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Reactivity of functionalized diphosphiranes and 1,3-diphosphapropenes towards Grignard reagents

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Abstract

The reaction of saturated and unsaturated organomagnesium compounds with the monohalogenated diphosphiranes, **1a–b**, and their isomers, the 1,3-diphosphapropenes, **2a–b**, leads to a series of substituted 1,3-diphosphapropenes and 1,3-diphosphadienes **4–8 (a–b)**, but with the dihalogeno-derivatives **1c–d** and **2c–d**, it gives quantitative yields of 1,3-diphospha-allene **9**. The reaction occurs *via* an anionic ring-opening involving an allylic anion intermediate **11a–b**, detected by ^{31}P NMR.

Introduction

It has been known for many years that cyclopropyl compounds undergo nucleophilic substitution with the greatest reluctance [1], and that ring-opening reactions generally take place instead of normal substitution. To the best of our knowledge, the few examples of substitution reactions without ring-opening concern the reaction of Grignard [2] and organolithium [3] reagents with cyclopropanes. In some cases, the reaction of preformed Grignard reagents with stabilized *gem*-dibromocyclopropanes gives monoreduced products (Fig. 1) [4].

The diphosphiranes, phosphorus analogues of cyclopropanes, are convenient models for a comparative study of reactivity in carbon and phosphorus three-membered rings. Our previous investigations in this area have shown the predominance of ring-opening reactions. Reactions with organolithium compounds [5], Lewis acids [6], under irradiation [7] or heating [8], lead to ring-opened products. In an extension of the scope of the reactivity of diphosphiranes we report their reactions towards saturated and unsaturated Grignard reagents. In order to facilitate comprehension of the mechanism, the reactivity of their photochemical isomers, 1,3-diphosphapropenes, towards the same reagents has also been studied.

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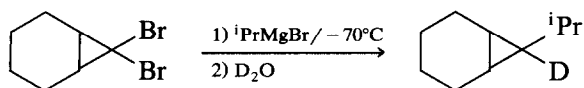


Fig. 1.

Results

We have already reported the synthesis of functionalized diphosphiranes **1a–d** by stereoselective cyclopropanation reactions of *trans*-diphosphene [9]. Irradiation at 300 nm of a degassed solution of **1a–d** in toluene or hexane for 2–4 h at room temperature gave quantitatively the corresponding 1,3-diphosphapropenes, **2a–d** (Fig. 2) [7].

(a) Reaction of Grignard reagents with monohalogenated diphosphiranes **1a–b** and 1,3-diphosphapropenes **2a–b**

The reaction of a large excess of organomagnesium bromide (50–100 molar eq) with the monohalogenated diphosphiranes **1a–b** in anhydrous diethylether or THF at room temperature for 4 h afforded the substituted 1,3-diphosphapropenes **4–8** (**a–b**) in low yields (Fig. 3). At lower temperature, the reaction does not proceed (*vide infra*). We could not detect the formation of diphosphirane **3** resulting from a substitution of a chlorine atom by the alkyl group without ring opening. The reaction of the same organomagnesium bromides with the 1,3-diphosphapropenes **2a–b** was carried out at room temperature for 2 h, but completion of the reaction does not require more than 5–10 equivalents of Grignard reagent and the resulting substituted 1,3-diphosphapropenes **4–8** were obtained in 70–80% yield (Fig. 3). Compounds **4–8** are stable and are purified by preparative thin-layer chromatography.

The allylic derivatives, 1,3-diphospha-1,5-hexadiene **7a** and 1,3-diphospha-1,5-heptadiene **8a** undergo a slow prototropic rearrangement in hexane solution at room temperature, leading to isomers **7'a** and **8'a**, respectively (Fig. 4). The same rearrangement is also observed during purification on silica gel. The substituent X^1 is a determining factor since such rearrangements were never observed for **7b** and **8b** ($X^1 = \text{Me}$).

