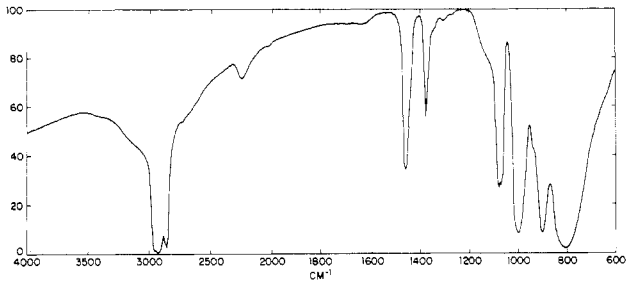

Figure 2. Infrared spectrum (mineral oil mull) of $(HO)_3W_{12}PO_{37}$.

Pure anhydrous phosphotungstic acid, exhibiting only the -11.0 ppm ^{31}P MAS NMR line (Figure 1c) was easily prepared by thermolysis of the hydrated acid (^{31}P, δ -14.7) at 215 °C under vacuum. The infrared spectrum of this material (Figure 2) is the same as that of the 215 °C thermolysis products of the alkyloxonium salts or the neutral esters referred to above.

Anhydrous phosphotungstic acid has been reported previously, and portions of its infrared spectra have been discussed.[3-5] One report[4] states that there is no appreciable difference between the anion absorption of the hydrated and dehydrated acids; another[3] reports that frequency changes occur in the 600-1100-cm^{-1} region upon dehydration. We agree with the latter except that we also note loss of degeneracy of the P-O stretching band, which would be expected upon protonation of the anion, and a new weak band at 2246 cm^{-1}. We have been unable to assign this band. It would be unreasonable to expect an O-H band at this frequency; nevertheless, we prepared $D_3W_{12}PO_{40}\cdot nD_2O$ and converted it to $(DO)_3W_{12}PO_{37}$ at 215 °C. The 2246-cm^{-1} band did not shift. We also observe a similar band in the spectrum of silicotungstic acid that has been thermolyzed at 205 °C under vacuum.

Other features of note in the infrared spectrum of $(HO)_3W_{12}PO_{37}$ are the absence of a normal water deformation band in the 1700-cm^{-1} region and a very broad band for hydrogen-bonded OH extending from about 3600 to 2400 cm^{-1}. The latter is more easily seen in a hexachlorobutadiene mull spectrum than in Figure 2, which is a mineral oil mull spectrum. It has also been discussed extensively by others.[3,4] $(HO)_3W_{12}PO_{37}$ dissolves easily in water, and normal $W_{12}PO_{40}^{3-}$ salts can be precipitated quantitatively from the solutions.

The infrared spectra of the $(RO)_3W_{12}PO_{37}$ esters are similar to that of $(HO)_3W_{12}PO_{37}$ except they lack the OH absorption as well as the band at 2246 cm^{-1}.

The question as to whether or not anhydrous phosphotungstic acid is truly anhydrous $(HO)_3W_{12}PO_{37}$ or is a partially hydrated species such as $H_3O(HO)_2W_{12}PO_{38}$ cannot be answered by analysis. We prefer the anhydrous formulation because of the preparation of the acid by thermolysis of the trialkyloxonium salts. These salts show no evidence of hydration and would not be expected to be hydrated because the excess trialkyloxonium cations present during their preparation (note that $[(CH_3)_3O]_3W_{12}PO_{40}$ was prepared from $[(Hex)_4N]_3W_{12}PO_{40}$ and $(CH_3)_3OBF_4$ in dichloroethane[1]) should serve as effective dehydrating agents. It is difficult to see how α- or β-elimination reactions from these anhydrous salts could lead to a hydrated acid.

