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Combining the chemistry of phospholes and phosphinines†

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Summary – Lithium 3,4-dimethylphospholide reacts (generally in the presence of Pd(0) and Ni(0) catalysts) with 2-bromo and 2,6-dibromophosphinines to give the corresponding 2-(3,4-dimethylphospholyl)- and 2,6-bis(3,4-dimethylphospholyl)phosphinines (**2**, **4**, **7**, **8**). When heating these phospholylphosphinines at *ca* 160 °C, the phosphinine ring migrates around the phosphole ring to give transient 5-(2-phosphininyl)-2*H*-phospholes which can be trapped as [4+2] cycloadducts by diphenylacetylene. The resulting phosphinine substituted 1-phosphanorbornadienes (**14–17**) can act as chelating ligands towards transition metals (Cr(0), Mo(0), W(0)). Prolonged heating at 180 °C of 2-(3,4-dimethylphospholyl)-4,5-dimethylphosphinine (**4**) affords the corresponding phosphinine-phospholyl-phospholyl-phosphinine chain as its P-P bonded dimer (**22**). The corresponding 2,2′-biphospholide dianion (**23**) can be prepared from **22** by cleavage of the two P-P bonds by Na-naphthalene in THF. Reaction of **23** with methyl iodide yields a phosphinine-phosphole-phosphole-phosphinine unit (**24**).

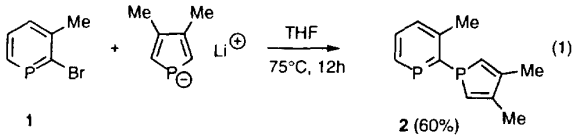
phosphorus-carbon heterocycle / phosphole / phosphinine / phosphanorbornadiene / palladium(0) catalyst / nickel(0) catalyst / cross-coupling reaction

Introduction

Like pyrroles and pyridines for nitrogen heterocycles, phospholes and phosphinines constitute the two most fundamental species of phosphorus heterocyclic chemistry. Structures associating pyrroles and pyridines are numerous as exemplified by some recently described pyridine-modified porphyrins [1]. On the contrary, molecules associating phospholes and phosphinines are unknown, and, in view of their potential in coordination chemistry and homogeneous catalysis, we felt it quite interesting to investigate their synthesis and their reactivity. This is the main subject of this report.

Results and discussion

In a preceding work [2] we have shown that 2-bromophosphinines are better substrates for nucleophilic substitution reaction than bromoarenes. However, the outcome of any nucleophilic attack onto a bromophosphinine is always difficult to predict because of the competition between the reaction at the C-Br bond and the reaction at the electrophilic phosphorus atom [3]. Anyhow, it seemed logical to start our investigations by the direct reaction of phospholide ions with 2-bromophosphinines. The results were surprisingly positive and we observed a reaction at the C-Br bond, which leads to the 2-(phospholyl)phosphinine (eq 1).



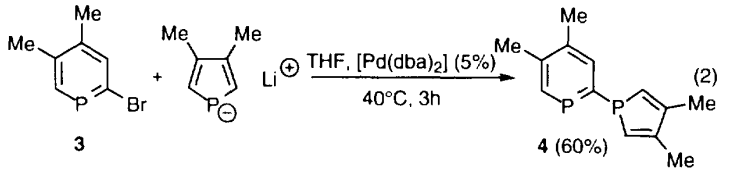
1 2 (60%) (1)

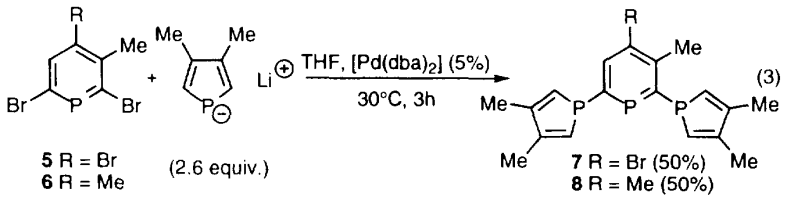
The 2-(phospholyl)phosphinine **2** displays a highly characteristic ^{31}P NMR spectrum ($CDCl_3$): AX system: δ_A +214.30, δ_X +0.6 ppm, ^2J (P_A-P_X) = 32.20 Hz. As already noted for 2-diphenylphosphino-3-methylphosphinine [4], the low value of the ^2J (P-P) coupling constant is a consequence of the 3-methyl substitution on the phosphinine ring. It must be recalled here that 3-methyl substitution activates the C_2-Br bond of **1** via a through-space destabilizing interaction [5]. Thus it was not surprising to find that the less reactive 2-bromo-4,5-dimethylphosphinine **3** gives less satisfactory results with lithium 3,4-dimethylphospholide. From a mechanistic standpoint, it is clear that the electronic delocalization within the phospholide ions permits this SnAr reaction by lowering their electron transfer ability. Indeed, in further experiments with other phosphides such as $LiPPh_2$, we mainly observed a redox process which leads to the corresponding 2,2′-biphosphinines.

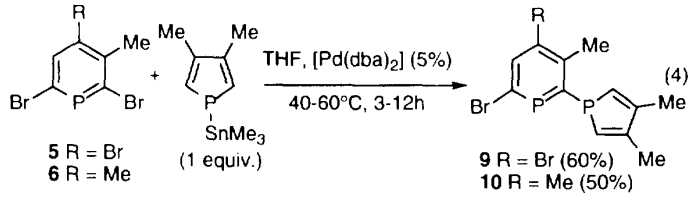
The direct SnAr reaction was not sufficiently general, and so we decided to investigate some transition metal-catalyzed cross-coupling reactions. We found that the addition of a palladium(0) catalyst to the bromophos-

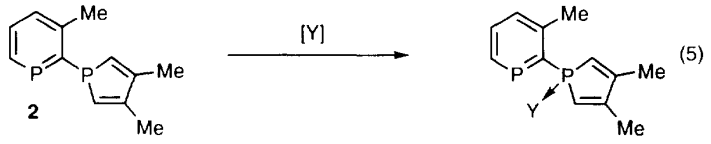
† Dedicated to prof Dr Marianne Baudler as a tribute to an outstanding phosphorus chemist.

* Correspondence and reprints









Y = $W(CO)_5$, THF, RT, 3h **11**
Y = $1/8S_8$, toluene, 70°C, 2h **12**

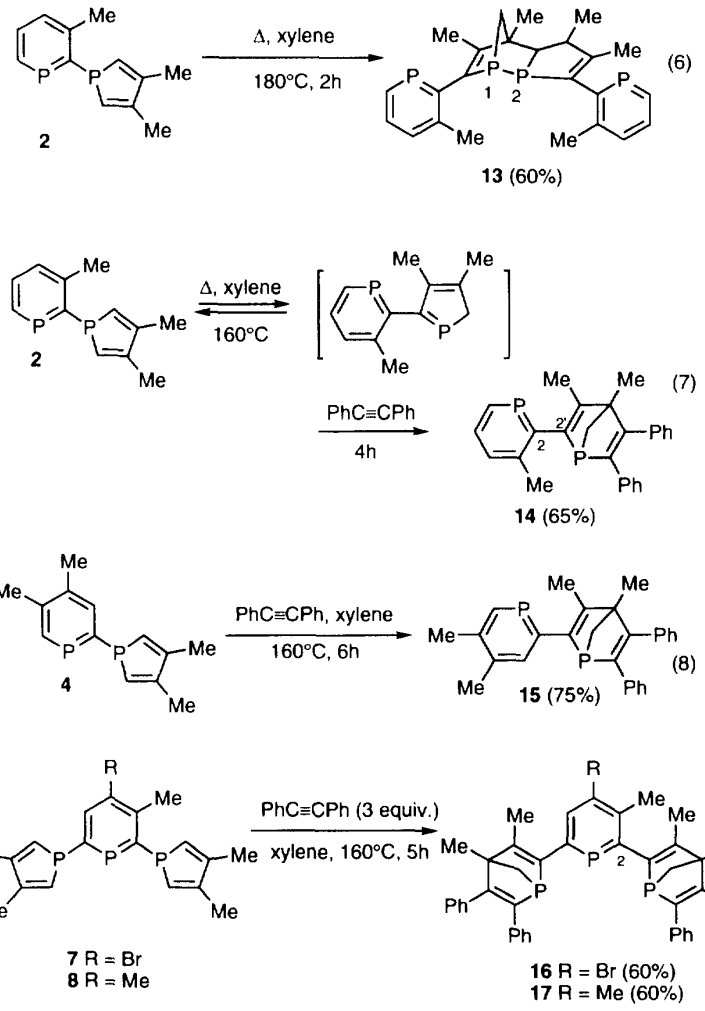
phinine and lithium phospholide reaction mixture induces a drastic improvement. The transformation of **1** into **2** takes place at 40 °C within 2 h using 5% of $Pd(dba)_2$ (dba = dibenzylideneacetone) as a catalyst. The final yield is identical with and without catalyst (60%). More significantly, this cross-coupling procedure can be efficiently transposed to 2-bromophosphinine **3** (eq 2) and to 2,6-dibromophosphinines **5** and **6** (eq 3).

As expected, the disappearance of the 3-methyl substitution in **4** leads to a sharp increase of the ^2J (P-P) coupling constant up to 81.60 Hz from 32.20 in **2**. This phenomenon allows us to easily ascribe the two phospholyl resonances of phosphinines **7** and **8**. Further investigations led to the discovery that $[Ni(dppe)Cl_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane) was even more active than $[Pd(dba)_2]$ as a catalyst. Phospholylphosphinines **2**, **4** and **8** were obtained in 75%, 75% and 60% yields respectively after 6 h (**2** and **4**) and 1 h (**8**) at room temperature. These cross-coupling reactions with nickel and palladium catalysts are so efficient that it is impossible to prevent the formation of **7** and **8** during the synthesis of the monophospholyl products **9** and **10** from 2,6-dibromophosphinines **5** and **6**. The use of the less reactive 1-trimethylstannylphosphole [6] allowed us to circumvent this limitation. As we demonstrated in a preceding work [5], the reaction takes place exclusively at the C_2 position (eq 4).

