(Na_2SO_4). Evaporation of the solvent left a pale yellow residue (110 mg). This was chromatographed on silica gel with ether–pentane (1:1), giving first the cubane **6** (37 mg, 39%) and then the cuneane **7** (32 mg, 34%). **6**: mp 112–113 °C; IR (KBr) ν 2991, 2982, 2938, 1695, 1415, 1383, 1093, 1041, 750, 569 cm^{-1}; ^1H NMR δ 4.34 (m, 4 H), 3.88 (m, 2 H), 2.79 ppm (s, 6 H); ^{13}C NMR δ 162.5, 67.8, 54.8, 42.6, 27.5 ppm; *m/e* 188 (P^+, 80), 162 (100). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.42; N, 14.88. Found: C, 70.11; H, 6.47; N, 14.72. **7**: mp 78–79 °C; IR (KBr) ν 3043, 3011, 2923, 1699, 1684, 1427, 1377, 1087, 923, 809, 750, 574, 467 cm^{-1}; ^1H NMR δ 3.07 (m, 2 H), 2.77 (s, 6 H), 2.63 ppm (m, 4 H); ^{13}c NMR δ 161.5 (s), 67.8 (s), 46.2 (d, J = 154 Hz), 3.16 (d, J = 180 Hz), 28.1 (q) ppm; *m/e* 188 (P^+, 10), 162 (100). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.42; N, 14.88. Found: C, 70.08; H, 6.31; N, 14.75.

3,5-Dinitro-3,5-diazahexacyclo[5.4.0.0^{2,6}.0^{2,10}.0^{6,9}.0^{8,11}]undecan-4-one (8). 100% Nitric acid (315 mg, 5.00 mmol)[14] was injected dropwise into a stirred solution of dry CH_2Cl_2 (3 mL) and acetic anhydride (510 mg, 5.00 mmol) at 0 °C under argon. After 30 min at 0 °C, the reaction mixture was allowed to warm to room temperature and then recooled to 0 °C. Powdered cubanourea **2** (65 mg, 0.41 mmol) solid was added all at once; stirring was continued at 0 °C for 2 h. Crushed ice was then added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The extract was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to give fine crystalline needles of **8** (83 mg, 82%): mp 210 °C dec, IR (KBr) ν 1802, 1573, 1310, 1160, 1140, 1015, 883, 729, 699 cm^{-1}; UV (CH_3CN) λ_{max} 279 nm (ϵ 5500); ^1H NMR δ 4.69 (m, 4 H), 4.19 ppm (m, 2 H); ^{13}C NMR δ 141.2, 63.1, 54.9, 43.6 ppm. Anal. Calcd for $C_9H_6N_4O_5$: C, 43.21; H, 2.41; N, 22.39. Found: C, 43.,07; H, 2.27; N, 22.13.

Single-crystal X-ray diffraction analysis of 3,5-dinitro-3,5-diazahexacyclo[5.4.0.0^{2,6}.0^{2,10}.0^{6,9}.0^{8,11}]undecan-4-one: $C_9H_6N_4O_5$, FW = 250.2; monoclinic space group $P2_1/c$; a = 9.669 (3), b = 5.972 (1), c = 16.584 (6) Å; β = 91.12 (3)°; vol. = 957.3 (5) Å^3; Z = 4; ρ_{calc} = 1.736 g/cm^3; λ(Mo Kα) = 0.71073 Å; μ = 1.36 cm^{-1}; F(000) = 512, T = 295 K.

A clear colorless 0.10 × 0.20 × 0.45 mm crystal, shaped like a rectangular prism, was used for data collection on an automated Nicolet R3m/V diffractometer with incident beam monochromator. Lattice parameters were determined from 30 centered reflections within 20 ≤ 2θ ≤ 30°. The data collection range of *hkl* was: 0 ≤ h ≤ 10, −6 ≤ k ≤ 0, −17 ≤ l ≤ 17, $(\sin(\theta)/\lambda)_{max}$ = 0.5384 Å^{-1}. Three standards were monitored every 60 reflections and exhibited a maximum random variation of 2.0% during data collection. A total of 1562 reflections were measured in the $\theta/2\theta$ mode with a variable 2θ scan rate, ranging from 10.0 to 31.2 deg/min. There were 1262 *unique* reflections, and 1121 were observed with $F_o > 3\sigma(F_o)$. The structure was solved by direct methods with the aid of program SHELXTL.[17] The full-matrix least-squares refinement varied 188 parameters: atom coordinates, anisotropic thermal parameters for all non-H atoms, and isotropic thermal parameters for the hydrogens. Final residuals were R = 0.034 and R_w = 0.041 with final difference Fourier excursions of 0.17 and −0.23 e Å^{-3}.

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Registry No. 1, 129103-49-7; **2**, 129103-50-0; **5**, 129103-52-2; **6**, 129103-53-3; **7**, 129103-54-4; **8**, 129103-55-5; cubane-1,2-dicarboxylic acid, 129103-51-1.

Supplementary Material Available: ^{13}C NMR spectra of compounds 1 and **5**; numbered ORTEP drawings of compounds **2** and 8; tables of atomic position parameters, Cartesian coordinates, bond distances, bond angles, torsion angles, and anisotropic thermal parameters for both X-ray structures (11 pages); tables of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Photochemistry of Functionalized Diphosphiranes

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The structure of the functionalized *trans*-diphosphiranes **1a–e**, obtained by reaction of halogenocarbenes with the *trans*-diphosphene is confirmed by X-ray diffraction. The photolysis of **1a–e** lead to the functionalized *cis*- and *trans*-1,3-diphosphapropenes **2a–e** as major products, via the diphosphiranyl **7** and the diphosphapropenyl **8** radical intermediates. The latter are characterized by ESR spectroscopy using the spin-trap method. The trans configuration of **2a** is also confirmed by X-ray diffraction. The mechanism of the ring-opening, involving P–P bond rupture, is discussed.

Whereas *gem*-dihalocyclopropanes are known to undergo thermally promoted skeletal rearrangements to 1,2-dihaloprop-2-ene derivatives[1] (Figure 1, reaction A), their photochemistry is different. For example, the irradiation of *gem*-dichloroarylcyclopropanes with UV light produces a dichlorocarbene (Figure 1, reaction B),[2] characteristic of reactions analogous to the photochemical fragmentation

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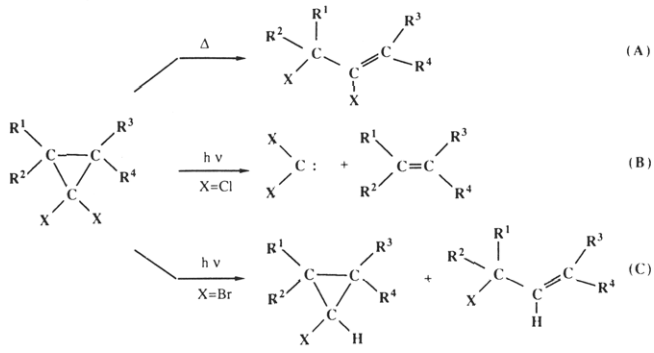
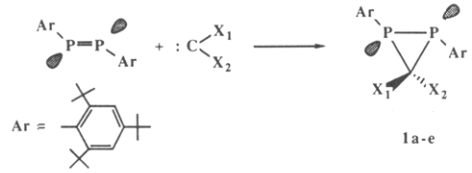


Figure 1. (A) Thermal ring opening of *gem*-dihalocyclopropanes (X = Cl, Br). (B) Photochemical fragmentation of *gem*-dichlorocyclopropanes. (C) Photochemical ring opening and photoreduction of *gem*-dibromocyclopropanes.



1	a	b	c	d	e
X_1	Cl	Ph	Me	Br	Ph
X_2	Cl	Cl	Cl	Br	Br

Figure 2. Synthesis of functionalized diphosphiranes **1a–e** by reaction of halocarbenes with the *trans*-diphosphene.

of arylcyclopropanes to arenes and methylene.[3] In contrast, the *gem*-dibromocyclopropanes are easily converted to the corresponding monobromocyclopropanes by a photoreduction process (Figure 1, reaction C).[4]

Diphosphiranes, the phosphorus analogues of cyclopropanes, provide unique opportunities for comparative studies. Previous work in our laboratory has focused on the study of the reactivity of these strained molecules.[5] Their reactions with organoalkali metals,[6] Lewis acids, and Brønsted acids,[7] as well as heating,[8] invariably lead to ring-opening products. Here, we report for the first time the photochemical reactions of functionalized diphosphiranes. This paper describes: (i) the X-ray crystal structure of precursor diphosphirane **1a**, (ii) the mechanisms for ring opening and/or fragmentation of these strained heterocycles under irradiation, (iii) ESR spectroscopic evidence of the reaction intermediates, and (iv) the X-ray crystal structure of functionalized 1,3-diphosphapropenes **2a**.