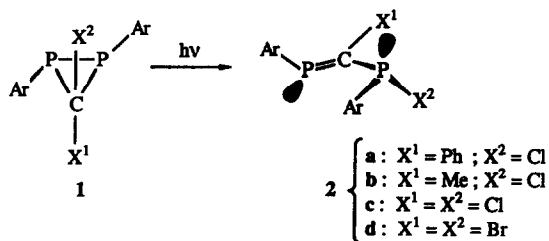


Fig. 2.

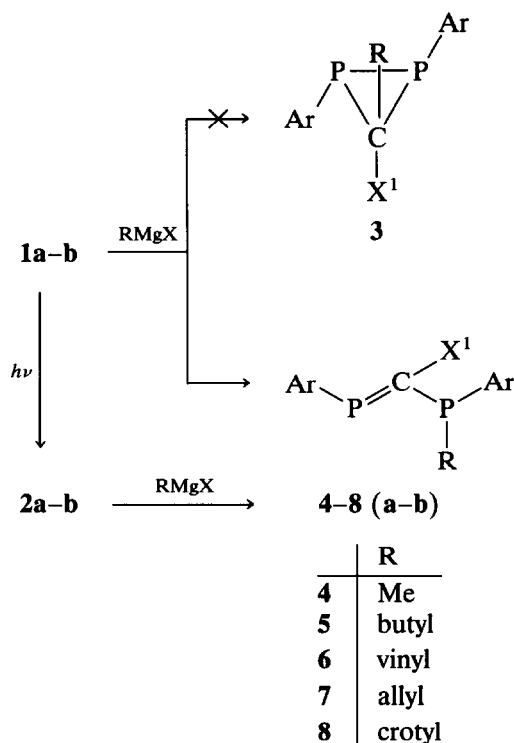


Fig. 3.

(b) Reaction of Grignard reagents with *gem*-dihalogenated diphosphiranes 1c-d and 1,3-diphosphapropenes 2c-d

The reaction of organomagnesium bromides with *gem*-dihalogenated diphosphiranes 1c-d in diethylether at 0°C for 2 h gives neither the substituted diphosphiranes 3, nor the substituted 1,3-diphosphapropenes 4-8, but the 1,3-diphosphaallene 9 [10] in 80% yield. The formation of allenes from *gem*-dihalogenocyclopropanes and Grignard reagents has already been described [11]. The reaction of organomagnesium bromides with the 1,3-diphosphapropenes 2c-d under the same conditions also led to 1,3-diphosphaallene 9 in 80-90% yield (Fig. 5).

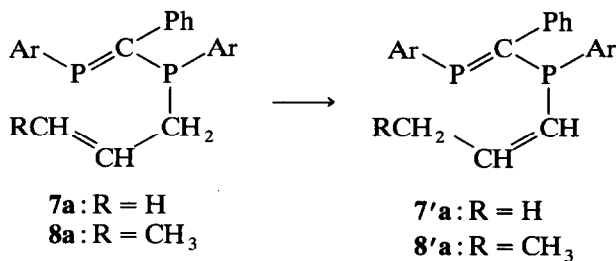


Fig. 4.

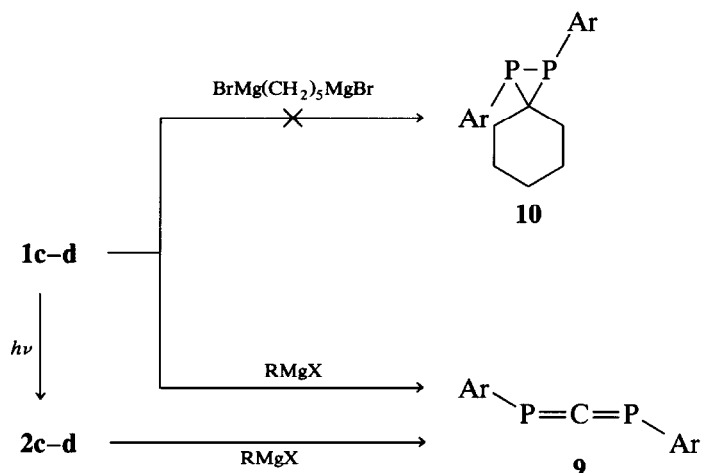


Fig. 5.