In all the phospholylphosphinines thus prepared, the lone pair of the phosphole unit is far more reactive than that of the phosphinine. As an example, **2** is easily complexed and sulfurized at the phospholyl phosphorus (eq 5).

However, by far the most interesting and characteristic property of phospholes concerns the 1H ↔ 2H phosphole interconversion via the concerted [1, 5] shift of the phosphorus substituent. As shown by experimental [7] and theoretical work [8], this shift is possible because the two species lie close in energy. When heterocyclic substituents are used, the connected position of the heterocycle is not modified as demonstrated with thienyl groups [9]. All these data led us to examine whether the phosphinine ring could play the role of the shifting substituent in this 1H ↔ 2H phosphole interconversion. As expected, we observed this shift and the simple heating of phosphinine **2** leads to the [4+2] 2*H*-phosphole dimer **13** (eq 6).

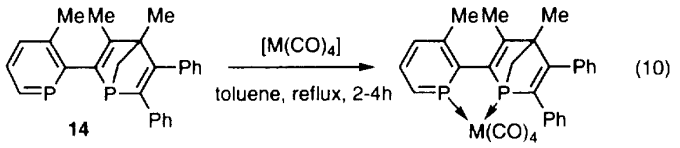
As shown by the ^{31}P NMR spectrum of **13**, the structure of this dimer is very similar to that obtained upon heating 1-phenyl-3,4-dimethylphosphole at 150 °C in the presence of $FeCl_2$ as a catalyst [10]. The presence of the P-P bond is demonstrated by the existence of a huge ^1J (P_1-P_2) coupling constant between the two upfield phosphorus resonances (221.0 Hz) and the connection of the phosphinines nucleus via their α-position



is confirmed by the presence of sizeable ^3J (P-P) couplings (51.75 and 34.90 Hz) between the sp^2 and sp^3 phosphorus resonances. The *exo* junction is likely since *endo* [4+2] phosphole dimers are known to rearrange to their *exo* isomers upon heating [7a]. Another interesting aspect of the reactivity of 2*H*-phospholes is their reaction with acetylenic derivatives which leads to 1-phosphanorbornadienes. We found that this [4+2] cycloaddition chemistry can be extended to the intermediate 2*H*-phospholyl-phosphinine. A number of new bi- and tridentate ligands with a phosphinine nucleus as sub-unit have thus been easily prepared in good yields (eqs 7–9).

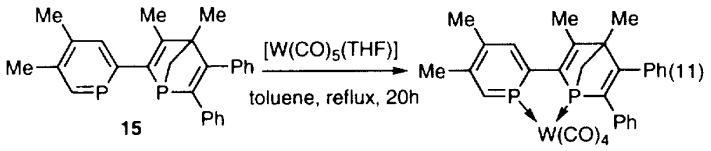
Whereas the ^{31}P NMR spectrum of **15** displays a well-resolved AX system (δ_A +183.60 ppm, δ_X −4.90 ppm, ^3J (P_A-P_X) = 33.40 Hz), the spectrum of **14** appears as 2 × 2 broad resonances *ca* +198.0 and −5.0 ppm at room temperature. At low temperature (−43 °C), it is resolved into two AX systems, mainly differing by their ^3J (P-P) coupling constants: δ_{A1} +199.10 ppm, δ_{X1} −4.20 ppm with ^3J (P_{A1}-P_{X1}) = 17.40 Hz and δ_{A2} +197.10 ppm, δ_{X2} −6.20 ppm with ^3J (P_{A2}-P_{X2}) = 14.10 Hz. We interpret this result as meaning that **14** is a mixture of two atropoisomers due to a restricted rotation around the C_2-$C_{2'}$ bridge. At room temperature, the mixture starts to equilibrate because the steric hindrance of the methyl substituents at C_3,$C_{3'}$ is not large enough to completely block the rotation. In line with our explanation, this mixture gives a series of $M(CO)_4$ chelates complexes (M = Cr, Mo, W, see below) as well-defined single products. The case of **16** and **17** is even more complicated since these compounds are mixtures of diastereomers (due to the two 1-phosphanorbornadiene units) and atropoisomers (due to the restricted rotation around the C_2-substituent axis). The use of 1-phosphanorbornadienes (1-phosphabicyclo[2.2.1]hepta-2,5-diene) in homogeneous catalysis is currently receiving increasing attention [11]. Ligands such as **14** and **15**, which associate a strong π-acceptor (the phosphinine) and a strong σ-donor (the phosphanorbornadiene), may be of some interest in this respect, provided that they can give stable chelates (eqs 10 and 11). The development of interesting coordination chemistry might be possible.

The possible synthesis of phosphole tetramers by thermolysis of 1-aryl-3,4-dimethylphospholes under rather drastic conditions [9, 12] constitutes another im-

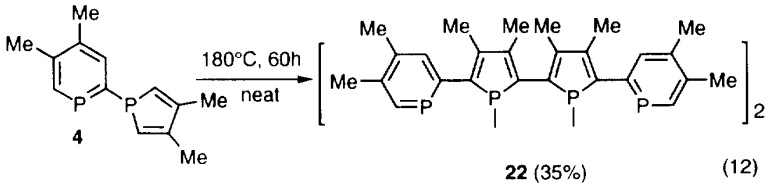


(10)

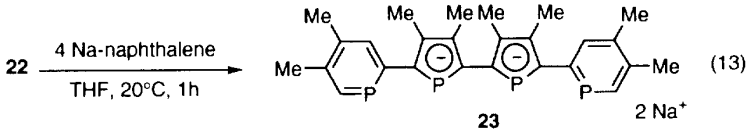
18 M = Cr (75%)
19 M = Mo (65%)
20 M = W (70%)



21 (70%)



22 (35%) (12)



(13)

portant feature of phosphole chemistry. A transposition of this reaction to 2-phospholylphosphinines would afford the very interesting α-connected phosphinine-phospholyl-phospholyl-phosphinine tetraphosphorus chain. We thus performed the thermolysis of **4** and got the expected tetramer structure **22** in a 35% yield (eq 12).

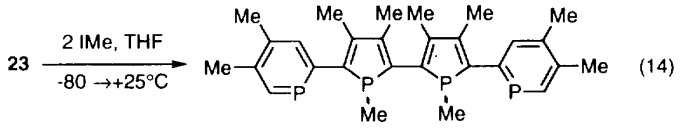
Surprisingly, in view of the known propensity of phosphinines to give stable radical anions [13], the cleavage of the two P-P bonds of **22** can be easily achieved by a stoichiometric amount of sodium naphthalenide in THF at room temperature (eq 13).

The dianion **23** displays a highly characteristic AA'XX' ^{31}P NMR spectrum: δP_A +174.60 ppm (phosphinine), δP_X +64.90 ppm (phospholide) with ^3J (P_A-P_X) = 55.0 Hz, ^6J (P_A-$P_{X'}$) = 1.0 Hz, ^3J (P_X-$P_{X'}$) = 72.0 Hz, ^9J (P_A-$P_{A'}$) = 0 Hz. All these values fall in the normal ranges. The dianion **23** has been identified further by reaction with methyl iodide (eq 14). The biphosphole **24** is obtained as a 90:10 mixture of two diastereomers. It has also been characterized as its *P,P'*-bis-sulfide **25** (eq 15).

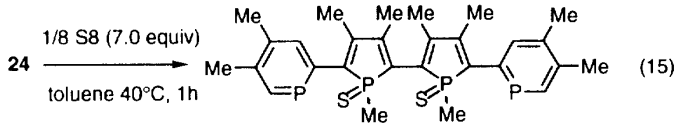
From all these experiments, it clearly appears that the phosphinine ring can replace an aryl substituent in any phosphole reaction primilary based on an aryl [1,5] P to C_α sigmatropic shift. A wide range of new ligands possessing both a normal P σ-donor and a phosphinine π-acceptor unit can thus be created. Their coordination chemistry will be investigated in due course.

Experimental section

Reactions were performed under nitrogen using oven-dried glassware. Dry tetrahydrofuran and toluene were obtained by distillation from Na/benzophenone, and dry hexane was obtained from P_2O_5. Silica gel (70-230 mesh) was used for chromatographic separations after drying overnight under vacuum (120 °C). Nuclear magnetic resonance spectra were obtained on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^1H, 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 (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P), and data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, b = broad), integration, and coupling constants in hertz. Mass spectra were obtained at 70 eV on a Shimadzu GC-MS QP 1000 spectrometer by the direct inlet method. Plasma desorption mass spectra of tetramer **22** was performed on a Depil-X time of flight mass built at the IPN (Institut de physique nucléaire at Paris XI Orsay University). 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: lithium-3,4-dimethylphospholide [14], $Pd(dba)_2$ [15], and $(dppe)NiCl_2$ [16].



24 (80% from **22**)



25 (80%)

2-(3,4-Dimethyl-1-phospholyl)-3-methylphosphinine **2**

A solution of lithium 3,4-dimethylphospholide (60 mmol) in 50 mL THF was added at room temperature to a solution of 2-bromophosphinine **1** (9.45 g, 50 mmol) in 50 mL THF. The catalyst (dppe)$NiCl_2$ (1 g, 2 mmol, 4% per mol of **1**) was then added and the mixture was stirred at room temperature for 6 h. After this period a ^{31}P NMR control indicated the quantitative conversion of **1**. Celite (10 g) was then added to the mixture and the solvent was evaporated *in vacuo*. The resulting coated celite was then loaded onto the top of a silica-gel-packed flash column for chromatography and phosphinine **2** was eluted with hexane/CH_2Cl_2 (95:5) as eluent. After evaporation of solvents, **2** was recovered as a colorless oxygen-sensitive oil. Yield 8.25 g (75%).

