JOC Article

Palladium Complexes of 1,3,5,7-Tetramethyl-2,4,8-trioxa-6-phenyl-6-phosphaadamantane: Synthesis, Crystal Structure and Use in the Suzuki and Sonogashira Reactions and the α-Arylation of Ketones

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Palladium complexes of 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phenyl-6-phosphaadamantane were prepared and characterized with Pd[1,3,5,7-tetramethyl-2,4,8-trioxa-6-phenyl-6-phosphaadamantane]$_2$·dba shown to be an effective catalyst for use in the Suzuki and Sonogashira reactions and the α-arylation of ketones. Couplings using this versatile complex proceeded in excellent yields under mild conditions.

The efficacy and scope of applicability of palladium-catalyzed cross-coupling chemistry[1] has been bolstered in recent years by the implementation of catalysts incorporating bulky, electron-rich phosphine ligands. These systems are particularly mild and extremely versatile,[2] permitting reactions such as the Suzuki,[3] Heck,[4] and Stille[5] couplings of even the least reactive coupling partners. Work in our laboratories has allowed for the development of a new class of sterically hindered tertiary phosphine based on a phosphaadamantane framework.[6] The use of a catalytic system incorporating $Pd_2(dba)_3$·$CHCl_3$ and 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phenyl-6-phosphaadamantane (PA-Ph, **1**) was shown to promote the Suzuki cross-coupling of aryl iodides, bromides, and chlorides with a variety of aryl boronic acids under mild conditions in high yields. The present paper builds on these initial results and describes the preparation and characterization of palladium complexes of **1** and reveals them to be effective catalysts for use in the Suzuki and Sonogashira reactions and the α-arylation of ketones.

Palladium complexes of 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phenyl-6-phosphaadamantane were readily prepared by dissolving (**1**) and $Pd_2(dba)_3$·$CHCl_3$ in toluene and stirring the resultant solution at room temperature for 2 h before diluting with hexane (a 10-fold volume) (Figure 1). Two crystalline products were obtained: brown crystals of Pd(PA-Ph)$_2$·dba (**2**) and small amounts of green Pd(PA-Ph)$_2$·O_2 (**3**). The major product **2** was physically separated from **3**, and both were characterized via MS and NMR. Integration of ^{1}H NMR spectrum of **2** clearly reveals the presence of both phosphaadamantanyl and dibenzylideneacetone (dba) moieties in a 2:1 ratio. Interestingly, the chemical shifts of the olefin protons of dba were clearly visible at 7.76 and 7.11 ppm and indicate that the dba is not coordinated with the Pd in solution. Contrast these chemical shifts with those reported by Stahl and co-workers wherein their (bathocupronine)Pd(η^2-dba) showed the coordinated olefinic protons at δ 4.47 and 4.24 ppm.[7] It would appear, therefore, that the dba is readily dissociated from the complex in solution to open two vacant coordination sites on the palladium (presumably occupied by solvent). Mass spectrometry of **2** reveals a base peak corresponding to the mass of a Pd-bisphosphine complex at $m/z = 690$. While crystals of the **2** failed to diffract, an X-ray structure of the bis(phospha-adamantanyl)peroxopalladium(II) complex (**3**) was obtained and is shown in Figure 2.[8,9] It should be noted that both **2** and **3** are air stable. Curiously, attempts at preparing solely Pd(PA-Ph)$_2$·dba under the strict exclusion of oxygen failed to result in the crystallization of either complex.

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[‡] Bruker-Nonius.
[§] Cytec Canada, Inc.

