Table I

substit (X)	k_X/k_H	log (k_X/k_H)	σ^a
OCH_3	1.548	0.1899	–0.27
CH_3	1.237	0.1269	–0.17
Cl	0.6598	–0.1806	0.23
Br	0.6356	–0.1968	0.23
NO_2	0.2093	–0.6140	0.78

[a] Taken from ref 5.

Table II

substit (X)	k_X/k_H	log (k_X/k_H)	σ^a
OCH_3	1.857	0.269	–0.27
CH_3	1.337	0.1261	–0.17
Cl	0.7185	–0.1435	0.23
NO_2	0.2762	–0.5587	0.78

[a] Taken from ref 5.

by mixing known volumes (0.50–0.30 μL) of the sulfide and decane solutions and measuring the GC areas.

For the oxidation experiments, 1.0-mL portions of the decane, phenyl methyl sulfide, and para-substituted phenyl methyl sulfide solutions were mixed at room temperature. To this mixture was added 0.50 mL of a freshly prepared[2] solution of dimethyldioxirane in acetone (0.06–0.08 M) dropwise, with shaking, in a 1-min period. The reaction mixtures were immediately analyzed by capillary GC. Each reaction mixture was analyzed at least three times. The relative rates of oxidation of the sulfides were calculated by using eq 3, where $[X_0]$ and $[H_0]$ are initial concentrations of

$$\frac{k_X}{k_H} = \frac{[X_0] - [X_1]}{[H_0] - [H_1]} \tag{3}$$

substituted and unsubstituted phenyl sulfides, respectively, and $[X_1]$ and $[H_1]$ are final concentrations of the same sulfides.

A summary of the relative rate so obtained is given in Table I.

These relative rate data were treated with the Hammett linear free energy relationship and gave a straight line plot with $\rho = -0.77 \pm 0.05$ (correlation coefficient = 0.984).

The gas chromatography conditions used in analyzing the oxidation mixture are available. See paragraph at end of paper about supplementary material.

b. Sulfoxides. Solutions of phenyl methyl sulfoxide (0.20 M) and the para-substituted phenyl methyl sulfoxide (0.20 M) in acetone were prepared separately in 10-mL volumetric flasks. An acetone solution of the internal standard, hexadecane, was also prepared (0.10 M). The relative GC responses of the individual sulfoxides with respect to hexadecane were determined by mixing 500-μL portions of phenyl methyl sulfoxide, a para-substituted phenyl methyl sulfoxide, and hexadecane solutions and then injecting 0.5-μL portions into the capillary GC (DB-1701).

The oxidation experiments were carried out by adding, dropwise, 200–500 μL of a freshly prepared solution of dimethyldioxirane (0.06–0.08 M) to a mixed solution of phenyl methyl sulfoxide and one of the para-substituted phenyl methyl sulfoxides. The oxidation reaction occurred instantaneously. Using a precision syringe, 0.5- or 1.0-μL portions of the oxidation mixtures were analyzed by using capillary GC. By studying the rates of oxidation at several different conversion levels, it was determined that conversions in the 10–25% range gave the best precision in determining relative rate constants. The relative rates were determined at least three times for each reaction pair. The relative rates were calculated in the same manner used in the sulfide oxidations. The reaction solutions were evaporated and the sulfone products were recrystallized from CH_2Cl_2–hexane to give nice crystals in each case. The individual sulfones were identified by comparing melting point, mass spectra, and ^1H NMR data with those of the authentic compounds. A summary of the relative rate data obtained is given in the Table II.

These data were treated with the Hammett linear free energy relationship and gave a straight line plot with $\rho = -0.76 \pm 0.025$ (correlation coefficient = 0.989).

The gas chromatography conditions used in analyzing the oxidation mixtures are available. See paragraph at the end of paper about supplementary material.

Acknowledgment. We are grateful to the National Institute of Environmental Health Sciences and the Office of Naval Research for financial support of this work. The Varian XL-300 NMR spectrometer was purchased with support from the National Science Foundation. We also acknowledge helpful discussions with Dr. David W. Larsen and Mr. John Boylan concerning the NMR experiments.

Supplementary Material Available: Full gas chromatography conditions and retention times for the oxidation mixtures (2 pages). Ordering information is given on any current masthead page.

Note Added in Proof: The labeling experiment described in ref 2 has been completed. The ^{13}C absorptions of 1 occur at 102.25 and 22.68 ppm, which are assigned to the ring and methyl carbons, respectively. These absorptions disappear upon addition of 1 drop of dimethyl sulfide to the NMR tube. Guided by our knowledge of the location of the 102 ppm peak, we have identified NMR spectrometer settings (5081 scans and a 10-s delay between pulses) which permit observation of the ring carbon absorption in 1 without ^{13}C enrichment as well as in other dioxiranes.

Palladium-Catalyzed Coupling of Aryl Halides with (Trimethylstannyl)diphenylphosphine and (Trimethylsilyl)diphenylphosphine

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The palladium-catalyzed reaction of aryl halides with either (trimethylsilyl)diphenylphosphine or (trimethylstannyl)diphenylphosphine gives aryldiphenylphosphines in good yields, under relatively mild conditions (50–70 °C, benzene). The reaction tolerates a number of functional groups including methyl ethers, esters, ketones, nitriles, anilides, and certain halogens. The nitro and aldehyde groups as well as compounds containing groups such as amino and hydroxyl are not tolerated.

