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Synthesis of Functionalized Phosphinines: Aromatization of Diels-Alder Adducts of *P*-Chloro-bis(trimethylsilyl)methylenephosphine

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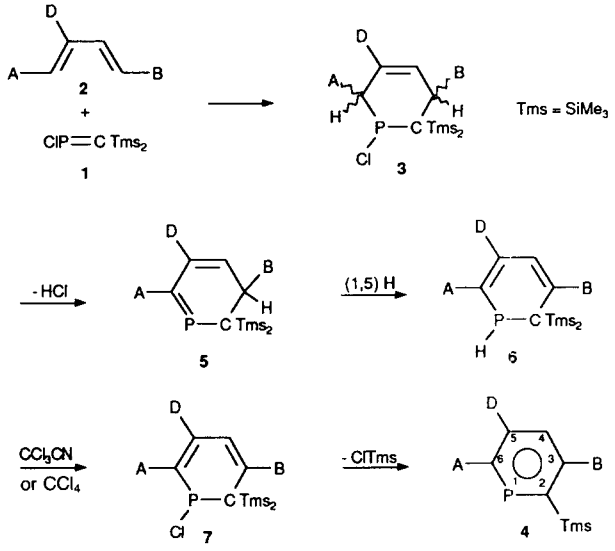
ABSTRACT

The Diels-Alder adducts of functionalized dienes with P-chloro-bis(trimethylsilyl)methylenephosphine can be aromatized, except in a few particular cases, thus opening a general route to functionalized phosphinines. The aromatization procedure differs with the substituents. Intermediates such as secondary cyclic phosphines could be characterized and even isolated. In some cases, aromatization and 1,5 sigmatropic shift of a trimethylsilyl group were observed and hydrogenolysis of the C–Si bond as well.

RESULTS AND DISCUSSION

In a preceding paper [1] we have shown that the Diels-Alder reaction of compound **1** with functionalized dienes **2** gives the adduct **3** in good yield. The aim of this paper is to show that aromatization of **3** can be achieved as predicted [2], thus opening a general and simple route to functionalized λ^3 phosphinines. For a long time, these compounds were rare [3]. Recently a general method of preparation starting from 1,3 λ^3-azaphosphinines has been described by Märkl and co-workers [4].

The "aromatization" of **3** to **4** generally follows Scheme 1 except for the adducts **3e** and **3f**. The



	A	B	D
a	H	OTms	H
b	H	Ph	OTms
c	H	CO_2Me	H
d	CO_2Me	CO_2Me	H [a]
e	H	OMe	OTms [b,c]
f	Me	CO_2Me	H [b]
g	CH_2-CH_2		OTms [d]

[a] **3d** is not isolated ; [b] the "aromatization" of **3e** and **3f** takes place by another way ; [c] **3e** leads to **4e** with A = B = H, D = OTms ; [d] Attempts to "aromatize" **3g** are failed.

SCHEME 1

Dedicated to Professor Dr. Rolf Appel on the occasion of his seventieth birthday.

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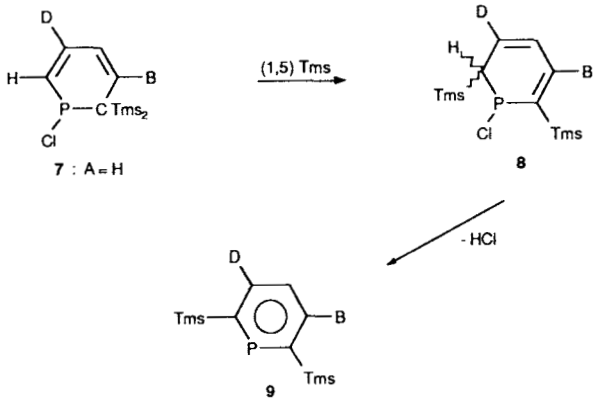
phosphinine **4g** corresponding to **3g** cannot be obtained.

The elimination of HCl from **3** occurs either spontaneously or by reaction with a base (DABCO or DBU), leading to the unstable phosphadiene **5** (when the reaction is monitored by ^{31}P NMR, an elusive signal above 200 ppm is sometimes observed). A 1.5 hydrogen shift leads to cyclic phosphine **6**, which is characterized and even isolated in a few cases. The halogenation of the latter with CCl_3CN [5] or CCl_4 [6] gives **7**, which loses ClTms to give the expected phosphinine **4**.

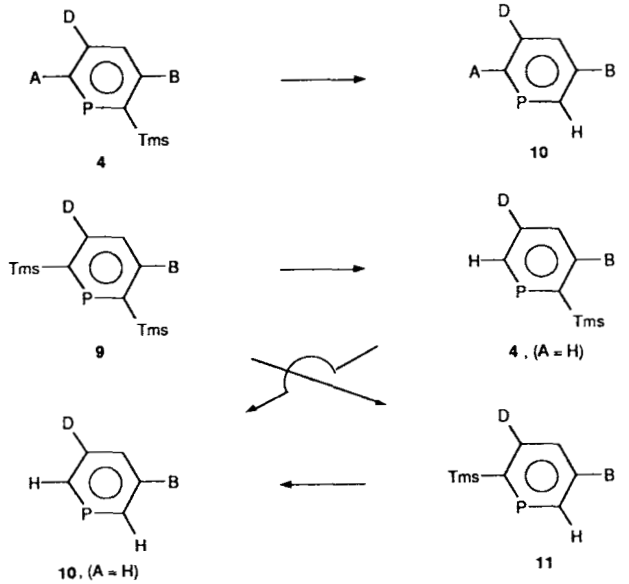
When A = H, the chlorophosphine **7** may react differently: the elimination of ClTms to give the compound **4** may compete with a 1.5 sigmatropic shift of the Tms group leading to compound **8**, which then loses HCl with the formation of **9** (Scheme 2).

It has also been observed that partial cleavage of the trimethylsilyl group from the primarily formed phosphinines may occur probably due to the presence of HCl (or hydrochlorides) in the reaction mixture. This C–Si cleavage was carried out in some cases with formic acid (Scheme 3).

In general, the yields are satisfactory. However, in some cases, the purification of the products is not easy and the efficiency of the present method decreases.



