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Hydrostannylation of Phosphaalkenes [1]

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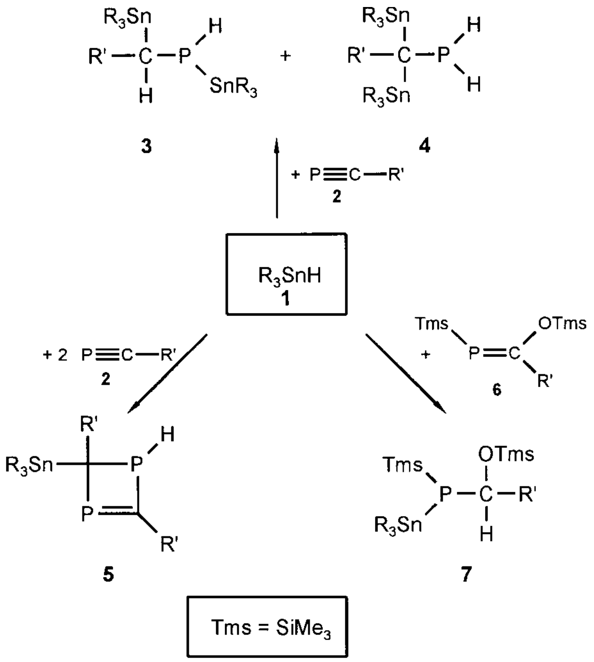
ABSTRACT: *Hydrostannylation reactions of the phosphaalkenes* **9**,**11**, *and* **21** *with the triorganotin hydrides* **1** *proceed by different routes. Whereas the triorganotin hydrides* **1a**,**b** *undergo regioselective 1,2-addition to the P/C double bond of the P-aminophosphaalkene* **9** *to furnish the 2-stannylphosphanes* **17a**,**b**, *the 1,2-addition products to the P-halophosphaalkenes* **11** *and* **21** *can only be postulated as the reactive intermediates* **20** *and* **23**, *respectively. The reactions of* **11** *with* **1a**,**b** *proceed with cleavage of the triorganotin halide via the diphosphene* **15** *to furnish the cyclophosphanes* **18** *and* **19**. *On the other hand, the hydrostannylation reactions of the phosphaalkene* **21** *are not selective, and the 1,3-diphosphetane* **22** *is isolated as one of the reaction products.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:453–460, 1998

INTRODUCTION

We have previously reported on the hydrostannylation reactions of selected, unsaturated, low-coordinated phosphorus compounds [2,3]. The product palette obtained from the hydrostannylation reactions of the phosphaalkynes **2** with the triorganotin hydrides **1** depends on the stoichiometry of the starting materials. An excess of the phosphaalkyne **2** favors formation of the 1,2-dihydro-1,3-diphosphete **5**, while further addition of the tin hydride **1** leads to complete saturation of the P/C triple bond and formation of the bis-stannyl-substituted phosphanes **3** and **4** [2].

Triorganotin hydrides undergo regioselective 1,2-addition with phosphaalkenes of the Becker-type **6** to yield the 1-stannylphosphanes **7** [3] (Scheme 1).

Other phosphaalkenes have as yet not been tested in hydrostannylation reactions. Previous investigations on the hydrozirconylation of the phosphaalkenes **9** and **11** with Schwartz's reagent **8** furnished different types of addition products [4,5].



SCHEME 1

Dedicated to Prof. Heinrich Nöth on the occasion of his seventieth birthday.

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Cp_2ZrHCl (**8**) undergoes addition to the P/C double bond of the *P*-aminophosphaalkene **9** to afford the metallaphosphacyclopropane **10** with transfer of the hydrogen atom from zirconium to phosphorus.

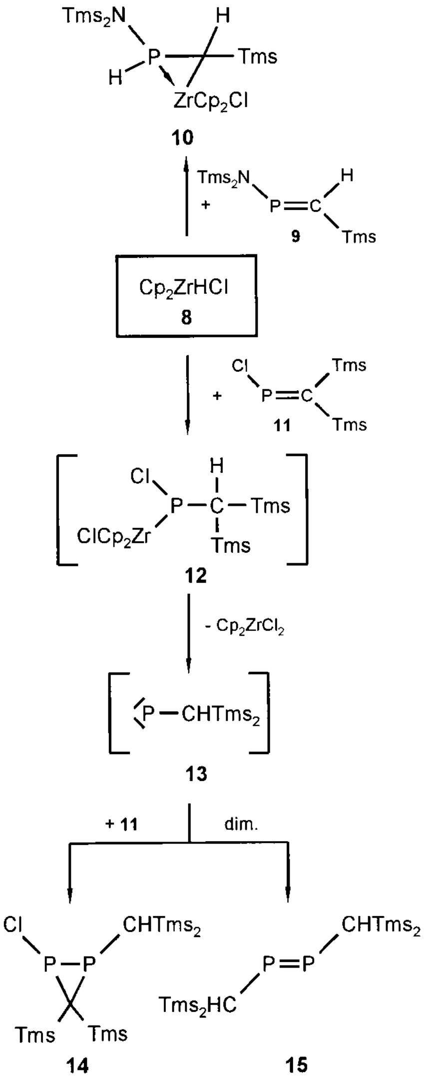
In the case of the *P*-chlorophosphaalkene **11**, the hydrogen atom is transferred from zirconium to the carbon atom of the P/C double bond. The primary addition product **12** then reacts through cleavage of Cp_2ZrCl_2 to afford the phosphinidene **13** that, in turn, undergoes stabilization by dimerization to the diphosphene **15.** The diphosphirane **14** is also formed in small amounts as the product of a trapping reaction of the phosphinidene **13** with the phosphaalkene **11** (Scheme 2).

