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New Reactivity of Phosphirenes (Phosphacyclopropenes). Synthesis of Allenylphosphines and of Functional Phosphirenes.

F. Nief* and F. Mathey

Laboratoire de Chimie du Phosphore et des Métaux de Transition, CNRS - UM 13, DCPH, Ecole Polytechnique, 91128 PALAISEAU CEDEX, FRANCE.

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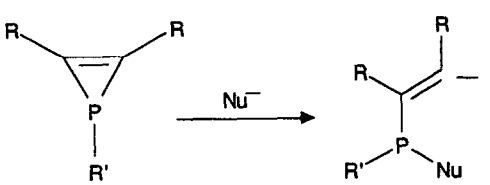
Abstract: *1-Mesityl 2,3-dimethylphosphirene* **1** *and 1-mesityl 2-methylphosphirene* **4** *can be easily prepared from mesityldichlorophosphine ($MesPCl_2$), $AlCl_3$, 2-butyne or propyne and Bu_3P. Because of the steric bulk of the mesityl substituent, n-butyllithium no longer reacts by nucleophilic addition onto the phosphorus atom of the phosphirene ring but instead, as a base, deprotonates the ring substituents. With* **1**, *an allenylphosphine anion results after ring opening, and this anion can be reacted with various electrophiles, whereas with* **4**, *the ring structure is conserved and a metalated phosphirene is obtained. This anion can be functionnalized by reaction with paraformaldehyde, ketones or aldehydes; phosphirene-alcools are obtained.*

Introduction

The phosphirene (phosphacyclopropene) ring system is receiving much attention at the present time, and work on this subject has been very recently reviewed[1]. However, the chemistry of this ring system has not been much developed, particularly as far as reactions of phosphirenes with electrophiles and nucleophiles are concerned, because these reagents will attack the phosphorus atom. For instance, reaction of nucleophiles with phosphirenes[2] results in ring opening into vinylphosphines, that are generally available by simpler routes[3] (scheme 1).

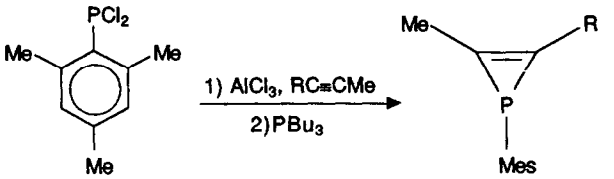


Scheme 1

We thought that substituting the phosphorus atom by a bulky group such as mesityl would shield the phosphorus lone pair and thus decrease the reactivity at phosphorus. In this paper, we describe a study of the reactivity of n-butyllithium with P-mesityl phosphirenes.

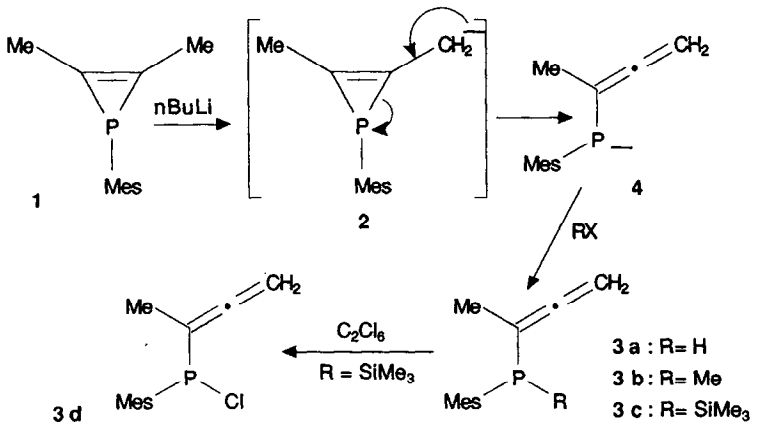
Results

Phosphirenes can now be considered as readily available heterocycles after Lochschmidt et al.[4] discovered that they can be easily one-pot prepared with $RPCl_2$, $AlCl_3$, an alkyne, and tributylphosphine. By using this method, we were able to obtain 1-mesityl 2,3-dimethylphosphirene **1** in good yield (scheme 2)



Scheme 2

Reaction of **1** with n-butyllithium has a totally different outcome than previously described: no reaction takes place when an equimolecular mixture of **1** and n-butyllithium was stirred at -80°C. On warming to room temperature, a ^{31}P NMR spectrum of the reaction mixture revealed the appearance of a peak at about -60 ppm, characteristic of a phosphide anion **4**. Upon subsequent treatment with methyl iodide, we obtained a stable, distillable compound for which all spectroscopic data pointed to an allenylphosphine structure **3b** (scheme 3).