SCHEME 2



SCHEME 3

Aromatization of **3a**

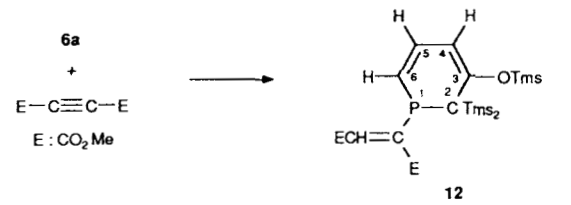
Compound **3a** reacts with DABCO at room temperature to give almost quantitatively the secondary phosphine **6a**, which is aromatized, after reaction with CCl_3CN at room temperature, to **4a** in 55% yield.

In order to test the capacity of the dienic phosphine in the Diels-Alder reaction, we reacted it with dimethyl acetylenedicarboxylate (Scheme 4): compound **12** was obtained quantitatively (NMR evaluation). This is not too surprising since the addition of secondary phosphines to alkynes is a known reaction [7].

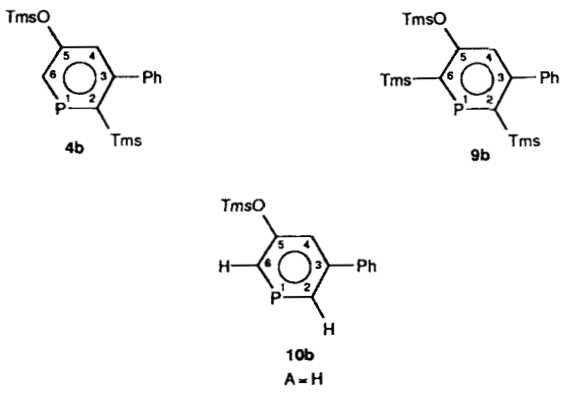
Aromatization of **3b**

After several attempts with different bases, the best results were obtained with DBU in boiling benzene. Compound **6b** was obtained in 77% yield (as estimated by ^{31}P NMR) and is only characterized by ^{31}P NMR.

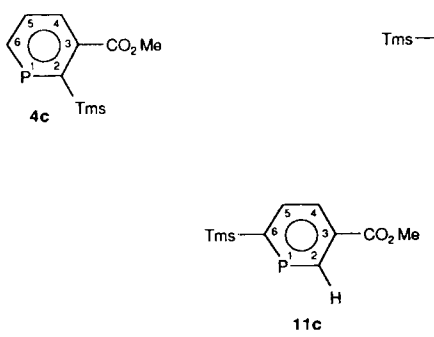
The aromatization of **6b** led to a mixture of which the composition depends on the experimental conditions as shown by ^{31}P NMR spectroscopy: hence, after 15 hours refluxing with CCl_4, **9b** (50%), **4b**



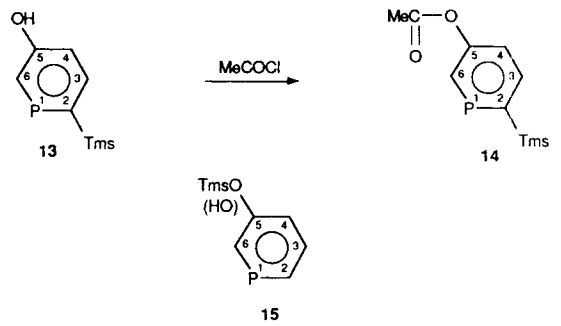
SCHEME 4



SCHEME 5



SCHEME 6



SCHEME 7

(35%), and **10b** (A = H) were principally formed (Scheme 5), while a solution of **6b** in acetonitrile gave, after 10 minutes at room temperature, mainly **4b** (63%) and **9b** (23%). These compounds were not separated but were characterized by ^{1}H NMR.

Aromatization of 3c

This compound reacted with DABCO in THF at room temperature to give mainly the secondary phosphine **6c** (80% by ^{31}P NMR), which could be purified by column chromatography.

The aromatization of **6c** was carried out in boiling CCl_4; the reproducibility of the results depend on the experimental procedure, which must be exactly followed (see experimental). A mixture of three phosphinines was obtained: **4c**, **9c**, and **11c** (Scheme 6), respectively 20, 50, and 30%, as evaluated by NMR spectroscopy. Each compound could be isolated by GLC and characterized by mass spectrometry and ^{1}H NMR (see Experimental).

Synthesis of Phosphinines from Dimethyl Muconate 2d

The reaction of **2d** with phosphaalkene **1** on refluxing with benzene for 40 h led quantitatively to phosphine **6d**, which was only characterized by ^{31}P NMR spectroscopy. This latter compound was formed by the general process shown in Scheme 1.

On boiling with CCl_4, the almost pure phosphine **6d** led quantitatively to **4d** (a pure compound after recrystallization). When the phosphaalkene was reacted with **2d** for a longer time (i.e. 56 hours), the phosphine **6d** was obtained with a mixture of phosphinines **4d** and **10d**. After refluxing with CCl_4, the crude product gave a mixture of **4d** and **10d**, which could be separated by GLC.

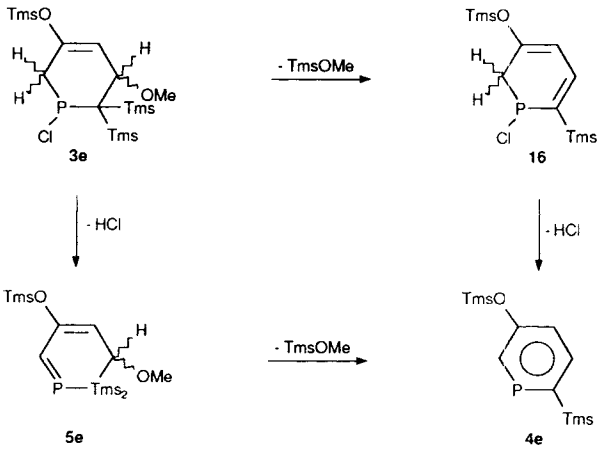
Aromatization of the Adduct 3e

After 3 h refluxing with benzene, adduct **3e** gave **4e** almost quantitatively (62% yield after distillation). Compound **4e** was characterized by its ^{31}P, ^{1}H, and ^{13}C NMR data (see Experimental), more particularly δ ^{31}P = 237, $^1J_{PC2}$ = 55 Hz, $^1J_{PC6}$ = 61 Hz, and $^2J_{PH6}$ = 34.5 Hz. The small coupling constants of H_6 with the other cyclic hydrogens, 2.3 and 0.6 Hz, show that no hydrogen is located on carbon 5 while H_3 and H_4 are on vicinal carbon atoms ($^3J_{H3H4}$ = 8.6 Hz). The same result was obtained when **3e** is treated with DABCO in benzene.

