γ-Functionalisation of the 1-Phosphanorbornadiene Structure

Frédéric Robin,[a] François Mercier,[a] Louis Ricard,[a] and François Mathey*[a]

Keywords: Phosphanorbornadiene / Allylic metalation / Allylic bromination / BIPNOR dioxide

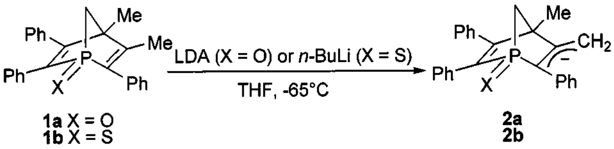
3-Methyl-substituted 1-phosphanorbornadiene oxides or sulfides such as **1a,b** are either metalated by a strong base (n-BuLi or LDA) or brominated by NBS at the methyl substituent. The reaction of the resulting delocalised carbanions **2a,b** takes place either at C-2 (H^+, MeI) or at the methylene group (Me_3SiCl, $ClPPh_2$, I_2). In the last case, γ-functional (**5a,b** or **6a,b**) or bridged (**7**) phosphanorbornadienes are obtained. Similarly, the reaction of 3-bromomethyl-1-phosphanorbornadiene oxides such as **8** with nucleophiles [$NaCH(CO_2Me)_2$, PhO^-, Me_2NH, $PhCH_2NH_2$] yields the corresponding γ-functional phosphanorbornadienes **9–12**. This chemistry has also been applied to the BIPNOR dioxide **13**.

Introduction

The 1-phosphanorbornadiene (1-phosphabicyclo[2.2.1]-hepta-2,5-diene) structure is now well established as a valuable source of phosphorus ligands for homogeneous catalysis. Powerful alkene hydrogenation and hydroformylation catalysts have been developed with rhodium.[1][2] They are approximately 10 times more active than their Ph_3P counterparts. Water-soluble phosphanorbornadienes have been prepared[3][4] and one of them, the so-called norbos,[3] is among the best ligands for the biphasic hydroformylation of propene. Since the bridgehead phosphorus atom of such structures cannot racemise, 1-phosphanorbornadienes have also been used in asymmetric catalysis.[5][6] The so-called BIPNOR[6] is one of the most efficient ligands for the enantioselective hydrogenation of functional alkenes. With such a background, it was obviously necessary to develop synthetic tools allowing to modulate the stereoelectronic and physicochemical properties of a preformed 1-phosphanorbornadiene. In a sister paper,[7] we have shown how it is possible to use the Stille cross-coupling reaction to graft functional groups on the C-2 position. In this paper, we describe several techniques allowing the introduction of functional groups on a β-methyl substituent. Among the possible uses of this remote γ-functionalisation are: 1) to provide the initial structure with some water solubility; 2) to graft this structure on a polymeric backbone; 3) to block the free rotation of a C-2−C-2′ dimeric structure so as to obtain atropisomers, etc. All these modifications must be achieved without significantly altering the stereoelectronic and catalytic properties of the phosphorus centre.

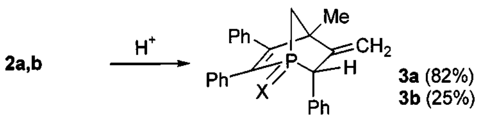
Results and Discussion

Our starting products have been the easily accessible 4,5-dimethyl-2,3,6-triphenyl-1-phosphanorborna-2,5-diene 1-oxide and 1-sulfide (**1a** and **1b**).[8] In these compounds, the 5-methyl group is activated by the P=O or P=S electron-withdrawing groups through the C-6=C-5 double bond. Allylic metalation can be easily achieved in such cases as already shown with the 3,4-dimethylphosphole sulfides.[9] Indeed, lithium diisopropylamide (LDA) and n-butyllithium cleanly convert **1a** and **1b**, respectively, into the corresponding delocalised carbanions **2a,b** at low temperature (Equation 1).

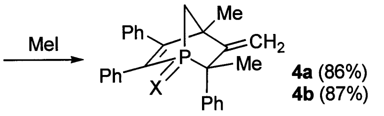


(1)

It appeared that butyllithium is less selective for X=O. These carbanions are selectively protonated and methylated at C-6 (Equations 2, 3).



(2)



(3)

Traces of **1a,b** are formed together with **3a,b**. The ^1H-NMR spectra of **3a,b** show a characteristic C*H*Ph resonance at $\delta = 4.41$ [$^2J(\text{H-P}) = 18.9$ Hz] and 4.34, [$^2J(\text{H-P}) = 15.5$ Hz], respectively, thus suggesting a similar stereochemistry at C-6.[10] The ^{13}C-NMR spectra of **4a,b** display the 6-CH_3 resonance at $\delta = 19.93$ [$^2J(\text{C-P}) = 18.1$ Hz] and 20.36, [$^2J(\text{C-P}) = 15.9$ Hz].

The stereochemistry of **3** and **4** was established by the X-ray crystal-structure analysis of **4a** (Figure 1). The proton and the methyl group on C-6 are in the *exo* position. This result is compatible with the observed values for the ^2J(H-P) couplings in **3a,b**.[10] When compared with the structure of a 1-phosphanorbornadiene oxide,[5] the structure of **4a** shows a significant shortening of the P−C bridge bond

---

[a] Laboratoire "Hétéroéléments et Coordination", UMR CNRS 7653, DCPH Ecole Polytechnique, F-91128 Palaiseau Cedex, France

1434−193X/99/0505−1091 $ 17.50+.50/0

from 1.819(3) to 1.791(1) Å. As expected, the P−C-1 bond is with 1.8606(9) Å longer than a P−C-sp^2 bond. The sum of the C−P−C angles increases from 281.5 in the 1-phosphanorbornadiene oxide[5] to 286.3° in **4a**, thus indicating some relief of ring strain in **4a**. The geometry of several lithiated phosphoryl-substituted carbanions has been shown to be close to planar on the basis of X-ray crystal-structure analyses,[11] ab initio calculations[12] and deuteration/alkylation experiments.[13] If we admit such a planar geometry for **2a** and **2b**, then the observed stereochemical preference for *exo* protonation and methylation reflects the lower steric hindrance of the *exo* versus the *endo* face of **2a** and **2b**.

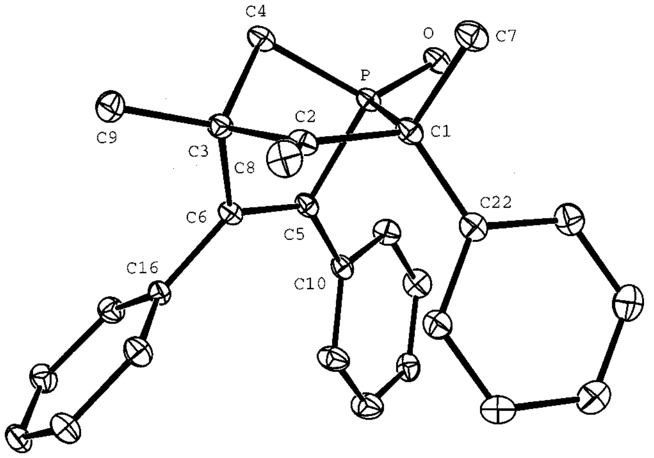
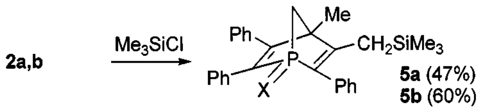
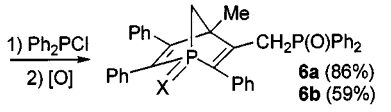


Figure 1. ORTEP drawing of the 1-phosphanorbornadiene oxide **4a**; selected bond lengths [Å] and angles [°]: P−O 1.4801(7), P−C1 1.8606(9), P−C4 1.791(1), P−C5 1.8128(9); C1−P−C5 99.80(4), C1−P−C4 93.53(4), C4−P−C5 93.01(4); O−P−C1−C7 48.3 ± 1

This steric control of the stereochemistry of the reactions of electrophiles with **2a** and **2b** is paralleled by a steric control of the regiochemistry. Whereas hard H$^+$ and soft MeI both react essentially at the α positions of the delocalised carbanions, both hard Me$_3$SiCl and soft Ph$_2$PCl react essentially at the γ positions (Equations 4, 5).