Experimental Section

Hydrated phosphotungstic and silicotungstic acids were obtained from Fisher Scientific Co. The preparation of $[(CH_3)_3O]_3W_{12}PO_{40}$ has been reported previously.[1] Infrared spectra were determined on a Perkin-Elmer 983 as mineral oil mulls unless otherwise noted. Solid-state ^{31}P NMR spectra were obtained at 121.4 MHz on a Bruker CXP-300 spectrometer. A Bruker MAS probe with 9-mm Delrin rotors was used. The observe coil was replaced with 3 $^1/_2$ turns of 14 gauge Au-plated Cu wire (11 mm i.d., 8 mm long). Magic-angle spinning at 4 kHz produces spectra free of detectable spinning sidebands, indicating that the chemical shift anisotropy is small, as expected for nearly symmetrical PO_4^{3-} groups.[6] Quantitative spectra were obtained with 30-90° pulses with a 4-10-s recycle delay, depending on the ^{31}P T_1 of the sample. Proton decoupling (γH_2 = 40 kHz) was employed. Proton cross-polarization was not used to obtain the quantitative spectra shown here but yields nonquantitative spectra more quickly (5-ms cross-polarization, 2-s recycle). Chemical shifts are reported in ppm downfield from external 85% phosphoric acid with an estimated precision of ±0.2 ppm. It is expected that the ^{31}P chemical shifts of the central phosphate groups in these compounds are well shielded from solvent effects so can be directly compared to solution values.

$[(C_2H_5)_3O]_3W_{12}PO_{40}$. Triethyloxonium tetrafluoroborate (6.0 g, 31.6 mmol) was added to a solution of phosphotungstic acid (14 g, 4.7 mmol) in acetonitrile (50 mL) in a nitrogen atmosphere. The mixture was stirred for 15 min and then filtered to obtain 12 g (80%) of $[(C_2H_5)_3O]_3W_{12}PO_{40}$, which was washed three times with acetonitrile and dried under vacuum at room temperature. The infrared spectrum was normal for a salt of $W_{12}PO_{40}^{3-}$. Anal. Calcd for $[(C_2H_5)_3O]_3W_{12}PO_{40}$: C, 6.78; H, 1.42. Found: C, 6.88, 6.86; H, 1.50, 1.47.

$(C_2H_5O)_3W_{12}PO_{37}$. One gram of $[(C_2H_5)_3O]_3W_{12}PO_{40}$ was heated at 150 °C under vacuum (nominal 0.1 mm) for 16 h to leave $(C_2H_5O)_3W_{12}PO_{37}$. Anal. Calcd for $(C_2H_5O)_3W_{12}PO_{37}$: C, 2.43; H, 0.51; O, 21.6; W, 74.4; P, 1.04. Found: C, 2.70, 2.76; H, 0.66; 0.66; O, 21.8, 22.0; W, 74.1, 74.9; P, 1.70, 1.60.

The infrared and ^{31}P MAS spectra and the slight contamination by $(HO)_3W_{12}PO_{37}$ they reveal are discussed above.

$(CH_3O)_3W_{12}PO_{37}$. $[(CH_3)_3O]_3W_{12}PO_{40}$ (4.8 g) was heated as above to leave 4.4 g of a solid residue that was primarily $(CH_3O)_3W_{12}PO_{37}$ by spectroscopic characterization as discussed above.

$(HO)_3W_{12}PO_{37}$. Hydrated phosphotungstic acid (20 g) was heated at 215 °C under vacuum (nominal 0.1 mm) for 16 h to leave a solid residue of $(HO)_3W_{12}PO_{37}$. Anal. Calcd for $(HO)_3W_{12}PO_{37}$: W, 76.6; O, 22.2. Found: W, 76.3, 76.0; O, 23.0, 23.2. Samples of $[(C_2H_5)_3O]_3W_{12}PO_{40}$ and $[(CH_3)_3O]_3W_{12}PO_{40}$ were thermolyzed similarly at 215 °C. The infrared spectra of the products were identical with that of $(HO)_3W_{12}PO_{37}$. The 215 °C thermolysis product from $[(C_2H_5)_3O]_3W_{12}PO_{40}$ (4.5 g) was stirred in water (15 mL) and filtered to remove 0.18 g of insoluble material. Addition of cesium chlorde to the filtrate precipitated $Cs_3W_{12}PO_{40}$ (4.5 g (97%)), identified by infrared analysis.