(1) *Metal-Catalyzed Cross Coupling Reactions;* Diederich, F., Stang, P., Eds.; Wiley-VCH: New York, 1998.
(2) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176.
(3) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem Soc.* **2000**, *122*, 4020; Yin, J.; Rainka, M. P.; Zhang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162.
(4) Littke, A. F.; Fu, G. C. *J. Org. Chem.* **1999**, *64*, 10.
(5) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2411.
(6) Adjabeng, G.; Brenstrum, T.; Wilson, J.; Frampton, C.; Robertson, A.; Hillhouse, J.; McNulty, J.; Capretta, A. *Org. Lett.* **2003**, *5*, 953.
(7) Stahl, S.; Thorman, J. L.; Nelson, R. C.; Kozee, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 7188−7189.
(8) Details regarding the crystal structure of Pd[1,3,5,7-tetramethyl-2,4,8-trioxa-6-phenyl-6-phosphaadamantane]$_2$·O_2 may be obtained from the Cambridge Crystallographic Data Centre (deposition no. 233089). It should be noted that crystals of Pd[1,3,5,7-tetramethyl-2,4,8-trioxa-6-(*o*-tolyl)-6-phosphaadamantane]$_2$·O_2 were also characterized (deposition no. 233088).
(9) Other η^2-peroxopalladium species have been reported in the literature including ref 7: Valentine, J. S. *Chem. Rev.* **1973**, *73*, 235. Yoshida, T.; Tatsumi, K.; Matsumoto, M.; Nakatsu, K.; Nakamura, A.; Fueno, T.; Otsuka, S. *Nouv. J. Chim.* **1979**, *3*, 761−774.

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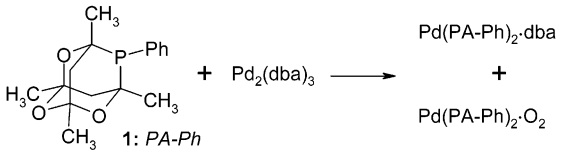


FIGURE 1. Synthesis of palladium/PA-Ph complexes.

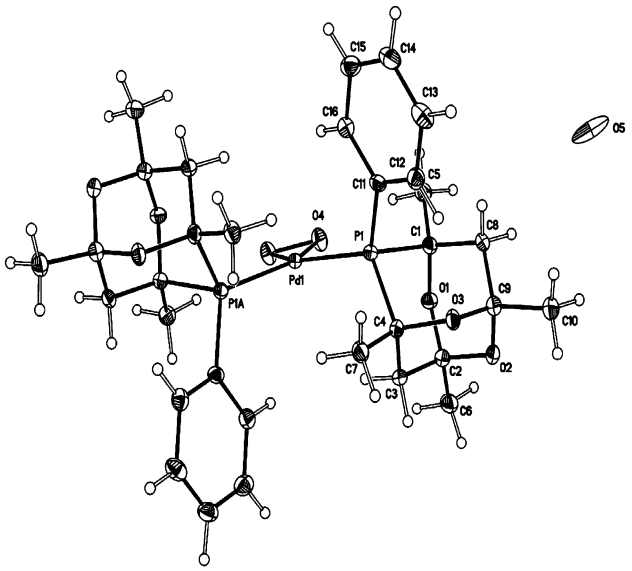
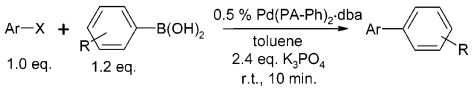
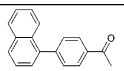
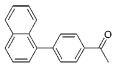
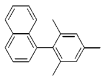


FIGURE 2. Structure of $Pd(PA\text{-}Ph)_2{\cdot}O_2$ (**3**).