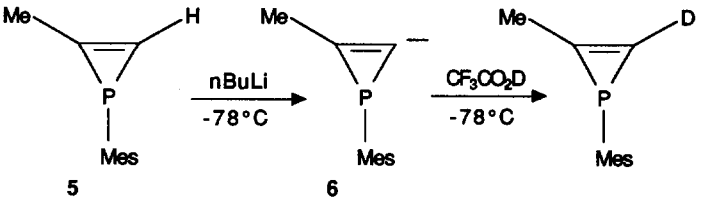


Scheme 3

In particular, one observes the central allenic carbon NMR resonance at ≈ 203 ppm. Functionnality can be introduced at phosphorus : reaction of anion **4** with Me_3SiCl gives the silylphosphine **3c** that can be isolated or in situ transformed into the chlorophosphine **3d** by further reaction with C_2Cl_6[5].

We next wanted to study the reactivity of a C-monosubstituted phosphirene such as **4**, in which there are two possible sites of attack by a base. Reaction of propyne with [$MesPCl_2.AlCl_3$] followed by Bu_3P affords 1-mesityl 2-methylphosphirene **5**. Reaction of **4** with base was monitored by variable-temperature NMR. This

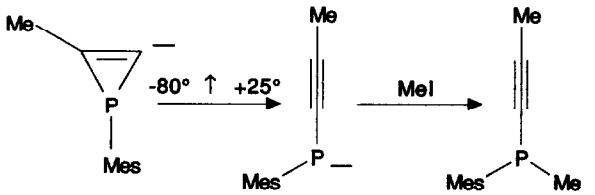
study reveals that 5 reacts with n-BuLi at -80°C and a signal at -210 ppm is observed. Quenching the reaction mixture with CF_3CO_2D at -80°C results in the reappearance of a resonance at the same chemical shift than in the starting material; in the ^1H coupled ^{31}P spectrum, this resonance now appears as a singlet whereas in the starting material it was a doublet with J = 22 Hz attributable to coupling with H_2. These observations constitute evidence that the resonance at -210 ppm corresponds to the metalated phosphirene 6 (scheme 4).



5 6

scheme 4

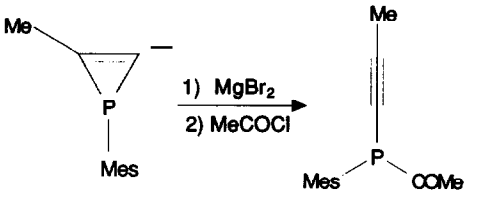
This high-field signal is the only resonance observed between -80°C and +10°C. At room temperature however, the anion 6 decomposes as indicated by the appearance of a new peak at -129 ppm attributable to a ring-opened alkynyl phosphide 7 that can be trapped with ICH_3; alkynyl phosphine 8 can be isolated in low yield (scheme 5).



6 7 8

scheme 5

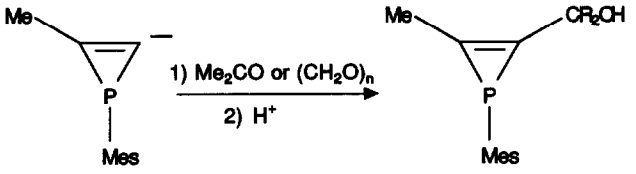
Anion 6 did react with CO_2 at -80°C and, after low temperature protonation, a ^{31}P NMR signal at -154 ppm appeared, corresponding to what we believe was a phosphirene-carboxylic acid, but the product decomposed upon attempted isolation even at 0°C. Likewise, the reaction of 6 with acid chlorides or anhydrides proved intractable. Reaction of acetyl chloride with 6 as a Grignard reagent (prepared by metal exchange of the lithiophosphirene with $MgBr_2$) resulted in ring opening and the obtention of acylphosphine 11 (scheme 6).



