Functionalisation of the 1-Phosphanorbornadiene Structure at the C2 Position by Stille Cross-Coupling Reactions

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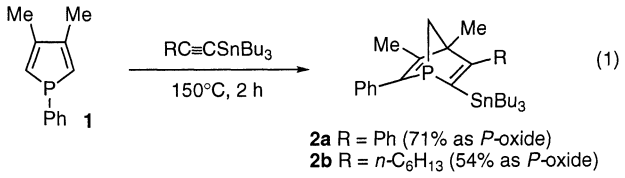
The reaction of alkynylstannanes with 1-phenyl-3,4-dimethylphosphole at 150 °C affords the corresponding 2-stannyl-1-phosphanorbornadienes (**2a,b**), in fair yield. Oxidation under mild conditions affords the corresponding phosphane oxides (**3a,b**), whereas more drastic conditions (H_2O_2, 15% in toluene at 80 °C) induce the oxidative cleavage of the P-CH_2 bond of the bridge to give a bicyclic phosphinate such as **4**. Treatement of **4** by iodine leads to a tin → iodine exchange. The X-ray crystal structure analysis of the resulting 1-phospha-2-oxabicyclo[2.2.2]octa-5,7-diene 1-oxide confirms the functionalisation at the α-position and the relief of ring strain taking place upon insertion of oxygen into the P-CH_2 bond of the norbornadiene. The 2-stannyl-1-phosphanorbornadiene 1-oxides (**3a,b**) readily undergo tin → iodine exchange. The resulting 2-iodo derivatives (**6a,b**) can be cross-coupled with 2-furyl-, 2-thienyl-, 2-pyrrolyl-, phenylethynyl-, and vinyl-tributylstannanes to give the corresponding 2-functional 1-phosphanorbornadiene 1-oxides in excellent yields (80–95%)

Introduction

The 1-phosphanorbornadiene (1-phosphabicyclo[2.2.1]-hepta-2,5-diene) structure shows some promise as a source of phosphorus ligands for transition metals in homogeneous catalysis. Thus, highly efficient rhodium catalysts have been prepared for the hydrogenation[1] and hydroformylation[2] of alkenes. Water-soluble versions of these catalysts have been synthesized.[3][4] Finally, one of the most efficient homochiral ligand for the asymmetric hydrogenation of functional alkenes, the so-called BIPNOR,[5] incorporates two 1-phosphanorbornadiene units coupled by the C2 positions. Considering this state of affairs, the development of synthetic methods for the functionalisation of a preformed 1-phosphanorbornadiene unit is obviously necessary in order to fine-tune the stereoelectronic characteristics of the phosphanorbornadiene ligands to the variety of catalytic transformations and substrates that might be envisaged. We describe here a method for the functionalisation of the C2 position based on the palladium-catalysed Stille cross-coupling reaction.[6]

Results and Discussion

The key finding which is at the basis of this work, is the successful transposition of the 1-phosphanorbornadiene synthesis[7][8] for the preparation of 2-stannyl-substituted derivatives. Indeed, transiently formed *2H*-phospholes regioselectively react with alkynylstannanes to afford the expected bicyclic structure (eq. 1).

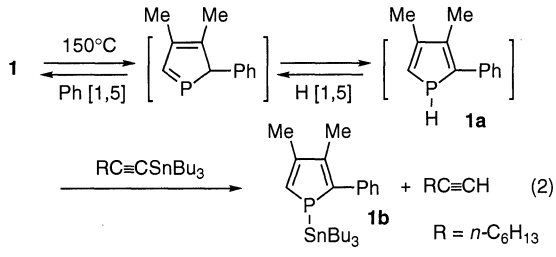


(1)

2a R = Ph (71% as *P*-oxide)
2b R = *n*-C_6H_{13} (54% as *P*-oxide)

In the two cases which have been studied, the ^{31}P-NMR spectrum of the crude reaction mixture showed the strong predominance of the α-regioisomers. The regiochemistry was established by the existence of a strong $^2J(^{31}P\text{-}^{119}Sn)$ coupling in the α case: **2a** [$\delta(^{31}P) = -9.24$ (hexane), $^2J(^{31}P\text{-}^{119}Sn) = 195.6$ Hz], **2b** [$\delta(^{31}P) = -11.70$ (toluene), $^2J(^{31}P\text{-}^{119}Sn) = 219.3$ Hz].

In the case of **2b,** besides the isomeric and oxidized by-products, an interesting resonance appeared on the crude spectrum at $\delta(^{31}P) = -50.45$ (hexane) with a huge $J(^{31}P\text{-}^{119}Sn)$ coupling of 617 Hz. The magnitude of the P-Sn coupling implies the presence of a P−Sn bond. These data are very close to those recorded for 1-stannylphospholes.[9] Our explanation is presented in eq. 2.



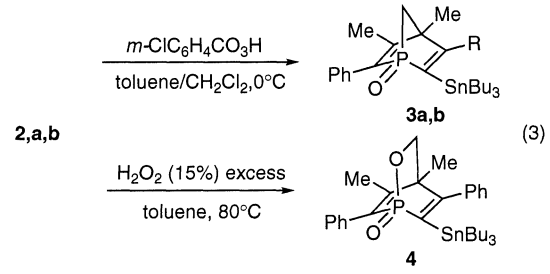
(2)

The highly acidic phosphole **1a**[10] is able to split the C−Sn bond to give the corresponding monosubstituted alkyne which is a much weaker acid than **1a** when R =

  1434−193X/98/1111−2683 $ 17.50+.50/0

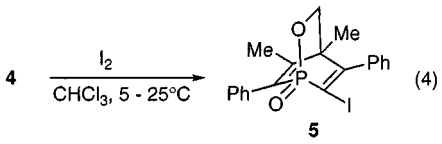
nC_6H_{13}. The relative amount of **1b** increases with the temperature. At 170°C, it becomes the major product of the reaction. Further identification was carried out by ^1H NMR and mass spectrometry.