RESULTS AND DISCUSSION

Hydrostannylation of Phosphaalkene 9 *with Triorganotin Hydride* 1

Treatment of the *P*-aminomethylenephosphane **9** with the triorganotin hydrides **1a,b** in pentane for 1 day at 20°C leads to the *P*-aminophosphanes **17a,b** in yields of 24–66%. Formation of the analogs of **7**—the *P*-amino-*P*-stannylphosphanes **16a,b**—was not observed (Scheme 3).

Microanalytical and mass spectroscopic data unequivocally demonstrate that the products **17** are 1:1 adducts of the starting materials. The NMR data of the *P*-aminophosphanes **17** provide concrete evidence for the regioselectivity of the reactions. In addition to an asymmetric carbon atom, compounds **17** also possess a chiral phosphorus atom. Thus, we may assume that two diastereomeric pairs of enantiomers, namely, **17A,B** and **17C,D**, are formed.



SCHEME 2

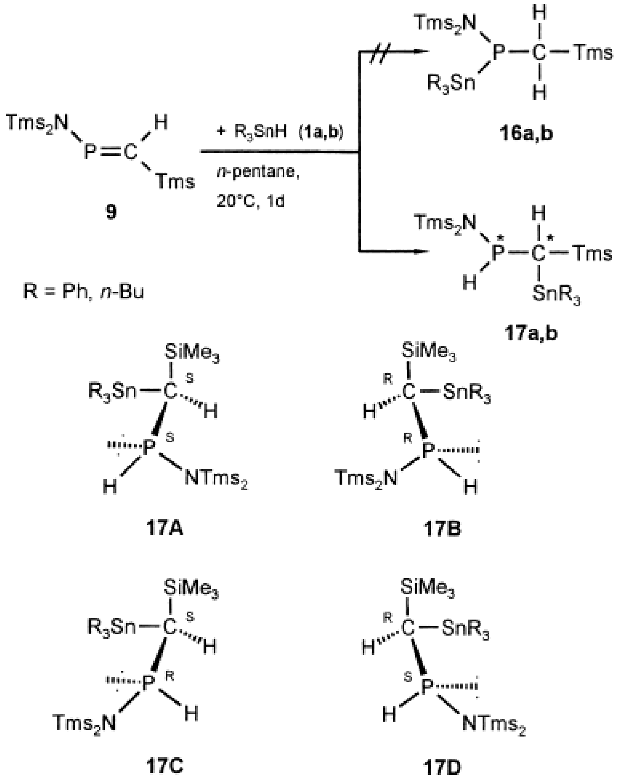
The NMR spectra confirm this assumption: the ^{31}P-NMR spectra of **17** each contain two signals with small $^2J_{P,Sn}$ coupling constants in the region expected for amino-substituted phosphanes [6,7]. In the proton, coupled ^{31}P-NMR spectra further splittings by large $^1J_{P,H}$ couplings provide firm evidence for the presence of a P–H bond. The double sets of signals are also seen in the ^{1}H-NMR spectra of **17.** On the basis of integration of the two trimethylsilyl proton signals, we obtained diastereomer ratios of 90:10 for **17a** and 70:30 for **17b.** The protons of the silyl groups give signals in the expected high field region, and small splitting or broadening by $^4J_{H,P}$ long-range couplings can be detected. In each case, the signal of the proton originating from the carbon atom of the double bond appears in the normal region for alkyl protons and is split into a doublet by a $^3J_{H,H}$ coupling of ca. 6 Hz. The signal for the proton transferred from tin to phosphorus is also characteristic and appears in each case in the region δ = 5.7–6.1 as a double doublet. The large splitting of over 200 Hz can be attributed to heteronuclear coupling with the adjacent phosphorus atom, while the small splitting of ca. 6 Hz corresponds to the already-mentioned $^3J_{H,H}$ coupling. The ^{13}C-NMR spectra are also in accord with the structure **17,** and each contains seven signals for each of the two diastereomers. Furthermore, assignment of the signals to the major and minor diastereomers is possible on the basis of the intensities. Each of the two diastereomers exhibits two signals for the trimethylsilyl groups (δ = 1.4–4.0), split into doublets by significant $^3J_{C,P}$ couplings. Aside from the signals of the triorganotin groups that provide signals in the regions expected for aromatic (**17a**) or alkyl carbon atoms (**17b**), there remain for each diastereomer the signals for the carbon atom adjacent to phosphorus with δ values of about 15, which can be clearly identified on the basis of the $^1J_{C,P}$ couplings of ca. 61 Hz. Although these spectroscopic data do allow an assignment of the signal sets to the major and minor diastereomers, they ultimately do not permit us to decide which signal set belongs to a specific diastereomeric enantiomer pair (**17A,B** or **17C,D**). Further confirmation for the regioselectivity of the hydrostannylation reaction is given by the observation of P–H valence vibrations in the IR spectra of the 2-stannylphosphanes **17**.