TABLE 1. Suzuki Coupling Reactions

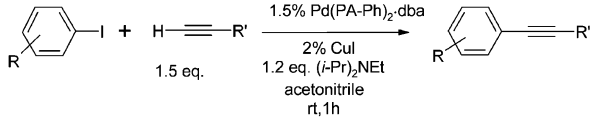


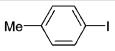
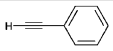
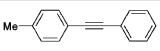
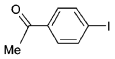
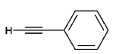
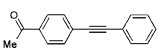
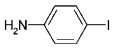
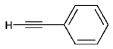
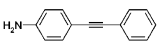
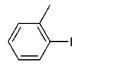
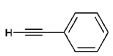
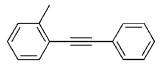
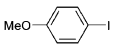
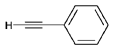
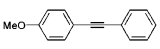
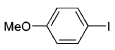
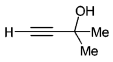
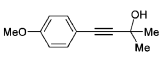
Entry	Aryl Halide	Boronic Acid	Product	Yield[a]
1				99%
2				99%
3				88%[b]
4				85%[c]

[a] Isolated yield. [b] 3% catalyst, 60 °C, 20 h. [c] 3% catalyst, 40 h.

The catalytic activity of the complexes was then determined. Satisfyingly, Suzuki cross-coupling of 4′-iodoacetophenone and 4′-bromoacetophenone with 1-naphthaleneboronic acid (Table 1, entries 1 and 2, respectively) using the $(PA\text{-}Ph)_2Pd{\cdot}dba$ complex (**2**) revealed extraordinary activity. In both cases, the reaction to form 4′-(1-naphthyl)acetophenone was completed within 10 min at room temperature with catalyst loadings as low as 0.5%. The $Pd(PA\text{-}Ph)_2{\cdot}dba$ complex was also used to effect the Suzuki coupling of 2-chlorotoluene with phenylboronic acid to yield 2-phenyltoluene (Table 1, entry 3) in 88% yield at a slightly milder temperature (60 °C)

TABLE 2. Sonogashira Reaction of Aryl Iodides



Entry	Aryl Iodide	Alkyne	Product	Yield[a]
1[b]				96%
2				93%
3				91%
4				93%
5[c]				94%
6				92%

[a] Isolated yields. [b] 0.75% catalyst. [c] Also successful with 1.2 equiv of Cs_2CO_3.

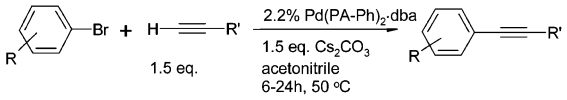
than previously described utilizing the PA-Ph/$Pd_2(dba)_3$ system.[6] Finally, the reaction of sterically hindered 2-bromomesitylene with 1-naphthaleneboronic acid (Table 1, entry 4) was catalyzed by **2** to afford an 85% conversion at room temperature. The η^2-peroxopalladium species **3** proved to be a less effective catalyst, requiring heat to promote the same reactions. This is not surprising since the $Pd(PA\text{-}Ph)_2{\cdot}O_2$ complex needs to undergo a reductive elimination of O_2 before the active palladium species is liberated and can undergo its first oxidative addition with the aryl halide.

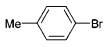
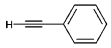
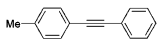
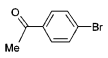
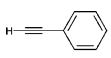
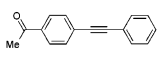
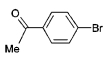
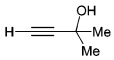
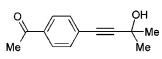
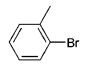
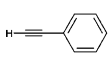
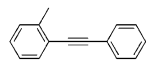
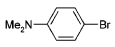
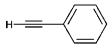
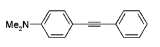
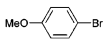
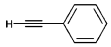
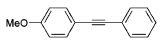
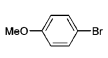
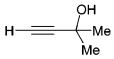
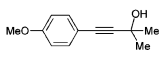
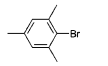
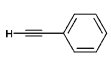
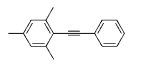
The Sonogashira reaction has proven to be an effective method for the synthesis of conjugated alkene/alkyne functionalities.[10] Application of the $Pd(PA\text{-}Ph)_2{\cdot}dba$ (**2**) complex to this class of organopalladium cross-coupling chemistry was highly successful. In the reactions involving aryl iodides, preliminary screening revealed that coupling could be effected in less than 1 h, in high yields, by using a combination of 1.5% $Pd(PA\text{-}Ph)_2{\cdot}dba$ and 2% CuI. Optimization of the reaction parameters revealed that acetonitrile was the best solvent and both diisopropylethylamine and Cs_2CO_3 were effective bases. These conditions were then applied to an array of aryl iodides and terminal alkynes (Table 2). The general protocol effected Sonogashira coupling of activated (entry 2), deactivated (entries 3, 5, and 6), and sterically demanding (entry 4) systems at room temperature, in approximately 1 h, in excellent yields. It should be noted that for reactions involving aryl iodides, omission of the copper cocatalyst necessitated longer reaction times (at room temperature) or heating to achieve comparable results.