The two phosphanorbornadienes **2a,b** were not kept as such but directly oxidized. Careful oxidation by *m*-chloroperbenzoic acid at 0°C afforded the expected P-oxides **3a,b** but, under more drastic conditions, with an excess of hydrogen peroxide at 80°C, an additional cleavage of the P−C7 bridge was observed (eq. 3).



(3)

That an oxidative cleavage has taken place on the P−CH_2 bond of the bridge as a result of the strain could be inferred from the spectroscopic data. For example, the molecular peak of **4** is found at *m*/*z* 612 vs 596 for **3a.** On the ^{13}C spectrum, the CH_2 bridge of **3a** appears as a doublet at 70.35 with a huge $^1J(^{13}C\text{-}^{31}P)$ coupling of 64.3 Hz. The OCH_2 bridge of **4** appears at 73.75 with a much smaller $^2J(^{13}C\text{-}^{31}P)$ coupling of 7.0 Hz. This oxidative cleavage is reminiscent of what occurs during the oxidation of a 7-phosphanorbornene structure. A similar cleavage of one P−C bridge bond was observed by several authors.[11][12] Upon reaction with iodine at room temperature, **4** is converted into the corresponding 2-iodo derivative **5** (eq. 4).



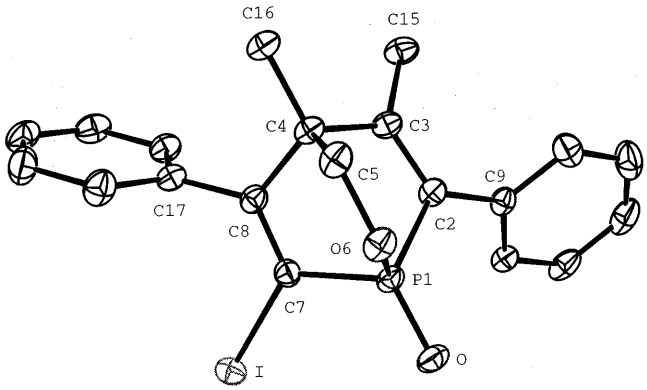
(4)

We were able to grow good crystals of **5** for X-ray analysis (Figure 1). The data confirm both the functionalisation at the C2 position and the insertion of oxygen into the former P−CH_2 bond of the bridge. That the reaction is driven by the relief of ring strain is obvious when comparing the data of **5** with those of the *meso*-BIPNOR disulfide, for example.[5] The sum of the intracyclic angles at the bridgehead carbon C4 is 323.8 in **5** vs 312.4° in the BIPNOR disulfide. Similarly, the sum of the intracyclic angles at P is 302.9 in **5** vs 280.5° in the BIPNOR disulfide.

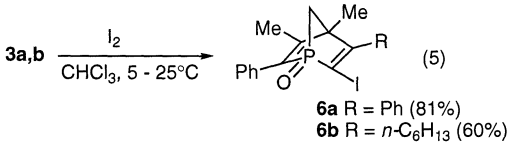
The direct use of the tin derivatives **3a,b** to perform Stille cross-coupling reactions was disappointing. Several side-reactions were observed (reduction...). Thus, we first converted **3a,b** into the corresponding iodo derivatives (eq. 5).

The C2(I) resonances of **6a,b** show the expected shielding: $\delta(^{13}C) = 96.93$ [d, $^1J(^{13}C\text{-}^{31}P) = 74.7$ Hz] for **6a** and 94.7 [d, $^1J(^{13}C\text{-}^{31}P) = 79.0$ Hz] for **6b**. All our experiments were performed with **6a**. The Stille cross-coupling reactions

Figure 1. ORTEP drawing of one molecule of **5**, as determined by a single crystal X-ray diffraction study[a]

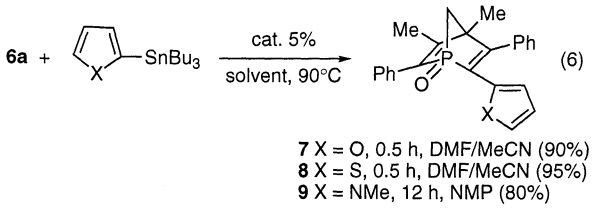


[a] Selected bond lengths (Å) and angles (°): P(1)−O 1.470(2), P(1)−C(2) 1.806(2), P(1)−O(6) 1.607(2), P(1)−C(7) 1.796(2), C(2)−C(3) 1.350(3), C(3)−C(4) 1.542(3), C(4)−C(5) 1.549(3), C(4)−C(8) 1.554(3), C(5)−O(6) 1.442(3), C(7)−C(8) 1.334(3), C(7)−I 2.090(3); O−P(1)−C(2) 119.86(9), O−P(1)−O(6) 112.05(9), O−P(1)−C(7) 119.0(1), C(2)−P(1)−O(6) 102.32(9), C(2)−P(1)−C(7) 100.76(9), O(6)−P(1)−C(7) 99.80(9), P(1)−C(2)−C(3) 111.3(1), P(1)−C(2)−C(9) 121.1(1), C(2)−C(3)−C(4) 116.7(2), C(3)−C(4)−C(5) 107.6(2), C(3)−C(4)−C(8) 109.3(2), C(5)−C(4)−C(8) 106.9(2), C(4)−C(5)−O(6) 114.0(2), P(1)−O(6)−C(5) 113.5(1), P(1)−C(7)−I 121.7(1), P(1)−C(7)−C(8) 113.6(2), C(4)−C(8)−C(7) 114.8(2).