Hydrostannylation of Phosphaalkene 11 *with Triorganotin Hydride* 1

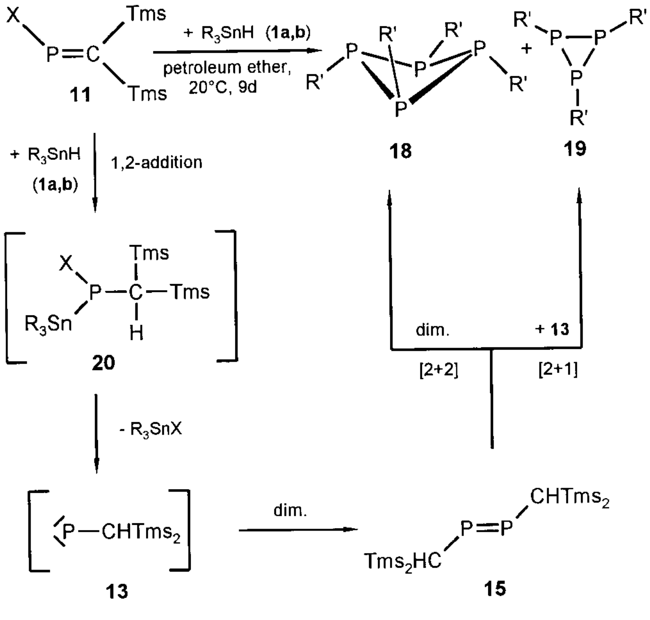
When an equimolar amount of the triorganotin hydride **1a,b** is added to a solution of the phosphaalkene **11a,b** in petroleum ether at 20°C, an immediate change in color of the reaction solution from yellow through orange to red is seen and, concomitantly, a white solid precipitates. When the course of the reaction is followed by ^{31}P-NMR spectroscopy, at first, and in addition to the signals of unreacted phosphaalkene **11** (δ = 341 for **11a** or 363 for **11b**), we see signals for the diphosphene **15** (δ = 515) [8] and the cyclic phosphanes **18** (δ = −14.6) and **19** (δ = −126.9 and −154.5; $^1J_{PP}$ = 194 Hz) [9]. After the mixture has been stirred at 20°C for 9 days, only signals for the cyclophosphanes **18** and **19** remain with **19** merely being present in small amounts as a side product. After collection of the solid by filtration, the cyclotetraphosphane **18** is isolated in the form of colorless crystals by crystallization from pentane at −30°C. Product **18** is poorly soluble in pentane, benzene, diethyl ether, dimethyl sulfoxide, and dichloromethane at room temperature (Scheme 4).

The two cyclophosphanes **18** and **19** had previously been prepared by Cowley from Tms_2CHPCl_2 and magnesium [9], but their data were only incompletely reported. We have now completely characterized the cyclotetraphosphane **18** by spectroscopy and confirmed its structure by X-ray crystallography (Figure 1).

The composition of **18** was unambiguously demonstrated by the presence of a molecular ion in the mass spectrum (m/z = 760, 36%) as well as by microanalysis, and its constitution was further supported by a high-resolution mass spectrum. The ^{31}P-NMR signals for the four equivalent phosphorus atoms appeared in the expected region (δ = −14.6) for cyclophosphanes [9–12]. The ^{13}C-NMR spectrum of **18** contained a pseudo-triplet signal at δ = 14.6 for the tertiary carbon atoms and a singlet signal in the high field region characteristic for carbon atoms of trimethylsilyl groups (δ = 3.5). The ^{1}H-NMR spectrum also contained only two signals at high field, and their integration ratio of 1:18 convincingly demonstrates the 1:1 composition from tin hydride and



SCHEME 3



X = Cl, Br; R = Ph, *n*-Bu, R' = $CH(SiMe_3)_2$

SCHEME 4

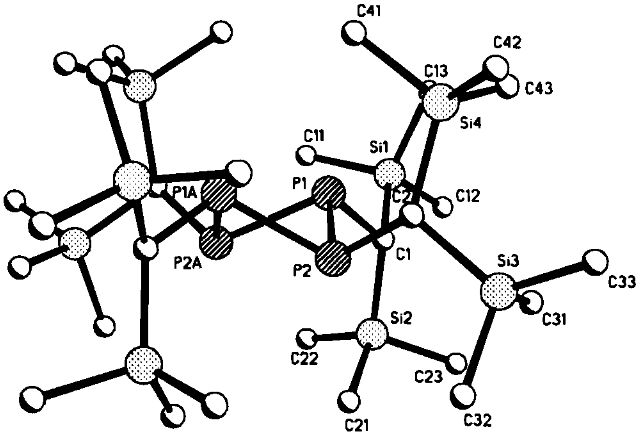


FIGURE 1 Molecular structure of **18** in the solid state.

TABLE 1 Selected Structural Parameters for **18.**

Bond Length		*Bond Angle*	
P1–P2	224.63 (10)	P1–P2–P1A	78.68 (4)
P2–P1A	224.48 (10)	P2A–P1–P2	78.58 (4)
P2–C2	187.1 (3)	C1–P1–P2	110.68 (10)
P1–C1	187.3 (3)	C2–P2–P1	110.01 (9)

Bond lengths in (pm), bond angles in (°), esd in parentheses.

TABLE 2 Atomic Coordinates and Equivalent Isotropic Displacement Parameters $10^3 \cdot pm^2$ for **18**

Atom	*x*	*y*	*z*	*U* (*eq*)
P1	479 (1)	2818 (1)	3191 (1)	34 (1)
P2	400 (1)	3887 (1)	2264 (1)	34 (1)
Si4	1040 (1)	938 (1)	2129 (1)	47 (1)
Si2	1018 (1)	5756 (1)	4166 (1)	52 (1)
Si3	1510 (1)	4185 (1)	2241 (1)	52 (1)
Si1	1179 (1)	2512 (1)	4728 (1)	51 (1)
C1	1033 (1)	3763 (3)	3995 (1)	39 (1)
C2	867 (1)	2932 (3)	1996 (1)	38 (1)
C11	506 (2)	2244 (5)	4774 (2)	76 (1)
C12	1773 (2)	3215 (5)	5571 (2)	74 (1)
C13	1432 (2)	731 (4)	4619 (2)	89 (1)
C21	744 (2)	6906 (4)	3397 (2)	71 (1)
C22	561 (2)	6128 (5)	4552 (2)	90 (1)
C23	1792 (2)	6357 (4)	4781 (2)	89 (1)
C31	1943 (2)	4542 (4)	3181 (2)	76 (1)
C32	1224 (2)	5939 (4)	1794 (2)	81 (1)
C33	2026 (2)	3474 (5)	1983 (3)	93 (1)
C41	415 (2)	−210 (4)	1975 (2)	67 (1)
C42	1240 (2)	332 (4)	1489 (2)	81 (1)
C43	1658 (2)	582 (4)	3016 (2)	76 (1)

phosphaalkene. As already mentioned, compound **18** was isolated in crystalline form from *n*-pentane at −30°C, thus making X-ray crystallographic analysis possible (Figure 1, Tables 1 and 2).

