Palladium(0)-Catalyzed Functionalization of Bromophosphinines

Pascal Le Floch, Duncan Carmichael, Louis Ricard, and François Mathey*

Contribution from the Laboratoire "Hétéroéléments et Coordination", URA CNRS 1499, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

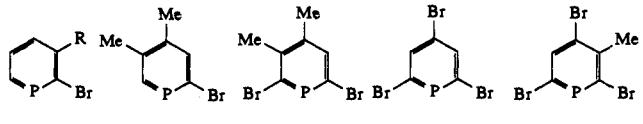
Received January 13, 1993®

Abstract: [PdL_2]-catalyzed (L = triphenyl- or trifurylphosphine) cross-coupling of 2,4,6-tribromo- or 2,6-dibromophosphinines with R–$SnMe_3$ derivatives yields the corresponding 2,6-di-R-phosphinines, where R = 2-furyl, 2-thienyl, 2-*N*-methylpyrrolyl, or C≡C—Ph. When R is 2-pyridyl, only the monosubstituted phosphinine is obtained. A similar cross-coupling reaction between 2,4,6-tribromo- or 2-bromophosphinines and (trimethylsilyl)diphenylphosphine gives either 2,6-bis(diphenylphosphino)- or 2-(diphenylphosphino)phosphinines according to the starting materials. In the case of 2,4,6-tribromophosphinines, the ortho selectivity of the functionalizations probably reflects an initial coordination of [PdL_2] to the phosphinine phosphorus.

The direct functionalization of preformed phosphinine rings is a key synthetic challenge of phosphorus heterocyclic chemistry because no general methodologies are available for the assembly of complex structures which contain phosphaarenes in place of arene or pyridine rings. Except for direct halogenation,[1a,b] no functionalization of C–H phosphaarenic bonds has ever been reported because reagents for electrophilic substitution and metalation reactions generally attack at the phosphorus lone pair or the P=C double bond. More success has been achieved with the carbon–halogen bonds of the readily available bromophosphinines,[1b,3,4] where two methodologies[4,5] permit the lithiation of ortho C—Br bonds. However, both require the masking of the phosphorus lone pair, and also of the P=C double bond in one case. In order to perform such metalations without protecting the heteroatom, Bickelhaupt et al. have studied the reaction of activated zinc with the more reactive 2-iodophosphinines,[6a,b] but the organozinc products display a limited reactivity and the synthesis of 2-iodophosphinines is cumbersome. Thus, more work is clearly needed to devise simple and convenient routes to functional phosphinines.

Results and Discussion

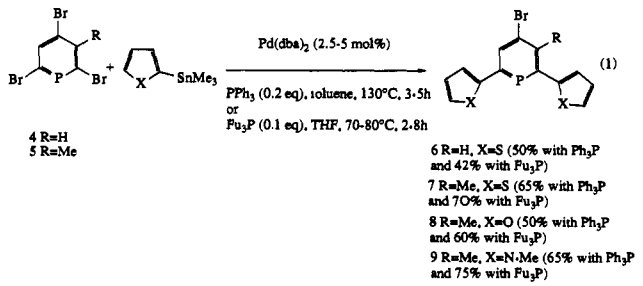
Several authors have recently described the insertion of Pt(0) and Pd(0) centers into the carbon–halogen bonds of *C,C*-dihalophosphaalkenes.[7,8] This suggested that bromophosphinines[1b,3,4] should be good candidates for palladium-catalyzed cross-coupling reactions, such as those amply described in the literature for haloarenes. We decided to investigate the Stille cross-coupling reaction[9] and allowed bromophosphinines **1–5** to react with a series of heteroaryl–trimethyltin derivatives in the presence of palladium(0) complexes.



1 a R = H
b R = Me

2 3 4 5

We immediately found that the tribromophosphinines **4** and **5** are better substrates than either mono- or dibromophosphinines **1–3** for this kind of coupling. Our catalysts were prepared in situ from $Pd(dba)_2$ (dba = dibenzylideneacetone) and a variety of 2e donors, including triphenylphosphine, triphenylarsine, and tri-2-furylphosphine, whose use has been recently reported by Farina and Krishnan.[10] The trifurylphosphine-based catalyst was very satisfactory and was systematically compared with its triphenylphosphine analogue for the coupling of **4** and **5**[1b] with furan, thiophene, and *N*-methylpyrrole derivatives. In each case, the coupling takes place at both ortho positions of the phosphinine ring (eq 1).



(1)

When monitoring the reactions by ^{31}P NMR, it was always possible to detect the transient formation of the monocoupled products[11] but we preferred to run these reactions until the dicoupled products were formed.

The X-ray crystal structure analysis of **7** (Figure 1) not only confirmed the 2,6-disubstitution of the phosphinine but also

* Abstract published in *Advance ACS Abstracts*, October 15, 1993.

(1) (a) Märkl, G.; Hock, K. *Tetrahedron Lett.* **1983**, *24*, 2645. (b) Le Floch, P.; Carmichael, D.; Mathey, F. *Bull. Soc. Chim. Fr.* **1992**, *129*, 291.

(2) For a recent review describing the chemistry of phosphinines, see: Märkl, G. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 1990, pp 220–257.

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

(4) Le Floch, P.; Carmichael, D.; Mathey, F. *Organometallics* **1991**, *10*, 2432.

(5) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1991**, *113*, 667.

(6) (a) Teunissen, H. T.; Bickelhaupt, F. *Tetrahedron Lett.* **1992**, *33*, 3537. (b) Teunissen, H. T.; Bickelhaupt, F. *Bull. Soc. Chim. Belg.* **1992**, *101*, 609. (c) Le Floch, P.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1993**, 789.

(7) Jun, H.; Young, V. G., Jr.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 9379.

(8) Romanenko, V. D.; Sanchez, M.; Sarina, T. V.; Mazieres, M. R.; Wolf, R. *Tetrahedron Lett.* **1992**, *33*, 2981.

(9) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. Kalinin, V. N. *Russ. Chem. Rev.* **1991**, *60*, 173. Kalinin, V. N. *Synthesis* **1992**, 413. Mitchell, T. N. *Synthesis* **1992**, 803.

(10) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585.

(11) 2-Furyl- and 2-thienylphosphinines are already known, see: Alcaraz, J.-M.; Deschamps, E.; Mathey, F. *Phosphorus Sulfur Relat. Elem.* **1984**, *19*, 45.

0002-7863/93/1515-10665$04.00/0

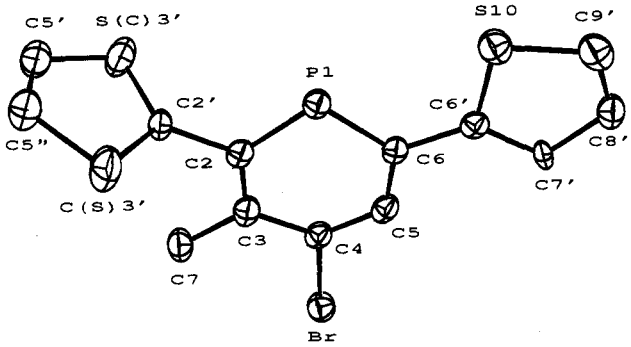
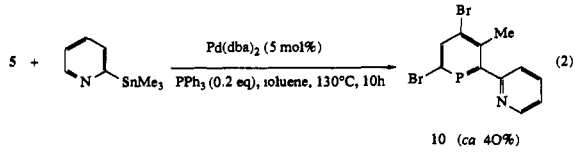


Figure 1. ORTEP drawing of **7** showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Important bond distances (Å) and angles (deg): P_1–C_2 1.734(4), P_1–C_6 1.735(5), C_2–C_3 1.383(7), C_3–C_4 1.421(6), C_4–C_5 1.362(5), C_5–C_6 1.399(7), C_3–C_7 1.501(6), C_4–Br 1.905(5), C_2–C_2' 1.503(6), C_6–C_6' 1.472(5); C_2–P_1–C_6 101.7(2), P_1–C_2–C_3 127.1(3), C_2–C_3–C_4 118.6(4), C_3–C_4–C_5 125.9(5), C_4–C_5–C_6 124.2(4), P_1–C_2–C_2' 113.9(3), P_1–C_6–C_6' 118.8(4).