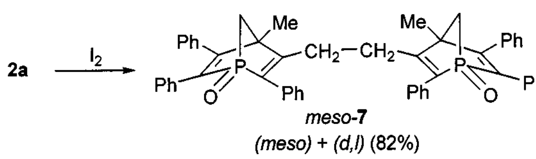


(4)



(5)

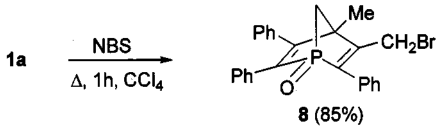
With Me$_3$SiCl, traces of the α-functional derivatives are also formed. In the ^{1}H-NMR spectrum of **5a**, the signal of the CH$_2$Si group appears as an ABX system: δ_A = 1.89, δ_B = 2.44 [$^2J(H_A\text{-}H_B)$ = 12.9 Hz, $^4J(H_B\text{-}P)$ = 3.2 Hz]. A similar phenomenon is observed on the ^{1}H-NMR spectrum of **5b**. In the case of **6a** and **6b**, the very low coupling between the two phosphorus nuclei rules out the α functionalisation: **6a**: $\delta^{31}P$ = 47.25 and 25.27 [^4J(P-P) = 8 Hz]; **6b**: $\delta^{31}P$ = 53.15 and 25.1 [^4J(P-P) = 8 Hz]. As in the preceding case, the two CH$_2$ protons appear to be sharply inequivalent. γ-Attack was also observed with iodine. In that case, a very interesting bis-1-phosphanorbornadiene **7** was obtained in good yield (Equation 6).



(6)

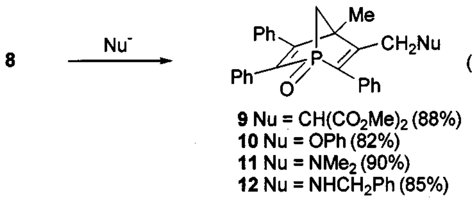
The mass spectrum of **7** shows the molecular peak at *m/z* 762. The ^{31}P-NMR spectrum shows the signals of the two isomers at δ = 45.29 and 44.96. Unfortunately, we were unable to separate these diastereomers.

Although leading to some original γ-functional 1-phosphanorbornadienes, the metalation route described above is clearly limited by the competition between α and γ attacks. Additional routes were thus needed. Allylic bromination provided a convenient alternative. The reaction of **1a** with *N*-bromosuccinimide indeed affords the bromomethyl derivative **8** in high yield (Equation 7).



(7)

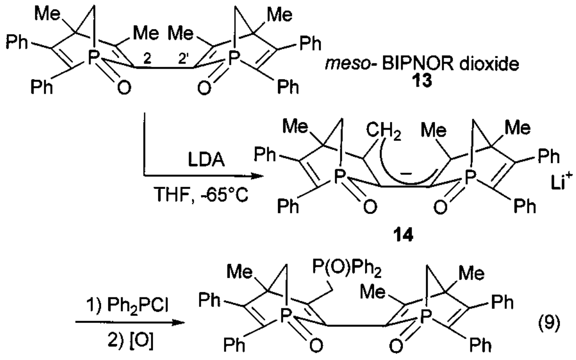
The mass spectrum of **8** shows the two expected molecular peaks at *m/z* 460 (^{79}Br) and 462 (^{81}Br) in the isotopic ratio. In the ^{1}H-NMR spectrum, the CH$_2$Br group gives a singlet at δ = 4.25 Compound **8** is a good precursor for a variety of γ-functional 1-phosphanorbornadienes. It cleanly reacts with mild nucleophiles such as sodium dimethyl malonate, phenoxide ion and amines (Equation 8).



(8)

In all of the resulting γ-functional 1-phosphanorbornadienes, the protons of the CH$_2$Nu substituent are sharply inequivalent.

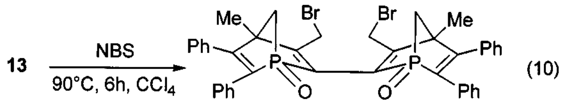
The *meso* isomer represents two thirds of the total amount of BIPNOR which is produced by the reaction of tolan with 3,3′,4,4′-tetramethyl-1,1′-biphospholyl.[6] Only the *d,l* enantiomers find some use as potent ligands in asymmetric catalysis. Thus, we decided to investigate the possible use of our γ-functionalisation methods to transform the *meso*-BIPNOR dioxide **13** into stable and potentially useful atropoisomers. The metalation route immediately appeared useless. Indeed, only mono-metalation can be achieved as shown by quenching the carbanion with Ph_2PCl (Equation 9).



15 (45%)

As expected, the ^{31}P-NMR spectrum of **15** displays three resonances at $\delta = 29.16$ (Ph_2PO), 46.06 and 51.06 in $CDCl_3$. We suspect that the impossibility to obtain the bis-anion results from a delocalisation of the negative charge all over the five carbon atoms through the bridge. The presence of some negative charge on C-3′ prevents the deprotonation of its methyl substituent.

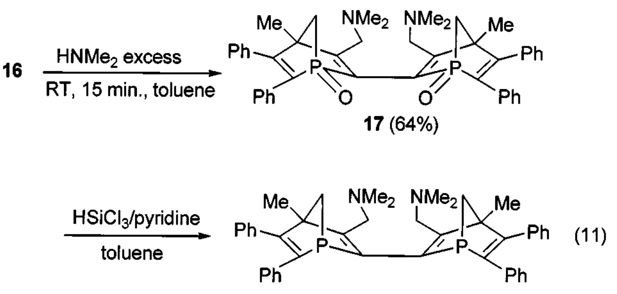
The bromination route proved more satisfactory. Allylic dibromination could be easily achieved with NBS (Equation 10).



16 (87%)

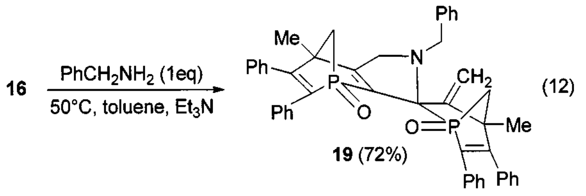
When monitoring the reaction by ^{31}P NMR, the initial formation of the monobromination product could be observed. It displays signals of two weakly coupled ^{31}P nuclei at $\delta = 45.94$ and 47.86 versus $\delta = 46.98$ for **16** in CCl_4. Contrary to the signals of the CH_2Br protons of **8**, those of **16** appear as two inequivalent sets at $\delta = 4.06$ and 4.42 [^2J(H-H) = 10.6 Hz].