^{31}P NMR ($CDCl_3$): δ 214.30 (d, ^2J (P-P) = 32.25, P of C_6H_6P), 0.60 (d, P of C_6H_8P).

^1H NMR ($CDCl_3$): δ 2.27 (d, 6H, ^4J (H-P) = 3.23, Me of C_6H_8P), 2.88 (d, 3H, ^4J (H-P) = 2.05, Me of C_6H_6P), 6.81 (dd, 2H, ^2J (H-P) = 36.87, ^4J (H-P) = 0.77, =CH of C_6H_8P), 7.43 (dd, 1H, ^4J (H-P) = 3.77, ^3J (H-H) = 8.22, H_4), 7.74 (dt, 1H, ^3J (H-H) = 9.97, ^3J (H-H) = 8.22, ^3J (H-P) = 8.22, H_5), 8.60 (dd, 1H, ^2J (H-P) = 38.81, ^3J (H-H) = 9.97, H_6).

^{13}C NMR ($CDCl_3$): δ 18.55 (d, ^3J (C-P) = 4.40, Me of C_6H_8P), 25.15 (d, ^3J (C-P) = 21.3, Me of C_6H_6P), 127.80 (d, ^3J (C-P) = 13.80, C_4), 132.0 (dd, ^1J (C-P) = 19.0, ^3J (C-P) = 4.35, =CH of C_6H_8P), 134.20 (dd, ^3J (C-P) = 12.30, C_5), 146.90 (dd, ^2J (C-P) = 19.70, ^3J (C-P) = 13.60, C_3), 148.90 (d, ^2J (C-P) = 9.25, =C- of C_6H_8P), 154.20 (d, ^1J (C-P) = 57.90, C_6), 162.70 (dd, ^1J (C-P) = 73.45, ^2J (C-P) = 21.65, C_2).

Mass spectrum *m/z* (relative intensity): 220 (M, 100).

2-(3,4-Dimethyl-1-phospholyl)-4,5-dimethylphosphinine **4**

The experimental procedure was the same as for the preparation of **2**. Lithium 3,4-dimethylphospholide (60 mmol) was reacted with 2-bromophosphinine **3** (10 g, 50 mmol) and (dppe)$NiCl_2$ (1 g, 2 mmol, 4% per mol of **3**) in 100 mL THF. After 6 h stirring at room temperature, celite (10 g) was added and the mixture was evaporated. Phosphinine **4** was recovered as a white solid after a chromatography with hexane/CH_2Cl_2 (95:5) as eluent. Yield 8.80 g (75%).

Mp: 70 °C.

^{31}P NMR ($CDCl_3$): δ 202.70 (d, ^2J (P-P) = 81.65, P of C_7H_8P), 2.90 (d, P of C_6H_8P).

^1H NMR ($CDCl_3$): δ 2.14 (d, 6H, ^4J (H-P) = 3.10, Me of C_6H_8P), 2.35 (d, 3H, ^4J (H-P) = 3.54, Me of C_7H_8P), 2.38 (s, 3H, Me of C_7H_8P), 6.57 (d, 2H, ^2J (H-P) = 38.31, =CH of C_6H_8P), 7.80 (dd, 1H, ^3J (H-P) = 13.45, ^3J (H-P) = 7.04, H_3), 8.40 (dd, 1H, ^2J (H-P) = 37.45, ^4J (H-P) = 3.01, H_6).

^{13}C NMR ($CDCl_3$): δ 18.40 (d, ^3J (C-P) = 3.30, Me of C_6H_8P), 22.90 (s, Me of C_7H_8P), 23.90 (d, J (C-P) = 2.40, Me of C_7H_8P), 130.65 (dd, ^1J (C-P) = 18.55, ^3J (C-P) = 1.90, =CH of C_6H_8P), 139.40 (dd, J (C-P) = 18.55, J (C-P) = 9.80, C_4 or C_5), 141.80 (dd, ^2J (C-P) = 23.75, ^2J (C-P) = 13.40, C_3), 143.95 (d, J (C-P) = 14.33, C_5 or C_4), 149.40 (d, ^2J (C-P) = 8.60, =C- of C_6H_8P), 156.80 (dd, ^1J (C-P) = 55.50, ^3J (C-P) = 8.0, C_6), 159.80 (dd, ^1J (C-P) = 63.80, ^1J (C-P) = 22.05, C_2).

Mass spectrum *m/z* (relative intensity): 234 (M, 100).

Anal calc for $C_{13}H_{16}P_2$: C, 66.67; H, 6.89. Found: C, 66.17; H, 6.84.

2,6-bis(3,4-Dimethyl-1-phospholyl)-3-methyl-4-bromophosphinine **7**

A solution of lithium 3,4-dimethylphospholide (37.50 mmol) in 25 mL THF was added to a solution of tribromophosphinine **5** (5 g, 14.4 mmol) in 50 mL THF. The catalyst $Pd(dba)_2$ (0.41 g, 0.72 mmol, 5% per mol of **5**) was then added and the mixture was heated at 30 °C for 3 h. Celite (3 g) was added and the solvent was evaporated leading a black residue which was deposited onto the top of a silica-gel-packed flash column for chromatography. A preliminary fraction eluted with hexane yielded traces of unreacted phosphinine **5**. A second fraction eluted with hexane/CH_2Cl_2 (4:1) as eluent afforded **7** as a white solid. Yield 2.95 g (50%).

Mp: 85 °C.

^{31}P NMR ($CDCl_3$): δ 217.95 (dd, ^2J ($P\text{-}P_B$) = 91.30, ^2J ($P\text{-}P_A$) = 32.30, P of C_6H_4PBr), 3.45 (d, P_A of C_6H_8P), 0.85 (d, P_B of C_6H_8P).

^1H NMR ($CDCl_3$): δ 2.13 (m, 12H, Me of C_6H_8P), 2.86 (d, 3H, ^4J (H-P) = 2.0, Me of C_6H_4PBr), 6.48 (d, 2H, ^2J (H-P) = 38.80, =CH of C_6H_8P), 6.59 (m, 2H, ^2J (H-P) = 37.97, =CH of C_6H_8P), 7.96 (dd, 1H, ^3J (H-P) = 11.74, ^3J (H-P) = 6.25, H_5).

^{13}C NMR ($CDCl_3$): δ 18.40 (d, ^3J (C-P) = 4.15, Me of C_6H_8P), 18.55 (d, ^3J (C-P) = 3.40, Me of C_6H_8P), 25.75 (d, ^3J (C-P) = 24.05, Me of C_6H_4PBr), 127.25 (d, ^1J (C-P) = 14.70, =CH of C_6H_8P), 129.50 (masked by the signal at 129.70, C_4), 129.70 (dd, ^1J (C-P) = 10.0, ^3J (C-P) = 3.16, =CH of C_6H_8P), 142.25 (dd, J (C-P) = 22.05, J (C-P) = 11.10, C_5), 145.20 (dd, ^2J (C-P) = 19.40, ^2J (C-P) = 13.10, C_3), 149.35 (d, ^2J (C-P) = 8.55, =C- of C_6H_8P), 149.90 (d, ^2J (C-P) =

9.50, =C- of C_6H_8P), 163.40 (dd, ^1J (C-P) = 74.15, ^1J (C-P) = 30.0, C_2 or C_6), 167.15 (ddd, ^1J (C-P) = 80.80, ^1J (C-P) = 26.40, ^3J (C-P) = 6.95, C_6 or C_2).

Mass spectrum m/z (relative intensity): 329 (M-Br, 100).

Anal calc for $C_{18}H_{20}P_3Br$: C, 52.84; H, 4.93. Found: C, 52.62; H, 4.91.

2,6-bis(3,4-Dimethyl-1-phospholyl)-3,4-dimethylphosphinine **8**

The experimental procedure was the same than for the synthesis of **7**. A solution of lithium 3,4-dimethylphospholide (46.30 mmol) in 25 mL THF was reacted with dibromophosphinine **6** (5 g, 17.8 mmol) and $Pd(dba)_2$ (0.51 g, 0.89 mmol, 5% per mol of **5**) in 50 mL THF. After 3 h of stirring at 30 °C, the mixture was purified by chromatography. Phosphinine **8** was eluted with hexane/CH_2Cl_2 (4:1) as eluent. **8** was recovered as a colorless solid. Yield 3.06 g (50%).

Mp: 75 °C.

^{31}P NMR ($CDCl_3$): δ 211.40 (dd, ^2J ($P\text{-}P_A$) = 91.65, ^2J ($P\text{-}P_B$) = 36.0, P of C_7H_7P), 1.55 (d, P_B of C_6H_8P), 1.40 (d, P_A of C_6H_8P).

^1H NMR ($CDCl_3$): δ 2.15 (m, 12H, Me of C_6H_8P), 2.37 (d, 3H, J (H-P) = 3.22, Me of C_7H_7P), 2.70 (d, 3H, J (H-P) = 1.61, Me of C_7H_7P), 6.53 (d, ^2J ($H\text{-}P_B$) = 38.33, =CH of $C_6H_8P_B$), 6.65 (ddq, 2H, ^2J (H-P) = 37.55, ^4J (H-P) = 1.79, ^4J (H-H) = 0.72, =CH of $C_6H_8P_A$), 7.64 (dd, 1H, ^3J (H-P) = 13.25, ^3J (H-P) = 6.60, H_5).

