Synthesis and Chemistry of 2-(Dibromophosphino)-4,5-dimethylphosphinine

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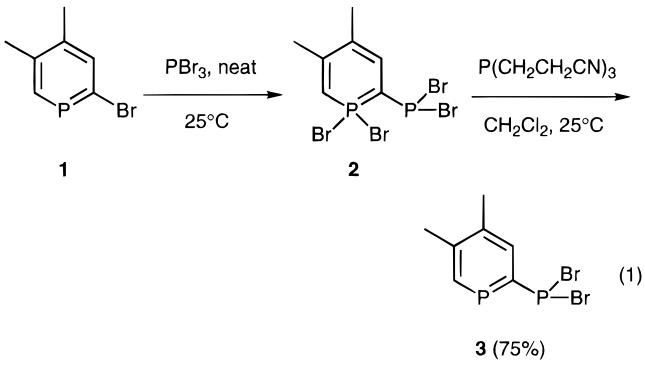
The reaction of PBr_3 with 2-bromo-4,5-dimethylphosphinine in the presence of traces of H^+ or O_2 leads to a transient 1,1-dibromo-λ^5-phosphinine whose reduction by $P(CH_2CH_2CN)_3$ gives the title compound (**3**). It is possible to transpose with **3** most of the classical reactions of phenyldibromophosphine despite the presence of the reactive phosphorus atom of the phosphinine nucleus. The reaction of **3** with 2 equiv of nucleophiles ($Nu^- = R^-$, RO^-, RS^-, R_2N^-) gives the expected 2-PNu_2 derivatives. The reduction of **3** by $LiAlH_4$ gives the primary phosphine **14** whose P-anion **15** is surprisingly stable. The phosphinine nucleus of **3** also withstands electrophilic conditions. Thus, the reaction of **3** with diphenylacetylene in the presence of $AlCl_3$ yields the expected phosphirenium salt, whose reduction leads to the 2-phosphirenylphosphinine **17**. A further ring expansion to the four-membered 1,2-dihydrophosphete **18** is also possible.

For some time now, a rising interest in the synthesis and coordination chemistry of 2-phosphinopyridines has been conspicuous in the literature.[1] Recently, the disclosure of an efficient process for the production of methyl acrylate from CO, methanol, and propyne using a palladium(II) complex of 2-(diphenylphosphino)pyridine as the catalyst[2] has definitively established the value of such phosphines in coordination chemistry. With such a background, it is not surprising that the isostructural 2-phosphinophosphinines have attracted some interest, although they are quite different from their nitrogen analogs from an electronic standpoint. Until now, synthetic efforts have mainly concentrated upon the preparation of 2-(diphenylphosphino)phosphinine derivatives.[3] The only exception concerns the synthesis in modest yields of the 2-(dichlorophosphino)-4,5-dimethylphosphinine from the corresponding 2-iodozinc derivative.[4] Since ready access to such dihalophosphinine derivatives is crucial for a wide-range evaluation of 2-phosphinophosphinines in coordination chemistry and homogeneous catalysis, we decided to look for a simple synthesis of these compounds.

Results and Discussion

We had previously noticed some parallelism between the reactivity of phosphinines and heterophospholes toward electrophiles. Thus, both phosphinines[5] and 1,2,3-diazaphospholes[6] react with bromine via Br_2-addition/HBr-elimination sequences to give bromo-substituted derivatives at the ring carbons. Since 1,2,3-diazaphospholes give PCl_2-substituted derivatives by direct reaction with PCl_3,[7] we decided to investigate the reaction of the readily available 2-bromo-4,5-dimethylphosphinine[8] (**1**) with PBr_3. The more reactive PBr_3 was selected rather than PCl_3 in order to avoid possible Br to Cl redistributions. We soon realized that PBr_3 indeed reacts with **1**, but only in the presence of traces of HBr and/or O_2. The initial product is the λ^5-phosphinine **2**, whose reduction by $P(CH_2CH_2CN)_3$ (chosen for its weak solubility and easy handling) gives the desired PBr_2-substituted phosphinine **3** in good yield (eq 1).



(1)

The 2-(dibromophosphino)phosphinine **3** has been characterized by ^1H, ^{13}C, and ^{31}P NMR and mass

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

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(5) Le Floch, P.; Carmichael, D.; Mathey, F. *Bull. Soc. Chim. Fr.* **1992**, *129*, 291.

(6) Högel, J.; Schmidpeter, A. *Chem. Ber.* **1985**, *118*, 1621.

(7) Luber, J.; Schmidpeter, A. *J. Chem. Soc., Chem. Commun.* **1976**, 887.

(8) Le Floch, P.; Ricard, L.; Mathey, F. *Polyhedron* **1990**, *9*, 991.

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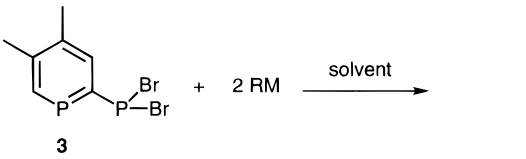
spectrometry. The most noteworthy spectral feature of **3** is its huge ^2J(P—P) coupling constant of 264 Hz. The corresponding PPh_2 derivative displays a much lower coupling of only 92.8 Hz.[3] We have already noticed the variability of such ^2J(P═C—P) couplings.[3] An inspection of the available data (see later) shows no simple correlation between this coupling and the electronegativity of the phosphino substituent. For example, the PCl_2 derivative displays a lower coupling than **3** at 238 Hz. Other factors such as the relative orientation of the phosphorus lone pairs certainly play a role, since blocking the free rotation around the phosphinine—PR_2 bond drastically reduces the observed values. We have no definitive indications concerning the mechanism leading to the formation of **2**. The only well-established fact is that pure degassed PBr_3 does not react with **1** under dry inert atmosphere (N_2 or argon). Admission of HBr or wet air into the flask initiates the reaction. Basically, an initial step almost certainly involves the catalyzed addition of Br—PBr_2 onto the formal P═C-(Br) double bond. Then, a 1,2-migration of bromine from C_2 to P leads to **2**. Such O_2-catalyzed additions of Br—PBr_2 onto unsaturated systems are not totally unprecedented. Some reports describe the synthesis of (bromovinyl)dibromophosphines from PBr_3 and terminal alkynes.[9]

Whatever its actual mechanism, the easy formation of **3** allowed us to prepare a large array of 2-phosphinophosphinines. Indeed, the phosphinine nucleus of **3** displays a surprising compatibility with various reagents used to transform the PBr_2 functionality. For example, whereas phosphinines are known to react easily with various organometallic derivatives at phosphorus,[10] it is possible to substitute the P—Br bond of **3** without destroying the aromatic nucleus, provided that a stoichiometric amount of organometallic species is used (eq 2).



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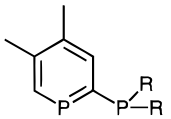


(2)

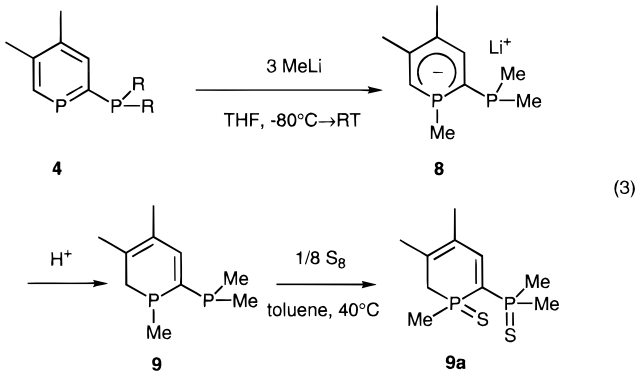
4 R = Me (M = MgBr, ether, 80%)

5  (M = ZnCl, ether : toluene, 70%)

6  (M = Li, toluene, 70%)

7 R = PhC≡C- (M = ZnCl, THF : toluene, 70%)

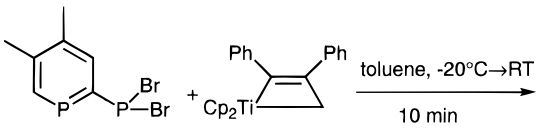
Phosphinines **4** and **6**, which are oxygen-sensitive, were also characterized as their $R_2P{\rightarrow}BH_3$ complexes **4a** and **6a**, respectively (see Experimental Section). Of course, an excess of organometallic species leads to the formation of a 1,2-dihydrophosphinine, as expected (eq 3).



