an extremely air-sensitive, colorless oil, bp 50 °C (0.005 mmHg); IR (film): ν = 3090, 2980, 2910, 2880, 2300, 1770, 1625, 1480, 1460, 1410, 1400, 1370, 1260, 1060, 910, 850, 770, 700, 640 cm^{-1}; ^1H NMR (C_6D_6): δ = 1.0 [s, 9H, $C(CH_3)_3$], 1.2 [s, 9H, $C(CH_3)_3$], 3.8 (d, $^1J_{H,P}$ = 202 Hz, 2H, PH_2), 4.9 (m, 2H, - CH = $C\underline{H}_2$), 6.5 (m, 1H, - $C\underline{H}$ = CH_2); ^{13}C NMR (C_6D_6): δ = 29.2 [s, $C(\underline{C}H_3)_3$], 29.7 [s, $C(\underline{C}H_3)_3$], 33.5 [s, $\underline{C}(CH_3)_3$], 34.9 [s, $\underline{C}(CH_3)_3$], 42.3 (s, C-3), 98.9 (d, $^1J_{C,P}$ = 38 Hz, C-1), 113.3 (s, CH = $\underline{C}H_2$), 142.3 (s, $\underline{C}H$ = CH_2), 145.1 (s, C-2); ^{31}P NMR (C_6D_6): δ = - 168.9 (t, $^1J_{H,P}$ = 202Hz); a correct elemental analysis could not be obtained because **7d** is extremely air-sensitive.

(2,3-Di-*tert*-butyl-3-methylcyclopropen-1-yl)mesitylphosphine (9a): **4e** (2.0 g, 6.3 mmol) gives 1.7 g (85%) **9a** as a mixture of diastereomers (ratio: *55:45*, ^{31}P NMR); colorless oil which partially crystallizes at room temperature; IR (film): ν = 2960, 2880, 2300, 1760, 1600, 1450, 1360, 1350, 1240, 1200, 1175, 1100, 1025, 940, 875, 845, 800 cm^{-1}; ^1H NMR (C_6D_6): δ = 1.27 [s, 9H, $C(CH_3)_3$], 1.32 [s, 9H, $C(CH_3)_3$], 1.36 [d, $^5J_{H,P}$ = 0.7 Hz, 9H, $C(CH_3)_3$], 1.39 [d, $^5J_{H,H}$ = 0.7 Hz, 9H, $C(CH_3)_3$], 1.52 (s, 3H, CH_3), 1.60 (dd, $^4J_{H,P}$ = 1.3 Hz, $^5J_{H,H}$ = 0.7 Hz, 3H, CH_3), 2.48, 2.49, 2.89, and 2.90 (each s, each 3H, 2′,6′-CH_3-phenyl), 2.49 (s, 6H, 4′-CH_3-phenyl), 5.57, 5.60 (each d, $^1J_{H,P}$ = 228 and 227 Hz, respectively, each 1H, PH), 7.16 (d, $^4J_{H,P}$ = 0.5 Hz, 4H, H-phenyl); ^{13}C NMR (C_6D_6): δ = 20.2 (s, $\underline{C}H_3$), 20.3 (s, $\underline{C}H_3$), 21.1 (s, 4′- $\underline{C}H_3$- phenyl), 23.3, 23.4 (each d, $^3J_{C,P}$ = 12.8 and 12.9 Hz, respectively, 2′,6′- $\underline{C}H_3$-phenyl), 29.3 [s, $C(\underline{C}H_3)_3$], 29.5 [s, $C(\underline{C}H_3)_3$], 29.7 [s, $C(\underline{C}H_3)_3$], 33.3 [s, $\underline{C}(CH_3)_3$], 36.0 (s, [s, $\underline{C}(CH_3)_3$], 36.1 [s, $\underline{C}(CH_3)_3$], 38.1 (s, C-3), 38.3 (d, $^2J_{C,P}$ = 4.7 Hz, C-3), 113.1 (d, $^1J_{C,P}$ = 40.7 Hz, C-1), 113.0 (d, $^1J_{C,P}$ = 40.6 Hz, C-1), 128.3 (d, $^2J_{C,P}$ = 2.7 Hz, C-2′), 128.4 (s, C-2′), 129.2 (d, $^3J_{C,P}$ = 4.1 Hz, C-3′), 138.8 (s, C-4′), 143,0 (d, $^1J_{C,P}$ = 13.1 Hz, C-1′), 143.2 (d, $^1J_{C,P}$ = 14.2 Hz, C-1′), 146.4 (d, $^2J_{C,P}$ = 6.6 Hz, C-2), 148.1 (d, $^2J_{C,P}$ = 9.6 Hz, C-2); ^{31}P NMR (C_6D_6): δ = –106.3 (d, $^1J_{H,P}$ = 228 Hz), –107.4 (d, $^1J_{H,P}$ = 227 Hz); Anal. Calcd for $C_{21}H_{33}P$ (316,5): C, 79.70; H, 10.51. Found: C, 79.1; H, 10.3.