6 11

scheme 6

Yet eventually, functionnalisation of the phosphirene ring could be achieved: reaction of anion **6** with a ketone at -80°C or even with dry paraformaldehyde at 0°C affords in fair yield respectively the tertiary and primary alcools **12** and **13** (scheme 7).



6

1 2: R = Me

1 3: R = H

scheme 7

Aldehydes also react, but in this case two diastereoisomeric secondary alcools are obtained, due to the chirality at phosphorus. Methylation of anion **6** with ICH_3 at -80°C affords a mixture of phosphirene **1** and alkynylphosphine **8** in a 1/1 ratio (estimated by ^{31}P NMR); at 0°C, **8** is favoured by a 9/1 ratio.

Discussion

Very likely because of steric crowding by the mesityl group, n-BuLi no longer reacts as a nucleophile with the phosphorus atom in **1** and **4**, but as a base deprotonates the ring substituents. In **1**, the resulting carbanion **2** is unstable, and rearranges into the more stable ring-opened allenylphosphide **4**. In **5**, the more acidic and more accessible vinylic proton on the ring is abstracted even at -80°C, the resulting metalated phosphirene **6** being stable up to +10°C. Above room temperature, **6** decomposes into the ring-opened (and therefore thermodynamically more stable) alkynylphosphide **7**. The relative stability of **6** could be of kinetic origin, because the activation barrier for the transformation of **6** into **7** might be higher in energy than for **3**→**4** due to the more extensive geometrical rearrangement required in the former case. Some metallacyclopropenes appear to be stable at room temperature[6]. Reaction of lithiophosphirene **6** with weak electrophiles is kinetically controlled, as evidenced by the ring structure being retained when **6** is reacted with carbonyl compounds. With the stronger electrophile ICH_3, there is a competition between the kinetic pathway leading to **1** and the thermodynamic pathway leading to **8**, the thermodynamic product being favoured at higher temperatures, as expected.

Conclusion

Although allenylphosphine oxides can be easily prepared[7], there was only few reported examples of trivalent allenylphosphines[8]. In this study, we expanded the range of these molecules and prepared in particular the secondary phosphine **3b** and the chlorophosphine **3d**. We also achieved direct functionnalization of the phosphirene ring for the first time, by preparing and isolating phosphirene-alcools **12** and **13**. Until now, only one ring-functionnal phosphirene (as a P→$W(CO)_5$ complex) existed[2].

EXPERIMENTAL PART

All reactions were performed under inert atmosphere (nitrogen or argon) with dry, deoxygenated solvents. NMR spectra were measured on a Bruker AC 200 spectrometer at 200.13 and 50.32 MHz for ^1H and ^{13}C respectively, and on a Bruker WP 80 spectrometer at 32.44 MHz for ^{31}P. Chemical shifts are expressed in ppm

downfield from internal TMS for ^{1}H and ^{13}C or external 85% H_3PO_4 for ^{31}P. Mass spectra were recorded at 70 eV on a Shimadzu GC/MS 1000 by the direct inlet method. Silicagel was used for chromatographic separations.

Mesityldichlorophosphine (MesPCl2) [9].