4 **8** (3)

9 **9a**

The intermediate delocalized carbanion **8** has been characterized by ^{31}P NMR spectroscopy. Diphosphine **9**, which is oxygen-sensitive, has also been characterized as its disulfide derivative **9a**. Besides the classical lithium, magnesium, and zinc organometallics, more exotic species can also be used. Thus, the reaction of **3** with titanacyclobutene, following a published synthesis of 1,2-dihydrophosphetes,[11] yields the expected four-membered ring **10** (eq 4).



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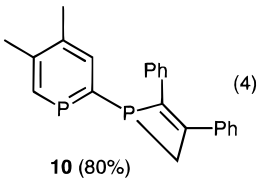
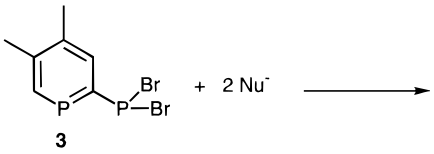


(4)

10 (80%)

Oxygen, sulfur, and nitrogen nucleophiles can also be used (eq 5).



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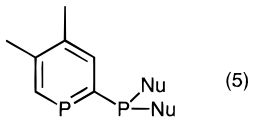


(5)

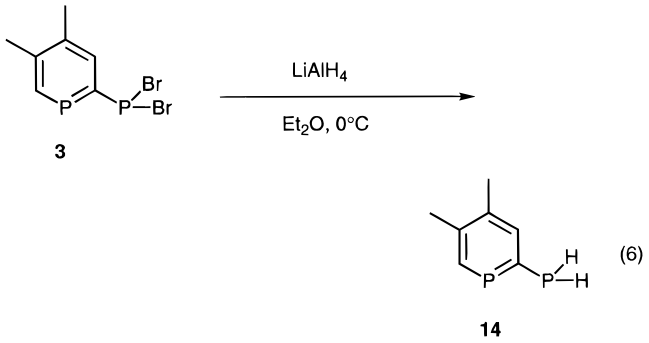
11 Nu = MeO (MeOH + Et_3N) (80%)
12 Nu = BuS (BuSH + Et_3N) (90%)
13 Nu = Et_2N (Et_2NH) (85%)

A further extension of the chemistry of **3** concerns the reduction to the corresponding primary phosphine **14** (eq 6).

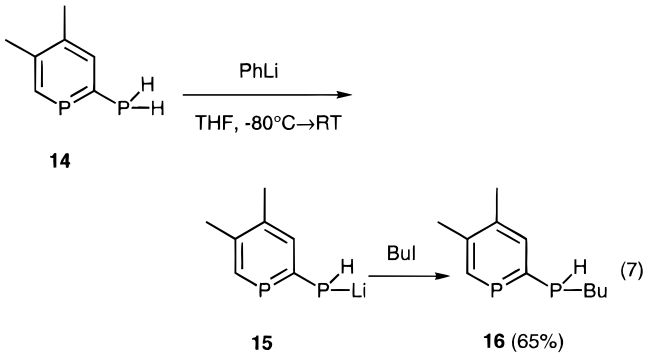
(9) Kruglov, A. S.; Oskotskii, E. L.; Dogadina, A. V.; Ionin, B. I.; Petrov, A. A. *Zh. Obshch. Khim.* **1978**, *48*, 1495; *Russ. J. Gen. Chem. (Engl. Transl.)* **1978**, 1371. Kruglov, A. S.; Dogadina, A. V.; Ionin, B. I.; Petrov, A. A. *Zh. Obshch. Khim.* **1978**, *48*, 705; *Russ. J. Gen. Chem. (Engl. Transl.)* **1978**, 649.

(10) Märkl, G.; Lieb, F.; Merz, A. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 87. Märkl, G.; Merz, A. *Tetrahedron Lett.* **1968**, 3611. Ashe, A. J., III; Smith, T. W. *Tetrahedron Lett.* **1977**, 407.

(11) Doxsee, K. M.; Chen, G. S.; Knobler, C. B. *J. Am. Chem. Soc.* **1989**, *111*, 9129. Tumas, W.; Suriano, J. A.; Marlow, R. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 75. Doxsee, K. M.; Hanavalt, E. M.; Chen, G. S.; Weakley, T. J. R.; Hope, H. Knobler, C. B. *Inorg. Chem.* **1991**, *30*, 3381.

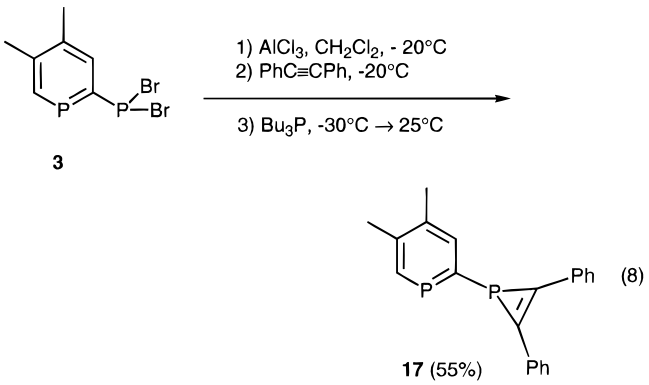


It is interesting to note that both the ^{31}P chemical shift (−116.2 ppm) and the $^{1}J(P—H)$ coupling (196.7 Hz) of the PH_2 group of **14** are very close to those of $PhPH_2$. Rather unexpectedly, it is possible to prepare a stable lithium phosphide from **14** using phenyllithium as base (eq 7).

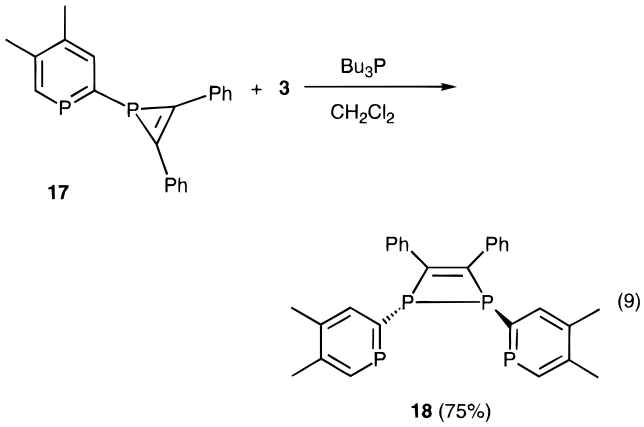


The surprising stability of **15** would suggest some bind of delocalization similar to that observed in 1-phosphaallylic anions.[12] However, this is probably not the case, since the $^{2}J(P—P)$ couplings are similar in **14** (57.3 Hz) and **15** (52.0 Hz). In any event, **15** is easily alkylated by butyl iodide to give the secondary phosphine **16**.

In order to complete our evaluation of the synthetic potential of **3**, we decided to carry out one series of transformations in the presence of a Lewis acid. As a model reaction, we selected the synthesis of phosphirenes from alkynes and dihalophosphines in the presence of aluminum trichloride.[13] The reaction proceeds rather well (eq 8).



Moreover, it is possible to go one step further and to transform the phosphirene **17** into the 1,2-dihydrophosphete **18**[14] (eq 9).



Thus, it is quite clear that the phosphinine nucleus of **3** withstands both nucleophilic and electrophilic conditions. A wide range of 2-phosphinophosphinines is consequently accessible by transposition of the known reactions of phenyldibromophosphine. The availability of these derivatives will be particularly useful for a systematic investigation of the coordination chemistry of this new class of bidentate ligands.