The *spiro*-diphosphirane can be prepared by cycloaddition of cyclopropyl sulfonium with diphosphene [10d,12]. In order to synthesise the *spiro*-diphosphirane **10** by cyclocondensation of diphosphiranes, the reaction of pentan-1,5-diyl dimagnesium dibromide with **1c-d** was attempted. Compound **9** was obtained as the sole product (Fig. 5).

Discussion

cis-trans Isomerization

The different atomic numbers of the substituents X^1 (C, Cl, and Br) change the designation of the compounds from *E* to *Z*. We have used *cis* and *trans* instead of the classical *Z* and *E* configuration nomenclature for the configuration about the $\text{P}=\text{C}$ double bond. However we maintain the usual *Z* and *E* nomenclature for confirmation about the $\text{C}=\text{C}$ double bond. The diphosphapropenes **4-8** were characterized by ^1H , ^{13}C and ^{31}P NMR spectroscopies. The chemical shift values of dicoordinated phosphorus in the range 220–260 ppm are characteristic of phosphalkanes, whereas the shifts of tricoordinated phosphorus (–11 to +15) are in the same range as those of phosphine compounds. The coupling constants, $^2J(\text{PP})$, (148–170 Hz) are in good agreement with the *trans* configuration about the $\text{P}=\text{C}$ double bond, consistent with the known analogues [4–9,13]. However, the compounds **4a**, **5a**, and **7a**, upon standing in hexane or benzene solution at room temperature undergo a partial *trans-cis* isomerisation (*cis* isomer: $42 < ^2J(\text{PP}) < 49$ Hz) (*ca.* 20–30% of *cis* isomer after one week at room temperature). The $\delta^{13}\text{C}$ of C_9 at low field (~ 188) is a doublet of doublets characteristic of a sp^2 carbon atom coupled with two inequivalent phosphorus atoms.

Cope rearrangement

Despite several attempts to show a possible Cope rearrangement of 1,3-diphospha-1,5-diene **7** and **8** (*ca.* 100°C, 20 h in toluene), we have never observed one.

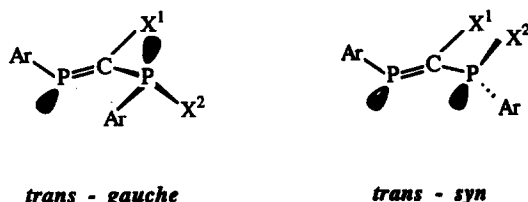
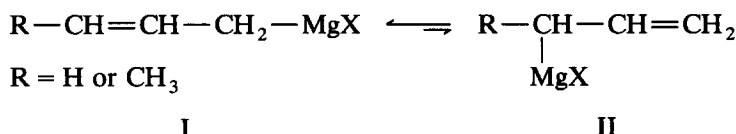


Fig. 6.

Allyl and crotyl magnesium chlorides exist at room temperature as rapidly equilibrating pairs of classical structures (forms I and II) with the equilibrium well to the left [14]:



