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# Copper-Catalyzed Synthesis of Unsymmetrical Triarylphosphines[†]

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**Abstract:** Various triarylphosphines have been prepared by coupling diphenylphosphine with aryl iodides with catalytic amounts of CuI in the presence of either $K_2CO_3$ or $Cs_2CO_3$, in good yields. This method can tolerate a variety of functional groups and does not require the use of expensive additives, or harsh reaction conditions, and is palladium free.

Arylphosphine ligands are extremely important for many reactions catalyzed by transition metals and are ubiquitous in organometallic chemistry.[1−3] Triarylphosphine ligands are well-known for their use in asymmetric catalysis as well as general metal-catalyzed procedures for aryl−carbon and aryl−heteroatom bond-forming reactions.[4−8] The classical methods of preparation of arylphosphines often involve reactions of aryl-Grignard or aryl-lithium reagents with phosphine halides, and are therefore intolerant to a wide variety of functional groups.[1,3] Many of these methods suffer the disadvantage of significant, if not exclusive oxidation to the phosphine oxide, often requiring an additional reductive step. More recently, palladium- and nickel-catalyzed procedures have emerged as a more tolerant method of preparing arylphosphines. However, in contrast to the volume of literature that exists for the formation of aryl−nitrogen and aryl−oxygen bonds using cross-coupling reactions with palladium catalysts, only a very few reports exist for the formation of arylphosphines, particularly unsymmetrical phosphines.[9−21]

In recent years, the DV group,[22−27] Buchwald group,[28−33] and others[34−38] have been developing copper-catalyzed cross-coupling reactions. These methods have demonstrated increased functional group tolerance and improvement over the traditional Ullmann-type reaction conditions.[39] In addition, there exists an economic attractiveness to develop copper-based methods, since they are the methods of choice for large and industrial scale reactions. We now report the extension of copper-catalyzed cross-coupling reactions for the formation of unsymmetrical triarylphosphines.

To establish the efficacy of copper-based catalysts for the formation of triarylphosphines, we first studied the cross-coupling reaction between iodobenzene and diphenylphosphine using [Cu(PPh$_3$)$_3$Br], [Cu(Phen)PPh$_3$Br], [Cu(Neocup)PPh$_3$Br], and [Cu(Neocup)$_2$Br·H$_2$O] as catalysts, toluene as the solvent, and $K_2CO_3$ as the base. We also studied the efficacy of the copper halides alone, as well as with ligands as additives, to catalyze this reaction (Table 1). We were pleased to find that both well-defined catalysts and copper halides with additives were found to catalyze this reaction. Moreover, we found that triphenylphosphine was formed in quantitative yields using

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[†] Dedicated to the memory of Prof. William E. McEwen.

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**TABLE 1. A Comparison of *Well-Defined* Copper(I) Complexes, Additives, and Copper(I) Salts**

| catalyst | GC yield |
|---|---|
| well-defined catalysts | |
| $Cu(PPh_3)_3Br$ | 83 |
| $Cu(neocup)PPh_3Br$ | 69 |
| $Cu(phen)PPh_3Br$ | 61 |
| $Cu(neocup)_2Br\cdot H_2O$ | 68 |
| additives | |
| CuI/phenanthroline | 99 |
| CuI/neocuproine | 60 |
| CuI/DMAP | 54 |
| copper(I) salts | |
| CuI | 99 |
| CuBr | 34 |
| CuCl | 58 |