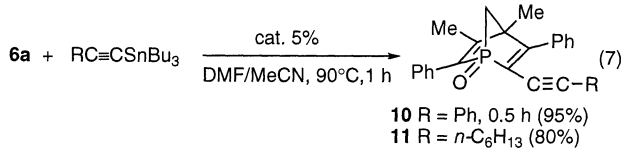


(5)

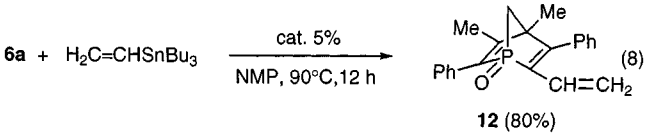
appeared to be efficient when using the $[Pd(Fu_3P)_2]$ + CuI catalyst introduced by Farina et al.[13] (eqs. 6−8).



(6)



(7)



(8)

Unfortunately, this functionalisation technique cannot be applied to the synthesis of 6,6′-bifunctional 2,2′-bis-(1-phosphanorbornadienyls)[14] which could show interesting properties in asymmetric catalysis.[5] Indeed, the P−P bond of the starting 1,1′-biphosphole[14] reacts with the C−Sn

bond of the alkynylstannane to give the corresponding 1-stannylphosphole. In spite of this restriction however, this Stille coupling provides an access to a huge variety of new functional and/or chelating ligands whose potential in homogeneous catalysis remains to be explored.

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

Experimental Section

All reactions were carried out under argon, and silica gel (70−230 mesh) was used for chromatographic separations. − NMR spectra were recorded on 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 parts per million downfield from internal TMS (^{1}H and ^{13}C) or external 85% H_3PO_4 (^{31}P). When noted, couplings with tin are measured for the ^{119}Sn isotope. − Routine mass spectra were obtained at 70eV by the direct inlet method, with a Shimadzu GC-MS QP 1000 spectrometer for all compounds. − Elemental analyses were performed by the "Service d'analyse du CNRS" at Gif-sur-Yvette, France. Oily compounds failed to give satisfactory analytical results. Tributyl(phenylethynyl)tin, 2-(tributylstannyl)thiophene, 2-(tributylstannyl)furan, tributyl(vinyl)tin were purchased from Aldrich. 2-(Tributylstannyl)*N*-methylpyrrole[15] was prepared according to literature procedures.

3,4-Dimethyl-2-phenyl-1-tributylstannylphosphole (**1b**): ^{31}P NMR (toluene): δ = −50.40 (m, $^1J_{P\text{-}Sn}$ = 617 Hz). − ^{1}H NMR ($CDCl_3$): δ = 6.5 (d, 1 H, $^2J_{H\text{-}P}$ = 40.8 Hz, =CH−P). − MS (^{120}Sn); *m/z* 478 [M^+], 421 [$M^+ - C_4H_9$), 343 [$M^+ - C_{10}H_{15}$), 188 [$M^+ - Sn(C_4H_9)_3$ + H).

4,5-Dimethyl-3,6-diphenyl-2-tributylstannyl-1-phosphanorbornadiene 1-Oxide (**3a**): A mixture of phenethynyltributylstannane (8.8 g, 22.5 mmol) and phosphole (4.2 g, 22.5 mmol) was heated at 150°C for 2 h in a sealed tube. A solution of the crude product containing mainly **2a** was treated at 0°C with a solution of 70% *m*Cl-C_6H_4-CO_3H (57.9 mmol) in CH_2Cl_2 that was previously dehydrated by treatment with anhydrous $MgSO_4$. Oxidation was instantaneous. The reaction mixture was treated at 0°C with a saturated sodium thiosulfate solution, then washed with sodium carbonate. After extraction with ether, drying with $MgSO_4$ and evaporation under reduced pressure, the residue was purified by column chromatography on silica gel (ethyl acetate as the eluent). 10.5 g of colorless oil was obtained (71% yield). − ^{31}P NMR (toluene): δ = 54.6 (m, $^2J_{P\text{-}Sn}$ = 75.5 Hz). − ^{1}H NMR ($CDCl_3$): δ = 0.7−1.2 (m, 27 H, butyl), 1.33 (s, 3 H, Me-C_4), 2.11 (d, 3 H, $^4J_{H\text{-}P}$ = 2.7 Hz, Me-C_5), 2.53 (m, 2 H, CH_2P), 7−7.5 (m, 10 H, H arom). − ^{13}C NMR ($CDCl_3$): δ = 10.81 (s, CH_2), 14.02 (s, Me), 15.27 (d, $^3J_{C\text{-}P}$ = 12.6 Hz, *Me*-C_5), 19.47 (d, $^3J_{C\text{-}P}$ = 20.4 Hz, *Me*-C_4), 27.58 (m, $^1J_{C\text{-}Sn}$ = 63.4 Hz, CH_2Sn), 29.40 (m, $^2J_{C\text{-}Sn}$ = 19.9 Hz, *CH_2*-CH_2Sn), 54.09 (d, $^2J_{C\text{-}P}$ = 35.4 Hz, C_4), 70.35 (d, $^1J_{C\text{-}P}$ = 64.3 Hz, C_7), 127.3−141.7 ($C_{sp}2$), 159.14 (d, $^2J_{C\text{-}P}$ = 15.2 Hz, C_5), 182.05 (d, $^2J_{C\text{-}P}$ = 5.2 Hz, C_3). − MS (^{120}Sn); *m/z*: 596 [M^+], 539 [$M^+ - C_4H_9$], 425 [$M^+ - (C_4H_9)_3$], 305 [$M^+ - Sn(C_4H_9)_3$].

