Synthesis and spectral properties of cyclopropyl-substituted phosphaalkenes

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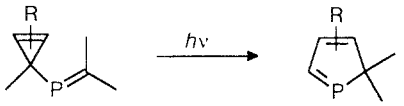
Cyclopropanecarboxylic acid chlorides **5a—d** react with tris(trimethylsilyl)phosphane **6** in benzene at −2 °C to form cyclopropylcarbonyl-bis(trimethylsilyl)phosphanes **7**. These products undergo silylic rearrangement at 25 °C to yield phosphaalkenes **8**. Compounds **8a,b,d** are formed as mixtures of *Z*- and *E*-isomers where the latter predominate. In the case of **8c**, the *Z*-isomer is formed exclusively.

Key words: phosphaalkenes, cyclopropyl-substituted, *E/Z*-isomerism.

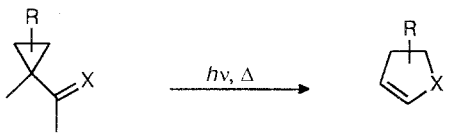
According to the isolobal principle, alkenes and phosphaalkenes (see the reviews in Ref. 2) are, formally, analogs whose chemical properties are much alike. In particular, the π-P=C bond can be involved in rearrangements typical of the C=C bond. For example, cyclopropenylphosphaalkenes **1** can undergo a photochemical transformation[3] into 2*H*-phospholes **2**, in analogy to the well known vinylcyclopropene—cyclopentadiene rearrangement.[4]



1 **2**

The present paper deals with the synthesis and study of the spectral properties of cyclopropyl-substituted phosphaalkenes. In particular, the latter are of interest for a study of the possibility of their transformation into phosphacyclopentenes in analogy to the vinylcyclopropane—cyclopentene rearrangement[4] (**3a→4a**). It is noteworthy that similar reactions involving double-bonded nitrogen (**3b→4b**) were found rather long ago.[5]

First, we studied the possibility of synthesizing *E,Z*-(R-trimethylsiloxymethylene)trimethylsilylphosphanes



3 **4**

X = CR'_2 (**a**), NR (**b**)

(Scheme 1) using the known reaction[6,7] of acyl halides with tris(trimethylsilyl)phosphane **6**. The synthesis of methylenephosphane $Me_3SiP{=}C(OSiMe_3)Bu^t$ **6**, which is stable when stored, from pyvaloyl chloride can be performed in two ways: either by keeping the reactants in an aprotic medium for one day at ~20 °C, or by boiling them for 6—7 h.[8] It has been shown in experiments with other carboxylic acid chlorides[9] that 1,3-silylic isomerization of the originally formed acylphosphane results in a phosphaalkene having the *E*-configuration of the substituents at the P=C bond. This compound then transforms into the *Z*-isomer, which is less sterically hindered and thus is more stable thermodynamically.

However, the reaction of cyclopropanecarboxylic acid chlorides **5a—d** with compound **6** did not allow us to synthesize phosphaalkenes **8** because of the easy oligomerization of the products formed. Nevertheless, we found that an efficient variant of the method considered is the treatment of compounds **5a—d** with phosphane **6** at temperatures from −3 to 0 °C for 20—30 min followed by heating the reaction mixtures obtained to ~20 °C. The yields of phosphaalkenes depend on both the temperature conditions and the nature of the solvent. We obtained the maximum yields of compounds **8** (75—95 %) when benzene was used as the solvent. If benzene is replaced by 1,2-dimethyxoethane, chloroform, aliphatic hydrocarbons (pentane, hexane), or their cyclic analogs, the yields of phosphaalkenes **8** decrease.

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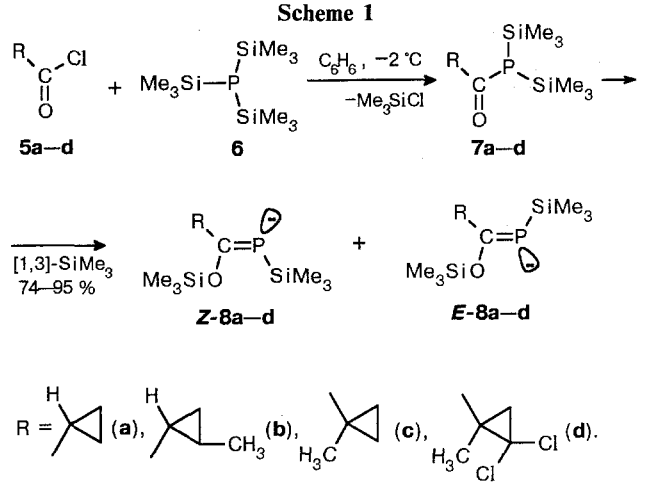
Scheme 1



The solutions of compounds **8a—d** in benzene are stable at 0°C for several days and can be used in further transformations. However, attempts to isolate these compounds in the individual state by evacuation and/or high-vacuum distillation always resulted in colorless polymeric products which we did not study.

1-Cyclopropylcarbonyl-bis(trimethylsilyl)phosphanes (**7a—d**), which are stable below −3°C, are the initial products of this reaction (see Scheme 1). The presence of these compounds in the products of the reaction performed in the temperature range from −3 to 0°C (yields 40—60%) can easily be detected by NMR (^{1}H, ^{13}C, ^{31}P, and ^{29}Si). Table 1 presents the compositions of the reaction mixtures obtained under the above conditions. It is interesting to note that a further decrease in temperature to −5°C in the case of 1-methyl-2,2-dichlorocyclopropanecarboxylic acid chloride makes it possible to obtain a solution of compound **7d** almost without an admixture of phosphaalkene **8d** (see Table 1, *cf.* **d** and **dd****).