Introduction

Triarylphosphines are an important class of compounds, both as ligands for various transition metals and as intermediates in organic synthesis. The numerous synthetic methods for preparation of triarylphosphines[1,2] can be divided into three major categories: the preparation from halophosphines and organometallic reagents, from meta-

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(1) *Organic Phosphorus Compounds*, 2nd ed.; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 1.

0022-3263/87/1952-0748$01.50/0

lated phosphines, and from Friedel–Crafts reactions.

The classical method for the preparation of triarylphosphines, the reaction of an aryl-Grignard reagent or an organolithium reagent with a chlorophosphine or an alkoxy-substituted phosphine, is satisfactory for compounds that are not base-sensitive. Phosphides displace halides[1,2] and sulfonate salts[1-3] from the corresponding aromatic compounds. However, the diphenylphosphide anion rapidly dealkylates alkyl aryl ethers and alkyl aryl thioethers to give the corresponding phenols and thiophenols.[4] Thus the preparation of triarylphosphines from metalated phosphines are limited to substrates that do not react with strong nucleophiles. The reaction of mono-, di- or trihalophosphines with an activated aromatic ring under Friedel–Crafts conditions[1,2,5-7] and the copper-catalyzed reaction of benzenediazonium tetrafluoroborate salts with halophosphines to give phosphonium salts (which can be reduced to phosphines) also are limited by the other functional groups that can be tolerated.

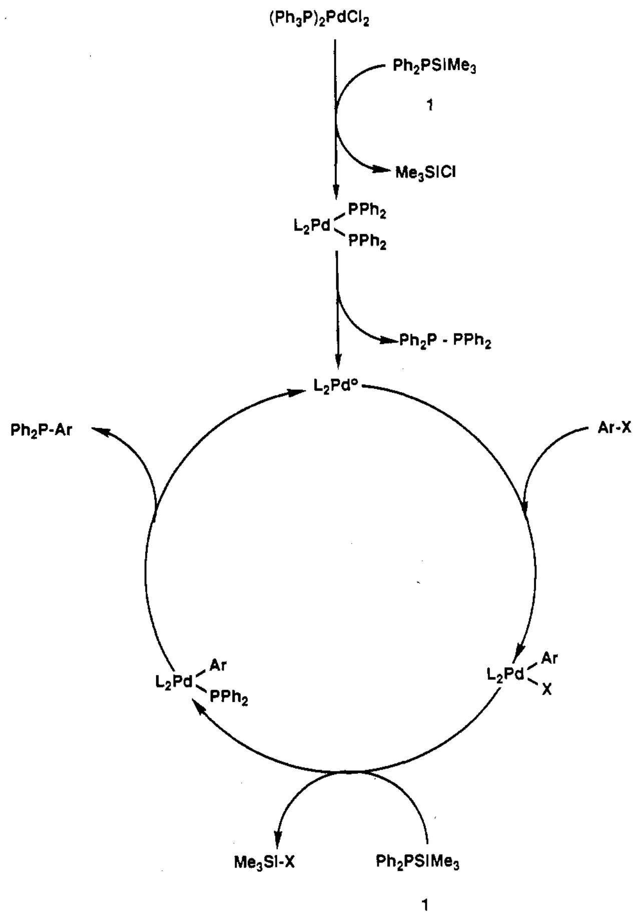
(Trimethylsilyl)diphenylphosphine (**1**) has been used to prepare a variety of phosphines.[8] Acid chlorides,[8,9] 2,3-dichloromaleic anhydride,[10] α-halocarbonyls,[11] and α-chloronitriles[12] all react with **1** to give the substituted diphenylphosphines. In addition, transition-metal halide complexes react with **1** to give transition-metal phosphide complexes.[13] The chemistry[14] of (trimethylstannyl)diphenylphosphine (**2**) is very similar to that of **1** but has not been explored as extensively. Although neither **1** nor **2** have been reported to react with palladium in any catalytic reaction, the palladium-catalyzed coupling of an aryl bromide with (tributylstannyl)diethylamine takes place in good yield.[15] Thus the coupling of **2** with aryl halides catalyzed by palladium could be expected to occur.

Results and Discussion

The reaction of 4-iodotoluene, (trimethylstannyl)diphenylphosphine (**2**), and 5 mol % bis(triphenylphosphine)palladium dichloride in benzene-d_6 gave cleanly the desired diphenyltolylphosphine in 75% isolated yield after 10 h at 50 °C (eq 1). In chloroform-d, no reaction occurred after 4.5 days at 50 °C. The reaction of (trimethylsilyl)diphenylphosphine (**1**) with 4-iodotoluene in the presence of a palladium catalyst also provided diphenyltolylphosphine.

Since the other three halotoluenes did not react with **1** or **2** under these conditions, an oxidative addition of 4-iodotoluene to palladium(0) catalyst appeared to be taking place. Oxidative addition reactions of aryl halides to palladium(0) show this selectivity at 50 °C.[16,17] No reaction of 4-iodotoluene with **1** or **2** in the absence of palladium occurred. The presence of a 10 M excess of a radical trap in the reaction (based on the amount of 4-iodotoluene) had no effect, indicating that a radical chain process was not involved.

Scheme I



The proposed catalytic cycle (Scheme I) is based on the known reaction of bis(triphenylphosphine)dichloropalladium with **1** to give the bis(diphenylphosphino)palladium(II) complex.[13c] The phosphine complex can undergo reductive elimination to give the necessary palladium(0) catalyst and tetraphenyldiphosphine. Tetraphenyldiphosphine was observed in the ^{31}P NMR spectra of the crude reaction mixtures in the same relative amount as the palladium catalyst added. The catalytic cycle requires oxidative addition,[16] a transmetalation reaction between **1** and the arylpalladium halide, and reductive elimination. The reductive elimination of an aryldiphenylphosphine from an arylpalladium–diphenylphosphine complex has been proposed[17] as an intermediate step in the reaction of the palladium complex with lithiodiphenylphosphide.