Mesityl-(2,3,3-tri-*tert*-butylcyclopropen-1-yl)phosphine (9b): **1b** (0.9 g, 3.0 mmol), **2b** (1.9 mL, 3.1 mmol), and chlorotrimethylsilane (0.4 mL, 3.1 mmol) followed by direct methanolysis of the crude **4f** gives 0.7 g (48%) **9b** as a colorless microcrystalline solid; mp 74 °C (from pentane); IR (KBr): ν = 2940, 2860, 2300, 1760, 1600, 1460, 1385, 1360, 1230, 1210, 1035, 960, 885, 850, 680 cm^{-1}; ^1H NMR (C_6D_6): δ = 1.05 [s, 9H, $C(CH_3)_3$], 1.20 [s, 18H, $C(CH_3)_3$], 2.10 (s, 3H, 4′-CH_3-phenyl), 2.55 (s, 6H, 2′,6′-CH_3-phenyl), 5.40 (d, $^1J_{H,P}$ = 230 Hz, 1H, PH), 6.85 (s, 2H, H-phenyl); ^{13}C NMR (C_6D_6): δ = 20.9 (s, 4′-$\underline{C}H_3$-phenyl), 23.4 (d, $^3J_{C,P}$ = 12.2 Hz, 2′,6′-$\underline{C}H_3$-phenyl), 30.3 [s, $C(\underline{C}H_3)_3$], 32.1 [s, $\underline{C}(CH_3)_3$], 32.9 [d, $^4J_{C,P}$ = 8.1 Hz, $C(CH_3)_3$], 39.3 [d, $^3J_{C,P}$ = 19.5 Hz, $\underline{C}(CH_3)_3$], 48.9 (d, $^2J_{C,P}$ = 4.4 Hz, C-3), 112.3 (d, $^2J_{C,P}$ = 43.6 Hz, C-2), 129.2 (s, C-4′), 129.4 (s, C-3′), 139.0 (s, C-2′), 143 (d, $^1J_{C,P}$ = 13.2 Hz, C-1′), 146.7 (d, $^1J_{C,P}$ = 12.2 Hz, C-1); ^{31}P NMR (C_6D_6): δ = –99.3 (d, $^1J_{H,P}$ = 230 Hz); MS (20 eV): *m/z* (%) = 358 (0.2, M^+), 301 [100, $M^+ - C(CH_3)_3$], 151 (7), 119 (2), 57 (29); Anal. Calcd for $C_{24}H_{39}P$ (358.5): C, 80.40; H, 10.96. Found: C, 78.7; H, 10.6.

(2,3-Di-*tert*-butyl-3-methylcyclopropen-1-yl)trimethylsilylphosphine (8): To a solution of **7a** (1.5 g, 7.6 mmol) in diethyl ether is added dropwise at –78 °C a solution of **2a** in diethyl ether (0.7 mL, 7.7 mmol). The mixture is allowed to warm to room temperature and stirring is continued for 3 h. Then, the mixture is cooled again to –78 °C and a solution of chlorotrimethylsilane in diethyl ether (1.0 mL, 7.9 mmol) is added. After warming to room temperature and removal of insoluble material by centrifugation, the diethyl ether solution is evaporated to give an oil which, upon bulb-to-bulb distillation, affords **8** as a colorless oil which consists of two diastereomers (ratio: *55:45*, ^{31}P NMR)l; bp 80 °C (0.005 mmHg); ^1H NMR (C_6D_6): δ = 0.40 [d, $^3J_{H,P}$ = 4.8 Hz, 9H, $Si(CH_3)_3$], 1.10 [s, 9H, $C(CH_3)_3$], 1.30 (s, 3H, CH_3), 1.35 [s, 9H, $C(CH_3)_3$], 3.30 (d, $^1J_{H,P}$ = 195 Hz,