On refluxing with methanol **4e** gave the easily oxidizable hydroxyphosphinine **13**, which was reacted with acetyl chloride to give **14**. When adduct **3e** was kept at room temperature for 20 h, a mixture of phosphabenzenes **4e** (90%) and **13** + **15** (10%) was obtained in 42% yield after distillation (Scheme 7). Compound **15** is characterized only by ^{31}P NMR spectroscopy: δ = 211.0; $^2J_{PH2} \approx {}^2J_{PH6}$ = 34, $^3J_{PH3}$ = 8.5 Hz, and $^4J_{PH4}$ = 2.5 Hz. Its structure is uncertain and it is not possible to say whether carbon 5 is substituted by the OH or OTms group.

Reaction Mechanism. Pellon and Hamelin [8] have directly obtained 3-hydroxy phosphininecarboxylic acid from diene **2e** and an in situ generated *P*-chloro phosphaalkene. They have discussed the mechanism of the formation of this phosphinine without being able to draw any definite conclusions about such a complex problem.

As far as our work is concerned (reactions in a neutral or basic medium), the simplest hypotheses are as found in Scheme 8.



SCHEME 8

Compounds **13** and **15** could be obtained from the easy cleavage of the O–Si or C–Si bond in an acidic medium.

When pyridine was used instead of DABCO, a 3:7 mixture of phosphinines **4e** and **9e** respectively (evaluated by ^{31}P NMR) was obtained and fully characterized by NMR and mass spectrometry.

Aromatization of **3f**

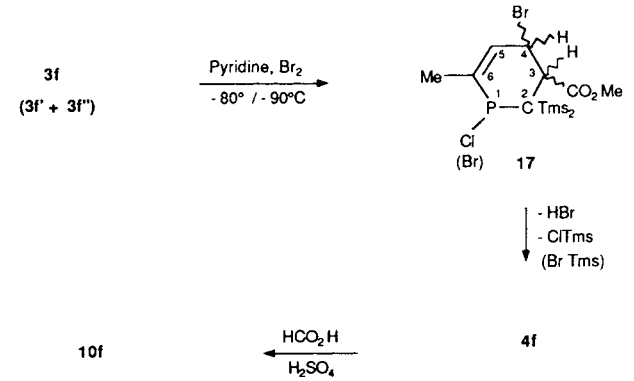
The general method described earlier fails to aromatize compounds **3f** (**3f'** + **3f"**, two diastereoisomers). Since the cycloaddition leading to **3f** is reversible, it is necessary to use mild experimental conditions. Different bases (NEt_3, DABCO, DBU, and pyridine) were used without success.

The phosphinine **4f** was obtained in a different way. Compounds **3f** (**3f'** + **3f"**) was reacted at −80/−90°C with the pyridine–bromine complex for about 45 minutes, after which time the reaction mixture was kept at room temperature for 15 h. A mixture of **17**, **4f**, and **10f**, respectively 63, 11, and 26% (as evaluated by NMR) was obtained. Before distillation, the major product **17** (*P*-chloro compound, one diastereoisomer) could be characterized by ^{31}P and ^{13}C NMR spectroscopy together with about 5 to 10% of the corresponding bromophosphine. Distillation led to a 1:1 mixture of phosphinines **4f** and **10f**. Refluxing this mixture with a mixture of formic and sulphuric acids gave **10f** only (Scheme 9).

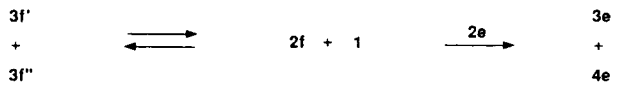
Compound **17** could be obtained with about 85% purity when the solvent of the crude product was completely eliminated at room temperature and the residue was dissolved in C_6H_6 or CCl_4 and filtered through silica gel.

The ^{31}P NMR data show that the two diastereoisomers **3f'** and **3f"** in boiling benzene and in the presence of Danishefsky's diene **2e** give a mixture of **3e** and **4e** (Scheme 10). Consequently, the cycloaddition of methyl sorbate to phosphaalkene **1** is reversible.

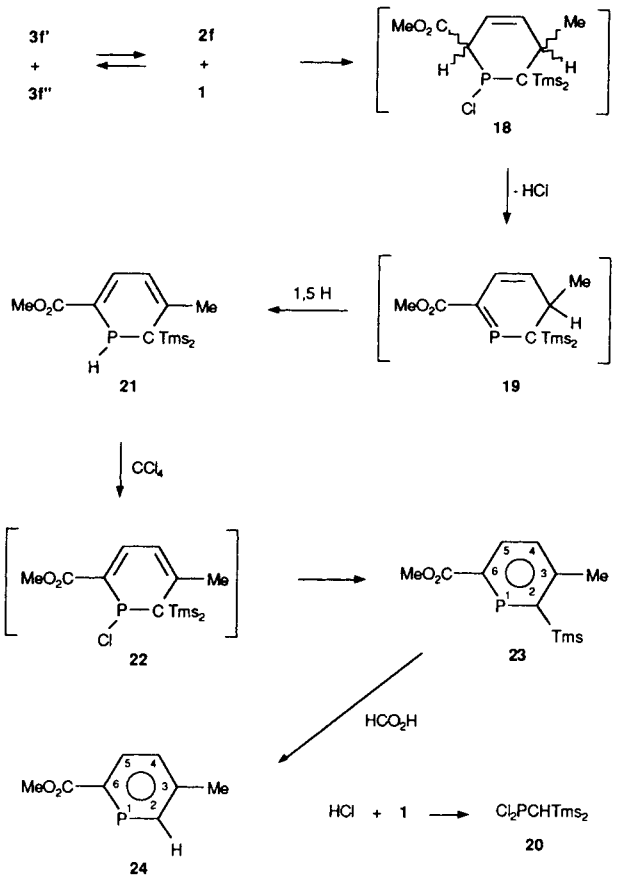
Heating the mixture of **3f'** and **3f"** in boiling benzene and in the presence of pyridine gave a mixture of the dichlorophosphine **20** (50%, $\delta\,^{31}P = 225$, easily obtained from phosphaalkene **1** and HCl) and the cyclic phosphine **21** (50%, $\delta\,^{31}P = -99.3$, $^1J_{PH} = 190.5$ Hz, characterized only by ^{31}P NMR). Attempts to minimize the formation of **20** by addition of a base (NEt_3, DABCO) failed. This was due to the rapid addition of HCl to **1**. The crude phosphine **21** with CCl_4, on refluxing with benzene, gave an 8:2 mixture of the two phosphabenzenes **23** and **24** respectively, probably via the chlorophosphine **22**, in about 20% yield. Compound **23** was transformed to **24** by the addition of formic acid and boiling with carbon tetrachloride (Scheme 11).



