New Methods for the Synthesis of $ArPdL_2I$ (L = Tertiary Phosphine) Complexes

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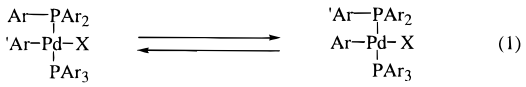
Received April 2, 1996⊗

Organopalladium $ArPdL_2I$ (L = tertiary phosphine) complexes (**1**) can be synthesized in one step from the precursors $Pd_2(dba)_3{\cdot}C_6H_6$ (**2**) (dba = *t,t*-dibenzylideneacetone) and (η^3-allyl)PdCp (**3**) (Cp = η^5-cyclopentadienide). Two advantages over previous synthetic methods are that this route requires only stoichiometric amounts of phosphine and that the desired complexes are easily isolated from reaction byproducts. The scope and generality of these reactions are investigated, and the synthesis of a number of new organic- and water-soluble complexes utilizing this methodology is discussed. Improved syntheses of water-soluble ligands $P(C_6H_5)_2(4\text{-}SO_3KC_6H_4)$ (**5**) and $As(C_6H_5)_2(4\text{-}SO_3KC_6H_4)$ (**6**) are presented as well.

Introduction

Organopalladium complexes $ArPdL_2X$ (L = tertiary phosphine, X = halide or sulfonate) play central roles as catalytic intermediates in a broad spectrum of cross-coupling reactions.[1] These complexes provide an attractive entry point into Pd-mediated cross-couplings, due to both enhanced catalytic activity relative to zerovalent PdL_n complexes[2] and ease of handling. Unlike zerovalent PdL_n compounds, $ArPdL_2X$ species are stable in air for hours to days, depending on the specific complex. A renewed interest in the stoichiometric reactivity of $ArPdL_2X$ compounds has arisen following the discovery that aryl moieties bound to the phosphorus atoms can interchange readily with the aryl group bound to the palladium center (eq 1).[3] This revelation



(1)

has potentially dramatic consequences for the synthesis of small molecules and polymers[4] utilizing palladium-mediated cross-couplings. Several recent investigations have attributed the formation of phosphine-derived byproducts in palladium-mediated cross-coupling reactions to this aryl−aryl interchange.[5] Furthermore, our own work suggests that incorporation of phosphine ligands into cross-coupling polymerizations can result not only in production of monofunctional aryl endcaps but also produce branched network structures by inadvertent generation of multifunctional phosphine monomers.[6] Given this wide range of potential consequences, a more detailed understanding of the aryl interchange process would be useful.

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⊗ Abstract published in *Advance ACS Abstracts,* August 1, 1996.

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(2) Whether or not a uniform scale for ranking the catalytic efficiency of Pd complexes exists in the context of cross-coupling remains an incompletely resolved issue. Numerous authors have reported that phosphine inhibition can play a role in limiting catalytic efficiency and/or employ stoichiometrically matched (1:2 Pd:P), entirely "ligandless", or even heterogeneous catalyst precursors. See: (a) Reference 1c,g,h and references therein. (b) Thompson, W. J.; Jones, J. H.; Lyle, P. A.; Thies, J. E. *J. Org. Chem.* **1988**, *53*, 2052. (c) Majeed, A. J.; Antonsen, O.; Benneche, T.; Undheim, K. *Tetrahedron* **1989**, *45*, 4. (d) Sandosham, J.; Undheim, K. *Acta Chem. Scand.* **1989**, *43*, 684. (e) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585 and references therein. (f) Banwell, M. G.; Cameron, J. M.; Collis, M. P.; Crisp, G. T.; Gable, R. W.; Hamel, E.; Lambert, J. N.; Mackay, M. F.; Reum, M. E.; Scoble, J. A. *Aust. J. Chem.* **1991**, *44*, 705. (g) Ali, N. M.; McKillop, A.; Mitchell, M. B.; Rebelo, R. A.; Wallbank, P. J. *Tetrahedron* **1992**, *48*, 8117. (h) Wallow, T. I.; Novak, B. M. *J. Org. Chem.* **1994**, *59*, 5034 and references therein. Alternatively, some reactions have been reported to proceed more readily in the presence of $Pd[P(C_6H_5)_3]_4$ or reaction mixtures containing excess phosphines. Use of these systems is ubiquitous; see reviews in ref 1. Catalyst stability in the presence of excess phosphines is sometimes invoked: some degree of catalyst tailoring to complement the reactivity of a given substrate appears to be necessary in instances when sterically hindered or complex multifunctional substrates are used.

Control of Pd:ligand stoichiometry is frequently accomplished by generating catalytic species *in situ*. For comprehensive discussions of subtleties that pertain to such processes as well as extensive compilations of methods employing *in-situ* generated catalysts; see: (i) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 8375. (j) Amatore, C.; Jutand, A.; Khalil, F.; M'Barki, M. A.; Mottier, L. *Organometallics* **1993**, *12*, 3168.

(3) (a) Kong, K.-C.; Cheng, C.-H. *J. Am. Chem. Soc.* **1991**, *113*, 6313. (b) Herrmann, W. A.; Brossmer, C.; Priermeier, T.; Öfele, K. *J. Organomet. Chem.* **1994**, *481*, 97.

(4) For reviews, see: (a) Schlüter, A. D.; Wegner, G. *Acta Polym.* **1993**, *44*, 59. (b) Tour, J. M. *Adv. Mater.* **1994**, *6*, 190.

(5) (a) O'Keefe, D. F.; Dannock, M. C.; Marcuccio, S. M. *Tetrahedron Lett.* **1992**, *33*, 6679. (b) Hunt, A. R.; Stewart, S. K.; Whiting, A. *Tetrahedron Lett.* **1993**, *34*, 3599. (c) Segelstein, B. E.; Butler, T. W.; Chenard, B. L. *J. Org. Chem.* **1995**, *60*, 12. Milstein has proposed that substrate-dependent structural changes of phosphine ligands during catalysis may complicate mechanistic investigations. (d) Milstein, D. *Chemtracts: Inorg. Chem.* **1991**, *3*, 356. Similarly, studies by Ceriotti *et al.* have demonstrated that an analogous ligand transformation *via* alkyl−aryl interchange renders a meaningful kinetic analysis of cyclohexene hydroformylation by Rh−phosphine complexes impossible. (e) Ceriotti, A.; Garlaschelli, L.; Longoni, G.; Malatesta, M. C.; Strumolo, D.; Fumagalli, A.; Martinengo, S. *J. Mol. Catal.* **1984**, *24*, 309.

S0276-7333(96)00256-7 CCC: $12.00

In this paper, we describe highly general, flexible, and functional-group-tolerant methods for synthesizing ArPdL$_2$I complexes (**1**). Such methods are necessary for synthesizing the variety of compounds required for substituent-effect studies of the aryl−aryl interchange and mechanistic investigations of Suzuki aryl cross-coupling reactions in aqueous media.[7] We report that the direct synthesis of ArPdL$_2$I complexes using Pd$_2$(dba)$_3$·C$_6$H$_6$ (**2**) (dba = *t*,*t*-dibenzylideneacetone) and (η^3-allyl)PdCp (**3**) (Cp = η^5-cyclopentadienide) as precursors provides high yields of the desired complexes from stoichiometric mixtures of the precursors, aryl iodides, and phosphines within minutes at room temperature. By employment of stoichiometric amounts of reagents, these routes minimize or eliminate the need for tedious and often intractable purification problems that can arise in traditional synthetic routes. Since these precursors are generic and tolerant of functional groups, ArPdL$_2$I complexes derivatized with nearly any combination of aryl moieties and substituted phosphines may be synthesized in one step. Finally, we demonstrate that **2** is a useful precursor for synthesizing water-soluble ArPdL$_2$I complexes in high yields. We note that the methods presented here may represent a convenient method for synthesizing chiral complexes,[8] since only stoichiometric amounts of potentially expensive phosphines are required.

Results and Discussion

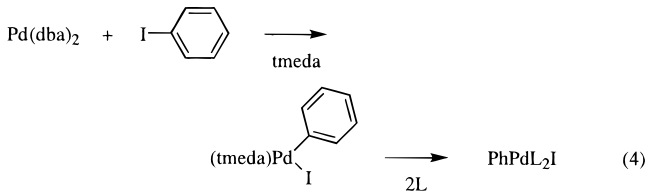
Synthetic Methodology. Given the specific importance of ArPd[P(C$_6$H$_5$)$_3$]$_2$I complexes, there are surprisingly few reports of synthetic alternatives to the traditional route involving oxidative addition of an aryl iodide to zerovalent Pd[P(C$_6$H$_5$)$_3$]$_4$[9] (eq 2). One such alterna-

$$\mathrm{Pd[P(C_6H_5)_3]_4} \xrightarrow[\mathrm{ArI}]{} \mathrm{ArPd[P(C_6H_5)_3]_2I} + 2\,\mathrm{P(C_6H_5)_3} \qquad (2)$$

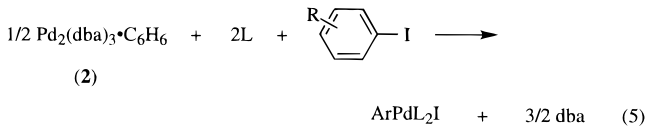
tive involves the use of strong reducing agents (eq 3) to

$$\mathrm{PdL_2X_2} \xrightarrow[2\ \mathrm{RLi}]{} \mathrm{'Pd^0L_2'} \xrightarrow[\mathrm{ArX}]{} \mathrm{ArPdL_2X} \qquad (3)$$

form the desired complexes.[10] Boersma *et al.*[11] have synthesized (C$_6$H$_5$)Pd(tmeda)I (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and reported it to be a useful precursor to bis(triphenylphosphine) species *via* ligand exchange reactions (eq 4). Treatment of the tmeda complex with 2 equiv of P(C$_6$H$_5$)$_3$ provided a 90% yield of (C$_6$H$_5$)Pd[(P(C$_6$H$_5$)$_3$]$_2$I.