The reaction of **16** with dimethylamine easily affords the 3,3′-bis(dimethylaminomethyl) derivative **17** (Equation 11).



18 (78%)

The two ^{31}P nuclei of **17** are inequivalent {AB system: $\delta_A = 46.10$ and $\delta_B = 44.00$ [$^3J_{AB}$ = 15.4 Hz]}, thus showing that the rotation of the two phosphanorbornadiene units around the C-2−C-2′ axis is slow on the NMR time scale at room temperature. This inequivalence disappears upon reduction to **18**. This observation indicates that **17** is probably a mixture of slowly interconverting atropisomers as is the BIPNOR disulfide.[6] In order to freeze completely the rotation around C-2−C-2′, we decided to investigate the reaction of **16** with a primary amine such as benzylamine, aiming to create a second bridge between the C-3 and C-3′ positions. Beside traces of the 3,3′-bis(benzylaminomethyl)-substituted derivative, the main product is the spirocyclic compound **19** (Equation 12).



The formula of **19** was established by X-ray crystal-structure analysis (Figure 2). The first S_N2 substitution is followed by an S_N2' substitution on the second bromoallyl unit. Very probably, the 3-CH_2NHCH_2Ph substituent initially formed cannot come close to the 3′-CH_2Br substituent of the second phosphanorbornadiene unit as a result of the blocked rotation around C-2−C-2′. Thus only a S_N2' substitution at C-3′ is possible. As already seen in the first part of this report, the reaction takes place on the less hindered *exo* face of the second phosphanorbornadiene.

As a temporary conclusion, it can be stated that both allylic metalation and allylic bromination are versatile and complementary routes to γ-functionalized 1-phosphanorbornadienes. The catalytic properties of these promising ligands remain to be explored

Experimental Section

All reactions were carried out under argon, and silica gel (70−230 mesh) was used for chromatographic separations. NMR spectra were recorded with a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in ppm downfield from internal TMS (^{1}H and ^{13}C) or external 85% H_3PO_4 (^{31}P). Routine mass spectra for all compounds were obtained at 70 eV by the direct inlet method, with a Hewlett−Packard GC 5890−11S 5989 B spectrometer. Elemental analyses were performed by the "Service d'analyse du CNRS" at Gif-sur-Yvette, France.

Compound 2a: To a magnetically stirred solution of **1a** (500 mg, 1.3 mmol) in 10 mL of THF at −60°C was added dropwise 3 mL of lithium diisopropylamide (0.5 M solution in hexane/THF, 50:50). The stirred solution was maintained at −60°C for 30 min.

Compound 2b: To a magnetically stirred solution, containing 700 mg (1.76 mmol) of **1a** in 20 mL of THF at −60°C was added dropwise *n*-butyllithium (2 mL of 1.1 M solution in hexane). The stirred solution was kept for 30 min at −60°C.

Compound 3a: To the purple solution of **2a** was added 1 mL of H_2O. The solution decolorised immediately and was allowed to warm to room temperature. The reaction mixture was extracted with 20 mL of CH_2Cl_2, washed with water (2 × 5 mL), dried with Na_2SO_4 and concentrated.The residue was purified by chromatography (AcOEt as eluent) to give 410 mg (82%) of **3a**. − ^{31}P NMR ($CDCl_3$): $\delta = 49.65$. − ^{1}H NMR ($CDCl_3$): $\delta = 1.39$ (s, 3 H, Me); 2.26−2.46 (m, 2 H, CH_2P); 4,41 (d, $J_{H,P} = 18.2$ Hz, 1 H, CH-Ph); 5.13 (d, $J = 1.9$ Hz, 1 H, C=CH_aH$_b$); 5.36 (q, $J = 1.9$ Hz, $J_{H,P} =$

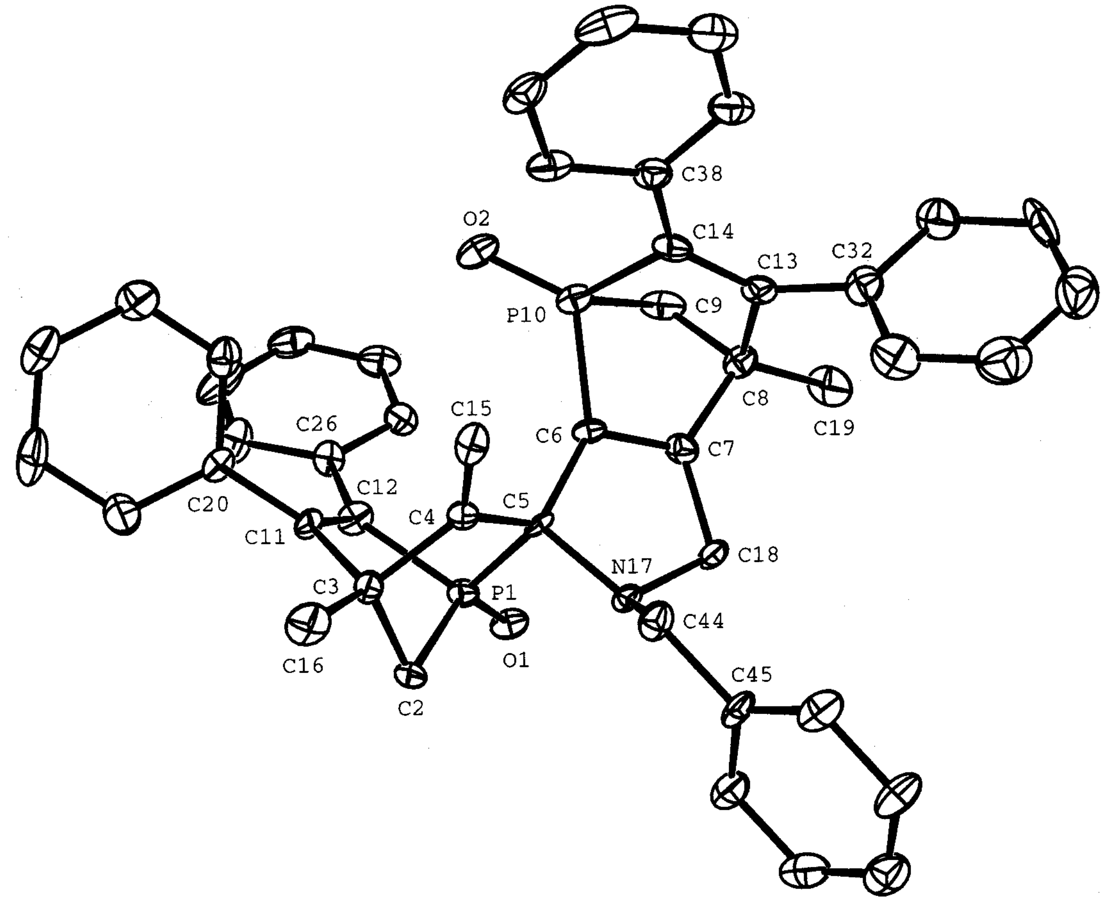


Figure 2. ORTEP drawing of the spirocyclic compound **19**

2.6 Hz, 1 H, C=CH_aH_b); 6.65−7.36 (m, 15 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.7 (d, $J_{C,P}$ = 18 Hz, Me); 46.8 (d, $J_{C,P}$ = 58.4 Hz, CH-Ph); 47.9 (d, $J_{C,P}$ = 21.9 Hz); 49.4 (d, $J_{C,P}$ = 63.9 Hz, CH_2); 111.9 (d, $J_{C,P}$ = 11.8 Hz, C=CH_2). − MS; *m/z* (%): 382 (100) [M]; 266 (35) [M − PhCHC=CH_2]; 204 (47) [M − PhC=CPh]. − R_f(AcOEt) = 0.15. − $C_{26}H_{23}OP$ (382.44): calcd. C 81.66, H 6.06; found C 81.65, H 6.06.