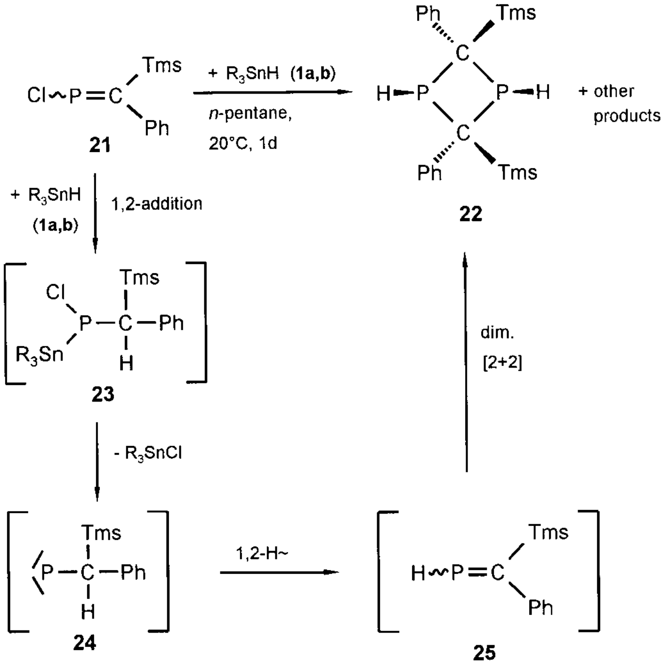
The crystals of cyclotetraphosphane **18** are monoclinic, space group C2/*c*. The most important feature of the crystal structure analysis is the nonplanar ring system. As in other cyclotetraphosphanes [13,14], the substituents at the phosphorus atom are arranged in an *"all-trans"* configuration. This means that the exocyclic groups are orientated so that each phosphorus atom and its bis(trimethylsilyl)methyl group lie on opposite sides of the central best plane. In comparison with other, less sterically overloaded cyclotetraphosphanes, the torsion angel PPPP in **18** is markedly increased to 47.9°. The folding angle along the P2-P2A axis amounts to 70°. The endocyclic ring angles P1-P2-P1A are relatively small, while the exocyclic C-P-P angles are widened. This is due to the steric effects of the voluminous bis(trimethylsilyl)methyl groups. The P–P bond lengths are in the normal range for P/P single bonds in cyclic polyphosphanes [13–15].

From a mechanistic point of view, the 1,2-addition product (**20**) of the triorganotin hydride **1** to the phosphaalkene **11** must be considered as the starting point of the reaction. In analogy to similar reaction sequences, such as the hydrozirconylation of **11** (Scheme 2), the next step is the α-elimination of triorganotin halide to afford **13** and dimerization of this species to the detected diphosphene **15.** Compounds of the latter type are known to be unstable and lead to cyclophosphanes analogous to **18** and **19** as the final products of an oligomerization [9]. Such a process may also be postulated here; thus, the cyclophosphanes **18** and **19** are the results of formal [2+2]- or [2+1]-cycloadditon reactions, respectively.

Hydrostannylation of Phosphaalkene 21 *with Triorganotin Hydride* 1

In contrast to that of the bis(trimethylsilyl)-substituted phosphaalkene **11,** reactions of the unsymmetrically substituted derivative **21** with triorganotin hydrides **1a,b** require reaction times of only 1 day. This higher reactivity is accompanied by a very mixed product pattern. After several work-up steps, including repeated crystallizations and removal of side products by distillation, we finally isolated the 1,3-diphosphacyclobutane **22** as one product of the hydrostannylation in the pure state and in a yield of 7% (Scheme 5).

The ^{31}P-NMR spectrum of **22** exhibits two singlet signals at δ = 69.0 and 41.3, the shifts of which are



R = Ph, *n*-Bu

SCHEME 5

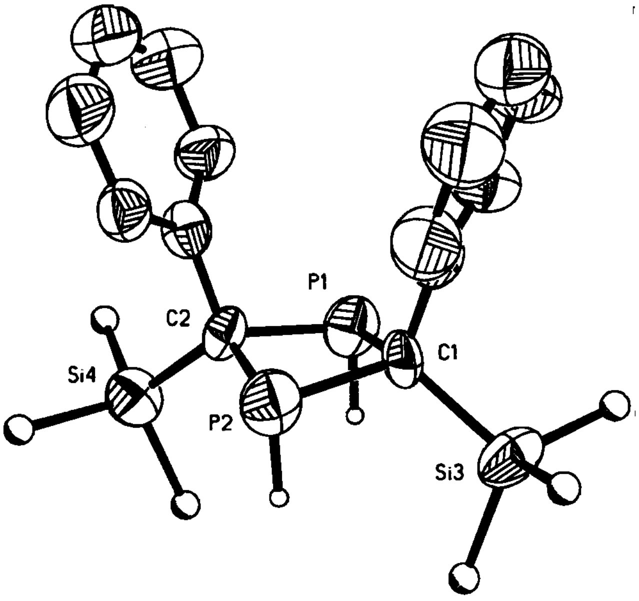


FIGURE 2 Molecular structure of **22** in the solid state.