A solution of mesitylmagnesium bromide prepared from bromomesitylene (39.8 g, 0.2 Mole) and magnesium (5g, 0.205 g-Atom) in THF (200 mL) was added dropwise during 1.5 hr to a solution of PCl_3 (31.5 g, 0.23 Mole) in n-hexane (600 mL) maintained in a dry ice-acetone bath at -78°C. A voluminous precipitate of magnesium salts soon appeared. After the end of the addition, the reaction mixture was poured while still cold on a medium-porosity glass frit and filtered by applying a 0.3 bar positive pressure of nitrogen. The precipitate was rinsed on the frit with cold hexane (200 mL), the filtrate was evaporated to dryness and the residue vacuum distilled. The colorless oil boiling at 87-90°C / 0.5 mm (30g, 0.136 Mole, 68%) was collected and solidified on standing, mp 30°C; it contained a small amount of MesPClBr (less than 5%, as estimated by ^{31}P NMR). NMR ($CDCl_3$): ^{1}H: 2.27 (CH_3 para), 2.70 (d, J_{PH}=4, CH_3 ortho), 6.88 (d, J_{PH}=4, H meta); $^{13}C\{^{1}H\}$: 21.20 (d, J=2, CH_3 ortho), 22.03 (CH_3 para), 130.59 (d, J=4, C meta), 131.82 (d, J=67, C ipso), 134.32 (C para), 143.26 (d, J=26, C ortho); $^{31}P\{^{1}H\}$: 164 ($MesPCl_2$), 159.1 (MesPClBr).

1-Mesityl 2,3-dimethylphosphirene, **1**.

A mixture of $MesPCl_2$ (7.04 g, 31.9 mMole) and $AlCl_3$ (4.3 g, 32 mMole) in dichloromethane (25 mL) was stirred at room temperature until homogeneous, then cooled at -78°C. A solution of 2-butyne (1.72 g, 31.9 mMole) in dichloromethane (20 mL) was added portionwise in 5 mn and stirred 15 min after the end of the addition; tributylphosphine (8 mL, 6.48 g, 32mMole) was then syringed into the reaction mixture at -78°C. The solution was then warmed up to room temperature, evaporated to dryness and the residue extracted with 3 x 25 mL of hexane. The extract was evaporated to dryness and the air-sensitive colourless product solidified on standing, mp 35°C (4.73 g, 23.2 mMole, 73%). NMR ($CDCl_3$): ^{1}H: 2.19 (CH_3 para), 2.32 (d, J_{PH}=4, CH_3—cycle), 2.53 (CH_3 ortho), 6.72 (H meta); $^{13}C\{^{1}H\}$: 12.18 (d, J=9, CH_3—cycle), 20.94 (CH_3 para), 21.55 (d, J=8.5, CH_3 ortho), 123.55 (d, J=44.5, C cycle), 128.33 (C meta), 136.74 (C para), 140.70 (d, J=9.5, C ortho), 141.75 (d, J=74, C ipso); $^{31}P\{^{1}H\}$: -181.2. Mass Spec. M/z 204 (M^+, 100%).

1-Mesityl 2-methylphosphirene, **5**.

Propyne gas was bubbled for 5 mn into a mixture of $MesPCl_2$ (4.42 g, 20 mMole) and $AlCl_3$ (2.26 g, 20 mMole) in dichloromethane (20 mL) at -78°C. After 15 mn of stirring at this temperature, Bu_3P (5 mL, 20 mMole) was syringed into the reaction mixture, which was worked up as described above, and the yellow residue thus obtained was short-path distilled at 150°C/0.2 mm Hg (oven temperature). Yield 2.0 g (10.5 mMole, 53%) of a colorless, air-sensitive oil that slowly turns yellow on storage even at -20°C. NMR ($CDCl_3$): ^{1}H: 2.17 (CH_3 para), 2.39 (dm, J_{PH}=3.5, CH_3—cycle), 2.48 (CH_3 ortho), 6.69 (H meta), 7.43 (d, J_{PH}=22, H—cycle). $^{13}C\{^{1}H\}$: 13.86 (d, J=10, CH_3—cycle), 20.70 (CH_3 para), 20.73 (d, J=8.5, CH_3 ortho), 113.38 (d, J=45, C cycle—H), 128.77 (C meta), 129.33 (d, J=47.5, C cycle—CH_3), 136.72 (C para), 140.25 (d, J=10, C ortho), 140.43 (d, J=72.5, C ipso); $^{31}P\{^{1}H\}$: -192.0. Mass Spec. M/z 190 (M^+, 100%).

Mesityl (1-methylallenyl) phosphine, **3a**.