Sonogashira coupling of aryl bromides was also effected using the $Pd(PA\text{-}Ph)_2{\cdot}dba$ complex. In this series, how-

(10) Tykwinski, R. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1566.; Sonogashira, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 3, Chapter 2.4. Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C. *Org. Lett.* **2000**, *2*, 1729. Bohm, V. P. W.; Herrmann, W. A. *Eur. J. Org. Chem.* **2000**, *22*, 3679.

TABLE 3. Copper-Free Sonogashira Reaction of Aryl Bromides



Entry	Aryl Bromide	Alkyne	Product	Yield[a]
1				95%
2				91%
3[b]				90%
4				93%
5				91%
6[c]				90%
7[b]				92%
8[c]				93%

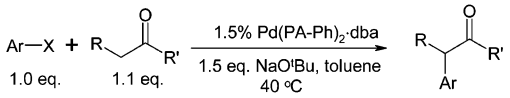
[a] Isolated yields. [b] 3.7% catalyst, 1.2 equiv of base. [c] 60 °C.

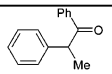
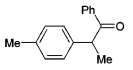
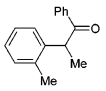
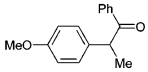
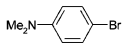
ever, addition of CuI was deleterious to the reaction. It was found that copper-free reactions of aryl bromides at 50 or 60 °C occurred efficiently, in high yield, and were complete within 6−20 h (entries 1−8, Table 3). The analogous reactions, using CuI as cocatalyst, were incomplete even after 24 h. It is unclear why the copper cocatalyst promotes the Sonogashira coupling of aryl iodides while hampering that of aryl bromides, although a plausible explanation could involve oxidation of the phosphine ligand by small amounts of Cu(II) present in the CuI. Since the oxidative addition of aryl bromides is slower than that of aryl iodides, the kinetics, in the former case, may be such that oxidation of the phosphine by Cu(II) now competes with the rate of oxidative addition and ultimately results in the poor yields obtained. Further mechanistic studies to explain this surprising result are currently underway.

The palladium-catalyzed α-arylation of ketones is another useful, general synthetic method[11] to which, it was envisaged, the Pd(PA-Ph)$_2$·dba (**2**) complex might be applied. Using the coupling of 4-bromoanisole with propiophenone for the initial screening allowed for rapid determination of the optimum reaction parameters such as solvent, base, temperature, and catalyst loading. While the reaction proceeded using various bases or solvents, the best results were obtained using NaO^{t}Bu as the base, toluene as the solvent, and a catalyst loading of 1.5%.