**SCHEME 1. Protocol for Copper(I)-Catalyzed Coupling of Substituted Iodobenzenes to Diphenylphosphine**

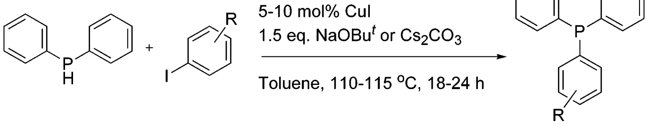
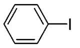
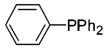
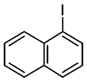
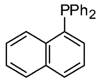
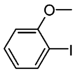
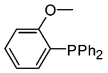
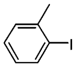
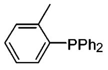
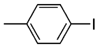
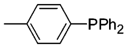
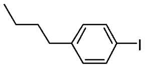
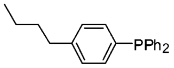
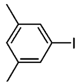
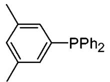
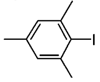
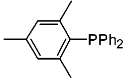
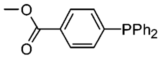
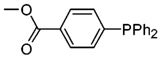
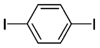
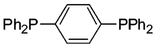
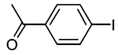
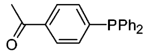
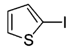
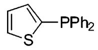


**TABLE 2. Optimization of Base for Coupling of Iodobenzene with Diphenylphosphine, Using CuI as the Catalyst**

| base | GC yield |
|---|---|
| $K_2CO_3$ | 99 |
| $K_3PO_4$ | 94 |
| $Cs_2CO_3$ | 88 |
| NaOMe | 63 |
| NaO*t*-Bu | 52 |
| NaOAc | 43 |
| KO*t*-Bu | 23 |
| $NEt_3$ | 0 |

**TABLE 3. Synthesis of Unsymmetrical Triarylphosphines**

| Entry | Aryl iodide | Product | Base | Isolated Yield |
|---|---|---|---|---|
| 1 |  |  | $K_2CO_3$ | 83 |
| 2 |  |  | $Cs_2CO_3$ | 91 |
| 3 |  |  | $Cs_2CO_3$ | 64 |
| 4 |  |  | $Cs_2CO_3$ | 76 |
| 5 |  |  | $Cs_2CO_3$ | 42 |
| 6 |  |  | $Cs_2CO_3$ | 70 |
| 7 |  |  | $Cs_2CO_3$ | 77 |
| 8 |  |  | $Cs_2CO_3$ | 71 |
| 9 |  |  | $Cs_2CO_3$ | 70 |
| 10 |  |  | $Cs_2CO_3$ | 71 |
| 11 |  |  | $Cs_2CO_3$ | 67 |
| 12 |  |  | $K_2CO_3$ | 63 |

CuI alone as the catalyst. This was contrary to our observation in other copper-catalyzed coupling reactions where there were substantial rate accelerations due to the ligands. We surmised that the product triphenylphosphine might form copper–phosphine complexes in situ, which in turn can accelerate the rate. If this were true, then we should observe substantial differences between reactions catalyzed by $Cu(PPh_3)_3Br$ and CuBr in the rate of formation of the product during the initial stages of the reaction. However, we found no differences in the rate of formation of triphenylphosphine in these reactions. Hence, we speculate that instead of triphenylphosphine, diphenylphosphine may be acting as a ligand throughout the reaction, contributing to the catalytic species.[40−44] Among the copper salts, we found CuI to be the most active catalyst (Table 1). Surprisingly, we have found no reports on the use of copper halides for the coupling of diphenylphosphine to aryl halides in the literature. In the absence of aryl halide, base, or catalyst there is no observed phosphine product as determined by GC.

We then screened various bases using CuI as the catalyst for the cross-coupling of iodobenzene with diphenylphosphine (Table 2). We found that $K_2CO_3$, $K_3PO_4$, and $Cs_2CO_3$ were the most effective bases while $NEt_3$, KO*t*-Bu, NaOMe, and NaOAc were less effective and often resulted in little or no observed triphenylphosphine by GC. However, we found that for several other aryl iodides, a significant amount of triarylphosphine oxide was observed when $K_2CO_3$ was used as the base. In these cases, we found that the amount of triarylphosphine oxide was minimized if $Cs_2CO_3$ was used as the base. Hence, we decided to use CuI (10 mol %) as the catalyst, $Cs_2CO_3$ as the base, and toluene as the solvent as a standard protocol for the formation of triarylphosphines.