3-Hexyl-4,5-dimethyl-6-phenyl-2-tributylstannyl-1-phosphanorbornadiene 1-Oxide (**3b**): The product was prepared by the same procedure as **3a**. **3b** was obtained as a yellow oil (54% yield). − ^{31}P NMR (dichloromethane): δ = 54.9 (m, $^2J_{P\text{-}Sn}$ = 85.5 Hz). − ^{1}H NMR ($CDCl_3$): δ = 1.2−1.65 (m, 43H), 2.0 (d, 3 H, $^4J_{H\text{-}P}$ = 2.7 Hz, Me-C_5), 2.40 (m, 2 H, CH_2P), 7.2−7.5 (m, 5 H, H arom). − ^{13}C NMR ($CDCl_3$): δ = 10.90 (s, CH_2, Bu), 13.97 and 14.08 (2s, Me, Bu), 14.39 (s, Me, Hex), 14.82 (d, $^3J_{C\text{-}P}$ = 13.2 Hz, *Me*-C_5), 18.18 (d, $^3J_{C\text{-}P}$ = 21.0 Hz, *Me*-C_4), 18.23 (s, CH_2), 23.00 (s, CH_2), 27.43 and 27.67 (2m, $^1J_{C\text{-}Sn}$ = 69.4 and 62.9 Hz, CH_2Sn), 28.34 (s, CH_2), 29.52 (m, $^2J_{C\text{-}Sn}$ = 19.7 Hz, *CH_2*-CH_2Sn), 32.15 (s, CH_2), 34.88 (d, $^3J_{C\text{-}P}$ = 21.2 Hz, *CH_2*-C_3), 53.70 (d, $^2J_{C\text{-}P}$ = 38.0 Hz, C_4), 70.54 (d, $^1J_{C\text{-}P}$ = 64.5 Hz), 127.4−138.52 ($C_{sp}2$), 159.30 (d, $^2J_{C\text{-}P}$ = 15.2 Hz, C_5), 183.19 (d, $^2J_{C\text{-}P}$ = 3.6 Hz, C_3). − MS (^{120}Sn); *m/z*: 604 [M^+], 547 [$M^+ - C_4H_9$], 435 [$M^+ - (C_4H_9)_2$], 313 [$M^+ - Sn(C_4H_9)_3$].

4,8-Dimethyl-5,7-diphenyl-6-tributylstannyl-1-phospha-2-oxabicyclo[2.2.2]octa-5,7-diene 1-Oxide (**4**): A mixture of phenethynyltributylstannane (8.8 g, 22.5 mmol) and phosphole (4.2 g, 22.5 mmol) was heated at 150°C for 2 h in a sealed tube. A solution of the resulting product in toluene was treated by an excess of hydrogen peroxide (15%) at 80°C for 15 min. After extraction with ether, drying with $MgSO_4$ and evaporation under reduced pressure, the residue was purified by column chromatography on silica (ethyl acetate as the eluent). 8.9 g of a colorless oil was obtained (65% yield). − ^{31}P NMR ($CDCl_3$): δ = 24.2 (m, $^2J_{P\text{-}Sn}$ = 70.2 Hz). − ^{1}H NMR ($CDCl_3$): δ = 0.65 -1.35 (m, 30H), 2.00 (s, Me-C_8), 3.72 (pseudo d, CH_2O), 7.0−7.4 (m, 10 H, H arom). − ^{13}C NMR ($CDCl_3$): δ = 11.05 (s, CH_2, Bu), 13.86 (s, Me, Bu), 16.74 (d, $^3J_{C\text{-}P}$ = 11.9 Hz, *Me*-C_8), 18.84 (s, *Me*-C_4), 27.35 (m, $^1J_{C\text{-}Sn}$ = 63.5 Hz, CH_2Sn), 29.26 (m, $^2J_{C\text{-}Sn}$ = 19.8 Hz, *CH_2*-CH_2Sn), 48.56 (m, $^3J_{C\text{-}P}$ = 47.3 Hz, C_4), 73.75 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, CH_2O), 127.3−141.4 ($C_{sp}2$), 156.54 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, C_8), 177.21 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, C_5). − MS (^{120}Sn); *m/z*: 612 [M^+], 555 [$M^+ - C_4H_9$], 321 [$M^+ - Sn(C_4H_9)_3$].