Results

The stereoselective cyclopropanation[5] of *trans*-diphosphene with halogenocarbenes gave various symmetrical and unsymmetrical functionalized diphosphiranes **1a–e** (Figure 2).

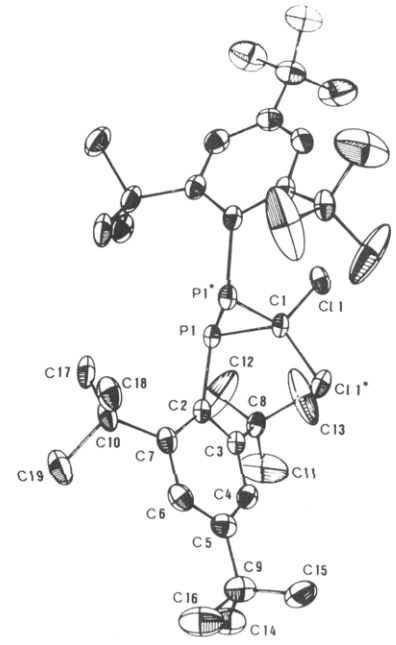


Figure 3. ORTEP diagram of the crystal structure of **1a** selected bond lengths (pm) and angles (deg): P(1)–P(1)*, 224.5 (2), P(1)–C(1) 186.3 (4), P(1)–C(2) 185.8 (4), C(1)–Cl(1) 176.6 (3); P(1)*–P(1)–C(1) 52.7 (2), P(1)–C(1)–P(1)* 74.3 (2), P(1)*–P(1)–C(2) 107.4 (1), C(1)–P(1)–C(2) 101.8 (1), Cl(1)–C(1)–Cl(1)* 110.6. Torsional angles (deg): P(1)*–P(1)–C(2)–C(7) 45.3, P(1)–C(2)–C(7)–C(6) 154.4. Dihedral angle between planes: ⟨P(1)P(1)*C(1)⟩–⟨C(2)C(3)C(4)C(5)C(6)C(7)⟩ 84.8°.

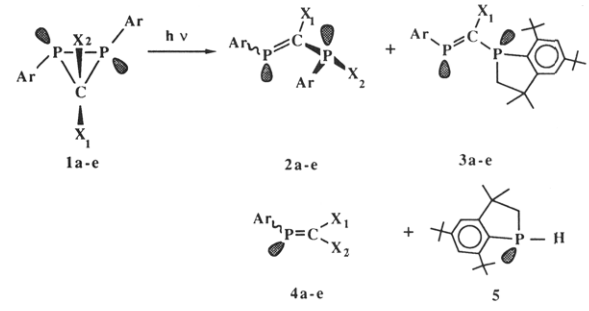
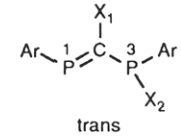
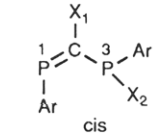


Figure 4. Photochemical products obtained by irradiation of diphosphiranes **1a–e**.

Table I. ^{31}P NMR Parameters of the Trans and Cis Functionalized 1,3-Diphosphapropenes 2a–e





	trans			cis		
	$\delta_{P(1)}$	$\delta_{P(3)}$	J_{PP}, Hz	$\delta_{P(1)}$	$\delta_{P(3)}$	J_{PP}, Hz
2a	276	75	106	288	83	45
2b	272	84	161	302	81	66
2c	273	84	143	281	76	53
2d	293	75	109	not detected		
2e	278	80	162	304	71	71

The X-ray structure of diphosphirane **1a** is presented in Figure 3. This chiral molecule in a trans configuration has a 2-fold crystallographic axis.

The irradiation at 300 nm of diphosphiranes **1a–e** (ca. 25 °C, 2–4 h) in degassed solutions of hexane or toluene gave largely 1,3-diphosphapropenes, **2**. Dehydrohalogenated 1,3-diphosphapropenes, **3**, phosphaalkenes, **4**, and

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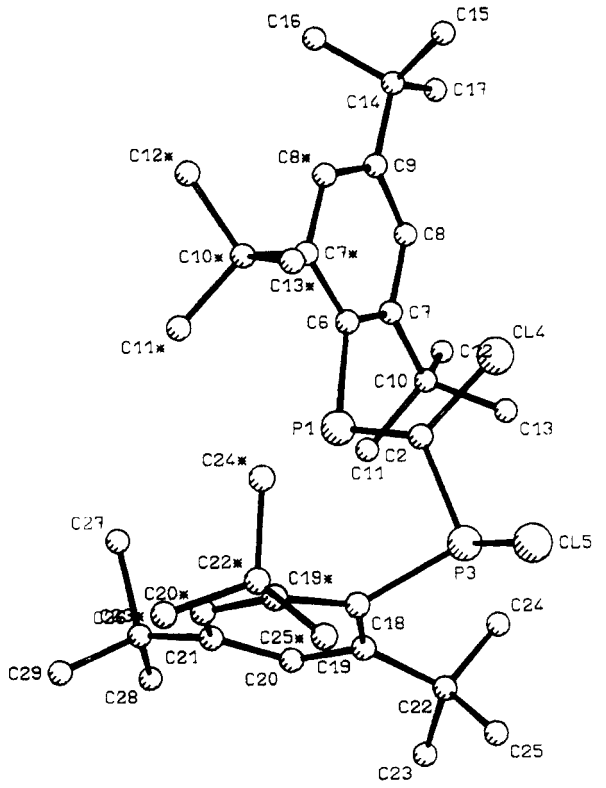


Figure 5. X-ray crystal structure of **2a**. Important bond lengths (pm) and angles (deg): P(1)–C(2) 166.1, P(3)–C(2) 181.8, P(3)–Cl(5) 189.0; P(3)–C(2)–P(1) 120.0, C(6)–P(1)–C(2) 104.7, C(18)–P(3)–C(2) 97.6. Torsional angles (deg): C(6)–P(1)–C(2)–Cl(4) 0.0, Cl(4)–C(2)–P(3)–Cl(5) 43.1, C(6)–P(1)–C(2)–P(3) –154.6, Cl(4)–C(2)–P(3)–C(18) 163.1.

phosphaindan, **5**, were also identified as minor products (Figure 4).

The 1,3-diphosphapropenes **2** were obtained in the cis and trans configurations[9,10] exhibiting different ^{31}P NMR parameters (Table I). The ratio of cis/trans isomers is about 10/90 and only the trans isomers could be isolated (owing to the difference of the atomic numbers of X_1 substituents (C, Cl, Br) that changes *E* to *Z*, we have used cis and trans instead of the classical *Z* and *E* configurational nomenclature).

The trans configuration of the 1,3-diphosphapropene **2a** obtained by photochemical reaction of **1a** is confirmed by X-ray diffraction study (Figure 5).

The *trans*-1,3-diphosphapropenes **2a–c** undergo simple methanolysis in the presence of triethylamine at room temperature to afford 1,3-diphosphapropenes **6a–c** in 50–90% yields. The ^{31}P NMR parameters for **6a–c** support the configurational integrity of the trans isomer.

1,3-Diphosphapropenes **3a–c**, obtained as byproducts, have been isolated and characterized as trans isomers. The phosphaalkenes, **4**, have also been isolated and characterized. Compounds **4b** and **4c** are mixtures of *Z* and *E* isomers. Due to its instability, compound **5** could only be characterized by ^{31}P NMR spectroscopy of the reaction mixture (δ ^{31}P = –79, J_{PH} = 172 Hz).