Experimental Section

Reactions were carried out under nitrogen using oven-dried glassware. Dry THF, toluene, and hexane were obtained by distillation from Na/benzophenone, and dry CH_2Cl_2 was obtained by distillation from P_2O_5. Silica gel (70−230 mesh) was used for chromatographic separations. Nuclear magnetic resonance spectra were obtained 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 external TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P) and coupling constants in Hertz. The following abreviations are used: s, singlet; d, doublet; t, triplet; q, quadruplet; b, broad. Mass spectra were obtained at 70 eV with a Shimadzu GC−MS QP 1000 spectrometer by the direct inlet method, and elemental analyses were performed by the "Service d'analyse du CNRS", at Gif-sur-Yvette, France. Starting materials were obtained from commercial suppliers or prepared according to literature methods.

1,1-Dibromo-λ^5-2-(dibromophosphino)-4,5-dimethylphosphinine (2) and 2-(Dibromophosphino)-4,5-dimethylphosphinine (3). 2-Bromophosphinine **1** (10 g, 50 mmol) was mixed with PBr_3 (12 g, 44 mmol, 0.88 equiv). The resulting solution was then stirred at room temperature. After 1 h, the reaction mixture became orange, which indicated that the condensation started (at this stage, if the solution is colorless, the solution can be kept in the air for a few seconds). After 15 h of stirring the reaction mixture became solid and 100 mL of freshly distilled hexane was added. The orange solid was then slowly dispersed into the solution in order to get a fine powder. After this operation, which requires about 30 min, the hexane solution (which contains a small amount of PBr_3) was eliminated by filtration under nitrogen and the resulting orange powder (compound **2**) was dissolved in 200 mL of dry CH_2Cl_2. Tris(2-cyanoethyl)phosphine (8.68 g, 45 mmol) was then added to this solution at room temperature. After 1 h of stirring, the mixture became yellow, which indicated the end of the reduction. The solution was then evaporated to the original volume, and 250 mL of dry and

(12) Niecke, E.; Nieger, M.; Wenderoth, P. *J. Am. Chem. Soc.* **1993**, *115*, 6989.
(13) Lochschmidt, S.; Mathey, F.; Schmidpeter, A. *Tetrahedra Lett.* **1986**, *27*, 2635.
(14) Ricard, L.; Maigrot, N.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 548.

degassed hexane was added. After filtration and evaporation of solvents, phosphinine **3** was recovered as a yellow powder which is sensitive to moisture. Yield: 11.70 g (75%).

2: orange powder; mp 60 °C; ^{31}P NMR (C_6D_6) δ 145.70 (d, ^2J(P−P) = 211.40, PBr_2), −47.55 (d, P of $C_7H_8PBr_2$); ^{1}H NMR (C_6D_6) δ 2.11 (dd, 3H, ^5J(H−P) = 3.33, ^4J(H−H) = 0.37, Me), 2.19 (d, 3H, ^4J(H−P) = 1.53, Me), 5.85 (dd, 1H, ^2J(H−P) = 12.72, ^4J(H−P) = 9.28, H_6), 7.62 (ddd, 1H, ^3J(H−P) = 50.30, ^3J(H−P) = 9.07, ^3J(H−H) = 0.37, H_3); ^{13}C NMR (C_6D_6) δ 20.30 (d, J(C−P) = 2.25, Me), 25.0 (d, J(C−P) = 20.40, Me), 92.95 (t, ^1J(C−P) = ^1J(C−P) = 81.75, C_2), 99.45 (dd, ^1J(C−P) = 86.80, ^3J(C−P) = 3.25, C_6), 121.25 (dd, ^3J(C−P) = 24.45, ^3J(C−P) = 2.40, C_4), 141.95 (dd, ^2J(C−P) = 7.0, ^2J(C−P) = 2.20 , C_3), 157.80 (s, C_5).

3: yellow solid: mp 40 °C; ^{31}P NMR ($CDCl_3$) δ 201.30 (d, ^2J(P−P) = 264.0, P of C_7H_8P), 153.70 (d, P of PBr_2); ^{1}H NMR ($CDCl_3$) δ 2.45 (d, 3H, J(C−P) = 3.50, Me), 2.50 (s, 3H, Me), 8.37 (dd, 1H, ^3J(H−P) = 11.45, ^3J(H−P) = 5.0, H_3), 8.51 (dd, 1H, ^2J(H−P) = 41.30, ^4J(H−P) = 6.85, H_6); ^{13}C NMR ($CDCl_3$) δ 23.10 (s, Me), 24.25 (s, Me), 140.86 (dd, J(C−P) = 17.50, J(C−P) = 4.75, C_4 or C_5), 141.51 (dd, ^2J(C−P) = 20.0, ^2J(C−P) = 12.35, C_3), 148.25 (d, J(C−P) = 13.70, C_5 or C_4), 154.15 (dd, ^1J(C−P) = 58.0, ^3J(C−P) = 22.80, C_6), 164.70 (dd, ^1J(C−P) = 71.52, ^1J(C−P) = 62.35, C_2); mass spectrum *m*/*z* (ion, relative intensity) 314 (M, 40), 254 (M − Br, 95). **3** was found to be too moisture sensitive to give satisfactory microanalytical data.

2-(Dimethylphosphino)-4,5-dimethylphosphinine (4). A solution of (dibromophosphino)phosphinine **3** (3.14 g, 10 mmol) in 10 mL of THF was quickly added at −80 °C to a solution of MeMgBr (22 mL, 22 mmol in ether). After 5 min of stirring, the resulting mixture was slowly warmed to room temperature and then stirred for 1 h. After the evaporation of solvents, 100 mL of a mixture of hexane and toluene (4:1) was added. After 10 min of stirring, the orange solution, which contains phosphinine **4**, was filtered under nitrogen. After evaporation of solvents, **4** was recovered as an orange, oxygen-sensitive oil. Yield: 1.46 g (80%).

4: ^{31}P NMR (C_6D_6) δ 196.55 (d, ^2J(P−P) = 55.05, P of C_7H_8P), −35.65 (d, PMe_2); ^{1}H NMR (C_6D_6) δ 1.55 (dd, 6H, ^2J(H−P) = 3.36, ^4J(H−P) = 0.71, P−Me), 1.92 (d, 3H, J(H−P) = 3.45, Me of C_7H_8P), 1.96 (s, 3H, Me of C_7H_8P), 7.83 (dd, 1H, ^3J(H−P) = 25.65, ^3J(H−P) = 14.41, H_3), 8.35 (d, 1H, ^2J(H−P) = 39.37, H_6); ^{13}C NMR ($CDCl_3$) δ 17.50 (t, ^1J(C−P) = ^3J(C−P) = 15.25, P−Me), 22.70 (s, Me of C_7H_8P), 23.65 (d, J(C−P) = 2.50, Me of C_7H_8P), 138.90 (dd, J(C−P) = 19.35, J(C−P) = 9.35, C_4 or C_5), 141.25 (dd, ^2J(C−P) = 28.85, ^2J(C−P) = 12.80, C_3), 143.45 (d, J(C−P) = 15.0, C_4 or C_5), 156.15 (dd, ^1J(C−P) = 55.10, ^3J(C−P) = 3.35, C_6), 173.30 (dd, ^1J(C−P) = 70.95, ^1J(C−P) = 23.65, C_2); mass spectrum *m*/*z* (ion, relative intensity) 184 (M, 11).

2-(Dimethylphosphinoborane complex)-4,5-dimethylphosphinine (4a). A solution of BH_3·SMe_2 complex (1.58 mL, 1.58 mmol, 1 M solution in toluene) was added to phosphinine **4** (0.18 g, 1 mmol) in 2 mL of toluene. After 90 min, a ^{31}P NMR control indicated the end of the complexation. Water (2 mL) was then added to destroy the excess complex, and the mixture was extracted with 3 mL of toluene. After separation, drying over $MgSO_4$, filtration under nitrogen, and evaporation of toluene, phosphinine **4a** was recovered as a pulverulent white solid. Yield: 0.15 g (75%).