1H, PH), 3.35 (d, $^1J_{H,P}$ = 204 Hz, 1H, PH); ^{13}C NMR (C_6D_6): δ = 0.4 [d, $^2J_{C,P}$ = 11.2 Hz, Si($\underline{C}H_3)_3$], 0.6 [d, $^2J_{C,P}$ = 10.7 Hz, Si($\underline{C}H_3)_3$], 20.8 (s, $\underline{C}H_3$), 21.8 (s, $\underline{C}H_3$), 29.2 [s, C($\underline{C}H_3)_3$], 29.8 [s, C($\underline{C}H_3)_3$], 33.3 [s, $\underline{C}(CH_3)_3$], 33.5 [s, $\underline{C}(CH_3)_3$], 36.1 [d, $^3J_{C,P}$ = 6.9 Hz, $\underline{C}(CH_3)_3$], 36.5 [d, $^3J_{C,P}$ = 8.8 Hz, $\underline{C}(CH_3)_3$], 108.3 (d, $^2J_{C,P}$ = 9.5 Hz, C-2), 109.2 (d, $^2J_{C,P}$ = 8.3 Hz, C-2), 145.3 (d, $^1J_{C,P}$ = 14.1Hz, C-1), 148.5 (s, C-1); ^{31}P NMR (C_6D_6): δ = –158.3 (d, $^1J_{H,P}$ = 195 Hz), –164.0 (d, $^1J_{H,P}$ = 204 Hz).

Reaction of* 1b *with Ynamines* 10a,b*; General Procedure:

A solution of the respective ynamine (**10a:** 1.0 g, 8.8 mmol; **10b:** 1.3 g, 10.0 mmol) in diethyl ether (20 mL) is added dropwise to a solution of **1b** (2.7 g, 8.8 mmol or 3.0 g, 10.0 mmol) at 0 °C. The reaction mixture is allowed to warm to room temperature and then stirred for 10 h. The solvent is evaporated under vacuum and the residue is recrystallized from pentane by cooling to –30 °C.

***N*-(4-*tert*-Butyl-1-mesityl-7,7-dimethyl-1-phosphaocta-1,3-dien-5-yn-2-yl)morpholine (11a):** Orange-red crystals; yield: 2.5 g (70%); mp 107 °C (dec.); IR (KBr): ν = 2950, 2900, 2840, 2200 (C≡C), 1590, 1580, 1450, 1370, 1350, 1330, 1300, 1270, 1250, 1230, 1210, 1140, 1115, 1105, 1030, 930, 900, 860, 850, 820, 650, 630 cm^{-1}; ^{1}H NMR (C_6D_6): δ = 1.00 [s, 9H, C($CH_3)_3$], 1.30 [s, 9H, C($CH_3)_3$], 2.30 (s, 3H, 4′- CH_3-phenyl), 2.70 (s, 6H, 2′,6′- CH_3-phenyl), 3.50 and 3.70 (m, 8H, H-morpholine), 6.05 (d,. $^3J_{H,P}$ = 6.6 Hz, 1H, H-3), 7.0 (broad, 2H, H-phenyl); ^{13}C NMR (C_6D_6): δ = 21.1 (s, 4′-$\underline{C}H_3$-phenyl), 23.7 (d, $^3J_{C,P}$ = 9.1, 2′,6′-$\underline{C}H_3$-phenyl), 28.9 [s, C($\underline{C}H_3)_3$], 28.4 [s, C($\underline{C}H_3)_3$], 31.2 [s, $\underline{C}(CH_3)_3$], 36.2 [s, $\underline{C}(CH_3)_3$], 49.8 (d, $^4J_{C,P}$ = 16.6 Hz, N-$\underline{C}H_2$-morpholine), 66.1 (d, $^5J_{C,P}$ = 3.0 Hz, O-$\underline{C}H_2$-morpholine), 77.5 (s, C-5), 105.8 (s, C-6), 128.4 (d, $^2J_{C,P}$ = 7.6 Hz, C-3), 128.6 (s, C-3′), 132.1 (d, $^3J_{C,P}$ = 6.5 Hz, C-4), 136.1 (d, $^1J_{C,P}$ = 38.1 Hz, C-1′), 136.9 (s, C-4′), 143.0 (d, $^2J_{C,P}$ = 6.1 Hz, C-2′), 194.7 (d, $^1J_{C,P}$ = 53.1Hz, C-2); ^{31}P NMR (C_6D_6): δ = 89.2 (s); Anal. Calcd for $C_{26}H_{38}NOP$ (411.6): C, 75.87; H, 9.31; N, 3.42. Found: C, 75.6; H, 9.1; N, 3.2.