6-Iodo-4,8-dimethyl-5,7-diphenyl-1-phospha-2-oxabicyclo[2.2.2]octa-5,7-diene 1-Oxide (**5**): A solution of iodine (0.1 mol / l.84 ml) was added dropwise at 4−5°C to a solution of **4** (5.1 g 8.4 mmol) in $CHCl_3$ (20 ml). The solution was stirred at room temperature for 12 h. The reaction mixture was treated at room temp. with a solution of KF in water for 1 h, then with a sodium thiosulfate solution, then washed with water. After extraction with ether, drying with $MgSO_4$ and evaporation under reduced pressure, the residue was purified by precipitation in hexane. 2.6 g of yellow solid was thus obtained (70% yield). − ^{31}P NMR ($CHCl_3$): δ = 14.6. − ^{1}H NMR ($CDCl_3$): δ = 1.22 (s, 3 H, Me-C_4), 2.06 (d, 3 H, $^4J_{H\text{-}P}$ = 1.7 Hz, Me-C_8), 3.87 (m, 2 H, CH_2O), 6.9−7.1 (m, 2 H, H arom), 7.3−7.5 (m, 8 H, H arom). − ^{13}C NMR ($CDCl_3$): δ = 16.78 (d, $^3J_{C\text{-}P}$ = 12.4 Hz, *Me*-C_8), 19.33 (s, *Me*-C_4), 49.43 (d, $^3J_{C\text{-}P}$ = 37.9 Hz, C_4), 74.03 (d, $^2J_{C\text{-}P}$ = 6.8 Hz, CH_2O), 91.7 (d, $^1J_{C\text{-}P}$ = 102.2 Hz, C_6-I), 126.7−139.7 ($C_{sp}2$), 157.54 (s, C_8), 170.22 (s, C_5). − MS; *m/z*: 448 [M^+], 321 [M^+ − I].

2-Iodo-4,5-dimethyl-3,6-diphenyl-1-phosphanorbornadiene 1-Oxide (**6a**): A solution of iodine (0.1 mol / l.84 ml) was added dropwise at 4−5°C to a solution of **3a** (2.1 g, 8.4 mmol) in $CHCl_3$ (20 ml). The solution was stirred at room temp. for 12 h. The reaction mixture was treated at room temp. with a solution of KF in water for 1 h, then with a sodium thiosulfate solution, then washed with water. After extraction with ether, drying with $MgSO_4$ and evaporation under reduced pressure, the residue was purified by precipitation with hexane. 2.9 g of yellow solid was thus obtained (81% yield). − ^{31}P NMR (CH_2Cl_2): δ = 45.8. − ^{1}H NMR ($CDCl_3$): δ = 1.45 (s, 3 H, Me-C_4), 2.13 (d, 3 H, $^4J_{H\text{-}P}$ = 2.8 Hz, Me-C_5), 2.70 (m, 2 H, CH_2P), 7.07 (m, 2 H, H arom), 7.42 (m, 8 H, H arom). − ^{13}C NMR ($CDCl_3$): δ = 15.67 (d, $^3J_{C\text{-}P}$ = 14.2 Hz, *Me*-C_5), 20.05 (d, $^3J_{C\text{-}P}$ = 18.5 Hz, *Me*-C_4), 53.80 (d, $^2J_{C\text{-}P}$ = 26.1 Hz, C_4), 67.62 (d, $^1J_{C\text{-}P}$ = 68.4 Hz, CH_2P), 96.94 (d, $^1J_{C\text{-}P}$ = 74.7 Hz, C_2-I); 127.4−137.3 ($C_{sp}2$), 138.17 (d, $^1J_{C\text{-}P}$ = 86.6 Hz, C_6), 160.00 (d, $^2J_{C\text{-}P}$ = 16.8 Hz, C_5), 173.30 (d, $^2J_{C\text{-}P}$ = 15.4 Hz, C_3). − MS; *m/z*:

432 [M^+], 305 [$M^+ - I$], 203 [$M^+ - C_8H_5I$]. – $C_{20}H_{18}IOP$ (432.24): calcd. C 55.55, H 4.19, P 7.16; found C 55.19, H 4.30, P 7.34.

3-Hexyl-2-iodo-4,5-dimethyl-6-phenyl-1-phosphanorbornadiene-1-Oxide (**6b**): The product was prepared by the same procedure as for **6a**. **6b** was obtained as a yellow oil (60% yield). – ^{31}P NMR (CH_2Cl_2): δ = 44.3. – ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, 3 H, Me), 1.28−1.31 (m, 8 H, 3 CH_2), 1.64 (d, 3 H, $^4J_{H-P}$ = 0.6 Hz, Me-C_4), 2.01 (d, 3 H, $^4J_{H-P}$ = 2.9 Hz, Me-C_5), 2.40 (m, 2 H, CH_2-C_3), 2.51 (m, 2 H, CH_2P), 7.25 -7.43 (m, 5 H, H arom). – ^{13}C NMR ($CDCl_3$): δ = 14.64 (s, Me, Hex), 15.39 (d, $^3J_{C-P}$ = 15.0 Hz, *Me*-C_5), 18.91 (d, $^3J_{C-P}$ = 18.6 Hz, *Me*-C_4), 23.15, 28.29, 29.71, 32.18 (4 s, 4 CH_2, Hex), 33.81 (d, $^3J_{C-P}$ = 10.5 Hz, CH_2-C_3), 53.05 (d, $^2J_{C-P}$ = 27.7 Hz, C_4), 67.98 (d, $^1J_{C-P}$ = 79.0 Hz, CH_2P), 94.71 (d, $^1J_{C-P}$ = 79 Hz, C_2-I), 128.07−129.22 (CH, Ph), 133.43 (d, $^2J_{C-P}$ = 9.1 Hz, Cipso, Ph), 138.04 (d, $^1J_{C-P}$ = 86.3 Hz, C_6), 160.01 (d, $^2J_{C-P}$ = 16.9 Hz, C_5), 173.90 (d, $^2J_{C-P}$ = 13.8 Hz, C_3). – MS; *m/z*: 440 [M^+], 313 [$M^+ - I$], 203 [$M - C_8H_{13}I$].