SCHEME 9



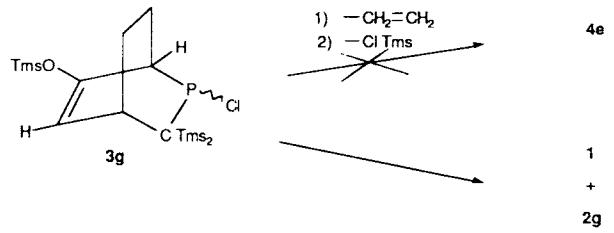
SCHEME 10



SCHEME 11

Attempts to Aromatize **3g**

This was attempted by the flash vacuum thermolysis (FVT) [9, 10] of **3g** in the hope of losing the ethylene bridge with simultaneous elimination of ClTms and the formation of the corresponding phosphinine. This type of reaction was not ob-



SCHEME 12

served. However, instead, retrocycloaddition took place giving the phosphaalkene **1** and the diene **2g**, which were easily characterized by ^{31}P and ^{1}H NMR (Scheme 12).

CONCLUSION

This work shows that the Diels-Alder reaction of *P*-chloro-bis(trimethylsilyl)methylenephosphine with dienes substituted by electron-donating or electron-withdrawing groups opens a general route to functionalized phosphinines.

The difficulty arises from the "aromatization" of the primary adduct, which is more or less complicated by a sigmatropic shift and/or the cleavage of the C–Si bond, thus giving a mixture of phosphabenzenes that is not always readily separable.

EXPERIMENTAL

During this work, the following NMR apparatus were used: Bruker WP 80 C, WP 80 DS, and AM 300. The mass spectra were carried out on a Varian Mat 311 (Centre de Mesures Physiques de l'Université de Rennes) and the determination of the exact masses by the peak matching technique. Elementary analyses were performed by the Laboratoire Central de Microanalyse du C.N.R.S. (Lyon). Merck 60 (230–400 mesh) silica gel was used for column chromatography. Preparative gas liquid chromatography was achieved on an Aerograph 700 apparatus.

The formation and the spectroscopic properties of adducts **3** have already been described [1].

Aromatization of Adduct **3a**

To Obtain Phosphine **6a**. Adduct **3a** was obtained at room temperature after 15 h reaction of 550 mg (2.45 mmol) of phosphaalkene **1** with 520 mg (3.66 mmol) of diene **2a**. After distillation of the excess **2a**, 300 mg (2.67 mmol) of freshly sublimed DABCO and 6 mL of benzene (distilled over Na/benzophenone) were added to the residue. The resulting mixture was then refluxed for 3.5 h. After cooling, filtration of the precipitate, and solvent removal, 780 mg of **6a** was obtained practically pure as an orange oil (96% yield). NMR ^{31}P (CCl_4), δ: −93.0 ($^{1}J_{PH}$ = 188, $^{2}J_{PH}$ = 57, $^{3}J_{PH}$ = 10); ^{1}H (CD_2Cl_2), δ: 4.46 (PH), 5.09 (H_4, $^{3}J_{HH}$ = 6.7), 5.25 (H_6, $^{3}J_{HH}$ = 11.1), 6.30 (H_5, $^{3}J_{HH}$ = 6.7 and 11.1); ^{13}C (CD_2Cl_2), δ: 35.9 (C_2, $^{1}J_{PC}$ = 42), 102.7 (C_4, $^{3}J_{PC}$ = 6.0), 106.1 (C_6, $^{1}J_{PC}$ = 16.0), 118.2 (C_5, $^{3}J_{PC}$ = 21), 158.1 (C_3, $^{2}J_{PC}$ = 4).

To Obtain Phosphinine **4a**. To a solution of 600 mg (1.9 mmol) of **6a** in 10 mL of benzene was added 0.2 mL (289 mg, 2 mmol) of CCl_3CN. After one night at room temperature and solvent removal, the residual yellow oil was purified by Kügelrohr distillation to give 250 mg of **4a** as a pale yellow oil (yield = 55%, bp = 180–220°C/0.2 mm Hg). Compound **4a**, which is unstable to air, was only characterized by NMR.

NMR ^{31}P (CCl_4), δ: 242 ($^{2}J_{PH}$ = 39.5); ^{1}H (CD_2Cl_2), δ: 6.70 (H_4, $^{3}J_{HH}$ = 8.7, $^{4}J_{PH}$ = 1.2), 7.57 (H_5, $^{3}J_{HH}$ = 8.7 and 9.8, $^{3}J_{PH}$ = 8.1), 8.15 (H_6, $^{3}J_{HH}$ = 9.8, $^{2}J_{PH}$ = 39.5); ^{13}C (CD_2Cl_2), δ: 0.4 [C–Si($\underline{C}H_3$)$_3$, $^{3}J_{PC}$ = 9.0], 0.9 [O–Si($\underline{C}H_3$)$_3$], 119.0 (C_4, $^{3}J_{PC}$ = 19), 137.6 (C_5, $^{2}J_{PC}$ = 14), 146.1 (C_6, $^{1}J_{PC}$ = 57), 155.1 (C_2, $^{1}J_{PC}$ = 77), 162.8 (C_3, $^{2}J_{PC}$ = 26).