Application of the optimum conditions determined allowed for smooth couplings of aryl bromides and

TABLE 4. α-Arylation of Ketones



Entry	Aryl Halide	Ketone	Product	Yield[a]
1[b]				93%
2				96%
3				95%
4				96%
5				95%
6[c]				93%
7				80%
8				87%
9[c,d]				75%
10[c,d]				78%

[a] Isolated yields. [b] 0.75% catalyst. [c] 70 °C. [d] 2.2% catalyst.

chlorides with either propiophenone or isobutyrophenone within a few hours in high yields. As Table 4 illustrates, the Pd(PA-Ph)$_2$·dba complex is not only an effective catalyst for the α-arylation of ketones but is also one of the most active systems reported to date. For example, the Pd(PA-Ph)$_2$·dba-catalyzed reaction of the unactivated 4-bromoanisole with propiophenone at 40 °C afforded the coupled product in 96% yield (Table 4, entry 4) in 24 h using NaO^{t}Bu as the base. A survey of the chemical literature has revealed that other leading ligands such as P(*t*-Bu)$_3$ effect the same reaction 20 °C higher at best.[9]

The Pd(PA-Ph)$_2$·dba system provides excellent yields with an array of electron-rich and hindered aryl bromides. For instance, the coupling of 2,4-dimethoxybromobenzene and propiophenone at 40 °C affords the coupled product in 80% isolated yield (Table 4, entry 7) while the reaction of sterically hindered 2-bromomesitylene with propiophenone at 40 °C affords an 87% yield

(11) Culkin, D. A.; Hartwig. J. F. *Acc. Chem. Res.* **2003**, *36*, 234.

of the diortho-substituted α-arylated ketone. Despite the additional steric crowding about the α-position in isobutyrophenone, reaction with electron-rich *N*,*N*-dimethyl-4-bromoaniline afforded a 93% yield of the coupled product (Table 4, entry 6). Finally, the Pd(PA-Ph)$_2$·dba-catalyzed α-arylation of ketones using aryl chlorides was also achieved. Entries 9 and 10 gave satisfactory results (comparable to those already described in the literature) at 70 °C.

Overall, the Pd(PA-Ph)$_2$·dba complex has been demonstrated to be an effective catalyst for the Suzuki reaction, the α-arylation of ketones, and the Sonogashira reaction and offers a number of advantages to other catalytic systems. The complex is simple to prepare, air stable, and provides an "all-in-one" system delivering both the metal and ligand required for reaction catalysis. Furthermore, the activity of the **2** is comparable to and, in some instances better than, other systems described in the chemical literature. Finally, the ability to alter the aryl moiety of the phosphaadamantane ligand affords the opportunity to sterically and electronically fine-tune the phosphine and hence generate palladium complexes with differing catalytic potential. Applications involving **2** in other palladium-promoted cross-coupling reactions are currently under investigation.

Experimental Section

Synthesis of the Palladium Complexes of 1,3,5,7-Tetramethyl-2,4,8-trioxa-6-phenyl-6-phosphaadamantane: Pd(PA-Ph)$_2$·dba (2) and Pd(PA-Ph)$_2$·O$_2$ (3). Pd$_2$(dba)$_3$·CHCl$_3$ (1.040 g, 1.0 mmol), PA-Ph (**1**) (2.340 g, 8.0 mmol), and toluene (70 mL) were placed in a round-bottom flask, and the dark-purple mixture was stirred under argon for 2 h. At that time, the original dark-purple color of the mixture became yellow. The reaction mixture was diluted with hexane (700 mL) and allowed to stand overnight. Two crystalline compounds were formed: brown needles [Pd(PA-Ph)$_2$·dba] and green microcrystals [Pd(PA-Ph)$_2$·O$_2$], the former being the major product. The two products were obtained in roughly 90% overall yield and separated manually. Pd(PA-Ph)$_2$·dba (**2**) showed: ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.76 (d, J = 16 Hz, 2H), 7.74−7.63 (m, 8H), 7.45−7.37 (m, 6H), 7.22−7.17(m, 6H), 7.11 (d, J = 16 Hz, 2H), 2.76 (dd, J = 13.5 & 4.5 Hz, 1H,), 1.84−1.78 (m, 4H), 1.58−1.55 (m, 2H), 1.52 (s, 6H), 1.47 (d, J = 14.5 Hz, 6H), 1.33 (s, 6H), 1.25 (d, J = 13.3 Hz, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 189.0, 143.4, 135.2, 135.1, 133.3, 130.6, 129.1, 129.0, 128.7, 128.3, 125.5, 97.7, 97.0, 96.4, 96.3, 74.6, 74.2, 73.9, 72.9, 43.3, 40.3, 40.3, 39.2, 27.5, 21.3; MS[FAB] *m*/*z* (RI) 692 (79), 691 (35), 690 (100), 689 (74), 688 (33). Pd(PA-Ph)$_2$·O$_2$ (**3**) showed: ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.92−7.86 (m, 4H), 7.32−7.23 (m, 6H), 2.50 (dd, J = 13.6, 4.4 Hz, 2H), 1.71−1.56 (m, 6H), 1.48 (s, 6H), 1.47 (d, J = 14.7 Hz, 6H), 1.33 (s, 6H), 1.04 (d, J = 13.3 Hz, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 2 × 134.6, 2 × 133.3, 2 × 131.1, 2 × 128.7, 96.7, 96.6, 96.2, 96.1, 74.5, 74.4, 74.0, 73.7, 43.8, 38.2, 27.7, 26.2; MS-[FAB] *m*/*z* (RI) 693 (29), 692 (79), 691 (35), 690 (100), 689 (74), 688 (33).