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Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Unsymmetrical, Chelating Ligands. Synthesis of 1-Mercapto-2-phosphinobenzenes with a Variety of Substituents on the Ligating Sites

Evan P. Kyba* and Clyde N. Clubb

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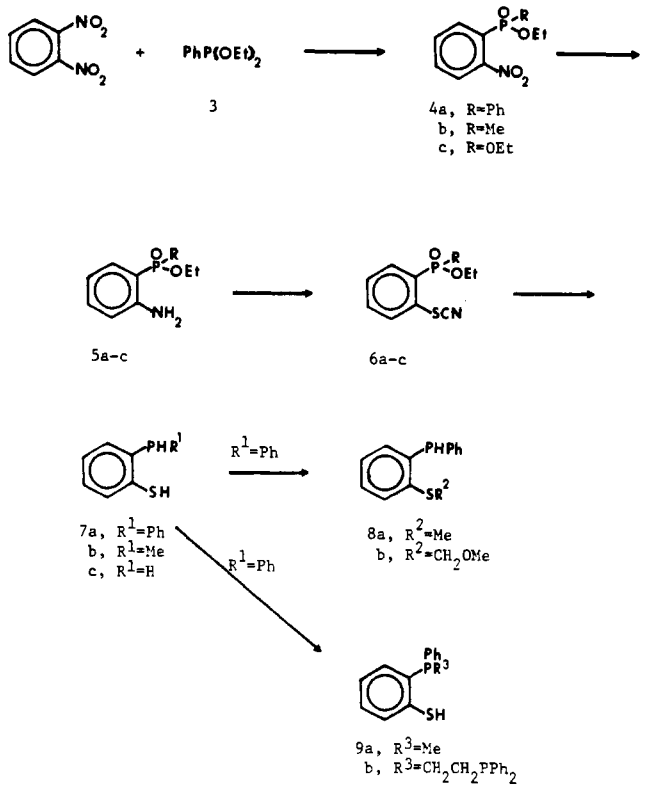
The synthesis of *o*-phenylenebis(ligand) (where L and L^1 contain heteroatoms such as phosphorus, arsenic, sulfur, ni-

Scheme I



trogen, and oxygen) of type **1** has been of interest to coordination chemists for a long time.[1] In general it is consid-

1 2

erably easier to synthesize symmetrical species (L = L^1)[2] than unsymmetrical ones, since in the latter, at some point in the synthesis, the two ortho positions must be differentiated, although there exist a number of different approaches to this problem.[1a] An even more difficult problem is the synthesis of species **2**, where the heteroatoms (i.e. ligands) are different and where each ligating site bears at least one hydrogen atom.[3] Such substitution would allow the elaboration of the ligating sites by S_N2-type chemistry,[4] as well as the formation of bis(μ-ligand) binuclear transition-metal complexes.[5]

Results and Discussion

We now report a synthesis of **2** with L = S and L^1 = PR that has reasonable generality. The first and key step, which forms the carbon–phosphorus bond, is an aromatic Arbuzov-type reaction, described previously by Cadogen et al.[6] Thus the reaction of 1,2-dinitrobenzene and diethyl phenylphosphonite (**3**) in acetonitrile at room temperature for 16 h gave the crystalline phosphinate derivative **4a** in 60% yield (Scheme I). Species **4b** and **4c** were prepared as described previously.[6] The nitro groups in **4a–c** were then reduced (Fe powder, aqueous ammonium chloride) to give the amines **5a–c** in yields of ca. 80%. These were diazotized and the resulting diazonium ions were treated with potassium thiocyanate/ferric chloride to give the thiocyanates **6a–c** in crude yields of 70–90%. Reduction of **6a–c** with lithium aluminum hydride then gave the phosphino thiols **7a–c** in yields in the range of 60–70%.

We have developed conditions that allow the alkylation of either the sulfur or the phosphorus center. Thus, reaction of **7a** with methyl iodide or chloromethyl methyl ether in alcoholic potassium hydroxide gave sulfur alkylation (**8a,b**) in essentially quantitative yields.[7] In contrast, attempts to carry out an alkylation reaction with the monolithium salt (1 equiv of *n*-butyllithium) of **7a** in tetrahydrofuran gave mixtures of products.