To a cold (-78°C) solution of **1** (780 mg, 3.81 mMole) in THF (10 mL) was added dropwise a solution of n-BuLi in hexane (3 mL of 1.3M, 3.9 mMole). The solution was warmed to room temperature,whereupon a red colour, corresponding to anion **4**, progressively appeared; the solution was further stirred for 10 mn and again cooled to -78°C. Trifluoroacetic acid (0.32 mL, 4.15 mMole) was then added dropwise. The reaction mixture was warmed to room temperature and solvent was stripped. The residue was extracted with hexane and evaporated to dryness, yielding **3a** (400 mg 1.95 mMole, 51%) as a very air-sensitive colorless oil, that was short-path distilled at 140°C/0.1 mm Hg (oven temperature). NMR ($CDCl_3$): ^{1}H: 1.70 (dt, J_{PH}=6, J_{HH}=3, CH_3—allenyl), 2.24

(CH_3 para), 2.44 (CH_3 ortho), 4.40 (br, CH_2), 4.83 (dt, J_{PH}=220, J_{HH}=2, H—P), 6.86 (H meta); $^{13}C\{^1H\}$: 18.53 (d, J=14, CH_3—allenyl), 21.02 (CH_3 para), 22.95 (d, J=11.5, CH_3 ortho), 71.12 (d, J=6, CH_2), 88.97 (d, J=12.5, C allenyl—P) 127.66 (d, J=15.3, Cipso), 128.85 (d, J=4, C meta), 138.42 (C para), 142.72 (d, J=12.5, C ortho), 207.97 (d, J=15, allenic C); $^{31}P\{^1H\}$: -75.8. The product was oxidised during the transfer to the mass spectrometer probe, as indicated by the molecular peak at M/z 206.

Mesityl (1-methylallenyl) methyl phosphine, 3b.

To a cold (-78°C) solution of anion 4 prepared as described above from 1 (700 mg, 3.42 mMole), n-BuLi in hexane (2.14 mL of 1.6M, 3.42 mMole), was added iodomethane (0.215 mL, 3.42 mMole). The reaction mixture was worked up as above, yielding 3b (470 mg, 2.15 mMole, 63%) as an air-sensitive colorless oil, that was short-path distilled at 145°C/0.1 mm Hg (oven temperature). NMR ($CDCl_3$): ^1H: 1.43 (d, J_{PH}=5, CH_3—P), 1.65 (dt, J_{PH}=9.5, J_{HH}=3, CH_3—allenyl), 2.24 (CH_3 para), 2.50 (CH_3 ortho), 4.64 (m, CH_2), 6.83 (H meta); $^{13}C\{^1H\}$: 9.31 (d, J=14, CH_3—P), 17.24 (d, J=27, CH_3—allenyl), 20.91 (CH_3 para), 22.34 (d, J=19, CH_3 ortho), 73.26 (CH_2), 94.29 (d, J=17, C allenyl—P) 128.34 (d, J=25, Cipso), 129.60 (d, J=4, C meta), 138.22 (C para), 145.31 (d, J=16.5, C ortho), 204.91 (d, J=8, allenic C); $^{31}P\{^1H\}$: -47.8. Mass spec. 218 (M^+, 30%), 150 (100%).

Mesityl (1-methylallenyl) trimethylsilylphosphine, 3c.

To a cold (-78°C) solution of anion 4 prepared as described above from 1 (1.11 g, 5.38 mMole), n-BuLi in hexane (4 mL of 1.35M, 5.40 mMole), was added Me_3SiCl (0.7 mL, 5.51 mMole). The reaction mixture was worked up as above, yielding 3c (1.39 g, 5.04 mMole, 63%) as an air-sensitive colorless oil. NMR ($CDCl_3$): ^1H: 0.20 (d, J_{PH}=5.5, CH_3—Si), 1.71 (dt, J_{PH}=9, J_{HH}=3, CH_3—allenyl), 2.23 (CH_3 para), 2.48 (CH_3 ortho), 4.55 (m, CH_2), 6.84 (H meta); $^{13}C\{^1H\}$: 0.40 (d, J=14, CH_3—Si), 20.77 (d, J=23.5, CH_3—allenyl), 21.30 (CH_3 para), 24.01 (d, J=16, CH_3 ortho), 72.35 (d, J=2, CH_2), 92.19 (d, J=15.5, C allenyl—P) 126.21 (d, J=21, Cipso), 129.54 (d, J=4.5, C meta), 138.23 (C para), 145.23 (d, J=13.5, C ortho), 206.36 (d, J=10.5, allenic C); $^{31}P\{^1H\}$: -78.6. Mass spec. 276 (M^+, 15%), 204 (100%).

