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Role of the Conformation in the Reactivity of 1,3-Diphosphapropenes

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ABSTRACT

The symmetrical and unsymmetrical 1,3-diphosphapropenes **3** *and* **4** *were obtained from the corresponding diphosphiranes* **1** *and* **2**. *The chemical behavior of these compounds has been studied. Phosphonium-phosphaalkenes* **7a** *and* **10a** *have been obtained in the reactions with aluminium trichloride. Whereas the symmetrical diphosphaallene* **13** *can be obtained by reaction of* **1** *or* **3** *with lithio compounds, the unsymmetrical diphosphaallene* **14** *cannot be prepared by a similar route. Reduction of* **3a** *and* **4a** *(obtained with a different conformation) by lithium aluminum hydride afforded phosphino-phosphaalkenes* **17a** *and* **18a** *(with a similar conformation); further dehydrochlorination with amines led to the symmetrical and unsymmetrical diphosphaallenes* **13** *and* **14**, *respectively. The formation of allenes strongly depends on the conformation of the starting diphosphapropenes.*

INTRODUCTION

We have prepared, by reaction of carbenoids with diphosphenes, two types of functionalized diphosphiranes, the symmetrical diphosphiranes **1** [1] and the unsymmetrical diphosphiranes **2** [2] (Scheme 1).

Due to the enthalpy difference ΔH (P–C)/ΔH (P–P) these phosphorus cyclopropane analogues generally undergo ring opening reactions with P–P bond cleavage. Thus, the photolysis of functionalized diphosphiranes **1** and **2** leads to new 1,3-diphosphapropenes functionalized on phosphorus [3].

In the case of compounds **1**, the photochemical opening reaction leads mostly to 1,3-diphosphapropenes **3** with a trans configuration (60–75%), but this reaction is neither stereospecific nor product selective: 1,3-diphosphapropenes with a cis configuration **3'** and byproducts (Scheme 2) are also obtained [4].

On the contrary, unsymmetrical diphosphiranes **2** undergo photochemical as well as thermal [2] regioselective ring opening reactions, since in the 1,3-diphosphapropenes **4** the P=C double bond is exclusively formed from the phosphorus atom substituted by the tri-*tert*-butyl phenyl group; moreover, these reactions are stereoselective since only the trans isomers are obtained [2] (Scheme 3). Contrary to the photochemical ring opening of **1**, no byproducts are observed.

The X-ray structure determinations display two different conformations for the trans 1,3-diphosphapropenes **3a** (gauche conformation) and **4a** (syn conformation), which induce very different NMR data [2–3]. It clearly appears that the kind of phosphorus substituents greatly influences the conformation and the reactivity. Therefore, we have studied and herein compare the chemical behavior of diphosphiranes **1** and **2** and 1,3-diphosphapropenes **3** and **4** toward nucleophiles, such as lithio compounds and hydrides, and toward Lewis acids.

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This paper is dedicated to Professor Dr. Rolf Appel on the occasion of his 70th birthday.

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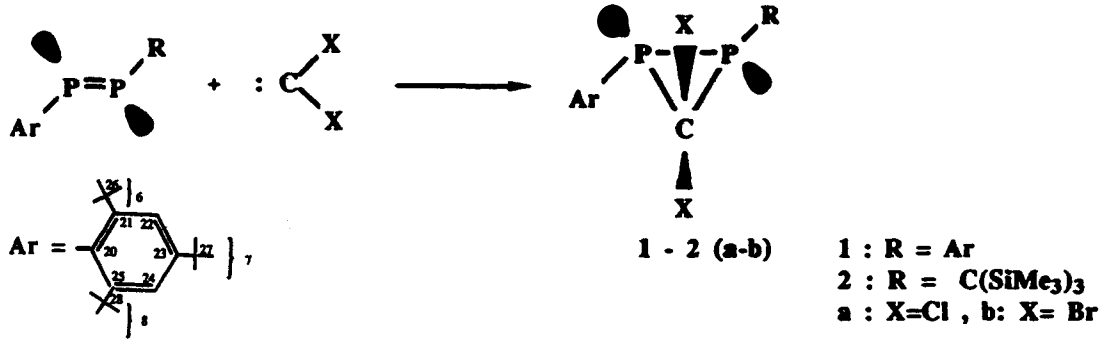