***N*-[4-*tert*-Butyl-1-mesityl-7,7-dimethyl-1-phosphaocta-1,3-dien-5-yn-2-yl]-*N*-methylaniline (11b):** Yellow crystals; yield: 2.2 g (50%); m.p. 75 °C (dec.); IR (KBr): ν = 2960, 2840, 2220 (C≡C), 1600, 1490, 1475, 1460, 1425, 1350, 1250, 1100, 1080, 1065, 1025, 850, 780, 695, 675 cm^{-1}; ^{1}H NMR (C_6D_6): δ = 0.70 [s, 9H, C($CH_3)_3$], 1.20 [s, 9H, C($CH_3)_3$], 2.10 (s, 3H, 4′-CH_3-phenyl), 2.6 (s, 6H, 2′,6′-CH_3-phenyl), 3.50 (d, $^5J_{H,P}$ = 4.5 Hz, 3H, N-CH_3), 5.90 (d, $^3J_{H,P}$ = 4.8 Hz, 1H, H-3), 6.9 (m, 7H, H-phenyl); ^{13}C NMR (C_6D_6): δ = 21.1 (s, 4′- $\underline{C}H_3$- phenyl), 23.8 (d, $^3J_{C,P}$ = 8.9 Hz, 2′,6′-$\underline{C}H_3$-phenyl), 28.3 [s, C($\underline{C}H_3)_3$], 28.6 [s, C($\underline{C}H_3)_3$], 31.2 [s, $\underline{C}(CH_3)_3$], 35.4 [s, $\underline{C}(CH_3)_3$], 43.0 (d, $^3J_{C,P}$ = 27.4 Hz, N-$\underline{C}H_3$), 77.7 (s, C-5), 124.3, 125.3, 128.0, 128.5 (each s, C-phenyl), 130.6 (d, $^3J_{C,P}$ = 7.5 Hz, C-4), 131.6 (d, $^2J_{C,P}$ = 8.1 Hz, C-3), 136.1 (d, $^1J_{C,P}$ = 36.5 Hz, C-1′), 137.0 (s, C-phenyl), 142.9 (d, $^2J_{C,P}$ = 6.1 Hz, C-2′), 148.5 (s, C-phenyl), 191.2 (d, $^1J_{C,P}$ = 50.5 Hz, C-2); ^{31}P NMR (C_6D_6): δ = 98.9 (s); Anal. Calcd for $C_{29}H_{38}NP$ (431.6): C, 80.70; H, 8.87; N, 3.26. Found: C, 80.2; H, 8.74; N, 3.1.

Reaction of* 1b *with Cyclobutadienes* 17a,b*; General Procedure:

A solution of **1b** (1.5 g, 5.0 mmol) and **17** (**17a:** 1.4 g, 5.0 mmol; **17b:** 1.6 g, 5.0 mmol) in pentane is stirred for several hours (**17a**) or 4 d (**17b**) until a precipitate is separated. The crystals are filtered, washed several times with pentane, and dried under vacuum.