TABLE 3 Selected Structural Parameters for **22.**

Bond Length		*Bond Angle*	
P1–C1	188.4 (6)	C1–P1–C2	87.0 (3)
P1–P2	269.1 (3)	P1–C1–P2	91.0 (3)
C1–C2	259.7	Folding angle of PCP planes	164.9

Bond lengths in (pm) bond angles in (°), esd in parentheses.

characteristic for 1,3-diphosphetanes [16,17]. The occurrence of two signals can be attributed to different stereoisomers of the 1,3-diphosphetane system, but an assignment of the signals to specific diastereomers is not possible. The direct adjacency of phosphorus and hydrogen atoms is confirmed in the coupled ^{31}P-NMR spectrum by the observation of $J_{P,H}$ couplings of 182 and 188 Hz. The same couplings are found in the low field signals of the ^{1}H-NMR spectrum. In addition, not-resolved multiplets for the phenyl protons are observed at $\delta = 7.1$–8.4 together with signals for the trimethylsilyl protons at high field ($\delta = 0.4$). The constitution of 22 is confirmed by the EI mass spectrum, which, in addition to an intense molecular ion peak at $m/z = 388$ (38%), also contains peaks for phenyl and silyl fragment ions as well as for [(Tms)(Ph)HC-PH^{+}] (29%).

A single crystal of one of the stereoisomers of 22 suitable for X-ray crystallography was obtained by crystallization from *n*-pentane at −30°C (Figure 2, Tables 3 and 4).

Crystals of the 1,3-diphosphetane 22 are monoclinic, space group $P2_1/n$. The four-membered ring exhibits a folding angle of 164.9° along the P-P; this is in marked contrast to the planar 2,4-diphenyl-2,4-bis(trimethylsiloxy)-1,3-diphosphetane [18]. The *cis* arrangement of the substituents and, especially, the large spatial requirements of the silyl groups are assumed to cause this folding. The P–C bond lengths in the ring are relatively large but still in the same order of magnitude of those in comparable compounds. The P-P and C-C separations of 269.1 and 259.7 pm, as compared to the van der Waals separations (370 and 340 pm), are similarly shortened to those in 2,4-diphenyl-2,4-bis(trimethylsiloxy)-1,3-diphosphetane. The angles in the rings of both 1,3-diphosphetanes are near to 90°, with the smaller angle always being found at phosphorus.

The hydrostannylation sequence of the *P*-chlorophosphaalkene 22 presumably also begins with the 1,2-addition of the tin hydride to the double bond of the phosphaalkene (to give 23). Immediate α-elimination of triorganotin chloride, which can be detected by mass spectroscopy, leads to the phosphinidine 24. A 1,2-shift of the proton from carbon to phosphorus favors formation of the kinetically unstabilized phosphaalkene 25. The tendency of head-to-tail dimerization of this type of phosphaalkene to give 1,3-diphosphetanes is well known [19]. The same process can be assumed for the present reaction.

TABLE 4 Atomic Coordinates and Equivalent Isotropic Displacement Parameters $10^3 \cdot pm^2$ for **22**

Atom	*x*	*y*	*z*	*U* (*eq*)
P1	5333 (4)	8159 (1)	1013 (1)	64 (1)
P2	1295 (4)	7775 (1)	824 (1)	69 (1)
Si3	4026 (5)	6921 (1)	−104 (1)	71 (1)
Si4	2337 (5)	9729 (1)	1274 (1)	64 (1)
C1	3739 (11)	7216 (4)	688 (2)	45 (3)
C2	2972 (11)	8530 (3)	1328 (2)	47 (3)
C11	4184 (18)	6421 (4)	1081 (3)	54 (3)
C12	2616 (16)	5849 (5)	1165 (3)	82 (4)
C13	2959 (20)	5104 (6)	1503 (4)	107 (4)
C14	4933 (25)	4940 (7)	1759 (4)	109 (6)
C15	6551 (19)	5491 (6)	1686 (3)	98 (4)
C16	6141 (15)	6221 (5)	1347 (3)	77 (3)
C21	3073 (17)	8234 (4)	1962 (3)	50 (4)
C22	1322 (18)	7949 (4)	2170 (3)	62 (5)
C23	1308 (17)	7696 (5)	2762 (4)	97 (4)
C24	3155 (25)	7740 (7)	3135 (4)	111 (7)
C25	4924 (22)	8031 (7)	2943 (4)	109 (6)
C26	4882 (13)	8280 (4)	2356 (3)	76 (3)
C51	4095 (11)	10327 (4)	1831 (3)	99 (3)
C52	2690 (13)	10171 (4)	534 (3)	108 (3)
C53	−389 (14)	9895 (4)	1403 (3)	82 (3)
C61	2360 (11)	5982 (4)	−340 (2)	90 (3)
C62	6880 (15)	6652 (6)	−154 (3)	101 (4)
C63	3182 (13)	7842 (4)	−616 (2)	116 (4)

EXPERIMENTAL

General

All experiments were carried out under argon (purity: >99.998%) in previously evacuated and baked out Schlenk vessels. The solvents were anhydrous and stored under argon until used. Melting points: Mettler FP 61 (heating rate 3°C/min), uncorrected. Elemental analyses: Perkin-Elmer EA 240. ^{1}H NMR: Varian EM 360 (60 MHz), and Bruker AC 200 and AMX 400; chemical shift relative to the solvent signals, calculated to TMS. ^{13}C NMR: Bruker AC 200 and AMX 400; chemical shift relative to the solvent signals, calculated to TMS. ^{31}P NMR: Bruker AC 200, external standard H_3PO_4. MS: Finnigan MAT 90 (70 eV). IR: Perkin-Elmer FT-IR Spectrometer Spectrum 1000. Chemicals: Triphenyltin hydride (**1a**) was prepared from triphenyltin chloride [20], and phosphaalkenes **9** [21], **11** [22], and **21** [23] were prepared as described in the literature. All other starting materials were purchased from commercial suppliers.