As expected, the resonance absorption of phosphorus in acylphosphanes **7** (δ from −80.3 to −102.8, *i.e.*, a weak-field shift in comparison to the signal of **6** is observed)[8] is in the same range of chemical shifts as that of 1-oxo-2,2-dimethylpropyl-[6] and 1-adamantylcarbonyl-bis(trimethylsilyl)phosphanes[10] (**7**, R = *t*-Bu or 1-Ad, respectively). The ^{1}H and ^{13}C NMR spectra of acylphosphanes **7** display characteristic doublets of silyl groups at the phosphorus atom: the coupling constants $^3J_{H,P}$ and $^2J_{C,P}$ are in the ranges 4.4—4.5 Hz and 10.1—11.1 Hz, respectively. The ^{1}H NMR spectra of the cyclopropane moieties (see Experimental) are analogous to the spectra of the original acid chlorides. The only exception is observed for compound **7c**. In this case, the signals of the $H_{MM'}$ protons are split additionally with coupling constants $^4J_{H,P}$ = 1.8 Hz, which implies that the $H_{MM'}$ protons interact directly with the phosphorus atom. Furthermore, the ^{13}C NMR spectrum of this compound contains similar $^3J_{C,P}$ coupling constants for the C atoms of the cyclopropane ring ($^3J_{C,P}$ = 6.1 Hz) and for the methyl group ($^3J_{C,P}$ = 8.1 Hz). The coupling constant for compound **7d** is ^3J (P,CH_3) = 9.1 Hz, and there is no coupling constant between the phosphorus and the C-2, C-3 atoms of the cyclopropane ring.

Table 1. Compositions of the reaction mixtures (%) obtained by the interaction of compounds **5** and **6** in benzene at −2°C (the conditions are given in Experimental).

Compound	5	7	*E*-8	*Z*-8	6
a	0	55	30	7	8
b	0	58	19	13	10
c	33	13	15	3	36
d	24	41	7	1	27
d**	24	49	0	0	27

* Determined by ^{1}H NMR at −2°C 20 min after mixing compounds **5** and **6**; mole ratio **5a—d**:**6** = 1.0:1.1.
** Measured at −5°C.

Of particular interest is the relation between the $^1J_{C,P}$ and $^2J_{C,P}$ coupling constants in the series of compounds **7**. In the case of 1-oxo-2,2,3,3-tetramethylbutyl-bis(trimethylsilyl)phosphane[11] (**7**, R = CBu^tMe_2) studied by ^{13}C NMR, the coupling constants $^1J_{C,P}$ and $^2J_{C,P}$ differ considerably and equal 64.4 and 25.7 Hz, respectively. The difference between these coupling constants is somewhat smaller for compounds **7c** ($^1J_{C,P}$ = 50.3 Hz, $^2J_{C,P}$ = 39.3 Hz) and **7d** ($^1J_{C,P}$ = 50.0 Hz, $^2J_{C,P}$ = 38.2 Hz). Compounds **7a** and **7b**, containing no substituents at position 1 of the cyclopropane rings, even display the opposite picture: the $^1J_{C,P}$ coupling constant (42.6 Hz for **7a**, 43.4 Hz for **7b**) is less than $^2J_{C,P}$ (52.3 and 51.3 Hz for **7a** and **7b**, respectively).

The structures of compounds **8a—d** were confirmed by NMR spectra of their solutions in benzene. The phosphaethylene moieties were unambiguously identified by resonance absorption in the ^{31}P NMR spectra at δ 81.1—131.1 and the signals of the olefinic carbon atoms in the ^{13}C NMR spectra (δ 212.2—222.0). The latter are observed as doublets with $^1J_{(P=C)}$ coupling constants in the range 57.5—66.4 Hz. These values are in good agreement with the data published for phosphaalkenes of this type.[6,7,10]

To determine the configuration of the substituents at the P=C bond in the series of compounds **8** we used the magnetic nonequivalence of the $OSiMe_3$ groups due to their different orientation relative to the unshared electron pair of the phosphorus atom. According to the data reported previously,[10] the $^4J_{(P=C-O-Si-C)}$ and $^5J_{(P=C-O-Si-C-H)}$ coupling constants are smaller for the *Z*-isomers, in which the $OSiMe_3$ group is in the *trans* position relative to the unshared electron pair of the phosphorus atom (^4J and ^5J are equal to 0), than for the *E*-isomers, in which the $OSiMe_3$ group is located on the same side as the unshared electron pair of phosphorus (6.0—6.1 and 1.0—1.2 Hz*, respectively).

The predominant formation of compounds **8a** and **8b** as *E*-isomers (*E*:*Z* = 4:1) and compound **8c** as the

* ^{13}C and ^{1}H NMR data were not obtained for ***E*-8c** due to its low concentration.

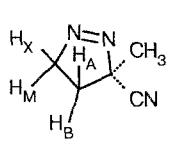
Z-isomer (according to ^{31}P NMR data, the content of the *E*-isomer is no more than 2—3 %) agrees with the previously observed[7] properties of phosphaalkenes of the $Me_3SiP{=}C(R)OSiMe_3$ type: in the case of primary and secondary substituents, the *E*-isomers are predominantly formed, while the *Z*-isomers are mainly formed with tertiary substituents. The fact that the content of the *E*-isomer in compound **8d** exceeds that of the *Z*-isomer (*E* : *Z* = 62 : 38) is an exception to the above law.

Experimental

^1H NMR spectra were recorded on Varian EM 390 (90 MHz) and Bruker AMX-400 (400 MHz) spectrometers using Me_4Si as the internal standard. ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (100.64 MHz), and ^{31}P NMR spectra were obtained on Bruker WP-200 (80.82 MHz) and Bruker AM-400 (161.6 MHz) spectrometers with 85 % H_3PO_4 as the external standard. IR spectra were obtained on a Perkin-Elmer 710B spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer EA240 analyzer.

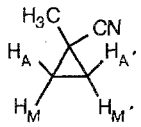
All experiments were carried out in a stream of argon (>99.998 % purity). The solvents were dehydrated. Freshly distilled reactants were used. Cyclopropanecarboxylic acid chlorides **5a—d** were obtained by treatment of the respective acids with $SOCl_2$ by the known procedure.[13] 1-Methylcyclopropanecarboxylic acid (**11**) was synthesized from methacrylonitrile and diazomethane *via* pyrazoline **9** (see below). The latter was transformed into 1-methyl-1-cyanocyclopropane **10**, hydrolysis of which gave acid **11** (overall yield > 65 % with respect to the original methacrylonitrile). Commercial grade 2-methylcyclopropanecarboxylic acid (Fluka, no. 66557) contained 92 % of the *trans*-isomer.