4a: ^{31}P NMR (C_6D_6) δ 200.60 (d, ^2J(P−P) = 54.95, P of C_7H_8P), 8.40 (m, P−BH_3); ^{1}H NMR (C_6D_6) δ 1.30 (d, 6H, ^2J(H−P) = 10.11, P−Me), 1.87 (d, 3H, J(H−P) = 3.67, Me of C_7H_8P), 1.93 (s, 3H, Me of C_7H_8P), 8.23 (dd, 1H, ^2J(H−P) = 41.07, ^4J(H−P) = 3.80, H_6), 8.28 (dd, 1H, ^3J(H−P) = 16.60, ^3J(H−P) = 6.27, H_3); ^{13}C NMR (C_6D_6) δ 15.45 (dd, ^1J(C−P) = 38.40, ^3J(C−P) = 10.20, P−$(Me)_2$), 22.60 (s, Me of C_7H_8P), 23.75 (d, J(C−P) = 2.45, Me of C_7H_8P), 140.30 (dd, J(C−P) = 18.91, J(C−P) = 12.60, C_4 or C_5), 142.00 (t, ^2J(C−P) = ^2J(C−P) = 12.85, C_3), 146.20 (dd, J(C−P) = 13.60, J(C−P) = 2.35, C_4 or C_5), 155.55 (dd, ^1J(C−P) = 54.05, ^3J(C−P) = 8.59, C_6), 158.25 (dd, ^1J(C−P) = 66.10, ^1J(C−P) = 41.25, C_2); mass spectrum *m*/*z* (ion, relative intensity) 198 (M, 26), 197 (M − 1, 42), 184 (M − BH_3, 100), 169 (M − BH_3 − Me, 41). Anal. Calcd for $C_9H_{17}BP_2$: C, 54.60; H, 8.65. Found: C, 54.40; H, 8.75.

2-(Bis(2-furyl)phosphino)-4,5-dimethylphosphinine (5). A solution of (2-furyl)ZnCl (prepared by methathesis with $ZnCl_2$ from the lithium derivative; 14 mmol, 2.2 equiv) in 40 mL of ether was slowly added at −40 °C to a solution of **3** (2.0 g, 6.36 mmol) in 70 mL of toluene. After the addition, the reaction mixture was slowly warmed at room temperature and then stirred for 1 h. After the evaporation of ether, 50 mL of toluene was added and the resulting solution was filtered under nitrogen. Phosphinine **5** was recovered as a colorless oxygen-sensitive oil after the removal of toluene. Phosphinine **5** can be definitively purified by rapid chromatography on silica gel with pure toluene as eluent. Yield: 1.28 g (70%).

5: ^{31}P NMR ($CDCl_3$) δ 205.05 (d, ^2J(P−P) = 104.0, P of C_7H_8P), −46.30 (d, P(furyl)$_2$); ^{1}H NMR ($CDCl_3$) δ 2.30 (d, 3H, J(H−P) = 3.60, Me), 2.38 (s, 3H, Me), 6.45 (q, 2H, ^3J(H−$H_{5'}$) = ^3J(H−$H_{3'}$) = ^3J(H−P) = 1.70, $H_{4'}$ of C_4H_3O), 6.95 (bs, 2H, $H_{3'}$ of C_4H_3O), 7.68 (d, 2H, ^3J(H−$H_{4'}$) = 1.70, $H_{5'}$ of C_4H_3O), 7.88 (dd, 1H, ^3J(H−P) = 14.95, ^3J(H−P) = 6.10, H_3), 8.45 (dd, 1H, ^2J(H−P) = 39.43, ^4J(H−P) = 3.95, H_6); ^{13}C NMR ($CDCl_3$) δ 23.05 (s, Me), 23.90 (d, J(C−P) = 2.50, Me), 111.45 (d, ^3J(C−P) = 6.15, $C_{4'}$ of C_4H_3O), 122.50 (d, ^2J(C−P) = 24.10, $C_{3'}$ of C_4H_3O), 139.50 (dd, J(C−P) = 18.15, J(C−P) = 8.70, C_4 or C_5), 141.55 (dd, ^2J(C−P) = 22.90, ^2J(C−P) = 13.50, C_3), 148.25 (s, $C_{5'}$ of C_4H_3O), 151.05 (t, ^1J(C−P) = ^3J(C−P) = 8.20, $C_{2'}$ of C_4H_3O), 156.05 (dd, ^1J(C−P) = 54.90, ^3J(C−P) = 9.40, C_6), 162.10 (dd, ^1J(C−P) = 65.60, ^1J(C−P) = 12.20, C_2); mass spectrum *m*/*z* (ion, relative intensity) 288 (M, 100). Anal. Calcd for $C_{15}H_{14}O_2P_2$: C, 62.51; H, 4.90. Found: C, 62.25; H, 4.80.

2-(Bis(2-thienyl)phosphino)-4,5-dimethylphosphinine (6). A solution of 2-thienyllithium (12.72 mmol) in 40 mL of ether was added dropwise at −80 °C to a solution of phosphinine **3** (2 g, 6.36 mmol) in 70 mL of toluene. At the end of the addition, the reaction mixture was slowly warmed at room temperature and stirred for an additional 1 h. After addition of NH_4Cl (0.33 g, 6.36 mmol), ether was evaporated and 50 mL of toluene was added before filtration under nitrogen. Phosphinine **6** was recovered as a yellow oxygen-sensitive oil after evaporation of toluene. Yield: 1.42 g (70%).

6: ^{31}P NMR (C_6D_6) δ 204.40 (d, ^2J(P−P) = 96.85, P of C_7H_8P), −28.85 (d, P$(C_4H_3S)_2$); ^{1}H NMR (C_6D_6) δ 1.98 (d, 3H, J(H−P) = 3.46, Me of C_7H_8P), 2.06 (s, 3H, Me of C_7H_8P), 6.95 (ddd, 2H, ^3J($H_{4'}$−$H_{5'}$) = 4.92, ^3J($H_{4'}$−$H_{3'}$) = 3.48, ^4J($H_{4'}$−P) = 1.31, $H_{4'}$ of C_4H_3S), 7.29 (dd, 2H, ^3J($H_{5'}$−$H_{4'}$) = 4.92, ^4J($H_{5'}$−$H_{3'}$) = 1.08, $H_{5'}$), 7.58 (ddd, 2H, ^3J($H_{3'}$−P) = 6.07, ^3J($H_{3'}$−$H_{4'}$) = 3.48, ^4J($H_{3'}$−$H_{5'}$) = 1.08, $H_{3'}$), 8.15 (dd, 1H, ^3J(H−P) = 13.94, ^3J(H−P) = 6.06, H_3), 8.43 (dd, 1H, ^2J(H−P) = 39.78, ^4J(H−P) = 3.19, H_6); ^{13}C NMR (C_6D_6): δ 22.65 (d, J(C−P) = 1.85, Me), 23.55 (d, J(C−P) = 3.25, Me), 128.90 (s, CH of C_4H_3S), 133.00 (s, CH of C_4H_3S), 137.15 (d, J(C−P) = 27.40, C−H of C_4H_3S), 139.30 (dd, J(C−P) = 18.20, J(C−P) = 9.20, $C_{2'}$ or C_4 or C_5), 140.50 (dd, J(C−P) = 26.95, J(C−P) = 8.60, $C_{2'}$ or C_4 or C_5), 142.05 (dd, ^2J(C−P) = 27.00, ^2J(C−P) = 13.30, C_3), 144.00 (d, J(C−P) = 14.00, C_4 or C_5), 156.35 (dd, ^1J(C−P) = 56.40, ^3J(C−P) = 8.75, C_6), 168.20 (dd, ^1J(C−P) = 67.05, ^1J(C−P) = 18.20, C_2); mass spectrum *m*/*z* (ion, relative intensity) 320 (M, 15).

2-(Bis(2-thienyl)phosphinoborane complex)-4,5-dimethylphosphinine (6a). The procedure is identical with that used for the synthesis of complex **4a**. Phosphinine **6** (0.32 g, 1 mmol) was reacted with BH_3·SMe_2 complex (1.58 mL, 1.58 mmol, 1 M solution in toluene) in 2 mL of toluene. After the conventional workup, phosphinine **6a** was isolated as a pulverulent oil. Yield: 0.30 g (90%).