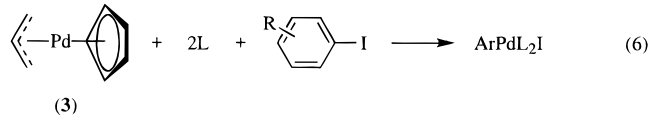


In the course of mechanistic investigations on palladium complexes, several researchers have used aryl iodides or electron-poor olefins to trap transient zerovalent "Pd(L)$_2$" species.[12] The similarity of this technique to the reports of Ishii *et al.*, who noted that Pd$_2$(dba)$_3$·solvent (solvent = C$_6$H$_6$ (**2**) or CHCl$_3$) complexes undergo a variety of ligand exchange and formal oxidative addition reactions[13] prompted us to consider **2** as a direct precursor. Given the lability of **2** and the rapid oxidative addition of aryl iodides to zerovalent palladium at room temperature,[14] a one-step, direct synthesis of ArPdL$_2$I complexes from **2** seemed feasible (eq 5). Indeed, studies presented in this paper show that



addition of a stoichiometric mixture of an aryl iodide and triarylphosphine to a solution of **2** gives a nearly quantitative yield of the desired ArPdL$_2$I complex in *ca.* 5−10 min at room temperature. Since our first preliminary disclosure on the use of this methodology,[2h] other researchers have used **2** as a precursor into ArPdL$_2$I (L = triphenylarsine) complexes[15] and (ArPdLBr)$_2$ (L = bulky phosphine) complexes.[16b]

A second one-step procedure was developed using (η^3-allyl)PdCp (**3**) as a precursor (eq 6). Shaw has shown



that **3** rapidly generates Pd[P(C$_6$H$_5$)$_3$]$_4$ in the presence of excess P(C$_6$H$_5$)$_3$.[17] Upon addition of a stoichiometric

(6) For preliminary disclosures, see: (a) Wallow, T. I.; Seery, T. A. P.; Goodson, F. E.; Novak, B. M. *Polym. Prep. (Am. Chem. Soc. Div. Polym. Chem.)* **1994**, *35* (1), 710. (b) Novak, B. M.; Wallow, T. I.; Goodson, F. E.; Loos, K. *Polym. Prep. (Am. Chem. Soc. Div. Polym. Chem.)* **1995**, *36* (1), 693.

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(12) For some examples, see: (a) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. (b) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174. (c) Ozawa, F.; Kurihara, K.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 399. (d) Ozawa, F.; Fujimori, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1986**, *5*, 2144. (e) Ozawa, F.; Kurihara, K.; Fujimori, M.; Hidaka, T.; Toyoshima, T.; Yamamoto, A. *Organometallics* **1989**, *8*, 180. (f) Reference 10b. (g) Mason, M. R.; Verkade, J. G. *Organometallics* **1992**, *11*, 2212. (h) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890. (i) Sakamoto, M.; Shimizu, I.; Yamamoto, A. *Chem. Lett.* **1995**, *1101*. Also, see ref 2i,j.

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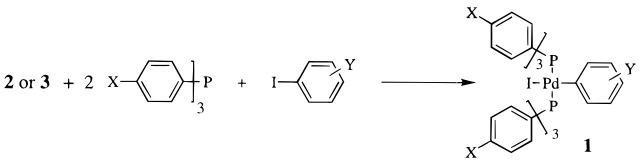
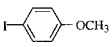
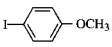
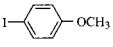
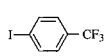
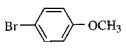
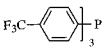
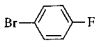
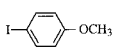
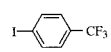
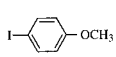
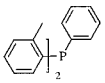
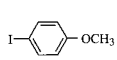
(17) Shaw, B. L. *Proc. Chem. Soc.* **1960**, 247.

Table 1. Synthesis of Organic-Soluble $ArPdL_2I$ Complexes



complex	X	Y	% yield from **2**	% yield from **3**
1a	H	4-OCH_3		90
1b	H	4-CH_3		87
1c	H	4-F		95
1d	H	4-NO_2	89	94
1e	H	4-CF_3	86	89
1f	H	2-CH_3		95
1g	H	2-OCH_3		99
1h	OCH_3	H		95
1i	OCH_3	4-CH_3		97
1j	OCH_3	4-F		98
1k	OCH_3	4-CF_3		94
1l	CH_3	H		85
1m	CH_3	4-OCH_3		87
1n	CH_3	4-F		93
1o	CH_3	4-CF_3		53
1p	F	H		91
1q	F	4-OCH_3		89
1r	F	4-CH_3		78
1s	F	4-CF_3		90
1t	CF_3	H	35	
1u	CF_3	4-OCH_3	73	77
1v	CF_3	4-CH_3	56	
1w	CF_3	4-F	80	
1x	CF_3	F_5	20	

Table 2. Synthesis of $ArPdL_2I$ Complexes: Scope and Limitations

Complex	*Ligand*	*Aryl Halide*	*% Yield from 2*	*% Yield from 3*
1y	$EtPPh_2$		--	90
1z			--	92
--			--	0
--			0	0
--			0	0
--			--	0
--			0	0
--			0	0
--			0	0
--			0	0

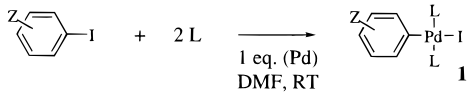
mixture of an aryl iodide and triphenylphosphine, **3** also gives a nearly quantitative yield of the desired $ArPdL_2I$ complex at room temperature. Recently, Yamamoto and co-workers were able to synthesize $ArPdL_2I$ complexes by oxidatively adding quaternary phosphonium salts to Pd(methyl acrylate)$(PMePh_2)_2$ providing another viable route to these compounds as well as some interesting insights into the mechanism of the aryl−aryl exchange reaction.[12i] However, the methodology from precursors **2** and **3** does have the important advantage of allowing the single-step synthesis of a number of different compounds containing a variety of ligands from a single palladium starting material.

Scope of Methodology. Representative syntheses of several $ArPdL_2I$ complexes (**1**) were carried out using both precursors; the results are summarized in Tables 1−3. In most cases (Table 1), complex **3** was the preferred precursor as only volatile byproducts are formed in the reaction, thus simplifying the purification of the desired products. However, **3** was found to be unreactive toward arsine-based ligands and was seen to decompose rapidly in the presence of water-solubilizing sulfonated phosphines. Consequently, for the synthesis of water-soluble complexes (Table 3), oxidative addition to precursor **2** was the preferred route.

Table 2 further illustrates the scope and generality of these procedures. Although the chelating 1,3-bis(diphenylphosphino)propane ligand promoted the reaction in the normal manner, 1,2-bis(diphenylphosphino)benzene failed to produce the target complex, presumably because of sterics (*vide infra*). The bulky, electron-poor perfluorotriphenylphosphine ligand also failed to yield identifiable complexes in the presence of either precursor. However, when tris(4-(trifluoromethyl)phenyl)phosphine was used as a ligand, the reactions proceeded as normal. When an aryl bromide was used in place of an aryl iodide, the result was a complex mixture of products from which the desired complex could not be isolated. Steric bulk on the phosphine ligands also had an adverse effect on the reactions, although ortho substituents on the aryl iodide appeared not to affect product formation. Hartwig has recently developed syntheses of several dimeric arylpalladium halide compounds with bulky phosphine ligands from a Pd^0L_2 precursor.[16] Researchers in his group also attempted to synthesize the bromide complexes directly from **2** but similarly had difficulties in isolating pure complexes in appreciable yields.[16b] The authors suggested that this might be due to dibenzylideneacetone insertions and subsequent β-hydrogen eliminations resulting in the formation of HBr. Running these reactions in the presence of triethylamine did produce pure complexes, but the yields were still no higher than those obtained from the Pd^0L_2 precursor.[16b]

Complexes **1a**−**f** have been synthesized previously (see Experimental Section); these are highly crystalline materials which can be readily purified from byproducts such as excess phosphines or dibenzylideneacetone. Thus, the methods developed here do not provide any special advantages over the known preparation of these compounds from $Pd[P(C_6H_5)_3]_4$. For organic-soluble complexes **1h**−**z**, however, the analogous PdL_4 species are not known or are not readily accessible, due largely to the expense or the nontrivial syntheses of the ligands. As a result, the preparation of these new compounds is made possible specifically by the methods described above. Preliminary studies on the aqueous systems showed the syntheses of complexes **1aa**−**ee** *via* analogous water-soluble PdL_3 precursors[7] to be unsatisfac-

Table 3. Synthesis of Water-Soluble $ArPdL_2I$ Complexes



complex	Z	ligand	% yield from **2**	% yield from **3**
1aa	−3-CO_2CH_3	$P[(C_6H_5)_3]_2(3\text{-}SO_3NaC_6H_4)$ (**4**)	94[a]	0
1bb	−4-CO_2CH_3	$P[(C_6H_5)_3]_2(4\text{-}SO_3KC_6H_4)$ (**5**)	95[a]	
1cc	−4-CO_2CH_3	$As[(C_6H_5)_3]_2(4\text{-}SO_3KC_6H_4)$ (**6**)	84[a]	
1dd	−4-NO_2	**5**	99	
1ee	−4-CF_3	**5**	99	

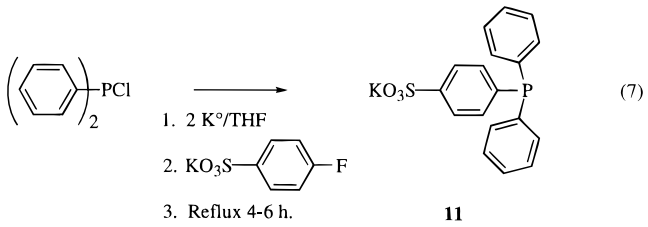
[a] Crude yield.

tory; the reactions went to completion, but as the solubilities of the products matched those of the liberated phosphines, purification of the complexes proved to be difficult. Consequently, the stoichiometric procedures presented in this paper provide a notable improvement in the synthesis of these compounds as well.