Methyl 1′,2,3,5′,6′-Penta-*tert*-butyl-2′-mesityl-[spiro(cyclopropene-1,3′-[2]phosphabicyclo[2.2.0]-hex-5-ene)]-4′-carboxylate (18a): Colorless crystals; yield: 1.5 g (52%); m.p. 175 °C; IR (KBr): ν = 3015, 2960, 2920, 1800, 1715 (C=O), 1600, 1460, 1390, 1355, 1235, 1130, 1105, 1070, 1020, 950, 850, 820, 805, 795, 750, 650, 630, 610 cm^{-1}; ^{1}H NMR (C_6D_6): δ = 1.30 [s, 9H, C($CH_3)_3$], 1.35 [s, 9H, C($CH_3)_3$], 1.50 [s, 9H, C($CH_3)_3$], 1.55 [s, broad, 9H, C($CH_3)_3$], 1.75 [s, 9H, C($CH_3)_3$], 2.10 (s, 3H, 4″-CH_3-phenyl), 3.10 (s, 6H, 2″,6″-CH_3-phenyl), 3.40 (s, 3H, OCH_3), 6.90 (d, $^4J_{H,P}$ = 2.0 Hz, 2H, H-phenyl); ^{13}C NMR (C_6D_6): δ = 20.9 (s, 4″-$\underline{C}H_3$- phenyl), 25.0, 28.0 (each s, broad, 2″,6″-$\underline{C}H_3$-phenyl), 31.5 [s, C($\underline{C}H_3)_3$], 32.6 [s, C($\underline{C}H_3)_3$], 33.1 [s, C($\underline{C}H_3)_3$], 32.6 [s, C($\underline{C}H_3)_3$], 33.23 [s, $\underline{C}(CH_3)_3$], 33.27 [s, $\underline{C}(CH_3)_3$], 33.9 [s, C($\underline{C}H_3)_3$], 34.0 [s, $\underline{C}(CH_3)_3$], 36.1 [d, $^2J_{C,P}$ = 25.6 Hz, $\underline{C}(CH_3)_3$], 42.4 (d, $^2J_{C,P}$ = 3.0 Hz, C-4′), 43.4 [s, C($\underline{C}H_3)_3$], 49.5 (s, O$\underline{C}H_3$), 68.0 (d, $^1J_{C,P}$ = 21.3 Hz, C-1′), 69.7 (d, $^1J_{C,P}$ = 24.2 Hz, C-3′, C-1), 121.8 (s, C-4″), 129.4 (each s, broad, C-3″, C-5″), 133.4 (d, $^1J_{C,P}$ = 67.2 Hz, C-1″), 136.6 (d, $^2J_{C,P}$ = 18.8 Hz, C-2), 144.2, 146.5 (each s, broad, C-2″ and

C-6′), 150.8 (s, C-6′), 155.6 (d, $^3J_{C,P}$ = 3.0 Hz, C-5′), 174.2 (s, C=O); ^{31}P NMR (C_6D_6): δ = 11.5 (s); Anal. Calcd for $C_{38}H_{59}O_2P$ (578.9): C, 78.84; H, 10.27. Found: C, 78.6; H, 10.2.

***tert.*-Butyl 1′,2,3,5′,6′-Penta-*tert*-butyl-2′-mesityl-[spiro(cyclopropene-1,3′-[2]phosphabicyclo-[2.2.0]hex-5-ene)]-4′-carboxylate (18b):** Pale yellow crystals; yield: 1.2 g (40%); m.p. 154 °C; IR (KBr): ν = 2960, 2910, 1790, 1700 (C=O), 1450, 1380, 1360, 1230, 1150, 1050, 1020, 850, 760, 640 cm^{-1}; ^{1}H NMR (C_6D_6): δ = 1.20 [s, 9H, C(CH$_3$)$_3$], 1.30 [s, 9H, C(CH$_3$)$_3$], 1.45 [s, broad, 9H, C(CH$_3$)$_3$], 1.50 [s, 9H, C(CH$_3$)$_3$], 1.55 [s, 9H, C(CH$_3$)$_3$], 1.70 [s, 9H, C(CH$_3$)$_3$], 2.10 (s, 3H, 4′′-CH$_3$-phenyl), 3.00 (s, 6H, 2′′,6′′-CH$_3$-phenyl), 6.7 (broad, 2H, H-phenyl); ^{13}C NMR (C_6D_6): δ = 20.9 (s, 4′′-CH$_3$-phenyl), 25.1 (s, broad, 2′′,6′′-CH$_3$-phenyl), 28.0 [s, C(CH$_3$)$_3$], 28.8 [s, broad, C(CH$_3$)$_3$], 31.5 [s, C(CH$_3$)$_3$], 31.7 [s, C(CH$_3$)$_3$], 32.8 [s, C(CH$_3$)$_3$], 33.4 [s, C(CH$_3$)$_3$], 33.8 [s, C(CH$_3$)$_3$], 34.0 [s, C(CH$_3$)$_3$], 34.3 [s, C(CH$_3$)$_3$], 34.5 [s, broad, C(CH$_3$)$_3$], 36.1 [d, $^2J_{C,P}$ = 25.4 Hz, C(CH$_3$)$_3$], 42.9 (s, C-4′), 69.7 (d, $^1J_{C,P}$ = 20.2 Hz, C-1′), 71.1 (d, $^1J_{C,P}$ = 24.9 Hz, C-3′/ C-1), 80.4 [s, (H$_3$C)$_3$CO], 121.0 (s, C-4′′), 130.0 (s, broad, C-3′′, C-5′′), 133.9 (d, $^1J_{C,P}$ = 69.2 Hz, C-1′′), 137.0 (d, $^2J_{C,P}$ = 17.4 Hz, C-2), 138.7 (s, C-3), 144.4, 146.9 (each s, broad, C-2′′ and C-6′′)150.5 (s, C-6′), 155.0 (d, $^3J_{C,P}$ = 4.8 Hz, C-5′), 173.3 (d, $^3J_{C,P}$ = 5.1 Hz, CO]; ^{31}P NMR (C_6D_6): δ = 7.7 (s); Anal. Calcd for $C_{41}H_{65}O_2P$ (621.0): C, 79.30; H, 10.55. Found: C, 79.2; H, 10.4.