6a: ^{31}P NMR (C_6D_6) δ 206.30 (d, ^2J(P−P) = 72.75, P of C_7H_8P), 8.00 (m, P−BH_3); ^{1}H NMR (C_6D_6) δ 1.68 (d, 3H, J(H−P) = 3.57, Me of C_7H_8P), 1.78 (s, 3H, Me of C_7H_8P), 6.65 (ddd, 2H, ^3J($H_{4'}$−$H_{5'}$) = 4.85, ^3J($H_{4'}$−$H_{3'}$) = 3.62, ^4J($H_{4'}$−P) = 1.58, $H_{4'}$ of C_4H_3S), 7.00 (ddd, 2H, ^3J($H_{5'}$−$H_{4'}$) = 4.85, ^3J($H_{5'}$−P) = 2.92, ^4J($H_{5'}$−$H_{3'}$) = 1.12, $H_{5'}$), 7.68 (ddd, 2H, ^3J(H−P) =

6.91, $^3J(H_{3'}-H_{4'}) = 3.62$, $^4J(H_{3'}-H_{5'}) = 1.12$, $H_{3'}$), 8.11 (dd, 1H, $^2J(H-P) = 41.17$, $^4J(H-P) = 4.87$, H_6), 8.40 (dd, 1H, $^3J(H-P) = 18.64$, $^3J(H-P) = 5.19$, H_3); ^{13}C NMR (C_6D_6) δ 22.60 (s, Me), 23.75 (d, $J(C-P) = 2.45$, Me), 129.35 (s, CH of C_4H_3S), 132.30 (dd, $^1J(C-P) = 61.30$, $^3J(C-P) = 4.10$, C_q of C_4H_3S), 135.20 (d, $J(C-P) = 2.40$, CH of C_4H_3S), 138.90 (d, $^3J(C-P) = 10.91$, CH of C_4H_3S), 140.35 (dd, $J(C-P) = 17.60$, $J(C-P) = 13.00$, C_4 or C_5), 142.30 (t, $^2J(C-P) = {}^2J(C-P) = 12.95$, C_3), 146.40 (dd, $J(C-P) = 13.60$, $J(C-P) = 2.50$, C_4 or C_5), 155.65 (dd, $^1J(C-P) = 55.05$, $^3J(C-P) = 10.75$, C_6), 157.60 (dd, $^1J(C-P) = 65.70$, $^1J(C-P) = 48.90$, C_2); mass spectrum *m/z* (ion, relative intensity) 334 (M, 15), 320 (M − BH_3, 100). Anal. Calcd for $C_{15}H_{17}BP_2S_2$: C, 53.91; H, 5.13. Found: C, 53.75; H, 5.10.

2-(Bis(phenylethynyl)phosphino)-4,5-dimethylphosphinine (7). A solution of (phenylethynyl)ZnCl (18 mmol) in 40 mL of THF was added dropwise at −80 °C to a solution of phosphinine **3** in a mixture of 20 mL of toluene and 10 mL of THF. At the end of the addition, the reaction mixture was slowly warmed to room temperature and then stirred for an additional 1 h. Celite (2 g) was then added, and the solvents were evaporated, yielding an orange powder. The resulting coated Celite was then loaded onto the top of a silica gel packed flash column for chromatography, and phosphinine **7** was eluted with a mixture of hexane and CH_2Cl_2 (3:1). After evaporation of solvents, **7** was recovered as a white solid. Yield: 2.24 g (70%).

7: ^{31}P NMR ($CDCl_3$) δ 205.10 (d, $^2J(P-P) = 133.30$, P of C_7H_8P), −57.35 (d, P of $P(CCPh)_2$); ^1H NMR ($CDCl_3$) δ 2.34 (d, 3H, $J(H-P) = 4.24$, Me of C_7H_8P), 2.37 (d, 3H, $J(H-P) = 1.80$, Me of C_7H_8P), 7.20−7.30 (m, 5H, C_6H_5), 8.16 (dd, 1H, $^3J(H-P) = 14.70$, $^3J(H-P) = 6.06$, H_3), 8.49 (dd, 1H, $^2J(H-P) = 39.13$, $^4J(H-P) = 4.51$, H_6); ^{13}C NMR ($CDCl_3$) δ 23.10 (s, Me), 24.00 (d, $J(C-P) = 2.60$, Me), 84.60 (dd, $^1J(C-P) = 11.0$, $^3J(C-P) = 4.85$, ≡C−), 107.35 (d, $^2J(C-P) = 5.70$, ≡C−), 123.15 (s, C_q of C_6H_5), 128.90 (s, CH of C_6H_5), 129.75 (s, CH of C_6H_5), 132.60 (s, CH of C_6H_5), 139.90 (dd, $J(C-P) = 28.10$, $J(C-P) = 9.30$, C_5 or C_4), 141.80 (dd, $^2J(C-P) = 25.80$, $^2J(C-P) = 13.70$, C_3), 144.85 (d, $J(C-P) = 14.0$, C_5 or C_4), 156.40 (d, $^1J(C-P) = 55.30$, $^3J(C-P) = 11.10$, C_6), 160.20 (dd, $^1J(C-P) = 63.45$, $^1J(C-P) = 10.60$, C_2); mass spectrum *m/z* (ion, relative intensity) 356 (M + 1, 30). Anal. Calcd for $C_{23}H_{18}P_2$: C, 77.52; H, 5.09. Found: C, 77.50; H, 5.05.

Anion 8 and 2-(Dimethylphosphino)-1-Methyl-4,5-dimethyl-1,6-dihydrophosphinine (9). MeLi (19.1 mL, molar solution in ether) was added at −80 °C to a solution of phosphinine **3** (2.0 g, 6.36 mmol) in 20 mL of THF. After 10 min of stirring at −80 °C, the resulting red solution was slowly warmed to room temperature and stirred for 10 min. The formation of anion **8** was checked by ^{31}P NMR. Addition of NH_4Cl led to the disappearance of the red color characteristic of **8**. After the evaporation of solvents, 30 mL of freshly distilled and degassed pentane was added and the resulting solution was filtered under nitrogen. Diphosphine **9** was isolated as a yellow oxygen-sensitive oil. Yield: 1.10 g (80%).

8: ^{31}P NMR (THF) δ −41.85 (d, $^2J(P-P) = 169.65$, P of $P(Me)_2$), −67.55 (d, P of $C_8H_{11}P$).

9: ^{31}P NMR (C_6D_6) δ −39.55 (d, $^2J(P-P) = 73.60$, P of $P(Me)_2$), −85.80 (d, P of $C_8H_{12}P$); ^1H NMR (C_6D_6) δ 0.87 (d, 3H, $^2J(H-P) = 4.13$, P−Me of $C_8H_{12}P$), 1.18 (d, 3H, $^2J(H-P) = 1.95$, Me of $P(Me)_2$), 1.20 (d, 3H, $^2J(H-P) = 1.95$, Me of $P(Me)_2$), 1.56 (s, 3H, Me), 1.66 (s, 3H, Me), 1.83 (d, 1H, $^2J(H_A-H_B) = 17.40$, H of CH_2), 2.19 (dd, 1H, $^2J(H_B-H_A) = 17.40$, $^2J(H_B-P) = 14.57$, H of CH_2), 6.64 (dd, 1H, $^3J(H-P) = 13.67$, $^3J(H-P) = 9.32$, H_3); ^{13}C NMR (C_6D_6) δ 8.50 (d, $^1J(C-P) = 18.30$, P−Me), 14.50 (m, Me of $P(Me)_2$), 19.50 (s, Me of $C_8H_{12}P$), 22.95 (s, Me of $C_8H_{12}P$), 29.80 (dd, $^1J(C-P) = 12.85$, $^3J(C-P) = 2.80$, CH_2), 125.80 (dd, $J(C-P) = 9.05$, $J(C-P) = 4.50$, C_4 or C_5 of $C_8H_{12}P$), 138.25 (dd, $^1J(C-P) = 32.85$, $^1J(C-P) = 23.80$, C_2), 142.10 (dd, $^2J(C-P) = 26.00$, $^2J(C-P) = 2.95$, =CH), 147.75 (d, $J(C-P) = 2.95$, C_5 or C_4); mass spectrum *m/z* (ion, relative intensity) 201 (M + 1, 38), 169 (M − 2 Me − H, 12). **9** was too moisture sensitive to give satisfactory microanalytical data.