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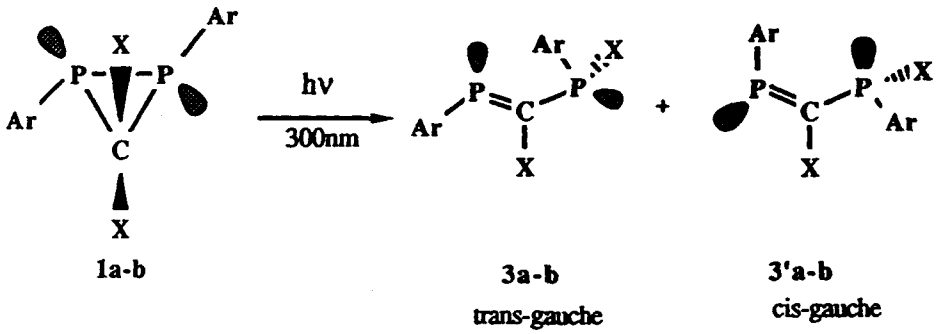

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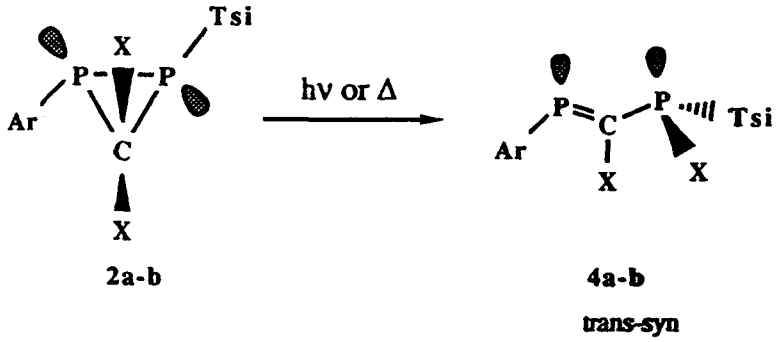


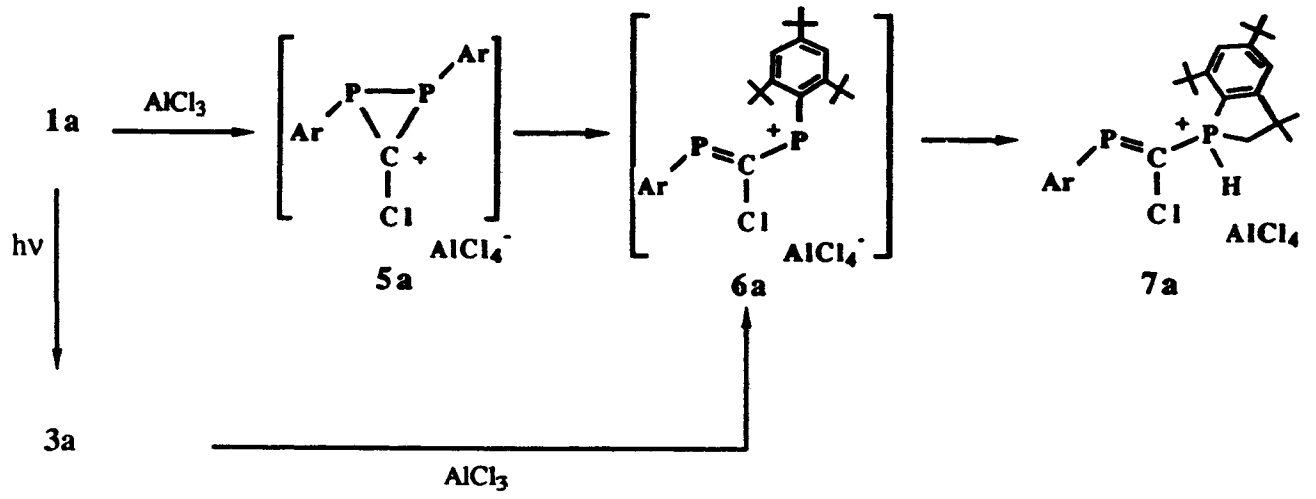
SCHEME 3

RESULTS AND DISCUSSION

Reaction with $AlCl_3$

The diphosphirane **1a** reacts at room temperature with aluminum trichloride to afford quantitatively the phosphonium-phosphaalkene **7a** characterized in solution by its physicochemical data [5]. Similar products were previously described starting from C-unsubstituted 1,3-diphosphapropenes [6]. Compound **7a** is formed via the presumed diphosphiranium ion **5** and diphosphaallyl cation **6**. The first step of this reaction is probably the heterolytic rupture of the C–Cl bond inducing the subsequent preferential P–P bond rupture (Scheme 4).