General Procedure for the Preparation of the Aminophosphanes 17a,b

Tin hydride **1** was added to a solution of phosphaalkene **9** in *n*-pentane (5 mL). The yellow color of phosphaalkene disappeared after stirring for 1 day at 20°C. The solvent was removed at 20°C/10^{-2} mbar. Product **17a** was obtained as a white solid after crystallization from *n*-pentane at −30°C, and aminophosphane **17b** was obtained as a colorless liquid after bulb-to-bulb distillation at 135°C/3 × 10^{-3} mbar.

*[(Trimethylsilyl)(triphenylstannyl)methyl)]bis(trimethylsilyl)aminophosphane (***17a***).* From 0.821 g (2.34 mmol) triphenyltin hydride (**1a**) and 0.65 g (2.34 mmol) [bis(trimethylsilyl)amino][(trimethylsilyl)methylene]phosphane (**9a**). Yield: 0.35 g (24%) mixture of two diastereomers in the ratio 90:10 as a white solid; mp 120.8°C. ^{1}H NMR (C_6D_6): *major diastereometer:* δ = 0.24 [s, b, 9H, $CSi(CH_3)_3$], 0.27 [d, $^4J_{HP}$ = 0.96 Hz, 18H, $N(Si(CH_3)_3)_2$], 2.38 (dd, $^2J_{H,P}$ = 7.26 Hz, $^3J_{H,H}$ = 5.81 Hz, 1H, PC–H), 5.86 (dd, $^1J_{H,P}$ = 219.44 Hz, $^3J_{H,H}$ = 5.81 Hz, 1H, PH), 7.16–7.21 (m, 9H, *meta-* + *para*-H), 7.75–7.78 (m, 6H, *ortho*-H); *minor diastereomer:* δ = 0.22 [s, b, 9H, $CSi(CH_3)_3$], 0.28 [d, $^4J_{H,P}$ = 0.97 Hz, 18H, $N(Si(CH_3)_3)_2$], 2.23 (dd, $^2J_{H,P}$ = 7.87 Hz, $^3J_{H,H}$ = 5.09 Hz, 1H, PC–H), 6.08 (dd, $^1J_{H,P}$ = 204.18 Hz, $^3J_{H,H}$ = 5.09 Hz, 1H, PH), 7.09–7.12 (m, 9H, *meta-* + *para*-H), 7.65–7.68 (m, 6H, *ortho*-H). ^{13}C{^{1}H} NMR (C_6D_6): *major diastereomer:* δ = 2.7 [d, $^3J_{C,P}$ = 4.0 Hz, $CSi(CH_3)_3$], 4.0 [d, $^3J_{C,P}$ = 6.4 Hz, $N(Si(CH_3)_3)_2$], 16.8 (d, $^1J_{C,P}$ = 61.0 Hz, P–CH), 129.0 (s, $^3J_{C,Sn}$ = 24.9 Hz, *meta*-C), 129.4 (s, $^4J_{C,Sn}$ = 10.4 Hz, *para*-C), 137.8 (s, $^2J_{C,Sn}$ = 36.1 Hz, *ortho*-C), 139.4 (d, $^3J_{C,P}$ = 3.2 Hz, *ipso*-C); *minor diastereomer:* δ = 1.8 [d, $^3J_{C,P}$ = 4.8 Hz, $CSi(CH_3)_3$], 3.8 [d, $^3J_{C,P}$ = 5.6 Hz, $N(Si(CH_3)_3)_2$], 128.7 (s, *meta*-C), 129.2 (s, *para*-C), 137.7 (s, $^2J_{C,Sn}$ = 37.7 Hz, *ortho*-C), P–CH and *ipso*-C could not be detected because of signal overlapping or low intensity. ^{31}P{^{1}H} NMR (C_6D_6): *major diastereomer:* δ = 8 (s, $^2J_{P,Sn}$ = 60 Hz, $^1J_{P,H}$ = 216 Hz), *minor diastereomer:* δ = 12 (s, $^2J_{P,Sn}$ = 124 Hz, $^1J_{P,H}$ = 199 Hz). IR (KBr): 3852 (s), 3742 (s), 2945 (m), 2356 (m), 2328 (m), 1959 (w, P–H), 1732 (m), 1480 (m), 1429 (s), 1260 (vs), 1074 (s), 903 (s), 835 (s), 727 (s), 698 (s). EI-MS (70 eV): *m/z* = 629 (11) [M^+], 552 (3) [M^+ − Ph], 355 (100) [M^+ − $SnPh_2$], 349 (22) [$SnPh_3^+$ − H], 279 (35) [M^+ − $SnPh_3$], 77 (24) [Ph^+], 73 (73) [Tms^+]. HR-MS: $C_{28}H_{44}NPSi_3{}^{120}Sn$: calcd: 629.1540; found: 629.1546.