As mentioned before, diphosphiranes **1** and 1,3-diphosphapropenes **2** do not react at low temperature with allylic Grignard reagents but reaction occurs at room temperature and gives the 1,3-diphospha-1,5-dienes **7** and **8**. Unlike Appel et al. [15], we have not detected the isomer arising from the direct substitution of form II. This result can be rationalised by the lower reactivity of substituted derivatives **2** (X¹ = Ph, Me) compared to the unsubstituted analogous (X¹ = H) of Appel, since for the latter, the reaction can occur at low temperature (−78°C). We explain this by the existence of two conformations having different reactivity. We have already demonstrated the presence of two *syn* and *gauche* conformations for *trans*-1,3-diphosphapropenes, distinguishable by their ²J(PP) coupling constants (Fig. 6) [8,16]. Whereas ²J(PP) for *trans-gauche* isomer is in the range of 100 Hz, for *trans-syn* isomer it is 350–450 Hz. Furthermore, the *syn* isomer, less stable than *gauche*, exhibits a higher reactivity towards nucleophiles such as methoxide, hydride, etc. [17]. We therefore suggest that the unsubstituted 1,3-diphosphapropene (X¹ = H) arising from dichloromethylene phosphine after dehydrohalogenation is *syn* (²J(PP) = 357 Hz) [15–17]. The absence of the Cope rearrangement is essentially due to steric hindrance around the C=C double bond in E configuration (main product), as also suggested by Appel [15].

In contrast, the allyl- and crotyl-substituted 1,3-diphosphapropenes **7a** and **8a**, in solution at room temperature for one week, undergo a prototropic rearrangement [18] and give the vinylic *Z* and *E* isomers.

Mechanism

The formation of the same substituted 1,3-diphosphapropenes **4–8** from diphosphiranes **1** and from their photochemical isomers **2** raises the problem of mechanism. The reaction could be either a concerted mechanism (simultaneous nucleophilic substitution, ring opening and loss of halogen), or prior ring opening followed by nucleophilic substitution (Fig. 7). The former can be excluded since we

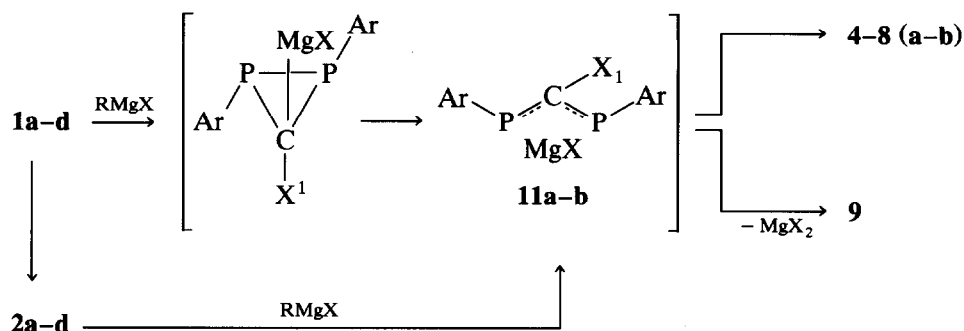


Fig. 7.

have never observed any substitution product from the *gem*-dihalogenodiphosphiranes **1** or their isomers **2**.

Recent calculations [19] and experimental results [5–7] indicate that radical and cationic ring opening of diphosphiranes (resulting from a homolytic or heterolytic rupture of the C–X bond followed by rupture of the P–P bond) give a mixture of *cis* and *trans* isomers, in contrast to anionic ring-opening reactions which lead to *trans*-1,3-diphosphapropenes only. The fact that only the *trans* isomers of **4–8** were observed at completion of the reaction suggests that the reaction of Grignard reagents with diphosphiranes **1** or their isomers **2** could involve an anionic ring opening followed by substitution at phosphorus *via* an allylic anion intermediate **11a–b**, detected by ^{31}P NMR spectroscopy (singlet at 54 ppm). We have already demonstrated such a mechanism in the case of organolithium reagents where the allylic intermediate has also been detected by ^{31}P NMR spectroscopy at low temperature [5]. The formation of allene **9** probably involves the same mechanism, and an unstable allylic anion intermediate.

Experimental

All reactions were performed under argon. All solvents were reagent grade and were purified, dried and degassed by standard techniques. The methyl-, butyl-, and crotyl-magnesium halides are prepared according to the procedure already described [20]. The vinyl, allyl and pentan-1,5-diyl Grignard reagents are commercially available. For TLC separation, Merck precoated preparative TLC plates (silica gel 60, 2 mm) and Merck precoated analytic TLC plates (silica gel 60, 0.2 mm) were used throughout. Yields of products were determined after crystallization and/or chromatography. The NMR spectra (^1H , ^{31}P , ^{13}C) were recorded on Bruker AM-300-WB, 250 WM, or AC 80 instruments. Mass spectra were obtained on a Ribermag R1010 (DCI/ NH_3).