Isomerization of* 18a,b *to* 20a,b*: General procedure:

A solution of **18a** (580 mg, 1.0 mmol) or **18b** (620 mg, 1.0 mmol) in 5 mL chloroform is stirred for 12 h. The chloroform solution is evaporated to give the colorless products which are dried under vacuum. The isomerization reaction can also performed in benzene but with a reaction time of several days.

Methyl 2,3,4-Tri-*tert*-butyl-1-(2,3-di-*tert*-butylcyclopropenylidene)-5-mesityl-5-phosphapenta-2,4-dienoate (20a): Colorless powder; yield:580 mg (100%); m.p. 201 °C; IR (KBr): ν = 3060, 2960, 1820, 1650, 1600, 1520, 1430, 1390, 1270, 1220, 1180, 1150, 1080, 1020, 930, 850, 835, 820, 805, 790, 775, 760, 740, 700, 660, 605 cm^{-1}; ^{1}H NMR (C_6D_6): δ = 1.10 [s, 9H, C(CH$_3$)$_3$], 1.38 [s, 9H, C(CH$_3$)$_3$], 1.39 [s, 9H, C(CH$_3$)$_3$], 1.40 [s, 9H, C(CH$_3$)$_3$], 1.51 [s, 9H, C(CH$_3$)$_3$], 2.12, 2.24, 2.39 (each s, each 3H, 2′′,4′′,6′′-CH$_3$-phenyl), 3.62 (s, 3H, OCH$_3$), 6.75 (s, 1H, H-phenyl), 6.78 (s, 1H, H-phenyl); ^{13}C NMR (C_6D_6): δ = 21.3 (s, 4′′- CH$_3$- phenyl), 24.0 (d, $^3J_{C,P}$ = 7.1Hz, 2′′-CH$_3$-phenyl), 25.0 (d, $^3J_{C,P}$ = 6.5 Hz, 6′′-CH$_3$-phenyl), 29.6, [s, C(CH$_3$)$_3$], 30.8, [s, C(CH$_3$)$_3$], 30.97 [s, C(CH$_3$)$_3$], 31.04 [s, C(CH$_3$)$_3$], 32.7 [s, C(CH$_3$)$_3$], 33.6 [s, C(CH$_3$)$_3$], 33.8 [s, C(CH$_3$)$_3$], 35.6 [s, C(CH$_3$)$_3$], 38.1 [d, $^3J_{C,P}$ = 8.0 Hz, C(CH$_3$)$_3$], 40.0 [s, C(CH$_3$)$_3$], 44.7 [d, $^2J_{C,P}$ = 15.4 Hz, C(CH$_3$)$_3$], 49.5 (s, OCH$_3$), 93.1 (s, C-1), 128.4, 128.6 (each s, C-3′′, C-5′′), 137.8 (s, C-4′′), 139.7, 140.3 (each s, C-2′′, C-6′′), 140.2 (d, $^1J_{C,P}$ = 5.3 Hz, C-1′′), 140.6 (d, $^2J_{C,P}$ = 5.8 Hz, C-3), 150.0, 151.0 (each s, broad, C-2′, C-3′), 151.7 (d, $^3J_{C,P}$ = 18.0 Hz, C-2), 152.9 (s, C-1′), 170.0 (s, broad, (s, CO), 211.0 (broad, C-4); ^{31}P NMR (C_6D_6): δ = 215.7 (s); Anal. Calcd for $C_{38}H_{59}O_2P$ (578.9): C, 78.84; H, 10.27. Found: C, 78.2; H, 10.0.