^{13}C NMR ($CDCl_3$): δ 18.40 (d, ^3J (C-P) = 4.10, Me of C_6H_8P), 18.55 (d, ^3J (C-P) = 4.20, Me of C_6H_8P), 21.45 (d, ^3J (C-P) = 25.80, C_3-*Me* of C_7H_7P), 23.90 (s, C_4-*Me* of C_7H_7P), 127.70 (d, ^1J (C-P) = 14.30, =CH of C_6H_8P), 130.05 (d, ^1J (C-P) = 11.30, =CH of C_6H_8P), 139.10 (ddd, ^3J (C-P) = 12.20, ^3J (C-P) = 8.95, ^3J (C-P) = 4.05, C_4), 140.90 (dd, ^2J (C-P) = 21.0, ^2J (C-P) = 11.45, C_5), 145.90 (dd, ^2J (C-P) = 18.25, ^2J (C-P) = 13.45, C_3), 148.75 (d, ^2J (C-P) = 9.90, =C- of C_6H_8P), 149.30 (d, ^2J (C-P) = 8.20, =C- of C_6H_8P), 161.45 (dd, ^1J (C-P) = 70.65, ^1J (C-P) = 24.90, C_2 or C_6), 164.70 (ddd, ^1J (C-P) = 78.20, ^1J (C-P) = 21.75, ^3J (C-P) = 7.60, C_6 or C_2).

Mass spectrum m/z (relative intensity): 344 (M, 75), 329 (M-Me, 5).

Anal calc for $C_{19}H_{23}P_3$: C, 66.28; H, 6.73. Found: C, 66.70; H, 6.50.

2,4-Dibromo-6-(3,4-dimethyl-1-phospholyl)-5-methylphosphinine **9**

1-Trimethylstannyl-3,4-dimethylphosphole (4.35 g, 15.84 mmol) was added to a solution of tribromophosphinine **5** (5 g, 14.4 mmol) and $Pd(dba)_2$ (0.41 g, 0.72 mmol, 5% per mol of **5**) in 50 mL THF. The resulting mixture was then heated at 40 °C for 12 h. After addition of celite (3 g) and evaporation of THF, the mixture was purified by chromatography. Phosphinine **9** was recovered as a colorless solid after elution with hexane/CH_2Cl_2 (4:1) as eluent and evaporation of solvents. Yield 3.26 g (60%).

^{31}P NMR ($CDCl_3$): δ 201.13 (d, ^2J (P-P) = 30.1, P of $C_6H_4PBr_2$), 1.87 (d, P of C_6H_8P).

^1H NMR ($CDCl_3$): δ 2.15 (d, 6H, ^4J (H-P) = 3.46, Me of C_6H_8P), 2.85 (d, 3H, ^4J (H-P) = 2.03, Me of $C_6H_4PBr_2$), 6.57 (dd, 2H, ^2J (H-P) = 38.25, ^4J (H-P) = 2.13, =CH of C_6H_8P), 8.19 (d, 1H, ^3J (H-P) = 4.27, H_3).

^{13}C NMR ($CDCl_3$): δ 18.60 (d, ^3J (C-P) = 3.50, Me of C_6H_8P), 25.35 (d, ^3J (C-P) = 24.25, Me of $C_6H_4PBr_2$), 127.30 (d, ^1J (C-P) = 14.90, =CH of C_6H_8P), 129.80 (dd, ^3J (C-P) = 18.1, ^3J (C-P) = 3.0, C_4), 141.80 (d, ^2J (C-P) = 12.60, C_3), 144.35 (dd, ^3J (C-P) = 19.90, ^2J (C-P) = 14.60, C_5), 150.40 (d, ^2J (C-P) = 8.90, =C- of C_6H_8P), 150.75 (d, ^1J (C-P) = 78.70, C_2), 169.05 (dd, ^1J (C-P) = 77.55, ^1J (C-P) = 28.50, C_6).

Anal calc for $C_{12}H_{12}P_2Br_2$: C, 38.13; H, 3.20. Found: C, 37.91; H, 3.43.

2-Bromo-6-(3,4-dimethyl-1-phospholyl)-4,5-dimethylphosphinine **10**

The experimental procedure was the same as for the synthesis of **9**. 1-Trimethylstannyl-3,4-dimethylphosphole (5.38 g, 19.58 mmol) was added to a solution of dibromophosphinine **6** (5 g, 17.8 mmol) and $Pd(dba)_2$ (0.51 g, 0.89 mmol, 5% per mol of **6**) in 50 mL THF. The resulting mixture was then heated at 60 °C for 3 h. After addition of celite (3 g) and evaporation of THF, the mixture was purified by chromatography. Phosphinine **10** was recovered as a colorless solid after elution with hexane as eluent and evaporation. Yield 2.77 g (50%).

Mp: 140 °C.

^{31}P NMR ($CDCl_3$): δ 193.60 (d, ^2J (P-P) = 31.70, P of C_7H_7PBr), −0.50 (d, P of C_6H_8P).

^1H NMR ($CDCl_3$): δ 2.15 (dd, 6H, ^4J (H-P) = 3.46, ^4J (H-H) = 0.82, Me of C_6H_8P), 2.39 (d, 3H, J (H-P) = 3.47, Me of C_7H_7PBr), 2.67 (d, 3H, J (H-P) = 1.87, Me of C_7H_7PBr), 6.59 (ddq, 2H, ^2J (H-P) = 37.90, ^4J (H-P) = 2.13, ^4J (H-H) = 0.82, =CH), 7.82 (d, 1H, ^3J (H-P) = 4.41, H_3).

^{13}C NMR ($CDCl_3$): δ 18.60 (d, ^3J (C-P) = 3.15, Me of C_6H_8P), 21.20 (d, ^3J (C-P) = 26.0, C_5-Me of C_7H_7PBr), 33.75 (s, Me of C_7H_7PBr), 127.75 (d, ^1J (C-P) = 15.20, =CH), 140.35 (d, ^2J (C-P) = 13.40, C_3), 141.85 (dd, J (C-P) = 15.40, C_4 or C_5), 144.60 (dd, J (C-P) = 19.05, C_5 or C_4), 148.0 (d, ^2J (C-P) = 9.1, =C-Me of C_6H_8P), 151.60 (d, ^1J (C-P) = 74.70, C_2), 166.85 (dd, ^1J (C-P) = 74.30, ^1J (C-P) = 23.60, C_6).

Mass spectrum m/z (relative intensity): 313 (M, 85), 233 (M-Br, 100).

Anal calc for $C_{13}H_{15}P_2Br$: C, 49.87; H, 4.83. Found: C, 48.97; H, 4.71.

Complex **11**

Phosphinine **2** (5 g, 22.8 mmol) was added to a solution of $W(CO)_5(MeCN)$ (9.15 g, 25.10 mmol) in 50 mL THF. After 3 h of stirring at room temperature, celite (4 g) was added and the THF was evaporated. The mixture was purified by chromatography. A preliminary fraction eluted with hexane as eluent yielded traces of $W(CO)_6$. A second fraction eluted with hexane/CH_2Cl_2 (3:1) as eluent yielded complex **11** as a yellow solid which was crystallized in pentane at 0 °C. Yield 9.28 g (75%).

Mp: 110 °C.

^{31}P NMR ($CDCl_3$): δ 215.06 (d, ^2J (P-P) = 79.0, P of C_6H_6P), 13.0 (d, ^1J (P-W) = 180.0, P of C_6H_8P).

^1H NMR ($CDCl_3$): δ 2.29 (s, 6H, Me of C_6H_6P), 2.92 (d, 3H, ^4J (H-P) = 36.31, Me of C_6H_8P), 6.92 (dd, 2H, ^2J (H-P) = 36.31, ^4J (H-P) = 2.56, =CH of C_6H_6P), 7.50 (m, 1H, H_4), 7.83 (dq, 1H, ^3J ($H\text{-}H_6$) = ^3J ($H\text{-}H_4$) = ^3J (H-P) = 9.90, ^5J (H-P) = 1.88, H_5), 8.64 (ddd, 1H, ^2J (H-P) = 41.10, ^3J (H-H) = 9.94, ^4J ($H\text{-}H_4$) or ^4J (H-P) = 4.23, H_6).

^{13}C NMR ($CDCl_3$): δ 17.95 (d, ^3J (C-P) = 11.10, Me of C_6H_6P), 26.0 (d, ^3J (C-P) = 11.50, Me of C_6H_8P), 129.35 (dd, ^2J (C-P) = 44.0, ^3J (C-P) = 13.65, =CH of C_6H_8P), 133.60 (dd, ^3J (C-P) = 19.40, ^3J (C-P) = 8.0, C_4), 135.80 (d, ^2J (C-P) = 12.0, C_5), 146.30 (dd, ^2J (C-P) = 13.40,

^2J (C-P) = 7.45, C_3), 150.10 (d, ^2J (C-P) = 10.0, =C- of C_6H_8P), 152.45 (dd, ^1J (C-P) = 56.80, ^3J (C-P) = 8.90, C_6), 161.10 (dd, ^1J (C-P) = 71.80, ^1J (C-P) = 27.30, C_2), 197.0 (d, ^2J (C-P) = 6.10, CO *cis*), 200.0 (d, ^2J (C-P) = 16.90, CO *trans*).

Anal calc for $C_{17}H_{14}O_5P_2W$: C, 37.52; H, 2.59. Found: C, 37.68; H, 2.46.

3,4-Dimethyl-1-(3-methyl-2-phosphininyl)phosphole 1-sulfide **12**

Sulfur (0.22 g, 6.84 mmol) was added to a solution of phosphinine **2** (1 g, 4.56 mmol) in 5 mL toluene. The resulting mixture was then heated at 70 °C for 2 h. After cooling and evaporation of toluene, the resulting brown mixture was chromatographed on silica gel. A preliminary fraction eluted with hexane allowed the separation of excess sulfur. A second fraction eluted with hexane/ether (3:1) as eluent afforded sulfide **12** as a yellow solid. Yield 0.74 g (65%).

Mp: 150 °C.

^{31}P NMR ($CDCl_3$): δ 212.55 (d, ^2J (P-P) = 104.85, P of C_6H_6P), 45.85 (d, ^2J (P-P) = 104.85, P=S).