Contrary to the case of photochemical [3] or anionic [7] ring opening reactions, the cationic intermediates **5** or **6** could not be detected. The short life of **6** is due to the instability of the phosphenium cation substituted by two carbon atoms (no species of this type have so far been reported); thus the oxidative addition of a neighboring tert-butyl group to the proximal electropositive phosphorus leading



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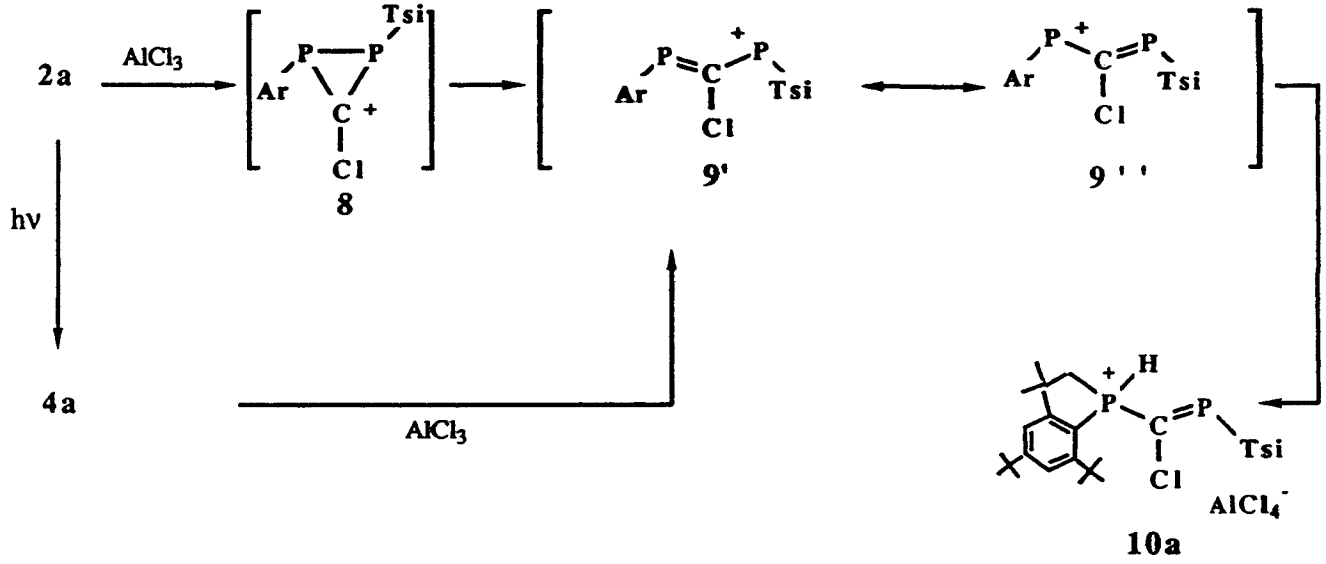


SCHEME 5

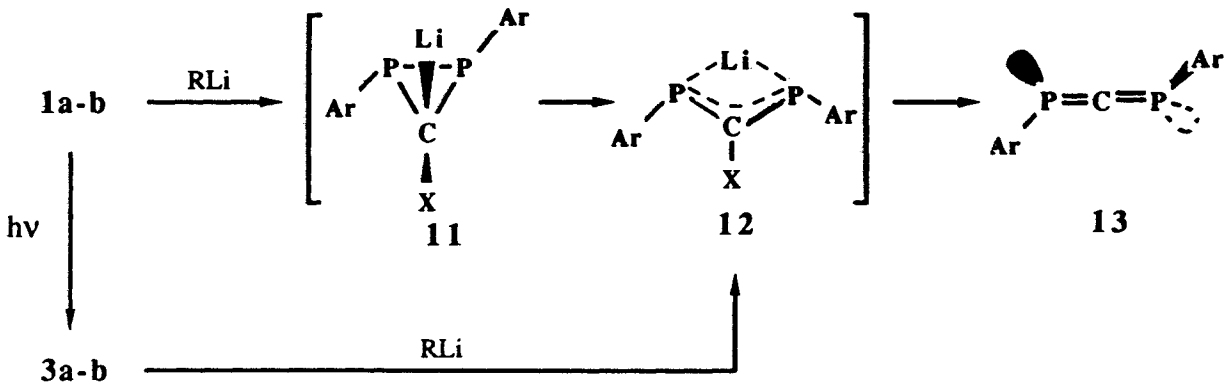
to the more thermodynamically favorable phosphonium ion **7a** occurs after the ring opening.