With use of our protocol various electron-withdrawing and electron-donating aryl iodides were successfully coupled to diphenylphosphine in good yields (Table 3). Base-sensitive functional groups such as methyl ketones (entry 11) and methyl esters (entry 9) are tolerated by this method. Ortho-substituted iodides also coupled well with this protocol (entries 3, 4, and 8), as well as bulky groups and multiple substitutions of the aryl iodide. In the case of entry 5, although the GC indicated the

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(40) A few copper−diphenylphosphine clusters have indeed been reported in the literature. However, they have not been studied for their reactivity in cross-coupling reactions. For structures of these compounds see refs 41−44.

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complete consumption of the starting materials our isolated yield of product was moderate. Since the boiling point (68 °C) of this compound is low, we believe that we incur loss of the product during isolation of the product (see Supporting Information). We also found that bromobenzene can be coupled with diphenylphosphine under the same conditions to form triphenylphosphine, but only in 10% yield.

In conclusion, we have reported a synthetic protocol for unsymmetrical triarylphosphines starting from aryl iodides and diphenylphosphine, using CuI as the catalyst and $Cs_2CO_3$ and $K_2CO_3$ bases. Our protocol tolerates a variety of functional groups, including base-sensitive groups. This method is palladium free and has shown a dramatic improvement in overall yields, and the reaction conditions are much less harsh than similar protocols based on phosphination.

## Experimental Section

**General Procedure.** In an argon-filled glovebox, a Pyrex glass tube (2.5 cm in diameter) equipped with a Teflon stir bar was charged with cesium carbonate (3.0 mmol) and CuI (10 mol % with respect to diphenylphosphine), sealed with a rubber septum, and taken out of the box and toluene (5 mL), the aryl halide (2.4 mmol), and diphenylphosphine (2.0 mmol) were injected into the tube through the septum. The reaction mixture was then heated at 110 °C for 24 h. The reaction mixture was then cooled to room temperature and filtered with dichloromethane to remove any insoluble residues. The filtrate was concentrated in vacuo; the residue was purified by flash chromatography on silica to obtain the analytically pure product.

**Triphenylphosphine (1).** The general procedure was used to convert iodobenzene and diphenylphosphine to the title product. Purification by flash chromatography (pentane/dichloromethane [2:1] as the eluent) gave the analytically pure product as a white solid (435 mg, 83% yield). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.34−7.22 (m, 15 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 137.2, 137.1, 133.8, 133.9, 128.8, 128.5, 128.4. $^{31}P$ NMR (121 MHz, $CDCl_3$) $\delta$ −4.96 (s). Anal. Calcd for $C_{18}H_{15}P$: C, 82.43; H, 5.76; P, 11.81. Found: C, 82.13; H, 5.78.

**Naphthalen-1-yldiphenylphosphane (2).**[45] The general procedure was used to convert 1-iodonaphthanlene and diphenylphosphine to the title product. Purification by flash chromatography (dichloromethane as the eluent) gave the analytically pure product as a white solid (567 mg, 91% yield). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.51−7.28 (m, 15 H), 7.85 (t, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 134.3, 134.1, 133.4, 133.4, 132.0, 129.5, 128.8, 128.7, 128.6, 128.5, 126.3, 126.0, 125.9, 125.5. $^{31}P$ NMR (121 MHz, $CDCl_3$) $\delta$ −16.66 (s). Anal. Calcd for $C_{22}H_{17}P$: C, 84.60; H, 5.49. Found: C, 84.35; H, 5.49.

**(2-Methoxyphenyl)diphenylphosphane (3).**[46] The general procedure was used to convert 2-iodoanisole and diphenylphosphine to the title product. Purification by flash chromatography (dichloromethane as the eluent) gave the analytically pure product as a white solid (373 mg, 64% yield). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.35−7.26 (m, 11 H), 6.90−6.82 (m, 2 H), 6.69−6.65 (t, 1 H), 3.73 (s, 3H; methyl protons). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 161.2, 161.0, 136.7, 136.6, 134.0, 133.7, 133.6, 130.3, 128.6, 128.4, 128.3, 125.6, 125.5, 121.0, 110.2, 110.2, 55.6. $^{31}P$ NMR (121 MHz, $CDCl_3$) $\delta$ −16.35 (s). Anal. Calcd for $C_{19}H_{17}OP$: C, 78.07; H, 5.86; P, 10.60, O, 5.47. Found: C, 78.19; H, 6.03; P, 10.4.