Compound 3b: 2 mL of water was added to the stirred purple solution of **2b** at −60°C. The decolorised mixture was allowed to warm to room temperature, then extracted with dichloromethane. The organic extracts were washed with 5 mL of water, dried with Na_2SO_4, and concentrated in vacuo to give a yellow oily 1:3 mixture of **1b** and **3b**. 180 mg (25%) of **3b** was isolated by chromatography (CH_2Cl_2 as eluent). − ^{31}P NMR ($CDCl_3$): δ = 54.48. − ^1H NMR ($CDCl_3$): δ = 1.41 (s, 3 H, Me); δ_a = 2.32, δ_b = 2.52 (ABX system, 2 H, CH_2, *J* = 11 Hz, $J_{Ha,P}$ = 6 Hz, $J_{Hb,P}$ = 10 Hz); 4.34 (d, $J_{H,P}$ = 15.5 Hz, 1 H, C*H*-Ph); δ_a = 5.13, δ_b = 5.35 (ABX, 2 H, C=CH_aH_b, *J* = 2.5 Hz, $J_{Hb,P}$ = 2.5 Hz); 6.57−7.41 (m, 15 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.88 (d, Me, $J_{C,P}$ = 13 Hz); 52.63 (d, $J_{C,P}$ = 15 Hz); 52.72 (d, $J_{C,P}$ = 43.7 Hz, C*H*-Ph); 53.77 (d, $J_{C,P}$ = 52 Hz, CH_2P); 111.96 (d, $J_{C,P}$ = 9.5 Hz, C = CH_2); 135.49 (d, $J_{C,P}$ = 33.5 Hz); 150.92 (d, $J_{C,P}$ = 3 Hz); 156.75 (d, $J_{C,P}$ = 15 Hz). − MS; *m/z* (%): 398 (100) [M]. − R_f(CH_2Cl_2) = 0.44.

Compound 4a: As with **3a**, 0.1 mL of iodomethane in 2 mL of THF was added to **2a** at −60°C. After warming to room temperature, the THF was removed in vacuo, then 10 mL of water was added and the mixture was extracted with 2 × 20 mL of Et_2O and the combined organic phases were dried with Na_2SO_4. The solution was concentrated in vacuo to give **4a**, which was recrystallized from hexane, to yield 450 mg (86%) of white crystals; m.p. 220°C. − ^{31}P NMR ($CDCl_3$): δ = 55.28. − ^1H NMR ($CDCl_3$): δ = 1.41 (s, 3 H, Me); 1.98 (d, $J_{H,P}$ = 14.4 Hz, 3 H, Me); 2.32−2.53 (m, 2 H, CH_2); 5.29 (s, 1 H, C=C$H_a$$H_b$); 5.6 (d, $J_{Hb,P}$ = 2.6 Hz, 1 H, C=$CH_a$$H_b$); 6.44−7.56 (m, 15 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.93 (d, $J_{C,P}$ = 18 Hz, Me); 26.99 (s, Me); 46.3 (d, $J_{C,P}$ = 62.6 Hz, *C*MePh); 47.52 (d, $J_{C,P}$ = 22.4 Hz); 49.08 (d, $J_{C,P}$ = 62.6 Hz, CH_2); 111.58 (d, $J_{C,P}$ = 10.5 Hz, C=CH_2). − MS; *m/z* (%): 396 (100) [M].

Compound 4b: After dropwise addition of a solution of 0.11 mL of IMe in 2 mL of THF, the same procedure was used as for **3b**. Purification of **4b** by chromatography (CH_2Cl_2 as eluent) gave 810 mg (87%) of a white crystalline product; m.p. 114°C. − ^{31}P NMR ($CDCl_3$): δ = 64.98. − ^1H NMR (C_6D_6): δ = 1.46 (s, 3 H, Me); 1.88 (d, $J_{H,P}$ = 17 Hz, Me); 1.93 and 2.12 (ABX, *J* = 11.5 Hz, $J_{Ha,P}$ = 5.8 Hz, $J_{Hb,P}$ = 9.9 Hz, 2 H, CH_2P); 5.32 (s, 1 H, =CH_2); 5.63 (d, 1 H, $J_{H,P}$ = 2.2 Hz, =CH_2); 6.31−7.66 (m, 15 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.35 (d, $J_{C,P}$ = 16 Hz, Me); 27.63 (s, C*Me*Ph); 49.8 (d, $J_{C,P}$ = 46 Hz, *C*MePh); 52.65 (d, $J_{C,P}$ = 17 Hz, *C*Me); 53.4 (d, $J_{C,P}$ = 51 Hz, CH_2P); 112.27 (d, $J_{C,P}$ = 9.2 Hz, = CH_2). − MS; *m/z* (%): 412 (100) [M]. − R_f(CH_2Cl_2) = 0.61. − $C_{27}H_{25}PS$ (412.54): calcd. C 78.61, H 6.11, P 7.51; found C 78.71, H 6.06, P 7.44.

Compound 5a: A solution of 0.1mL (1.6 mmol) of chlorotrimethylsilane in 2mL of THF was added dropwise at −60°C to **2a**. The solution was allowed to warm to room temperature and the organic mixture was extracted as for **3a**. The oily residue was chromatographed (AcOEt as eluent). **1a** was eluted first, then **5a** (280 mg, 47%) and finally **3a**. − **5a:** ^{31}P NMR ($CDCl_3$): δ = 46.79. − ^{1}H NMR ($CDCl_3$): δ = 0 (s, 9 H, Me_3Si); 1.35 (s, 3 H, Me); δ_a = 1.89, δ_b = 2.44 (ABX, J = 12.9 Hz, $J_{Hb,P}$ = 3.2 Hz, 2 H, CH_aH_b-Si); 2.75 (m, 2 H, CH_2P); 6.99−7.40 (m, 15 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.2 (s, Me_3Si); 20.25 (d, $J_{C,P}$ = 13.7 Hz, CH_2-Si); 20.35 (d, $J_{C,P}$ = 18.3 Hz, Me); 49.98 (d, $J_{C,P}$ = 27.5 Hz); 67.15 (d, $J_{C,P}$ = 70.2 Hz, CH_2P). − MS; *m/z* (%): 454 (60) [M]; 382 (100) [M − TMS + 1]. − R_f(AcOEt) = 0.53.