^{1}H NMR ($CDCl_3$): δ 1.58 (d, 6H, ^4J (H-P) = 0.86, Me of C_6H_8PS), 3.01 (s, 3H, Me of C_6H_6P), 6.49 (d, 2H, ^2J (H-P) = 30.26, =CH of C_6H_8PS), 7.20 (m, 1H, H_4), 7.48 (m, 1H, H_5), 8.27 (ddd, 1H, ^2J (H-P) = 41.47, ^3J (H-H) = 10.02, ^4J (H-P) = 5.60, H_6).

^{13}C NMR ($CDCl_3$): δ 17.10 (d, ^3J (C-P) = 18.05, Me of C_6H_8PS), 24.85 (d, ^3J (C-P) = 9.15, Me of C_6H_6P), 125.25 (dd, ^1J (C-P) = 83.85, ^3J (C-P) = 9.10, =CH of C_6H_8PS), 134.55 (dd, ^3J (C-P) = 18.95, ^3J (C-P) = 10.20, C_4), 137.10 (dd, ^2J (C-P) = 12.20, ^4J (C-P) = 2.55, C_5), 150.0 (dd, ^2J (C-P) = 13.40, ^2J (C-P) = 4.15, C_3), 151.0 (d, ^2J (C-P) = 19.40, =C- of C_6H_8PS), 152.20 (dd, ^1J (C-P) = 42.05, ^3J (C-P) = 13.70, C_6), 160.10 (dd, ^1J (C-P) = 70.25, ^1J (C-P) = 64.05, C_2).

Anal calc for $C_{12}H_{14}P_2S$: C, 57.14; H, 5.59. Found: C, 57.35; H, 5.31.

Dimer **13**

Phosphinine **2** (2 g, 9.13 mmol) was heated in 10 mL xylene at 180 °C for 2 h. After cooling and evaporation of the solvent the resulting mixture was purified by chromatography with hexane/Et_2O (98.8:1.5) as eluent. Dimer **13** was recovered as a colorless oil after evaporation of the solvents. Yield 1.1 g (55%).

^{31}P NMR ($CDCl_3$): δ 202.10 (dd, ^3J ($P_{1''}$-P_2) = 34.90, ^4J ($P_{1''}$-P_1) = 10.20, $P_{1''}$), 201.40 (d, ^3J ($P_{1'}$-P_1) = 51.75, $P_{1'}$), 29.55 (dd, ^1J (P_2-P_1) = 221.05, ^4J (P_2-$P_{1''}$) = 34.90, P_2), −36.60 (ddd, ^1J (P_1-P_2) = 221.05, ^3J ($P_{1'}$-P_1) = 51.75, ^4J (P_1-$P_{1''}$) = 10.20, P_1).

^{1}H NMR ($CDCl_3$): δ 1.34-1.67 (m, 12H, 4 × Me), 2.42-3.0 (m, 10H, 2 × Me of C_6H_6P, CH_2, H_5 and H_6), 7.33-7.50 (m, 2H, $H_{4'}$ and $H_{4''}$ of C_6H_6P), 7.50–7.70 (m, 2H, $H_{5'}$ and $H_{5''}$ of C_6H_6P), 8.50 (dd, 1H, ^2J (H-P) = 38.25, ^3J (H-H) = 10.08, $H_{6'}$ or $H_{6''}$ of C_6H_6P), 8.51 (dd, 1H, ^2J (H-P) = 38.46, ^3J (H-H) = 9.84, $H_{6'}$ or $H_{6''}$ of C_6H_6P).

^{13}C NMR ($CDCl_3$): δ 13.35, 16.20, 19.25 (s, 3 × Me), 22.40 (d, J (C-P) = 4.85, Me), 23.05 (d, J (C-P) = 4.75, Me), 23.55 (d, J (C-P) = 2.30, Me), 40.05 (d, J (C-P) = 15.70, C_7), 47.60 (s, C_5), 54.60 (d, ^1J (C-P) = 22.40, C_6), 63.20 (s, bridging CH_2), 132.70 (d, J (C-P) = 17.70, $C_{4',4''}$ or $C_{5',5''}$ of C_6H_6P), 133.15 (d, J (C-P) = 14.45, $C_{4',4''}$ or $C_{5',5''}$ of C_6H_6P).

Mass spectrum m/z (relative intensity): 440 (M, 2), 220 (M/2 retro-Diels-Alder, 100).

Anal calc for $C_{24}H_{28}P_4$: C, 65.46; H, 6.41. Found: C, 64.71; H, 5.98.

2-(5,6-Diphenyl-3,4-dimethyl-1-phosphanorbornadienyl)-3-methylphosphinine **14**

Phosphinine **2** (5 g, 22.72 mmol) and diphenylacetylene (6.06 g, 34.10 mmol) were heated in 20 mL xylene at 160 °C for 4 h. After this period, celite (2 g) was added and xylene was evaporated. The resulting coated celite was deposited onto the top of a column for chromatography. A first fraction eluted with hexane afforded excess diphenylacetylene. A second fraction eluted with pentane/ether (98:2) as eluent yielded phosphinine **14** as a yellow powder after evaporation of solvents. Yield 5.87 g (65%).

Mp: 50–60 °C.

^{31}P NMR ($CDCl_3$, −43 °C): δ 199.10 (d, ^3J (P-P) = 17.40, P of C_6H_6P), −4.24 (d, P of $C_{20}H_{18}P$) et 197.10 (d, ^3J (P-P) = 14.15, P of C_6H_6P), −6.21 (d, P of $C_{20}H_{18}P$).

^{1}H NMR ($CDCl_3$): δ 1.45 (s, 3H, Me of $C_{20}H_{18}P$), 1.95 (m, 3H, ^4J (H-P) = 2.65, Me of $C_{20}H_{18}P$), 2.2–2.5 (m, 5H, Me of C_6H_6P and bridging CH_2), 7.06–7.50 (m, 11H, CH of C_6H_5 and H_4), 7.69 (dt, 1H, ^3J (H-H) = 9.65, ^3J (H-P) = ^3J (H-H) = 8.79, H_5), 8.63 (dd, 1H, ^2J (H-P) = 38.06, ^3J (H-H) = 9.65, H_6).

^{13}C NMR ($CDCl_3$): δ 15.75 (s, Me of $C_{20}H_{18}P$), 21.20 (s, Me of $C_{20}H_{18}P$), 23.35 (d, ^3J (C-P) = 3.0, Me of C_6H_6P), 65.45 (m, bridging CH_2), 71.90 (s, $C_{4'}$), 126.70–128.9 (m, CH of C_6H_5), 132.50 (d, J (C-P) = 17.22, C_4 or C_5), 132.90 (d, J (C-P) = 14.60, C_5 or C_4), 134.80 (d, J (C-P) = 21.0, Cq of C_6H_5 or C_3), 138.35 (d, J (C-P) = 19.60, Cq of C_6H_5 or C_3), 139.25 (s, Cq of C_6H_5 or C_3), 153.10 (d, ^1J (C-P) = 54.35, C_6), 153.10 (m, $C_{2'}$ et $C_{6'}$ masked by C_6), 158.60 (d, ^2J (C-P) = 9.55, $C_{3'}$), 162.15 (s, $C_{5'}$), 168.85 (dd, ^1J (C-P) = 50.25, ^3J (C-P) = 17.0, C_2).

Mass spectrum m/z (relative intensity): 398 (M, 100), 220 (M-PhCCPh, 100).

Anal calc for $C_{26}H_{24}P_2$: C, 78.38; H, 6.07. Found: C, 78.70; H, 6.55.

2-(5,6-Diphenyl-3,4-dimethyl-1-phosphanorbornadienyl)-4,5-dimethylphosphinine **15**

Phosphinine **2** (6 g, 25.64 mmol) and diphenylacetylene (6.84 g, 38.46 mmol) were heated in 20 mL xylene at 160 °C for 6 h. After this period, celite (2 g) was added and xylene was evaporated before chromatography. A preliminary fraction eluted with hexane afforded excess of diphenylacetylene. A second fraction eluted with hexane/CH_2Cl_2 (3:1) as eluent yielded phosphinine **15** as a yellow powder after evaporation of solvents. Yield 7.92 g (75%).

Mp: 95 °C.

^{31}P NMR ($CDCl_3$): δ 183.60 (d, ^3J (P-P) = 33.40, P of C_7H_8P), −4.95 (d, P of $C_{20}H_{18}P$).

^{1}H NMR ($CDCl_3$): δ 1.38 (s, 3H, Me of $C_{20}H_{18}P$), 2.13 (dd, 3H, ^4J (H-P) = 2.35, ^5J (H-P) = 0.69, =C-*Me* of $C_{20}H_{18}P$), 2.15–2.24 (m, 2H, bridging CH_2), 2.34 (d, 3H, J (H-P) = 3.59, Me of C_7H_8P), 2.41 (s, 3H, Me of C_7H_8P), 6.97–7.36 (m, 10H, 2 × C_6H_5), 7.61 (d, 1H, ^3J (H-P) = 5.85, H_3), 8.43 (d, 1H, ^2J (H-P) = 38.24, H_6).