The palladium-catalyzed reactions of **1** and **2** with aryl halides are highly catalytic and are routinely carried out by using 1.0–2.5 mol % catalyst. The method of introduction of palladium makes little difference since the reactions using either palladium bis(dibenzylideneacetone), bis(triphenylphosphine)palladium dichloride, or bis(ace-

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(2) *Organophosphorous Chemistry*, The Royal Chemical Society: London; 1969–1983, Vol. 1–15.

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(4) Mann, F. G.; Pragnell, M. J. *J. Chem. Soc.* **1965**, 4120.

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(6) Sollott, G. P.; Howard, E. *J. Org. Chem.* **1962**, *27*, 4034.

(7) Protopopov, I. S.; Kraft, M. Y. *Zh. Obshch. Khim.* **1963**, *33*, 3050.

(8) Armitage, D. A. *Organosilanes in Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 2, p 146.

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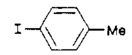
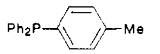
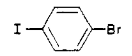
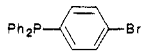
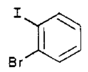
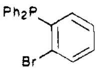
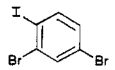
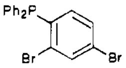
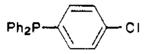
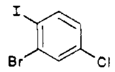
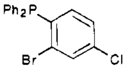
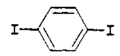
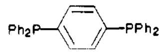
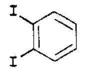
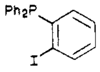
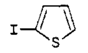
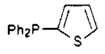
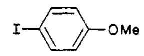
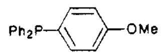
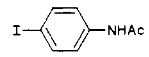
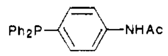
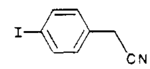
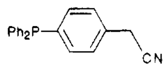
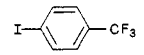
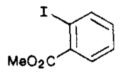
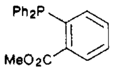
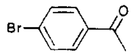
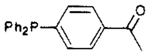
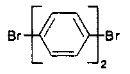
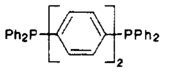
(16) Stille, J. K. in *Chemistry of the Metal–Carbon Bond*; Hartley, F. R.; Patai, S., Eds.; Wiley: Chichester, UK, 1985; Vol. 2, p 625.

(17) Sokolov, V. I.; Troitskaya, L. L. *J. Organomet. Chem.* **1980**, *202*, C58.

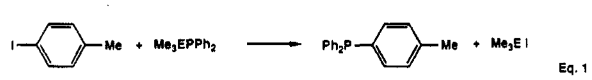
Table I. Phosphination of Aryl Halides

entry	ArX	$ArPPh_2$	catalyst[a]	temp, °C	time, h	yield,[b] %
1			B (2.5)	60	36	83
2			B (2.5)	65	14	85
3			B (2.5)	70	100	82
4			B (2.5)	60	183	86
5			A (2.0)	65	62	94
6			B (2.0)	60	38	90
7			B (2.8)	50	53	87 (89)
8			A (2.0)	60	73	20
9			B (1.0)	50	36	76 (97)
10			B (2.5)	60	28	79 (94)
11			B (2.5)	60	24	55
12			B (2.5)	60	28	80
13			B (2.5)	60	28	69
14			B (2.5)	60	28	65 (96)
15			B (2.5)	105	24	65
16			B (5.0)	105	60	40

[a] Catalyst A: bis(triphenylphosphine) palladium dichloride. Catalyst B: bis(acetonitrile)palladium dichloride; number in parentheses was the mol % catalyst used based on amount of aryl halide. [b] All yields are isolated yields; numbers in parentheses are NMR yields.

tonitrile)palladium dichloride as the catalyst gave similar yields.

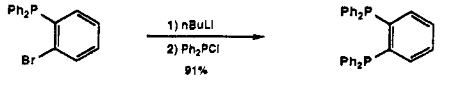
Although the stannylphosphine reacted about twice as fast as the silyl phosphide, **1** was favored over **2** as a diphenyl phosphide source since the starting trimethylsilyl chloride is cheaper, and trimethylsilyl compounds are not as toxic as trimethylstannyl derivatives.



3 **4** Eq. 1

	E	yield
1	Si	83%
2	Sn	74%

The coupling reaction is quite general and can be used to prepare a wide variety of aryldiphenylphosphines (Table I). The aryl iodides were obtained from commercial sources or prepared from the corresponding commercially available aryl amines. Because bromotoluene and chlorotoluene are not phosphinated under the standard reaction conditions, aryl iodides containing chloro and bromo substituents were selectively phosphinated at iodide to give the corresponding aryldiphenylphosphines (entries 2–6). Treating 1,4-diiodobenzene with 2 equiv of **1** gave high yields of the 1,4-bis(diphenylphosphino)benzene (entry 7). However, treating 1,2-diiodobenzene with 2 equiv of **1** gave only a low yield of (2-iodophenyl)diphenylphosphine (entry 8) and none of the 1,2-bis(diphenylphosphino)benzene. Using **2** instead of **1** gave similar results. This compound was obtained from a two-step procedure. Phosphination of 2-bromoiodobenzene (entry 3) gave, in good yield, (2-(bromophenyl)diphenylphosphine. Halogen–metal exchange of (2-bromophenyl)diphenylphosphine with *n*-butyllithium followed by quenching with chlorodiphenylphosphine gave the desired 1,2-bis(diphenylphosphino)benzene in high overall yield (eq 2). Other substituted aryl iodides were generally phosphinated in good yields (entries 9–14), regardless of the electronic nature of the substituent. Aryl bromides could be phosphinated at higher temperatures in moderate yields (entries 15 and 16). Although the actual yield of product was high as determined by ^{31}P NMR (entries 7, 9, 10, 14), some product was lost upon isolation.