Compound 5b: 0.3 mL (2.4 mmol) of chlorotrimethylsilane in 2 mL of THF was added to **2b** at −60°C. The solution was allowed to warm to room temperature and the organic products were extracted as for **3b**. Purification by chromatography of the residue (CH_2Cl_2 as eluent) gave **5b** (350 mg, 60%) and **3b**, m.p. 137°C. − **5b:** ^{31}P NMR ($CDCl_3$): δ = 53.92. − ^{1}H NMR ($CDCl_3$): δ = 0 (s, 9 H, Me_3Si); 1.39 (s, 3 H, Me); δ_a = 1.86, δ_b = 2.42 (ABX, J = 12.8 Hz, $J_{H,P}$ = 3.1 Hz, 2 H, CH_aH_b-Si); δ_a = 2.74, δ_b = 2.87 (ABX, J = 9.2 Hz, $J_{Ha,P}$ = 7.6 Hz, $J_{Hb,P}$ = 7.3 Hz, 2 H, CH_aH_bP); 6.96−7.38 (m, 15 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.5 (s, 3 Me, Me_3Si); 20.18 (d, $J_{C,P}$ = 12.1 Hz, CH_2-Si); 20.61 (d, $J_{C,P}$ = 16.6 Hz, Me); 56.47 (d, $J_{C,P}$ = 19.7 Hz); 70.73 (d, $J_{C,P}$ = 59 Hz, CH_2P). − MS; *m/z* (%): 470 (77) [M]; 455 (8) [M − Me]; 292 (65) [M − PhC=CPh]; 186 (100) [Phosphole]. − R_f(CH_2Cl_2) = 0.54. − $C_{29}H_{31}PSSi$ (470.69): calcd. C 74.00, H 6.64; found C 74.15, H 6.74.

Compound 6a: 0.3 mL (1.7 mmol) of Ph_2PCl in 2 mL of THF was added to **2a**. The same work-up as with **3a** and quantitative oxidation in air gave **6a** (650 mg, 86%) as a white solid, m.p. 122°C. − ^{31}P NMR ($CDCl_3$): δ_a = 47.25, δ_b = 25.27 (AX, J = 8 Hz). − ^{1}H NMR ($CDCl_3$): δ = 1.61 (s, 3 H, Me); δ_a = 2.78, δ_b = 2.88 (ABX, J = 9.7 Hz, $J_{Ha,P}$ = 21 Hz, $J_{Hb,P}$ = 21 Hz, 2 H, CH_2P); 3.31−4.20 [m, 2 H, CH_2-P(O)]; 6.94−7.66 (m, 25 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.77 (d, $J_{C,P}$ = 18.7 Hz, Me); 31.73 [dd, $CH_2P(O)$, $J_{C,P}$ = 62.8 Hz, $J_{C,P}$ = 13.5 Hz]; 50.43 (d, $J_{C,P}$ = 26.5 Hz); 68.6 (d, CH_2, $J_{C,P}$ = 70.3 Hz); 139.49 (d, $J_{C,P}$ = 77.9 Hz); 143.92 (dd, $J_{C,P}$ = 80.9 Hz, $J_{C,P}$ = 10.7 Hz); 155.5 (dd, $J_{C,P}$ = 16.8 Hz, $J_{C,P}$ = 12.2 Hz); 164.45 (d, $J_{C,P}$ = 18.1 Hz). − MS; *m/z* (%): 582 (46) [M]; 381 (17) [M − $P(O)Ph_2$]; 201 (100) [$P(O)Ph_2$]. − $C_{38}H_{32}O_2P_2$ (582.62): calcd. C 78.34, H 5.54, P 10.63; found C 76.31, H 5.61, P 10.45.

Compound 6b: 0.4 mL (2.2 mmol) of Ph_2PCl in 3 mL of THF was added to **2b**. The crude solid was oxidized quantitatively as in the case of **3b**. **6b** (600 mg, 60%) was purified by chromatography (CH_2Cl_2/AcOEt, 80:20 as eluent). − ^{31}P NMR ($CDCl_3$): δ_a = 53.15, δ_b = 25.1 (AX, J = 8 Hz). − ^{1}H NMR ($CDCl_3$): δ = 1.68 (s, 3 H, Me); 2.82−3.00 (m, 2 H, CH_2P); 3.28−4.10 [m, 2 H, CH_2-P(O)]; 6.81−7.65 (m, 25 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.15 (d, $J_{C,P}$ = 16.4 Hz, Me); 32.07 [dd, $J_{C,Pa}$ = 63.3 Hz, $J_{C,Pb}$ = 11.7 Hz, CH_2-P(O)]; 56.9 (d, $J_{C,P}$ = 18.7 Hz, C-4); 71.6 (d, $J_{C,P}$ = 59.5 Hz, CH_2P). − MS; *m/z* (%): 598 (35) [M]; 566 (10) [M − S]; 420 (64) [M − PhC=CPh].

Compound 7: I_2 (400 mg, 1.6 mmol) was added to a solution of **2a** at −60°C and the mixture was allowed to warm to room temperature. 10 mL of H_2O was added and the products were extracted with 2 × 20 mL of Et_2O. The organic layer was washed with a solution of sodium thiosulfate (2 M), dried with Na_2SO_4 and stripped to dryness in vacuo. After chromatography (AcOEt as eluent), **7** (410 mg, 82%) was obtained as a (50:50) mixture of two diastereoisomers. − ^{31}P NMR ($CDCl_3$): δ = 45.29 and 44.96. − ^{1}H NMR ($CDCl_3$): δ = 1.03 and 1.14 (s, 6 H, 2Me). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 18.86 and 19.22 (d, $J_{C,P}$ = 13.4 Hz, Me); 27.88 and 28.14 (d, $J_{C,P}$ = 13.3 Hz, CH_2-CH_2); 49.41 (d, $J_{C,P}$ = 27.3 Hz); 68.86 and 69.22 (d, $J_{C,P}$ = 68.7 Hz, CH_2P). − MS; *m/z* (%): 762 (80) [M]; 584 (30) [M − PhC=CPh]; 381 (70) [M/2]; 363 (100) [M/2 − H_2O + 1]; 178 (100) [PhC=CPh].

Compound 8: A suspension of 500 mg of **1a** (1.3 mmol) in 20 mL of CCl_4 was placed in a three-necked flask containing a magnetic stirring bar. The suspension was refluxed until the solution was homogeneous, whereupon it was treated with 280 mg (1.6 mmol) of solid *N*-bromosuccinimide. After stirring at reflux for 30 min, the solution was allowed to cool to room temperature. The precipitate was filtered off through a plug of CH_2Cl_2-dampened Celite which was subsequently washed with CH_2Cl_2. The resulting solution was extracted with 20 mL of HCl (1 N), then 2 × 20 mL of H_2O and dried with Na_2SO_4. The organic extracts were concentrated in vacuo and hexane was added to give a white solid. Recrystallisation from hexane/CH_2Cl_2 gave **8** (510 mg, 85%), m.p. 162°C. − ^{31}P NMR ($CDCl_3$): δ = 45.6. − ^{1}H NMR ($CDCl_3$): δ = 1.58 (s, 3 H, Me); 2.78−2.98 (m, 2 H, CH_2P); 4.25 (s, 2 H, CH_2Br); 7.05−7.65 (m,15 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 18.69 (d, $J_{C,P}$ = 18.5 Hz, Me); 26.37 (d, $J_{C,P}$ = 15.7 Hz, CH_2Br); 49.07 (d, $J_{C,P}$ = 26.2 Hz); 70.21 (d, $J_{C,P}$ = 70.15, CH_2P); 138.25 (d, $J_{C,P}$ = 79.56 Hz); 144.66 (d, $J_{C,P}$ = 77.85 Hz); 157 (d, $J_{C,P}$ = 17.2 Hz); 163.58 (d, $J_{C,P}$ = 16.3 Hz). − MS; *m/z* (%): 461 (16) [M]; 382 (46) [M − Br]; 204 (80) [M − Br − tolane]; 178 (100) [PhC=CPh]. − $C_{26}H_{22}BrOP$ (461.34): calcd. C 67.69, H 4.81, P 6.71; found C 66.72, H 4.89, P 6.71.