^{13}C NMR ($CDCl_3$): δ 16.70 (d, ^3J (C-P) = 6.60, Me of $C_{20}H_{18}P$), 21.80 (s, Me of $C_{20}H_{18}P$), 23.15 (s, Me of C_7H_8P), 23.70 (d, J (C-P) = 3.0, Me of C_7H_8P), 65.40 (s, bridging CH_2), 73.20 (d, ^2J (C-P) = 4.80, $C_{4'}$), 127.0, 127.50, 128.40, 128.70, 128.95, 129.10 (CH

of C_6H_5), 136.70 (d, ^2J (C-P) = ^3J (C-P) = 11.30, C_3), 138.55 (d, ^2J (C-P) = 19.44, C_4 or C_5), 139.56 (d, ^2J (C-P) = 12.60, Cq of C_6H_5),139.70 (d, ^3J (C-P) = 3.75, Cq of C_6H_5), 141.60 (d, J (C-P) = 15.80, C_5 or C_4), 152.10 (dd, J (C-P) = 23.95, J (C-P) = 22.0, $C_{2'}$), 153.0 (d, ^1J (C-P) = 26.90, $C_{6'}$), 154.80 (d, ^1J (C-P) = 51.80, C_6), 157.95 (d, J (C-P) = 8.80, $C_{3'}$), 162.0 (s, $C_{5'}$), 166.80 (dd, ^1J (C-P) = 47.50, ^2J (C-P) = 19.70, C_2).

Mass spectrum m/z (relative intensity): 412 (M, 40), 234 (M-PhCCPh, 90).

Anal calc for $C_{27}H_{26}P_2$: C, 78.63; H, 6.35. Found: C, 78.35; H, 5.97.

2,6-bis(5,6-Diphenyl-3,4-dimethyl-1-phosphanorbornadienyl)-4-bromo-5-methylphosphinine **16**

Phosphinine **7** (5 g, 12.22 mmol) and diphenylacetylene (6.52 g, 36.66 mmol) were heated in 10 mL xylene at 160 °C for 6 h. After this period, celite (2 g) was added and xylene was evaporated before chromatography. A first fraction eluted with hexane afforded excess of diphenylacetylene. A second fraction eluted with hexane/CH_2Cl_2 (3:1) as eluent yielded phosphinine **16** as a yellow powder after evaporation of solvents. Yield 5.61 g (60%).

Mp: 125 °C.

^{31}P NMR ($CDCl_3$) (4 diastereomers): δ 190.10 (t, ^3J (P-P) = 20.0, P of C_6H_4PBr), 189.70 (t, ^3J (P-P) = 20.0, P of C_6H_4PBr), 187.10 (dd, ^3J (P-P) = 16.0, ^3J (P-P) = 9.70, P of C_6H_4PBr), 186.65 (dd, ^3J (P-P) = 17.0, ^3J (P-P) = 11.0, P of C_6H_4PBr), −1.60 to −3.10 (m, 4 × $C_{20}H_{18}P$), −4.0 to −5.10 (m, 4 × $C_{20}H_{18}P$).

^{1}H NMR ($CDCl_3$): δ 1.30–1.50 (m, 6H, 2 × Me of $C_{20}H_{18}P$), 1.70–2.20 (m, 9H, 2 × Me of $C_{20}H_{18}P$ and Me of C_6H_4PBr), 2.30–2.60 (m, 4H, 2 bridging CH_2), 6.9–7.50 (m, 20H, CH of C_6H_5), 7.9–8.1 (m, 1H, H_5).

Mass spectrum m/z (relative intensity): 765 (M, 44), 685 (M-Br, 8), 588 (M-$C_{14}H_{10}$, 35), 507 (588-Br, 20), 408 (588-$C_{14}H_{10}$, 35), 329 (408-Br, 100).

Anal calc for $C_{46}H_{40}P_3Br$: C, 72.16; H, 5.27. Found: C, 72.48; H, 5.55.

2,6-bis(5,6-Diphenyl-3,4-dimethyl-1-phosphanorbornadienyl)-3,4-dimethylphosphinine **17**

Phosphinine **8** (6 g, 17.44 mmol) and diphenylacetylene (9.31 g, 52.32 mmol) were heated in 15 mL xylene at 160 °C for 6 h. After this period, celite (2 g) was added and xylene was evaporated before chromatography. A preliminary fraction eluted with hexane afforded excess of diphenylacetylene. A second fraction eluted with hexane/CH_2Cl_2 (3:1) as eluent yielded phosphinine **17** as a yellow powder after evaporation of solvents. Yield 7.32 g (60%).

Mp: 90 °C.

^{31}P NMR ($CDCl_3$) (4 diastereomers): δ 180.0–181.0 (m, 2×C_7H_7P), 178.20 (dd, ^3J (P-P) = 30.0, ^3J (P-P) = 18.0, P of C_7H_7P), 177.50 (dd, ^3J (P-P) = 30.0, ^3J (P-P) = 18.0, P of C_7H_7P), −2.0 to −3.80 (m, 4×$C_{20}H_{18}P$), −5.0 to −6.0 (m, 4 × $C_{20}H_{18}P$).

^{1}H NMR ($CDCl_3$): δ 1.37 (s, 6H, 2 × Me of $C_{20}H_{18}P$), 1.85–1.90 (m, 6H, 2×Me of $C_{20}H_{18}P$), 2.07 (m, 4H, 2 bridging CH_2), 2.24–2.38 (m, 6H, 2 × Me of C_7H_7P), 7.0–7.49 (m, 21H, CH of C_6H_5 and H_5).

Mass spectrum m/z (relative intensity): 700 (M, 40), 522 (M-$C_{14}H_{10}$, 30), 344 (522-$C_{14}H_{10}$).

Anal calc for $C_{47}H_{43}P_3$: C, 80.56; H, 6.18. Found: C, 81.05; H, 6.48.

[2-(5,6-Diphenyl-3,4-dimethyl-1-phosphanorbornadienyl)-3-methylphosphinine]tetracarbonylchromium complex **18**

Phosphinine **14** (1 g, 2.51 mmol) was added to a freshly prepared solution of $Cr(CO)_5$THF (2.76 mmol) in 20 mL THF. The THF was then evaporated and 10 mL of toluene was added. The resulting mixture was then heated at reflux for 18 h. After this period a ^{31}P NMR control indicated the total disappearance of phosphinine **14** and the quantitative formation of complex **18**. After evaporation of the solvent, the mixture was purified by chromatography. A first fraction eluted with pentane afforded traces of $Cr(CO)_6$. A second fraction eluted with pentane/CH_2Cl_2 (4:1) as eluent yielded complex **18** as an orange powder. Yield 1.06 g (75%).

Mp: >250 °C.

^{31}P NMR ($CDCl_3$): δ 260.90 (d, ^3J (P-P) = 24.30, P of C_6H_6P), 95.70 (d, P of $C_{20}H_{18}P$).

^{1}H NMR ($CDCl_3$): δ 1.47 (s, 3H, Me of $C_{20}H_{18}P$), 2.26 (dd, 3H, ^4J (H-P) = 4.47, ^5J (H-P) = 2.10, Me of $C_{20}H_{18}P$), 2.41 (d, 3H, ^4J (H-P) = 2.51, Me of C_6H_6P), 2.51 (ABX, 1H, ^2J (H_A-H_B) = 9.93, ^2J (H_A-P) = 2.20, H_A of bridging CH_2), 2.66 (ABX, 1H, ^2J (H_B-H_A) = 9.93, ^2J (H_B-P) = 2.31, H_B of bridging CH_2), 6.90–7.34 (m, 11H, CH of C_6H_5 and H_4), 7.49 (ddd, 1H, ^3J (H-P) = 21.60, ^3J (H-H_6) = 10.0, ^3J (H-H_4) = 8.50, H_5), 8.35 (dd, 1H, ^2J (H-P) = 25.70, ^3J (H-H_5) = 10.0, H_6).

^{13}C NMR ($CDCl_3$): δ 19.05 (d, ^3J (C-P) = 7.30, Me of $C_{20}H_{18}P$), 21.0 (d, ^3J (C-P) = 7.05, Me of $C_{20}H_{18}P$), 25.45 (d, ^3J (C-P) = 4.80, Me of C_6H_6P), 68.75 (s, $C_{4'}$ of $C_{20}H_{18}P$), 69.60 (dd, ^1J (C-P) = 33.30, ^3J (C-P) = 5.67, bridging CH_2), 127.0–129.10 (m, C_6H_5), 129.80 (d, ^3J (C-P) = 25.40, C_4 of C_6H_6P), 134.45 (d, ^2J (C-P) = 17.90, C_5), 135.40 (d, ^2J (C-P) = 14.0, Cq of C_6H_5), 136.30 (d, ^3J (C-P) = 7.30, Cq of C_6H_5), 140.85 (dd, ^2J (C-P) = 12.70, ^3J (C-P) = 9.60, C_3 of C_6H_6P), 146.80 (t, ^1J (C-P) = ^3J (C-P) = 8.10, C_6), 146.80 ($C_{3'}$ masked by C_6), 147.95 (dd, ^1J (C-P) = 42.85, ^2J (C-P) = 26.45, C_2), 154.10 (dd, ^1J (C-P) = 24.40, ^3J (C-P) = 4.60, $C_{6'}$), 156.50 (dd, ^1J (C-P) = 32.75, ^2J (C-P) = 18.80, $C_{2'}$), 163.20 (d, ^2J (C-P) = 4.30, $C_{5'}$), 216.40 (dd, ^2J (C-P) = 20.80, ^2J (C-P) = 13.95, CO *trans* to P), 219.85 (dd, ^2J (C-P) = 18.15, ^2J (C-P) = 10.95, CO *trans* to P), 226.15 (dd, ^2J (C-P) = 12.10, ^2J (C-P) = 4.85, CO *cis* to P), 228.20 (d, ^2J (C-P) = 12.65, CO *cis* to P).

Mass spectrum, m/z (relative intensity): 398 (M-$Cr(CO)_4$, 56), 220 (398-PhCCPh, 100).

Anal calc for $C_{30}H_{24}O_4P_2Cr$: C, 64.06; H, 4.30. Found: C, 63.99; H, 4.28.