Disulfide 9a. Sulfur (0.19 g, 6 mmol) was added to a solution of diphosphine **9** (0.40 g, 2 mmol) in 10 mL of toluene. After 2 h of heating at 40 °C, toluene was evaporated and 5 mL of CH_2Cl_2 was added. The solution was filtered to remove excess sulfur, and 2 g of Celite was added. The solvent was then evaporated, yielding a yellow powder. The resulting coated silica gel was then loaded onto the top of a silica gel packed flash column for chromatography. The first fraction eluted with hexane yielded traces of sulfur. Disulfide **9a** was then eluted with a CH_2Cl_2/MeOH (80:20) mixture. After evaporation of solvents, **9a** was recovered as a white solid. Yield: 0.18 g, (80%).

9a: ^{31}P NMR (C_6D_6) δ 36.00 (d, $^2J(P-P) = 19.95$, S=P(Me)$_2$), 21.60 (d, S=P−Me); ^1H NMR (C_6D_6) δ 1.11 (d, 3H, $^2J(H-P) = 5.40$, Me of $P(Me)_2$), 1.16 (d, 3H, $^2J(H-P) = 7.16$, Me of $P(Me)_2$), 1.34 (s, 3H, Me−P), 1.90 (d, 1H, partially masked by the signal at 1.92 ppm, H_A of CH_2), 1.92 (d, 3H, $J(H-P) = 13.57$, Me), 2.17 (d, 3H, $J(H-P) = 13.86$, Me), 2.46 (t, 1H, $^2J(H_B-H_A) = {}^2J(H_B-P) = 18.51$, H_B of CH_2) 7.83 (dd, 1H, $^3J(H-P) = 31.28$, $^3J(H-P) = 25.88$, H_3); mass spectrum *m/z* (ion, relative intensity) 264 (M, 76), 249 (M − Me, 17). Anal. Calcd for $C_{10}H_{18}P_2S_2$: C, 45.44; H, 6.86. Found: C, 45.75; H, 6.95.

2-(3,4-Diphenyl-1,2-dihydro-1-phosphetenyl)-4,5-dimethylphosphinine (10). A solution of **3** (2 g, 6.36 mmol) in 20 mL of toluene was added at −20 °C to a solution of titanacycle in 50 mL of toluene. After 10 min of stirring, the reaction mixture was slowly warmed at room temperature and then stirred for an additional 20 min. After filtration under a nitrogen atmosphere, 5 g of Celite was added and the solvents were evaporated. Phosphinine **10** was then purified by chromatography on silica gel. The first fraction eluted with hexane allowed the elimination of traces of diphenylacetylene. Phosphinine **10** was then eluted with a mixture of hexane and toluene (80:20). After evaporation of solvents, **10** was recovered as a colorless oil. Yield: 1.76 g (80%).

10: ^{31}P NMR (C_6D_6) δ 206.60 (d, $^2J(P-P) = 84.10$, P of C_7H_8P), −12.55 (d, P of $C_{15}H_{12}P$); ^1H NMR (C_6D_6) δ 2.03 (d, 3H, $J(H-P) = 3.53$, Me of C_7H_8P), 2.06 (s, 3H, Me of C_7H_8P), 2.90 (ddd, 1H, $J(H_B-H_A) = 14.45$, $^2J(H-P) = 3.51$, $^4J(H-P) = 1.32$, H_B of CH_2), 3.08 (dd, 1H, $^2J(H_A-H_B) = 14.45$, $^2J(H_A-P) = 9.21$, H_A of CH_2), 7.10−7.30 (m, 10H, CH of C_6H_5), 8.17 (dd, 1H, $J(H-P) = 11.86$, $J(H-P) = 7.07$, H_3), 8.44 (d, 1H, $^2J(H-P) = 37.94$, H_6); ^{13}C NMR (C_6D_6) δ 21.85 (s, Me of C_7H_8P), 22.90 (s, Me of C_7H_8P), 30.30 (dd, $^1J(C-P) = 10.60$, $^3J(C-P) = 6.00$, CH_2), 126.95−129.20 (m, CH of C_6H_5), 136.50 (d, $J(C-P) = 10.45$, C_q of C_6H_5), 136.95 (d, $J(C-P) = 3.30$, C_q of C_6H_5), 138.50 (dd, $^1J(C-P) = 18.60$, $^3J(C-P) = 8.05$, C_4 or C_5), 141.25 (dd, $J(C-P) = 26.00$, $J(C-P) = 13.60$, C_3), 142.35 (d, $^2J(C-P) = 8.35$, =C−), 143.90 (d, $J(C-P) = 14.50$, C_4 or C_5), 146.30 (dd, $^1J(C-P) = 8.70$, $^2J(C-P) = 2.30$, =C−), 156.45 (dd, $^1J(C-P) = 56.45$, $^3J(C-P) = 7.45$, C_6), 165.80 (dd, $^1J(C-P) = 66.80$, $^1J(C-P) = 43.40$, C_2); mass spectrum *m/z* (ion, relative intensity) 346 (M, 100). Anal. Calcd for $C_{22}H_{20}P_2$: C, 76.29; H, 5.82. Found: C, 76.15; H, 5.75.

2-(Dimethoxyphosphino)-4,5-dimethylphosphinine (11). Dibromophosphinine **3** (2 g, 6.36 mmol) was dissolved in a mixture of 20 mL of THF and triethylamine (3.85 g, 38.16 mmol, 6 equiv). After the mixture was cooled to −10 °C, a solution of MeOH (0.52 g, 12.7 mmol) in 5 mL of THF was added dropwise. At the end of the addition, the reaction mixture was stirred for 10 min at −10 °C and then slowly warmed to room temperature. After the evaporation of solvents and excess triethylamine, 20 mL of dry and deoxygenated hexane was added and the solution was filtered. The same operation was repeated twice. Phosphinine **11** was recovered as a yellow oxygen-sensitive oil after the evaporation of hexane. Yield: 1.10 g (80%).

11: ^{31}P NMR ($CDCl_3$) δ 203.62 (d, $^2J(P-P) = 96.40$, P of C_7H_8P), 163.45 (d, $P(OMe)_2$); ^1H NMR ($CDCl_3$) δ 1.92 (d, 3H,

J(H−P) = 3.50, Me), 1.95 (s, 3H, Me), 7.97 (dd, 1H, ^3J(H−P) = 10.90, ^3J(H−P) = 7.05, H_3), 8.38 (dd, 1H, ^2J(H−P) = 39.30, ^4J(H−P) = 2.38, H_6); ^{13}C NMR ($CDCl_3$) δ 22.80 (s, Me), 23.95 (d, J(C−P) = 3.50, Me), 53.20 (d, ^2J(C−P) = 8.50, OMe), 139.25 (dd, J(C−P) = 18.30, J(C−P) = 7.60, C_4 or C_5), 139.90 (dd, ^2J(C−P) = 27.50, ^2J(C−P) = 13.70, C_3), 145.15 (d, J(C−P) = 13.80, C_5 or C_4), 156.60 (dd, ^1J(C−P) = 55.05, ^3J(C−P) = 4.70, C_6), 168.90 (dd, ^1J(C−P) = 68.85, ^1J(C−P) = 35.20, C_2); mass spectrum *m/z* (ion, relative intensity) 216 (M, 60), 201 (M − Me, 50), 196 (M − 2 Me, 30), 93 ($P(OMe)_2^+$, 100). Anal. Calcd for $C_9H_{14}O_2P_2$: C, 50.01; H, 6.53. Found: C, 49.75; H, 6.54.