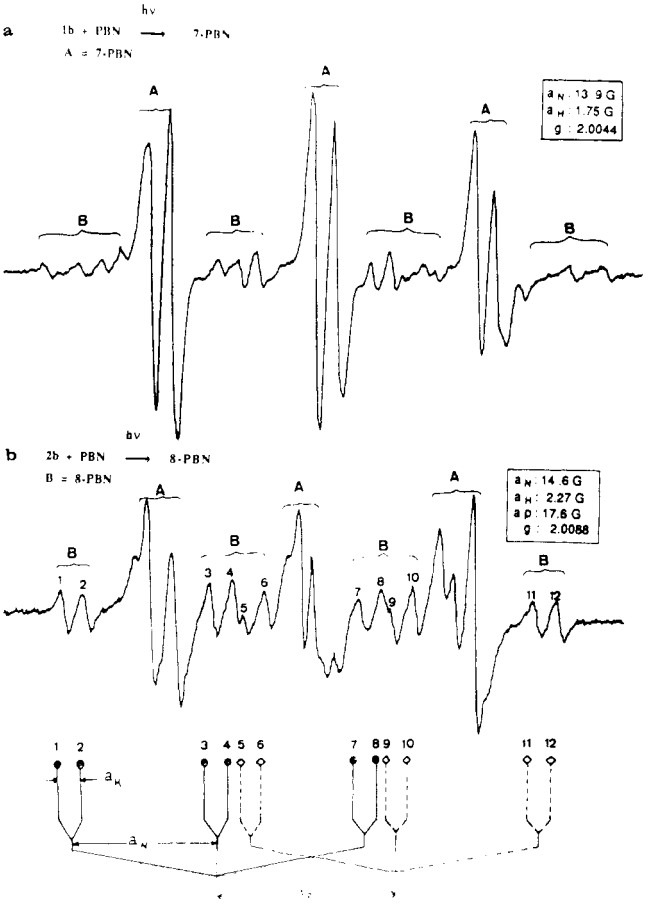
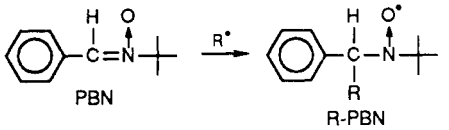


Figure 6. ESR spectra of spin-trap addition (PBN) to the diphosphirane **1b** (a), and the 1,3-diphosphapropene **2b** (b), according to the general reaction:



The diphosphiranyl, **7**, and 1,3-diphosphapropenyl, **8**, radical intermediates were detected and characterized by ESR, using spin-trapping methods (Figures 6, 7).

Discussion

Generally, the experimental and theoretical approach of the electrocyclic reactions are well described in the chemistry of cyclopropanes,[11] but there are only few electrocyclic reactions in "heteroelementary chemistry" and in particular organophosphorus chemistry.[12] The functionalized diphosphiranes possess a skeletal disymmetry and serve as an appropriate model for a comparative study.

The intracyclic P–P and P–C bond lengths of diphosphirane **1a** are longer than those of the unfunctionalized homologue, diphosphamethylenecyclopropane.[13] This lengthening is probably a consequence of the presence of bulky substituents on phosphorus atoms. Indeed, with the

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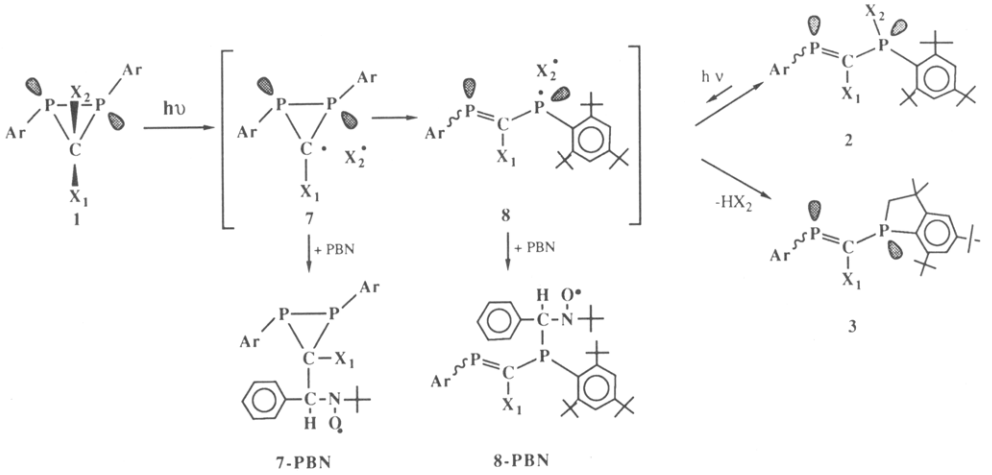

Figure 7. Mechanism of the ring-opening reaction of diphosphiranes.

thiadiphosphirane[14] which has the same substituents on phosphorus, the P–P bond length is identical with **1a**.

Addition of carbene on diphosphene leads to a lengthening of the P–P bond but also induces a slight modification of the ($P_1P^*_1C_2$) angle (107° instead of 104°). This fact, confirmed by ab initio calculations[15] about cyclopropanation reaction, is consistent with a perpendicular approach of the carbene to the $C_2P_1P^*_1C^*_2$ plane.

Since the bond enthalpy values are different (ΔH_{P-P} = 53 kcal mol^{-1} and ΔH_{P-C} = 63 kcal mol^{-1}),[16] the homolytic rupture of the C–X bond under irradiation induces a weakening of the cycle and leads to the ring opening by the preferential P–P bond rupture.

The ^{31}P NMR spectra of the 1,3-diphosphapropenes **2a–e**, **3a–c**, **6a–c** are characterized by chemical shifts at low fields for dicoordinated phosphorus atoms (230–303.5 ppm) whereas the tricoordinated phosphorus atoms have a chemical shift at ~6–124 ppm.

These 1,3-diphosphapropenes show in each case an AX spin system with a coupling constant $^2J_{PCP}$ varying between 106 (**2a**) and 162 Hz (**2e**). In the same way, we observe a decrease of the $^2J_{PCP}$ coupling constants for the 1,3-diphosphapropenes with an electron-withdrawing substituent on the carbon atom (**2b–2a**: ΔJ = 60 Hz).

The configuration around the P=C double bond was determined using the empirical rule developed by Fluck.[17] When the tricoordinated phosphorus atom is syn to the lone pair of the dicoordinated phosphorus atom around the P=C double bond (trans), $^2J_{PCP}$ is larger than that of the tricoordinated phosphorus atom in the anti position (cis).

The $^2J_{PCP}$ values in **3** are 50–150 Hz larger than those in **2**. The $^2J_{PCP}$ values for 1,3-diphosphapropenes also increase with temperature. So, for compounds **2** and **6**, we observe a variation of $^2J_{PP}$ by 10 and 32 Hz, respectively.

The trans configuration of 1,3-diphosphapropene **2a** has been confirmed by crystal structure analysis. Figure 5 indicates that **2a** has a π symmetry plane containing C(26), C(21), C(18), Cl(5), Cl(4), C(2), P(1), C(6), C(9), and C(14) whereas the tricoordinated phosphorus atom P(3) occupies two statistically equivalent positions with respect to this plane: the distance P(3)-π is 67 pm. The two Ar substituents are nearly orthogonal to this symmetry plane (93.3° and 82.9°, respectively, for the substituents directly bonded to P(2) and P(3)). The bond lengths $d_{P=C}$ equal to 167 pm and d_{P-C} in the range 181.0–190.8 pm are in good agreement with the published structure of 1,3-diphosphapropenes.[18] However, the conformation of **2a** is different from the conformation of the similar 1,3-diphosphapropenes obtained by thermal ring opening of unsymmetrical diphosphiranes:[8] in particular **2a** has a gauche conformation in which the tricoordinated phosphorus P(3) lone pair is approximatively orthogonal to the π plane.