For each of the coupling protocols described, a general procedure is provided as well as one specific example. All other experimental procedures are available in the Supporting Information.

General Procedure for the Pd(PA-Ph)$_2$·dba-Catalyzed Suzuki Coupling Reactions. The aryl halide (1 mmol), arylboronic acid (1.2 mmol), K$_3$PO$_4$ (2.4 mmol), Pd(PA-Ph)$_2$·dba (4.6 mg, 0.0050 mmol), and toluene (3 mL) were added to the reaction vessel, and the mixture was stirred at room temperature (or heated as required) under argon and the course of the reaction monitored by TLC. At the conclusion of the reaction, the reaction mixture was loaded onto small plug of silica gel and washed with copious amounts of Et$_2$O or EtOAc. The washings are concentrated and purified by column chromatography on silica gel. **4′-(1-Naphthyl)acetophenone (Table 1, Entries 1 and 2).** Pd(PA-Ph)$_2$·dba (4.6 mg, 0.0050 mmol), K$_3$PO$_4$ (509 mg, 2.4 mmol), 1-naphthaleneboronic acid (142 mg, 1.20 mmol), and either 4′-bromoacetophenone (199 mg, 1.00 mmol) or 4′-iodoacetophenone (246 mg, 1.00 mmol) in toluene (3 mL) were used. Both reactions were complete after 10 min and after workup and column chromatography (20% EtOAc in hexane) yielded 245 mg (99% in both cases) of the title compound as a white solid. Compound showed: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.10 (d, J = 8.1 Hz, 2H), 8.00−7.80 (m, 3H), 7.61 (d, J = 8.3 Hz, 2H), 7.58−7.40 (m, 4H), 2.69 (s, 3H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 198.0, 145.9, 139.1, 136.0, 133.9, 2 × 130.4, 5 × 128.4, 127.0, 126.5, 126.1, 125.6, 125.4, 26.8; MS[EI+] *m*/*z* (RI) 246 (100), 231 (72), 202 (68); HRMS for C$_{18}$H$_{14}$O calcd 246.1045, obsd 246.1051.