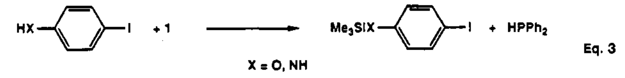


Eq. 2

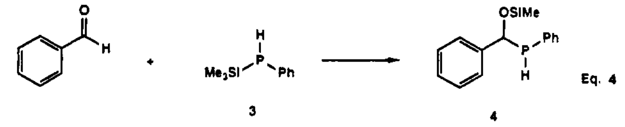
Many functional groups are tolerated by this phosphination reaction. Ester, ketone, and trifluoromethyl groups were not affected (entries 13–15). The byproduct of these coupling reactions, trimethylsilyl iodide, did not cleave the methyl ether in either 4-methoxyiodobenzene or (4-

methoxyphenyl)diphenylphosphine (entry 10), even though aryl methyl ethers are cleaved under similar reaction conditions.[18] A benzyl cyanide survived intact (entry 12), although 1 is a good nucleopile and readily displaces benzyl bromides.[19] N-Acylated anilines reacted slowly (entry 11).

Hydroxyl, amino, nitro, and aldehyde are not tolerated. 4-Iodophenol and 4-iodoaniline cleaved the silicon–phosphorus bond in 1 to give diphenylphosphine and the corresponding trimethylsilylated product (eq 3). Chloronitrobenzene reacted with 1 to give a mixture of aniline-derived products.[20] Benzaldehyde reacted with (trimethylsilyl)phenylphosphine (3) to give compound 4 (eq 4).[21]



Eq. 3



Eq. 4

Experimental Section

^1H NMR spectra were obtained on an IBM WP-200 spectrometer (200 MHz) or an IBM WP-270 spectrometer (270 MHz), with tetramethylsilane (0.00 ppm), dimethyl sulfoxide (Me_2SO, 2.49 ppm), benzene (7.15 ppm), or chloroform (7.24 ppm) as the internal standard. The ^{13}C NMR spectra were obtained on an IBM WP-200 spectrometer (50.3 MHz) or an IBM WP-270 spectrometer (67.9 MHz), with tetramethylsilane (0.00 ppm), Me_2SO (39.50 ppm), chloroform (77.00 ppm), or benzene (128.00 ppm) as the internal standard. The ^{31}P NMR spectra were obtained on an IBM WP-200 spectrometer (81.0 MHz) with 85% phosphoric acid (0.0 ppm) as the external reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, b = broad), coupling constant in hertz, and integration. The multiplicity reported in the $^{13}C\{^1H\}$ spectra refer to the ^{31}P–^{13}C coupling. Unless otherwise stated, the spectra were obtained in deuteriochloroform.

Starting materials were obtained from commercial suppliers or prepared according to standard procedures. Tetrahydrofuran (THF), diethyl ether (ether), and benzene were freshly distilled under nitrogen from sodium/benzophenone prior to use. All reactions were carried out under an inert atmosphere (nitrogen or argon) and in flame-dried glassware unless otherwise stated.

All melting and boiling points are uncorrected. Medium pressure liquid chromatography (MPLC) was performed with an ISCO Model UA-5 absorbance/fluorescence monitor equipped with a Type 6 optical unit and a Model 1133 multiplexer–expander using Woelm silica gel, 240–400 mesh. Elemental analyses were performed by Micro-Tech Laboratories of Skokie, IL., Atlantic Microlab, Inc. of Atlanta, GA or Galbraith Laboratories, Inc. of Knoxville, TN.

(Trimethylstannyl)diphenylphosphine (2),[22] bis(acetonitrile)palladium dichloride ($(MeCN)_2PdCl_2$),[23] bis(triphenylphosphine)palladium dichloride ($(Ph_3P)_2PdCl_2$),[24] (4-iodophenyl)acetonitrile,[25] methyl 2-iodobenzoate,[26] and 4-iodoacetanilide[27] were prepared according to literature methods.

General Method for Preparation of Iodoaromatics from Aniline Derivatives. To a mixture of 100 mmol of the aniline derivative, 225 mL of water, and 60 mL of concentrated sulfuric acid cooled to less than 10 °C in an ice bath was added a solution of 6.90 g (100 mmol) of sodium nitrite in 30 mL of water while maintaining the temperature at less than 10 °C. The mixture was stirred for 30 min. The cooled solution was poured into a solution of 20.8 g (125 mmol) of potassium iodide in 100 mL of water. After the addition was complete, the water was heated to 60 °C. The black solution was cooled and chloroform was added. The organic layer was separated and washed with 10% sodium hydroxide, 1 M sodium thiosulfate, 10% hydrochloric acid, water, saturated sodium bicarbonate, and saturated sodium chloride. The organic layer was dried over magnesium sulfate. The solvent was removed under reduced pressure to give the crude iodoaromatic compounds: 4-bromoiodobenzene, mp 91–93 °C (lit.[28] mp 89–90 °C), 2-bromoiodobenzene,[28] 2,4-dibromoiodobenzene, mp 43–45 °C (lit.[29] mp 45–46 °C), 2-bromo-4-chloroiodobenzene, mp 32–35 °C (lit.[30] mp 33 °C).