Mechanism. (a) Formation of 1,3-Diphosphapropenes 2 and 3. Contrary to 1-chlorocyclopropyl radical observed only at low temperature,[19] we could not detect nor identify short-lived free radicals in the temperature range –90 to 30 °C, when the compound **1b** in toluene is irradiated in situ in the ESR cavity. So, we have employed the spin-trapping technique using α-phenyl *tert*-butyl nitrone (PBN), which reacts with the free radical, giving rise to a relatively stable ESR-observable "spin adduct".[20] In toluene, the photolysis of PBN did not produce significant concentration of nitroxide radicals. When the diphosphirane **1b** was irradiated (ca. 25 °C, toluene) in the presence of PBN, we detected the persistent radical consistent with nitrogen and β-hydrogen hyperfine coupling of α-substituted-benzyl *tert*-butyl nitroxide, **7-PBN** (a_N = 13.90 G, a_H = 1.75 G, g = 2.0044) (Figures 6a and 7). Furthermore, we observe the presence of a more complex ESR spectrum whose radical intensity increases with time. This spectrum consists principally of a 1:1:1 triplet due to splitting by hydrogen and phosphorus coupling. The structure of the nitrosyl was believed to be the "spin adduct" **8-PBN** (a_N = 14.6 G, a_H = 2.27 G, a_P = 17.6 G, g = 2.0088). **8-PBN** is actually produced under irradiation, after addition of 1,3-diphosphapropene **2b** to the latter solution (Figures 6b and 7). Contrary to the results of Janzen,[21] under our conditions, chlorine atoms are not

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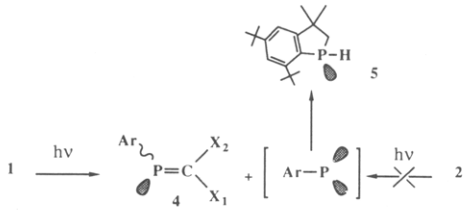

Figure 8. The formation of the phosphaalkene **4** and the phosphaindan **5** occurs only starting from **1**.

trapped by PBN (a_N = 12.10 G, a_H = 0.75 G, a_{Cl} = 4.88, 6.05 G). From this result, we can conclude that the mechanism of the ring opening of diphosphirane is the consequence of the homolytic rupture of the C–X bond leading to the diphosphiranyl radical **7**. This unstable radical, after the preferential P–P bond rupture, gives the 1,3-diphosphapropenyl radical **8**. The unsaturated radical **8** undergoes two competitive reactions: (i) an equilibration arising from reversible attack due to the coming back of the halogen radical on the phosphorus atom, leading to 1,3-diphosphapropene, **2**, and (ii) a dehydrohalogenation supported by a classical radical rearrangement of *tert*-butyl group affording to 1,3-diphosphapropene, **3**.[22]

The anionic ring opening reactions of diphosphiranes lead to the *trans*-1,3-diphosphapropenes only.[6] The ring opening of the diphosphiranyl radical gives a mixture of cis and trans isomers **2**. These two isomers arise neither from the previous cis ⇌ trans isomerization of the diphosphiranes **1a–e**[23] nor from a **2** cis ⇌ **2** trans equilibrium (under the same conditions, the irradiation of **2** trans did not afforded **2** cis), but presumably they are the consequence of the nonselectivity of the ring-opening process.

(b) Formation of Phosphaalkenes, 4. The presence of phosphaalkenes, **4** and phosphaindan, **5**, as byproducts arises from a fragmentation reaction analogous to the photochemical fragmentation of arylcyclopropanes,[3] cyclotrigermanes,[24] or cyclotrisilanes.[25] This fragmentation, which is the consequence of the rupture of P–P and P–C bonds, generates an unstable phosphinidene. The latter, stabilized by oxidative addition, leads to the phosphaindan **5**.[22b,26] This reaction, related to cheletropic reactions,[27] is the "reverse" reaction of the synthesis of diphosphirane. Indeed, under the same reaction conditions, we have checked that the irradiation of 1,3-diphosphapropenes, **2**, does not lead to phosphaalkenes, **4**, and phosphaindan, **5** (Figure 8).

Conclusion

Owing to the leaving groups on the intracyclic carbon atom and to the presence of bulky substituents on the phosphorus atoms, the functionalized diphosphiranes **1a–e** are convenient models for the study of the P–P bond rupture.

Under irradiation, the electrocyclic ring opening is the main reaction whereas the fragmentation is the side reaction (cheletropic reaction). Thus, these diphosphiranes are good precursors for original functionalized 1,3-diphosphapropenes. Furthermore, we have never observed photoreduction reactions. The difference of the photochemical behavior of diphosphiranes **1a–e** and *gem*-dihalocyclopropanes is presumably the consequence of the stability and reactivity of their respective cyclic radicals (diphosphiranyl and cyclopropyl).

To the best of our knowledge, in the field of the three-membered ring chemistry, these reactions are the first example of electrocyclic reactions involving P–P bonds.

Experimental Section

General Details. Usual chemical reagents were purchased from Aldrich or Fluka. All solvents were reagent grade and were purified by standard procedures before use. 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 this work. The yields of the products, described in the Experimental Section, were determined after crystallization and/or chromatography. The *cis*-**2** isomers were not isolated, and the relative yields were determined by ^{31}P NMR analysis compared to the trans isomers. The NMR spectra (^1H, ^{31}P, ^{13}C) were recorded on a Bruker AM-300-WB, 250 WM, or AC 80 NMR spectrometer. UV–visible spectra were measured on a Cary 2300 or a Beckman S 260 spectrophotometer. Mass spectra were obtained on a Varian 311A (Field Desorption, FD). ESR spectra were obtained on a Bruker ER 200 spectrometer. Melting points were determinated on a Kofler apparatus and are uncorrected. The purity of all title compounds was judged to be higher than 90% by ^{13}C and ^1H NMR spectral determinations (See the supplementary material).

Irradiation Procedures. The functionalized diphosphiranes **1a–e** are prepared according to the procedure described.[5] The measured UV absorption of the diphosphiranes **1** in hexane are λ (ε, mol^{-1} L cm^{-1}): **1a**, 284 nm (10 200); **1b**, 283 nm (8800); **1c**, 270 nm (8923); **1d**, 300 nm (7110). Irradiation of solutions of diphosphiranes in degassed solvents was carried out using as light source a Rayonet photochemical reactor, at 300 nm at room temperature.

Crystal data for 1a: $C_{37}Cl_2P_2H_{58}$; M = 635.729; monoclinic space group $C2/c$ with a = 19.509 (9) Å, β = 102.6 (2)°, V = 3755 Å^3, D_c = 1.124 g cm^{-3}, Z = 4; Mo Kα radiation (λ = 0.710 73), μ(Mo Kα) = 2.774 cm^{-1}.

The structure was solved by the direct method and refined using 2295 reflections > 3σ(I) on the 3281 independent reflections measured at −50 °C on a CAD 4-Enraf Nonius diffractometer. All the calculations were performed on a Vax-730 Digital computer, using SDP (Structure Determination Package of Enraf Nonius). In spite of the small value of the absorption coefficient, an empirical correction of absorption was performed as the Lorentz polarization contribution.

Only the half molecule was refined because of the presence of a crystallographic 2-fold direct axis. The hydrogen atoms were only introduced in the calculation, but not refined, all the other atoms were anisotropically refined. The R values are R_1 = 0.062, R_2 = 0.060 for 186 variables.

Compound 2a. A solution of **1a** (200 mg, 0.32 mmol) in degassed toluene (4 mL) was irradiated at 300 nm for 5 h. The reaction mixture was evaporated to dryness in vacuum. Pentane was added, and the suspension was filtered on Celite. Recrystallization from pentane afforded pure **2a**, as yellow crystals (100 mg, 50%): mp 184 °C; ^1H NMR (80.13 MHz, C_6D_6) δ 1.27 (s, 9 H, *p*-*t*-Bu), 1.28 (s, 9 H, *p*-*t*-Bu), 1.38 (s, 9 H, *o*-*t*-Bu), 1.48 (s, 9 H, *o*-*t*-Bu), 1.70 (s, 18 H, *o*-*t*-Bu), 7.53 (m, 4 H, Ar); ^{13}C NMR (62.86 MHz, C_6D_6) δ 171.6 (dd, $^1J_{CP1}$ = 98.5 Hz, $^1J_{CP3}$ = 88.0 Hz, C_2), 161.2 (d, $^2J_{CP3}$ = 17.5 Hz, C_{19}), 155.1 (d, $^2J_{CP3}$ = 5.0 Hz, C_{19*}), 155.0 (s, C_7), 154.0 (s, C_{7*}), 151.3 (s, C_9 and C_{21}), 136.2 (d, $^1J_{CP1}$ = 66.0 Hz, C_6), 133.0 (dd, $^1J_{CP3}$ = 77.0 Hz, $^3J_{CP1}$ = 11.0 Hz, C_{18}), 123.7 (d, $^3J_{CP3}$ = 7.5 Hz, C_{20} and C_{20*}), 123.0 (s, C_8), 122.6 (s, C_{8*}), 39.9 (d, $^3J_{CP3}$ = 7.0 Hz, C_{22} and C_{22*}), 38.7 (s, C_{14} and C_{26}), 35.5 (s, C_{10}), 35.4 (s, C_{10*}), 34.8 (d, $^4J_{CP3}$ = 8.0 Hz, C_{23-25} and $C_{23*-25*}$), 33.4 (d, $^4J_{CP1}$ = 7.0 Hz, C_{11-13}), 33.3 (s, $C_{11*-13*}$), 31.7 (s, C_{15-17}), 31.6 (s, C_{27-29}); ^{31}P NMR (32.44 MHz, C_6D_6) δ 275.5 (P_1), 74.5 (P_3), $^2J_{PP}$ = 106 Hz; MS ($C_{37}H_{58}P_2Cl_2$) m/e 635 (M^+, ^{35}Cl).