General Procedure for the Sonogashira Cross-Coupling Reactions. All liquid reagents (phenylacetylene, 2-methyl-3-butyn-2-ol, diisopropylethylamine, aryl iodides, and aryl bromides) and solvents were degassed under argon prior to use. The palladium source, Cs$_2$CO$_3$, and CuI (if required) were placed in an oven-dried reaction tube. The reaction tube was sealed with a rubber septum, evacuated, and refilled with argon. Next, the aryl halide (if a liquid; if a solid, then the aryl halide was added prior to the evacuation−refill cycle), the alkyne, and acetonitrile were added. The reaction was stirred under argon at the indicated temperature for the indicated amount of time. At the conclusion of the reaction, the reaction mixture was diluted with Et$_2$O or EtOAc, filtered through a pad of silica gel with copious washings, concentrated, and purified by column chromatography on silica gel. **4-(Phenylethynyl)toluene (Table 2, Entry 1).** Following the general procedure, using Pd(PA-Ph)$_2$·dba (7 mg, 0.0075 mmol), 4-iodotoluene (218 mg, 1.00 mmol), phenylacetylene (0.165 mL, 1.50 mmol), CuI (4 mg, 0.02 mmol), (*i*-Pr)$_2$NEt (0.210 mL, 1.20 mmol), and acetonitrile (1 mL). After 1 h at room temperature, workup and column chromatography (hexane) yielded 188 mg (96%) of the title compound as a white solid. The compound showed: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.55−7.46 (m, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.40−7.26 (m, 3H), 7.16 (d, J = 8.1 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 138.4, 4 × 131.6, 2 × 129.2, 2 × 128.4, 128.1, 123.5, 120.2, 89.6, 88.8, 21.5; MS-[EI+] *m*/*z* (RI) 192 (100), 191 (42); HRMS for C$_{15}$H$_{12}$ calcd 192.0939, obsd 192.0940.

General Procedure for the Pd(PA-Ph)$_2$·dba-Catalyzed Ketone Arylation Reactions. (PA-Ph)$_2$Pd·dba (**2**, 0.015 mmol), NaO^{t}Bu (1.50 mmol), and the aryl halide (if a solid) were placed in a reaction vessel containing a magnetic stir bar. The reaction vessel was evacuated and then refilled with argon. Toluene (1.5 mL) was added followed by the aryl halide (if a liquid), the ketone, and the remaining toluene (1.5 mL) [or THF (0.5 mL)]. The reaction was stirred at the indicated temperature for the indicated amount of time and was monitored by ^{1}H NMR. At the conclusion of the reaction, the mixture was diluted with CH$_2$Cl$_2$ or EtOAc, filtered through a pad of silica gel with copious washings, concentrated, and purified by column chromatography on silica gel. **1,2-Diphenylpropan-1-one (Table 4, Entry 1).** (PA-Ph)$_2$Pd·dba (7 mg, 0.0075 mmol), NaO^{t}Bu (144 mg, 1.50 mmol), bromobenzene (0.105 mL, 1.00 mmol), propiophenone (0.146 mL, 1.10 mmol), and toluene/THF (1.5 mL: 0.5 mL) were used. After 20 h at 40 °C, workup and column chromatography (5% EtOAc in hexane) gave 195 mg (93%) of the title compound as a pale yellow liquid. The compound showed: ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.00 (d, J = 7.2 Hz, 2H), 7.43−7.22 (m, 8H), 4.73 (q, J = 6.9 Hz, 1H), 1.59 (d, J = 6.8 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 200.2, 141.4, 136.4, 132.8, 2 × 128.9, 2 × 128.7, 2 × 128.4, 2 × 127.7, 126.8, 47.8, 19.5; MS[EI+] *m*/*z* (RI) 210 (4), 105 (100); HRMS for C$_{15}$H$_{14}$O calcd 210.1045, obsd 210.1046.

Acknowledgment. We thank Cytec Canada, Inc., and the Natural Sciences and Engineering Research Council of Canada for financial support.

Supporting Information Available: Experimental procedures for compounds shown in Table 1, entries 3 and 4, Table 2, entries 2−6, Table 3, entries 1−8, and Table 4, entries 2−10; IR spectra for compounds shown Table 3, entries 5−7; and ^{1}H NMR spectra for all compounds described. This material is available free of charge via the Internet at http://pubs.acs.org.

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