Compound 9: 50 mg of NaH (60% in oil) was degreased using 2 × 2 mL of pentane. Then 5 mL of THF was added and the suspension was cooled to 0°C in an ice bath. 180 μL of $CH_2(COOMe)_2$ (1.6 mmol) was added and the mixture was stirred vigorously for 30 min at 0°C. 500 mg of **8** (1.1 mmol) in 5 mL of THF was added dropwise at 0°C, and the mixture was allowed to warm to room temperature. Stirring was continued for a further 30 min before H_2O (5 mL) was added. The resulting mixture was extracted with 2 × 20 mL of CH_2Cl_2. The combined organic phases were washed with H_2O, dried with Na_2SO_4 and stripped of solvent in vacuo. The white solid **9** was recrystallized from AcOEt to give 500 mg (88%), m.p. 212°C. − ^{31}P NMR ($CDCl_3$): δ = 46.00. − ^{1}H NMR ($CDCl_3$): δ = 1.47 (s, 3 H, Me); 2.77 (m, 2 H, CH_2P); 3.15 [m, 2 H, CH_2-$CH(CO_2Me)_2$]; 3.45−3.56 [m, 1 H, $CH(CO_2Me)_2$]; 3.52 (s, Me, CO_2Me); 3.56 (s, Me, CO_2Me); 7.04−7.43 (m, 15 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.66 (d, $J_{C,P}$ = 18.7 Hz, Me); 27.35 [d, $J_{C,P}$ = 13.6 Hz, CH_2-$CH(CO_2Me)_2$]; 49.75 (s, CH); 53.20 (s, Me, CO_2Me); 53.26 (s, Me, CO_2Me); 69.18 (d, $J_{C,P}$ = 69.8 Hz, CH_2P); 169.14 (s, C=O, CO_2Me); 169.27 (s, C=O, CO_2Me). − MS; *m/z* (%): 512 (100) [M]. − $C_{31}H_{29}O_5P$ (512.54): calcd. C 72.65, H 5.70; found C 72.09, H 5.67.

Compound 10: 450 mg of **8** (1.0 mmol) was dissolved in 10 mL of dimethyl ketone. 100 mg of PhOH (1.1 mmol) and 200 mg of K_2CO_3 (1.5 mmol) were added. The resulting mixture was heated at 70°C for 2 h. The suspension was filtered through a plug of CH_2Cl_2-dampened Celite which was subsequently washed with CH_2Cl_2. The organic solution was concentrated and 380 mg (82%) of **10** precipitated with AcOEt. − ^{31}P NMR ($CDCl_3$): δ = 49.2. − ^{1}H NMR ($CDCl_3$): δ = 1.48 (s, 3 H, Me); 2.88 (m, 2 H, CH_2); δ_a = 4.71 and δ_b = 4.79 (ABX, J = 10.3 Hz, $J_{Ha,P}$ = 1.2 Hz, $J_{Hb,P}$ = 1.2 Hz, 2 H, CH_2-OPh); 6.79−7.47 (m, 20 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.11 (d, $J_{C,P}$ = 18.4 Hz, Me); 49.18 (d, $J_{C,P}$ = 26.4 Hz, C-4); 63.2 (d, $J_{C,P}$ = 15 Hz, CH_2-OPh); 70.67 (d, $J_{C,P}$ = 70.1 Hz, CH_2P); 138.5 (d, $J_{C,P}$ = 79.5 Hz); 146.0 (d, $J_{C,P}$ = 77.8 Hz); 157.06 (d, $J_{C,P}$ = 16.3 Hz); 164.26 (d, $J_{C,P}$ = 15.8 Hz). − MS; *m/z* (%): 474 (20) [M]; 381 (100) [M − OPh]. − $C_{32}H_{27}O_2P$ (474.54): calcd. C 80.99, H 5.73, P 6.53; found C 80.27, H 5.77, P 6.52.

Compound 11: 300 mg of **8** (0.65 mmol) was dissolved in 10 mL of toluene and 1 mL (2.0 mmol) of Me_2NH in C_6H_6 (2 M) was added at room temperature. The mixture was then stirred for 1 h. The precipitated ammonium salt was filtered off on Celite and the solvent was evaporated in vacuo. The residual oil was purified by chromatography (AcOEt as eluent). Recrystallisation from CH_2Cl_2/toluene gave 250 mg (90%) of **11**, m.p. 162°C. ^{31}P NMR ($CDCl_3$): $\delta = 45.93$. − ^1H NMR ($CDCl_3$): $\delta = 1.54$ (s, 3 H, Me), 2.07 [s, 6 H, N(Me)$_2$]; $\delta_a = 2.68$ and $\delta_b = 2.82$ (ABX, $J = 9.5$ Hz, $J_{Ha,P} = 9.5$ Hz, $J_{Hb,P} = 9.5$ Hz, 2 H, CH_2P); $\delta_a = 3.28$ and $\delta_b = 3.37$ [ABX, $J = 12.5$ Hz, $J_{Ha,P} = 1.5$ Hz, $J_{HbP} = 1.5$ Hz, 2 H, $CH_2N(Me)_2$]; 7.12−7.49 (m, 15 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 19.13$ (d, $J_{C,P} = 18.9$ Hz, Me); 45.85 [s, 2Me, N(Me)$_2$]; 49.47 (d, $J_{C,P} = 27.3$ Hz, C-4); 55.4 [d, $J_{C,P} = 13.6$ Hz, $CH_2N(Me)_2$]; 71.3 (d, $J_{C,P} = 70.3$ Hz, CH_2P); 137.54 (d, $J_{C,P} = 78.8$ Hz); 143.34 (d, $J_{C,P} = 77.2$ Hz); 160.82 (d, $J_{C,P} = 16.5$ Hz); 165 (d, $J_{C,P} = 14.6$ Hz). − MS; *m/z* (%): 426 (46) [M + 1]; 382 (88) [M + 1 − N(Me)$_2$]; 58 (100) [$CH_2N(Me)_2$]. − $C_{28}H_{28}NOP$ (425.51): calcd. C 79.04, H 6.63, P 7.28; found C 79.06, H 6.63, P 7.07.