Under similar conditions, the same final product **7a** is obtained from 1,3-diphosphapropene **3a** and $AlCl_3$ [5] (Scheme 4).

The reaction of $AlCl_3$ with diphosphirane **2a** under the same experimental conditions leads to the phosphonium-phosphaalkene **10a**, which has been spectroscopically identified in solution. This compound with the trisyl group on the dicoordinated phosphorus is less stable than its homologous **7a**, and decomposes in solution after one week at room temperature. With the objective to prepare the phosphenium cation **9'**, we have added $AlCl_3$ at room temperature directly to **4a**. Owing to the substitution of the electropositive phosphorus by the very bulky trisyl group, and the impossibility of an oxidative addition, we thought that the phosphenium cation **9'** might be stable. Actually, addition of $AlCl_3$ does not afford the expected **9'**, but the phosphonium-phosphaalkene **10a** exclusively. The contributing canonical structures **9'** and **9''** provide a convenient visualization of the precursor of **10a** (Scheme 5).

Reaction with Lithio Compounds

As in the case of gem-dihalogenocyclopropanes, the reaction of lithio compounds (BuLi, MeLi) with diphosphiranes **1a–b** quantitatively affords the corresponding allene **13** (possibly via intermediates **11** and **12**) (Scheme 6) [8, 9]; such a diphosphaallene has already been prepared by other routes [10]. In this reaction, we have not been able to detect a



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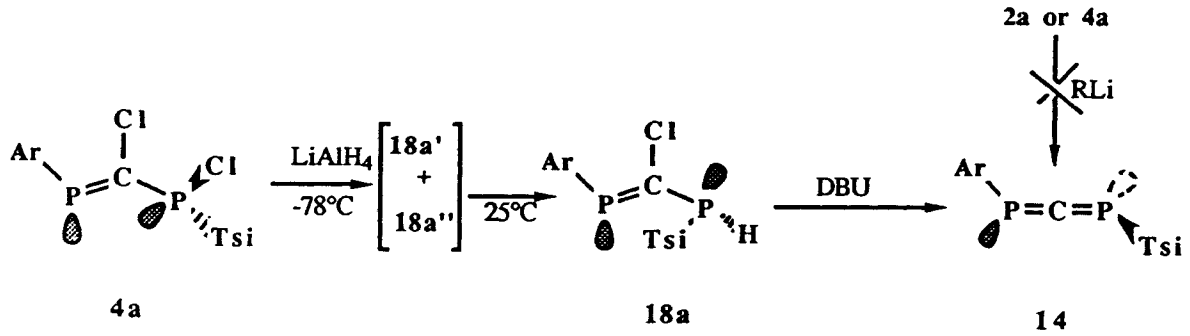


SCHEME 7

diphosphiranic carbene intermediate: no trapping adduct or dimer form of the carbene has been observed [8].

Moreover, the diphosphaallene **13** can be obtained quantitatively from diphosphapropenes **3a–b** (prepared by photolysis of **1a–b**), which present a trans gauche conformation. From this result, it seems that **13** is obtained via intermediate **12**; when X is a methyl or a phenyl group similar intermediates can be trapped [7]. This mechanism of allene formation has recently been confirmed by theoretical calculations performed by Bachrach and colleagues [11].

With the aim to prepare unsymmetrical diphosphaallenes (only one compound of this type has been recently described [12]), we have attempted to bring about the reaction of methyllithium with diphosphirane **2a** and diphosphapropene **4a** under the same experimental conditions as for **1** and **3** (0°C in Et_2O). However, we have not obtained the corresponding allene **14** (Scheme 7), but only unidentified products.