Addition of **6a** *to Dimethyl Acetylenedicarboxylate.* A solution of 55 mg of the alkyne in 0.4 mL of benzene was added under nitrogen over 1 min to a magnetically stirred solution of 126 mg of the dienic secondary phosphine **6a** in 0.4 mL of benzene. The reaction was exothermic. After stirring (5 min) and solvent removal, a solution of the residue (solvent 100 mL of a 9:1 mixture of CH_2Cl_2 and diethyl ether) was filtered through silica gel to give 125 mg of **12** as a yellow oil that is practically pure (^{31}P and ^{1}H NMR). NMR ^{31}P (CD_2Cl_2), δ: −40.8; ^{1}H (CD_2Cl_2), δ: 2.98 and 3.20 ($CO_2C\underline{H}_3$), 4.80 (H_4, $^{3}J_{HH}$ = 7), 5.20 (H_6, $^{3}J_{HH}$ = 11, $^{2}J_{PH}$ = 56), 6.15 (H_5, $^{3}J_{HH}$ = 7 and 11, $^{3}J_{PH}$ = 12.5), 6.37 (=CHCO$_2$Me, $^{3}J_{PH}$ = 11).

Aromatization of Adduct **3b**

To Obtain Phosphine **6b**. A 573 mg (3.7 mmol) sample of DBU was added dropwise under argon to a solution of 1.67 g (3.7 mmol) of adduct **2b** in 2 mL of benzene (distilled over Na-benzophenone). After one night at room temperature, the DBU's hydrochloride was filtered off under argon to leave, after solvent elimination, 1.15 g of an orange oil. ^{31}P NMR shows that the only phosphorus compound in the crude product is **6b** (δ: −65.8).

To Obtain Phosphinines **4b**, **9b**, *and* **10b**. This can be achieved in two ways: (i) A solution of 545 mg (3.7 mmol) of CCl_3CN in 5 mL of dry benzene was added dropwise under argon to crude **6b**. After 10 min at room temperature, phosphinines **4b** (63%) and **10b** (24%) were obtained (ratio estimated by ^{31}P NMR). (ii) A solution of 300 mg of **6b** in 5 mL of CCl_4 was refluxed for 15 h giving a mixture consisting of mainly **10b** (50%), **4b** (35%), and **9b** (5%) as estimated by ^{31}P NMR.

4b: Mass spectrometry: Molecular ion of weak intensity at m/z = 332 ($C_{17}H_{25}Si_2OP$). NMR ^{31}P (CD_2Cl_2), δ: 245.5; ^{1}H (CD_2Cl_2), cyclic protons, δ:

6.85 (H_4, $^4J_{HH}$ = 2.2, $^4J_{PH}$ = 0.7), 8.10 (H_6, $^4J_{HH}$ = 2.2, $^2J_{PH}$ = 35.5).

9b: NMR ^{31}P (CD_2Cl_2), δ: 274.7; ^1H (CD_2Cl_2), cyclic proton, δ: 6.73 (H_4).

10b: Mass spectrometry: Calculated molecular mass for $C_{20}H_{33}OPSi_3$: 404.158, found: 404.158. NMR ^{31}P (CD_2Cl_2), δ: 212.4; ^1H (CD_2Cl_2), cyclic protons δ: 8.00 (H_6, $^2J_{PH}$ = 35.0), 8.50 (H_2, $^2J_{PH}$ = 39.0, $^4J_{HH}$ = 2.2), the signal corresponding to H_4 is masked under those of **4b** and **9b**.

Aromatization of Adduct **3c**

To Obtain the Phosphine **6c**. A 631 mg sample (5.6 mmol, 1.5 equivalents) of freshly sublimed DABCO was added to a solution of 1.265 g (3.7 mmol) of adduct **3c** in 10 mL of anhydrous THF. After three days, the hydrochloride of DABCO formed was filtered off. THF was eliminated under vacuum. The obtained phosphine **6c** was purified by column chromatography on silica gel and characterized by ^{31}P NMR spectroscopy (C_6H_6, δ: −99.9, $^1J_{PH}$ = 195, $^2J_{PH}$ = 59).

To Obtain Phosphinines **4c**, **9c**, *and* **11c**. A solution of phosphine **6c** in 5 mL of CCl_4 (distilled over P_2O_5) was refluxed overnight under argon. After solvent removal, the residue was distilled under vacuum in a Kugelrohr apparatus (bp = 150–170°C/0.005 mm Hg) to give 375 mg of a 2:3:5 mixture of phosphinines **4c**, **11c**, and **9c**, respectively. Distillation was ineffective for their separation, which was achieved by preparative GLC (column 5% SE 30 on chromosorb W, 6.1 m long, 9.5 mm diameter, flow rate: 150 mL/min, carrier gas: H_2, oven temperature: 225°C, injector temperature: 260°C and detector temperature: 275°C). The retention times of **4c**, **11c**, and **9c** are 5.4, 10.9, and 19.2 min., respectively.

4c: Mass spectrometry: Calculated molecular mass for $C_{10}H_{15}O_2SiP$: 226.058, found: 226.058. NMR ^{31}P (C_6H_6), δ: 241.1; ^1H (CD_2Cl_2), δ: 0.68 ($Si(C\underline{H}_3)_3$, $^4J_{PH}$ = 1), 3.91 ($CO_2C\underline{H}_3$), 7.95 (H_5, $^3J_{HH}$ = 9.8 and 8.2), 8.02 (H_4, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 1, $^4J_{PH}$ = 2), 8.73 (H_6, $^2J_{PH}$ = 38.8, $^3J_{HH}$ = 9.8 and $^4J_{HH}$ = 1).