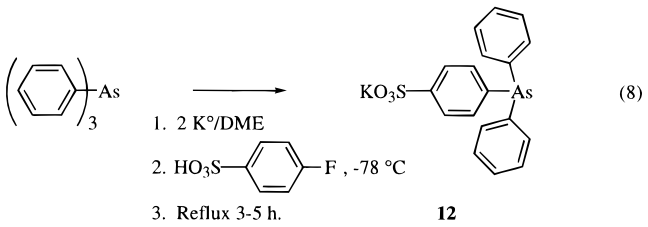
Water soluble compound **1aa** appears to be noncrystalline, and the removal of trapped solvents has proven to be difficult. In order to overcome this problem, we prepared more symmetric analogs. Substitution of highly crystalline phosphine **5** in place of phosphine **4** and use of methyl 4-iodobenzoate as an aryl iodide instead of the corresponding 3-isomer produced crystalline complex **1bb**, which could be obtained in analytical purity. Arsine complex **1cc** and phosphine complexes **1dd,ee** were prepared in the same manner. Ironically, neither **1bb** nor **1cc** is stable in unbuffered water for more than approximately 30 min at room temperature, due to apparent ester hydrolysis and subsequent acid-promoted decomposition. Solutions prepared in aqueous bicarbonate solution or methanol are stable for several hours at room temperature and for days when stored at −20 °C. Both complexes **1dd,ee** are water stable. However, they are potent surfactants and are best prepared as stock solutions in aqueous mixtures with alcohols or acetone to suppress foaming.

Synthesis of $P(C_6H_5)_2(4\text{-}SO_3KC_6H_4)$ (5) and $As(C_6H_5)_2(4\text{-}SO_3KC_6H_4)$ (6). The *meta*-substituted monosulfonated triphenylphosphine $P(C_6H_5)_2(3\text{-}SO_3NaC_6H_4)$ (**4**) has been used extensively as a supporting ligand for water-soluble transition-metal complexes.[18] Its *para*-isomer, **5**, offers several advantages over **4**, including improved crystallinity of both the ligand and its metal complexes, simplified spectroscopic characteristics, and convenience of preparation and purification. The analogous *para*-substituted monosulfonated triphenylarsine **6** is also easily prepared; its corresponding *meta*-isomer has not been described previously. Both **5** and **6** have been known for some time; however, they have not found use until very recently,[19] since classical preparations have yielded both ligands only as byproducts formed under forcing conditions.[20]

Ligands **5** and **6** can be produced under mild conditions and in good yields by reaction of potassium 4-fluorobenzenesulfonate with potassium diphenylphosphide or -arsenide, respectively. Reaction yields are highly dependent on both the choice of solvent and the preparative routes used to generate potassium diphenylphosphide and -arsenide. The most effective synthesis of **5** employs chlorodiphenylphosphine in THF as shown in eq 7, while **6** is more readily prepared from



(7)



(8)

triphenylarsine in DME (eq 8). Negligible yields are obtained *via* the reduction of either $P(C_6H_5)_3$ or $As(C_6H_5)_3$ in THF or diethyl ether. THF displays poor stability in the presence of extremely reactive anions such as phenylpotassium at room temperature,[21] while diethyl ether is too nonpolar to facilitate reduction of the phosphine and arsine. Synthesis of **5** from $P(C_6H_5)_3$ in analogy to eq 7 proceeds in only 28% yield. This poor yield appears to result from reaction of the phosphide anion with DME. Anhydrous 4-fluorobenzenesulfonic acid was found to be a convenient source of protons for selectively quenching phenylpotassium in the preparation of **6**.

Recrystallization from water affords analytically pure **5** and **6** in 66% and 62% yields, respectively. Phosphine **5** forms a stable hydrate, while the arsine crystallizes without associated water. This difference is reflected

(18) For reviews, see: (a) Kalck, P.; Monteil, F. *Adv. Organomet. Chem.* **1992**, *34*, 219. (b) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524. (c) Li, C.-J. *Chem. Rev.* **1993**, *93*, 2023.

(19) A modern synthesis of **5** has been developed recently using a nucleophilic aromatic substitution similar to the method presented here. See: (a) Herd, O.; Langhans, K. P.; Stelzer, O.; Weferling, N.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1058. (b) Herd, O.; Hessler, A.; Langhans, K.; Stelzer, O. *J. Organomet. Chem.* **1994**, *475*, 99. Instead of employing reducing metals, the authors generate potassium diphenylphosphide in KOH/DMSO by deprotonation of diphenylphosphine, an approach which has been used previously for the alkylation of primary and secondary phosphines. See: (c) Tsvetkov, E. N.; Bondarenko, N. A.; Malakhova, I. G.; Kabachnik, M. I. *Synthesis* **1986**, 198 and references therein. On balance, the two methods appear to be similar in terms of synthetic ease and reaction yield.

(20) (a) Schindlbauer, H. *Monatsh. Chem.* **1965**, *96*, 2051. (b) Schindlbauer, H.; Lass, H. *Monatsh. Chem.* **1968**, *99*, 2460.

(21) See: Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 972 and references therein.

in their respective palladium complexes: lyophilization yields arsine complex **1cc** as a completely anhydrous powder, whereas small amounts of water are very difficult to remove even from lyophilized samples of phosphine complexes **1bb,dd,ee**.

Conclusion

To summarize, the precursors $Pd_2(dba)_3{\cdot}C_6H_6$ (**2**) (dba = *t,t*-dibenzylideneacetone) and (η^3-allyl)PdCp (**3**) (Cp = η^5-cyclopentadienide) provide a convenient route into $ArPdL_2I$ complexes. This methodology is tolerant of a variety of functional groups, although it does not appear to be a good method for the synthesis of the analogous bromides or for complexes with sterically bulky or extremely electron-poor phosphines. From these precursors, we have successfully synthesized a number of organic and water soluble complexes for mechanistic studies of the aryl−aryl exchange reaction and of Suzuki coupling reactions in aqueous media. These investigations will be discussed in further disclosures.

Experimental Section

General Methods. Schlenk-line or drybox (Vacuum Atmospheres Inc. HE-43-2 drybox equipped with a HE 493 Dry Train; maintained under positive argon pressure) techniques were used for all manipulations. ^{1}H NMR spectra were acquired at 300, 400, or 500 MHz using Bruker AM-series and AMX-series spectrometers; proton-decoupled ^{13}C, ^{19}F, and ^{31}P spectra were obtained at corresponding frequencies. ^{1}H and ^{13}C chemical shifts are reported relative to tetramethylsilane, ^{31}P chemical shifts are reported relative to 85% phosphoric acid, and ^{19}F chemical shifts are reported relative to fluorobenzene ($\delta = -113.1$). THF, DME, diethyl ether, hexanes, and toluene were purified by distillation from sodium/benzophenone and used immediately. DMF was dried over 4 Å molecular sieves, filtered, and vacuum distilled prior to use. Water and alcohols were deoxygenated by prolonged sparging with an argon stream. Aryl halides were obtained from Aldrich and sublimed or distilled prior to use. Organic soluble phosphines except phenyldi-*o*-tolylphosphine were used as received from Strem Chemicals. Phenyldi-*o*-tolylphosphine was prepared from a literature procedure.[22] Mass spectra were performed by the U.C. Berkeley Mass Spectrometry Laboratory. Analytical data were obtained by the elemental analysis facilities at the University of California at Berkeley and the University of Massachusetts at Amherst.

Palladium Complex Synthesis. Complexes **2**[13a] and **3**[23] were synthesized by standard methods. *Caution!* Complex **3** is a modestly air-stable, highly volatile organometallic. While we are unaware of documented health risks associated with **3** in particular, volatile transition metal complexes, specifically those of the nickel triad, can be quite toxic. Complex **3** has a painful, piercingly noxious odor and should be handled accordingly. ^{1}H, ^{19}F, and ^{31}P NMR characterization of complexes **1a**−**ee** was quite straightforward. ^{13}C NMR spectra were complicated by multiple couplings and ^{13}C−^{31}P virtual coupling.[24] In combination with the limited solubility of complexes **1a**−**ee**, these effects hampered the detection of weak, multiply split, or overlapping resonances. As a result, complete ^{13}C NMR spectral assignments were not possible in many cases. Partial tabulations are included, where appropriate. Complexes **1a**−**ee** are not particularly robust and decompose thermally over the course of hours (for complexes made from electron-donating aryl iodides) to several weeks (for complexes made from electron-withdrawing aryl iodides) at room temperature even when stored under argon. Consequently, care should be taken to prechill solvents used in the preparation of these materials, and the exposure of the complexes to ambient temperatures should be limited as much as possible. They are, however, indefinitely stable when stored under argon at −30 °C.