General Procedure for the Coupling of **6a** *with Tributyltin Derivatives:* A solution of [$Pd(dba)_2$] (5% mol) and tri-2-furylphosphane (20% mol) in 1 ml of anhydrous degassed DMF, CH_3CN or NMP was stirred for 10 min at room temp. **6a**, the tributyltin derivative and CuI were introduced and the flask was then heated at 80−90°C. The evolution of the crude reaction mixture was monitored by GC on a Varian 3400 apparatus equipped with a WCOT (25 m, 0.25 mm) capillary column and a CP-SiP-SCB stationary phase between 40 and 220°C. Addition of a 1 M aqueous solution of KF with stirring for 30 min, dilution with EtOAc and filtration were followed by evaporation of the filtrate and purification by flash chromatography (silica gel) or by recrystallization. When NMP or DMP were employed, the mixture was washed with water and, after extraction with ether, dried with $MgSO_4$ and evaporated under reduced pressure.

2-Furyl-4,5-dimethyl-3,6-diphenyl-1-phosphanorbornadiene 1-Oxide (**7**): The product was prepared by the general procedure in DMF or CH_3CN and was purified by recrystallization from ethyl acetate. A yellow solid was obtained (90% yield). – ^{31}P NMR (CH_3CN): δ = 45.5. – ^{1}H NMR ($CDCl_3$): δ = 1.35 (s, 3 H, Me-C_4), 2.12 (d, 3 H, $^4J_{H-P}$ = 2.8 Hz, Me-C_5), 2.65 (m, 2 H, CH_2P), 6.32 (dd, 1 H, $H_{\beta'}$ furyl), 6.74 (d, 1 H, H_β furyl), 7.05−7.44 (m, 11 H, H arom). – ^{13}C NMR ($CDCl_3$): δ = 15.65 (d, $^3J_{C-P}$ = 13.8 Hz, *Me*-C_5), 19.24 (d, $^3J_{C-P}$ = 18,8 Hz, *Me*-C_4), 49.44 (d, $^2J_{C-P}$ = 27.4 Hz, C_4), 66.86 (d, $^1J_{C-P}$ = 71.2 Hz, CH_2P), 111.75 and 111.99 (2 s, $C_{\beta\beta'}$ furyl), 127.8−129.5 ($C_{sp}2$), 133.68 (d, $^3J_{C-P}$ = 8.8 Hz, $C_{3'}$), 136.60 (d, $^2J_{C-P}$ = 13.9 Hz, $C_{6'}$), 137.67 (d, $^1J_{C-P}$ = 85.7 Hz, C_6), 143.41 (s, $C_{\alpha'}$ furyl), 148.77 (d, $^1J_{C-P}$ = 61.5 Hz, C_2), 158.60 (d, $^2J_{C-P}$ = 12.7 Hz, C_5 or C_3), 161.74 (d, $^2J_{C-P}$ = 16.4 Hz, C_3 or C_5). – MS; *m/z*: 372 [M^+], 357 [$M^+ - CH_3$], 204 [M^+ − Ph-C=C-furyl], 256 [M^+ − Me-C=C-Ph]. – $C_{24}H_{21}O_2P$ (372.40): calcd. C 77.34, H 5.68, O 8.59, P 8.31; found C 77.05, H 5.97, O 8.75, P 8.00.

4,5-Dimethyl-3,6-diphenyl-2-thienyl-1-phosphanorbornadiene 1-Oxide (**8**): The product was prepared by the general procedure in DMF or CH_3CN and was purified by column chromatography on silica gel (ethyl acetate/hexane, 50:50 as the eluent) and recrystallization from ethyl acetate. A yellow solid was obtained (95% yield). – ^{31}P NMR (CH_3CN): δ = 49.2. – ^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 3 H, Me-C_4), 2.11 (d, 3 H, $^4J_{H-P}$ = 2.9 Hz, Me-C_5), 2.69 (m, 2 H, CH_2P), 6.95 (dd, 1 H, $^3J_{H-H}$ = 5.1 Hz, $^3J_{H-H}$ = 3.7 Hz, $H_{\beta'}$ thienyl), 7.04−7.49 (m, 11 H, H arom), 7.83 (m, 1H). – ^{13}C NMR ($CDCl_3$): δ = 15.83 (d, $^3J_{C-P}$ = 13.7 Hz, *Me*-C_5), 19.36 (d, $^3J_{C-P}$ = 18.5 Hz, *Me*-C_4) (in that case, the assignments of the Me resonances were checked by ^{1}H^{13}C correlation experiments) 49.27 (d, $^2J_{C-P}$ = 26.7 Hz, C_4), 66.75 (d, $^1J_{C-P}$ = 70 Hz, CH_2P), 127.3−137.0 ($C_{sp}2$), 138.49 (d, $^1J_{C-P}$ = 84 Hz, C_6), 159.14 (d, $^2J_{C-P}$ = 15.3 Hz, C_5 or C_3), 161.82 (d, $^2J_{C-P}$ = 16.4 Hz, C_3 or C_5). – MS; *m/z*: 388 [M^+], 272 [$M^+ - CH_3$-C=C-Ph], 204 [M^+ − Ph-C=C-Th]. – $C_{24}H_{21}OPS$ (388.47): calcd. C 74.19, H 5.44, P 7.97; found C 74.10, H 5.45, P 8.01.