(Trimethylsilyl)diphenylphosphine (1). This compound was prepared by a modification of the reported procedure.[31] To a mechanically stirred mixture of 65.5 g (250 mmol) of triphenylphosphine and 6.10 g (875 mmol) of freshly cleaned lithium wire was added 200 mL of THF. The mixture was stirred overnight. The dark red solution was cannulated away from the excess lithium wire and 54.3 g (63.5 mL, 500 mmol) of trimethylsilyl chloride was added dropwise with cooling. The slurry was filtered through a Celite pad and the solvents were removed under reduced pressure. The residue was distilled under reduced pressure to give (trimethylsilyl)benzene, bp 168–170 °C, 760 mmHg, and 58.6 g (91%) of 1, bp 119–120 °C, 0.2 mm Hg (lit.[32] bp 126–127 °C, 1.0 mmHg): ^1H NMR (270 MHz) δ 7.61–7.55 (m, 4 H), 7.21–7.12 (m, 6 H), 0.22 (d, J_{PH} = 4.7 Hz, 9 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 136.60 (d, J = 17.7 Hz), 134.13 (d, J = 17.6 Hz), 128.64 (d, J = 7.4 Hz), 127.63, -0.99 (d, J = 11.8 Hz); ^{31}P NMR δ -56.2 (lit.[33] ^{31}P NMR δ -56.8).

General Procedure for Obtaining NMR Yields. A 10-mm NMR tube containing 0.25 mmol of triphenylphosphine, 0.5 mmol of aryl halide, and 2.6 mg (0.010 mmol) of $(MeCN)_2PdCl_2$ was sealed with a septum, under nitrogen. Then 0.5 mL of benzene-d_6 and 3.0 mL of benzene were added via syringe followed by 155 mg (0.150 mL, 0.6 mmol) of 1. The homogeneous solutions were placed in an oil bath at 60 °C and ^{31}P NMR spectra were then obtained at intervals, and the ratio between the triphenylphosphine and the product was determined by integration of the ^{31}P peaks.

General Procedure for Preparation of Aryldiphenylphosphines from Aryl Iodides. Into a flask was placed the aryl iodide and 0.025 equiv of $(MeCN)_2PdCl_2$. The flask was sealed with a septum and then evacuated and filled with argon three times. Enough benzene was added to make a 0.5 M solution of aryl iodide, and 1.05 equiv of 1 was added via syringe into the flask. The solution turned deep purple. The flask was placed into an oil bath at 50–70 °C, after a given time an aliquot was removed, and it was determined by ^{31}P NMR that the reaction was finished. Chloroform was added to the cooled reaction mixture. The organic layer was washed with saturated sodium bicarbonate, water, and saturated sodium chloride and dried over magnesium sulfate. The solvents were removed under reduced pressure to give a black oil. The black oil was dissolved in chloroform, silica gel (2 g per 1 g of oil) was added, and the chloroform was removed under reduced pressure. The coated silica gel was then loaded onto the top of a silica gel packed flash column for chromatography.

(4-Methylphenyl)diphenylphosphine (Entry 1, Table I). Method 1. The reaction was carried out with 1.09 g (5.00 mmol)

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of 4-iodotoluene and 2.5 mol % of $(MeCN)_2PdCl_2$ at 60 °C as described in the general procedure. The crude product was chromatographed (silica gel, hexanes) to give 1.15 g (83%) of white solid, mp 64–66 °C (lit.[34] mp 63.5–65 °C): ^1H NMR (270 MHz) δ 7.37–7.19 (m, 14 H), 2.40 (s, 3 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 138.77, 137.75, (d, J = 11.7 Hz), 134.08 (bs), 133.64 (d, J = 19.7 Hz), 129.33 (d, J = 6.2 Hz), 128.45 (apparent t, J = 5.8 Hz), 21.22; ^{31}P NMR δ –5.3 (lit.[35] ^{31}P NMR δ –6.0).

Method 2. The reaction was carried out with 561 mg (1.61 mmol) of 4-iodotoluene and 1.6 mol % of $(MeCN)_2PdCl_2$ at 50 °C as described in the general procedure above except **2** was used in place of **1**. The crude product was chromatographed (silica gel, hexanes) to give 327 mg (74%) of product, which was identical with that prepared above.

(4-Bromophenyl)diphenylphosphine (Entry 2, Table I). The reaction was carried out with 5.66 g (20.0 mmol) of 4-bromoiodobenzene and 2.5 mol % of $(MeCN)_2PdCl_2$ at 65 °C. The crude product was chromatographed (silica gel, hexanes) to give 5.8 g (85%) of product, which was recrystallized from absolute ethanol (10 mL/g) to give 3.4 g of white solid, mp 83–84 °C (lit.[36] mp 79–80 °C): ^1H NMR (270 MHz) δ 7.46 (dd, J = 2.0, 8.2 Hz, 2 H), 7.37–7.27 (m, 10 H), 7.17 (dd, J = 7.0, 8.3 Hz, 2 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 136.83 (d, J = 11.9 Hz), 135.24 (d, J = 20.0 Hz), 133.74 (d, J = 20.1 Hz), 131.68 (d, J = 5.9 Hz), 128.94, 128.63 (d, J = 7.9 Hz), 123.41; ^{31}P NMR δ –5.4 (lit.[37] ^{31}P NMR δ –4.8).