Ligand Synthesis. *Meta*-substituted phosphine **4** was synthesized according to the literature procedure.[25] Chlorodiphenylphosphine was obtained commercially, stored in a drybox, and used without further purification. Triphenylarsene was sublimed before use. Metallic potassium was stripped of hydroxides and freshly cut in a drybox. Anhydrous 4-fluorobenzenesulfonic acid was obtained by stripping water from the crystalline hydrate at 50 °C *in vacuo*, followed by two Kugelrohr distillations. The anhydrous acid is an intensely hygroscopic colorless liquid and must be handled with complete exclusion of moisture. A 0.373 M stock solution was prepared in toluene and stored at −20 °C in a Teflon stopcock equipped Schlenk tube. Potassium 4-fluorobenzenesulfonate was prepared by titrating an aqueous solution of the acid with potassium bicarbonate, followed by recrystallization from water. The resulting crystals were rinsed with cold water, dried *in vacuo* at 80 °C for several hours, then ground into a fine powder, and once again dried *in vacuo* at 80 °C overnight.

Preparation of Organic-Soluble Pd Complexes 1a−z. General Procedure from Precursor 2. THF solutions of **2** (92.0 mg, 0.0926 mmol), aryl iodide (0.185 mmol), and ligand (0.370 mmol) were chilled to −30 °C and then combined in a 20 mL scintillation vial equipped with a stirbar. The reaction was allowed to stir at room temperature until the deep violet color faded to a bright yellow (generally 5−15 min), after which the solvent was then removed with a rotary evaporator leaving a yellow solid mass. This was dissolved in a minimum amount of cold toluene (prechilled to −30 °C) and filtered onto a plug of silica in a pipette with cold toluene as eluent. The product eluted with the solvent front as a pale yellow band leaving behind dibenzylideneacetone as an intense yellow band. The solution was filtered through a 0.2 μm PTFE membrane and then concentrated, layered with hexanes (2−4 volumes), and chilled to −30 °C overnight. The resulting crystals were collected via filtration and dried *in vacuo* or by lyophilization from benzene.

General Procedure from Precursor 3. THF solutions (1 mL) of **3** (39.4 mg, 0.185 mmol), aryl iodide (0.185 mmol), and ligand (0.370 mmol) were chilled to −30 °C and then combined in a 20 mL scintillation vial equipped with a stirbar. The reaction was allowed to stir at room temperature until the deep orange-red color faded to a pale yellow (generally 5−15 min), after which the solution was filtered through a 0.2 μm PTFE membrane, concentrated, layered with hexanes, and chilled to −30 °C overnight. The resulting crystalline mass was then collected via filtration and dried *in vacuo* or by lyophilization from benzene.

(4-Methoxyphenyl)Pd[P(C_6H_5)$_3$]$_2$I (1a).[3] Synthesized from 3. The above general procedure was followed by utilizing 19.8 mg (0.0925 mmol) of **3**, 21.7 mg (0.0925 mmol) of 4-iodoanisole, 48.5 mg (0.185 mmol) of triphenylphosphine, and dry, degassed CH_2Cl_2 as solvent. A 72.0 mg amount of a pale

(22) Bennett, M. A.; Longstaff, P. A. *J. Am. Chem. Soc.* **1969**, *91*, 6266.

(23) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 342.

(24) $^2J_{P-P}$ coupling in square-planar Pd(II) diphosphine complexes produces AXX′ or A[X]$_2$ spin systems observable in {^{1}H} ^{13}C NMR spectra. In the limit where $^2J_{P-P}$ is large, ^{13}C resonances resolve into apparent triplets. For discussions, see: (a) Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 1975. (b) Pregosin, P. S.; Kunz, R. *Helv. Chim. Acta* **1975**, *58*, 423. (c) Verstuyft, A. W.; Nelson, J. H.; Cary, L. W. *Inorg. Chem.* **1976**, *15*, 732. (d) Verstuyft, A. W.; Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1976**, *15*, 1128. (e) Pregosin, P. S., Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer: Berlin, 1979; pp 65−74.

(25) (a) Ahrland, S.; Chatt, J.; Davies, N. R.; Williams, A. A. *J. Chem. Soc.* **1958**, *90*, 276. Very recently, notable improvements in the synthesis of *m*-sulfonated triarylphosphines have been realized by using $H_2SO_4/SO_3/B(OH)_3$ as the sulfonating medium. (b) Herrmann, W. A.; Albanese, G. P.; Manetsberger, R. B.; Lappe, P.; Bahrmann, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 811.

greenish-yellow powder, **1a**, was recovered (0.0832 mmol, 90%): ^{1}H NMR ($CDCl_3$) δ 3.48 (s, 3H), 5.92 (d, J = 8.6Hz, 2H), 6.40 (m, 2H), 7.24 (apparent t, J_{app} = 7.1 Hz, 12H), 7.29 (apparent t, J_{app} = 7.2 Hz, 6H), 7.50 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 55.4, 114.5, 127.7 (apparent t, J_{app} = 5.2 Hz), 129.7, 132.3 (apparent t, J_{app} = 23.0 Hz), 134.9 (apparent t, J_{app} = 6.2 Hz), 135.7, additional resonances not resolved; ^{31}P NMR ($CDCl_3$) δ 22.9. Anal. Calcd for $C_{43}H_{37}IOP_2Pd$: C, 59.71; H, 4.31. Found: C, 59.84; H, 4.24.

(4-Methylphenyl)Pd[P(C_6H_5)$_3$]$_2$I (1b).[26] **Synthesized from 3.** The above general procedure was followed using 39.4 mg (0.185 mmol) of **3**, 40.4 mg (0.185 mmol) of 4-iodotoluene, 97.0 mg (0.370 mmol) of triphenylphosphine, and dry, degassed CH_2Cl_2 as solvent. This yielded 137.2 mg of a pale greenish-yellow powder, **1b** (0.162 mmol, 87%): ^{1}H NMR ($CDCl_3$) δ 1.91 (s, 3H), 6.07 (d, J = 7.6 Hz, 2H), 6.40 (dt, J = 8.0 Hz, J = 2.2 Hz, 2H), 7.22 (m, 12H), 7.30 (t, J = 7.6 Hz, 6H), 7.49 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 20.1, 127.7 (apparent t, J_{app} = 5.1 Hz), 128.9 129.6, 131.0, 132.3 (apparent t, J_{app} = 22.9 Hz) 134.9 (apparent t, J_{app} = 6.3 Hz), 135.5 (br m) additional resonances not resolved; ^{31}P NMR ($CDCl_3$) δ 22.6.

(4-Fluorophenyl)Pd[P(C_6H_5)$_3$]$_2$I (1c).[27] **Synthesized from 3.** The above general procedure was followed using 39.4 mg (0.185 mmol) of **3**, 41.1 mg (0.185 mmol) of 4-fluoroiodobenzene, and 97.0 mg (0.370 mmol) of triphenylphosphine to yield 150.1 mg of **1c** as greenish-white flakes (0.176 mmol, 95%): ^{1}H NMR ($CDCl_3$) δ 6.02 (m, 2H), 6.48 (m, 2H), 7.25 (t, J = 7.3 Hz, 12H), 7.33 (t, J = 7.3 Hz, 6H), 7.51 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 114.5 (d, J_{C-F} = 18.9 Hz), 127.8 (apparent t, J_{app} = 5.1 Hz), 129.8, 132.0 (apparent t, J_{app} = 23.4 Hz), 134.9 (apparent t, J_{app} = 6.2 Hz), 135.8 (m), 151.6, 160.2 (d, $^1J_{C-F}$ = 239.5 Hz); ^{19}F NMR ($CDCl_3$) δ −125.1; ^{31}P NMR ($CDCl_3$) δ 22.9.

(4-Nitrophenyl)Pd[P(C_6H_5)$_3$]$_2$I (1d).[9a] **Synthesized from 2.** A solution of 4-iodonitrobenzene (0.052 g, 0.204 mmol) and triphenylphosphine (0.106 g, 0.408 mmol) in 3 mL of THF was added to a solution of $Pd_2(dba)_3{\cdot}C_6H_6$ (**2**) (0.100 g, 0.101 mmol) in 2 mL of THF. The reaction was complete within 5 min; the solution was filtered through a 0.2 μm PTFE membrane which was rinsed with additional THF until any precipitated product had redissolved. The filtrate was concentrated, two volumes of hexanes were added, and the flask was chilled for several hours (−30 °C) to yield 0.170 g of complex **1d** as a crystalline mono-THF solvate (0.179 mmol, 89%).

Synthesized from 3. A solution of 4-iodonitrobenzene (0.052 g, 0.204 mmol) and triphenylphosphine (0.106 g, 0.408 mmol) in 3 mL of THF was added to a solution of (η^3-allyl)-PdCp (**3**) (0.043 g, 0.202 mmol) in 2 mL of THF. The reaction was stirred for 5 min and then filtered, concentrated, layered with hexanes, and chilled to −30 °C. Collection of the crystalline deposit yielded 0.181 g of complex **1d** as the THF solvate (0.191 mmol, 94%): ^{1}H NMR ($CDCl_3$) δ 6.86 (d, J = 8.7 Hz, 1H), 7.03 (d, J = 8.7 Hz, 1H), 7.25 (m, 6H), 7.35 (m, 3H), 7.55 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 120.8, 127.9 (apparent t, J_{app} = 5.1 Hz), 130.2, 131.3 (apparent t, J_{app} = 23.7 Hz), 134.8 (apparent t, J_{app} = 6.2 Hz), 135.8, 143.7, 176.9, additional resonances not resolved; ^{31}P NMR ($CDCl_3$) δ 23.2.