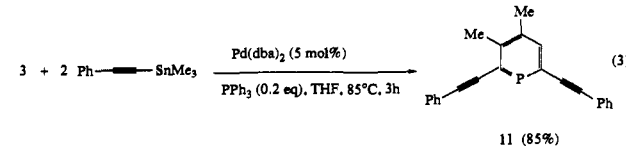
revealed several interesting details. The alteration between short and long C–C bonds in the phosphinine ring is clearly more pronounced in **7** than in the parent species.[12] Moreover, the thiophene opposite to the methyl substituent (S_{10}) is strictly coplanar with the phosphorus ring, whereas the other (S_3') is twisted from the phosphinine plane. A steric repulsion between the methyl group and the S_3' ring is visible from the P–C_α–C(S) angles (118.8° for S_{10} and only 113.9° for S_3'), and the bridge between the S_{10}-thiophene and phosphinine is shorter than the bridge with the S_3' thiophene [1.472(5) *vs* 1.503(6) Å]. It seems more probable that packing effects and steric hindrance by the methyl substituent are responsible for this situation rather than intramolecular conjugative interactions. The distance between the parallel P_1S_{10} planes of two vicinal molecules is only 3.510(1) Å, and the two molecules are head to tail so that the S_{10} thiophene lies above the phosphinine ring of the second molecule. Clearly, it is tempting to suggest that intermolecular charge transfer may be responsible for this stacking (Figure 2), although further work will be required to clarify this point.

In contrast to the five-membered ring series, the cross-coupling of **5** with 2-(trimethylstannyl)pyridine yielded only the rather unstable monocoupled pyridylphosphinine **10**, whose substitution at C_2 is likely, but not definitively proven (eq 2). The limited lifetime of **10** in solution precluded a full stereochemical assignment by nuclear Overhauser effect spectroscopy.

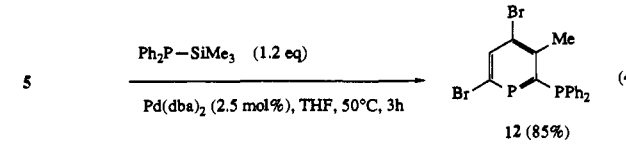


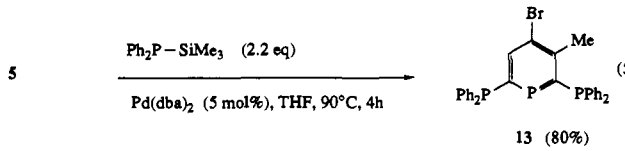
Some Pd(II) chelates with 2-pyridylphosphinine have been described recently,[13] and it is known that Pd(0) chelates perform poorly in the catalysis of the Stille reaction.[10] We therefore propose that the reaction stops after the first cross-coupling because the catalyst is inactivated by chelation of **10** to Pd(0).

Preliminary experiments on the palladium-catalyzed cross-coupling of 2-thienyltrimethyltin with phosphinine **3** showed a much lower reactivity than with **4** and **5**. However, it was possible to couple a stannyl-substituted alkyne efficiently with **3**[1b] (eq 3). Unfortunately, alkynation reactions could not be extended to monobromophosphinines such as **1** and **2**.



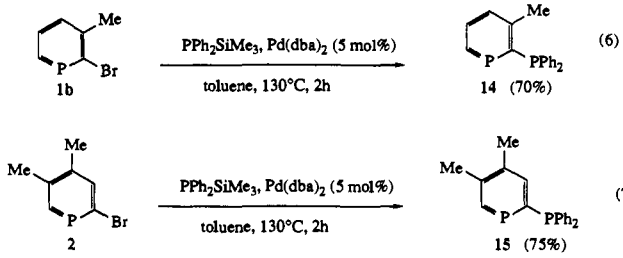
Palladium(0) complexes are known to catalyze the formation of P–C bonds from aryl halides and (trimethylsilyl)phosphines.[14] The transposition of this reaction to the tribromophosphinine **5** was again successful, as is shown in eqs 4 and 5. In this case, we isolated both the mono- and disubstituted products.





The ^{31}P NMR spectrum of **13** displays some interesting characteristics: δ –2.32 (d, ^2J(P–P) = 158.6 Hz, P_6), –2.43 (d, ^2J(P–P) = 36.6 Hz, P_2), 239.09 (dd, cyclic P). The assignment of the P_2 and P_6 resonances was made on the basis of ^1H–^{31}P shift correlation experiments which showed that the phosphinine hydrogen is coupled with P_6 [^3J(H–P_6) = 9.32 Hz] and not with P_2. The enormous difference between the ^2J(P–P_6) and ^2J(P–P_2) coupling constants is probably the result of restricted rotation of the PPh_2 group at C_2. Since the ^2J(P–P) coupling is small (35.4 Hz) in **12**, we can deduce that the initial substitution takes place on the side of the methyl substituent. Thus, we have further indirect confirmation of the structure of 2-pyridylphosphinine (**10**).

We were somewhat surprised when it was possible to extend this phosphination reaction to monobromophosphinines such as **1b** and **2**[3,4] (eqs 6 and 7). Compound **15** has already been



described,[4] and the new phosphinophosphinine **14** displays the characteristically low ^2J(P–P) coupling constant of 30.5 Hz which follows logically from our previous assignments for **12** and **13**. The comparison between the experimental conditions of reactions **4**, **6**, and **7** clearly underlines that phosphination is more difficult for monobromo- than for tribromophosphinines. Since we find that C–C bonds appear to be less easy to form than C–P bonds, we propose that, for monobromophosphinines, the palladium insertion products are formed at 130 °C but decompose faster than they react with stannanes. In the case of the phosphination reaction, the presence of a large excess of silyl phosphine stabilizes the palladium insertion products so that they react with the very reactive Si–P bond faster than they decompose.

(12) Ashe, A. J., III *Acc. Chem. Res.* **1978**, *11*, 153.
(13) Schmid, B.; Venanzi, L. M.; Albinati, A.; Mathey, F. *Inorg. Chem.* **1991**, *30*, 4693.
(14) Tunney, S. E.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 748.