[2-(5,6-Diphenyl-3,4-dimethyl-1-phosphanorbornadienyl)-3-methylphosphinine]tetracarbonylmolybdenum complex **19**

Phosphinine **14** (1 g, 2.51 mmol) was added to a freshly prepared solution of $Mo(CO)_5$(MeCN) (0.764 g, 2.76 mmol) in 15 mL toluene. The resulting mixture was then heated at reflux for 3 h. After this period, a ^{31}P NMR control indicated the total disappearance of phosphinine **14**. After the usual treatment with celite the mixture was purified by chromatography. A preliminary fraction eluted with hexane as eluent afforded traces of unreacted $Mo(CO)_6$. A second fraction eluted with hexane/CH_2Cl_2 (3:1) as eluent yielded complex **19** as a yellow powder. The complex was crystallized in CH_2Cl_2 at −20 °C. Yield 1 g (65%).

Mp: >250 °C.

^{31}P NMR ($CDCl_3$): δ 230.50 (d, ^3J (P-P) = 9.0, P of C_6H_6P), 65.70 (d, P of $C_{20}H_{18}P$).

^{1}H NMR ($CDCl_3$): δ 1.36 (s, 3H, Me of $C_{20}H_{18}P$), 2.10 (dd, 3H, ^4J (H-P) = 4.60, ^5J (H-P) = 2.02, Me of $C_{20}H_{18}P$), 2.26 (d, 3H, ^4J (H-P) = 2.50, Me of C_6H_6P), 2.50 (ABX, 1H, ^2J (H_A-H_B) = 10.0, ^2J (H_A-P) = 3.0, H_A of bridging CH_2), 2.58 (ABX, 1H, ^2J (H_B-H_A) = 10.0, ^2J (H_B-P) = 2.73, H_B of bridging CH_2), 6.81–7.22 (m, 11H, CH of C_6H_5 and H_4), 7.35 (m, 1H, H_5), 8.22 (dd, 1H, ^2J (H-P) = 26.90, ^3J (H-H) = 9.90, H_6).

^{13}C NMR ($CDCl_3$): δ 19.45 (d, J (C-P) = 5.50, Me of $C_{20}H_{18}P$), 21.10 (d, J (C-P) = 7.20, Me of $C_{20}H_{18}P$), 25.45 (d, ^3J (C-P) = 4.40, Me of C_6H_6P), 69.45 (s, $C_{4'}$), 70.25 (dd, ^1J (C-P) = 32.55, ^3J (C-P) = 5.0, bridging CH_2), 127.30–130.90 (m, CH of C_6H_5), 133.10 (d, ^3J (C-P) = 19.70, C_4), 134.30 (d, ^2J (C-P) = 18.05, C_5), 135.65 (d, ^2J (C-P) = 15.05, Cq of C_6H_5), 136.90 (d, ^3J (C-P) = 7.80, Cq of C_6H_5), 141.35 (t, ^2J (C-P) = ^3J (C-P) = 10.70, C_3), 146.55 (d, ^2J (C-P) = 11.35, $C_{3'}$), 147.05 (t, ^1J (C-P) = ^3J (C-P) = 5.75, C_6), 148.60 (dd, ^1J (C-P) = 39.10, ^2J (C-P) = 25.45, C_2), 155.85 (dd, ^1J (C-P) = 22.95, ^3J (C-P) = 3.05, $C_{6'}$), 156.70 (dd, ^1J (C-P) = 29.90, ^2J (C-P) = 16.06, $C_{2'}$), 162.95 (t, ^2J (C-P) = ^4J (C-P) = 4.70, $C_{5'}$), 205.50 (dd, ^2J (C-P) = 25.20, ^2J (C-P) = 9.90, CO *cis* to P), 209.05 (dd, ^2J (C-P) = 12.05, ^2J (C-P) = 6.15, CO *cis* to P), 215.0 (dd, ^2J (C-P) = 26.50, ^2J (C-P) = 9.35, CO *trans* to P), 216.85 (dd, ^2J (C-P) = 33.15, ^2J (C-P) = 9.35, CO *trans* to P).

Anal calc for $C_{30}H_{24}O_4P_2Mo$: C, 59.42; H, 3.99. Found: C, 59.21; H, 4.96.

[2-(5,6-Diphenyl-3,4-dimethyl-1-phosphanorbornadienyl)-3-methylphosphinine]tetracarbonyltungsten complex **20**

Phosphinine **14** (1 g, 2.51 mmol) was added to a freshly prepared solution of $W(CO)_5$(MeCN) (1.0 g, 2.76 mmol) in 15 mL toluene and the resulting solution was heated at reflux for 20 h. After cooling, the mixture was purified by chromatography. A preliminary fraction eluted with hexane afforded traces of unreacted $W(CO)_6$. A second fraction eluted with hexane/CH_2Cl_2 (4:1) as eluent yielded complex **20** as an orange powder. Yield 1.22 g (70%).

Mp: >250 °C.

^{31}P NMR ($CDCl_3$): δ 201.55 (^1J (P-W) = 238.0, P of C_6H_6P), 43.27 (^1J (P-W) = 231.90, P of $C_{20}H_{18}P$).

^{1}H NMR ($CDCl_3$): δ 1.50 (s, 3H, Me of $C_{20}H_{18}P$), 2.23 (dd, 3H, ^4J (H-P) = 4.66, ^5J (H-P) = 2.15, Me of $C_{20}H_{18}P$), 2.41 (d, 3H, ^4J (H-P) = 2.61, Me of C_6H_6P), 2.48 (ABX, 1H, ^2J (H_A-H_B) = 9.95, ^2J (H_A-P) = 3.0, H_A of bridging CH_2), 2.53 (ABX, 1H, ^2J (H_B-H_A) = 9.95, ^2J (H_B-P) = 2.70, H_B of bridging CH_2), 6.95–7.35 (m, 11H, CH of C_6H_6 and H_4 of C_6H_6P), 7.51 (ddd, 1H, ^3J (H-P) = 22.37, ^3J (H-H) = 9.96, ^3J (H-H) = 8.54, H_5), 8.28 (dd, 1H, ^2J (H-P) = 25.67, ^3J (H-H) = 9.96, H_6).

^{13}C NMR ($CDCl_3$): δ 20.0 (d, ^3J (C-P) = 7.30, Me of $C_{20}H_{18}P$), 21.55 (d, ^3J (C-P) = 7.63, Me of $C_{20}H_{18}P$), 26.10 (d, ^3J (C-P) = 4.55, Me of C_6H_6P), 69.95 (s, $C_{4'}$), 71.05 (dd, ^1J (C-P) = 36.40, ^3J (C-P) = 5.55, bridging CH_2), 127.70–129.90 (m, CH of C_6H_5), 130.80 (d, ^3J (C-P) = 26.55, C_4), 135.25 (d, ^2J (C-P) = 17.80, C_5), 135.75 (d, ^2J (C-P) = 14.45, Cq of C_6H_5), 136.95 (d, ^3J (C-P) = 8.55, Cq of C_6H_5), 141.90 (t, ^2J (C-P) = ^3J (C-P) = 10.25, C_3), 145.10 (dd, ^1J (C-P) = 14.35, ^3J (C-P) = 7.0, C_6), 146.15 (d, ^2J (C-P) = 16.70, $C_{3'}$), 149.70 (dd, ^1J (C-P) = 36.90, ^3J (C-P) = 30.35, C_2), 155.60 (dd, ^1J (C-P) = 27.70, ^3J (C-P) = 24.15, $C_{2'}$), 156.15 (dd, ^1J (C-P) = 23.15, ^3J (C-P) = 4.15, $C_{6'}$), 163.35 (t, ^3J (C-P) = ^4J (C-P) = 5.10, $C_{5'}$), 197.25 (dd, ^2J (C-P) = 11.35, ^2J (C-P) = 8.85, CO *cis* to P), 200.90 (dd, ^2J (C-P) = 6.45, ^2J (C-P) = 3.0, *cis* to P), 205.85 (dd, ^2J (C-P) = 25.0, ^2J (C-P) = 6.25, CO *trans* to P), 207.90 (dd, ^2J (C-P) = 32.10, ^2J (C-P) = 6.90, CO *trans* to P).

Anal calc for $C_{30}H_{24}O_4P_2W$: C, 51.90; H, 3.48. Found: C, 52.50; H, 3.70.

[2-(5,6-Diphenyl-3,4-dimethyl-1-phosphanorbornadienyl)-4,5-dimethylphosphinine]tetracarbonyltungsten complex **21**

Phosphinine **14** (1.5 g, 3.64 mmol) was added to a freshly prepared solution of $W(CO)_5$(MeCN) (1.46 g, 4.0 mmol) in 20 mL toluene and the resulting solution was then heated at reflux for 20 h. After cooling the mixture was purified by chromatography. A preliminary fraction eluted with hexane afforded traces of unreacted $W(CO)_6$. A second fraction eluted with hexane/CH_2Cl_2 (4:1) as eluent yielded complex **21** as an orange powder. Yield 1.80 g (70%).

Mp: >250 °C.

^{31}P NMR ($CDCl_3$): δ 191.60 (s, ^1J (P-W) = 284.85, P of C_7H_8P), 44.95 (s, ^1J (P-W) = 230.50, P of $C_{20}H_{18}P$).

^{1}H NMR ($CDCl_3$): δ 1.50 (s, 3H, Me of $C_{20}H_{18}P$), 2.35 (s, 3H, Me of $C_{20}H_{18}P$), 2.40 (s, 3H, Me of C_7H_8P), 2.50 (ABX, 1H, ^2J (H_A-H_B) = 9.75, ^2J (H_A-P) = 1.85, H_A of bridging CH_2), 2.55 (m, 3H, Me C_7H_8P), 2.75 (ABX, 1H, ^2J (H_B-H_A) = 9.75, ^2J (H_B-P) = 1.10, H_B of bridging CH_2), 6.95–7.30 (m, 10H, CH of C_6H_5), 8.10 (d, 1H, ^3J (H-P) = 6.25, H_3), 8.20 (d, 1H, ^2J (H-P) = 12.60, H_6).