General procedure for the synthesis of substituted 1,3-diphosphapropenes **4–8**

An excess of Grignard reagent (5–10 eq. for **2**; 50–100 eq. for **1**) in diethylether (in THF for vinylmagnesium bromide) was added dropwise to a solution of **1** or **2** (0.10 mmol) in 10 mL of dry ether (THF). The mixture was stirred at room temperature for 1–2 h for **2** (2–4 h for **1**), then evaporated to dryness under

Compd	4	5	6	7	8
R	$-\underset{\alpha}{\text{CH}_3}$	$-\underset{\alpha}{\text{CH}_2}-\underset{\beta}{\text{CH}_2}-\underset{\gamma}{\text{CH}_2}-\underset{\delta}{\text{CH}_3}$	$-\underset{\alpha}{\text{CH}}=\underset{\beta}{\text{CH}_2}$	$-\underset{\alpha}{\text{CH}_2}-\underset{\beta}{\text{CH}}=\underset{\gamma}{\text{CH}_2}$	$-\underset{\alpha}{\text{CH}_2}-\underset{\beta}{\text{CH}}=\underset{\gamma}{\text{CH}}-\underset{\delta}{\text{CH}_3}$

5b; yellow oil; yield = 70%; R_f = 0.6; MS (FD) m/e = 636 ($M^+ + 1$); ^{31}P NMR (32.44 MHz, C_6D_6) δ 239.5 (P_A); 6.5 (P_X); $^2J(\text{PP})$ = 152 Hz; ^1H NMR (80.13 MHz, C_6D_6) δ 0.85 (m, 3H, CH_3); 0.88 (m, 3H, CH_3); 1.12 (m, 2H, C_α); 1.20 (m, 4H, C_β , C_γ); 1.26 (s, 9H, p - ^tBu); 1.32 (s, 9H, p - ^tBu); 1.42 (s, 9H, o - ^tBu); 1.56 (s, 9H, o - ^tBu); 1.64 (s, 9H, o - ^tBu); 1.68 (s, 9H, o - ^tBu); ^{13}C NMR (75.43 MHz, C_6D_6) δ 188.8 (dd, $^1J(\text{CP})$ = 75 Hz; $^1J(\text{CP})$ = 49 Hz, C_9); 161.0 (s, C_2); 155.2 (d, $^2J(\text{CP})$ = 28 Hz, C_2); 154.8 (s, C_2); 153.9 (s, C_2); 151.0 (d, $^4J(\text{CP})$ = 2 Hz, C_4); 149.6 (s, C_5); 138.7 (d, $^1J(\text{CP})$ = 69 Hz, C_1); 129.5 (dd, $^1J(\text{CP})$ = 67 Hz, $^3J(\text{CP})$ = 6 Hz, C_1); 123.1 (s, C_3); 122.5 (m, 2C_3); 122.0 (s, C_3); 40.5 (broad s, C_5); 40.1 (broad s, C_5); 39.5 (d, $^3J(\text{CP})$ = 4 Hz, C_5); 38.5 (s, C_5); 34.5 (s, 6C_7); 34.3 (s, C_6); 33.8 (s, C_6); 33.3 (broad

s, $6C_7$); 31.9 (d, $^3J(\text{CP}) = 10.0$ Hz, C_7); 31.5 (s, $3C_8$); 31.35 (d, $^2J(\text{CP}) = 16$ Hz, C_β); 31.30 (s, $3C_8$); 25.5 (dd, $^2J(\text{CP}) = 20$ Hz, $^2J(\text{CP}) = 14$ Hz, C_{10}); 25.0 (d, $^1J(\text{CP}) = 16$ Hz, C_α); 14.2 (s, C_δ).