We were even more interested in being able to alkylate the phosphorus atom in the presence of the unprotected[7] sulfur nucleophilic site. To effect this, we made use of the much higher nucleophilicity of the phosphide compared to the sulfide anion; we illustrate the procedure by describing the synthesis of two chiral ligands, **9a,b**. Treatment of **7a** with 2 equiv of *n*-BuLi at −78 °C, followed by the addition of 1 equiv of MeI and a standard workup, gave the chiral, bidentate ligand **9a** in 76% yield. A similar procedure, but with (2-chloroethyl)diphenylphosphine as the alkylating agent at 0 °C, followed by chromatographic workup, gave the chiral, functionalized derivative of the well-known, commercially available diphos ligand.

Experimental Section

General Information. Proton magnetic resonance spectra were obtained on $CDCl_3$ solutions on a Varian EM-390 or a Varian FT-80 spectrometer. Carbon-13 and proton-decoupled phosphorus-31 NMR spectra were determined on $CDCl_3$ solutions on a Varian FT-80 spectrometer at 20.1 and 32.4 MHz, respectively. Chemical shifts are given in ppm relative to Me_4Si for ^{13}C and relative to 85% H_3PO_4 for ^{31}P NMR spectra. Chemical shifts upfield of the standard are defined as negative.

Infrared spectra (IR) were recorded on a Perkin-Elmer 298 grating spectrophotometer.

Mass spectra (MS or HRMS) were determined on a CEC-21-100 high-resolution instrument or a Du Pont 21-491 instrument at 70 eV.

Unless noted, all of the reactions, manipulations, and purification steps involving phosphines were performed under a dry nitrogen or argon atmosphere. Air-sensitive liquids were transferred by Teflon flexneedles with use of nitrogen pressure or by syringe. All concentrations of solutions were carried out on a rotary evaporator under water aspiration pressures unless otherwise noted. Solutions were dried with anhydrous magnesium sulfate.

Ethyl methyl(2-nitrophenyl)phosphinate (**4b**),[6] diethyl (2-nitrophenyl)phosphonate (**4c**),[6] and diethyl (2-aminophenyl)phosphonate (**5c**)[8] were prepared as described previously.

Ethyl Phenyl(2-nitrophenyl)phosphinate (4a). Diethyl phenylphosphonite (139 g, 0.702 mol) was added over 3 h to a stirred solution of 1,2-dinitrobenzene (100 g, 0.595 mol) in acetonitrile (700 mL) at 0 °C. The resulting solution was allowed to warm to room temperature, stirred for 16 h, and then concentrated. The residue was crystallized from diethyl ether to give **4a** (103 g, 60%) as tan crystals: mp 65–68 °C (lit.[9] mp 71–72 °C); ^1H NMR δ 8.2 (m, 1 H), 7.8 (m,

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(3) Syntheses of such compounds have been published, but one step involves the photolysis of liquid ammonia solutions of 1-iodo-2-X-benzenes [X = NH_2, OH, SC(S)(OEt)], a relatively inconvenient procedure. See: (a) Issleib, K.; Vollmer, R.; Oehme, H.; Meyer, H. *Tetrahedron Lett.* **1978**, 441. (b) Issleib, K.; Vollmer, R. *Z. Chem.* **1978**, *12*, 451.
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(7) Species **8b** represents a sulfur-protected compound in which the protecting CH_2OMe group is quite stable to strong bases and acids for moderate lengths of time. Deprotection can be effected quantitatively with the use of *n*-BuS^-/DMF. For experimental details, see: Kyba, E. P.; Clubb, C. N.; Larson, S. B.; Schueler, V. J.; Davis, R. E. *J. Am. Chem. Soc.*, in press.
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5 H), 7.5 (m, 3 H), 4.1 (m, 2 H), 1.3 (t, 3 H); ^{31}P NMR δ 26.9 (s); MS *m/e* 291 (M^+).

Ethyl Phenyl(2-aminophenyl)phosphinate (5a). Ethyl phenyl(2-nitrophenyl)phosphinate (103 g, 0.354 mol) was added to a mixture of iron powder (57.3 g, 1.03 mol) and ammonium chloride (15.1 g, 0.282 mol) in water (250 mL) under reflux. The resulting mixture was stirred and boiled under reflux for 16 h and then made basic with 10% aqueous sodium hydroxide. This mixture was extracted with ethyl acetate (3 × 300 mL), and the combined organic extracts were washed with brine and 10% aqueous sodium cyanide (125 mL). The dried solution was concentrated to give crude **5a** as an orange oil (79.4 g, 85%): ^{1}H NMR δ 7.8 (m, 2 H), 7.3 (m, 5 H), 6.6 (m, 2 H), 4.3 (br s, 2 H), 4.2 (m, 2 H), 1.4 (t, J = 6 Hz, 3 H); ^{31}P NMR δ 35.5 (s); IR (neat) ν_{NH} 3320, 3420 cm^{-1}; HRMS *m/e* 261.0926 (calcd 261.0919).