Reaction with Methanol and $LiAlH_4$

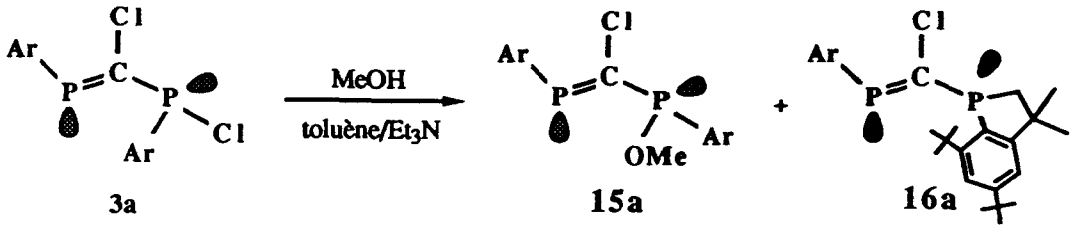
When a toluene solution of diphosphapropene **3a** is heated with an excess of methanol and triethylamine at 40°C for 72 h, derivatives **15a** and **16a** are obtained in the ratio 50/50 (Scheme 8). Derivative **15a**, obtained as a stable compound in a trans configuration, has been isolated by the usual workup. The nucleophilic substitution reaction is rather slow because of the very bulky substituents on phosphorus.

A reaction of the same type from the diphosphapropene **4a** substituted by two different groups on phosphorus has not been observed under similar experimental conditions, not even by heating at 70°C for 60 h.

Diphosphapropene **3a**, treated with an excess of $LiAlH_4$ (10 eq) in refluxing ether, gives the secondary phosphino-phosphaalkene **17a** (75%) together with phosphaallene **13** (25%) (Scheme 9). Heating **17a** for 6 h at 70°C in toluene with an excess of triethylamine quantitatively affords the allene **13**.

Compound **4a** easily reacts with one equivalent of $LiAlH_4$ in Et_2O to give the stable derivative **18a** (δP_2: 271.0, δP_3: −22.4, $^2J_{PP}$: 89 Hz, $^1J_{PH}$: 235 Hz, $^3J_{PH}$: 13 Hz) (Scheme 7). A selective irradiation in ^1H NMR unambiguously proved that the hydrogen is located on the phosphorus substituted by the trisyl group ($^4J_{H-C-Si-C-P_3}$ = 0.7 Hz).

Addition of one equivalent of DBU to **18a** at room temperature leads to the unsymmetrical allene **14**, which has not been isolated in a completely



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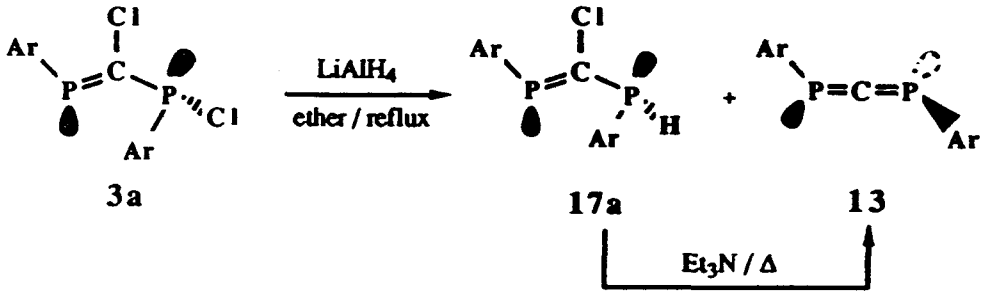

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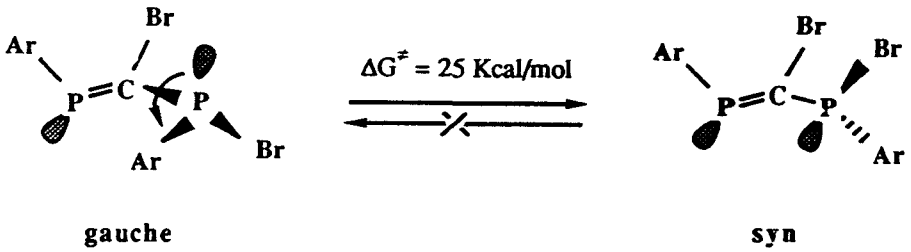

SCHEME 10

pure form, but has been unambiguously characterized by ^{31}P NMR data (δP_A: 169.0, δP_B: 145.7, $^2J_{PP}$: 4.6 Hz).

The lack of reactivity of MeOH with **4a** must be due to the very large steric hindrance of the trisyl group. On the other hand, in the reduction, we have observed the fixation of the smallest nucleophile H^- on the phosphorus substituted by this group: the steric bulk of the trisyl group does not prevent this reaction. From these two reactions, an S_{N^2} mechanism seems the most likely. As MeOH reacts only with **3a** and not with **4a**, which has the same moiety Ar–P=C(Cl)–P<, an S'_{N^2} mechanism seems to be excluded. Such a mechanism has been found by Karsch and colleagues but with other experimental conditions and different starting materials ($tBuO^-$ and Ar–P=CH–P(Cl)Ar) [13].