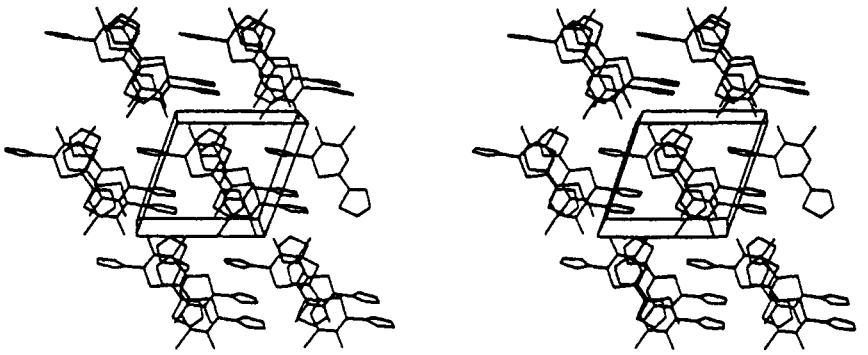
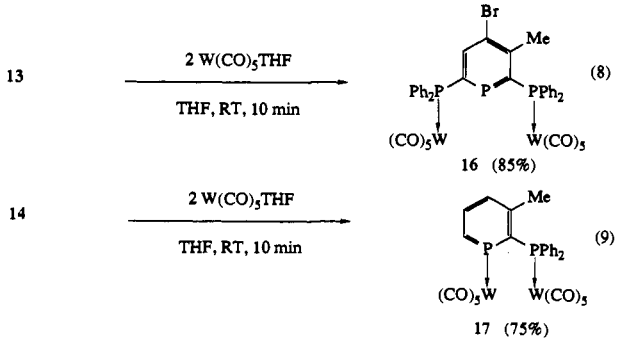


Figure 2. Stereoview of the packing of **7** in the direction of the *b* axis of the unit cell.

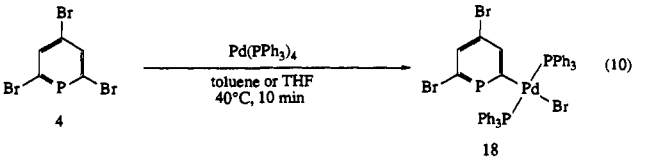
Preliminary testing of the coordination ability of **13** and **14** was performed with $W(CO)_5(THF)$. Both phosphinines act as bidentate ligands, via the two PPh_2 units for **13** and via the cyclic phosphorus and the PPh_2 unit for **14** (eqs 8 and 9). Some other



phosphinophosphinines have been described in the literature,[15] and given their combination of strong π-acceptor and σ-donor phosphorus atoms, these ligands obviously have a promising potential in coordination chemistry.

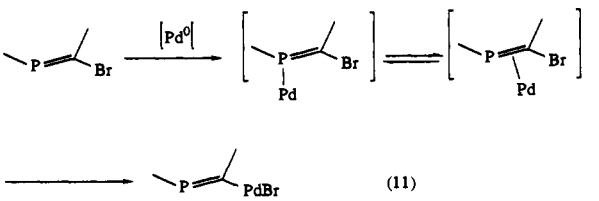
From a mechanistic standpoint, the most intriguing aspects of this work concern the tribromophosphinines **4** and **5** and why they undergo coupling exclusively in the ortho positions (eqs 1, 2, 4, and 5). For **5**, the preference for substitution at the more hindered C_2 position poses an additional problem (eqs 2 and 4).

In an attempt to clarify these points, we investigated the reaction of $Pd(PPh_3)_4$ with **4** and **5** by ^{31}P NMR spectroscopy. The reaction with **4** leads to a single product whose $^{31}P\{^1H\}$ NMR spectrum displays an AX_2 pattern δ A 202.9, δ X 25.4, J(A–X) 38.6 (toluene); the A component is further split to a doublet of doublets (J(A–H) 13.3 and 3.0) in the ^{31}P proton-coupled spectrum. The chemical shift of the low-field signal is quite characteristic of an sp^2-hybridized phosphorus atom. It excludes any possibility that the product involves a phosphinine π complex or that the aromaticity of the phosphinine has been destroyed because very large upfield shifts (ca. 150 ppm)[16a,b] would be observed in both of these cases. The high-field signal indicates the presence of two equivalent triphenylphosphine ligands, and the magnitude of their J(A–X) coupling to the phosphinine requires that the palladium is connected either to the phosphinine phosphorus or to the α carbons of the ring. However, because the proton-coupled spectrum shows that the phosphinine phosphorus is coupled differently with the two ring protons, all symmetrical structures must be excluded. Thus, only the second hypothesis is acceptable, and we are led to propose the formulation indicated in eq 10.

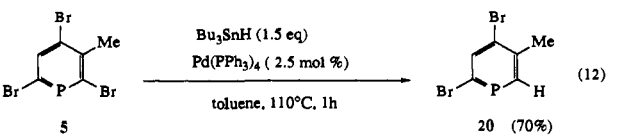


Unfortunately we have been unable to obtain single crystals of **18** which would allow us to definitively establish its structure by X-ray diffraction.

As the symmetry and coupling constant arguments outlined above convincingly exclude the insertion of the palladium into the C_4–Br bond, it only remains to explain why $Pd(PPh_3)_2$ should insert exclusively into the ortho C–Br linkages. We feel that a two-step mechanism is involved, whose first step involves a coordination of the electron-deficient palladium to the P=C moiety, either at phosphorus or at the double bond. Both types of complexes are known to equilibrate readily,[16a] and in the second step, insertion into the C–Br bond can take place as a result of the close proximity of the metal and the carbon–halogen bond in the π complex. It seems reasonable to suppose that orthoselectivity results from a directed transfer of the complexed Pd(0) onto the P=C moiety (eq 11).



The picture concerning **5** is not yet clear. According to ^{31}P NMR spectroscopy, the reaction of **5** with $Pd(PPh_3)_4$ at 40 °C yields two complexes **19a,b** in a ca. 40:60 ratio. **19a**:δ 211.5 [dt, J(P–P) = 35.8 Hz, J(P–H) = 13.3 Hz, ring P], 25.0 (d, PPh_3). **19b**: 202.7 [t, J(P–P) = 41.3 Hz, ring P], 25.0 (d, PPh_3). Above 80 °C, only **19b** is formed. The reduction of **5** by Bu_3SnH in the presence of $Pd(PPh_3)_4$ exclusively takes place at the more hindered C_2 position (eq 12). The rather unstable phosphinine **20** was



unambiguously characterized by ^1H NMR, ^{31}P NMR, and mass spectrometry. The ^1H spectrum ($CDCl_3$) establishes the substitution pattern: δ 2.57 (dd, 3H, ^4J(H–P) = 1.47 Hz, ^4J(H–H) = 0.6 Hz, Me), 8.40 (d, 1H, ^3J(H–P) = 4.14 Hz, Hβ), 8.44 (dq,

(15) (a) Holah, D. G.; Hughes, A. N.; Knudsen, K. L.; Perrier, R. *J. Heterocycl. Chem.* **1988**, *25*, 155. (b) Märkl, G.; Dörges, Ch.; Riedl, Th. *Tetrahedron Lett.* **1990**, *32*, 4589.

(16) (a) van der Knaap, Th. A.; Bickelhaupt, F.; Kraaykamp, J. G.; van Koten, G.; Bernards, J. P. C.; Edzes, H. T.; Veeman, W. S.; de Boer, E.; Baerends, E. J. *Organometallics* **1984**, *3*, 1804. (b) Nief, F.; Charrier, C.; Mathey, F.; Simalty, M. *J. Organomet. Chem.* **1980**, *187*, 277.