^{13}C NMR ($CDCl_3$): δ 15.80 (d, ^3J (C-P) = 7.45, Me of $C_{20}H_{18}P$), 21.40 (d, ^3J (C-P) = 8.00, Me of $C_{20}H_{18}P$), 23.50 (d, J (C-P) = 3.80, Me of C_7H_8P), 24.15 (d, J (C-P) = 9.35, Me of C_7H_8P), 70.65 (s, $C_{4'}$ of $C_{20}H_{18}P$), 70.80 (dd, ^1J (C-P) = 34.45, ^3J (C-P) = 5.30, bridging CH_2), 127.60–130.0 (m, CH of C_6H_5), 134.0 (dd, ^3J (C-P) = 12.15, ^3J (C-P) = 9.35, C_3), 136.20 (d, J (C-P) = 6.15, Cq of C_6H_5), 136.65 (s, Cq of C_6H_5), 145.95 (d, ^2J (C-P) = 17.95, $C_{3'}$ of $C_{20}H_{18}P$), 147.25 (dd, ^1J (C-P) = 14.75, ^4J (C-P) = 8.40, C_6 of C_7H_8P), 147.70–148.55 (m, C_2, C_4, C_5 of C_7H_8P), 153.55 (dd, ^1J (C-P) = 26.50, ^3J (C-P) = 5.25, $C_{6'}$ of $C_{20}H_{18}P$), 154.60 (dd, ^1J (C-P) = 30.75, ^2J (C-P) = 28.00, $C_{2'}$ of $C_{20}H_{18}P$), 162.70 (s, $C_{5'}$ of $C_{20}H_{18}$), 197.45 (dd, ^2J (C-P) = 11.0, ^2J (C-P) = 8.40, CO *cis* to P), 199.80 (dd, ^2J (C-P) = 10.60, ^2J (C-P) = 4.60, CO *cis* to P), 206.0 (dd, ^2J (C-P) = 24.90, ^2J (C-P) = 6.35, CO *trans* to P), 208.15 (dd, ^2J (C-P) = 32.05, ^2J (C-P) = 6.05, CO *trans* to P).

Anal calc for $C_{31}H_{26}O_4P_2W$: C, 52.57; H, 3.70. Found: C, 53.40; H, 3.90.

Tetramer **22**

Phosphinine **3** (10 g, 42.92 mmol) was heated with 4-bromo-*N*,*N*-dimethylaniline (1.20 g, 6.38 mmol) at 180 °C for 60 h. After cooling, 150 mL CH_2Cl_2 was added and the mixture was stirred for 30 min. Tetramer **22**, which is insoluble in CH_2Cl_2, was collected by filtration. After a second washing with 40 mL CH_2Cl_2, the orange powder was dryed *in vacuo*. The tetramer was crystallized in hot chlorobenzene. Yield 3.5 g (35%).

Mp: >250 °C.

^{31}P NMR ($CDCl_3$): δ 186.55 (pseudo-t, ΣJ (P-P) = 66.65, P of C_7H_8P), −5.85 (pseudo-t, P of $C_{20}H_{18}P$).

^{1}H NMR ($CDCl_3$): δ 2.12 (s, 12H, Me of C_6H_6P), 2.29 (s, 12H, Me of C_6H_6P), 2.40 (d, 12H, J (H-P) = 3.02, Me

of C_7H_8P), 2.47 (s, 12H, Me of C_7H_8P), 7.68 (pseudo-d, 4H, ^3J (H-P) = 5.34, H_3), 8.47 (pseudo-d, 4H, ^2J (H-P) = 38.73, H_6).

Mass spectrum (plasma desorption): 929.8 (M + 1), 928.8 (M).

Anal calc for $C_{52}H_{56}P_8$ (+ 2 C_6H_5Cl): C, 66.62; H, 5.76. Found: C, 65.59; H, 5.73.

Dianion **23** *and 2,2'-biphosphole* **24**

Tetramer **22** (3 g, 3.23 mmol) was added to a solution of naphthalene sodium (13 mmol) in 30 mL THF at room temperature. After 1 h of stirring at 25 °C, a ^{31}P NMR control indicated the quantitative formation of dianion **23**. The reaction mixture was then cooled to −80 °C and methyl iodide (1.83 g, 12.92 mmol) was added. After 10 min of stirring at −80 °C, the mixture was slowly warmed to room temperature and allowed to stir for an additional 20 min. After evaporation of THF, 20 mL dry deoxygenated hexane was added and the mixture was stirred for 30 min. After filtration and evaporation of hexane, biphosphole **24** was recovered as a yellow oil which is slightly sensitive to oxidation. Yield 2.55 g (80%).

23 ^{31}P NMR (THF): δ 174.60 (AA'XX', ^9J (A-A') = 0, ^3J (A-X) = 55.0, ^6J (A-X') = 1.0, ^3J (X-X') = 72.0 , P of C_7H_8P); 64.90 (AA'XX', P of C_6H_6P).

5,5'-bis(4,5-Dimethyl-2-phosphininyl)-3,3',4,4'-tetramethyl-2,2'-biphosphole **24**

^{31}P NMR (C_6D_6) (major diastereomer): δ 186.0 (AA'XX', ^9J (A-A') = 0, ^3J (X-X') = 55.5, ^3J (A-X) = 43.0, ^6J (A-X') = 1.0, P of C_7H_8P), 7.80 (AA'XX', P of C_6H_6P).

^{31}P NMR (C_6D_6) (minor diastereomer): δ 186.75 and −2.05 (coupling constants were not determined).

^1H NMR ($CDCl_3$): δ 1.25 (s, 6H, Me-P), 1.96 (s, 6H, Me of C_6H_6P), 2.01 (s, 6H, Me of C_6H_6P), 2.03 (s, 6H, Me of C_7H_8P), 2.24 (d, J (H-P) = 0.97, Me of C_7H_8P), 7.81 (d, 2H, ^3J (H-P) = 5.35, H_3), 8.37 (d, 2H, ^2J (H-P) = 38.56, H_6).

^{13}C NMR ($CDCl_3$): δ 8.40 (pseudo-t, ΣJ (C-P) = 15.75, Me-P), 16.10 (d, ^3J (C-P) = 4.70, Me of C_6H_6P), 17.20 (s, Me of C_6H_6P), 23.0 (s, Me of C_7H_8P), 23.45 (d, ^3J (C-P) = 2.90, Me of C_7H_8P), 137.60 (pseudo-t, C_3), 140.10 (d, ^3J (C-P) = 16.55, C_4), 141.50 (d, ^2J (C-P) = 15.75, C_5), 141.70 (pseudo-t, ΣJ (C-P) = 19.45, $C_{2'}$ or $C_{5'}$ of C_6H_6P), 142.50 (pseudo-t, ΣJ (C-P) = 21.10, $C_{2'}$ or $C_{5'}$ of C_6H_6P), 145.0 (pseudo-t, ΣJ (C-P) = 22.65, $C_{3'}$ or $C_{4'}$ of C_6H_6P), 151.40 (d, ΣJ (C-P) = 23.70, $C_{3'}$ or $C_{4'}$ of C_6H_6P), 156.15 (d, ^1J (C-P) = 52.15, C_6), 165.90 (pseudo-t, ΣJ (C-P) = 65.45, C_2).

Mass spectrum, m/z (relative intensity): 494 (M, 100), 479 (M-Me, 30).

5,5'-bis(4,5-Dimethyl-2-phosphininyl)-3,3',4,4'-tetramethyl-2,2'-biphosphole 1,1'-disulfide **25**

Biphosphole **24** (2 g, 4.05 mmol) was reacted with sulfur (0.9 g, 28.35 mmol) in 10 mL toluene at 40 °C for 1 h. After cooling, celite (1 g) was added and the solvent was evaporated before chromatography. A preliminary fraction eluted with hexane as eluent afforded excess of sulfur. A second fraction eluted with CH_2Cl_2/hexane (7:3) as eluent yielded **25** as a yellow solid. Yield 1.80 g (80%).

^{31}P NMR ($CDCl_3$): δ 190.10 (pseudo-d, ΣJ (P-P) = 11.25, C_7H_8P), 50.55 (pseudo-d, C_7H_6PS).

^1H NMR ($CDCl_3$): δ 1.83-2.11 (m, 18H, Me of C_7H_6PS), 2.38 (d, 6H, J (H-P) = 3.44, Me of C_7H_8P), 2.43 (s, 6H, Me of C_7H_8P), 8.03 (d, 2H, ^3J (H-P) = 5.0, H_3), 8.50 (d, 2H, ^2J (H-P) = 38.44, H_6).

^{13}C NMR ($CDCl_3$): δ 15.55 (dd, ΣJ (C-P) = 16.25, Me of C_7H_6PS), 17.15 (d, ΣJ (C-P) = 11.95, Me of C_7H_6PS), 20.10 (d, ΣJ (C-P) = 48.90, Me-P), 23.10 (s, Me of C_7H_8P), 23.90 (d, J (C-P) = 3.35, Me of C_7H_8P), 138.55 (dd, ^2J (C-P) = 11.15, ^3J (C-P) = 3.60, C_3), 137.60-139.45 (d, m, =CH of C_7H_6PS), 140.35 (d, ^2J (C-P) = 16.50, C_4), 143.65 (d, ^3J (C-P) = 15.15, C_5), 145.60 (dd, ΣJ (C-P) = 24.15, =C- of C_7H_6PS), 153.10 (dd, ΣJ (C-P) = 32.75, =C- of C_7H_6PS), 155.70 (d, ^1J (C-P) = 52.25, C_6), 158.65 (dd, ^1J (C-P) = 48.35, ^2J (C-P) = 9.70, C_2).

Mass spectrum, m/z (relative intensity): 558 (M, 90), 525 (M-S-1, 100).

Anal calc for $C_{28}H_{34}P_4S_2$: C, 60.21; H, 6.14. Found: C, 60.24; H, 6.42.

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