3-Cyano-3-methyl-4,5-dihydro-3*H*-pyrazole (9). A solution of diazomethane prepared from *N*-nitroso-*N*-methylurea (46.0 g, 0.45 mol), KOH (78 g), water (78 mL), and ether (70 mL) was added over 2—3 h at ~20 °C with stirring to methacrylonitrile (16.8 g, 0.25 mol) in ether (20 mL). The excess ether was removed in a rotor evaporator, and the residue was distilled *in vacuo* to give 23.5 g (86 %) of compound **9**, b.p. 35—36 °C (0.001 Torr). **(Caution!** The compound decomposes explosively above 95 °C). Found (%): C, 55.1; H, 6.5. $C_5H_7N_3$. Calculated (%): C, 55.03; H, 6.48. Mol. mass 109.13. IR, ν/cm^{-1}: 3000, 2975, 2950, 2260.



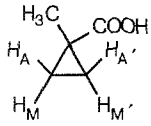
^1H NMR (C_6D_6), δ: 0.90 (ddd, 1 H, X-part of an ABMX-system, $^2J_{HH} = {}^2J_{XM} = -12.0$ Hz, $^3J_{HH} = {}^3J_{XB} = 5.0$ Hz, $^2J_{HH} = {}^2J_{XA} = 7.8$ Hz); 1.09 (s, 3 H, CH_3); 1.35 (ddd, 1 H, M-part of an ABMX-system, $^2J_{HH} = {}^2J_{MX} = -12.0$ Hz, $^3J_{HH} = {}^2J_{MB} = 10$ Hz, $^3J_{HH} = {}^3J_{MA} = 7.5$ Hz); 3.96 (qd, 1 H, A-part of an ABMX-system, $^3J_{HH} = {}^3J_{AX} = 7.8$ Hz, $^3J_{HH} = {}^3J_{AM} = 7.5$ Hz, $^2J_{HH} = {}^2J_{AB} = -17.5$ Hz); 4.06 (qd, 1 H, B-part of a ABMX-system, $^3J_{HH} = {}^3J_{BX} = 5.0$ Hz, $^3J_{HH} = {}^3J_{BM} = 10.0$ Hz, $^2J_{HH} = {}^2J_{BA} = -17.5$ Hz). ^{13}C NMR (C_6D_6), δ: 22.9 (q, CH_3,, $^1J_{CH} = 129$ Hz); 29.5 (t, CH_2, $^1J_{CH} = 129$ Hz); 78.1 (t, CH_2, $^1J_{CH} = 129$ Hz); 82.9 (s, >C<); 119.8 (s, CN).

1-Cyano-1-methylcyclopropane (10). A solution of compound **9** (19.5 g, 0.179 mol) in CCl_4 (100 mL) was refluxed for 45—50 h. The solvent was distilled off, and the residue was distilled to give 11.8 g (82 %) of compound **10**, b.p. 126—127 °C. Found (%): C, 74.1; H, 8.7. C_5H_7N. Calculated (%): C, 74.03; H, 8.70. Mol. mass 81.12. IR, ν/cm^{-1}: 2900—3010, 2245.



^1H NMR (C_6D_6), δ: 0.10 (m, 2 H, AA'-part of an AA'MM'-system, $^3J_{HH} = {}^3J_{AA'} = {}^3J_{A'A} = 9.0$ Hz, $^3J_{HH} = J_{AM'} = J_{A'M} = 7.1$ Hz, $^2J_{HH} = {}^2J_{AM} = {}^2J_{A'M'} = -4.1$ Hz); 0.65 (m, 2 H, MM'-part of an AA'MM'-system, $^3J_{HH} = {}^3J_{MM'} = {}^3J_{M'M} = 10.5$ Hz, $^3J_{HH} = {}^3J_{MA'} = {}^3J_{M'A} = 7.1$ Hz, $^2J_{HH} = {}^2J_{MA} = {}^2J_{M'A'} = -4.1$ Hz); 0.80 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 4.46 (>C<); 14.6 (2 CH_2); 20.7 (CH_3); 124.0 (CN).

1-Methylcyclopropanecarboxylic acid (11). Nitrile **10** (8.1 g, 0.1 mol) was refluxed with 25 % NaOH (35 mL) until ammonia evolution ceased (2—3 h). The mixture was cooled, neutralized with 20 % H_2SO_4, and diluted with a twofold volume of water. The mixture was distilled (bath temperature 150—155 °C) and the fraction with b.p. 95 °C (a mixture of water and acid **11**) was collected. The crystals that precipitated on cooling were filtered off and dried. The yield of **11** was 9.8 g (99 %), m.p. 36 °C. Found (%): C, 59.9; H, 8.00. $C_5H_8O_2$. Calculated (%): C, 60.05; H, 8.06. Mol. mass 100.12.

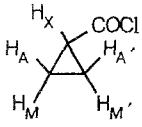


^1H NMR (CCl_4), δ: 0.68 (m, 2 H, AA'-part of an AA'MM'-system, $^3J_{HH} = {}^3J_{AA'} = {}^3J_{A'A} = 8.8$ Hz, $^3J_{HH} = J_{AM'} = J_{A'M} = 6.9$ Hz, $^2J_{HH} = {}^2J_{AM} = {}^2J_{A'M'} = -4.0$ Hz); 1.26 (m, 2 H, MM'-part of an AA'MM'-system, $^3J_{HH} = {}^3J_{MM'} = {}^3J_{M'M} = 9.8$ Hz, $^3J_{HH} = {}^3J_{MA'} = {}^3J_{M'A} = 6.9$ Hz, $^2J_{HH} = {}^2J_{MA} = {}^2J_{M'A'} = -4.0$ Hz); 1.30 (s, 3H, CH_3); 12.06 (s, 1 H, COOH).