Compound 12: The same procedure as for **11** was employed using H_2NCH_2Ph as the base. The reaction mixture was heated at 50°C for 1 h. Chromatography gave 270 mg (85%) of a white solid. − ^{31}P NMR ($CDCl_3$): $\delta = 46.16$. − ^1H NMR ($CDCl_3$): $\delta = 1.41$ (s, 3 H, Me); 2.57−2.78 (m, 2 H, CH_2); 3.35−3.73 (m, 4 H, CH_2N); 6.98−7.30 (m, 20 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 19.21$ (d, $J_{C,P} = 19$ Hz, Me); 46.12 (d, $J_{C,P} = 13.7$ Hz, CH_2-N); 49.34 (d, $J_{C,P} = 27.3$ Hz); 54.57 (s, NCH_2-Ph); 70.42 (d, $J_{C,P} = 70.1$ Hz,CH_2P); 138.58 (d, $J_{C,P} = 79$ Hz); 142.16 (d, $J_{C,P} = 79$ Hz); 161.55 (d, $J_{C,P} = 15$ Hz); 164.09 (d, $J_{C,P} = 16$ Hz). − MS; *m/z* (%): 487 (15) [M]; 382 (70) [M − $NHCH_2Ph$ + 1]; 91 (100) [$PhCH_2$].

Compound 15: To a magnetically stirred solution of **13** (500 mg, 0.82 mmol) in 20 mL of THF at −60°C were added dropwise 0.4 mL of TMEDA and 4.8 mL of lithium diisopropylamide (0.5 M solution in hexane/THF, 50:50). The stirred solution was maintained at −60°C for 30 min and 0.3 mL of Ph_2PCl (1.7 mmol) was then added. The solution, which decolorised immediately, was then allowed to warm to room temperature. The reaction mixture was extracted with 20 mL of Et_2O, washed with water (2 × 5 mL), dried with Na_2SO_4 and concentrated in vacuo. **15** was oxidized during crystallization from AcOEt; yield 300 mg (45%). − ^{31}P NMR ($CDCl_3$): $\delta = 29.16$ [$Ph_2P(O)$-]; 46.06 (P-2); 51.06 (P-1). − MS; *m/z* (%): 811 (50) [M + 1]; 610 (100) [M − $Ph_2P(O)$ + 1].

Compound 16: A suspension of 2.45 g (4.0 mmol) of **13** in 100 mL of CCl_4 was placed in a three-necked flask containing a magnetic stirring bar. The suspension was refluxed until the solution was homogeneous. Solid NBS (1.7 g, 10 mmol) was added and the mixture was stirred at reflux for 6 h. The solution was then allowed to cool to room temperature. The precipitate was removed using a plug of CH_2Cl_2-dampened Celite which was subsequently washed with CH_2Cl_2. The filtrate was shaken with 40 mL of HCl (1 N) and 2 × 20 mL of H_2O and dried with Na_2SO_4. The organic phases were concentrated in vacuo and Et_2O was added to give a white solid. Recrystallisation from hexane/CH_2Cl_2 gave 2.7 g of **16** (87%), m.p. 242°C. − ^{31}P NMR ($CDCl_3$): $\delta = 48.14$. − ^1H NMR ($CDCl_3$): $\delta = 1.46$ (s, 6 H, 2 Me); 2.82−2.86 (m, 4 H, CH_2P); 4.06 (d, $J = 10.5$ Hz, 2 H, CH_2Br); 4.45 (d, $J = 10.5$ Hz, 2 H, CH_2Br); 7.07−7.36 (m, 20 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 18.58$ (m, Me); 24.87 (m, CH_2Br); 50.13 (m); 71.0 (d, $J_{C,P} = 72$ Hz, CH_2P); 137.14 (d, $J_{C,P} = 81.28$ Hz, C sp^2); 138.25 (d, $J_{C,P} = 80.7$ Hz, C sp^2); 163.4 (m, C-β sp^2); 164.9 (m, C-β sp^2). − MS; *m/z* (%): 608 (60) [M − 2 Br]; 430 (50) [M − 2 Br − tolan,]; 178 (100) [PhC=CPh]. − $C_{40}H_{34}Br_2O_2P_2$ (768.46): calcd. C 62.52, H 4.46; found C 61.65, H 4.41.

Compound 17: 350 mg (0.45 mmol) of **16** was dissolved in 10 mL of toluene. An excess of $NHMe_2$ (1 mL of a 2 M solution in C_6H_6, 2.0 mmol) was added dropwise at room temperature. The resulting mixture was stirred for 15 min. The precipitate was filtered and the solvent was evaporated in vacuo. The crude product was chromatographed (AcOEt/MeOH, 90:10) to give **17** (250 mg, 64%) as a white solid. − ^{31}P NMR ($CDCl_3$): $\delta_a = 46.09$, $\delta_b = 44.0$ (AB, $J = 15.4$ Hz). − ^1H NMR ($CDCl_3$): $\delta = 1.43$ (s, 3 H, Me); 1.47 (s, 3 H, Me); 1.56 (s, 6 H, NMe_2); 2.28 (s, 6 H, NMe_2); 2.58−3.56 (m, 8 H, CH_2); 7.16−7.45 (m, 20 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 19.02$ (d, $J_{C,P} = 18.2$ Hz, Me); 19.88 (d, $J_{C,P} = 18.1$ Hz, Me); 45.87 (s, NMe_2); 46.30 (s, NMe_2); 49.97 (d, $J_{C,P} = 27.1$ Hz, C-4); 50.59 (d, $J_{C,P} = 27.3$ Hz, C-4); 59.08 (d, $J_{C,P} = 13.5$ Hz, CH_2-N); 60.02 (d, $J_{C,P} = 13.7$ Hz, CH_2-N); 69.24 (d, $J_{C,P} = 69.7$ Hz, CH_2P); 73.55 (d, $J_{C,P} = 69.5$ Hz, CH_2P); 127.89−166.72 (m). − MS; *m/z* (%): 696 (4) [M]; 651 (100) [M − NMe_2 − 1].

Compound 18: A solution of $HSiCl_3$ (0.15 mL, 1.5 mmol) in CH_2Cl_2 (3 mL) was added at 0°C under N_2 to a solution of pyridine (0.26 mL, 3 mmol) in CH_2Cl_2 (4 mL). To the resulting mixture was added dropwise a solution of **17** in CH_2Cl_2 (10 mL). At the end of the addition, the mixture was heated at 50°C for 3 h. Monitoring of the reaction by ^{31}P-NMR spectroscopy showed complete reduction of **17**. The resulting suspension was treated with 30% NaOH (2 mL). **18** was extracted with CH_2Cl_2,washed with H_2O, dried with Na_2SO_4 and concentrated. After the solvent was removed, the organic residue was flash-chromatographed on silica gel with CH_2Cl_2 as eluent. − ^{31}P NMR ($CDCl_3$) $\delta = -6.79$. − ^1H NMR ($CDCl_3$): $\delta = 1.41$ (s, 6 H, Me); 1.89 (s, 12 H, NMe_2); 2.04−2.15 (m, 4 H, CH_2P); $\delta_a = 2.90$, $\delta_b = 3.07$ (AB, $J = 12.5$ Hz, 4 H, CH_2-N); 7.02−7.29 (m, 20 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.0$ (s, Me); 45.93 (s, 4 Me); 57.96 (s, CH_2-N); 67.41 (s, CH_2P); 71.70 (d, $J_{C,P} = 2.8$ Hz, *C*Me); 126.82−163.04 (m). − MS; *m/z* (%): 665 (2) [M]; 620 (18) [M − NMe_2 − 1]; 576 (20) [M − 2 NMe_2 − 1]; 398 (55) [M − 2 NMe_2 − 1 − tolan]; 178 (100) [tolan].