Mesityl (1-methylallenyl) chlorophosphine, 3d.

To a solution of trimethylsilylphosphine 3c (530 mg, 1.92 mMole) in THF (10 mL) was added hexachloroethane (460 mg, 1.94 mMole) After 3 h of stirring at room temperature, solvent was stripped, the residue was extracted with hexane and the solvent evaporated to dryness, leaving 3d as an air-sensitive yellow oil (250 mg, 1.05 mMole, 55%), that was short-path distilled at 170°C/0.1 mm Hg (oven temperature). NMR ($CDCl_3$): ^1H: 1.85 (dt, J_{PH}=8.5, J_{HH}=3, CH_3—allenyl), 2.26 (CH_3 para), 2.56 (d, J_{PH}≈2, CH_3 ortho), 4.57 (dq, J_{PH}=5, J_{HH}=3, CH_2), 6.85 (H meta); $^{13}C\{^1H\}$: 15.70 (d, J=28.5, CH_3—allenyl), 20.98 (CH_3 para), 21.99 (d, J=22.5, CH_3 ortho), 74.65 (CH_2), 94.92 (d, J=40.5, C allenyl—P) 128.35 (d, J=44.5, Cipso), 129.81 (d, J=4 C meta), 141.31 (C para), 144.70 (d, J=16.5, C ortho), 205.45 (d, J=13, allenic C); $^{31}P\{^1H\}$: 73.2. Mass spec 238/240 (M^+, 50%), 185/187 (100%).

Mesityl methyl propynylphosphine, 8.

To a cold (-78°C) solution of phosphirene 5 (500 mg, 2.63 mMole) in THF (10 mL) was added n-BuLi (1.65 mL of 1.6M hexane solution, 2.64mMole). The solution was stirred at room temperature for 1 h, and iodomethane (0.17 mL, 2.73 mMole) was syringed into the reaction mixture, that was evaporated to dryness and extracted with hexane, yielding 8 (140 mg, 0.68 mMole, 26%) as a colorless air-sensitive oil, that was purified by column chromatography (hexane). NMR ($CDCl_3$): ^1H: 1.43 (d, J_{PH}=6, CH_3—P), 1.92 (d, J_{PH}=2, CH_3 propynyl), 2.22 (CH_3 para), 2.64 (CH_3 ortho), 6.85 (H meta); $^{13}C\{^1H\}$: 5.15 (CH_3 propynyl) 11.51 (d, J=10, CH_3—P), 20.80 (CH_3 para), 22.64 (d, J=19.5, CH_3 ortho), 77.65 (acetylenic C—P), 103.08 (d, J=5,

acetylenic C) 128.88 (d, J=11, Cipso), 129.45 (d, J=5, C meta), 139.29 (C para), 143.82 (d, J=17, C ortho); $^{31}P\{^1H\}$: -71.9.

Mesityl acetyl propynylphosphine, **11**.

To a cold (-78°C) solution of anion **6** prepared as described above with **5** (570 mg, 3 mMole) and n-BuLi (1.9 mL of 1.6M hexane solution, 3.04 mMole) was added solid $MgBr_2$ (550 mg, 2.99 mMole). The reaction mixture was warmed to 0°C, where it became homogeneous. Acetyl chloride (0.25 mL, 3.50 mMole) was then syringed into the solution. Solvent was stripped, and the residue was chromatographed (toluene/ethyl acetate 90/10). **11** was obtained as a white solid, mp 58°C (410 mg, 1.77 mMole, 59%). NMR ($CDCl_3$): ^1H: 2.02 (CH_3 propynyl), 2.26 (CH_3 para), 2.37 (d, J_{PH}=6.5, CH_3 acetyl), 2.50 (CH_3 ortho), 6.93 (H meta); $^{13}C\{^1H\}$: 5.42 (CH_3 propynyl), 21.00 (CH_3 para), 23.07 (d, J=15.5, CH_3 ortho), 31.09 (d, J=41, CH_3 acetyl), 71.27 (d, J=8, acetylenic C—P), 107.48 (d, J=5.5, acetylenic C) 125.07 (Cipso), 129.44 (d, J=6, C meta), 141.05 (C para), 144.60 (d, J=16.5, C ortho), 220.07 (d, J=31, CO); $^{31}P\{^1H\}$: -33.8. Mass spec. M/z 232 (M^+, 60%), 189 (M^+-acetyl, 100%).