Synthesis of acid chlorides 5a—d (general procedure)

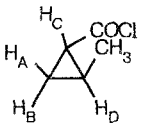
A cyclopropanecarboxylic acid (1.0 mol) and $SOCl_2$ (1.5 mol) were mixed. When the exothermic reaction and gas evolution ceased, the mixture was boiled for 2—3 h. The excess $SOCl_2$ was distilled off, and the acid chloride that formed was distilled.

Cyclopropanecarboxylic acid chloride (5a). Yield up to 95 %, b.p. 122—123 °C.



^1H NMR (C_6D_6), δ: 0.43 (m, 2 H, AA'-part of an AA'MM'X-system, $^3J_{HH} = {}^3J_{AA'} = {}^3J_{A'A} = 9.2$ Hz, $^3J_{HH} = {}^3J_{AM'} = {}^3J_{A'M} = 7.6$ Hz, $^2J_{HH} = {}^2J_{AM} = {}^2J_{A'M'} = -4.5$ Hz, $^3J_{HH} = {}^3J_{AX} = {}^3J_{A'X} = 7.9$ Hz); 0.90 (m, 2 H, MM'-part of an AA'MM'X-system, $^3J_{HH} = {}^3J_{MM'} = {}^3J_{M'M} = 10.0$ Hz, $^3J_{HH} = {}^3J_{MA'} = {}^3J_{M'A} = 7.6$ Hz, $^2J_{HH} = {}^2J_{MA} = {}^2J_{M'A'} = -4.5$ Hz, $^3J_{HH} = {}^3J_{MX} = {}^3J_{M'X} = 4.4$ Hz); 1.54 (tt, 1 H, X-part of an AA'MM'X-system, $^3J_{HH} = {}^3J_{XA} = {}^3J_{XA'} = 7.9$ Hz, $^3J_{HH} = {}^3J_{XM} = {}^3J_{XM'} = 4.4$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 12.1 (2 CH_2); 23.8 (CH); 174.5 (COCl).

***trans*-2-Methylcyclopropanecarboxylic acid chloride (5b).** Yield up to 90 %, b.p. 75 °C (120 Torr).

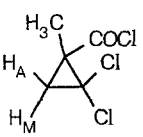


^1H NMR (C_6D_6), δ: 0.40 (ddd, A-part of an ABCD-system, $^3J_{HH} = {}^3J_{AD} = 8.2$ Hz, $^2J_{HH} = {}^2J_{AB} = -4.5$ Hz, $^3J_{HH} = {}^3J_{AC} = 8.2$ Hz); 0.63 (d, 3 H, CH_3, $^3J_{HH} = {}^3J_{DCH_3} = 6.0$ Hz); 1.16 (ddd, B-part of an ABCD-system, $^3J_{HH} = {}^3J_{BD} = 9.0$ Hz, $^2J_{HH} =$

$^2J_{BA}$ = −4.5 Hz, $^3J_{HH}$ = $^3J_{BC}$ = 4.5 Hz); 1.36 (dddd, 1 H, D-part of an ABCD-system, $^3J_{HH}$ = $^3J_{DCH_3}$ = 6.0 Hz, $^3J_{HH}$ = $^3J_{DA}$ = 8.2 Hz, $^3J_{HH}$ = $^3J_{DB}$ = 9.0 Hz, $^3J_{HH}$ = $^3J_{DC}$ = 4.1 Hz); 1.46 (ddd, 1 H, C-part of an ABCD-system, $^3J_{HH}$ = $^3J_{CA}$ = 8.2 Hz, $^3J_{HH}$ = $^3J_{CB}$ = 4.5 Hz, $^3J_{HH}$ = $^3J_{CD}$ = 4.1 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 17.0 (CH_3); 20.6 (CH_2); 21.9 ($\underline{C}HCH_3$); 31.9 ($\underline{C}HCOCl$); 173.6 (COCl).

1-Methylcyclopropanecarboxylic acid chloride (5c). Yield up to 95 %, b.p. 129—130 °C. The spin system is analogous to that of compound **11**. ^1H NMR (C_6D_6), δ: 0.29 (m, 2 H, AA′-part of an AA′MM′-system, $^3J_{HH}$ = $^3J_{AA'}$ = $^3J_{A'A}$ = 8.9 Hz, $^3J_{HH}$ = $J_{AM'}$ = $J_{A'M}$ = 7.3 Hz, $^2J_{HH}$ = $^2J_{AM}$ = $^2J_{A'M'}$ = −4.8 Hz); 0.98 (s, 3 H, CH_3); 1.21 (m, 2 H, MM′-part of an AA′MM′- system, $^3J_{HH}$ = $^3J_{MM'}$ = $^3J_{M'M}$ = 9.9 Hz, $^3J_{HH}$ = $^3J_{MA'}$ = $^3J_{M'A}$ = 7.3 Hz, $^2J_{HH}$ = $^2J_{MA}$ = $^2J_{M'A'}$ = -4.8 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 19.5 (2 CH_2); 20.1 (CH_3); 28.7 (>C<); 177.8 (COCl).

2,2-Dichloro-1-methylcyclopropanecarboxylic acid chloride (5d). Yield up to 95 %, b.p. 22 °C (10^{-4} Torr). IR, ν/cm^{-1}: 3090, 2980, 1775, 775, 625. Found (%): C, 32.20; H, 2.70. $C_5H_5Cl_3O_1$. Calculated (%): C, 32.03; H, 2.69. Mol. mass 187.45.



^1H NMR (C_6D_6), δ: 1.00 (d, 1 H, A-part of an AM-system, $^2J_{HH}$ = $^2J_{AM}$ = −8.1 Hz); 1.29 (s, 3 H, CH_3); 1.95 (d, 1 H, M-part of an AM-system, $^2J_{HH}$ = $^2J_{MA}$ = −8.1 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 19.2 (CH_3); 32.4 (CH_2); 44.1 (>C<); 62.5 (s, CCl_2); 171.2 (s, COCl).