(4-(Trifluoromethyl)phenyl)Pd[P(C_6H_5)$_3$]$_2$I (1e).[9c,d] **Synthesized from 2.** The above procedure for **1d** employing 4-iodobenzotrifluoride (0.056 g, 0.204 mmol) triphenylphosphine (0.106 g, 0.408 mmol), and $Pd_2(dba)_3{\cdot}C_6H_6$ (**2**) (0.100 g, 0.101 mmol) yielded 0.169 g of complex **1e** as a mono-THF solvate (0.173 mmol, 86%).

Synthesized from 3. The above procedure for **1d** yielded 0.175 g of complex **1e** as a mono-THF solvate (0.180 mmol, 89%): ^{1}H NMR ($CDCl_3$) δ 6.39 (d, J = 8.0 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 7.24 (m, 6H), 7.31 (m, 3H), 7.51 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 123.3 (m), 124.9 (q, $^1J_{C-F}$ = 265.5 Hz), 127.9 (apparent t, J_{app} = 5.1 Hz), 130.0, 131.6 (apparent t, J_{app} = 23.5 Hz), 134.8 (apparent t, J_{app} = 6.2 Hz), 135.7 (apparent t, J_{app} = 4.9 Hz), additional resonances not resolved; ^{19}F NMR ($CDCl_3$) δ −61.7; ^{31}P NMR ($CDCl_3$) δ 23.7. Anal. Calcd for $C_{43}H_{34}F_3IP_2Pd$: C, 57.20; H, 3.80. Found: C, 57.09; H, 3.94.

(2-Methylphenyl)Pd[P(C_6H_5)$_3$]$_2$I (1f).[28] **Synthesized from 3.** The above general procedure was followed using 39.4 mg (0.185 mmol) of **3**, 40.4 mg (0.185 mmol) of 2-iodotoluene, and 97.0 mg (0.370 mmol) of triphenylphosphine to yield 0.149 g of **1f** as a pale greenish-yellow powder (0.175 mmol, 95%): ^{1}H NMR ($CDCl_3$) δ 1.82 (s, 3H), 6.08 (d, J = 7.0 Hz, 1H), 6.26 (apparent t, J_{app} = 7.2 Hz, 1H), 6.39 (apparent t, J_{app} = 7.2 Hz, 1H), 6.86 (m, 1H), 7.22 (apparent t, J_{app} = 7.5 Hz, 12H), 7.31 (apparent t, J_{app} = 7.4 Hz, 6H), 7.46 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 15.3, 122.9, 124.1, 127.7 (apparent t, J_{app} = 5.0 Hz), 129.7, 130.4, 132.1 (apparent t, J_{app} = 22.8 Hz), 134.8, 134.9 (apparent t, J_{app} = 6.1 Hz), 141.2, 159.8; ^{31}P NMR ($CDCl_3$) δ 22.7. Anal. Calcd for $C_{43}H_{37}IP_2Pd$: C, 60.83; H, 4.39. Found: C, 60.99; H, 4.33.

(2-Methoxyphenyl)Pd[P(C_6H_5)$_3$]$_2$I (1g). Synthesized from 3. The above general procedure was followed using 39.4 mg (0.185 mmol) of **3**, 43.3 mg (0.185 mmol) of 2-iodoanisole, and 97.0 mg (0.370 mmol) of triphenylphosphine yielding 0.159 g of **1g**, a pale greenish-yellow powder (0.184 mmol, 99%): ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 3H), 5.40 (dd, J = 8.1 Hz, J = 1.3 Hz, 1H), 6.17 (apparent t, J_{app} = 7.2 Hz, 1H), 6.37 (apparent t, J_{app} = 7.3 Hz, 1H), 6.86 (m, 1H), 7.21 (m, 12H), 7.28 (apparent t, J_{app} = 7.3 Hz, 6H), 7.52 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 53.6, 109.2, 120.0, 124.0, 127.5 (apparent t, J_{app} = 5 Hz), 129.5, 132.6 (apparent t, J_{app} = 22.8 Hz), 134.2, 134.8 (apparent t, J_{app} = 6.4 Hz), 146.0, 159.0; ^{31}P NMR ($CDCl_3$) δ 23.1. Anal. Calcd for $C_{43}H_{37}IOP_2Pd$: C, 59.71; H, 4.31. Found: C, 59.47; H, 4.24.

(Phenyl)Pd[P(4-methoxyphenyl)$_3$]$_2$I (1h). Synthesized from 3. The above general procedure was followed using 39.4 mg (0.185 mmol) of **3**, 37.8 mg (0.185 mmol) of iodobenzene, and 130.2 mg (0.370 mmol) of tris(4-methoxyphenyl)phosphine to yield 0.169 g of **1h**, a white powdery solid (0.166 mmol, 90%): ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 18H), 6.24 (apparent t, J_{app} = 7.4 Hz, 2H), 6.36 (t, J = 7.2 Hz, 1H), 6.56 (m, 2H), 6.74 (d, J = 8.6 Hz, 12H), 7.37 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 55.2, 113.4 (apparent t, J_{app} = 5.7 Hz), 121.6, 124.1 (apparent t, J_{app} = 25.2 Hz), 127.3, 136.2 (apparent t, J_{app} = 6.9 Hz), 160.6, 161.2, one additional resonance not resolved; ^{31}P NMR ($CDCl_3$) δ 19.5. Anal. Calcd for $C_{48}H_{47}IO_6P_2Pd$: C, 56.79; H, 4.67. Found: C, 56.89; H, 4.93.

(4-Methylphenyl)Pd[P(4-methoxyphenyl)$_3$]$_2$I (1i). Synthesized from 3. The above general procedure was followed using 39.4 mg (0.185 mmol) of **3**, 40.4 mg (0.185 mmol) of 4-iodotoluene, and 130.2 mg (0.370 mmol) of tris(4-methoxyphenyl)phosphine to yield 0.184 g of **1i** as a white powdery solid (0.179 mmol, 97%): ^{1}H NMR ($CDCl_3$) δ 1.96 (s, 3H), 3.79 (s, 18 H), 6.12 (d, J = 7.5 Hz, 2H), 6.40 (m, 2H), 6.76 (d, J = 8.8 Hz, 12H), 7.40 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 20.2, 55.2, 113.3 (apparent t, J_{app} = 5.4 Hz), 124.1 (apparent t, J_{app} = 25.5), 128.4, 130.5, 135.6, 136.3 (apparent t, J_{app} = 6.9 hz), 155.3, 160.5; ^{31}P NMR ($CDCl_3$) δ 19.1. Anal. Calcd for $C_{49}H_{49}IO_6P_2Pd$: C, 57.19; H, 4.76. Found: C, 56.94; H, 4.90.

(4-Fluorophenyl)Pd[P(4-methoxyphenyl)$_3$]$_2$I (1j). Synthesized from 3. The above general procedure was followed using 39.4 mg (0.185 mmol) of **3**, 41.1 mg (0.185 mmol) of *p*-fluoroiodobenzene, and 130.2 mg (0.370 mmol) of tris(4-methoxyphenyl)phosphine to yield 0.188 g of **1j** as a white powdery solid (0.182 mmol, 98%): ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 18H), 6.05 (app t, J = 9.2 Hz, 2H), 6.45 (m, 2H), 6.76 (d, J = 8.8 Hz, 12H), 7.39 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 55.2, 113.4 (apparent t, J_{app} = 5.5 Hz), 113.9 (d, J_{C-F} = 18.9 Hz), 123.8 (apparent t, J_{app} = 25.6 Hz), 135.9 (apparent dt, J_{app} = 5.5 Hz, J_{app} = 5.1 Hz), 136.2 (apparent t, J_{app} = 6.9 Hz) 136.2 (apparent t, J_{app} = 6.9 Hz), 153.9, 160.0 (d, $^1J_{C-F}$ = 237.3 Hz), 160.7; ^{19}F NMR ($CDCl_3$) δ −125.5; ^{31}P NMR ($CDCl_3$) δ 19.4 (d,

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J_{P-F} = 3.2 Hz). Anal. Calcd for $C_{48}H_{46}FIO_6P_2Pd$: C, 55.80; H, 4.49. Found: C, 55.78; H, 4.49.

(4-(Trifluoromethyl)phenyl)Pd[P(4-methoxyphenyl)$_3$]$_2$I (1k). Synthesized from 3. The above general procedure was followed by utilizing 19.8 mg (0.0925 mmol) of **3**, 25.2 mg (0.0925 mmol) of 4-iodobenzotrifluoride, and 65.1 mg (0.185 mmol) of tris(4-methoxyphenyl)phosphine. This yielded 0.094 mg (0.087 mmol, 94%) of **1k** as a pale yellow powder: ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 18H), 6.44 (d, J = 8.0, 2H), 6.69 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 8.8 Hz, 12H), 7.39 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 55.1, 122.8 (br), 123.4 (apparent t, J_{app} = 25.7 Hz), 135.7 (br), 136.1 (apparent t, J_{app} = 7.0 Hz), 160.8, additional resonances not resolved; ^{19}F NMR ($CDCl_3$) δ −61.8; ^{31}P NMR ($CDCl_3$) δ 19.5. Anal. Calcd for $C_{49}H_{46}F_3IO_6P_2Pd$: C, 54.34; H, 4.28. Found: C, 54.20; H, 4.33.