1H, ^2J(H–P) = 38.6 Hz, ^4J(H–H) = 0.6 Hz, Hα). The absence of coupling between H_α and H_β demonstrates their para disposition.[3]

Although the mechanism proposed in eq 11 implies that the steric effect of the methyl substituent at C3 should be minimal, we have no explanation for the selectivity in favor of C_2 and cannot define with certainty the structure of **19a,b**. If these products result from the insertion of Pd into the C_6–Br and C_2–Br bonds, then it is not clear why the reduction exclusively takes place at C_2. More work is obviously needed to clarify these points. In spite of these mechanistic uncertainties, it is nonetheless obvious that these palladium-catalyzed derivatization reactions of bromophosphinines dramatically increase the availability of functional phosphinines. We are starting a systematic investigation of the chemistry of these new species.

Experimental Section

Reactions were carried out under nitrogen using oven-dried glassware. Dry THF and toluene 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 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 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: dibromo(dibromomethyl)phosphine,[17] bis(dibenzylideneacetone)palladium,[18] tri-2-furylphosphine,[19] 2-(trimethylstannyl)thiophene,[20] 2-(trimethylstannyl)furan,[21] 2-(trimethylstannyl)pyrrole,[22] 2-(trimethylstannyl)pyridine,[23] (phenylethynyl)trimethylstannane,[24] (trimethylsilyl)diphenylphosphine.[25]

2-Bromophosphinine (1a). A nitrogen-flushed 3-L three-necked flask cooled to −15 °C was charged with triethylamine (200 mL) and THF (75 mL). Butadiene (ca. 1 L) was subsequently condensed into the mixture by allowing the gas to pass over the cold surface of a dry ice condenser cooled to −78 °C. The bromophosphine Br_2PCHBr_2[17] (120 g) was then added dropwise to the rapidly stirred solution over a period of 2 h, at a temperature between −10 and −5 °C.

After the addition, the product was stirred for 1 h and brought gently to 25 °C to allow the butadiene to evaporate. The residue was treated with triethylamine (100 mL) and THF (100 mL) and heated to 40 °C for 1.5 h. After evaporation of the solvents on a rotary evaporator, the mixture was extracted with hexane (2 × 1 L) and filtered. Evaporation of the filtrate gave crude 2-bromophosphinine, which was purified by rapid chromatography under a slight nitrogen pressure on a silica column (20 × 2.5 cm), using hexane (ca. 1.5 L) as the solvent. Yield: 28 g (48%) colorless oil. ^{31}P NMR ($CDCl_3$): δ 210.40. ^{1}H NMR ($CDCl_3$): δ 7.42 (dddd, 1H, ^3J(H_3–H_4) = 8.63, ^3J(H_4–H_5) = 7.98, ^4J(H_4–P) = 4.55, ^4J(H_4–H_6) = 1.48, H_4), 7.82 (m, 1H, ^3J(H_5–H_6) = 9.88, ^3J(H_5–H_4) = 7.98, ^4J(H_5–H_3) = 0.84, ^3J(H_5–P) = 9.28, H_5), 8.10 (dddd, 1H, ^3J(H_3–H_4) = 8.63, ^5J(H_3–H_6) = 0.30, ^3J(H_3–H_5) = 0.84, ^3J(H_3–P) = 4.04, H_3), 8.61 (dddd, 1H, ^2J(H_6–P) = 39.92, ^3J(H_6–H_5) = 9.88, ^4J(H_6–H_4) = 1.48, ^5J(H_6–H_3) = 0.30 H). ^{13}C NMR ($CDCl_3$) (assignments by ^{13}C–^{1}H shift correlation): δ 131.16 (d, J(C–P) = 17.49, C_4), 131.89 (d, J(C–P) = 13.81, C_5), 138.11 (d, J(C–P) = 13.57, C_3), 152.75 (d, J(C–P) = 68.5, C_2), 157.47 (d, J(C–P) = 56.92, C_6). Mass spectrum, m/z (ion, relative intensity): 176 (M + 1, 100). **1a** has also been analyzed as its $W(CO)_5$ complex. **1a**→$W(CO)_5$: yellow solid. Mp: 90 °C. ^{31}P NMR ($CDCl_3$): δ 186.20, ^1J(^{31}P–^{183}W) = 286.36. ^{1}H NMR ($CDCl_3$): δ 7.27 (dddd, 1H, ^3J(H_4–H_3) = 8.9, ^3J(H_4–H_5) = 8.1, ^4J(H_4–P) = 7.5, ^4J(H_4–H_6) = 1.3, H_4), 7.78 (dddd, 1H, ^3J(H_5–H_6) = 10.1, ^3J(H_5–P) = 23.4, ^3J(H_5–H_3) = 1, H_5), 8.21 (ddd, 1H, ^3J(H_3–P) = 13.6, H_3), 8.38 (ddd, 1H, ^2J(H_6–P) = 26.5, H_6). ^{13}C NMR ($CDCl_3$): δ 128.16 (d, J(C–P) = 26.35, C_3 or C_5), 135.85 (d, J(C–P) = 16.95, C_5 or C_3), 140.91 (d, J(C–P) = 10.73, C_4), 147.62 (d, J(C–P) = 12.43, C_2), 152.41 (d, J(C–P) = 15.38, C_6), 193.99 (d, ^2J(C–P) = 9.19, CO *cis*), 198.22 (d, ^2J(C–P) = 33.48, CO *trans*). Mass spectrum, m/z (ion, relative intensity): 499 (M, 55), 350 (M − 5CO, 100). Anal. Calcd for $C_{10}H_4BrO_5PW$: C, 24.07; H, 0.81. Found: C, 24.01; H, 0.93.

2,4,6-Tribromophosphinine (4). A solution of bromine (9.6 g, 6 × 10^{-2} mol, 3.5 equiv) in 10 mL of CH_2Cl_2 was added slowly (10 min) to bromophosphinine **1a** (3.0 g, 1.71 × 10^{-2} mol) in 100 mL of CH_2Cl_2 at −20 °C. After 10 min of stirring at −20 °C, the solution was warmed to room temperature and diluted with THF (50 mL). After cooling to −20 °C, triethylamine (9.6 g, 8.55 × 10^{-2} mol, 5.0 equiv) was added over a 5-min period and the mixture was stirred for 1 h before being returned gently to 25 °C (30 min). The solvents and the excess of triethylamine were then evaporated, and the black residue was quickly purified by chromatography on silica gel with hexane as the eluent. Yield: 3.70 g (65%), white solid. Mp: 90 °C. ^{31}P NMR ($CDCl_3$): δ 195.97. ^{1}H NMR ($CDCl_3$): δ 8.21 (d, 2H, ^3J(H–P) = 4.54, H_3 and H_5). ^{13}C NMR ($CDCl_3$): δ 126.34 (d, ^3J(C–P) = 15.35, C_4), 139.32 (d, ^2J(C–P) = 14.54, C_3 and C_5), 154.71 (d, ^1J(C–P) = 75.91, C_2 and C_6). Mass spectrum, m/z (ion, relative intensity): 332 (M − 1, 100). Anal. Calcd for $C_5H_2Br_3P$: C, 18.03; H, 0.61. Found: C, 18.25; H, 0.75.