Crystal Data for 2a. A crystal of approximate size 0.2 × 0.2 × 0.2 mm was mounted on a Syntex $P2_1$ diffractometer. X-ray diffraction measurements were performed at room temperature with graphite monochromated Mo Kα radiation (0.710 69 Å).

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Lattice parameters refined using 15 reflections in the range $4 < 2\theta < 16°$: $a = 11.745$ (5) Å, $b = 16.255$ (9) Å, $c = 10.032$ (6) Å, $\beta = 97.87$ (4)°, $v = 1897$ (2) Å^3. Monoclinic system, C_m space group $C_{37}H_{58}P_2Cl_2$, $M = 635.7$ g, $Z = 2$, $D_{calc} = 1.11$ g cm^{-3}; μ(Mo Kα) = 0.28 mm^{-1}.

Intensities were measured by the $\omega - 2\theta$ scan method. No absorption correction was applied to the data. Standard reflection (0,4,0) checked every 50 reflections indicated a total loss in intensity of 8% and a linear decay correction was applied. A total of 3734 reflections was collected of which 2032 were unique (R_{inf} = 0.038) and 1096 with $I \geq 2.5\sigma(I)$ were used for structure determination. $F(000) = 678$; $2\theta_{max} = 52°$; $0 \leq h \leq 14$; $-19 \leq k \leq 19$ and $-11 \leq l \leq 7$.

Considering the initial ambiguity of the space group C and Z value, the structure was solved by direct methods using SHELX-86 in the P_1 group. For that purpose, the lattice parameters were modified as $a' = b' = 10.027$ Å, $c' = 10.032$ Å, $\alpha' = \beta' = 94.6°$ and $\gamma' = 108.3°$. Indexes were transformed by the matrix:

$$\begin{matrix} 1/2 & -1/2 & 0 \\ 1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{matrix}$$

Atomic parameters were refined in this group P_1 with the SHELX-76 program to a value of $R = 0.13$. A mirror plane clearly appeared in the molecule showing that C_m is the correct space group with the following atoms in the mirror plane: P(1), C(2), Cl(4), Cl(5), C(6), C(9), C(14), C(18), C(21), and C(26).

The refinement was completed in the monoclinic space group, and a local disorder was detected concerning the atoms P(3), C(15), C(16), C(17), C(27), C(28), and C(29). For them, the mirror is only a pseudoplane of symmetry.

All hydrogen atoms were located in theoretical position (1.08 Å from carbon). Refinements were performed using least-squares methods with F scattering factors as given in the *International Tables for X-ray Crystallography*. Observed structure factors were weighted by the scheme: $w = 1/[\sigma^2(F) + 0.00023F^2]$. Final values obtained: $R = 0.063$; $R_w = 0.053$; $(\Delta/\sigma)_{max} < 1$, S (goodness of fit) = 1.61, and $-0.3 < \Delta\rho < +0.3$ e Å^{-3}.

Compound 2b. A solution of **1b** (135 mg, 0.2 mmol) in degassed hexane (3 mL) was irradiated at 300 nm for 4 h at room temperature. The pale yellow solution became more intense.

The compound **2b** was obtained as yellow crystals by recrystallization in hexane at −20 °C (75 mg, 55%): mp 208 °C; ^{1}H NMR (80.13 MHz, C_6D_6) δ 1.19 (s, 9 H, *p*-*t*-Bu), 1.26 (s, 9 H, *p*-*t*-Bu), 1.35 (s, 18 H, *o*-*t*-Bu), 1.76 (s, 18 H, *o*-*t*-Bu), 6.80 (m, 5 H, phenyl), 7.4 (d, $^4J_{HP}$ = 2.9 Hz, 2 H, Ar), 7.6 (d, $^4J_{HP}$ = 2.9 Hz, 2 H, Ar); ^{13}C NMR (75.43 MHz, C_6D_6) δ 190.3 (dd, $^1J_{CP1}$ = 82.0 Hz, $^1J_{CP3}$ = 76.0 Hz, C_2), 158.5, 156.0, 154.5, 153.9 (4 s, C_7, C_{7*}, C_{19}, and C_{19*}), 150.0 (s, C_9 and C_{21}), 140.5 (d, $^3J_{CP3}$ = 13.0 Hz, C_{30}), 137.1 (d, $^1J_{CP1}$ = 75.0 Hz, C_6), 133.5 (dd, $^1J_{CP3}$ = 79.0 Hz, $^3J_{CP1}$ = 14.0 Hz, C_{18}), 127.0 (s, C_{31} and C_{31*}), 126.2 (s, C_{32} and C_{32*}), 123.4, 123.0, 122.9, 122.7 (4 s, C_8, C_{8*}, C_{20}, and C_{20*}), 122.5 (s, C_{33}), 39.7 (d, $^3J_{CP3}$ = 5.0 Hz, C_{10} and C_{10*}), 38.4 (d, $^3J_{CP3}$ = 7.0 Hz, C_{22} and C_{22*}), 34.5 (s, C_{23-25} and $C_{23*-25*}$), 34.4 (s, C_{11-13}), 34.1 (s, $C_{11*-13*}$), 33.8 (s, C_{14}), 33.1 (s, C_{26}), 31.5 (s, C_{15-17}), 31.4 (s, C_{27-29}); ^{31}P NMR (32.44 MHz, C_6D_6) δ 275.2 (P_1), 84.2 (P_3), $^2J_{PP}$ = 163 Hz; MS ($C_{43}H_{63}P_2Cl$) *m*/*e* 678 ($M^+ + 1$, ^{35}Cl).

Compound 2c. The same procedure as described for **2a** was used. Starting from **1c** (200 mg, 0.326 mmol), **2c** was obtained as yellow crystals by recrystallization from pentane (100 mg, 50%): mp 179–180 °C; ^{1}H NMR (300.13 MHz, C_6D_6) δ 1.28 (s, 9 H, *p*-*t*-Bu), 1.30 (s, 9 H, *p*-*t*-Bu), 1.35 (s, 9 H, *o*-*t*-Bu), 1.45 (s, 9 H, *o*-*t*-Bu), 1.7 (dd, $^3J_{HP1}$ = 13.3 Hz, $^3J_{HP3}$ = 7.5 Hz, Me), 1.73 (s, 18 H, *o*-*t*-Bu), 7.48 (m, 2 H, Ar), 7.56 (d, 2 H, $^4J_{HP}$ = 2.5 Hz, Ar); ^{13}C NMR (62.86 MHz, C_6D_6) δ 186.8 (dd, $^1J_{CP1}$ = 77.0 Hz, $^1J_{CP3}$ = 71.5 Hz, C_2), 161.3, 155.2 (2 br s, C_{19} and C_{19*}), 154.2, 154.0 (2 s, C_7 and C_{7*}), 150.5 (s, C_9 and C_{21}), 138.9 (d, $^1J_{CP1}$ = 73.5 Hz, C_6), 135.2 (dd, $^1J_{CP3}$ = 79.0 Hz, $^3J_{CP1}$ = 12.5 Hz, C_{18}), 123.3 (d, $^3J_{CP3}$ = 7.0 Hz, C_{20} and C_{20*}), 122.6 (s, C_8), 122.3 (s, C_{8*}), 39.9 (d, $^3J_{CP3}$ = 5.0 Hz, C_{22} and C_{22*}), 38.8 (s, C_{14} and C_{26}), 35.5 (s, C_{10}), 35.4 (s, C_{10*}), 34.9 (d, $^4J_{CP3}$ = 8.0 Hz, C_{23-25} and $C_{23*-25*}$), 33.1 (s, C_{11-13}), 33.0 (s, $C_{11*-13*}$), 31.8 (s, C_{15-17}), 31.7 (s, C_{27-29}), 24.6 (dd, $^2J_{CP1}$ = 27.5 Hz, $^2J_{CP3}$ = 14 Hz, C_{30}); ^{31}P NMR (121.49 MHz, C_6D_6) δ 272.5 (P_1), 84.0 (P_3), $^2J_{PP}$ = 142 Hz, $^3J_{P1H}$ = 13.3 Hz, $^3J_{P3H}$ = 7.6 Hz; MS ($C_{38}H_{61}P_2Cl$) *m*/*e* 614 (M^+, ^{35}Cl).