(2-Bromophenyl)diphenylphosphine (Entry 3, Table I). The reaction was carried out with 11.3 g (40.0 mmol) of 2-bromoiodobenzene and 2.5 mol % of $(MeCN)_2PdCl_2$ at 70 °C. The crude product was chromatographed (silica gel, hexanes→benzene/hexanes (1:1)) to give 11.1 g (82%) of white solid, mp 112–114 °C (lit.[38] mp 113–114.5 °C): ^1H NMR (270 MHz) δ 7.61–7.58 (m, 1 H), 7.38–7.27 (m, 10 H), 7.21–7.18 (m, 2 H), 6.79–6.77 (m, 1 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 139.09 (d, J = 11.8 Hz), 136.00 (d, J = 10.2 Hz), 134.47, 134.02 (d, J = 19.7 Hz), 132.99, 130.27, 130.07, 129.82, 128.62 (d, J = 7.5 Hz), 127.35; ^{31}P NMR δ –4.4.

(2,4-Dibromophenyl)diphenylphosphine (Entry 4, Table I). The reaction was carried out with 21.7 g (60.0 mmol) of 2,4-dibromoiodobenzene and 2.5 mol % of $(MeCN)_2PdCl_2$ at 60 °C. The crude product was chromatographed (silica gel, hexanes→benzene/hexanes (1:1)) to give 1.6 g (7%) of recovered iodide and 21.6 g (86%) of product. The product was recrystallized from absolute ethanol (40 mL/g) to give 19.2 g of white solid, mp 146.0–146.5 °C: ^1H NMR (270 MHz) δ 7.79 (dd, J = 1.9, 3.2 Hz, 1 H), 7.41–7.26 (m 11 H), 6.65 (dd, J = 2.2, 8.2 Hz, 1 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 138.41 (d, J = 14.5 Hz), 135.35 (d, J = 9.2 Hz), 134.07, 133.77, 130.57, 130.13, 129.15, 128.72 (d, J = 6.6 Hz), 123.38; ^{31}P NMR δ –5.0. Anal. Calcd for $C_{18}H_{13}Br_2P$: C, 51.46; H, 3.12. Found: C, 51.22; H, 3.27.

(4-Chlorophenyl)diphenylphosphine (Entry 5, Table I). The reaction was carried out with 2.39 g (10.0 mmol) of 4-chloroiodobenzene and 2 mol % of $(Ph_3P)_2PdCl_2$ at 65 °C. The crude product was chromatographed (silica gel, hexanes) to give 2.82 g (94%) of white solid, mp 44–46 °C (lit.[39] mp 44–45 °C): ^1H NMR (270 MHz) δ 7.41–7.25 (m); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 136.95 (d, J = 10.3 Hz), 136.21 (d, J = 12.3 Hz), 135.14 (bs), 134.85, 133.72 (d, J = 19.7 Hz), 128.91–128.56 (m); ^{31}P NMR δ –5.5 (lit.[37] ^{31}P NMR δ –6.6).

(2-Bromo-4-chlorophenyl)diphenylphosphine (Entry 6, Table I). The reaction was carried out with 31.7 g (100 mmol) of 2-bromo-4-chloroiodobenzene and 2 mol % of $(MeCN)_2PdCl_2$ at 60 °C. The crude product was chromatographed (silica gel, hexanes→benzene/hexanes (1:1)) to give 33.8 g (90%) of product, which was recrystallized from absolute ethanol (25 mL/g) to give 27.7 g of white solid, mp 130.0–130.5 °C: ^1H NMR (270 MHz) δ 7.64 (dd, J = 2.1, 3.2 Hz, 1 H), 7.41–7.26 (m, 10 H), 7.20 (dd, J = 2.0, 8.3 Hz, 1 H), 6.72 (dd, J = 2.3, 8.3 Hz, 1 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 135.70, 135.33 (d, J = 18.4 Hz), 133.96 (d, J = 18.1 Hz), 132.66, 130.44, 129.96, 129.17, 128.75 (d, J = 6.9 Hz), 127.69; ^{31}P NMR δ –5.0. Anal. Calcd for $C_{18}H_{13}BrClP$: C, 57.55; H, 3.49. Found: C, 57.64; H, 3.54.

1,4-Bis(diphenylphosphino)benzene (Entry 7, Table I). The reaction was carried out with 825 mg (2.50 mmol) of 1,4-diiodobenzene and 2.8 mol % of $(MeCN)_2PdCl_2$ for 52.5 h. The crude product was chromatographed (silica gel, hexanes→hexanes/benzene (1:1)) to give 970 mg (87%) of white solid, mp 166–168 °C (lit.[40] mp 166–168 °C): ^1H NMR (270 MHz) δ 7.38–7.33 (m, 20 H), 7.28 (dd, J = 3.7, 4.6 Hz, 4 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 138.23 (d, J = 12.6 Hz), 137.03 (d, J = 11.4 Hz), 133.90 (d, J = 19.7 Hz), 133.60 (d, J = 6.0 Hz), 133.32 (d, J = 7.0 Hz), 128.86, 128.56 (d, J = 6.3 Hz), 128.34; ^{31}P NMR δ –4.82.