6a–b are not stable and decompose in solution. Consequently, they have not been isolated. The yields were determined with ^{31}P NMR spectra of the reaction mixtures. **6a**: 15%; ^{31}P NMR (32.44 MHz, C_6D_6) δ 236.2 (P_A); 5.3 (P_X); $^2J(\text{PP}) = 164$ Hz; **6b**: 40%; ^{31}P NMR (32.44 MHz, C_6D_6) δ 237 (P_A); 15 (P_X); $^2J(\text{PP}) = 164$ Hz.

7a: yield = 90%; $R_f = 0.68$ (eluent: hexane/dichloromethane 95/5); MS (DCI/ NH_3) $m/e = 683$ ($M^+ + 1$); ^{31}P NMR (32.44 MHz, C_6D_6) δ 239.6 (P_A); 6.4 (P_X); $^2J(\text{PP}) = 164$ Hz; ^1H NMR (250 MHz, C_6D_6) δ 1.17 (s, 9H, p - ^1Bu); 1.24 (s, 9H, p - ^1Bu); 1.39 (s, 9H, o - ^1Bu); 1.45 (s, 9H, o - ^1Bu); 1.75 (s, 9H, o - ^1Bu); 1.77 (s, 9H, o - ^1Bu); 3.56 (m, 5H, allyl); 6.40 (m, 5H, Ph); 7.40 (m, 4H, Ar); ^{13}C NMR “ J mod.” (62.9 MHz, C_6D_6) δ 188.4 (dd, $^1J(\text{CP}) = 79$ Hz, $^1J(\text{CP}) = 45$ Hz, C_9); 155.5 (m, $2C_2$); 150.8 (s, $2C_2$); 150.7 (s, C_4); 149.8 (s, C_4); 141.0 (dd, $^2J(\text{CP}) = 18$ Hz, $^2J(\text{CP}) = 14$ Hz, C_{10}); 137.4 (d, $^1J(\text{CP}) = 70$ Hz, C_1); 135.7 (dd, $^2J(\text{CP}) = 18$ Hz, $^4J(\text{CP}) = 5.5$ Hz, C_β); 126.6 (s, C_{13}); 126.4 (s, C_{12}); 126.3 (s, C_{11}); 125.5 (s, C_3); 123.08 (s, C_3); 122.7 (s, C_3); 120.4 (s, C_3); 117.2 (d, $^3J(\text{CP}) = 14$ Hz, C_7); 39.4 (s, C_5); 37.0 (f(t), $|J(\text{CP})| = 25$ Hz, C_α); 34.8 (s, C_5); 34.6 (s, C_7); 34.4 (s, C_7); 34.3 (d, $^4J(\text{CP}) = 5$ Hz, C_7); 33.0 (d, $^4J(\text{CP}) = 4$ Hz, C_7); 32.0 (s, C_5); 31.6 (s, C_8); 31.28 (s, C_8); 31.20 (s, C_5); Anal. Found: C, 79.14; H, 10.58. $\text{C}_{46}\text{H}_{68}\text{P}_2$ calcd.: C, 80.89; H, 10.04.

7b: $R_f = 0.65$ (eluent: hexane/dichloromethane: 95/5); MS (DCI/ NH_3): $m/e = 620$ ($M^+ + 1$); ^{31}P NMR (32.44 MHz, C_6D_6) δ 227.8 (P_A); 3.9 (P_X); $^2J(\text{PP}) = 153$ Hz.