*[(Trimethylsilyl)(tributylstannyl)methyl)]bis(trimethylsilyl)aminophosphane (***17b***).* From 0.713 g (2.45 mmol) tributyltin hydride (**1b**) and 0.68 g (2.45 mmol) [bis(trimethylsilyl)amino][(trimethylsilyl)-methylene]phosphane (**9b**). Yield: 0.92 g (66%) mixture of two diastereomers in the ratio 70:30 as a col-

orless liquid; bp 135°C/3 × 10^{-2} mbar. ^{1}H NMR (C_6D_6): *major diastereomer:* $\delta = 0.33$ [s, b, 9H, $CSi(CH_3)_3$], 0.36 [d, $^4J_{H,P} = 0.98$ Hz, 18H, $N(Si(CH_3)_3)_2$], 0.92–1.74 (m, 28H, Bu_3Sn and PC–H), 5.73 (dd, $^1J_{H,P} = 210.70$ Hz, $^3J_{H,H} = 6.10$ Hz, 1H, PH); *minor diastereomer:* $\delta = 0.25$ [d, $^4J_{H,P} = 1.22$ Hz, 18H, $N(Si(CH_3)_3)_2$], 0.29 [d, $^4J_{H,P} = 1.71$ Hz, 9H, $CSi(CH_3)_3$], 0.92–1.74 (m, 28H, Bu_3Sn and PC–H), 5.96 (dd, $^1J_{H,P} = 201.66$ Hz, $^3J_{H,H} = 6.35$ Hz, 1H, PH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): *major diastereomer:* $\delta = 2.31$ [d, $^3J_{C,P} = 4.5$ Hz, $CSi(CH_3)_3$], 3.75 [d, $^3J_{C,P} = 5.3$ Hz, $N(Si(CH_3)_3)_2$], 10.75 (d, $^3J_{C,P} = 4.5$ Hz, $SnCH_2$), 13.78 [s, $Sn(CH_2)_3\underline{C}H_3$], 14.30 (d, $^1J_{C,P} = 60.1$ Hz, P–CH), 27.71 (s, $SnCH_2\underline{C}H_2$), 29.56 (s, $\underline{C}H_2CH_3$); *minor diastereomer:* $\delta = 1.36$ [d, $^3J_{C,P} = 6.3$ Hz, $CSi(CH_3)_3$], 3.69 [d, $^3J_{C,P} = 7.6$ Hz, $N(Si(CH_3)_3)_2$], 11.59 (d, $^3J_{C,P} = 2.7$ Hz, $SnCH_2$), 12.33 (d, $^1J_{C,P} = 63.3$ Hz, P–CH), 13.80 [s, $Sn(CH_2)_3\underline{C}H_3$], 27.86 (s, $SnCH_2\underline{C}H_2$), 29.61 (s, $\underline{C}H_2CH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): *major diastereomer:* $\delta = 7$ (s, $^2J_{P,Sn} = 69$ Hz, $^1J_{P,H} = 210$ Hz); *minor diastereomer:* $\delta = 13$ (s, $^2J_{P,Sn} = 105$ Hz, $^1J_{P,H} = 201$ Hz). IR (film): 2956 (s), 2284 (w, P–H), 1618 (w), 1464 (m), 1250 (s), 982 (s), 681 (m). EI-MS (70 eV): $m/z = 570$ (1) [M^+], 512 (43) [$M^+ - Bu$], 400 (31) [$M^+ - 3Bu$], 278 (100) [$M^+ - SnBu_3$], 73 (80) [Tms^+]. HR-MS: $C_{22}H_{56}NPSi_3{}^{120}Sn$: calcd: 569.2480; found: 569.2477. Anal. calcd: C, 46.47; H, 9.93; N, 2.46. Found: C, 46.49; H, 9.82; N, 2.67.

General Procedures for the Preparation of the Tetrakis[bis(trimethylsilyl)methyl]cyclotetraphosphane (**18**) To a solution of phosphaalkene **11** in 5 mL of petroleum ether was added an equimolar amount of triorganotin hydride **1**. The color of the reaction solution changed from yellow through orange to red. After the mixture had been stirred for 9 days at 20°C, the precipitated triorganotin halide was filtered off and all volatile compounds were removed in vacuo. The residue was taken up in *n*-pentane and tetrakis[bis(trimethylsilyl)methyl] cyclotetraphosphane (**18**) was crystallized at −30°C.

Method A: From 430 mg (1.91 mmol) [bis(trimethylsilyl)methylene]chlorophosphane (**11a**) and 555 mg (1.91 mmol) tributyltin hydride (**1b**); yield: 110 mg (30%) **18.**

Method B: From 350 mg (1.30 mmol) [bis(trimethylsilyl)methylene]bromophosphane (**11b**) and 456 mg (1.30 mmol) triphenyltin hydride (**1a**); yield: 160 mg (66%) **18.**

Method C: From 340 mg (1.26 mmol) [bis(trimethylsilyl)methylene]bromophosphane (**11b**) and 366 mg (1.26 mmol) tributyltin hydride (**1b**); yield: 140 mg (58%) **18.** Melting point 155°C. ^{1}H NMR (C_6D_6): $\delta = 0.39$ [s, 72H, $Si(CH_3)_3$], 0.56 [m, 4H, $C\underline{H}Si(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 3.54$ [s, $Si(CH_3)_3$], 14.61 [pt, $|J_{C,P}| = 35.3$ Hz, $\underline{C}HSi(CH_3)$]. $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -14.6$ (s). EI-MS (70 eV): $m/z = 760$ (36) [M^+], 601 (36) [$M^+ - CHTms_2$], 380 (68) [$Tms_2HC-P=P-CHTms_2{}^+$], 307 (22) [$Tms_2HC\text{-}P=P\text{-}CHTms^+$], 73 (100) [$Tms^+$]. HR-MS: $C_{28}H_{76}P_4Si_8$: calcd: 760.3051; found: 760.3032. Anal. calcd: C, 44.16; H, 10.06. Found: C, 44.03; H, 10.08.