(2-Iodophenyl)diphenylphosphine (Entry 8, Table I). The reaction was carried out with 3.3 g (10 mmol) of 1,2-diiodobenzene and 2 mol % of $(Ph_3P)_2PdCl_2$ at 60 °C. The crude product was chromatographed (silica gel, hexanes) to give 0.60 g (20%) of product, which was recrystallized from absolute ethanol to give a white solid, mp 119–120 °C: ^1H NMR (270 MHz) δ 7.91 (ddd, J = 1.0, 3.1, 7.8 Hz, 1 H), 7.39–7.27 (m, 11 H), 7.02 (dt, J = 2.0, 7.6 Hz, 1 H), 6.79 (td, J = 2.0, 7.6 Hz, 1 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 139.87, 136.54 (d, J = 11.7 Hz), 134.22, 134.10 (d, J = 23.4 Hz), 130.08, 128.94, 128.74, 128.62, 128.25, 107.10 (d, J = 41.5 Hz); ^{31}P NMR δ +9.1. Anal. Calcd for $C_{18}H_{14}IP$: C, 55.69; H, 3.64. Found: C, 55.79; H, 3.66.

2-(Diphenylphosphino)thiophene (Entry 9, Table I). The reaction was carried out with 3.15 g (1.66 mL, 15.0 mmol) of 2-iodothiophene and 1 mol % of $(MeCN)_2PdCl_2$ at 50 °C. The crude product was chromatographed (silica gel, hexanes) to give 3.75 g (94%) of crude product, which was chromatographed (MPLC, 2% ethyl acetate/hexanes) to give 3.04 g (76%) of white solid, mp 44–46 °C (lit.[41] mp 36–38 °C): ^1H NMR (270 MHz) δ 7.66 (d, J = 4.5 Hz, 1 H), 7.59–7.51 (m, 4 H), 7.46–7.44 (m, 6 H), 7.38–7.36 (m, 1 H), 7.23 (t, J = 4.5 Hz, 1 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 138.48, 138.09 (d, J = 9.5 Hz), 136.08 (d, J = 25.2 Hz), 133.06 (d, J = 19.7 Hz), 131.78, 128.50 (d, J = 22.0 Hz), 128.31, 127.90 (d, J = 7.2 Hz); ^{31}P NMR δ –18.9 (lit.[42] ^{31}P NMR δ –19.3).

(4-Methoxyphenyl)diphenylphosphine (Entry 10, Table I). The reaction was carried out with 351 mg (1.50 mmol) of 4-methoxyiodobenene and 2.5 mol % of $(MeCN)_2PdCl_2$ at 60 °C. The crude product was chromatographed (silica gel, hexanes→benzene/hexanes (1:1)) to give 346 mg (79%) of white solid, mp 63–65 °C (lit.[43] mp 64.5–65.5 °C): ^1H NMR (270 MHz) δ 7.32–7.24 (m, 12 H), 6.89 (d, J = 8.5 Hz, 2 H), 3.80 (s, 3 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 160.61, 138.23 (d, J = 12.1 Hz), 135.57 (d, J = 20.6 Hz), 133.46 (d, J = 18.9 Hz), 128.39, 128.30–127.98 (m), 114.41 (d, J = 8.6 Hz), 55.12; ^{31}P NMR δ –6.3 (lit.[37] ^{31}P NMR δ –6.1).

4-(Diphenylphosphino)acetanilide (Entry 11, Table I). The reaction was carried out with 1.31 g (5.00 mmol) of 4-iodoacetanilide and 2.5 mol % of $(MeCN)_2PdCl_2$ at 60 °C. The crude product was chromatographed (silica gel, hexanes→50% ethyl acetate/hexanes) to give 870 mg (55%) of white solid, mp 117–119 °C: ^1H NMR (270 MHz) δ 7.69 (bs, 1 H), 7.51 (d, J = 8.1 Hz, 2 H), 7.34–7.24 (m, 12 H), 2.17 (s, 3 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 168.35, 138.77, 137.04 (d, J = 9.1 Hz), 134.69 (d, J = 20.3 Hz), 133.61 (d, J = 19.6 Hz), 132.10 (bs), 128.77, 128.51 (d, J = 7.2 Hz), 119.90 (bs), 24.46; ^{31}P NMR δ –5.8.

[4-(Diphenylphosphino)phenyl]acetonitrile (Entry 12, Table I). The reaction was carried out with 365 mg (1.50 mmol) of (4-iodophenyl)acetonitrile and 2.5 mol % of $(MeCN)_2PdCl_2$ at 60 °C. The crude product was chromatographed (silica gel, hexanes→5% ethyl acetate/hexanes) to give 362 mg (80%) of a colorless oil that crystallized on standing, mp 85.5–87.5 °C: ^1H NMR (270 MHz) δ 7.34–7.21 (m, 14 H), 3.68 (s, 2 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 137.84 (d, J = 13.1 Hz), 134.24 (d, J = 18.8 Hz), 133.58 (d, J = 18.9 Hz), 130.46, 128.75, 128.44 (d, J = 7.0 Hz), 127.91 (d, J = 6.1 Hz), 117.20, 23.17; ^{31}P NMR δ –5.3. Anal. Calcd for $C_{20}H_{16}NP$: C, 79.72; H, 5.35. Found: C, 80.01; H, 5.56.

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[4-(Trifluoromethyl)phenyl]diphenylphosphine (Entry 13, Table I). The reaction was carried out with 412 mg (1.50 mmol) of 4-(trifluoromethyl)iodobenzene and 2.5 mol % of $(MeCN)_2PdCl_2$ at 60 °C. The crude product was chromatographed (silica gel, hexanes) to give 342 mg (69%) of a colorless oil that crystallized on standing, mp 51–53 °C (lit.[44] mp 55–57 °C): ^{1}H NMR (270 MHz) δ 7.56 (bd, J = 8.4 Hz, 2 H), 7.42–7.29 (m, 12 H); $^{13}C\{^{1}H\}$ NMR (67.9 MHz) δ 160.61, 138.23 (d, J = 12.1 Hz), 135.57 (d, J = 20.6 Hz), 133.46 (d, J = 18.9 Hz), 128.39, 128.30–127.98 (m), 114.41 (d, J = 8.6 Hz), 55.12; ^{31}P NMR δ −4.7.