4,5-Dimethyl-2-(N-methylpyrrolyl)-3,6-diphenyl-1-phosphanorbornadiene 1-Oxide (**9**): The product was prepared by the general procedure in NMP and was purified by precipitation with pentane. A yellow solid was obtained (80% yield). – ^{31}P NMR ($CDCl_3$): δ = 47.27. – ^{1}H NMR ($CDCl_3$): δ = 1.47 (s, 3 H, Me-C_4), 2.16 (d, 3 H, $^4J_{H-P}$ = 2.8 Hz, Me-C_5), 2.72 (m, 2 H, CH_2P), 3.25 (s, 3 H, Me-N), 5.90 and 5.99 (2 m, 2 H, $H_{\beta\beta'}$ pyrrolyl), 6.51 (m, 1 H, $H_{\alpha'}$ pyrrolyl), 6.96−7.39 (m, 10 H, H arom). – ^{13}C NMR ($CDCl_3$): δ = 15.56 (d, $^3J_{C-P}$ = 13.9 Hz, *Me*-C_5), 19.87 (d, $^3J_{C-P}$ = 18.4 Hz, *Me*-C_4), 35.70 (s, Me-N), 50.01 (d, $^2J_{C-P}$ = 27.3 Hz, C_4), 68.19 (d, $^1J_{C-P}$ = 68.9 Hz, CH_2P), 108.84 (s, $C_{\beta'}$ pyrrolyl), 111.92 (d, $^3J_{C-P}$ = 4.3 Hz, C_β pyrrolyl), 124.62 (s, $C_{\alpha'}$ pyrrolyl), 127.98 -136.73 ($C_{sp}2$), 138.82 (d, $^1J_{C-P}$ = 82.8 Hz, C_6), 161.13 (d, $^2J_{C-P}$ = 16.8 Hz, C_5 or C_3), 164.17 (d, $^2J_{C-P}$ = 17.8 Hz, C_3 or C_5). – MS; *m/z*: 385 [M^+], 370 [$M^+ - CH_3$), 306 [M^+ − N(Me)Pyr), 269 [$M^+ - CH_3$-C=C-Ph], 204 [M^+ − Ph-C=C-N(Me)Pyr]. – $C_{25}H_{24}NOP$ (385.45): calcd. C 77.9, H, 6.27, O 4.17, P 8.03, N 3.63; found C 77.85, H 6.15, O 4.30, P 8.12, N 3.58.

4,5-Dimethyl-2-phenethynyl-3,6-diphenyl-1-phosphanorbornadiene 1-Oxide (**10**): The product was prepared by the general procedure in DMF or CH_3CN and was purified by recrystallization from ethyl acetate. A white solid was obtained (95% yield). – ^{31}P NMR (CH_3CN): δ = 46.3. – ^{1}H NMR ($CDCl_3$): δ = 1.54 (s, 3 H, Me-C_4), 2.20 (d, 3 H, $^4J_{H-P}$ = 2.8 Hz, Me-C_5), 2.72 (m, 2 H, CH_2P), 7.2−7.5 (m, 15 H, H arom). – ^{13}C NMR ($CDCl_3$): δ = 15.58 (d, $^3J_{C-P}$ = 13.9 Hz, *Me*-C_5), 19.72 (d, $^3J_{C-P}$ = 18.4 Hz, *Me*-C_4), 50.02 (d, $^2J_{C-P}$ = 26.2 Hz, C_4), 68.72 (d, $^1J_{C-P}$ = 68.9 Hz, CH_2P), 83.11 (d, $^3J_{C-P}$ = 7.7 Hz, C_{sp}), 102.93 (d, $^2J_{C-P}$ = 6.3 Hz, C_{sp}), 124.65 (d, $^1J_{C-P}$ = 89.9 Hz, C_2), 128.2−132.4 ($C_{sp}2$), 133.52 (d, $^3J_{C-P}$ = 9.3 Hz, $C_{3'}$), 135.16 (d, $^2J_{C-P}$ = 13.0 Hz, $C_{6'}$), 138.55 (d, $^1J_{C-P}$ = 85.2 Hz, C_6), 160.43 (d, $^2J_{C-P}$ = 16.6 Hz, C_5), 172.02 (d, $^2J_{C-P}$ = 16.5 Hz, C_3). – MS; *m/z*: 406 [M^+], 391 [$M^+ - CH_3$], 329 [M^+ − Ph], 290 [$M^+ - CH_3$-C=C-Ph], 204 [M^+ − Ph-C=C-C≡C-Ph].