2,4-Bis(trimethylsilyl)-2,4-diphenyl-1,3-diphosphacyclobutane (**22**)

To a solution of 560 mg (2.45 mmol) of [(trimethylsilyl)(phenyl)methylene]chlorophosphane (**21**) in 5 mL of *n*-pentane was added 712 mg (2.45 mmol) of tributyltin hydride (**1b**). After the mixture had been stirred for 1 day at 20°C, the precipitated triorganotin halide was filtered off and all volatile compounds were removed in vacuo. The residue was taken up in *n*-pentane, and 2,4-bis(trimethylsilyl)-2,4-diphenyl-1,3-diphosphacyclobutane (**22**) was crystallized at −30°C. The crystals were washed with *n*-pentane several times and recrystallized. By-products were removed at 100°C/7 × 10^{-3} mbar by bulb-to-bulb distillation. Yield: 20 mg (4.2%, referred to **21**) colorless crystals.

The same procedure was followed with 1140 mg (5.01 mmol) of [(trimethylsilyl)(phenyl)methylene] chlorophosphane (**21**) in 5 mL of petroleum ether and 1750 mg (5.01 mmol) of triphenyltin hydride (**1a**). Yield: 70 mg (7% referred to **21**) colorless crystals. Melting point 98°C. ^{1}H NMR (60 MHz) (C_6D_6): $\delta = 0.4$ (s, 18H, Tms), 7.02 (d, $|^1J_{H,P} + {}^3J_{H,P}| = 182$ Hz, 1H, P–H), 7.31 (d, $|^1J_{H,P} + {}^3J_{H,P}| = 188$ Hz, 1H, P–H), 7.1–8.4 (m, 10H, Ph–H). $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 41.3$ (s, $|^1J_{H,P} + {}^3J_{H,P}| = 182$ Hz), 69.0 (s, $|^1J_{H,P} + {}^3J_{H,P}| = 188$ Hz). EI-MS (70 eV): $m/z = 388$ (38) [M^+], 315 (3) [$M^+ - Tms$], 195 (29) [$(Tms)(Ph)HC\text{-}PH^+$], 77 (3) [Ph^+], 73 (100) [Tms^+].

Crystal Structure Analysis of **18** *[24]*

Crystal Data. $C_{28}H_{76}P_4Si_8$; M = 761.49 g/mol; temperature 293 K; wavelength 71.073 pm; crystal system monoclinic; space group C2/c; crystal dimensions 0.5 × 0.3 × 0.3 mm, $a = 2664.0(2)$ pm, $\alpha = 90°$, $b = 932.20(7)$ pm, $\beta = 121.197(6)°$, $c = 2278.0(2)$ pm, $\gamma = 90°$, $V = 4.8390(7)$ nm^3, $\mu = 0.371$ mm^{-1}, $Z = 4$, $d_{calc} = 1.045$ g/cm^3.

Data Collection. Data were collected using an automatic four-circle diffractometer (Siemens P4, Mo-Kα radiation, graphite monochromator). Exact lattice constants were determined from the least-squares refinement of the 2 Θ values of 40 reflections.

Structure Solution and Refinement. Structure solution and refinement were performed by direct methods (SHELXS 86 [25]) and by full-matrix least-squares on F^2 (SHELXL-93 [26]), respectively. A total of 4191 reflections ($R_{int} = 0.0495$) were measured in the range $1.79° \leq \Theta \leq 22.50°$, of which 2498 with $I \geq 2\sigma\ (I)$ were considered in the refinement. The number of parameters was 181. Hydrogen atoms were included at geometrically calculated positions. The structure refinement converged at $R1 = 0.0372$ and $wR2 = 0.0890$; the difference Fourier synthesis on the basis of the final structural model showed a maximum of 308 e/nm^3 and a minimum of -228 e/nm^3, and the goodness-of-fit was 1.055.

Crystal Structure Analysis of **22** *[24]*

Crystal Data. $C_{20}H_{30}P_2Si_2$; M = 388.56 g/mol; temperature 293 K; wavelength 0.71073 pm; crystal system monoclinic; space group $P2_1/n$; crystal dimensions 0.35 × 0.20 × 0.15 mm, $a = 6.5638(10)$ pm, $\alpha = 90°$, $b = 15.448(2)$ pm, $\beta = 98.11\ (3)°$, $c = 22.970(5)$ pm, $\gamma = 90°$, $V = 2.3058(7)$ nm^3, $\mu = 0.293$ mm^{-1}, $Z = 4$, $d_{calc} = 1.119$ g/cm^3.

Data Collection. Data were collected using an automatic four-circle diffractometer (Siemens P4, Mo-Kα radiation, graphite monochromator). Exact lattice constants were determined from the least-squares refinement of the 2 Θ values of 41 reflections.

Structure Solution and Refinement. Structure solution and refinement were performed by direct methods (SHELXS 86 [25]) and by full-matrix least-squares on F^2 (SHELXL-93 [26]), respectively. A total of 2815 reflections ($R_{int} = 0.0414$) were measured in the range $1.59° \leq \Theta \leq 22.50°$, of which 1073 with $I \geq 2\sigma\ (I)$ were considered in the refinement. The number of parameters was 225. Hydrogen atoms, except for H1 and H2, were included at geometrically calculated positions. The structure refinement converged at $R1 = 0.0489$ and $wR2 = 0.1019$; the difference Fourier synthesis on the basis of the final structural model showed a maximum of 0.248 e/nm^3 and a minimum of -0.141 e/nm^3, and the goodness-of-fit was 1.139.

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