Compound 2d. A solution of **1d** (150 mg, 0.2 mmol) in degassed hexane (3 mL) was irradiated at 300 nm for 3 h. The reaction mixture was filtered on Celite, the solvent was removed, and **2d** was obtained as yellow oil (120 mg, 80%): ^{1}H NMR (80.13 MHz, C_6D_6) δ 1.27 (s, 9 H, *p*-*t*-Bu), 1.28 (s, 9 H, *p*-*t*-Bu), 1.37 (s, 9 H, *o*-*t*-Bu), 1.49 (s, 9 H, *o*-*t*-Bu), 1.72 (s, 18 H, *o*-*t*-Bu), 7.51 (m, 4 H, Ar); ^{13}C NMR (75.43 MHz, C_6D_6) δ 162.1 (dd, $^1J_{CP}$ = 104.0 Hz, $^1J_{CP}$ = 99.0 Hz, C_2), 154.6 (s, C_7), 154.0 (s, C_{7*}), 153.9 (s, C_{19}), 153.2 (s, C_{19*}), 151.1 (s, C_9 and C_{21}), 139.9 (dd, $^1J_{CP}$ = 68.0 Hz, $^3J_{CP}$ = 3.5 Hz, C_6), 132.9 (dd, $^1J_{CP}$ = 85.5 Hz, $^3J_{CP}$ = 11.5 Hz, C_{18}), 123.2 (br s, C_{20} and C_{20*}), 122.8 (s, C_8), 122.4 (s, C_{8*}), 39.86 (d, $^3J_{CP}$ = 7.0 Hz, C_{22} and C_{22*}), 38.3 (s, C_{14} and C_{26}), 35.2 (broad s, C_{10} and C_{10*}), 34.6 (d, $^4J_{CP}$ = 8.2 Hz, C_{23-25} and $C_{23*-25*}$), 33.3 (d, $^4J_{CP}$ = 7.6 Hz, C_{11}–C_{13}), 33.0 (d, $^4J_{CP}$ = 3.0 Hz, C_{11*}–C_{13*}), 31.4 (s, C_{15-17}), 31.2 (s, C_{27-29}); ^{31}P NMR (32.44 MHz, C_6D_6) δ 293.4 (P_1), 75.0 (P_3), $^2J_{PP}$ = 109 Hz; MS ($C_{37}H_{58}P_2Br_2$) *m*/*e* 723 (M^+, ^{79}Br).

Compounds **3a–c**, obtained as byproducts from the recrystallization filtrate, were separated and purified on precoated plates (silica gel 60F 254).

Compound 3a: yellow crystals (40 mg, 21%); R_f = 0.55 (dichloromethane/hexane, 10/90, as eluent); mp 174–176 °C; ^{1}H NMR (300.13 MHz, C_6D_6) δ 1.19 (s, 3 H, Me), 1.26 (s, 18 H, *p*-*t*-Bu), 1.50 (s, 3 H, Me), 1.56 (s, 9 H, *o*-*t*-Bu), 1.57 (s, 9 H, *o*-*t*-Bu), 1.69 (s, 9 H, *o*-*t*-Bu), 2.27 (dd, H_A, $^2J_{HAHB}$ = 14.4 Hz, $^2J_{HAP3}$ = 28.2 Hz), 2.44 (dd, H_B, $^2J_{HBHA}$ = 14.4 Hz, $^2J_{HBP3}$ = 2.9 Hz), 7.20 (d, 2 H, $^4J_{HP}$ = 1.7 Hz, Ar), 7.54 (m, 2 H, Ar); ^{13}C NMR (75.43 MHz, C_6D_6) δ 176.7 (dd, $^1J_{CP}$ = 76.9 Hz, $^3J_{CP}$ = 74.6 Hz, C_2), 159.6 (br s, C_{19*}), 154.6 (s, C_7), 153.6 (br s, C_{7*}), 153.5 (s, C_{19}), 153.0, 150.7 (s, C_9 and C_{21}), 136.5 (dd, $^1J_{CP}$ = 65.2 Hz, $^3J_{CP}$ = 25.0 Hz, C_6), 131.4 (dd, $^1J_{CP}$ = 20.2 Hz, $^3J_{PC}$ = 19.6 Hz, C_{18}), 122.8 (d, $^3J_{CP}$ = 4.2 Hz, C_{20}), 122.5 (s, C_8 and C_{8*}), 118.8 (s, C_{20*}), 45.7 (d, J_{CP} = 5.5 Hz, C_{22*}), 42.2 (t, J_{CP} = 11.7 Hz, C_{23*}), 38.3 (d, J_{CP} = 8.2 Hz, C_{22}), 37.8 (s, C_{14} and C_{26}), 35.0 (s, C_{10}), 34.4 (d, J_{CP} = 4.2 Hz, C_{10*}), 33.7 (d, J_{CP} = 7.0 Hz, C_{11-13}), 33.3 (d, J_{CP} = 6.6 Hz, $C_{11*-13*}$), 33.0 (d, J_{CP} = 8.6 Hz, C_{23-25}), 31.5 (s, C_{15-17}), 31.4 (s, C_{27-29}), 22.7 (s, C_{24*}), 14.3 (s, C_{25*}); ^{31}P NMR (121.49 MHz, C_6D_6) δ 284 (P_1), 19.75 (P_3), $^2J_{PP}$ = 267.0 Hz, $^2J_{HAP3}$ = 28.0 Hz, $^2J_{HBP3}$ = 3.3 Hz; MS ($C_{37}H_{57}P_2Cl$) *m*/*e* 599 (M^+, ^{35}Cl).

Compound 3b: yellow oil (13 mg, 10%); R_f = 0.9 (dichloromethane as eluent); ^{1}H NMR (300.13 MHz, C_6D_6) δ 1.27 (s, 9 H, *p*-*t*-Bu), 1.31, 1.34 (s, 2 Me), 1.36 (s, 9 H, *p*-*t*-Bu), 1.38 (s, 9 H, *o*-*t*-Bu), 1.47 (s, 9 H, *o*-*t*-Bu), 1.89 (s, 9 H, *o*-*t*-Bu), 6.80 (m, 5 H, phenyl), 7.19 (d, 2 H, $^4J_{HP}$ = 1.75 Hz, Ar), 7.53 (m, 2 H, Ar); ^{13}C NMR (75.43 MHz, C_6D_6) δ 187.4 (m, C_2), 158.6 (br s, C_{19*}), 155.3 (s, C_7), 154.6 (s, C_{7*}), 153.7 (d, J_{CP} = 15.0 Hz, C_{19}), 153.1, 149.9 (s, C_9 and C_{21}), 142.4 (d, J_{CP1} = 15.0 Hz, C_{30}), 137.5 (br s, C_6), 134.0 (br s, C_{18}), 126.3, 124.1 (s, C_{31} and C_{32}), 122.9 (d, $^3J_{CP}$ = 6.0 Hz, C_{20}), 122.3 (s, C_8 and C_{8*}), 121.5 (s, C_{33}), 119.3 (s, C_{20*}), 45.9 (d, $^3J_{CP}$ = 6.8 Hz, C_{22*}), 39.9 (t, J_{CP} = 11.0 Hz, C_{23*}), 38.6 (br s, C_{22}), 35.1 (s, C_{14} and C_{26}), 35.0 (d, $^3J_{CP}$ = 3.7 Hz, C_{10}), 34.3 (d, $^3J_{CP}$ = 6.0 Hz, C_{10*}), 34.0 (d, $^4J_{CP}$ = 8 Hz, C_{11-13} and $C_{11*-13*}$), 33.5 (d, $^4J_{CP}$ = 9.0 Hz, C_{23-25}), 31.9 (s, C_{15-17}), 31.3 (s, C_{27-29}), 23.0 (s, C_{24*}), 14.6 (s, C_{25*}); ^{31}P NMR (121.49 MHz, C_6D_6) δ 267.6 (P_1), 17.4 (P_3), $^2J_{PP}$ = 207 Hz; MS ($C_{43}H_{62}P_2$) *m*/*e* 640 (M^+).