Ethyl Methyl(2-aminophenyl)phosphinate (5b). Ethyl methyl(2-nitrophenyl)phosphinate (3.34 g, 14.6 mmol) was reduced as described above to give **5b** (2.2 g, 76%) as an orange oil (crude): ^{1}H NMR δ 7.2 (m, 2 H), 6.7 (m, 2 H), 5.5 (br s, 2 H), 4.0 (m, 2 H), 1.6 (d, J = 2 Hz, 3 H), 1.3 (t, J = 6 Hz, 3 H); ^{31}P NMR δ 47.1 (s); IR (CCl_4) ν_{NH} 3330, 3425 cm^{-1}; HRMS *m/e* 199.0768 (calcd 199.0762).

Ethyl Phenyl(2-thiocyanatophenyl)phosphinate (6a). Sodium nitrite (14.1 g, 0.204 mol) in water (60 mL) was added (35 min) from an ice-jacketed addition funnel to a stirred mixture of amine **3a** (53.0 g, 0.203 mol) in 6 N hydrochloric acid (200 mL), which was maintained at less than 5 °C. Ferric chloride (17.1 g, 0.105 mol) and potassium thiocyanate (63.6 g, 0.655 mol) in water (80 mL) were added, and the resulting mixture was stirred at room temperature for 2 h. The dark tarry material was then extracted with dichloromethane (3 × 300 mL), and the combined organic extracts were washed with water (5 × 300 mL) and 10% aqueous sodium cyanide (2 × 100 mL). The solution was dried and concentrated to give crude **6a** as a brown oil (50.5 g, 82%): ^{1}H NMR δ 7.9–7.2 (m, 9 H), 4.3 (m, 2 H), 1.4 (t, J = 6 Hz, 3 H); ^{31}P NMR δ 29.7 (s), 26.6 (s), ratio 8:1; IR (neat) ν_{SCN} 2140 cm^{-1}; HRMS *m/e* 303.0476 (calcd 303.0483).

Ethyl Methyl(2-thiocyanatophenyl)phosphinate (6b). Ethyl methyl(2-aminophenyl)phosphinate (12.0 g, 60.3 mmol) was diazotized and reacted with KSCN/$FeCl_3$ as described above for **6a**, with the amounts of reagents and solvents scaled down by a factor of 3.4, to give crude **6b** as an orange oil (10.6 g, 73%): ^{1}H NMR δ 8.0–7.3 (m, 4 H), 4.0 (m, 2 H), 2.7 (d, J = 1.5 Hz, 3 H), 1.3 (t, J = 6 Hz, 3 H); ^{31}P NMR δ 41.6 (s), 41.3 (s), 38.1 (s), ratio 1:12:1; IR (neat) ν_{SCN} 2160 cm^{-1}; HRMS *m/e* 241.0333 (calcd 241.0326).

Diethyl (2-Thiocyanatophenyl)phosphonate (6c). Diethyl (2-aminophenyl)phosphonate (15.4 g, 67.2 mmol) was diazotized and reacted with KSCN/$FeCl_3$ as described above for **6a**, with the amounts of reagents and solvents scaled down by a factor of 3.0, to give crude **6c** as an amber oil (16.8 g, 92%): ^{1}H NMR δ 8.1–7.2 (m, 4 H), 4.15 (m, 4 H), 1.3 (t, J = 6 Hz, 6 H); ^{31}P NMR δ +14.7 (s); IR (neat) ν_{SCN} 2170 cm^{-1}; HRMS *m/e* 271.0437 (calcd 271.0432).