General Procedure for the Preparation of 6–10. Method A Using PPh_3 as the Ligand. Tribromophosphinine (5 × 10^{-3} mol of 4 or 5) was added at room temperature to $Pd(PPh_3)_4$ prepared in situ from $Pd(dba)_2$ (0.14 g, 2.5 × 10^{-4} mol, 5 mol %) and PPh_3 (0.26 g, 1.0 × 10^{-3} mol, 0.2 equiv) in 30 mL of toluene. After 10 min of stirring, the stannane (1.5 × 10^{-2} mol, 3 equiv) was added and the flask was immersed in a bath at 130 °C. After 5 h for **6** and **7**, 4 h for **8**, 3 h for **9**, and 10 h for **10**, the flask was cooled to room temperature and the solution was concentrated in vacuo. The black residue was then dissolved in dichloromethane (5 mL), silica gel (ca. 2 g per 1 g of oil) was added, and the dichloromethane was removed under reduced pressure. The coated silica gel was then loaded onto the top of a silica gel packed flash column for chromatography. For the synthesis of **9**, 1.25 × 10^{-4} mol of $Pd(dba)_2$ and 5 × 10^{-4} mol of PPh_3 were also used successfully.

Method B Using (2-furyl)$_3$P as the Ligand. The procedure is analogous to method A. Tribromophosphinine (5 × 10^{-3} mol) was added to a THF solution (30 mL) containing $Pd(dba)_2$ (2.5 × 10^{-4} mol, 5 mol %) and (2-furyl)$_3$P (0.11 g, 5 × 10^{-4} mol, 0.1 equiv). After 10 min of stirring, the corresponding stannane (1.5 × 10^{-2} mol, 3 equiv) was added and the solution was heated (at 80 °C for the preparation of **6** and **7** and at 70 °C for the preparation of **8** and **9**). After 8 h for **6** and **7** (4 h for **8** and 2 h for **9**), the flask was cooled, the solution was concentrated, and the residue was chromatographed. For the preparation of **9**, 1.25 × 10^{-4} mol of $Pd(dba)_2$ and 2.5 × 10^{-4} mol of (2-furyl)$_3$P were also used successfully.

2,6-Bis(2-thienyl)-4-bromophosphinine (6). Phosphinine **6** was isolated after chromatography with hexane as the eluent. Yield: 0.85 g (50%, method A), 0.71 g (42%, method B), yellow solid. Mp: 75 °C. ^{31}P NMR ($CDCl_3$): δ 174.88. ^{1}H NMR ($CDCl_3$): δ 7.10–7.50 (m, 6H, CH of 2 × C_4H_3S), 8.03 (d, 2H, ^3J(H–P) = 5.20, H_3 and H_5). ^{13}C NMR ($CDCl_3$): δ 125.19 (d, ^3J(C–P) = 15.36, C_3' of C_4H_3S), 127.11 (d, ^3J(C–P) = 16.0, C_4), 127.74 (d, ^4J(C–P) = 4.98, C_5' of C_4H_3S), 129.13 (s, C_4' of C_4H_3S), 133.49 (d, ^2J(C–P) = 12.24, C_3), 145.30 (d, ^2J(C–P) = 29.44, C_2' of C_4H_3S), 164.71 (d, ^1J(C–P) = 53.14, C_2). Mass spectrum, m/z (ion, relative intensity): 340 (M, 100). Anal. Calcd for $C_{13}H_8BrPS_2$: C, 45.92; H, 2.36. Found: C, 45.67; H, 2.19.

2,6-Bis(2-thienyl)-3-methyl-4-bromophosphinine (7). Phosphinine **7** was isolated after chromatography with hexane as the eluent. Yield: 1.14 g (65%, method A), 1.24 g (70%, method B), yellow solid. Mp: 100 °C. ^{31}P NMR ($CDCl_3$): δ 191.79. ^{1}H NMR ($CDCl_3$): δ 2.59 (d, 3H, ^4J(H–P) = 2.15, Me), 7.01–7.46 (m, 6H, 2 × C_4H_3S), 8.27 (d, 1H, ^3J(H–P) = 4.83, H_5). ^{13}C NMR ($CDCl_3$): δ 23.47 (s, Me), 124.99 (d, ^3J(C–P) = 14.90, C_7' of C_4H_3S), 126.71 (d, ^5J(C–P) = 4.54, C_9 of C_4H_3S), 127.02 (s, C_4' or C_5' of C_4H_3S), 127.43 (s, C_5' or C_4' of C_4H_3S), 127.88 (s, C_3' of C_4H_3S), 128.53 (s, C_8' of C_4H_3S), 130.63 (d, ^3J(C–P) = 15.49, C_4), 141.80 (d, ^2J(C–P) = 12.67, C_3), 143.30 (d, ^2J(C–P) = 30.95, C_2' or C_6' of C_4H_3S), 144.35 (d, ^2J(C–P) = 27.24, C_6' or C_2' of C_4H_3S),

(17) Prischenko, A. A.; Gromov, A. V.; Lusikov, Y. N.; Borisenko, A. A.; Lazhko, E. I.; Klaus, K.; Lutsenko, I. F. *J. Gen. Chem. USSR* **1984**, *54*, 1354.
(18) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1990**, *28*, 110.
(19) Allen, D. W.; Taylor, B. F. *J. Chem. Soc., Dalton Trans.* **1982**, 51.
(20) Gopinatham, S.; Gopinatham, G.; Gupta, J. *Indian J. Chem.* **1974**, *12*, 623.
(21) Kubevics, E.; Erchak, N. P.; Popelis, J.; Dipaus, I. *Zh. Obshch. Khim.* **1977**, *47*, 802.
(22) Bailey, T. R. *Tetrahedron Lett.* **1986**, *37*, 4407.
(23) Yamamoto, Y.; Yanagi, A. *Heterocycles* **1981**, *16*, 1161.
(24) (a) Jones, K.; Lappert, M. F. *J. Organomet. Chem.* **1965**, *3*, 295. (b) Mitchell, T. N. *J. Organomet. Chem.* **1977**, *141*, 289. (c) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138.
(25) Appel, R.; Geisler, K. *J. Organomet. Chem.* **1976**, *112*, 61.

160.72 (d, ^1J(C–P) = 52.75, C_2 or C_6), 163.29 (d, ^1J(C–P) = 50.28, C_6 or C_2). Mass spectrum, *m/z* (ion, relative intensity): 353 (M, 100). Anal. Calcd for $C_{14}H_{10}BrPS_2$: C, 47.63; H, 2.85. Found: C, 47.44; H, 2.94.