During the reduction of **4a**, two diphosphapropene intermediates **18a'** and **18a"** have been observed at low temperature. The major one, **18a'**, appears at −70°C and disappears after some hours at 20°C; its NMR data are dependent on the temperature:

−70°C	δP_2: 283.5	δP_3: −29.9	$^2J_{PP}$: 56 Hz
+30°C	δP_2: 285.7	δP_3: −29.8	$^2J_{PP}$: 74 Hz

Above −20°C, the minor intermediate **18a"** appears in the reaction mixture and disappears after 24 h at room temperature:

18a" δP_2: 290.3 δP_3: −25.1 $^2J_{PP}$: 45 Hz

The intermediates **18a'** and **18a"** could be unstable conformational isomers or could be due to a low temperature interaction between aluminum and diphosphapropene **4a** π electrons [14]. Whatever the stereochemistry occurring in this reduction of **4a** (inversion or retention [15]), the attack of the hydride ion destabilizes the syn conformation and leads to **18a** in a gauche conformation. The ^{31}P NMR data of the latter are comparable to those of **17a** and **3a**.

The conformational change **4a** (syn) → **18a** (gauche) is proved by the great variation of $^2J_{PP}$: **4a** (457 Hz) **18a** (89 Hz). In a similar reaction the reduction of **3a** gives **17a**; both compounds present very close $^2J_{PP}$: **3a** (109 Hz) **17a** (102 Hz).

Thus it seems that allene **14** can be prepared only from a diphosphapropene in the suitable gauche conformation, close to that of the allene. The gauche → syn rotameric transformation has been evidenced and measured (25 kcal/mol [16]), but the reverse reaction has never been observed (Scheme 10). This irreversibility probably prevents the allene formation.

Such a result confirms the previously proposed mechanism [5, 11], which involves the preliminary diphosphirane ring opening to give the corresponding diphosphaallyl intermediate, instead of a carbenic insertion.

EXPERIMENTAL

All manipulations were carried out in an argon atmosphere using standard Schlenk and vacuum techniques. Solvents were dried by distillation from sodium-benzophenone immediately prior to use. ^1H and ^{31}P NMR spectra were recorded on Bruker AC80 and Bruker WM250 spectrometers, respectively, at 80.13 MHz and 250.13 MHz and ^{13}C NMR spectra on a Bruker WM250 at 62.86 MHz. The numbering of the carbons appears in Scheme 1. Mass spectra were taken on a Nermag R10-10H spectrometer. Chromatographies were carried out on silica columns (silica 60F, 70–230 mesh) or on Chromatotron.

The functionalized 1,3-diphosphapropenes **3a–b** [3] and **4a–b** [2] were prepared according to the previously described procedure, and diphosphapropene **15a** was prepared by reaction of **3a** with MeOH [3].

*Synthesis of 1-[1-Chloro-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]-3,3-dimethyl-5,7-di-*tert*-butyl-1-phosphoniaindane* **7a**

From diphosphirane **1a**. To a solution of **1a** (0.130 g; 0.205 mmol) in 6 mL of degassed CH_2Cl_2, stirred at 0°C, was added $AlCl_3$ (0.030 g, 0.224 mmol). The starting yellow solution turned dark; the reaction mixture was allowed to warm to room temperature.

From diphosphapropene **3a**. To a solution of **3a** (0.052 g; 0.082 mmol) in degassed CH_2Cl_2 (2 mL) was added $AlCl_3$ (0.012 g, 0.090 mmol) at room temperature.

7a (90%): NMR: ^{31}P (32.44 MHz): δP_2 = 342, δP_3 = 25, $^2J_{PP}$ = 133 Hz, $^1J_{P3H}$ = 532 Hz; ^{27}Al (20.88 MHz): δ = 103, $AlCl_4^-$; MS (DCI) $C_{37}H_{58}P_2Cl$, *m/e* = 599 (M^+).