Synthesis of acyl-bis(trimethylsilyl)phosphanes 7 (general procedure)

A solution of acyl halide **5** (0.09 mol) in C_6H_6 (45 mL) was added under argon at −2 °C with stirring to tris(trimethylsilyl)phosphane **6** (0.1 mol). The solution was kept for 20—30 min to give a mixture containing compound **7** as the major component. The composition of the mixture was determined by ^1H NMR (see Table 1).

1-Cyclopropylcarbonyl-bis(trimethylsilyl)phosphane (7a). The spin system of the protons of the cyclopropane ring is similar to the spin system of the protons in compound **5a**. ^1H NMR (C_6D_6, −2 °C), δ: 0.35 (d, 18 H, P—Si(CH_3)$_3$, $^3J_{PH}$ = 4.4 Hz); 0.48 (m, 2 H, AA′-part of an AA′MM′X-system, $^3J_{HH}$ = $^3J_{AA'}$ = $^3J_{A'A}$ = 9.1 Hz, $^3J_{HH}$ = $^3J_{AM'}$ = $^3J_{A'M}$ = 7.5 Hz, $^2J_{HH}$ = $^2J_{AM}$ = $^2J_{A'M'}$ = −4.4 Hz, $^3J_{HH}$ = $^3J_{AX}$ = $^3J_{A'X}$ = 7.8 Hz); 1.09 (m, 2 H, MM′-part of an AA′MM′X-system, $^3J_{HH}$ = $^3J_{MM'}$ = $^3J_{M'M}$ = 9.90 Hz, $^3J_{HH}$ = $^3J_{MA'}$ = $^3J_{M'A}$ = 7.5 Hz, $^2J_{HH}$ = $^2J_{MA}$ = $^2J_{M'A'}$ = −4.4 Hz, $^3J_{HH}$ = $^3J_{MX}$ = $^3J_{M'X}$ = 4.4 Hz); 2.11 (tt, 1 H, X-part of an AA′MM′X-system, $^3J_{HH}$ = $^3J_{XA}$ = $^3J_{XA'}$ = 7.8 Hz, $^3J_{HH}$ = $^3J_{XM}$ = $^3J_{XM'}$ = 4.4 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, −2 °C), δ: 1.89 (d, P—Si—CH_3, $^2J_{PC}$ = 10.3 Hz); 11.6 (s, 2 CH_2); 28.1 (d, CH, $^2J_{PC}$ = 53.2 Hz); 221.3 (d, C=O, J_{PC} = 42.6 Hz). ^{31}P NMR (C_6D_6, −2 °C), δ: −80.3.

***trans*-(2-Methyl-1-cyclopropylcarbonyl)-bis(trimethylsilyl)-phosphane (7b).** The spin system of the protons of the cyclopropane ring is similar to the spin system of the protons in compound **5b**. ^1H NMR (C_6D_6, −2 °C), δ: 0.33 (d, 18 H, P—Si(CH_3)$_3$, $^3J_{PH}$ = 4.5 Hz); 0.45 (ddd, 1 H, A-part of an ABCD-system, $^3J_{HH}$ = $^3J_{AD}$ = 6.2, Hz, $^2J_{HH}$ = $^2J_{AB}$ = −3.5 Hz, $^3J_{HH}$ = $^3J_{AC}$ = 7.9 Hz); 0.84 (d, 3 H, CH_3, $^3J_{HH}$ = $^3J_{DCH_3}$ = 6.0 Hz); 1.32 (ddd, 1 H, B-part of an ABCD-system, $^3J_{HH}$ = $^3J_{BD}$ = 8.5 Hz, $^2J_{HH}$ = $^2J_{BA}$ = −3.5 Hz, $^3J_{HH}$ = $^3J_{BC}$ = 4.3 Hz); 1.44 (dddd, D-part of an ABCD-system, $^3J_{HH}$ = $^3J_{DCH_3}$ = 6.0 Hz, $^3J_{HH}$ = $^3J_{DA}$ = 6.2 Hz, $^3J_{HH}$ = $^3J_{DB}$ = 8.5 Hz, $^3J_{HH}$ = $^3J_{DC}$ = 3.9 Hz); 1.97 (ddd, 1 H, C-part of an ABCD-system, $^3J_{HH}$ = $^3J_{CA}$ = 7.9 Hz, $^3J_{HH}$ = $^3J_{CB}$ = 4.3 Hz, $^3J_{HH}$ = $^3J_{CD}$ = 3.9 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, −2 °C), δ: 1.9 (d, P—Si—CH_3, $^2J_{PC}$ = 11.1 Hz); 18.0 (s, CH_3); 19.8 (s, CH_2); 20.5 (s, $\underline{C}HCH_3$); 37.1 (d, CH, $^2J_{PC}$ = 51.3 Hz); 220.1 (d, C=O, $^1J_{PC}$ = 43.3 Hz). ^{31}P NMR (C_6D_6, −2 °C), δ: −80.6.

(1-Methyl-1-cyclopropylcarbonyl)-bis(trimethylsilyl)-phosphane (7c). The spin system of the protons of the cyclopropane ring is similar to the spin systems of the protons in compounds **11** and **5c**. ^1H NMR (C_6D_6, −2 °C), δ: 0.28 (d, 18 H, P—Si(CH_3)$_3$, $^3J_{PH}$ = 4.4 Hz); 0.47 (m, 2 H, AA′-part of an AA′MM′-system, $^3J_{HH}$ = $^3J_{AA'}$ = $^3J_{A'A}$ = 9.2 Hz, $^3J_{HH}$ = $J_{AM'}$ = $J_{A'M}$ = 6.6 Hz, $^2J_{HH}$ = $^2J_{AM}$ = $^2J_{A'M'}$ = −5.0 Hz); 1.27 (s, 3 H, CH_3); 1.32 (m, 2 H, MM′-part of an AA′MM′-system, $^3J_{HH}$ = $^3J_{MM'}$ = $^3J_{M'M}$ = 10.3 Hz, $^3J_{HH}$ = $^3J_{MA'}$ = $^3J_{M'A}$ = 7.5 Hz, $^2J_{HH}$ = $^2J_{MA}$ = $^2J_{M'A'}$ = −5.0 Hz, $^4J_{MP}$ = $^4J_{M'P}$ = 1.8 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, −2 °C), δ: 2.0 (d, P—Si—CH_3, $^3J_{PC}$ = 11.1 Hz); 17.2 (d, 2 CH_2, $^3J_{PC}$ = 6.1 Hz); 20.7 (d, CH_3, $^3J_{PC}$ = 8.1 Hz); 33.4 (d, OC-$\underline{C}$-CH_3, $^2J_{PC}$ = 39.2 Hz); 223.5 (d, C=O, $^1J_{PC}$ = 50.3 Hz). ^{31}P NMR (C_6D_6, −2 °C), δ: −102.8.