2,6-Bis(2-furyl)-3-methyl-4-bromophosphinine (8). Phosphinine **8** was isolated after chromatography with hexane as the eluent. Yield: 0.80 g (50% method A), 0.96 g (60%, method B), yellow solid. Mp: 120 °C. ^{31}P NMR ($CDCl_3$): δ 185.11. ^{1}H NMR ($CDCl_3$): δ 2.59 (d, 3H, ^4J(H–P) = 2.1, Me), 6.49–6.54 (m, 2H, H_3' and H_7' of C_4H_3O), 6.59 (ddd, 1H, ^5J(H–P) = ^3J(H–H) = 0.87, ^3J(H–H) = 3.31, H_4' or H_8' of C_4H_3O), 6.88 (bd, 1H, ^3J(H–H) = 3.38, H_8' or H_4' of C_4H_3O), 7.52–7.54 (m, 1H, H_5' or H_9' of C_4H_3O), 7.59–7.61 (m, 1H, H_9' or H_5' of C_4H_3O), 8.36 (d, 1H, ^3J(H–P) = 4.93, H_5). ^{13}C NMR ($CDCl_3$): δ 24.20 (s, Me), 107.354 (d, ^3J(C–P) = 12.20, C_3' or C_7' of C_4H_3O), 111.25 (d, ^3J(C–P) = 10.55, C_7' or C_3' of C_4H_3O), 112.20 (s, C_4' or C_8' of C_4H_3O), 112.90 (s, C_8' or C_4' of C_4H_3O), 131.54 (d, ^3J(C–P) = 13.57, C_4), 133.79 (d, ^2J(C–P) = 13.99, C_5), 141.72 (d, ^2J(C–P) = 13.67, C_3), 143.93 (d, ^4J(C–P) = 13.99, C_5' or C_9' of C_4H_3O), 143.99 (d, ^4J(C–P) = 13.57, C_9' or C_5' of C_4H_3O), 154.72 (d, ^2J(C–P) = 30.67, C_2' or C_6' of C_4H_3O), 154.83 (d, ^2J(C–P) = 30.92, C_6' or C_2' of C_4H_3O), 156.54 (d, ^1J(C–P) = 50.15, C_2 or C_6), 159.05 (d, ^1J(C–P) = 48.62, C_6 or C_2). Mass spectrum, *m/z* (ion, relative intensity): 320 (M – 1, 100). Anal. Calcd for $C_{14}H_{10}BrO_2P$: C, 52.38; H, 3.14 Found: C, 52.40; H, 3.39.

2,6-Bis(*N*-methyl-2-pyrolyl)-3-methyl-4-bromophosphinine (9). Phosphinine **9** was isolated after chromatography with hexane/CH_2Cl_2 (5/1) as the eluent. Yield: 1.12 g (65%, method A), 1.30 g (75%, method B), yellow oil. ^{31}P NMR ($CDCl_3$): δ 199.47. ^{1}H NMR ($CDCl_3$): 2.38 (d, 3H, ^4J(H–P) = 2.19, Me), 3.44 (s, 3H, N–Me), 3.81 (d, 3H, ^5J(H–P) = 0.6, N–Me), 6.15–6.40 (m, 4H, H_3', H_7', H_4', H_8' of 2 × C_5H_6N), 6.81 (m, 2H, H_5', H_9' of C_5H_6N), 8.17 (d, 1H, ^3J(H–P) = 4.77, H_5). ^{13}C NMR ($CDCl_3$): δ 23.48 (s, Me), 34.79 (s, N–Me), 36.41 (d, ^4J(C–P) = 10.28, N–Me), 108.43 (s, C_4' or C_8' of C_5H_6N), 108.99 (s, C_8' or C_4' of C_5H_6N), 110.90 (d, ^3J(C–P) = 6.07, C_3' or C_7' of C_5H_6N), 111.07 (d, ^3J(C–P) = 4.86, C_7' or C_3' of C_5H_6N), 126.42 (s, C_5' or C_9' of C_5H_6N), 129.69 (d, ^4J(C–P) = 2.64, C_9' or C_5' of C_5H_6N), 130.08 (d, ^3J(C–P) = 13.66, C_4), 133.58 (d, ^2J(C–P) = 30.55, C_2' or C_6' of C_5H_6N), 134.61 (d, ^2J(C–P) = 24.50, C_6' or C_2' of C_5H_6N), 138.57 (d, ^2J(C–P) = 10.63, C_5), 143.01 (d, ^2J(C–P) = 11.93, C_3), 160.54 (d, ^1J(C–P) = 56.20, C_2 or C_6), 162.31 (d, ^1J(C–P) = 50.42, C_6 or C_2). Mass spectrum, *m/z* (ion, relative intensity): 346 (M – 1, 100). Anal. Calcd for $C_{16}H_{16}BrN_2P$: C, 55.38; H, 4.64. Found: C, 55.22; H, 4.87.

2-Pyridyl-3-methyl-4,6-dibromophosphinine (10). Phosphinine **10** was isolated after chromatography with hexane/Et_2O (5/1) as the eluent. Yield: 0.70 g (40%, method A), orange solid (slightly air sensitive). ^{31}P NMR ($CDCl_3$): δ 200.47. ^{1}H NMR ($CDCl_3$): δ 2.45 (d, 3H, ^4J(H–P) = 1.97, Me), 7.72 (d, 1H, ^3J(H–H) = 7.85, H_3' of C_5H_5N), 7.84 (dd, 1H, ^3J(H–H) = 7.85, ^3J(H–H) = 4.72, H_5' of C_5H_5N), 8.32 (t, 1H, ^3J(H–H) = 7.85, H_4' of C_5H_5N), 8.50 (d, 1H, ^3J(H–H) = 4.72, H_6' of C_5H_5N), 8.97 (d, 1H, ^3J(H–P) = 5.41, H_5). ^{13}C NMR ($CDCl_3$): δ 23.75 (s, Me), 124.50 (s, C_5' of C_5H_5N), 126.50 (d, ^3J(C–P) = 7.02, C_3' of C_5H_5N), 130.97 (d, ^3J(C–P) = 15.65, C_4), 140.91 (s, C_4' of C_5H_5N), 141.99 (d, ^2J(C–P) = 12.49, C_3), 142.69 (d, ^2J(C–P) = 13.34, C_5), 146.92 (s, C_6' of C_5H_5N), 149.56 (d, ^1J(C–P) = 48.29, C_6), 156.80 (d, ^2J(C–P) = 27.05, C_2'), 168.54 (d, ^1J(C–P) = 68.54, C_2). Mass spectrum, *m/z* (ion, relative intensity): 344 (M – 1, 100).

2,6-Bis(phenylethynyl)-3,4-dimethylphosphinine (11). Dibromophosphinine **3** (2.0 g, 7.11 × 10^{-3} mol) was added at room temperature to a solution of $Pd(PPh_3)_4$ prepared in situ from $Pd(dba)_2$ (0.20 g, 3.55 × 10^{-4} mol, 5 mol %) and triphenylphosphine (0.37 g, 1.42 × 10^{-3} mol, 0.2 equiv) in 20 mL of THF. After a period of 10 min at room temperature, (phenylethynyl)trimethylstannane (3.70 g, 1.42 × 10^{-2} mol, 2 equiv) was added and the flask was immersed in a bath at 85 °C. After 3 h of stirring at this temperature, the flask was cooled and the solution was concentrated in vacuo. The black residue obtained was then purified by chromatography on silica gel (see method A) with hexane/CH_2Cl_2 (4/1) as the eluent. Yield: 1.95 g (85%), white powder. Mp: 145 °C. ^{31}P NMR ($CDCl_3$): δ 220.82. ^{1}H NMR ($CDCl_3$): δ 2.49 (d, 3H, J(H–P) = 3.5, Me), 2.70 (d, 3H, J(H–P) = 2.35, Me), 7.42–7.48 (m, 6H of 2 × C_6H_5), 7.61–7.67 (m, 4H of 2 × C_6H_5), 7.85 (d, 1H, ^3J(H–P) = 5.23, H_5). ^{13}C NMR ($CDCl_3$): δ 20.33 (s, Me), 23.71 (s, Me), 90.37 (d, J(C–P) = 31.32, ≡C—), 90.99 (d, J(C–P) = 30.76, ≡C—), 96.42 (d, J(C–P) = 7.28, ≡C—), 100.76 (d, J(C–P) = 7.85, ≡C—), 129.02 (s, CH of 2 × C_6H_5), 132.07, 132.15, 132.2 (s, CH of 2 × C_6H_5), 134.15, 134.55 (s, C ipso of C_6H_5), 139.49 (d, ^2J(C–P) = 11.80, C_5), 140.74 (d, J(C–P) = 13.07, C_4 or C_3), 145.74 (d, J(C–P) = 12.49, C_3 or C_4), 148.66 (d, ^1J(C–P) = 44.53, C_2 or C_6), 150.00 (d, ^1J(C–P) = 46.94, C_6 or C_2). Mass spectrum, *m/z* (ion, relative intensity): 325 (M + 1, 100). Anal. Calcd for $C_{23}H_{17}P$: C, 85.26; H, 5.28. Found: C, 84.57; H, 5.11.