Compound 3c: white crystals (50 mg, 26%); mp 192–194 °C; R_f = 0.20 (dichloromethane/hexane, 10/90, as eluent); ^{1}H NMR (300.13 MHz, C_6D_6) δ 1.20 (s, 3 H, Me), 1.29 (s, 9 H, *p*-*t*-Bu), 1.30 (s, 9 H, *p*-*t*-Bu), 1.32 (dd, $^3J_{HP1}$ = 14.7 Hz, $^3J_{HP3}$ = 9.8 Hz, Me), 1.38 (s, 3 H, Me), 1.55 (s, 18 H, *o*-*t*-Bu), 1.65 (s, 9 H, *o*-*t*-Bu), 2.18 (dd, $^2J_{HBHA}$ = 14.3 Hz, $^2J_{HBP3}$ = 2.5 Hz, H_B), 2.34 (dd, $^2J_{HAHB}$ = 14.3 Hz, $^2J_{HAP3}$ = 26.3 Hz, H_A), 7.19 (d, 2 H, $^4J_{HP}$ = 1.75 Hz, Ar), 7.53 (m, 2 H, Ar); ^{13}C NMR (75.43 MHz, C_6D_6) δ 189.6 (dd, $^1J_{CP}$ = 57.1 Hz, $^3J_{CP}$ = 48.6 Hz, C_2), 159.2 (br s, C_{19*}), 154.5 (s, C_7), 153.6 (s, C_{7*}), 153.2 (d, J_{CP} = 15.0 Hz, C_{19}), 152.3, 149.8 (s, C_9 and C_{21}), 139.5 (dd, $^1J_{CP}$ = 71.8 Hz, $^3J_{CP}$ = 30.0 Hz, C_6), 133.0 (dd, $^1J_{CP}$ = 24.3 Hz, $^3J_{CP}$ = 22.6 Hz, C_{18}), 122.7 (d, $^3J_{CP}$ = 6.0 Hz, C_{20}), 122.0 (s, C_8 and C_{8*}), 118.6 (s, C_{20*}), 45.7 (d, $^3J_{CP}$ = 4.7 Hz, C_{22*}), 42.2 (t, J_{CP} = 11.6 Hz, C_{23*}), 38.3 (d, $^3J_{CP}$ = 4.7 Hz, C_{22}), 37.9 (s, C_{14}), 37.8 (s, C_{26}), 34.9 (d, $^3J_{CP}$ = 3.7 Hz, C_{10}), 34.5 (d, $^3J_{CP}$ = 3.8 Hz, C_{10*}), 33.5 (d, $^4J_{CP}$ = 8 Hz, C_{11-13}), 33.2 (d, $^4J_{CP}$ = 7.0 Hz, $C_{11*-13*}$), 32.9 (d, $^4J_{CP}$ = 9.0 Hz, C_{23-25}), 31.55 (s, C_{15-17}), 31.46 (s, C_{27-29}), 22.8 (d, $^2J_{CP}$ = 15.7 Hz, C_{30}), 22.7 (s, C_{24*}), 14.3 (s, C_{25*}); ^{31}P NMR (121.49 MHz, C_6D_6) δ 279.4 (P_1), 7.7 (P_3), $^2J_{PP}$ = 306 Hz, $^3J_{P1H}$ = 15 Hz, $^3J_{P3H}$ = 26 Hz; MS ($C_{38}H_{60}P_2$) *m*/*e* 578 (M^+).

The same procedure as described for **3a–c** was used to purify the phosphaalkenes **4a–c**.

Compound 4a: yellow crystals (5 mg, 4%); R_f = 0.90 (dichloromethane/hexane, 10/90, as eluent); ^{1}H NMR (80.13 MHz, C_6D_6) δ 1.27 (s, 9 H, *p*-*t*-Bu), 1.49 (s, 9 H, *o*-*t*-Bu), 1.50 (s, 9 H, *o*-*t*-Bu), 7.54 (d, 2 H, $^4J_{HP}$ = 1.6 Hz, Ar); ^{31}P NMR (32.44 MHz, C_6D_6) δ 232.3; MS ($C_{19}H_{29}PCl_2$) *m*/*e* 358 (M^+, ^{35}Cl) (see ref 28).

Compound 4b: yellow crystals (4 mg, 5%); R_f = 0.5 (dichloromethane as eluent); ^{1}H NMR (80.13 MHz, C_6D_6) δ 0.90 (s, 9 H, *p*-*t*-Bu), 1.23 (s, 18 H, *o*-*t*-Bu), 6.80 (m, 5 H, phenyl), 7.20 (m, 2 H, Ar); ^{13}C NMR (75.43 MHz, C_6D_6) δ *Z* isomer 170.1 (d, $^1J_{CP}$ = 58.7 Hz, C_2), 154.4 (s, C_7 and C_{7*}), 150.36 (s, C_9), 141.9 (d, $^2J_{CP}$ = 18.8 Hz, C_{30}), 135.7 (d, $^1J_{CP}$ = 58.0 Hz, C_6), 126.6 (s, C_{31} and C_{31*}), 125.7 (s, C_{32} and C_{32*}), 122.5 (s, C_8 and C_{8*}), 119.7 (s, C_{33}), 38.2 (s, C_{10} and C_{10*}), 35.1 (s, C_{14}), 32.8 (d, $^4J_{CP}$ = 6.8 Hz, C_{11-13} and $C_{11*-13*}$), 31.5 (s, C_{15-17}); *E* isomer 167.6 (s, C_2), 155.08 (s, C_7 and C_{7*}), 151.22 (s, C_9), 130.4 (d, $^1J_{CP}$ = 54 Hz, C_6); ^{31}P NMR (32.44 MHz, C_6D_6) δ 228.1 (*Z* isomer), 238.8 (*E* isomer); MS ($C_{25}H_{34}PCl$) *m*/*e* 401 (M^+, ^{35}Cl).

Compound 4c: white oil (6 mg, 5%); R_f = 0.75 (dichloromethane/hexane, 10/90, as eluent); the NMR parameters were slightly different that the same product described by Appel and Coll:[27] ^{1}H NMR (80.13 MHz, C_6D_6) δ 1.34 (s, 27 H, *o*-*t*-Bu), 1.49 (s, 27 H, *o*-*t*-Bu and *p*-*t*-Bu), 1.80 (d, 3 H, $^3J_{PH}$ = 11.9 Hz, Me of *E* isomer), 2.40 (d, 3 H, $^3J_{PH}$ = 23.3 Hz, Me of *Z* isomer), 7.25 (d, 2 H, $^4J_{PH}$ = 1.1 Hz, Ar), 7.40 (d, 2 H, $^4J_{PH}$ = 1.5 Hz, Ar); ^{13}C NMR (75.43 MHz, $CDCl_3$) δ 175.00 (d, $^1J_{CP}$ = 46.8 Hz, C_2), 169.00 (d, $^1J_{CP}$ = 58.1 Hz, C_2), 153.65 (d, $^2J_{CP}$ = 46.0 Hz, 2 C_7), 150.70 (d, $^2J_{CP}$ = 26.4 Hz, 2 C_{7*}), 150.00 (s, 2 C_9), 135.45 (d, $^1J_{CP}$ = 51.3 Hz, C_6), 135.20 (d, $^1J_{CP}$ = 55.8 Hz, C_6), 121.87 (s, 2 C_8), 119.50 (s, 2 C_{8*}), 37.90 (d, $^3J_{CP}$ = 4.0 Hz, 2 C_{10}), 35.00 (d, $^3J_{CP}$ = 3.5 Hz, 2 C_{10*}), 33.75 (s, C_{14}), 33.64 (s, C_{14}), 32.55 (dd, $^4J_{CP}$ = 6.9 Hz, 2 C_{11-13} and 2 $C_{11*-13*}$), 31.61 (s, C_{15-17}), 31.36 (s, $C_{15*-17*}$), 29.60 (d, $^2J_{CP}$ = 19.5 Hz, C_{30}), 28.86 (d, $^2J_{CP}$ = 17.6 Hz, C_{30}); ^{31}P NMR (32.44 MHz, C_6D_6) δ 224.8 (q, $^3J_{PH}$ = 12.0 Hz, *E* isomer, 50%), 225.3 (q, $^3J_{PH}$ = 23.0 Hz, *Z* isomer, 50%); MS ($C_{20}H_{32}PCl$) *m*/*e* 338 (M^+, ^{35}Cl).

Compound 6a. To a stirred solution of **2a** (70 mg, 0.11 mmol) in toluene (2 mL) were added methanol (3 mL) and triethylamine (0.5 mL). The mixture was heated at 40 °C for 72 h. The reaction led to a mixture of compounds **6a** (50%) and **3a** (50%).