Compound 19: 310 mg of **16** (0.4 mmol) was dissolved in 5 mL of toluene. Et_3N (0.2 mL) was subsequently added and the mixture was heated at 50°C. 0.05 mL (0.5 mmol) of $PhCH_2NH_2$ in 5 mL of toluene was added dropwise and the stirring was continued for 15 min. After filtration, the solvent was evaporated in vacuo. The crude product was recrystallized from CH_2Cl_2/Et_2O to give 210 mg (72%) of **19** as a white crystalline solid, m.p. 166°C. − ^{31}P NMR ($CDCl_3$): $\delta = 51.20$ and 41.22. − ^1H NMR ($CDCl_3$): $\delta = 1.02$ (s, 3 H, Me); 1.15 (s, 3 H, Me); 2.18−2.55 (m, 4 H, CH_2P); 3.41−4.26 (m, 4 H, CH_2-N); 5.20 (d, $J_{H,P} = 3.3$ Hz, 1 H, C=CH_2); 5.24 (s, 1 H, C=CH_2); 6.82−7.59 (m, 25 H, ArH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 18.72$ (d, $J_{C,P} = 15$ Hz, Me); 20.07 (d, $J_{C,P} = 16.1$ Hz, Me); 45.97 (d, $J_{C,P} = 19.8$ Hz, *C*Me); 47.92 (d, $J_{C,P} = 19.7$ Hz, *C*Me); 49.63 (d, $J_{C,P} = 59.9$ Hz, CH_2P); 54.95 (s, N-CH_2-Ph); 56.72 (dd, $J_{C,P} = 14.5$ Hz, $J_{C,P} = 3$ Hz, CH_2-N); 67.33 (d, $J_{C,P} = 72.7$ Hz, CH_2P); 74.33 (dd, $J_{C,P} = 68.5$ Hz, $J_{C,P} = 7.7$ Hz, *C*N); 113.52 (d, $J_{C,P} = 10$ Hz, C=CH_2); 128.07−180.6 (m). − MS; *m/z* (%): 713 (16) [M]; 178 (66) [PhC=CHPh]; 91 (100) [CH_2Ph]. − $C_{47}H_{41}NO_2P_2 \cdot 0.15CH_2Cl_2$ (726.54): calcd. C 77.95, H 5.73, P 8.53; found C 77.41, H 5.93, P 8.85.

X-ray Structure Determination for 4a and 19:[14] Crystals suitable for X-ray diffraction were obtained from diclhloromethane/hexane

Table 1. Crystallographic data for **4a** and **19**

	4a	**19**
Empirical formula	$C_{27}H_{25}OP$	$C_{48}H_{43}Cl_2NO_2P_2$
M_r	396.47	$C_{48}H_{43}Cl_2NO_2P_2$
Crystal size [mm]	0.28 × 0.28 × 0.28	0.31 × 0.31 × 0.28
Crystal system	monoclinic	triclinic
Space group	$P2_1$	$P-1$
a [Å]	8.554(1)	12.622(1)
b [Å]	13.422(1)	13.292(1)
c [Å]	18.581(2)	13.978(1)
α [°]	90	74.01(1)°
β [°]	101.42(1)	64.02(1)
γ [°]	90	87.83(1)
V [Å^3]	2090.93(69)	2017.28(19)
Z	4	2
ρ [g cm^{-3}]	1.259	1.315
μ [mm^{-1}]	12.5	2.8
F(000)	840	836
Radiation	Cu	Mo
λ [Å]	1.54184	0.71073
$2\theta_{max}$ [°]	120	56.1
	$h = -9$ to 9	$h = -15$ to 16
	$k = -15$ to 0	$k = -16$ to 17
	$l = -20$ to 0	$l = 0$ to 18
Data measured	3364	10188
Data observed for $F^2 > 3\sigma F^2$	2917	2765
Refinement on	F	F
No. of parameters	362	496
Hydrogen atoms	refined isotropically	included as fixed contributions
R	0.042	0.066
Rw	0.078	0.078
S	1.86	1.33
Max/min difference peak [e Å^3]	0.22(6)/−0.50(6)	0.91(9)/−0.22(9)

solutions of the compounds. Data were collected at 123 ± 0.5 K with an Enraf Nonius CAD4 diffractometer. The crystal structures were solved and refined using the Enraf Nonius MOLEN package. Crystal data are assembled in Table 1.

Acknowledgments

This work was supported by CNRS, Ecole Polytechnique and Rhône-Poulenc.

---

[1] F. Mathey, D. Neibecker, A. Brèque (SNPE), Fr. Pat. 2588197, Oct. 3, **1985**; *Chem. Abstr.* **1987**, *107*, 219468v.

[2] D. Neibecker, R. Réau, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 500.

[3] W.A. Herrmann, C.W. Kohlpaintner, R.B. Manatsberger, H. Bahrmann, H. Kottmann, *J. Mol. Catal., A* **1995**, *97*, 65.

[4] S. Lelièvre, F. Mercier, F. Mathey, *J. Org. Chem.* **1996**, *61*, 3531.

[5] A. Brèque, J.-M. Alcaraz, L. Ricard, F. Mathey, A. Tambuté, P. Macaudière, *New. J. Chem.* **1989**, *13*, 369.

[6] F. Robin, F. Mercier, L. Ricard, F. Mathey, M. Spagnol, *Chem. Eur. J.* **1997**, *3*, 1365.

[7] V. Mouriès, F. Mercier, L. Ricard, F. Mathey, *Eur. J. Org. Chem.* **1998**, 2683.

[8] F. Mathey, F. Mercier, C. Charrier, J. Fischer, A. Mitschler, *J. Am. Chem. Soc.* **1981**, *103*, 4595.

[9] F. Mathey, *Tetrahedron Lett.* **1973**, 3255; *Tetrahedron* **1974**, *30*, 3127; *Tetrahedron* **1976**, *32*, 2395; B. Deschamps, F. Mathey, *Organometallics* **1992**, *11*, 1411.

[10] The ^2J[H-P(X)] couplings are under the control of the H−C−P−X dihedral angle, see: W.G. Bentrude, W.N. Setzer, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis* (Eds.: J. G. Verkade and L. D. Quin), VCH, Deerfield Beach, FL, **1987**, p. 381.

[11] S. E. Denmark, R. L. Dorow, *J. Am. Chem. Soc.* **1990**, *112*, 864; S. E. Denmark, P. C. Miller, S. R. Wilson, *J. Am. Chem. Soc.* **1991**, *113*, 1468.

[12] C. J. Cramer, S. E. Denmark, P. C. Miller, R. L. Dorow, K. A. Swiss, S. R. Wilson, *J. Am. Chem. Soc.* **1994**, *116*, 2437; D. R. Armstrong, D. Barr, M. G. Davidson, G. Hutton, P. O'Brien, R. Snaith, S. Warren, *J. Organomet. Chem.* **1997**, *529*, 29.

[13] Y. L. Bennani, S. Hanessian, *Tetrahedron* **1996**, *52*, 13837.

[14] Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-104043 and -104044. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Received October 16, 1998
[O98453]