2-(Diphenylphosphino)-3-methyl-4,6-dibromophosphinine (12). Tribromophosphinine **5** (2.5 g, 7.2 × 10^{-3} mol) was added at room temperature to a solution of (trimethylsilyl)diphenylphosphine (2.0 g, 7.92 × 10^{-3} mol, 1.1 equiv) and $Pd(dba)_2$ (0.1 g, 1.74 × 10^{-4} mol, 2.5 mol %) in 50 mL of THF. After a period of 5 min at room temperature, the flask was immersed in a bath at 50 °C. After 3 h of stirring at this temperature, the flask was cooled and the solution was concentrated in vacuo. The orange residue obtained was then purified by chromatography on silica gel with hexane/Et_2O (5/1) as the eluent. Yield: 2.76 g (85%), yellow powder (slightly sensitive toward oxidation). Mp: 120 °C. ^{31}P NMR ($CDCl_3$): δ 212.10 (d, ^2J(P–P) = 35.45 Hz, =P—), –4.86 (d, Ph_2P). ^{1}H NMR ($CDCl_3$): δ 2.48 (d, 3H, ^4J(H–P) = 1.95 Hz, Me), 7.14–7.30 (m, 10 H, 2 × C_6H_5), 8.17 (d, 1H, ^3J(H–P) = 4.21 Hz, H_5). ^{13}C NMR ($CDCl_3$): δ 24.46 (d, ^3J(C–P) = 27.57 Hz, Me), 129.11, 129.26, 129.94 (s, CH of C_6H_5), 134.62 (d, ^2J(C–P) = 18.96 Hz, C_5), 135.24 (d, ^1J(C–P) = 10.46 Hz, C ipso of C_6H_5), 141.40 (d, ^3J(C–P) = 12.58 Hz, C_4), 145.71 (dd, ^2J(C–P) = 22.05 Hz, ^2J(C–P) = 14.08 Hz, C_3), 150.18 (d, ^1J(C–P) = 77.87 Hz, C_6), 173.63 (dd, ^1J(C–P) = 80.83 Hz, ^1J(C–P) = 30.34 Hz, C_2). Anal. Calcd for $C_{18}H_{14}Br_2P$: C 47.82; H, 3.12. Found: C, 47.75; H, 3.17.

2,6-Bis(diphenylphosphino)-3-methyl-4-bromophosphinine (13). Tribromophosphinine **5** (0.50 g, 1.44 × 10^{-3} mol) was added at room temperature to a solution of (trimethylsilyl)diphenylphosphine (0.82 g, 3.16 × 10^{-3} mol, 2.2 equiv) and $Pd(dba)_2$ (0.04 g, 7.2 × 10^{-5} mol, 5 mol %) in 10 mL of THF. After a period of 5 min at room temperature, the flask was immersed in a bath at 90 °C. After 4 h, the flask was cooled, the black solution was concentrated in vacuo, and the residue was quickly purified by chromatography (see method A) on degassed silica gel. A first fraction eluted with hexane yielded a small amount of diphenylphosphine and a second fraction eluted with hexane/Et_2O (5/1) yielded **13**. Yield: 0.7 g (80%), yellow powder (slightly sensitive toward oxidation). Mp: 150 °C. ^{31}P NMR ($CDCl_3$): δ 239.09 (dd, ^2J(P–P_2) = 36.6, ^2J(P–P_6) = 158.6, =P—), –2.32 (d, P_6), –2.43 (d, P_2). ^{1}H NMR ($CDCl_3$): δ 2.82 (d, 3H, ^4J(H–P) = 1.89, Me), 7.34–7.64 (m, 20H, 4 × C_6H_5), 8.12 (dd, 1H, ^3J(H–P_6) = 9.32, ^3J(H–P) = 5.93, H_5). ^{13}C NMR ($CDCl_3$): δ 25.27 (d, ^3J(H–P_2) = 27.50, Me), 128.85–130.28 (m, CH of 4 × C_6H_5 and C_4), 134.07–135.11 (m, CH of 4 × C_6H_5), 136.13 (t, J(C–P) = 9.75, C ipso of C_6H_5), 137.41 (dd, J(C–P) = 13.17, J(C–P) = 9.24, C ipso of C_6H_5), 143.39 (dd, ^2J(C–P) = 10.39, ^2J(C–P) = 15.11, C_5), 147.45 (dd, ^2J(C–P) = 22.69, ^2J(C–P) = 12.32, C_3), 167.57 (dd, ^1J(C–P) = 73.25, ^1J(C–P) = 30.52, C_2 or C_6), 171.73 (ddd, ^1J(C–P) = 85.45, ^1J(C–P) = 27.46, ^3J(C–P) = 12.21, C_6 or C_2). Mass spectrum, *m/z* (ion, relative intensity): 557 (M, 32), 477 (M – Br, 13), 183 (M – 2PPh_2 – 4, 100).

General Procedure for the Preparation of 14 and 15. Bromophosphinine **1b** or **2** (5 × 10^{-3} mol) was added at room temperature to a solution of (trimethylsilyl)diphenylphosphine (1.63 g, 6.35 × 10^{-3} mol, 1.3 equiv) and $Pd(dba)_2$ (0.15 g, 2.64 × 10^{-4} mol, 5 mol %) in 10 mL of toluene. After 5 min of stirring at room temperature, the flask was immersed in a bath at 130 °C. After 2 h, the flask was cooled, the mixture was concentrated in vacuo, and the residue was quickly chromatographed (see method A) on silica gel. A first fraction eluted with hexane yielded small amounts of diphenylphosphine and traces of unreacted bromophosphinine. A second fraction eluted with hexane/Et_2O (9/1) yielded **14** or **15**. **15**, which has been already characterized (see ref 4), was recovered as a yellow viscous oil. Yield: 1.08 g (75%). **14** was recovered as a yellow powder. Yield: 1.00 g (70%). Mp: 70 °C. ^{31}P NMR: δ 222.90 (d, ^2J(P–P) = 30.55, =P—), –7.32 (d, PPh_2). ^{1}H NMR ($CDCl_3$): δ 2.60 (t, 3H, ^4J(H–P) = ^4J(H–P_2) = 1.92, Me), 7.25–7.47 (m, 11H, CH of 2 × C_6H_5 and H_4), 7.79 (dt, 1H, ^3J(H–H) = 9.95, ^3J(H–H) = ^3J(H–P) = 8.18, H_5), 8.63 (dd, 1H, ^2J(H–P) = 40.31, ^3J(H–H) = 9.95, H_6). ^{13}C NMR ($CDCl_3$): δ 24.74 (d, ^3J(C–P) = 25.15, Me), 128.95, 129.09, 129.49, (s, CH of 2 × C_6H_5), 132.11 (dd, J(C–P) = 18.34, J(C–P) = 3.89, C ipso of C_6H_5), 133.70 (d, ^1J(C–P) = 12.07, C ipso of C_6H_5), 134.79 (d, J(C–P) = 20.36, C_4 or C_5), 136.52 (t, J(C–P) = J(C–P_2) = 9.29, C_5 or C_4), 148.53 (dd, ^2J(C–P) = 13.48, ^2J(C–P) = 22.81, C_3), 153.08 (d, ^1J(C–P) = 57.61, C_6), 167.14 (dd, ^1J(C–P) = 75.95, ^1J(C–P_2) = 23.53, C_2). Mass spectrum, *m/z* (ion, relative intensity): 294 (M, 100). Anal. Calcd for $C_{18}H_{16}P_2$: C, 73.46; H, 5.48. Found: C, 73.26; H, 5.19.