Methyl 2-(Diphenylphosphino)benzoate (Entry 14, Table I). The reaction was carried out with 414 mg (1.50 mmol) of methyl 2-iodobenzoate and 2.5 mol % of $(MeCN)_2PdCl_2$ at 60 °C. The crude product was chromatographed (silica gel, hexanes→5% ethyl acetate/hexanes) to give 309 mg (65%) of white solid, mp 97–98.5 °C (lit.[45] mp 96–97 °C): ^{1}H NMR (270 MHz) δ 8.05–7.99 (m, 1 H), 7.39–7.20 (m, 12 H), 6.94–6.88 (m, 1 H), 3.70 (s, 3 H); $^{13}C\{^{1}H\}$ NMR (67.9 MHz) δ 167.22, 140.59, 138.00 (d, J = 11.3 Hz), 134.19, 133.89 (d, J = 21.6 Hz), 131.73 (bs), 130.56, 128.45 (apparent t, J = 7.7 Hz), 128.10, 51.73; ^{31}P NMR δ −3.5 (lit.[45] ^{31}P NMR δ −5.1).

(4-Acetylphenyl)diphenylphosphine (Entry 15, Table I). The reaction was carried out with 299 mg (1.50 mmol) of 4-acetylbromobenzene and 2.5 mol % of $(MeCN)_2PdCl_2$ in toluene at 105 °C. The crude product was chromatographed (silica gel, hexanes→5% ethyl acetate/hexanes) to give 297 mg (65%) of white solid, mp 118–120 °C (lit.[46] mp 118–119 °C): ^{1}H NMR (270 MHz) δ 7.84 (d, J = 7.9 Hz, 2 H), 7.35–7.20 (m, 12 H), 2.53 (s, 3 H); for $^{13}C\{^{1}H\}$ NMR data, see ref 47; ^{31}P NMR δ −4.3.

4,4′-Bis(diphenylphosphino)biphenyl (Entry 16, Table I). The reaction was carried out with 1.56 g (5.00 mmol) of 4,4′-dibromobiphenyl and 5 mol % of $(MeCN)_2PdCl_2$ in toluene at 105 °C. The crude product was chromatographed (silica gel, hexanes→20% ethyl acetate/hexanes) to give 1.05 g (40%) of white solid, mp 185–186 °C (lit.[40] mp 192.5–194 °C): ^{1}H NMR (270 MHz) δ 7.61 (d, J = 7.3 Hz, 4 H), 7.45–7.37 (m, 24 H); $^{13}C\{^{1}H\}$ NMR (67.9 MHz) δ 140.77, 137.24 (d, J = 10.9 Hz), 136.71 (d, J = 11.3 Hz), 134.22 (d, J = 19.6 Hz), 133.81 (d, J = 19.6 Hz), 128.80, 128.57 (d, J = 6.0 Hz), 127.06 (d, J = 7.3 Hz); ^{31}P NMR δ −5.5.

1,2-Bis(diphenylphosphino)benzene. To a cooled (−78 °C) solution of 1.02 g (3.00 mmol) of (2-bromophenyl)diphenylphosphine in 30 mL of THF was added dropwise 1.7 mL (3.0 mmol) of a 1.8 M solution of *n*-butyllithium in hexanes. The solution was stirred at −78 °C for 30 min and then 660 mg (3.00 mmol) of chlorodiphenylphosphine was added dropwise. The solution was allowed to warm to room temperature; then chloroform was added to the solution. The organic layer was washed with water and saturated sodium chloride and then dried over magnesium sulfate. The solvents were removed under reduced pressure. The oil was dissolved in chloroform, silica gel was added, and the chloroform was removed under reduced pressure. The coated silica gel was then loaded onto the top of a silica gel packed flash column and eluted with hexanes→30% ethyl acetate/hexanes. The solvents were removed under reduced pressure to yield 1.22 g (91%) of product, mp 179–181 °C (lit.[48] mp 183–185 °C): ^{1}H NMR (270 MHz) δ 7.39–7.17 (m, 20 H), 7.13–7.03 (m, 4 H); $^{13}C\{^{1}H\}$ NMR (67.9 MHz) δ 137.26, 134.12–134.01 (m), 133.73 (t, J = 9.9 Hz), 129.03, 128.47–128.07 (m); ^{31}P NMR δ −13.2 (lit.[49] ^{31}P NMR δ −14.3).

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Direct Photoamination of Arenes with Ammonia and Primary Amines in the Presence of Electron Acceptors[1]

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Direct photoamination of phenanthrene, 9-methoxyphenanthrene, anthracene, naphthalene, and several substituted naphthalenes with ammonia or primary amines in the presence of *m*-dicyanobenzene occurs to give aminated dihydroarenes in fairly good yields. *m*-Dimethoxybenzene and biphenyl are photoaminated in lower yields. A suggested mechanism for the photoamination involves the nucleophilic attack of ammonia and amines on aromatic cation radicals generated by photochemical electron transfer to *m*-dicyanobenzene. The present photoamination is applied to direct introduction of various functionalized primary amines containing the vinyl, cyano, hydroxy, acetylamino, and ethoxycarbonyl groups.

Photochemical electron transfer has received much attention as a convenient method for generation of ion radicals, thus having potential application to organic synthesis.[2] To apply photochemical electron transfer synthetically, we have extensively explored the possibility

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