***tert.*-Butyl 2,3,4-Tri-*tert*-butyl-1-(2,3-di-*tert*-butylcyclopropenylidene)-5-mesityl-5-phosphapenta-2,4-dienoate (20b):** Colorless crystals; yield: 620 mg (100%); m.p. 198 °C; IR (KBr): ν = 2960, 1820, 1710, 1670, 1605, 1520, 1480, 1460, 1390, 1360, 1270, 1230, 1170, 1060, 1030, 860, 780 cm^{-1}; ^{1}H NMR (C_6D_6): δ = 1.25 [s, 9H, C(CH$_3$)$_3$], 1.35 [s, 18H, C(CH$_3$)$_3$], 1.40 [s, 9H, C(CH$_3$)$_3$], 1.50 [s, 18H, C(CH$_3$)$_3$], 2.05, 2.20, 2.40 (each s, each 3H, 2′′,4′′,6′′-CH$_3$-phenyl), 6.75 (s, 2H, H-phenyl); ^{13}C NMR (C_6D_6): δ = 21.0 (s, 4′′-CH$_3$-phenyl), 23.7 (d, $^3J_{C,P}$ = 7.6Hz, 2′′-CH$_3$-phenyl), 24.9 (d, $^3J_{C,P}$ = 5.5 Hz, 6′′-CH$_3$-phenyl), 28.8 [s, C(CH$_3$)$_3$], 29.7 [s, C(CH$_3$)$_3$], 30.9 [s, C(CH$_3$)$_3$], 31.0 [s, C(CH$_3$)$_3$], 32.5 [s, C(CH$_3$)$_3$], 33.4 [s, C(CH$_3$)$_3$], 33.7 [s, C(CH$_3$)$_3$], 35.9 [s, C(CH$_3$)$_3$], 37.8 [d, $^3J_{C,P}$ = 6.4 Hz, C(CH$_3$)$_3$], 39.3 [s, C(CH$_3$)$_3$], 44.4 [d, $^2J_{C,P}$ = 14.6 Hz, C(CH$_3$)$_3$], 78.2 [s, OC(H$_3$C)$_3$], 94.0 (s, C-1), 128.2, 128.3 (each s, C-3′′, C-5′′), 137.4 (s, C-4′′), 139.7 (s, C-2′′), 140.2 (d, $^1J_{C,P}$ = 6.2 Hz, C-1′′), 140.3 (d, $^2J_{C,P}$ = 5.5 Hz, C-5′′), 142.0 (s, C-1′), 143.2 (d, $^2J_{C,P}$ = 7.5 Hz, C-3), 149.4, 151.1 (each s, C-2′, C-3′), 151.6 (d, $^3J_{C,P}$ = 14.3 Hz, C-2), 169.7 (s, CO], 210.5 (d, $^1J_{C,P}$ = 52.9 Hz, C-4); ^{31}P NMR (C_6D_6): δ = 215.4 (s); Anal. Calcd for $C_{41}H_{65}O_2P$ (621.0): C, 79.30; H, 10.55. Found: C, 78.3; H, 10.2.

***X-Ray Crystal Structure Analysis of* 11a:**

Crystal data: $C_{26}H_{38}NOP$, M_r = 411.5; orthorhombic; space group $Pna2_1$; a = 16.346(2), b = 9.712(1), c = 16.091(2) Å; V = 2554.5 Å^3; Z = 4; $D_{calc.}$ = 1.070 g cm^{-3}; μ = 1.2 cm^{-1}. *Data collection:* The data collection was performed using an automatic four circle diffractometer (Enraf Nonius CAD4). Crystal dimensions: 0.3×0.35×0.5 mm. The measurements were made in the range $2° \leq \Theta \leq 25°$, Mo K_α (graphite monochromator), a total of 2579 reflections were obtained of which 2337 were independent reflections. Structure solution and refinement: The structure was solved using direct methods (SHELXS-86)[27] and refined with a full matrix least squares method (SHELX-76)[28] . All hydrogen atoms were calculated geometrically. The anisotropic refinement with 1513 reflections [$I > 2\sigma(I)$] converged at R = 0.069 and R_w = 0.060. The difference Fourier synthesis on the basis of the final structural model showed a maximum of 0.21 eÅ^{-3} and a minimum of -0.23 eÅ^{-3} [29].

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