**Diphenyl-*p*-tolylphosphane (4).**[14] The general procedure was used to convert 4-iodotoluene and diphenylphosphine to the title product. Purification by flash chromatography (pentane/dichloromethane [3:1] as the eluent) gave the analytically pure product as a white solid (232 mg, 42% yield). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.31−7.14 (m, 14 H), 2.34 (s, 3H; methyl protons). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 138.8, 137.6, 137.5, 134.0, 133.8, 133.7, 133.5, 133.5, 133.4, 129.8, 129.4, 129.3, 128.6, 128.5, 128.4, 128.2, 128.2, 128.1, 21.3. $^{31}P$ NMR (121 MHz, $CDCl_3$) $\delta$ -5.87 (s). Anal. Calcd for $C_{19}H_{17}P$: C, 82.59; H, 6.20; P, 11.21. Found: C, 82.62; H, 6.37; P, 11.4.

**Diphenyl-*o*-tolylphosphane (5).**[47] The general procedure was used to convert 2-iodotoluene and diphenylphosphine to the title product. Purification by flash chromatography (pentane/dichloromethane [3:1] as the eluent) gave the analytically pure product as a white solid (420 mg, 76% yield). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.32−7.21 (m, 12 H), 7.09−7.04 (t, 1H), 6.79−6.75 (m, 1H), 2.39 (s, 3H; methyl protons). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 142.3, 142.0, 136.3, 136.2, 135.9, 134.1, 133.9, 132.7, 130.1, 130.0, 128.7, 128.6, 128.5, 126.0, 21.1. $^{31}P$ NMR (121 MHz, $CDCl_3$) $\delta$ −13.23 (s). Anal. Calcd for $C_{19}H_{17}P$: C, 82.59; H, 6.20; P, 11.21. Found: C, 82.44; H, 6.11; P, 11.1.

**(4-Butylphenyl)diphenylphosphane (6).** The general procedure was used to convert 1-butyl-4-iodo-benzene and diphenylphosphine to the title product. Purification by flash chromatography (hexane/dichloromethane [10:1] as the eluent) gave the analytically pure product as a colorless oil (443 mg, 70% yield). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.29−7.12 (m, 14 H), 2.59 (t, 2H), 1.59 (t, 2H), 1.34 (m, 2H), 0.91 (t, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 143.2, 137.1, 137.0, 133.4, 133.2, 133.1, 133.0, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 124.8, 34.9, 32.9, 22.1, 13.6. $^{31}P$ NMR (121 MHz, $CDCl_3$) $\delta$ −16.73 (s). Anal. Calcd for $C_{22}H_{23}P$: C, 82.99; H, 7.28. Found: C, 82.72; H, 7.30.

**(3,5-Dimethylphenyl)diphenylphosphane (7).**[14] The general procedure was used to convert 1-Iodo-3,5-dimethylbenzene and diphenylphosphine to the title product. Purification by flash chromatography (pentane/dichloromethane [3:1] as the eluent) gave the analytically pure product as a colorless oil (447 mg, 77% yield). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.31−7.30 (m, 10 H), 6.96−6.92 (m, 3 H), 2.24 (s, 6H; methyl protons). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 138.0, 137.9, 137.5, 137.4, 136.7, 136.6, 133.8, 133.6, 131.6, 131.4, 130.6, 128.5, 128.3, 128.4. $^{31}P$ NMR (121 MHz, $CDCl_3$) $\delta$ −5.20 (s). Anal. Calcd for $C_{20}H_{19}P$: C, 82.74; H, 6.60. Found: C, 82.55; H, 6.69.