(Phenyl)Pd[P(4-methylphenyl)$_3$]$_2$I (1l). Synthesized from 3. The above general procedure was applied using 39.4 mg (0.185 mmol) of **3**, 37.8 mg (0.185 mmol) of iodobenzene, and 112.4 mg (0.370 mmol) of tri-*p*-tolylphosphine to yield **1l** as a yellow crystalline mass. Residual solvent was removed via lyophilization from benzene (0.145 g, 0.158 mmol, 85%): ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 18H), 6.17 (app t, J = 7.5 Hz, 2H), 6.32 (t, J = 7.2 Hz, 1H), 6.54 (m, 2H), 7.01 (d, J = 7.7 Hz, 12H), 7.35 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 21.4, 121.3, 127.5, 128.4 (apparent t, J_{app} = 5.2 Hz), 129.3 (apparent t, J_{app} = 23.7 Hz), 134.8 (apparent t, J_{app} = 6.3 Hz), 136.1 (br), 139.5, 159.7; ^{31}P NMR ($CDCl_3$) δ 21.1. Anal. Calcd for $C_{48}H_{47}IP_2Pd$: C, 62.72; H, 5.15. Found: C, 62.92; H, 5.21.

(4-Methoxyphenyl)Pd[P(4-methylphenyl)$_3$]$_2$I (1m). Synthesized from 3. The above general procedure was applied using 39.4 mg (0.185 mmol) of **3**, 43.3 mg (0.185 mmol) of iodoanisole, and 112.4 mg (0.370 mmol) of tri-*p*-tolylphosphine to yield **1m** as yellow needlelike crystals. Residual solvent was removed by freeze-drying the product from benzene (0.153g, 0.161 mmol, 87%): ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 18H), 3.47 (s, 3H), 5.89 (d, J = 8.6 Hz, 2H), 6.35 (m, 2H), 7.02 (d, J = 7.7 Hz, 12H), 7.37 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 21.4, 55.3, 114.1, 128.4 (apparent t, J_{app} = 5.1 Hz), 129.3 (apparent t, J_{app} = 23.8), 134.6, 134.8 (apparent t, J_{app} = 6.2 Hz), 135.7, 136.6, 139.5; ^{31}P NMR ($CDCl_3$) δ 21.0. Anal. Calcd for $C_{49}H_{49}IOP_2Pd$: C, 62.01; H, 5.20. Found: C, 61.70; H, 5.20.

(4-Fluorophenyl)Pd[P(4-methylphenyl)$_3$]$_2$I (1n). Synthesized from 3. The above general procedure was applied using 39.4 mg (0.185 mmol) of **3**, 41.1 mg (0.185 mmol) of 4-fluoroiodobenzene, and 112.4 mg (0.370 mmol) of tri-*p*-tolylphosphine to yield **1n** as a yellow crystalline mass. Residual solvent was removed by freeze-drying the product from benzene (0.162 g, 0.173 mmol, 93%): ^{1}H NMR ($CDCl_3$) δ 2.30, (s, 12H), 5.98 (d, J = 7.4 Hz, 2H), 6.43 (m, 2H), 7.02 (d, J = 8.0 Hz, 12H), 7.37 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 21.3, 114.0 (d, J_{C-F} = 18.9 Hz), 128.5 (apparent t, J_{app} = 5.3 Hz), 129.1 (apparent t, J_{app} = 24.2 Hz), 134.8 (apparent t, J_{app} = 6.5 Hz), 135.8 (m), 139.7, 152.6, additional resonances not resolved; ^{19}F NMR ($CDCl_3$) δ −125.6; ^{31}P NMR ($CDCl_3$) δ 21.1 (d, J_{P-F} = 3.8 Hz). Anal. Calcd for $C_{48}H_{46}FIP_2Pd$: C, 61.52; H, 4.95. Found: C, 61.20; H, 4.98.

(4-(Trifluoromethyl)phenyl)Pd[P(4-methylphenyl)$_3$]$_2$I (1o). Synthesized from 3. The above general procedure was applied using 19.8 mg (0.0925 mmol) of **3**, 25.2 mg (0.0925 mmol) of 4-iodobenzotrifluoride, and 56.2 mg (0.185 mmol) of tri-*p*-tolylphosphine to yield **1o** as a pale yellow, feathery precipitate (48.6 mg, 0.0492 mmol, 53%): ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 18H), 6.32 (d, J = 8.0 Hz, 2H), 6.64 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 7.6 Hz, 12H), 7.38 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 122.9 (q, J_{C-F} = 3.9 Hz), 123.6 (br), 128.6 (apparent t, J_{app} = 5.3 Hz), 128.7 (apparent t, J_{app} = 24.2 Hz), 134.7 (apparent t, J_{app} = 6.5 Hz), 135.7 (apparent t, J_{app} = 4.9 Hz), 140.0, additional resonances not resolved; ^{19}F NMR ($CDCl_3$) δ −62.0; ^{31}P NMR ($CDCl_3$) δ 21.3. Anal. Calcd for $C_{49}H_{46}F_3IP_2Pd$: C, 59.62; H, 4.70. Found: C, 59.35; H, 4.87.

(Phenyl)Pd[P(4-fluorophenyl)$_3$]$_2$I (1p). Synthesized from 3. The above general procedure was applied using 39.4 mg (0.185 mmol) of **3**, 37.8 mg (0.185 mmol) of iodobenzene, and 117.0 mg (0.370 mmol) of tri-*p*-fluorophenylphosphine to yield **1p** as bright yellow crystals. These were then freeze-dried from benzene in order to remove solvent of crystallization (0.158 g, 0.168 mmol, 91%): ^{1}H NMR ($CDCl_3$) δ 6.32 (apparent t, J_{app} = 7.3 Hz, 2H), 6.45 (t, J = 7.2 Hz, 1H), 6.53 (m, 2H), 6.95 (apparent t, J_{app} = 8.8 Hz, 12 H), 7.41 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 115.4 (apparent dt, J_{app} = 21.2 Hz, J_{app} = 5.5 Hz), 122.5, 127.3 (apparent td, J_{app} = 24.4 Hz, J_{app} = 3.3 Hz), 128.3, 135.8 (apparent t, J_{app} = 4.8 Hz), 136.7 (apparent dt, J_{app} = 8.0 Hz, J_{app} = 7.1 Hz), 159.3, 163.8 (d, $^1J_{C-F}$ = 250.6 Hz); ^{19}F NMR ($CDCl_3$) δ −109.3; ^{31}P NMR ($CDCl_3$) δ 20.9. Anal. Calcd for $C_{42}H_{29}F_6IP_2Pd$: C, 54.43; H, 3.67. Found: C, 54.28; H, 3.64.

(4-Methoxyphenyl)Pd[P(4-fluorophenyl)$_3$]$_2$I (1q). Synthesized from 3. The above general procedure was applied using 78.8 mg (0.370 mmol) of **3**, 86.6 mg (0.370 mmol) of iodoanisole, and 234.0 mg (0.740 mmol) of tri-*p*-fluorophenylphosphine to yield **1q** as pale greenish-yellow feathery crystals (0.320 g, 0.329 mmol, 89%): ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 3H), 6.02 (d, J = 8.5 Hz, 2H), 6.33 (d, J = 8.5 Hz, 2H), 6.96 (apparent t, J_{app} = 8.5 Hz, 12H), 7.42 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 55.4, 114.8, 115.4 (apparent dt, J_{app} = 21.4 Hz, J_{app} = 5.5 Hz), 125.8, 127.4 (apparent t, J_{app} = 24.1 Hz), 135.5 (br m), 136.8 (apparent dt, J_{app} = 7.9 Hz, J_{app} = 7.4 Hz), 156.6, 163.8 (d, $^1J_{C-F}$ = 252.5 Hz), additional resonances not resolved; ^{19}F NMR ($CDCl_3$) δ −109.3; ^{31}P NMR ($CDCl_3$) δ 20.8. Anal. Calcd for $C_{43}H_{31}F_6IOP_2Pd$: C, 53.97; H, 3.26. Found: C, 53.70; H, 3.12.

(4-Methylphenyl)Pd[P(4-fluorophenyl)$_3$]$_2$I (1r). Synthesized from 3. The above general procedure was applied using 19.8 mg (0.0925 mmol) of **3**, 20.2 mg (0.0925 mmol) of iodotoluene, and 58.5 mg (0.185 mmol) of tri-*p*-fluorophenylphosphine to yield **1r** as pale greenish-yellow feathery crystals (69.1 mg, 0.0722 mmol, 78%): ^{1}H NMR ($CDCl_3$) δ 1.98 (s, 3H), 6.19 (d, J = 6.0 Hz, 2H), 6.35 (d, J = 6.1 Hz, 2H), 6.95 (m, 12H), 7.41 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 20.1, 115.3 (apparent dt, J_{app} = 21.3 Hz, J_{app} = 5.7 Hz), 127.3 (apparent td, J_{app} = 24.2 Hz, J_{app} = 3.3 Hz), 129.3, 132.0, 135.3 (apparent t, J_{app} = 5.2 Hz), 136.8 (apparent dt, J_{app} = 7.7 Hz, J_{app} = 7.4 Hz), 153.5, 163.9 (d, $^1J_{C-F}$ = 252.3 Hz); ^{19}F NMR ($CDCl_3$) δ −109.5; ^{31}P NMR ($CDCl_3$) δ 20.6. Anal. Calcd for $C_{43}H_{31}F_6IOP_2Pd$: C, 53.97; H, 3.27. Found: C, 53.93; H, 3.62.