*Synthesis of 1-[1-Chloro-2-[tris(trimethylsilyl)methyl]2-phosphaethenyl]-3,3-dimethyl-5,7-di-*tert*-butyl-1-phosphoniaindane* **10a**

From diphosphapropene **4a**. To a solution of **4a** (0.050 g; 0.081 mmol) in degassed CH_2Cl_2 (2 mL) cooled at −80°C contained in a NMR tube was added 0.9 equivalent of $AlCl_3$ (0.010 g, 0.075 mmol). The reaction was followed by NMR spectroscopy between −80° and 30°C. The formation of **10a** was observed at 30°C: δP_2 = 369, δP_3 = 60, $^2J_{PP}$ = 212 Hz, $^1J_{P3H}$ = 541 Hz). ^{27}Al NMR displays a unique signal at δ: 103 ppm, characteristic of the $AlCl_4^-$ anion. Compound **10a** gradually decomposes at room temperature in the reaction mixture to give unidentified products. Starting from diphosphirane **2a** under the same conditions we obtained the same results.

From diphosphirane **2a**. Under the same conditions we obtained the same results.

*Synthesis of 1,3-Bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphaallene* **13**

From diphosphiranes **1a** *and* **1b**. To a solution of **1b** (0.320 g; 0.442 mmol) in Et_2O (5 mL) cooled at 0°C were added dropwise 3 equivalents of a 1.6 M solution of methyllithium in Et_2O (0.9 mL, 1.32 mmol). The resulting brown suspension was stirred for 1 h at room temperature, then evaporated to dryness. After addition of pentane, the reaction mixture was filtered through celite, and the filtrate was concentrated in vacuo. Crude product was purified by chromatography on silica in hexane (R_f: 0.7). Light yellow crystals of **13** (0.190 g, 76%) were obtained.

Starting from **1a**, the best yield of **13** requires a 1/10 ratio of **1a**/MeLi.

From 1,3-diphosphapropenes **3a** *and* **3b**. To a solution of **3a** (0.052 g; 0.082 mmol) in Et_2O (5 mL) cooled to 0°C, was added dropwise 1 equivalent of a 1.6 M solution of methyllithium in Et_2O. The reaction mixture was allowed to warm to room temperature, then Et_2O was evaporated in vacuo. Diphosphaallene **13** was purified as previously described [10].

NMR: ^1H (80.13 MHz, C_6D_6): δ = 1.31 (s, 18 H, *p*-tBu); 1.48 (m, 36 H, *o*-tBu); 7.4 (s, 4 H, Ar); ^{13}C (62.86 MHz, $CDCl_3$): δ = 276.2 (t, $^1J_{CP}$ = 58 Hz, C_1); 153.2 (C_{21}, C_{25}); 149.6 (C_{23}); 129.5 (dd, $^1J_{CP}$ = 73 Hz; $^3J_{CP}$ = 28 Hz, C_{20}); 121.7 (C_{22}, C_{24}); 37.9 (C_{26}, C_{28}); 34.8 (C_{27}); 33.1 (C_6); 31.4 (C_8); 29.7 (C_7); ^{31}P (32.44 MHz, C_6D_6): δ = 141.6; MS (FD) $C_{37}H_{58}P_2$, *m/e* = 565 (M^+).

*Synthesis of 1-(2,4,6-tri-*tert*-butylphenyl)-3-[tris(trimethylsilyl)methyl]-1,3-diphosphaallene* **14**

To 25 mg of **18a** (0.043 mmol) in 2.5 mL of toluene were added 2 equivalents of freshly distilled DBU. The reaction mixture was stirred overnight at room temperature. ^{31}P NMR analysis showed the formation of the expected diphosphaallene **14** (δP_A = 169.0, δP_B = 145.7 $^2J_{PP}$ = 4.6 Hz.

*Synthesis of 2-Chloro-1,3-bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphapropene* **17a**