(2,2-Dichloro-1-methyl-1-cyclopropylcarbonyl)-bis(trimethylsilyl)phosphane (7d). ^1H NMR (C_6D_6, −2 °C), δ: 0.29 (d, 18 H, P—Si(CH_3)$_3$, $^3J_{PH}$ = 4.5 Hz); 0.86 (d, 1 H, A-part of an AM-system, $^2J_{HH}$ = $^2J_{AM}$ = −7.1 Hz); 1.50 (s, 3 H, CH_3); 2.36 (d, 1 H, M-part of an AM-system, $^2J_{HH}$ = $^2J_{MA}$ = −7.1 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, −2 °C), δ: 2.1 (d, P—Si—CH_3, $^2J_{PC}$ = 10.1 Hz); 20.8 (d, CH_3, $^3J_{PC}$ = 9.1 Hz); 30.7 (s, CH_2); 44.7 (d, >C<, $^2J_{PC}$ = 38.2 Hz); 63.6 (s, CCl_2); 218.7 (d, C=O, $^1J_{PC}$ = 50.0 Hz). ^{31}P NMR (C_6D_6, −2 °C), δ: −82.6.

Synthesis of phosphaalkenes 8a—d (general procedure)

A solution of acyl halide **5** (0.09 mol) in C_6H_6 (50 mL) was added under argon at −2 °C with stirring to tris(trimethylsilyl)phosphane **6** (0.1 mol). The mixture was kept for 10—15 min and then heated to ~20 °C to give a light-yellow solution of a phosphaalkene (**8a,b**) or a colorless solution (**8c,d**). The yields were 75—95 %.

***E,Z*-(Cyclopropyltrimethylsiloxymethylene)trimethylsilylphosphane (8a).** Yield 16.4 g (74 %), *E* : *Z* = 81 : 19. The spin systems of the protons of the cyclopropane ring are similar to the spin system of the protons in compound **7a**.

***E*-8a**: ^1H NMR (C_6D_6, −2 °C), δ: 0.34 (d, 9 H, O—Si(CH_3)$_3$, $^5J_{PH}$ = 1.2 Hz); 0.41 (d, 9 H, P—Si(CH_3)$_3$, $^3J_{PH}$ = 4.0 Hz); 0.60 (m, 2 H, AA′-part of an AA′MM′X-system, $^3J_{HH}$ = $^3J_{AA'}$ = $^3J_{A'A}$ = 9.2 Hz, $^3J_{HH}$ = $^3J_{AM'}$ = $^3J_{A'M}$ = 7.6 Hz, $^2J_{HH}$ = $^2J_{AM}$ = $^2J_{A'M'}$ = −4.5 Hz, $^3J_{HH}$ = $^3J_{AX}$ =

$^3J_{A'X}$ = 7.6 Hz); 1.11 (m, 2 H, MM'-part of an AA'MM'X-system, $^3J_{HH}$ = $^3J_{MM'}$ = $^3J_{M'M}$ = 9.9 Hz, $^3J_{HH}$ = $^3J_{MA'}$ = $^3J_{M'A}$ = 7.6 Hz, $^2J_{HH}$ = $^2J_{MA}$ = $^2J_{M'A'}$ = −4.5 Hz, $^3J_{HH}$ = $^3J_{MX}$ = $^3J_{M'X}$ = 4.6 Hz); 2.34 (ttd, 1 H, X-part of an AA'MM'X-system, $^3J_{HH}$ = $^3J_{XA}$ = $^3J_{XA'}$ = 7.6 Hz, $^3J_{HH}$ = $^3J_{XM}$ = $^3J_{XM'}$ = 4.6 Hz, $^3J_{PHX}$ = 2.5 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, −2 °C), δ: 0.2 (d, O—Si—CH_3, $^4J_{PC}$ = 6.1 Hz); 1.8 (d, P—Si—CH_3, $^2J_{PC}$ = 10.5 Hz); 10.2 (s, 2 CH_2); 26.4 (d, CH, $^2J_{PC}$ = 14.5 Hz); 222.0 (d, P=C, $^1J_{PC}$ = 59.0 Hz). ^{31}P NMR (C_6D_6, −2 °C), δ: 100.2.