6a was separated and purified on silica plate (dichloromethane/hexane, 20/80, as eluent): R_f = 0.8; white crystals (30 mg, 50%); ^{1}H NMR (80.13 MHz, C_6D_6) δ 1.28 (s, 9 H, *p*-*t*-Bu), 1.34 (s, 9 H, *p*-*t*-Bu), 1.46 (s, 9 H, *o*-*t*-Bu), 1.49 (s, 9 H, *o*-*t*-Bu), 1.74 (s, 18 H, *o*-*t*-Bu), 3.72 (d, 3 H, $^3J_{HP3}$ = 14.3 Hz, MeO), 7.52 (m, 2 H, Ar), 7.6 (m, 2 H, Ar); ^{13}C NMR (62.86 MHz, C_6D_6) δ 175.7 (dd, $^1J_{CP}$ = 92.0 Hz, $^3J_{CP}$ = 65.5 Hz, C_2), 159.0 (br s, C_7), 158.0 (br s, C_{7*}), 155.4 (s, C_{19}), 153.8 (s, C_{19*}), 153.1 (s, C_9), 150.8 (s, C_{21}), 136.7 (d, $^1J_{CP}$ = 68.0 Hz, C_6), 135.7 (dd, $^1J_{CP}$ = 45.8 Hz, $^3J_{CP}$ = 10.0 Hz, C_{18}), 123.7 (br s, C_8 and C_{8*}), 122.8 (s, C_{20}), 122.5 (s, C_{20*}), 59.7 (d, J_{CP} = 31.1 Hz, C_{34}), 39.2 (br s, C_{14} and C_{26}), 38.8 (d, J_{CP} = 7.5 Hz, C_{10} and C_{10*}), 35.5 (br s, C_{22} and C_{22*}), 34.0 (br s, C_{11-13} and $C_{11*-13*}$), 33.6 (d, J_{CP} = 6.4 Hz, C_{23-25}), 33.1 (d, J_{CP} = 6.6 Hz, $C_{23*-25*}$), 31.8 (s, C_{15} and C_{17}); ^{31}P NMR (32.44 MHz, C_6D_6) δ 259.8 (P_1), 115.1 (P_3), $^2J_{PP}$ = 85.0 Hz; MS ($C_{38}H_{61}P_2OCl$) *m*/*e* 631 (M^+, ^{35}Cl).

Compound 6b. To a stirred solution of **2b** (70 mg, 0.1 mmol) in dry toluene (4 mL) were added triethylamine (120 μL, 7 equiv) and methanol (3 mL). After 20 h at room temperature, the solvent was removed. **6b** was purified on silica plates (dichloromethane/hexane, 30/70): R_f = 0.70; yellow crystals (54 mg, 80%); ^{1}H NMR (80.13 MHz, C_6D_6) δ 1.24 (s, 9 H, *p*-*t*-Bu), 1.30 (br s, 18 H, *o*-*t*-Bu), 1.42 (s, 9 H, *p*-*t*-Bu), 1.55 (br s, 18 H, *o*-*t*-Bu), 3.50 (d, 3 H, $^3J_{HP3}$ = 14.0 Hz, MeO), 6.80 (br s, 5 H, phenyl), 7.50 (m, 4 H, Ar); ^{13}C NMR (75.43 MHz, C_6D_6) δ 194.0 (dd, $^1J_{CP3}$ = 50.0 Hz, $^1J_{CP2}$ = 76.5 Hz, C_2), 158.3 (d, J_{CP} = 32.0 Hz, C_7), 156.6 (br s, C_{7*}), 156.0 (s, C_{19}), 154.4 (s, C_{19*}), 151.9 (s, C_9), 149.5 (s, C_{21}), 142.1 (t-like, $^2J_{CP}$ = 14.0 Hz, C_{30}), 138.0 (d, $^1J_{CP}$ = 74.0 Hz, C_{18}), 136.7 (dd, $^1J_{CP}$ = 52.0 Hz, $^3J_{CP}$ = 14.0 Hz, C_6), 126.9 (s, C_{31} and C_{31*}), 125.4 (s, C_{32} and C_{32*}), 124.4 (s, C_{33}), 122.7 (s, C_8 and C_{8*}), 122.4 (s, C_{20} and C_{20*}), 59.0 (d, J_{CP} = 30.2 Hz, C_{34}), 39.1 (s, C_{10} and C_{10*}), 38.5 (s, C_{22}), 38.2 (s, C_{22*}), 34.7 (br s, C_{11-13}), 34.58 (s, $C_{11*-13*}$), 34.0 (s, C_{23-25}), 33.9 (s, $C_{23*-25*}$), 33.1 (s, C_{14}), 33.04 (s, C_{26}), 31.6 (s, C_{15-17}), 31.59 (s, C_{27-29}); ^{31}P NMR (32.44 MHz, C_6D_6) δ 259.3 (P_1), 124.0 (P_3), $^2J_{PP}$ = 141.5 Hz; MS ($C_{44}H_{66}P_2O$) *m*/*e* 672 (M^+).

Compound 6c. To a stirred solution of **2c** (100 mg, 0.136 mmol) in toluene (2 mL) were added methanol (3 mL) and triethylamine (0.5 mL). The mixture was stirred at room temperature for 72 h. The solvent was removed, and **6c** was purified on silica plates (dichloromethane/hexane, 5/95, as eluent): R_f = 0.55; yellow crystals (90 mg, 90%); mp 205 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 1.14 (dd, 3 H, $^3J_{HP1}$ = 14.0 Hz, $^3J_{HP3}$ = 8.4 Hz, Me), 1.25 (s, 9 H, *p*-*t*-Bu), 1.27 (s, 9 H, *p*-*t*-Bu), 1.30 (s, 9 H, *o*-*t*-Bu), 1.34 (s, 9 H, *o*-*t*-Bu), 1.41 (s, 9 H, *o*-*t*-Bu), 1.66 (s, 9 H, *o*-*t*-Bu), 3.86 (d, 3 H, $^3J_{HP3}$ = 14.4 Hz, MeO), 7.30 (m, 4 H, Ar); ^{13}C NMR (62.86 MHz, $CDCl_3$) δ 189.0 (dd, $^1J_{CP1}$ = 73.0 Hz, $^1J_{CP3}$ = 45.0 Hz, C_2), 157.6 (br s, C_7), 156.7 (br s, C_{7*}), 154.3 (s, C_{19}), 153.4 (s, C_{19*}), 151.2 (s, C_9), 149.3 (s, C_{21}), 139.0 (dd, $^1J_{CP1}$ = 74.0 Hz, $^3J_{CP3}$ = 3.0 Hz, C_6), 137.2 (dd, $^1J_{CP3}$ = 54.0 Hz, $^3J_{CP1}$ = 13.0 Hz, C_{18}), 122.4 (s, C_{20}), 121.6 (s, C_8 and C_{8*}), 121.2 (d, $^3J_{CP3}$ = 12.0 Hz, C_{20*}), 58.8 (d, $^2J_{CP3}$ = 32 Hz, C_{34}), 38.84 (s, C_{14}), 38.83 (s, C_{26}), 38.2 (s, C_{10}), 38.1 (s, C_{10*}), 34.9 (s, C_{22}), 34.8 (s, C_{22*}), 33.1 (s, C_{23-25}), 32.7 (d, J_{CP1} = 7.5 Hz, C_{11-13}), 32.2 (d, J_{CP1} = 7.5 Hz, $C_{11*-13*}$), 31.6 (s, $C_{23*-25*}$), 31.3 (s, C_{15-17}), 31.2 (s, C_{27-29}), 22.1 (dd, $^2J_{CP1}$ = 15.0 Hz, $^2J_{CP3}$ = 22.0 Hz, C_{30}); ^{31}P NMR (121.49 MHz, C_6D_6) δ 258.3 (P_1), 123.1 (P_3), $^2J_{PP}$ = 136 Hz, $^3J_{P1H}$ = 13.7 Hz; MS ($C_{39}H_{64}P_2O$) *m*/*e* 610 (M^+).

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Supplementary Material Available: ^{1}H and/or ^{13}C NMR spectra for compounds **2a–d**, **3a–c**, **4a–c**, and **6a–c**, and X-ray data for compounds **1a** and **2a** (34 pages). Ordering information is given on any current masthead page.

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