To a suspension of $LiAlH_4$ (0.100 g; 2.632 mmol, excess) in Et_2O was added at room temperature a solution of **3a** (0.170 g; 0.267 mmol). The reaction mixture was heated for 1 h at reflux, then Et_2O was evaporated in vacuo and replaced by hexane. The suspension was filtered through celite. A NMR study showed the formation of **17a** (75%) and **13** (25%). These two stable derivatives could not be separated by chromatography on silica gel plates in hexane because of close R_f values (**17a**: 0.55 and **13**: 0.4). However, **17a** could be obtained in 95% purity by using Chromatotron. NMR: ^1H (80.13 MHz, C_6D_6) δ 1.28 (s, 9H, *p-t*-Bu), 1.30 (s, 9H, *p-t*-Bu), 1.45 (s, 9H, *o-t*-Bu), 1.50 (s, 9H, *o-t*-Bu), 1.66 (s, 18H, *o-t*-Bu), 6.45 (dd, $^1J_{HP3}$ = 232 Hz, $^3J_{HP2}$ = 23.7 Hz, 1H, PH), 7.60 (d, $^4J_{HP}$ = 1.2 Hz, 2H, Ar), 7.70 (d, $^4J_{HP}$ = 2.3 Hz, 2H, Ar); ^{13}C (62.86 MHz, C_6D_6) δ 170.8 (dd, $^1J_{CP2}$ = 88.0 Hz, $^1J_{CP3}$ = 53.0 Hz, C_1), 156.3 (m, C_{31} and C_{35}), 154.6 (s, C_{21}), 154.2 (s, C_{25}), 151.8 (s, C_{23} or C_{33}), 151.0 (s, C_{33} or C_{23}), 136.5 (d, $^1J_{CP2}$ = 68.0 Hz, C_{20}), 134.0 (m, C_{30}), 122.7 (s, C_{22} or C_{24}), 122.6 (s, C_{32} or C_{34}), 38.8 (s, C_{36} and C_{38}), 38.6 (s, C_{27} and C_{37}), 35.4 (s, C_{26} and C_{28}), 34.7 (m, C_6 and C_8), 33.8 (d, $^4J_{CP3}$ = 6.0 Hz, C_{16}), 33.1 (d, $^4J_{CP3}$ = 6.0 Hz, C_{18}), 31.8 (s, C_{17} and C_7); ^{31}P (32.44 MHz, C_6D_6) δP_2 = 263, δP_3 = −32, $^2J_{PP}$ = 102 Hz, $^1J_{P3H}$ = 232 Hz, $^3J_{P2H}$ = 23 Hz; MS (FD) ($C_{37}H_{59}Cl\ P_2$): *m/e* = 601 (M^+, ^{35}Cl).

*Synthesis of 2-Chloro-1-(2,4,6-tri-*tert*-butylphenyl)-3-[tris(trimethylsilyl)methyl]-1,3-diphosphapropene* **18a**

To a solution of **4a** (0.075 g; 0.121 mmol) in Et_2O cooled to 0°C was added 1 equivalent of $LiAlH_4$ (1 M solution in Et_2O). The reaction mixture was stirred for 1 h at 0°C then warmed to room temperature and filtered through celite. Solvents were evaporated in vacuo and crude products were purified by chromatography on silica plates (R_f: 0.35 in hexane). Compound **18a** was obtained as a yellow oil (0.065 g, 91%). NMR: ^1H (250.13 MHz, C_6D_6) δ 0.35 (d, $^4J_{HP3}$ = 0.7 Hz, 27H, $(SiMe_3)_3$), 1.32 (s, 9H, *p-t*-Bu), 1.54 (d, $^5J_{HP2}$ = 0.5 Hz, 9H, *o-t*-Bu), 1.62 (d, $^5J_{HP2}$ = 0.8 Hz, 9H, *o-t*-Bu), 5.82 (dd, $^1J_{HP3}$ = 235 Hz, $^3J_{HP2}$ = 13.2 Hz, 1H, PH), 7.57 (d, 2H, $^4J_{HP}$ = 1.4 Hz, 2H, Ar); ^{13}C RMN (62.86 MHz, C_6D_6) δ 172.2 (dd, $^1J_{CP}$ = 93.5 Hz, $^1J_{CP}$ = 64.5 Hz, C_1), 154.9 (s, C_{21} or C_{25}), 154.0 (s, C_{25} or C_{21}), 151.4 (s, C_{23}), 137.7 (d, $^1J_{CP}$ = 65.6 Hz, C_{20}), 123.2 (s, C_{24} or C_{22}), 122.3 (s, C_{22} or C_{24}), 38.7 (s, C_{27}), 34.7 (m, C_{26} and C_{28}), 33.6 (s, C_6 or C_8), 33.5 (s, C_8 or C_6), 31.8 (s, C_7), 4.3 (d, $^3J_{CP}$ = 4.6 Hz, Me_3Si); ^{31}P (32.44 MHz, C_6D_6) δP_2 = 270, δP_3 = −22, $^2J_{PP}$ = 86 Hz, $^1J_{P3H}$ = 236 Hz, $^3J_{P2H}$ = 13 Hz; MS (FD) ($C_{29}H_{57}Cl\ P_2Si_3$): *m/e* = 587 (M^+).

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