2-(Bis(butylthio)phosphino)-4,5-dimethylphosphinine (12). A solution of phosphinine **3** (3.14 g, 10 mmol) was added dropwise at 0 °C to a mixture of *n*-butanethiol (1.8 g, 20 mmol) and triethylamine (5.05 g, 50 mmol) in 5 mL of THF. After 5 min of stirring, the reaction mixture was warmed to room temperature and stirred for an additional 10 min. After evaporation of solvents and excess triethylamine, 50 mL of dry and deoxygenated hexane was added and the resulting solution was filtered under a nirrogen atmosphere. The same extraction was repeated with 50 mL of hexane. Phosphinine **12** was recovered as an oxygen-sensitive yellow oil after evaporation of hexane. Yield: 3.0 g (90%).

12: ^{31}P NMR ($CDCl_3$) δ 201.20 (d, ^2J(P−P) = 104.55, P of C_7H_8P), 80.60 (d, P of $P(SBu)_2$); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 6H, ^3J(H−H) = 7.30, Me of Bu), 1.42 (dq, 4H, ^3J(H−H) = 7.30, CH_2 of Bu), 1.68 (dt, 4H, ^3J(H−H) = 7.30, CH_2 of Bu), 2.37 (d, 3H, J(H−P) = 3.88, Me of C_7H_8P), 2.40 (s, 3H, Me of C_7H_8P), 2.60−3.00 (m, 4H, CH_2−S), 8.09 (dd, 1H, ^3J(H−P) = 12.27, ^3J(H−P) = 6.07, H_3), 8.46 (dd, 1H, ^2J(H−P) = 39.76, ^4J(H−P) = 3.96, H_6); ^{13}C NMR ($CDCl_3$) δ 14.25 (s, Me of Bu), 22.40 (s, CH_2 of Bu), 23.00 (s, Me of C_7H_8P), 23.85 (d, J(C−P) 3.60, Me of C_7H_8P), 33.00 (d, ^3J(C−P) = 18.20, CH_2 of Bu), 33.80 (d, ^2J(C−P) = 4.45, CH_2−S), 139.30 (dd, J(C−P) = 18.25, J(C−P) = 7.50, C_4 or C_5), 140.40 (dd, ^2J(C−P) = 24.50, ^2J(C−P) = 12.40, C_3), 144.40 (d, J(C−P) = 14.10, C_4 or C_5), 155.50 (dd, ^1J(C−P) = 46.50, ^3J(C−P) = 7.70, C_6), 165.50 (dd, ^1J(C−P) = 65.10, ^1J(C−P) = 39.20, C_2); mass spectrum *m/z* (ion, relative intensity) 332 (M, 45), 275 (M − Bu, 25), 219 (M − 2 Bu + 1, 50). **12** was too moisture sensitive to give satisfactory microanalytical data.

2-(Bis(diethylamino)phosphino)-4,5-dimethylphosphinine (13). Diethylamine (2.77 g, 38 mmol) in 10 mL of THF was added dropwise at −20 °C to a solution of phosphinine **3** (2 g, 6.36 mmol) in 2 mL of THF. At the end of the addition, the reaction mixture was stirred at −20 °C for an additional 20 min and then slowly warmed to room temperature. After evaporation of THF and excess amine, 30 mL of dry and deoxygenated hexane was added and the solution was filtered under a nitrogen atmosphere. The same extraction was repeated twice. Phosphinine **13** was recovered as a yellow oxygen-sensitive oil after evaporation of hexane. Yield: 1.61 g (85%).

13: ^{31}P NMR ($CDCl_3$) δ 204.60 (d, ^2J(P−P) = 85.65, P of C_7H_8P), 100.40 (d, $P(NEt_2)_2$); ^{1}H NMR ($CDCl_3$) δ 1.20 (t, 3H, ^3J(H−H) = 7.07, Me of Et), 2.17 (s, 3H, Me), 2.18 (d, 3H, J(H−P) = 3.75, Me), 3.22 (m, 4H, CH_2), 7.94 (dd, 1H, ^3J(H−P) = 6.68, ^3J(H−P) = 9.90, H_3), 8.53 (dd, 1H, ^2J(H−P) = 39.90 ^4J(H−P) = 4.15, H_6); ^{13}C NMR ($CDCl_3$) δ 14.90 (s, Me of Et), 22.50 (s, Me of C_7H_8P), 22.96 (d, J(C−P) = 2.85, Me of C_7H_8P), 43.05 (d, ^2J(C−P) = 16.35, CH_2), 138.30 (dd, J(C−P) = 18.30, J(C−P) = 3.05, C_4 or C_5), 139.0 (dd, J(C−P) = 18.25, J(C−P) = 18.30, C_3), 141.45 (d, J(C−P) = 3.05, C_5 or C_4), 156.50 (dd, ^1J(C−P) = 54.90, ^3J(C−P) = 2.80, C_6), 171.70 (dd, ^1J(C−P) = 65.90, ^1J(C−P) = 13.85, C_2); mass spectrum *m/z* (ion, relative intensity) 298 (M, 30), 226 (M − NEt_2 − Et, 90). **13** was too moisture sensitive to give satisfactory microanalytical data.

Phosphinophosphinine 14. A solution of phosphinine **3** (6.28 g, 20 mmol) in 100 mL of THF was added dropwise at 0 °C to a suspension of $LiAlH_4$ (0.88 g, 23 mmol) in 200 mL of ether. At the end of the addition, the reaction mixture was warmed to room temperature and then stirred for 10 min. Then, excess hydride was destroyed by addition of 1.6 mL of water. Finally, the resulting yellow solution was then stirred with $MgSO_4$. After filtration under nitrogen and evaporation of solvents, a yellow viscous oil which contains phosphinine **14** and salts was obtained. Dry and deoxygenated hexane (250 mL) was then added, and the solution was filtered under nitrogen. After evaporation of hexane, **14** was recovered as a yellow oxygen-sensitive oil. Yield: 2.65 g (85%).

14: ^{31}P NMR (C_6D_6) δ 209.30 (d, ^2J(P−P) = 57.30, P of C_7H_8P), −116.25 (d, PH_2); ^{1}H NMR (C_6D_6) δ 1.84 (d, 3H, J(H−P) = 3.64, Me), 1.91 (s, 3H, Me), 4.27 (d, 2H, ^1J(H−P) = 196.70, PH_2), 7.66 (dd, 1H, ^3J(H−P) = 12.27, ^3J(H−P) = 7.06, H_3), 8.16 (dd, 1H, ^2J(H−P) = 37.35, ^4J(H−P) = 1.93, H_6); ^{13}C NMR (C_6D_6) δ 22.55 (s, Me), 23.55 (s, Me), 139.65 (dd, J(C−P) = 19.00, J(C−P) = 8.55, C_4 or C_5), 142.50 (C_4 or C_5 masked by C_3), 143.60 (dd, ^2J(C−P) = 26.05, ^2J(C−P) = 14.00, C_3), 154.40 (dd, ^1J(C−P) = 64.55, ^1J(C−P) = 15.25, C_2), 157.05 (dd, ^1J(C−P) = 55.75, ^3J(C−P) = 3.70, C_6); mass spectrum *m/z* (ion, relative intensity) 156 (M, 100), 123 (M − PH_2, 41). **14** was too moisture sensitive to give satisfactory microanalytical data.

2-(Lithiophosphino)-4,5-dimethylphosphinine (15) and 2-(Butylphosphino)-4,5-dimethylphosphinine (16). A solution of phenyllithium (10 mL, molar solution in ether) was added dropwise at −80 °C to a solution of phosphinine **14** (1.56 g, 10 mmol) in 30 mL of THF. The resulting red solution was then stirred at −80 °C for 10 min and slowly warmed to room temperature. A ^{31}P NMR control unequivocally indicated the formation of the anion **15**. The reaction with butyl iodide (1.87 g, 10 mmol) was carried out, dropwise, at −80 °C. When the addition was complete, the reaction mixture was slowly warmed to room temperature before the evaporation of solvents. The viscous red oil obtained was partially dissolved in 50 mL of hexane, and the resulting solution was filtered under nitrogen. After evaporation of hexane, phosphinine **16** was recovered as an orange, oxygen-sensitive oil. Yield: 1.38 g (70%).