11c: Mass spectrometry: Calculated molecular mass for $C_{10}H_{15}O_2SiP$: 226.058, found: 226.058. NMR ^{31}P (C_6H_6), δ: 230.7; ^1H (CD_2Cl_2), δ: 0.38 ($Si(C\underline{H}_3)_3$, $^4J_{PH}$ = 1.3), 3.80 ($CO_3C\underline{H}_3$), 8.15 (H_4, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 1.4, $^4J_{PH}$ = 1.8), 8.24 (H_5, $^3J_{HH}$ = 8.2, $^5J_{HH}$ = 1, $^3J_{PH}$ = 9.8), 9.50 (H_2, $^4J_{HH}$ = 1.4, $^5J_{HH}$ = 1, $^2J_{PH}$ = 36.3).

9c: Mass spectrometry: Calculated molecular mass for $C_{13}H_{23}O_2Si_2P$: 283.074, found: 283.074, NMR ^{31}P (C_6H_6), δ: 265.0; ^1H (CD_2Cl_2), δ: 0.37 and 0.39 ($Si(C\underline{H}_3)_3$, 3.90 ($CO_2C\underline{H}_3$), 7.92 (H_4, $^3J_{HH}$ = 8.3, $^4J_{PH}$ = 1.3), 8.13 (H_5, $^3J_{HH}$ = 8.3, $^3J_{PH}$ = 9.4).

Compound **9c** crystallizes in the chromatographic receiver. It melts at 54°C and is stable enough for elementary analysis; Anal. Cal. for $C_{13}H_{23}O_2Si_2P$: C, 52.35; H, 7.72. Found: C, 52.07; H, 7.70.

Synthesis of Phosphinines from Dimethyl Muconate **2d**

Formation of the Phosphine **6d**. A 417 mg (3.72 mmol) sample of sublimed DABCO was introduced under argon into a two-necked Schlenk's flask predried under vacuum followed by 10 mL of freshly distilled benzene (distilled from Na/benzophenone) and 634 mg (3.73 mmol) of dimethyl muconate. The reaction mixture was heated to reflux; 837 mg (3.73 mmol) of phosphaalkene **1** in 2 mL of anhydrous benzene was then added dropwise over a few minutes and the resulting mixture was refluxed for 40 h. At this time, the medium acquired a deep brown coloration. The hydrochloride of DABCO formed was filtered off and the benzene eliminated under vacuum. The formation of phosphine **6d**, characterized by ^{31}P NMR spectroscopy, is almost quantitative.

6d: NMR ^{31}P (C_6H_6), δ = −100.4, $^1J_{PH}$ = 110.

Remark: The reaction conditions must be strictly adhered to in order to give reproducible results. For example, increasing the reaction time to 56 h leads to the formation of small quantities of phosphinines **4d** and **10d**.

To Obtain Phosphinines **4d** *and* **10d**. After filtration of the reaction mixture (previously described, 56 h reaction) and concentration of the filtrate, the resulting solution was refluxed overnight with 5 mL of CCl_4 (distilled over P_2O_5). The solvent was removed and the residue was distilled in a Kugelrohr apparatus (bp = 165–170°C/0.05 mm Hg). The product obtained (410 mg) was a 3:7 mixture of **10d** and **4d**, respectively, which could not be separated by distillation. Their separation was achieved by preparative GLC (column 5% SE 30 on chromosorb W; flow rate: 150 mL/min; length: 6.10 m; diameter: 9.5 mm; carrier gas: H_2; temperatures of oven, injector, and detector: 225°, 260°, and 275°C, respectively. Retention time: 9.3 min for **10d** and 19.8 min for **4d**.

Remark: Starting from 535 mg of **2d** and after 40 h, practically pure phosphine **6d** was obtained and was refluxed in CCl_4 overnight. After elimination of the solvent, the residue crystallized partially. Recrystallization from *n*-hexane gave 140 mg of phosphinine **4d**; mp = 87°C.

4d: Mass spectrometry: Molecular ion of weak intensity at m/z = 284. Calculated mass for $C_{11}H_{14}O_4SiP$ ($M^+ - \cdot CH_3$): 269.040, found 269.040.

Anal. Calc. for $C_{12}H_{17}O_4SiP$: C, 50.70; H, 5.98. Found: C, 50.43; H, 5.89.

NMR ^{31}P (C_6H_6), δ: 255.1, ^1H (CD_2Cl_2): 0.42 ($Si(C\underline{H}_3)_3$, $^4J_{PH}$ = 2.3), 3.94, and 3.96 ($CO_2C\underline{H}_3$), 8.01 (H_4, $^3J_{HH}$ = 8.8), 8.58 (H_5, $^3J_{HH}$ = 8.8).

10d: Mass spectrometry: Calculated molecular mass for $C_9H_9O_4P$: 212.024, found: 212.024. NMR

^{31}P (C_6H_6), δ: 221.0; ^{1}H (CD_2Cl_2): 3.90 and 3.95 ($CO_2C\underline{H}_3$), 8.30 (H_4, $^{3}J_{HH}$ = 8.8, $^{4}J_{HH}$ = 1.4), 8.66 (H_5, $^{3}J_{HH}$ = 8.8, $^{3}J_{PH}$ = 8.2, $^{5}J_{HH}$ = 0.6), 9.55 (H_2, $^{2}J_{PH}$ = 39.0, $^{4}J_{HH}$ = 1.4, $^{5}J_{HH}$ = 0.6).

Aromatization of Adduct **3e**

To Obtain **4e**. A solution of 1.55 g (7.0 mmol) of phosphaalkene **1** and 1.90 g (9.1 mmol, 1.5 mL) of Danishefsky's diene in 14 mL of benzene (distilled over Na/benzophenone) was refluxed for 2 h. After cooling and solvent elimination, the residue was distilled under vacuum.

4e: Yellow-greenish oil, 1.10 g, yield = 62%, bp: 75–78°C/0.1–0.2 mm Hg, slowly transforms in air. Mass spectrometry: Calculated molecular mass for $C_{11}H_{21}OSi_2P$: 255.087, found: 255.088. NMR ^{31}P (C_6H_6), δ: 237.0; ^{1}H (CD_2Cl_2), δ: 6.81 (H_4, $^{4}J_{PH}$ = 1.8, $^{3}J_{HH}$ = 8.6, $^{5}J_{HH}$ = 0.6), 7.93 (H_6, $^{2}J_{PH}$ = 34.5, $^{4}J_{HH}$ = 2.3, $^{5}J_{HH}$ = 0.6). ^{13}C (CD_2Cl_2), δ: 123.4 (C_4, $^{3}J_{PC}$ = 20), 142.3 (C_3, $^{2}J_{PC}$ = 16), 142.5 (C_6, $^{1}J_{PC}$ = 61), 159.5 (C_5, $^{2}J_{PC}$ = 4), 161.6 (C_2, $^{1}J_{PC}$ = 55).