4,5-Dimethyl-2-octynyl-3,6-diphenyl-1-phosphanorbornadiene 1-Oxide (**11**): The product was prepared by the general procedure in DMF or CH_3CN and was purified by column chromatography on silica gel (ethyl acetate/hexane, 50:50 as the eluent). A yellow oil was obtained (80%). – ^{31}P NMR ($CDCl_3$): δ = 43.0. – ^{1}H NMR ($CDCl_3$): δ = 0.85 (t, 3 H, Me, Hex), 1.22−1.42 (m, 8 H, 4 CH_2), 1.48 (s, 3 H, Me-C_4), 2.17 (d, 3 H, $^4J_{H-P}$ = 2.8 Hz, Me-C_5), 2.34 (m, 2 H, CH_2C≡), 2.65 (m, 2 H, CH_2P), 7.2−7.4 (m, 10 H, H arom). – ^{13}C NMR ($CDCl_3$): δ = 14.47 (s, Me, Hex), 15.29 (d, $^3J_{C-P}$ = 14.0 Hz, *Me*-C_5), 19.42 (d, $^3J_{C-P}$ = 18.3 Hz, *Me*-C_4), 20.62, 22.91, 28.75, 31.67 (4 s, 4 CH_2), 49.45 (d, $^2J_{C-P}$ = 25.9 Hz, C_4), 68.27 (d, $^1J_{C-P}$ = 68.5 Hz, CH_2P), 73.70 (d, $^3J_{C-P}$ = 8.4 Hz, C_{sp}), 105.11 (d, $^2J_{C-P}$ = 6.5 Hz, C_{sp}), 125.18 (d, $^1J_{C-P}$ = 88.7 Hz, C_2), 127.8−128.9 ($C_{sp}2$), 133.42 (d, $^3J_{C-P}$ = 8.9 Hz, $C_{3'}$), 135.02 (d, $^2J_{C-P}$ = 13.7 Hz, $C_{6'}$), 138.18 (d, $^1J_{C-P}$ = 84.4 Hz, C_6), 160.15 (d, $^2J_{C-P}$ = 16.6 Hz, C_5), 169.98 (d, $^2J_{C-P}$ = 16.7 Hz, C_3). – MS; *m/z*: 414 [M^+], 399 [$M^+ - CH_3$], 344 [$M^+ - (CH_2)_5$], 204 [M^+ − $C_{16}H_{18}$].

4,5-Dimethyl-3,6-diphenyl-2-vinyl-1-phosphanorbornadiene 1-Oxide (**12**): The product was prepared by the general procedure in NMP and was purified by column chromatography on silica gel (ethyl acetate/hexane, 80:20 as the eluent). A white solid was ob-

tained (80%). – ^{31}P NMR (NMP): δ = 46.2. – ^{1}H NMR ($CDCl_3$): δ = 1.36 (s, 3 H, Me-C_4), 2.11 (d, 3 H, $^{4}J_{H\text{-}P}$ = 2.8 Hz, Me-C_5), 2.62 (m, 2 H, CH_2P), 5.33 (m, 1 H, =CH), 6.30 (m, 2 H, $=CH_2$), 7.0 (m, 2 H, H arom), 7.3 (m, 8 H, H arom). – ^{13}C NMR ($CDCl_3$): δ = 15.58 (d, $^{3}J_{C\text{-}P}$ = 13.7 Hz, *Me*-C_5), 19.36 (d, $^{3}J_{C\text{-}P}$ = 18.3 Hz, *Me*-C_4), 48.95 (d, $^{2}J_{C\text{-}P}$ = 27.4 Hz, C_4), 67.54 (d, $^{1}J_{C\text{-}P}$ = 69.4 Hz, CH_2P), 120.89 (d, $^{3}J_{C\text{-}P}$ = 4.5 Hz, $=CH_2$), 127.8–135.3 ($C_{sp}2$), 137.54 (d, $^{1}J_{C\text{-}P}$ = 80.4 Hz, C_2 or C_6), 138.56 (d, $^{1}J_{C\text{-}P}$ = 83.8 Hz, C_6 or C_2), 160.89 (d, $^{2}J_{C\text{-}P}$ = 16.6 Hz, C_5 or C_3), 163.48 (d, $^{2}J_{C\text{-}P}$ = 15.6 Hz, C_3 or C_5). – MS; *m*/*z*: 332 [M^+], 317 [$M^+ - CH_3$], 204 [M^+ – Ph-C=C-CH=CH_2]. – $C_{22}H_{21}OP$ (332.38): calcd. C 79.48, H 6.37, O 4.83, P 9.32; found C 79.1, H 6.32, O 5.06, P 9.52.

X-ray Structure Determination of **5**: Crystals of **5**, $C_{20}H_{18}IO_2P$ were grown from a ethyl acetate-hexane solution of the compound. Data were collected at −150 ± 0.5°C on an Enraf Nonius CAD4 diffractometer using Mo-K_α radiation (λ = 0.71073Å) and a graphite monochromator . The crystal structure was solved and refined using the Enraf Nonius MOLEN package. The compound crystallises in space group *P*21/*n* (14), *a* = 9.436(1), *b* = 16.816(2), *c* = 11.755(1) Å, β = 104.7(1)°; *V* = 1804.39(64) Å^3; *Z* = 4; d_{calc} = 1.650 g/cm^3; μ = 18.5 cm^{-1}; *F*(000) = 888. A total of 5707 unique reflexions were recorded in the range 2° ≤ 2θ ≤ 60.0° of which 1143 were considered as unobserved [$F^2 < 3.0\sigma(F^2)$], leaving 4564 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were refined isotropically in the final stages of least-squares while using anisotropic temperature factors for all other atoms. A nonPoisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were R = 0.029, R_ω = 0.051, *G.O.F.* = 1.11.

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