1-Mercapto-2-(phenylphosphino)benzene (7a). Ethyl phenyl(2-thiocyanatophenyl)phosphinate (26.0 g, 85.8 mmol) in ether (70 mL) was added (3 h) to LAH (12.0 g, 1.26 mol H^-) in ether (200 mL) at −78 °C. The mixture was allowed to warm to room temperature, stirred for 16 h, and quenched with 12 N hydrochloric acid (50 mL) followed by water (150 mL). After the layers were separated, the aqueous portion was extracted with ether (3 × 150 mL), dried, and concentrated. The residue was distilled under vacuum to give **7a** as a colorless air-sensitive oil (39.1 g, 69%): bp 127–130 °C (20 μm); ^{1}H NMR δ 7.6–6.9 (m, 9 H), 5.2 (d, J = 222 Hz, 1 H), 3.8 (br s, 1 H); ^{31}P NMR δ −47.6 (s, ^{1}H coupled, d, J = 223 Hz); HRMS *m/e* 218.0315 (calcd 218.0319).

1-Mercapto-2-(methylphosphino)benzene (7b). Ethyl methyl(2-thiocyanatophenyl)phosphinate (3.0 g, 12.4 mmol) in THF (15 mL) was added to LAH (2.4 g, 0.25 mol) in THF (22 mL) at −78 °C. The resulting mixture was boiled under reflux for 16 h and then quenched with 6 N hydrochloric acid (30 mL). The layers were separated, and the aqueous portion was extracted with ether (3 × 30 mL). The combined organic extracts were dried, concentrated, and distilled under vacuum to give **7b** (1.2 g, 63%) as a colorless, air-sensitive oil: bp 56–58 °C (18 μm); ^{1}H NMR δ 7.5–7.0 (m, 4 H), 4.2 (br d, J = 202 Hz, 1 H), 3.8 (br s, 1 H), 1.35 (d, J = 3 Hz, 3 H); ^{31}P NMR δ −75.0 (s, ^{1}H coupled, d, J = 210 Hz); ^{13}C NMR (partial) δ 4.5 (d, J = 12.3 Hz, P–CH_3); HRMS *m/e* 156.0158 (calcd 156.0163).

1-Mercapto-2-phosphinobenzene (7c). Diethyl (2-thiocyanatophenyl)phosphonate (16.8 g, 62.0 mmol) was reduced by using the procedure described above for **7b** except that all quantities (except time) were scaled up by a factor of 5. Compound **7c** was obtained as a colorless air-sensitive liquid (5.2 g, 61%): bp 71–72 °C (410 μm) [lit.[3b] bp 74 °C (400 μm)]; ^{1}H NMR δ 7.6–6.5 (m, 4 H), 3.9 (d, J = 205 Hz, 2 H), 3.6 (s, 1 H); ^{31}P NMR δ −127.0 (s, ^{1}H coupled, dt, J = 205, 6 Hz); HRMS *m/e* 142.0003 (calcd 142.0006).

2-(Phenylphosphino)phenyl Methyl Sulfide (8a). Potassium hydroxide (4.0 g) in absolute ethanol (90 mL) and THF (90 mL) was added to 1-mercapto-2-(phenylphosphino)benzene (10.3 g, 47.3 mmol), and the resulting mixture was cooled to −78 °C. Methyl iodide (6.7 g, 47 mmol) was added, and the solution was stirred and allowed to warm to room temperature (1 h). The mixture was concentrated, and the residue was partitioned between water (50 mL) and ether (3 × 70 mL). The combined organic extracts were dried, concentrated, and distilled under vacuum to give **8a** (8.7 g, 80%) as a colorless air-sensitive oil: bp 150 °C (14 μm); ^{1}H NMR δ 7.2 (m, 9 H), 5.3 (d, J = 223 Hz, 1 H), 2.35 (s, 3 H); ^{31}P NMR δ −49.3 (s, ^{1}H coupled, d, J = 220 Hz); HRMS *m/e* 232.0479 (calcd 232.0476).