The assignment of the signals was confirmed by selective decoupling. The same applies for the other products.

To Obtain **13**. A solution of 1.10 g (4.3 mmoles) of **4e** in 5 mL of methanol (distilled over sodium) was refluxed for 40 min. After distillation, 0.43 g of **13** was obtained as a white solid (mp = 60–66°C, bp = 68–72°C/0.01 mm Hg, yield = 54%) decomposing rapidly in air. It was only characterized by NMR spectroscopy.

NMR ^{31}P (C_6H_6), δ: 238.0; ^{1}H (CCl_4), δ: 7.00 (OH), 7.01 (H_4, $^{3}J_{HH}$ = 8.6), 7.83 (H_3, $^{3}J_{HH}$ = 8.6, $^{3}J_{PH}$ = 10.4), 8.02 ($^{2}J_{PH}$ = 33.0).

To Obtain **14**. A solution of 0.20 mL of CH_3COCl in 5 mL of CCl_4 was added over 30 min at room temperature to a magnetically stirred solution of 400 mg (2.17 mmol) of **13** and 0.5 mL (363 mg, 3.59 mmoles) of NEt_3 in 5 mL of CCl_4. After 15 h and distillation, 350 mg of **14** was obtained as a colourless oil (bp = 160–165°C/0.2 mm Hg, yield = 71%) characterized by NMR spectroscopy only.

NMR ^{31}P (C_6H_6), δ: 240.5; ^{1}H (CCl_4): 0.35 ($Si(C\underline{H}_3)_3$, $^{4}J_{PH}$ = 0.9), 2.27 ($C\underline{H}_3CO$), 7.11 (H_4, $^{3}J_{HH}$ = 8.5, $^{4}J_{HH}$ = 2.2), 8.06 (H_3, $^{3}J_{PH}$ = 10.2, $^{3}J_{HH}$ = 8.5, $^{5}J_{HH}$ = 0.6), 8.32 (H_6, $^{2}J_{PH}$ = 34.0, $^{4}J_{HH}$ = 2.2, $^{5}J_{HH}$ = 0.6).

Reaction of Adduct **3e** *in the Presence of Pyridine.* A solution of 0.1 mL of pyridine in 5 mL of benzene was added dropwise under argon to a magnetically stirred boiling solution of 455 mg of adduct **3e** in 5 mL of benzene. After 12 h at room temperature, the solvent was eliminated. 278 mg of a 3:7 mixture of phosphinines **4e** and **9e** respectively was obtained. Compound **9e** was not isolated but was characterized by NMR and mass spectroscopy.

9e: Mass spectrometry: Calculated molecular mass for $C_{14}H_{29}OSi_3P$: 328.126, found: 328.125, NMR ^{31}P (CCl_4), δ: 269.0; ^{1}H (CD_2Cl_2), δ: cyclic protons only 6.69 (H_4, $^{3}J_{HH}$ = 8.6), 7.64 (H_3, $^{3}J_{HH}$ = 8.6, $^{3}J_{PH}$ = 9.8); ^{13}C (CD_2Cl_2), δ: 118.2 (C_4, $^{3}J_{PC}$ = 21), 142.2 (C_3, $^{2}J_{PC}$ = 13), 155.1 (C_6, $^{1}J_{PC}$ = 86), 159.7 (C_2, $^{1}J_{PC}$ = 79). The signal of C_5 cannot be assigned.

Aromatization of Adducts **3f′** *and* **3f″**

Preparation of the Pyridine–Bromine Complex. A solution of 1 mL of Br_2 in 20 mL of petroleum ether was added dropwise over 30 min to a magnetically stirred solution of 1.6 mL of pyridine in 15 mL of petroleum ether. After 30 min at room temperature, the resulting orange solid was filtered off, washed with 20 mL of petroleum ether and dried under vacuum: mp = 66°C; weight obtained = 3.8 g (81% yield).

To Obtain the Chlorophosphine 17. An orange solution of 2.6 g (1.03 equivalents) of the pyridine–bromine complex and 1 mL of pyridine in 100 mL of CH_2Cl_2 was added dropwise over 45 min to a magnetically stirred solution (cooled between −80°C and −90°C) of 3.7 g of the mixture of adducts **3f′** and **3f″** in 50 mL of CH_2Cl_2. After 15 h at room temperature and after removal of the solvent, 20 mL of benzene or CCl_4 was added to the residue. The precipitate was filtered off and washed with 20 mL more solvent in small portions. After removal of the solvent, the ^{31}P NMR of the crude product (a red viscous oil, 1.5 g) showed that it is a mixture of **17** (63%), **4f** (11%), and **10f** (26%).

17: NMR ^{31}P (C_6D_6), δ: 85.3; ^{13}C (CCl_4), δ: 2.6 ($^{3}J_{PC}$ = 7) and 3.7 ($^{3}J_{PC}$ = 10) (2 ($\underline{C}H_3)_3Si$ groups), 19.0 ($\underline{C}H_3$–C_6, $^{2}J_{PC}$ = 38, $^{1}J_{CH}$ = 128), 28.2 (C_2, $^{1}J_{PC}$ = 76), 48.4 (C_4, $^{1}J_{CH}$ = 139), 51.1 (C_3, $^{2}J_{PC}$ = 2, $^{1}J_{CH}$ = 156), 51.4 ($CO_2\underline{C}H_3$, $^{1}J_{CH}$ = 147), 134.4 (C_5, $^{1}J_{CH}$ = 163), 136.8 (C_6, $^{1}J_{PC}$ = 39), 172.8 ($\underline{C}O_2CH_3$).

Remark: **17** (P–Cl compound) contains a small quantity of (P–Br) compounds. This quantity depends on the experimental conditions.