15: ^{31}P NMR (THF) δ 170.95 (d, ^2J(P−P) = 52.00, P of C_7H_8P), −68.0 (ddd, ^1J(P−H) = 162.10, ^2J(P−P) = 52.0, ^3J(P−H_3) = 9.50, PHLi).

16: ^{31}P NMR (C_6D_6) δ 206.55 (d, ^2J(P−P) = 47.70, P of C_7H_8P), −45.95 (d, P−H); ^{1}H NMR (C_6D_6) δ 0.90−2.00 (m, 9H, butyl), 2.10 (d, 3H, J(H−P) = 3.54, Me of C_7H_8P), 2.13 (s, 3H, Me of C_7H_8P), 4.77 (ddt, 1H, ^1J(H−P) = 206.52, ^3J(H−P) = 15.66, ^3J(H−H) = 6.75, P−H), 8.00 (dd, 1H, ^3J(H−P) = 11.80, ^3J(H−P) = 7.35, H_3), 8.45 (d, 1H, ^2J(H−P) = 37.05, H_6); ^{13}C NMR (C_6D_6) δ 14.55 (s, Me of C_4H_9), 22.80 (s, Me of C_7H_8P), 23.75 (s, Me of C_7H_8P), 24.85 (d, J(C−P) = 8.55, CH_2), 26.75 (dd, ^1J(C−P) = 12.35, ^3J(C−P) = 8.85, CH_2−P), 31.00 (d, J(C−P) = 7.70, CH_2), 139.40 (dd, J(C−P) = 18.55, J(C−P) = 9.20, C_4 or C_5), 143.00 (m, C_3), 143.60 (m, C_4 or C_5 masked by C_3), 157.10 (dd, ^1J(C−P) = 55.85, ^3J(C−P) = 9.60, C_6), 163.30 (dd, ^1J(C−P) = 66.70, ^1J(C−P) = 19.40, C_2); mass spectrum *m/z* (ion, relative intensity) ICP − NH_3, 229 (M + 16, 9), 214 (M + 2, 13), 213 (M + 1, 100). **16** was too moisture sensitive to give satisfactory microanalytical data.

2-(2,3-Diphenylphosphirenyl)-4,5-dimethylphosphinine (17). Aluminum chloride (1.74 g, 12.72 mmol) was added at −20 °C to a solution of phosphinine **3** (4 g, 12.72 mmol) in 100 mL of CH_2Cl_2. The resulting orange solution was stirred at −20 °C for 20 min. A solution of tolane (2.40 g, 12.72 mmol) in 40 mL of CH_2Cl_2 was then added dropwise (at this stage an elevation of the temperature must be avoided). The resulting solution was then transferred via a cannula to a solution of Bu_3P (3.34 g, 16.52 mmol, 1.3 equiv) in 60 mL of CH_2Cl_2 at −20 °C and stirred for 10 min. After warming to room temperature, the CH_2Cl_2 was evaporated and 60 mL of a mixture of hexane and toluene (60:40) was added. The solution which contains phosphinine **17** and traces of tolane was then filtered under nitrogen. After evaporation of solvents, the yellow residue obtained was dissolved in 30 mL of CH_2Cl_2 and 6 g of Celite was added. The resulting coated Celite which was obtained after evaporation was then loaded onto the top

of a silica gel packed flash column for chromatography. The first fraction eluted with hexane yielded traces of tolane. A second fraction eluted with a mixture of hexane and CH_2Cl_2 (60:40) yielded phosphinine **17** as a yellow solid after evaporation of solvents. Yield: 2.32 g (55%).

17: mp 70 °C; ^{31}P NMR (C_6D_6) δ −178.10 (d, ^2J(P−P) = 84.45, P of $C_{14}H_{10}P$), 205.30 (d, P of C_7H_8P); ^{1}H NMR (C_6D_6) δ 1.88 (d, 3H, J(H−P) = 3.56, Me), 1.91 (s, 3H, Me), 7.0−7.15 (m, 6H, CH of C_6H_5), 7.95−8.00 (m, 4H, CH of C_6H_5), 8.10 (dd, 1H, ^3J(H−P) = 11.70, ^3J(H−P) = 7.20, H_3), 8.23 (d, 1H, ^2J(H−P) = 36.09, H_6); ^{13}C NMR (C_6D_6) δ 22.70 (s, Me), 23.65 (s, Me), 125.45 (dd, ^1J(C−P) = 45.55, ^3J(C−P) = 6.40, =C−P of $C_{14}H_{10}P$), 129.80−130.10 (m, C_q and CH of C_6H_5), 131.75 (s, CH of C_6H_5), 139.0 (dd, J(C−P) = 18.90, J(C−P) = 6.90, C_4 or C_5), 140.70 (dd, ^2J(C−P) = 29.0, ^2J(C−P) = 13.45, C_3), 144.20 (d, J(C−P) = 14.95, C_5 or C_4), 156.50 (dd, ^1J(C−P) = 56.52, ^3J(C−P) = 6.85, C_6), 173.0 (dd, ^1J(C−P) = 72.90, ^1J(C−P) = 67.30, C_2); mass spectrum *m*/*z* (ion, relative intensity) 332 (M, 100). Anal. Calcd for $C_{21}H_{18}P_2$: C, 75.90; H, 5.46. Found: C, 75.60; H, 5.45.

1,2-Bis(2-(4,5-dimethylphosphininyl))-3,4-diphenyl-1,2-dihydro-1,2-diphosphete (18). Dibromophosphinine **3** (2.07 g, 6.62 mmol) was added to a solution of phosphinine **17** (2 g, 6.62 mmol) in 30 mL of CH_2Cl_2 at −20 °C. The yellow solution obtained was then stirred for 10 min at −20 °C before warming to room temperature. Tributylphosphine was used as reducing agent. The solution of adduct was slowly added via a cannula to a solution of Bu_3P (1.74 g, 8.61 mmol, 1.3 equiv) in CH_2Cl_2 at −20 °C. After 10 min of stirring the reaction mixture was warmed to room temperature and the solvents were evaporated. A yellow oil which contains phosphinine **18**, $Bu_3P^+Br^-$ and $Bu_3P{\cdot}HBr$ was obtained. Phosphinine **18** was extracted with a mixture of hexane and toluene (60:40) (3 × 30 mL). After evaporation of solvents, phosphinine **18** was purified by chromatography on silica gel. The first fraction eluted with hexane allowed the separation of small traces of phosphorus impurities. A second fraction eluted with a mixture of hexane and CH_2Cl_2 (1:1) yielded phosphinine **18**, which was recovered as a yellow solid after evaporation of solvents. Yield: 2.41 g (75%).

18: mp 210 °C; ^{31}P NMR ($CDCl_3$) δ 214.30 (AA′XX′, $\sum J$(P−P) = 128.60, P of C_7H_8P), −21.50 (AA′XX′, P of diphosphete); ^{1}H NMR ($CDCl_3$) δ 1.74−1.76 (m, 12H, Me), 6.90−7.05 (m, 6H, CH of C_6H_5), 7.76−7.80 (m, 4H, CH of C_6H_5), 8.03−8.22 (m, 4H, $H_{3,3'}$ and $H_{6,6'}$); ^{13}C NMR ($CDCl_3$) δ 21.70 (s, Me), 22.80 (s, Me), 127.30−128.50 (m, CH of C_6H_5), 136.20 (pt, $\sum J$(C−P) = 16.10, C_q of C_6H_5), 138.45 (dt, $\sum J$(C−P) = 25.35, C_4 or C_5), 142.70 (m, $\sum J$(C−P) = 43.65, C_3), 143.95 (pd, $\sum J$(C−P) = 15.05, C_4 or C_5), 147.80 (dt, $\sum J$(C−P) = 26.72, =C−P), 156.15 (dt, $\sum J$(C−P) = 64.65, C_6), 161.05 (dq, $\sum J$(C−P) = 112.95, C_2); mass spectrum *m*/*z* (ion, relative intensity) 486 (M, 85), 209 ($Ph_2C_2P^+$, 100). Anal. Calcd for $C_{28}H_{26}P_4$: C, 69.14; H, 5.39. Found: C, 69.05; H, 5.35.

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