(4-(Trifluoromethyl)phenyl)Pd[P(4-fluorophenyl)$_3$]$_2$I (1s). Synthesized from 3. The above general procedure was applied using 19.8 mg (0.0925 mmol) of **3**, 25.2 mg (0.0925 mmol) of 4-iodobenzotrifluoride, and 58.5 mg (0.185 mmol) of tri-*p*-fluorophenylphosphine to yield **1s** as pale greenish-yellow feathery crystals (84.3 mg, 0.0834 mmol, 90%): ^{1}H NMR ($CDCl_3$) δ 6.55 (d, J = 7.9 Hz, 2H), 6.68 (d, J = 7.9 Hz, 2H), 6.97 (t, J = 8.6 Hz, 12H), 7.58 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 115.6 (apparent dt, J_{app} = 21.3 Hz, J_{app} = 5.7 Hz), 123.7, 126.5 (apparent td, J_{app} = 24.8 Hz, J_{app} = 3.6 Hz), 135.6 (apparent t, J_{app} = 5.1 Hz), 136.7 (apparent dt, J_{app} = 7.6 Hz, J_{app} = 7.3 Hz), 164.0 (d, $^1J_{C-F}$ = 253.6 Hz), additional resonances overlap; ^{19}F NMR ($CDCl_3$) δ −108.6, −62.3; ^{31}P NMR ($CDCl_3$) δ 20.9. Anal. Calcd for $C_{43}H_{28}F_9IP_2Pd$: C, 51.09; H, 2.80. Found: C, 50.99; H, 2.99.

(Phenyl)Pd[P(4-(trifluoromethyl)phenyl)$_3$]$_2$I (1t). Synthesized from 2. The above general procedure was followed utilizing 92.0 mg (0.0925 mmol) of **2**, 37.8 mg (0.185 mmol) of iodobenzene, and 172.4 mg (0.370 mmol) of tris(4-(trifluoromethyl)phenyl)phosphine to yield 80.3 mg of **1t** as pale yellow feathery crystals (0.0646 mmol, 35%): ^{1}H NMR ($CDCl_3$) δ 6.28 (apparent t, J_{app} = 7.5 Hz, 2H), 6.43 (d, J = 7.3 Hz, 1H), 6.47 (m, 2H), 7.58 (m, 24H); ^{13}C NMR 9$CDCl_3$) δ 123.5 (q, $^1J_{C-F}$ = 271.2 Hz), 125.1 (m), 129.1, 132.6 (q, J_{C-F} = 32.6 Hz), 134.6 (apparent t, J_{app} = 22.9 Hz), 134.9 (apparent t, J_{app} = 6.6 Hz); 135.4 (apparent t, J_{app} = 5.1 Hz); 157.8, additional resonances not resolved; ^{19}F NMR ($CDCl_3$) δ −63.2; ^{31}P NMR ($CDCl_3$) δ

23.2. Anal. Calcd for $C_{48}H_{29}F_{18}IP_2Pd$: C, 46.38; H, 2.36. Found: C, 46.05; H, 2.43.

(4-Methoxyphenyl)Pd[P(4-(trifluoromethyl)phenyl)$_3$]$_2$I (1u). Synthesized from 2. The above general procedure was followed utilizing 92.0 mg (0.0925 mmol) of **2**, 43.3 mg (0.185 mmol) of 4-iodoanisole, and 172.4 mg (0.370 mmol) of tris(4-(trifluoromethyl)phenyl)phosphine to yield 0.172 g of **1u** as pale yellow feathery crystals (0.135 mmol, 73%).

Synthesized from 3. The above general procedure was applied using 19.8 mg (0.0925 mmol) of **3**, 21.7 mg (0.0925 mmol) of 4-iodoanisole, and 86.3 mg (0.185 mmol) of tris(4-(trifluoromethyl)phenyl)phosphine to yield **1u** as pale yellow feathery crystals (91.2 mg, 77%): ^{1}H NMR ($CDCl_3$) δ 3.44 (s, 3H), 5.97 (d, J = 8.4 Hz, 2h), 6.27 (m, 2H), 7.60 (m, 24 H); ^{13}C NMR ($CDCl_3$) δ 54.8, 115.4, 123.5 (q, $^1J_{C-F}$ = 271.2 Hz), 125.1 (m), 132.6 (q, $^?J_{C-F}$ = 32.8 Hz), 134.8 (apparent t, J_{app} = 22.4 Hz), 135.0 (apparent t, J_{app} = 6.6 Hz), 157.0; ^{19}F NMR ($CDCl_3$) δ −63.2; ^{31}P NMR ($CDCl_3$) δ 23.0. Anal. Calcd for $C_{49}H_{31}F_{18}IOP_2Pd$: C, 46.23; H, 2.46. Found: C, 45.97; H, 2.58.

(4-Methylphenyl)Pd[P(4-(trifluoromethyl)phenyl)$_3$]$_2$I (1v). Synthesized from 2. The above general procedure was followed by utilizing 92.0 mg (0.0925 mmol) of **2**, 40.4 mg (0.185 mmol) of 4-iodotoluene, and 172.4 mg (0.370 mmol) of tris(4-(trifluoromethyl)phenyl)phosphine to yield 0.131 g of **1v** as a white, fluffy precipitate (0.104 mmol, 56%): ^{1}H NMR ($CDCl_3$) δ 1.90 (s, 3H), 6.11 (d, J = 7.5 Hz, 2H), 6.28 (m, 2H), 7.54 (d, J = 8.0 Hz, 12H), 7.61 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 19.6, 123.5 (q, $^1J_{C-F}$ = 271.2 Hz), 125.1 (m), 130.1, 132.6 (q, J_{C-F} = 32.2 Hz), 134.8 (apparent t, J_{app} = 22.2 Hz), 134.9 (apparent t, J_{app} = 5.1 Hz), 135.0 (apparent t, J_{app} = 6.7 Hz), 152.1, additional resonances not resolved; ^{19}F NMR ($CDCl_3$) δ −63.2; ^{31}P NMR ($CDCl_3$) δ 22.9. Anal. Calcd for $C_{49}H_{31}F_{18}IP_2Pd$: C, 46.82; H, 2.49. Found: C, 46.81; H, 2.59.

(4-Fluorophenyl)Pd[P(4-(trifluoromethyl)phenyl)$_3$]$_2$I (1w). Synthesized from 2. The above general procedure was followed by utilizing 92.0 mg (0.0925 mmol) of **2**, 41.1 mg (0.185 mmol) of 4-fluoroiodobenzene, and 172.4 mg (0.370 mmol) of tris(4-(trifluoromethyl)phenyl)phosphine to yield 0.187 g of **1w** as pale yellow, feathery crystals (0.148 mmol, 80%): ^{1}H NMR ($CDCl_3$) δ 6.12 (apparent t, J_{app} = 8.9 Hz, 2H), 6.39 (m, 2H), 7.60 (m, 24H); ^{13}C NMR ($CDCl_3$) δ 115.9 (d, J_{C-F} = 19.6 Hz), 123.4 (q, $^1J_{C-F}$ = 271.1 Hz), 125.2 (q, J_{C-F} = 3.7 Hz), 123.9 (q, J_{C-F} = 32.7 Hz), 134.5 (apparent t, J_{app} = 23.0 Hz), 135.0 (apparent t, J_{app} = 6.6 Hz), 135.4 (q, J_{C-F} = 5.7 Hz), 149.8, 160.7 (d, $^1J_{C-F}$ = 245.7); ^{19}F NMR ($CDCl_3$) δ −122.3 (s, 1F), −61.5 (s, 18F); ^{31}P NMR ($CDCl_3$) δ 22.9. (J_{P-F} = 4.5 Hz). Anal. Calcd for $C_{48}H_{28}F_{19}IP_2Pd$: C, 45.72; H, 2.24. Found: C, 45.38; H, 2.30.

(Pentafluorophenyl)Pd[P(4-(trifluoromethyl)phenyl)$_3$]$_2$I (1x). Synthesized from 2. The above general procedure was followed by utilizing 92.0 mg (0.0925 mmol) of **2**, 54.3 mg (0.185 mmol) of iodopentafluorobenzene, and 172.4 mg (0.370 mmol) of tris(4-(trifluoromethyl)phenyl)phosphine to yield 49.0 mg of **1x** as bright yellow cubic crystals (0.0367 mmol, 20%): ^{1}H NMR ($CDCl_3$) δ 7.50 (d, J = 8.1 Hz, 12H), 7.70 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 123.3 (q, $^1J_{C-F}$ = 271.2 Hz); 125.3 (m), 133.5 (q, J_{C-F} = 32.9 Hz), 134.0 (apparent t, J_{app} = 24.7 Hz), 134.7 (apparent t, J_{app} = 6.6 Hz), additional resonances not resolved; ^{19}F NMR ($CDCl_3$) δ −160.0 (apparent t, J_{app} = 21.7Hz, 2F), −158.8 (t, J = 19.0 Hz, 1F), −117.8 (d, J = 24.8 Hz, 2F), −61.6 (s, 18F); ^{31}P NMR ($CDCl_3$) δ 22.2. Anal. Calcd for $C_{48}H_{24}F_{23}IP_2Pd$: C, 43.25; H, 1.81. Found: C, 43.47; H, 2.12.