Complexation of Phosphinines 13 and 14 with $W(CO)_5$(THF). Phosphinines **13** or **14** (1 × 10^{-3} mol) diluted in 10 mL of THF were added to a solution of $W(CO)_5$ in THF (2.2 × 10^{-3} mol prepared from 0.70 g of $W(CO)_6$ in 120 mL of THF by irradiation at 254 nm). After 15 min of stirring at room temperature, the THF was evaporated under

reduced pressure and the orange–brown residue was purified by chromatography on silica gel (see method A). A first fraction eluted with hexane yielded a small amount of $W(CO)_6$ and a second fraction eluted with hexane/CH_2Cl_2 (1/1) (for **16**) or hexane/CH_2Cl_2 (9/1) (for **17**) yielded the complex as a yellow powder. **16**: Yield: 1.00 g (85%). Mp: 180 °C. ^{31}P NMR ($CDCl_3$): δ 236.20 (dd, ^2J(P–P) = 108.19, ^2J(P–P) = 124.64, =P—), 27.27 (d, $^2J(^{31}P\text{-}^{183}W)$ = 245.47, $Ph_2P\rightarrow W(CO)_5$), 23.63 (d, $^1J(^{31}P\text{–}^{183}W)$ = 249.36, $Ph_2P\rightarrow W(CO)_5$). ^1H NMR ($CDCl_3$): δ 2.51 (d, 3H, ^4J(H–P) = 1.34, Me), 7.38–7.63 (m, 20H, CH of 4 × C_6H_5), 8.14 (dd, ^3J(H–P) = 14.28, ^3J(H–P) = 5.07, H_5). ^{13}C NMR ($CDCl_3$): δ 29.42 (d, ^3J(C–P) = 9.6, Me), 128.91, 129.09, 129.28 (s, CH of C_6H_5), 130.87, 131.08 (s, CH of C_6H_5), 131.62 (d, ^3J(C–P) = 12.06, C_4), 132.91, 133.15 (s, CH of C_6H_5), 133.78, 134.02 (CH of C_6H_5), 134.33, 134.68, 134.78, 134.98, 135.13, 135.47, 135.58 (C ipso of C_6H_5, J(C–P) not estimated), 143.52 (t, ^2J(C–P) = 8.08, C_5), 147.55 (dd, ^2J(C–P) = 11.13, ^2J(C–P) = 7.41, C_3), 164.37 (ddd, ^1J(C–P) = 75.6, ^1J(C–P) = 20.46, ^3J(C–P) = 10.46, C_2 or C_6), 168.02 (ddd, ^1J(C–P) = 82.91, ^1J(C–P) = 20.27, ^3J(C–P) = 12.82, C_6 or C_2). Anal. Calcd for $C_{40}H_{24}BrO_{10}P_3W_2$: C, 39.86; H, 2.01. Found: C, 40.05; H, 1.90. **17**: Yield: 0.50 g (75%). Mp: 125 °C. ^{31}P NMR ($CDCl_3$): δ 178.05 (d, ^2J(P–P) = 44.47, $^1J(^{31}P\text{–}^{183}W)$ = 262.65, =P→W(CO)$_5$), 24.01 (d, $^1J(^{31}P\text{–}^{183}W)$ = 344.8, $Ph_2P\rightarrow W(CO)_5$). ^1H NMR ($CDCl_3$): δ 2.29 (d, 1H, ^4J(H–P) = 4, Me), 7.34–7.90 (m, 12H, CH of C_6H_5, H_4 and H_5), 8.78 (ddd, 1H, ^2J(H–P) = 31.22, ^3J(H–H) = 10.02, ^4J(H–P) = 4.57, H_6). Anal. Calcd for $C_{28}H_{16}O_{10}P_2W_2$: C, 35.68; H, 1.71. Found: C, 35.52; H, 1.49.

2,4-Dibromo-5-methylphosphinine (20). Tribromophosphinine **5** (1 g, 2.88 × 10^{-3} mol) was added at room temperature to a solution of $Pd(PPh_3)_4$ prepared in situ from $Pd(dba)_2$ (0.04 g, 7.2 × 10^{-5} mol, 2.5 mol %) and PPh_3 (0.075 g, 2.88 × 10^{-4} mol, 0.1 equiv) in 15 mL of toluene. After 2 min of stirring, Bu_3SnH (1.25 g, 4.32 × 10^{-3} mol, 1.5 equiv) was added and the resulting solution was heated at 110 °C for 1 h. After cooling and evaporation of the solvent in vacuo, the viscous residue was purified by chromatography on silica gel with pentane as the eluent. Phosphinine **20** was recovered as a slightly air-sensitive colorless oil. Yield: 0.54 g (70%). ^{31}P NMR ($CDCl_3$): δ 203.48. ^1H NMR ($CDCl_3$): see text. Mass spectrum, m/z (ion, relative intensity): 267 (M, 100).

X-ray Structure Determination for 7. Crystals of **7**, $C_{14}H_{10}BrPS_2$, were grown at −18 °C from an ether solution of the compound. Data were collected at −150 ± 0.5 °C on an Enraf Nonius CAD4 diffractometer. The crystal structure was solved and refined using the Enraf Nonius MOLEN package. The compound crystallizes in space group $P2_1/m$: a = 9.939(1) Å, b = 7.018(1) Å, c = 10.411(1) Å, β = 109.21(1)°; V = 685.74(27) Å^3; Z = 2; d_{calcd} = 1.711 g/cm^3; Cu Kα radiation (λ = 1.541 84 Å), graphite monochromator; μ = 78.7 cm^{-1}; F(000) = 352. A total of 1458 unique reflections were recorded in the range $2° \leq 2\theta \leq 150.0°$, of which 75 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 1383 for solution and refinement. A direct method solution of the structure yielded a model for the phosphinine ring and one of the thiophene moieties. One of the thiophene rings and the phosphinine are contained in a plane of symmetry; the second thiophene is perpendicular to that plane. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were R = 0.052, R_w = 0.092, and GOF = 2.18.

Supplementary Material Available: Tables of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.