***Z*-8a**: ^1H NMR (C_6D_6, −2 °C), δ: 0.20 (s, 9 H, O—Si$(CH_3)_3$); 0.24 (d, 9 H, P—Si$(CH_3)_3$, $^3J_{PH}$ = 4.8 Hz); 0.63 (m, 2 H, AA'-part of an AA'MM'X-system, $^3J_{HH}$ = $^3J_{AA'}$ = $^3J_{A'A}$ = 8.6 Hz, $^3J_{HH}$ = $^3J_{AM'}$ = $^3J_{A'M}$ = 7.6 Hz, $^2J_{HH}$ = $^2J_{AM}$ = $^2J_{A'M'}$ = −4.0 Hz, $^3J_{HH}$ = $^3J_{AX}$ = $^3J_{A'X}$ = 7.7 Hz); 1.17 (m, 2 H, MM'-part of an AA'MM'X-system, $^3J_{HH}$ = $^3J_{MM'}$ = $^3J_{M'M}$ = 9.20 Hz, $^3J_{HH}$ = $^3J_{MA'}$ = $^3J_{M'A}$ = 7.6 Hz, $^2J_{HH}$ = $^2J_{MA}$ = $^2J_{M'A'}$ = −4.0 Hz, $^3J_{HH}$ = $^3J_{MX}$ = $^3J_{M'X}$ = 4.4 Hz); 2.64 (ttdd, 1 H, X-part of an AA'MM'X-system, $^3J_{HH}$ = $^3J_{XA}$ = $^3J_{XA'}$ = 7.7 Hz, $^3J_{HH}$ = $^3J_{XM}$ = $^3J_{XM'}$ = 4.4 Hz, $^3J_{PHX}$ = 1.1 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, −2 °C), δ: 1.0 (d, P—Si—CH_3, $^2J_{PC}$ = 8.3 Hz); 1.3 (s, O—Si—CH_3); 11.7 (s, 2 CH_2); 24.4 (d, CH, $^2J_{PC}$ = 30.7 Hz); 220.3 (d, P=C, $^1J_{PC}$ = 65.4 Hz). ^{31}P NMR (C_6D_6, −2 °C), δ: 84.1.

***E,Z*-(*trans*-2-Methylcyclopropyltrimethylsiloxymethylene)-trimethylsilylphosphane (8b).** Yield 18.5 g (79 %), *E* : *Z* = 82 : 18. The spin systems of the protons of the cyclopropane ring are similar to the spin system of the protons in compound **7b**.

***E*-8b**: ^1H NMR (C_6D_6, −2 °C), δ: 0.31 (d, 9 H, O—Si—$(CH_3)_3$, $^5J_{PH}$ = 1.0 Hz); 0.38 (d, 9 H, P—Si—CH_3, $^3J_{PH}$ = 4.0 Hz); 0.46 (ddd, 1 H, A-part of an ABCD-system, $^3J_{HH}$ = $^3J_{AD}$ = 6.1 Hz, $^2J_{HH}$ = $^2J_{AB}$ = −3.5 Hz, $^3J_{HH}$ = $^3J_{AC}$ = 8.0 Hz); 0.97 (d, 3 H, CH_3, $^3J_{HH}$ = $^3J_{DCH_3}$ = 6.0 Hz); 1.30 (ddd, 1 H, B-part of an ABCD-system, $^3J_{HH}$ = $^3J_{BD}$ = 9.2 Hz, $^2J_{HH}$ = $^2J_{BA}$ = −3.5 Hz, $^3J_{HH}$ = $^3J_{BC}$ = 4.5 Hz); 1.40 (dddd, 1 H, D-part of an ABCD-system, $^3J_{HH}$ = $^3J_{DCH_3}$ = 6.0 Hz, $^3J_{HH}$ = $^3J_{DA}$ = 6.1 Hz, $^3J_{HH}$ = $^3J_{DB}$ = 9.2 Hz, $^3J_{HH}$ = $^3J_{DC}$ = 4.1 Hz); 2.09 (ddd, 1 H, C-part of an ABCD-system, $^3J_{HH}$ = $^3J_{CA}$ = 8.0 Hz, $^3J_{HH}$ = $^3J_{CB}$ = 4.5 Hz, $^3J_{HH}$ = $^3J_{CD}$ = 4.1 Hz, $^3J_{PH}$ = $^3J_{PC}$ = 2.7 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, −2 °C), δ: 0.26 (d, O—Si—CH_3, $^4J_{PC}$ = 6.0 Hz); 1.96 (d, P—Si—CH_3, $^2J_{PC}$ = 10.7 Hz); 18.2 (s, CH_3); 18.4 (s, CH_2); 18.5 (s, $\underline{C}HCH_3$); 35.6 (d, $\underline{C}HC$=P, $^2J_{PC}$ = 13.1 Hz); 221.7 (d, P=C, $^1J_{PC}$ = 57.8 Hz). ^{31}P NMR (C_6D_6, −2 °C), δ: 97.2.

***Z*-8b**: ^1H NMR (C_6D_6, −2 °C), δ: 0.22 (s, 9 H, O—Si—$(CH_3)_3$); 0.38 (d, 9 H, P—Si—CH_3, $^3J_{PH}$ = 5.0 Hz); 0.46 (ddd, 1 H, A-part of an ABCD-system, $^3J_{HH}$ = $^3J_{AD}$ = 6.1 Hz, $^2J_{HH}$ = $^2J_{AB}$ = −3.1 Hz, $^3J_{HH}$ = $^3J_{AC}$ = 8.1 Hz); 0.95 (d, 3 H, CH_3, $^3J_{HH}$ = $^3J_{DCH_3}$ = 6.0 Hz); 1.40 (ddd, 1 H, B-part of an ABCD-system, $^3J_{HH}$ = $^3J_{BD}$ = 8.6 Hz, $^2J_{HH}$ = $^2J_{BA}$ = −3.1 Hz, $^3J_{HH}$ = $^3J_{BC}$ = 4.3 Hz); 1.52 (dddd, 1 H, D-part of an ABCD-system, $^3J_{HH}$ = $^3J_{DCH_3}$ = 6.0 Hz, $^3J_{HH}$ = $^3J_{DA}$ = 6.1 Hz, $^3J_{HH}$ = $^3J_{DB}$ = 8.6 Hz, $^3J_{HH}$ = $^3J_{DC}$ = 4.0 Hz); 2.15 (ddd, 1 H, C-part of an ABCD-system, $^3J_{HH}$ = $^3J_{CA}$ = 8.1 Hz, $^3J_{HH}$ = $^3J_{CB}$ = 4.5 Hz, $^3J_{HH}$ = $^3J_{CD}$ = 4.1 Hz, $^3J_{PH}$ = $^3J_{PC}$ = 3.9 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, −2 °C), δ: 1.1 (d, P—Si—CH_3, $^2J_{PC}$ = 8.6 Hz); 1.30 (s, O—Si—CH_3); 18.0 (s, CH_3); 18.2 (s, CH_2); 18.3 (s, $\underline{C}HCH_3$); 33.1 (d, $\underline{C}HC$=P, $^2J_{PC}$ = 27.2 Hz); 220.2 (d, P=C, $^1J_{PC}$ = 64.0 Hz). ^{31}P NMR (C_6D_6, −2 °C), δ: 81.1.