17 (P–Br): NMR ^{31}P (C_6D_6) δ: 90.0; Mass spectrometry; molecular ion: m/z = 472 ($C_{14}H_{27}O_2PSi_2{}^{79}Br_2$).

To Obtain the Compounds **4f** *and* **10f**. Those phosphinines were previously identified in the preceding mixture. Distillation led to 1.04 g of a 1:1 mixture of phosphinines **4f** and **10f** (bp = 90–94°C/0.5 mm Hg). Redistillation of this mixture gave 530 mg of pure **4f** (bp = 145°C/0.4 mm Hg, yield = 36%).

Refluxing 165 mg of the 1:1 mixture of **4f** and **10f** with a mixture of formic and sulphuric acids (4 mL and 1 mL, respectively) for 0.5 h led to **10f** only. The crude product was extracted with 2 ×

15 mL of $CHCl_3$. The organic layer was washed with 3 × 20 mL of saturated NaCl aqueous solution. After drying over $NaSO_4$ and elimination of the solvent, the solid residue was sublimed at 50–55°C under 0.05 mm Hg). Pure **10f** was obtained, mp: 54°C (75 mg).

4f: Mass spectrometry. Calculated molecular mass for $C_{11}H_{17}O_2SiP$: 240.074, found: 240.076. NMR ^{31}P (CD_2Cl_2), δ: 238.0; ^1H (CD_2Cl_2), δ: 0.41. ($Si(C\underline{H}_3)_3$), $^4J_{PH}$ = 0.2), 2.73 ($C\underline{H}_3$–C_6, $^3J_{PH}$ = 14), 3.88 ($CO_2C\underline{H}_3$), 7.65 (H_5, $^3J_{PH}$ = 5.6, $^3J_{HH}$ = 8.6), 7.92 (H_4, $^3J_{HH}$ = 8.6, $^4J_{PH}$ = 2.6).

10f: Mass spectrometry. Calculated molecular mass for $C_8H_9O_2P$: 168.034, found: 168.034. Anal. calcd. C, 57.14; H, 5.36. Found: C, 57.06; H, 5.45. NMR ^{31}P (CD_2Cl_2), δ: 204.8; ^1H (CD_2Cl_2), δ: 2.80 ($C\underline{H}_3$–C_6, $^3J_{PH}$ = 15), 7.78 (H_5, $^3J_{PH}$ = 6, $^3J_{HH}$ = 8.7, $^5J_{HH}$ = 0.4), 8.14 (H_4, $^3J_{HH}$ = 8.7, $^4J_{PH}$ = 3.3, $^4J_{HH}$ = 1.5), 9.40 (H_2, $^2J_{PH}$ = 37, $^4J_{HH}$ = 1.5, $^5J_{HH}$ = 0.4).

Reversibility of the Cycloaddition of Methyl Sorbate with Phosphaalkene **1**. This was demonstrated in the following way: a solution of 390 mg (1.1 mmol) of a mixture of **3f'** and **3f"** in 1 mL of C_6D_6 and 220 mg (1.3 mmol, 1.1 eq) of diene **2e** was heated at 80°C for 1 h. The ^{31}P NMR spectrum showed the formation of **3e** and **4e** in a 3:7 ratio and the complete disappearance of adducts **3f'** and **3f"**.

To Obtain Phosphine **21**. A solution of 330 mg (2.6 mmol) of diene **2f** in 5 mL of anhydrous benzene was added under magnetic stirring at room temperature to 416 mg (1.8 mmol) of **1**. After 3 h, 6 mL of benzene and 5 mL of pyridine were added to the reaction mixture, which was then refluxed for 15 h. ^{31}P NMR showed the formation of a 1:1 mixture of **21** and the dichlorophosphine **20**. The crude solution was filtered through silica gel (elution with 60 mL of benzene). After distillation of benzene, 500 mg of a viscous oil containing a mixture of diene **2f** and phosphine **21** in a 3:7 ratio and 10–15% unidentified products were obtained as evaluated by NMR spectroscopy. The different attempts to minimize the formation of **20** failed and the change of the nature of the base or its concentration did not solve the problem.

To Obtain Phosphinines **23** and **24**. From the previously obtained product, methyl sorbate was eliminated by heating over an oil bath (90°C under 0.2 mm Hg) to give 241 mg of a red oil which was dissolved in 5 mL of benzene and treated with 0.1 mL of CCl_4. The resulting solution was refluxed for 24 h. After benzene elimination and Kugelrohr distillation, 90 mg of a yellowish oil was obtained (bp = 135–155°C/0.1 mm Hg). NMR showed that it is a 4:1 mixture of **23** and **24** (yield ≈ 20%). This mixture, when reacted with formic acid in boiling CCl_4, gave only **24** (yield ≈ 40%).

23: NMR (CCl_4), ^{31}P, δ: 249.0; ^1H (C_6D_6), δ: 0.38 ($Si(C\underline{H}_3)_3$, $^4J_{PH}$ = 2.0), 2.25 ($C\underline{H}_3$–C_3, $^4J_{PH}$ = 2.0), 3.91 ($CO_2C\underline{H}_3$), 7.24 (H_4, $^3J_{HH}$ = 8.5, $^4J_{PH}$ = 2.2), 8.28 (H_5, $^3J_{HH}$ = 8.5, $^3J_{PH}$ = 4.0).

24: Mass spectrometry: Calculated molecular mass for $C_8H_9O_2P$ = 168.034, found = 168.034. NMR ^{31}P (CCl_4), δ = 220.0; ^1H (CCl_4), δ: 2.55 ($C\underline{H}_3$–C_3), 3.91 ($CO_2C\underline{H}_3$), 7.32 (H_4, $^3J_{HH}$ = 8.8), 8.35 (H_5, $^3J_{HH}$ = 8.8, $^3J_{PH}$ = 4.0), 8.50 (H_2, $^2J_{PH}$ = 40.0).

Attempts to Aromatize **3g**

FVT at 350°C and 500°C under 0.1 mm Hg on 100 mg of **3g** were carried out. The signal corresponding to **3g** at 129 ppm (^{31}P NMR) completely disappeared and only the signal corresponding to phosphaalkene **1** was observed (^{31}P NMR, δ = 343).

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