((2-(Phenylphosphino)phenyl)thio)methyl Methyl Ether (8b). Chloromethyl methyl ether (1.75 g, 21.7 mmol) was added to **7a** (4.74 g, 21.7 mmol) and potassium hydroxide (2.4 g, 42 mmol) in 95% ethanol (70 mL) at −78 °C. The resulting mixture was warmed to room temperature, concentrated, and partitioned between water (100 mL) and ether (3 × 50 mL). The ethereal extracts were dried and concentrated, and the residue was distilled under vacuum to give **8b** (4.31 g, 76%) as a colorless air-sensitive oil: bp 150–160 °C (10 μm); ^{1}H NMR δ 7.3 (m, 9 H), 5.3 (d, J = 220 Hz, 1 H), 4.83 (s, 2 H), 3.35 (s, 3 H); ^{31}P NMR δ −47.0 (s; ^{1}H coupled, d, J = 225 Hz); ^{13}C NMR (partial) δ 77.9 (d, $^4J_{PC}$ = 4 Hz), 55.9 (s); HRMS *m/e* 262.0574 (calcd 262.0581).

1-Mercapto-2-(methylphenylphosphino)benzene (9a). A solution of **7a** (2.67 g, 12.2 mmol) in ether (40 mL) at −78 °C was treated with a 1.92 M hexane solution of *n*-butyllithium (13.0 mL, 25.0 mmol) followed by methyl iodide (765 μL, 12.3 mmol) and then allowed to warm to room temperature. This mixture was quenched with 15% aqueous ammonium chloride (10 mL) and extracted with ether (3 × 50 mL), and the extract concentrated. The residue was dissolved in ether (50 mL) and extracted with 12% aqueous potassium hydroxide (20 mL). The aqueous phase was separated, acidified with 6 N hydrochloric acid, and extracted with ether (3 × 50 mL). The dried ethereal extracts were concentrated, and the residue was distilled under vacuum to give **9a** (2.15 g, 76%) as a faintly yellow oil: bp 147–151 °C (18 μm); ^{1}H NMR δ 7.2 (m, 9 H), 4.3 (br s, 1 H), 1.6 (d, $^2J_{PH}$ = 4 Hz, 3 H); ^{31}P NMR δ −34.7; ^{13}C NMR (partial) δ 11.4 (d, $^1J_{PC}$ = 14 Hz); HRMS *m/e* 232.047 02 (calcd 232.047 56).

1-Mercapto-2-((2-diphenylphosphinoethyl)phenylphosphino)benzene (9b). A solution of **7a** (1.59 g, 7.3 mmol) in THF (30 mL) at 0 °C was treated with a 2.05 M hexane solution of *n*-butyllithium (7.1 mL, 14.6 mmol), followed by (2-chloroethyl)diphenylphosphine[9] (2.65 g, 10.7 mmol) in THF (40 mL). The mixture was warmed to room temperature, stirred for 0.5 h, and then quenched with 20% aqueous ammonium chloride (5 mL). The layers were separated, and the organic layer was dried and concentrated. The oily residue was chromatographed on alumina (150 g). Elution with hexane/dichloromethane (7:3, v/v) gave the starting (2-chloroethyl)diphenylphosphine. Further elution with dichloromethane gave **9b** (1.80 g, 58%) as a slightly yellow glass: ^{1}H NMR δ 7.25 (m, 19 H), 4.05 (br s, 1 H), 2.05 (m, 4 H); ^{31}P NMR δ −12.4 (d, $^3J_{PP}$ = 33 Hz), −22.1 (d, $^3J_{PP}$ = 33 Hz); ^{13}C NMR (partial) δ 23.6 (m); HRMS *m/e* 430.1062 (calcd 430.1074).

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Registry No. **3**, 1638-86-4; **4a**, 65000-89-7; **4b**, 23081-49-4; **4c**, 13294-40-1; **5a**, 93383-23-4; **5b**, 31238-61-6; **5c**, 31238-50-3; **6a**, 93383-24-5; **6b**, 93383-25-6; **6c**, 93383-26-7; **7a**, 93383-27-8; **7b**, 93383-28-9; **7c**, 70048-90-7; **8a**, 93383-29-0; **8b**, 93383-30-3; **9a**, 93383-31-4; **9b**, 93383-32-5; 1,2-dinitrobenzene, 528-29-0; methyl iodide, 74-88-4; chloromethyl methyl ether, 107-30-2; (2-chloroethyl)diphenylphosphine, 5055-11-8.

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