1-Mesityl 2-methyl 3-(dimethylhydroxymethyl)phosphirene, **12**.

To a cold (-78°C) solution of anion **6** prepared as described above with **5** (480 mg, 2.52 mMole) and n-BuLi (1.65 mL of 1.6M hexane solution, 2.64 mMole) was added dry acetone (0.22 mL, 3 mMole). The reaction mixture was warmed to room temperature, and excess solid powdered NH_4Cl was added. The solution was filtered, evaporated to dryness, and the residue dissolved in toluene and chromatographed (toluene/ethyl acetate 70:30). The main fraction was collected and evaporated to dryness, leaving **12** as an air-sensitive, colorless oil (300 mg, 1.21 mMole, 48%). NMR ($CDCl_3$): ^1H: 1.44 (CH_3—alcool), 2.17 (CH_3 para), 2.42 (d, J_{PH}=3.5, CH_3—cycle), 2.54 (CH_3 ortho), 2.6 (br.s., exch. with D_2O, OH), 6.70 (H meta); $^{13}C\{^1H\}$: 12.50 (d, J=9, CH_3—cycle), 20.79 (CH_3 para), 21.81 (d, J=10.5, CH_3 ortho), 28.99 (d, J=25, CH_3—alcool), 70.70 (d, J=8, C alcool), 123.41 (d, J=45, C cycle—CH_3), 128.32 (C meta), 133.38 (d, J=49.5, C cycle), 136.77 (C para), 140.16 (d, J=76, C ipso), 140.62 (d, J=10, C ortho); $^{31}P\{^1H\}$: -172.1. Mass Spec. M/z 248 (M^+, 20%), 233 (100%).

1-Mesityl 2-methyl 3-hydroxymethylphosphirene, **13**.

A cold (-78°C) solution of anion **6** prepared as described above with **5** (520 mg, 2.73 mMole) and n-BuLi (1.71 mL of 1.6M hexane solution, 2.74 mMole) was warmed to 0°C (ice/water bath). Excess dry paraformaldehyde (500 mg) was then added. After 3 h of stirring, excess solid powdered NH_4Cl was added, and the solution was filtered, evaporated to dryness, and the residue dissolved in toluene and chromatographed (toluene/ethyl acetate 50:50). The main fraction was collected and evaporated to dryness, leaving **13** as an air-sensitive, slightly yellow oil (220 mg, 1.0 mMole, 36%). NMR ($CDCl_3$): ^1H: 2.18 (CH_3 para), 2.32 (m, CH_3—cycle), 2.46 (CH_3 ortho), 3.25 (br.s., exch. with D_2O, OH), 4.68 (br.d, J_{AB}=16, H_A of CH_2), 4.81 (br.d, J_{AB}=16, H_B of CH_2), 6.70 (H meta); $^{13}C\{^1H\}$: 12.74 (d, J=9, CH_3—cycle), 20.79 (CH_3 para), 21.38 (d, J=9.5, CH_3 ortho), 58.87 (d, J=10, CH_2), 125.50 (d, J=47.5, C cycle), 126.44 (d, J=48, C cycle), 128.22 (C meta), 136.80 (C para), 140.30 (d, J=10, C ortho), 140.70 (d, J=74, C ipso); $^{31}P\{^1H\}$: -176.8. Mass Spec. M/z 220 (M^+, 25%), 149 (100%).

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