***E,Z*-(1-Methylcyclopropyltrimethylsiloxymethylene)trimethylsilylphosphane (8c).** Yield 19.7 g (84 %), *E* : *Z* = 98 : 2. The spin system of the protons of the cyclopropane ring in compound ***Z*-8c** is similar to the spin system of the protons in compound **7c**.

***E*-8c**: ^{31}P NMR (C_6D_6, −2 °C), δ: 114.0.

***Z*-8c**: ^1H NMR (C_6D_6, −2 °C), δ: 0.25 (s, 9 H, O—Si—$(CH_3)_3$); 0.27 (d, 9 H, P—Si—CH_3, $^3J_{PH}$ = 4.3 Hz); 0.48 (m, 2 H, AA'-part of an AA'MM'-system, $^3J_{HH}$ = $^3J_{AA'}$ = $^3J_{A'A}$ = 8.8 Hz, $^3J_{HH}$ = $J_{AM'}$ = $J_{A'M}$ = 5.9 Hz, $^2J_{HH}$ = $^2J_{AM}$ = $^2J_{A'M'}$ = −4.3 Hz, $^4J_{PH}$ = $^4J_{PA}$ = 1.8 Hz); 1.05 (m, 2 H, MM'-part of an AA'MM'-system, $^3J_{HH}$ = $^3J_{MM'}$ = $^3J_{M'M}$ = 10.0 Hz, $^3J_{HH}$ = $^3J_{MA'}$ = $^3J_{M'A}$ = 5.9 Hz, $^2J_{HH}$ = $^2J_{MA}$ = $^2J_{M'A'}$ = −4.3 Hz, $^4J_{PH}$ = $^4J_{PM}$ = $^4J_{PM'}$ = 2.2 Hz); 1.20 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, −2 °C), δ: 0.95 (d, P—Si—CH_3, $^2J_{PC}$ = 8.1 Hz); 1.56 (s, O—Si—CH_3); 16.7 (d, 2 CH_2, $^3J_{PC}$ = 16.1 Hz); 24.5 (d, CH_3, $^3J_{PC}$ = 4.1 Hz); 28.6 (d, OC-$\underline{C}$-CH_3, $^2J_{PC}$ = 31.2 Hz); 220.9 (d, P=C, $^1J_{PC}$ = 66.4 Hz). ^{31}P NMR (C_6D_6, −2 °C), δ: 116.1.

***E,Z*-[(2,2-Dichloro-1-methylcyclopropyl)trimethylsiloxymethylene]trimethylsilylphosphane (8d).** Yield 27.8 g (94 %), *E* : *Z* = 62 : 38. The spin system of the protons of the cyclopropane ring is similar to the spin system of the protons in compound **7d**.

***E*-8d**: ^1H NMR (C_6D_6, −2 °C), δ: 0.26 (d, 9 H, P—Si—CH_3, $^3J_{PH}$ = 4.7 Hz); 0.37 (d, 9 H, O—Si—$(CH_3)_3$, $^5J_{PH}$ = 1.0 Hz); 1.23 (d, 1 H, A-part of an AM-system, $^2J_{HH}$ = $^2J_{AM}$ = $^2J_{MA}$ = −7.1 Hz); 1.51 (s, 3 H, CH_3); 1.92 (d, 1 H, M-part of an AM-system, $^2J_{HH}$ = $^2J_{MA}$ = $^2J_{AM}$ = −7.1 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, −2 °C), δ: 0.24 (d, O—Si—CH_3, $^4J_{PC}$ = 6.1 Hz); 2.39 (d, P—Si—CH_3, $^2J_{PC}$ = 12.2 Hz); 23.2 (d, CH_3, $^3J_{PC}$ = 4.6 Hz); 35.4 (s, CH_2); 44.3 (d, OC$\underline{C}$$CH_3$, $^2J_{PC}$ = 13.7 Hz); 63.7 (d, CCl_2, $^3J_{PC}$ = 3.0 Hz); 216.2 (d, P=C, $^1J_{PC}$ = 59.4 Hz). ^{31}P NMR (C_6D_6, −2 °C), δ: 123.2.

***Z*-8d**: ^1H NMR (C_6D_6, −2 °C), δ: 0.29 (d, 9 H, P—Si—CH_3, $^3J_{PH}$ = 4.7 Hz); 0.34 (s, 9 H, O—Si$(CH_3)_3$); 1.26 (d, 1 H, A-part of an AM-system, $^2J_{HH}$ = $^2J_{AM}$ = $^2J_{MA}$ = −7.4 Hz); 1.45 (s, 3 H, CH_3); 2.25 (d, 1 H, M-part of an AM-system, $^2J_{HH}$ = $^2J_{MA}$ = $^2J_{AM}$ = −7.4 Hz, $^4J_{PH}$ = $^4J_{PM}$ = 4.2 Hz, $^4J_{PH}$ = $^4J_{PA}$ = 1.5 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, −2 °C), δ: 0.76 (d, P—Si—CH_3, $^2J_{PC}$ = 9.2 Hz); 1.74 (s, O—Si—CH_3); 22.4 (d, CH_3, $^3J_{PC}$ = 4.6 Hz); 36.0 (d, CH_2, $^3J_{PC}$ = 27.2 Hz); 42.0 (d, OC$\underline{C}$$CH_3$, $^2J_{PC}$ = 33.2 Hz); 65.7 (d, CCl_2, $^3J_{PC}$ = 18.1 Hz); 212.2 (d, P=C, $^1J_{PC}$ = 63.4 Hz). ^{31}P NMR (C_6D_6, −2 °C), δ: 131.1.

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