**Diphenyl(2,4,6-trimethylphenyl)phosphane (8).**[48] The general procedure was used to convert 2-iodo-1,3,5-trimethylbenzene and diphenylphosphine to the title product. Purification by flash chromatography (pentane/dichloromethane [3:1] as the eluent) gave the analytically pure product as a colorless oil (432 mg, 71% yield). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.37−7.20 (m, 10 H), 6.90 (s, 2 H), 2.27 (s, 3H; methyl protons), 2.18 (s, 6H; methyl protons). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 145.6, 145.4, 140.0, 139.9, 136.7, 136.5, 131.6, 131.3, 129.9, 129.9, 129.0, 128.3, 128.3, 127.4, 23.8, 23.6, 21.1. $^{31}P$ NMR (121 MHz, $CDCl_3$) $\delta$ −16.39 (s). Anal. Calcd for $C_{21}H_{21}P$: C, 82.87; H, 6.95. Found: C, 82.70; H, 7.25.

**4-Diphenylphosphanylbenzoic Acid Methyl Ester (9).**[49] The general procedure was used to convert 4-Iodobenzoic acid methyl ester and diphenylphosphine to the title product. Purification by flash chromatography (pentane/ethyl acetate [3:1] as the eluent) gave the analytically pure product as a white solid (448 mg, 70% yield). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.98−7.95 (d, 2 H), 7.36−7.32 (m, 12 H), 3.89 (s, 3H; methyl protons). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 166.8, 144.1, 143.9, 136.2, 136.1, 134.1, 133.8, 133.3, 133.0, 130.0, 129.3, 129.2, 129.1, 128.7, 128.6, 52.1. $^{31}P$ NMR (121 MHz, $CDCl_3$) $\delta$ −5.04 (s). Anal. Calcd for $C_{20}H_{17}OP$: C, 74.99; H, 5.35; P, 9.67. Found: C, 74.99; H, 5.46, P, 9.7.

**1,4-Bis(diphenylphosphanyl)benzene (10).**[16] The general procedure was used to convert *p*-diiodobenzene and diphenyl-

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phosphine to the title product. Purification by flash chromatography (pentane/dichloromethane [2:1] as the eluent) gave the title product as an off-white solid (634 mg, 71% yield). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.36−7.31 (m, 24 H). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$) $\delta$ 138.0, 136.8, 136.7, 136.5, 134.0, 133.7, 133.3, 133.2, 128.9, 128.6, 128.5. $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ −5.20 (s). HRMS EI calcd for $C_{30}H_{24}P_2$ 446.1353, found 446.1353.

**1-(4-(Diphenylphosphanyl)phenyl)ethanone (11).**[16] The general procedure was used to convert 4-iodoacetophenone and diphenylphosphine to the title product. Purification by flash chromatography (pentane/dichloromethane [1:6] as the eluent) gave the title product as an off-white solid (409 mg, 67% yield). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.29−7.38 (m, 12 H), 7.86−7.89 (dd, 2 H; $J$ = 1.51 and 6.97 Hz), 3.89 (s, 3H; methyl protons). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$) $\delta$ 197.8, 144.5, 144.3, 136.8, 136.1, 136.0, 134.1, 133.8, 133.4, 133.2, 129.2, 129.0, 128.8, 128.7, 128.0, 127.9, 26.6. $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ −3.81 (s). Anal. Calcd for $C_{20}H_{17}OP$: C, 78.93; H, 5.63; P, 10.18. Found: C, 78.73; H, 5.70, P, 10.0.

**Diphenylthiophenylphosphane (12).**[16] The general procedure was used to convert 4-iodoanisole and diphenylphosphine to the title product. Purification by flash chromatography (pentane/dichloromethane [3:1] as the eluent) gave the analytically pure product as an off-white solid (338 mg, 63% yield). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.58−7.10 (m, 13 H). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$) $\delta$ 138.0, 137.8, 136.5, 136.2, 133.2, 132.9, 132.0, 128.8, 128.6, 128.5, 128.4, 128.1, 127.9. $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ −19.49 (s). Anal. Calcd for $C_{16}H_{13}PS$: C, 71.62; H, 4.88; P, 11.54. Found: C, 71.71; H, 5.00; P, 11.6.

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**Supporting Information Available:** General experimental procedures and the synthesis of well-defined copper(I) complexes and a crystallographic information file (CIF) for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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