8a: yield = 90%; $R_f = 0.65$; MS (DCI/ NH_3): $m/e = 697$ ($M^+ + 1$); ^{31}P NMR (32.44 MHz, C_6D_6) δ 239.6 (P_A); 8.5 (P_X); $^2J(\text{PP}) = 164$ Hz, and 238.7 (P_A); 7.7 (P_X); $^2J(\text{PP}) = 163$ Hz; ^{13}C NMR “ J Mod” (62.89 MHz, C_6D_6) δ 188.0 (dd, $^1J(\text{CP}) = 81.0$ Hz, $^1J(\text{CP}) = 47.5$ Hz, C_9); 187.7 (dd, $^1J(\text{CP}) = 80.9$ Hz, $^1J(\text{CP}) = 47.2$ Hz, C_9); 155.5 (broad s, C_2); 150.7 (m, C_2); 150.6 (s, C_4); 149.8 (s, C_4); 141.0 (dd, $^2J(\text{CP}) = 17.5$ Hz, $^2J(\text{CP}) = 13.5$ Hz, C_{10}); 137.6 (d, $^1J(\text{CP}) = 70.4$ Hz, C_1); 137.56 (d, $^1J(\text{CP}) = 71.4$ Hz, C_1); 127.0 (m, C_7); 126.2 (s, C_{11}); 126.3 (s, C_{12}); 126.4 (s, C_{13}); 125.4 (s, C_3); 125.1 (s, C_3); 122.6 (s, C_3); 122.0 (d, $^2J(\text{CP}) = 4$ Hz, C_β (Z)); 120.4 (d, $^2J(\text{CP}) = 10.0$ Hz, C_β (E)); 120.2 (s, C_3); 38.4 (m, C_α (E)); 35.6 (f(t), ($^1J(\text{CP}) + ^3J(\text{CP}) = 25$ Hz, C_α (Z)); 35.4 (d, $J(\text{CP}) = 6.0$ Hz, C_5); 34.8 (s, C_5); 34.3 (s, C_7); 34.2 (s, C_7); 34.1 (s, C_7); 33.9 (s, C_7); 32.3 (s, C_5); 31.6 (s, C_8); 31.3 (s, C_8); 30.7 (s, C_6); 30.3 (s, C_5); 30.2 (d, $J(\text{CP}) = 3$ Hz, C_5); 18.5 (d, $J(\text{CP}) = 1.3$ Hz, C_δ (Z)); 13.5 (d, $J(\text{CP}) = 4.0$ Hz, C_δ (E)).

8b: yield = 80%; MS (DCI/ NH_3): $m/e = 634$ ($M^+ + 1$); ^{31}P NMR (32.44 MHz, C_6D_6) δ 242.6 (P_A); 5.3 (P_X); $^2J(\text{PP}) = 150$ Hz, and 231.6 (P_A); 5.5 (P_X); $^2J(\text{PP}) = 148$ Hz.

7'a: MS (DCI/ NH_3) $m/e = 683$ ($M^+ + 1$); ^{31}P NMR (32.44 MHz, C_6D_6) δ 246.0 (P_A); -12.0 (P_X); $^2J(\text{PP}) = 153$ Hz, and 244.0 (P_A); 3.5 (P_X); $^2J(\text{PP}) = 154$ Hz.

8'a: MS (DCI/ NH_3) $m/e = 697$ ($M^+ + 1$); ^{31}P NMR (32.44 MHz, C_6D_6) δ 247.0 (P_A); -11.0 (P_X); $^2J(\text{PP}) = 154$ Hz, and 245.0 (P_A); 4.0 (P_X); $^2J(\text{PP}) = 157$ Hz.

General procedure for the synthesis of 1,3-diphosphaallene 9

An excess of Grignard reagent (5–10 equiv. for **1**; 4 equiv. for **2**) in diethylether (in THF for vinylmagnesium bromide) was added dropwise to a solution of **1** or **2** (0.15 mmol) in 10 mL of dry ether (THF). The mixture was stirred at room temperature for 1–2 h for **2** (2–4 h for **1**), then evaporated to dryness under vacuum. The residue was taken up in anhydrous hexane and the suspension was filtered through Celite. The filtrate was concentrated and purified on a dry silica gel column (eluent: hexane) affording compound **9** in 80–90% yield.

9: $R_f = 0.7$ (eluent: hexane); ^{31}P NMR (32.44 MHz, C_6D_6) δ 141.0.

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