(4-Methylphenyl)Pd[(ethyl)P(phenyl)$_2$]$_2$I (1y). Synthesized from 3. The above general procedure was applied using 39.4 mg (0.185 mmol) of **3**, 40.4 mg (0.185 mmol) of 4-iodotoluene, and 79.3 mg (0.370 mmol) of ethyldiphenylphosphine to yield **1y** as a greenish-white precipitate: ^{1}H NMR ($CDCl_3$) δ 0.86 (dt, J = 8.3 Hz, J = 7.5 Hz, 6H), 2.04 (s, 3H), 2.06 (m, 4H), 6.35 (d, J = 7.6 Hz, 2H), 6.41 (m, 2H), 7.26 (m, 8H), 7.33 (apparent t, J_{app} = 7.2 Hz, 4H), 7.48 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 9.1, 20.5, 22.5 (apparent t, J_{app} = 14.3 Hz), 127.8 (apparent t, J_{app} = 5.0 Hz), 128.5, 129.5, 131.6 (apparent t, J_{app} = 21.3 Hz), 133.8 (apparent t, J_{app} = 5.7 Hz), 135.5 (apparent t, J_{app} = 4.9 Hz), 141.2, 149.9; ^{31}P NMR ($CDCl_3$) δ 17.0. Anal. Calcd for $C_{35}H_{37}IP_2Pd$: C, 55.83; H, 4.95. Found: C, 56.02; H, 5.10.

(4-Methylphenyl)Pd(1,3-bis(diphenylphosphino)propane)I (1z). Synthesized from 3. The above general procedure was applied using 39.4 mg (0.185 mmol) of **3**, 40.4 mg (0.185 mmol) of 4-iodotoluene, and 78.8 mg (0.185 mmol) of 1,3-bis(diphenylphosphino)propane to yield **1z** as pale green-yellow crystals which turned pinkish upon exposure to ambient temperature. The crystals were then freeze-dried from benzene in order to remove solvent of crystallization (0.125 g, 0.170 mmol, 92%): ^{1}H NMR ($CDCl_3$) δ 1.85 (m, 2H), 1.99 (s, 3H), 2.39 (m, 2H), 2.51 (m, 2H), 6.39 (m, 2H), 6.74 (td, J_t = 8.0 Hz, J_d = 2.6 Hz, 2H), 7.12 (td, J_t = 7.8 Hz, J_d = 2.4 Hz, 4H), 7.28 (m, 6H), 7.41 (m, 6H), 7.81 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.0, 20.4, 27.1 (broad), 28.6 (dd, J = 24.6 Hz, 7.4 Hz), 128.0 (d, J = 10.6 Hz), 128.2, 128.4 (d, J = 9.6 Hz), 130.1, 130.5, 130.9, 132.8, 133.1 (d, J = 10.7 Hz), 133.7 (d, J = 11.0 Hz), 136.6, additional resonances not resolved; ^{31}P NMR ($CDCl_3$) δ −10.6 (d, J_{PP} = 53.2 Hz), 10.9 (d, J_{PP} = 53.2 Hz). Anal. Calcd for $C_{43}H_{33}IP_2Pd$: C, 55.42; H, 4.51. Found: C, 55.17; H, 4.54.

Preparation of Water-Soluble Complexes 1aa−ee. ((3-Methoxycarbonyl)phenyl)Pd[P(C$_6$H$_5$)$_2$(3-SO$_3$NaC$_6$H$_4$)]$_2$I (1aa). A solution of methyl 3-iodobenzoate (0.250 g, 0.955 mmol) and monosulfonated triphenylphosphine (**4**) (0.695 g, 1.91 mmol) dissolved in 7.5 mL of DMF was added to a slurry of $Pd_2(dba)_3{\cdot}C_6H_6$ (**2**) (0.470 g, 0.48 mmol) in 2.5 mL of DMF. All **2** dissolved over the course of 1 h to yield a homogeneous yellow solution. The solution was filtered through a 0.2 μm PTFE membrane to remove traces of metallic Pd. Complex **1aa** was precipitated as a slush by addition of several volumes of ether. Repeated ethereal washes yielded a free-flowing powder, which was collected by filtration and dried *in vacuo* to give 0.999 g of complex **1aa** (0.910 mmol, 94%) suitable for routine use. Similar reactions using **4** in the presence of precursor **3** failed to yield identifiable products. Highly purified material was obtained by dissolving **1aa** in warm (40 °C) methanol, filtering, concentrating the solution *in vacuo*, and chilling (−20 °C). The resulting powder was free of detectable impurities other than trapped methanol by ^{1}H and ^{31}P NMR: ^{1}H NMR (DMSO-d_6) δ 3.57 (s, 3H), 6.30 (apparent t, J_{app} = 7.7 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 6.89 (br d, J = 7.7 Hz, 1H), 6.92 (br s, 1H), 7.26 (m, 8H), 7.31 (m, 12 H), 7.44 (apparent t, J_{app} = 7.7 Hz, 2H), 7.71 (d, J = 7.7 Hz, 2H), 7.82 (br d, J = 7.7 Hz, 2H), 7.98 (br s, 2H); ^{13}C NMR (DMSO-d_6) δ 51.3, 122.7, 126.3, 127.8, 128.0, 128.8, 129.8, 130.8 (br), 133.9, 136.0, 136.7, 139.0, 148.0, 166.0, additional resonances not resolved; ^{31}P NMR (DMSO-d_6) δ 24.8. Anal. Calcd for $C_{44}H_{35}INa_2O_8P_2PdS_2$: C, 48.17; H, 3.21. Found: C, 48.73; H, 3.26.

((4-Methoxycarbonyl)phenyl)Pd[P(C$_6$H$_5$)$_2$(4-SO$_3$KC$_6$H$_4$)]$_2$I (1bb). The above procedure for **1aa** was employed using $Pd_2(dba)_3{\cdot}C_6H_6$ (**2**) (0.150 g, 0.151 mmol) **5** (0.232 g, 0.583 mmol) and methyl 4-iodobenzoate (0.082 g, 0.310 mmol). This yielded 0.322 g of complex **1bb** (0.285 bbb, 95%), which was then recrystallized from aqueous THF by quickly adding just enough water to a warm (*ca.* 50 °C) THF suspension (*ca.* 10 mL of THF) to dissolve the complex. The solution was rapidly cooled to −20 °C to yield pale yellow-green leaves as a mono-THF solvate. Lyophilization from water gave a solvate-free powder: ^{1}H NMR (CD_3OD) δ 3.73 (s, 3H), 6.80 (dm, J = 7.9 Hz, 2H), 6.86 (d, J = 7.9 Hz, 2H), 7.28 (m, 8H), 7.38 (m, 4H), 7.54 (m, 12H), 7.70 (d, J = 8.1 Hz, 4H); ^{13}C NMR insufficient solubility; ^{31}P NMR (CD_3OD) δ 22.3; Anal. Calcd for $C_{44}H_{35}IK_2O_8P_2PdS_2$: C, 45.33; H, 2.83. Calcd for the monohydrate: C, 44.63; H, 2.96. Found: C, 45.02; H, 3.38.

((4-Methoxycarbonyl)phenyl)Pd[As(C$_6$H$_5$)$_2$(4-SO$_3$KC$_6$H$_4$)]$_2$I (1cc). An identical procedure employing $Pd_2(dba)_3{\cdot}C_6H_6$ (**2**) (0.150 g, 0.151 mmol), **6** (0.259 g, 0.610 mmol), and methyl 4-iodobenzoate (0.082 g, 0.310 mmol) yielded 0.307 g of complex **1cc** (0.252 mmol, 84%). This material was

recrystallized from aqueous THF to yield pale yellow leaves as a mono-THF solvate. Lyophilization from water gave a solvate-free powder: ^{1}H NMR (CD_3OD) δ 3.75 (s, 3H), 6.87 (d, J = 7.8 Hz, 2H), 6.94 (d, J = 7.8 Hz, 2H), 7.31 (m, 4H), 7.39 (m, 2H), 7.45 (multiple resonances, 6H), 7.73 (d, J = 8.0 Hz, 2H); ^{13}C NMR insufficient solubility. Anal. Calcd for $C_{44}H_{35}As_2IK_2O_8PdS_2$: C, 43.42; H, 2.90. Found: C, 43.63; H, 2.84.

(4-Nitrophenyl)Pd[P(C_6H_5)$_2$(4-$SO_3KC_6H_4$)]$_2$I (1dd). An identical procedure employing $Pd_2(dba)_3{\cdot}C_6H_6$ (**2**) (0.100 g, 0.101 mmol), **5** (0.155 g, 0.390 mmol), and 4-iodonitrobenzene (0.052 g, 0.206 mmol) yielded 0.232 g of complex **1dd** (0.199 mmol, 99%). A portion of this material was recrystallized from aqueous THF to yield pale yellow-green leaves as a mono-THF solvate. Lyophilization of the solvate from 90:10 water:methanol gave a solvate-free powder in 99% recovery based on the crude material: ^{1}H NMR (CD_3OD) δ 6.92 (dm, J = 8.8 Hz, 1H), 7.04 (d, J = 8.8 Hz, 1H), 7.35 (m, 4H), 7.45 (m, 2H), 7.56 (m, 6H), 7.86 (m, 4H); ^{13}C NMR insufficient solubility; ^{31}P NMR (CD_3OD) δ 23.5. Anal. Calcd for $C_{42}H_{32}IK_2NO_8P_2PdS_2$: C, 45.19; H, 2.89; N, 1.25. Calcd for the monohydrate: C, 44.47; H, 3.02; N, 1.23. Found: C, 44.80; H, 3.21; N, 1.47.

(4-(Trifluoromethyl)phenyl)Pd[P(C_6H_5)$_2$(4-$SO_3KC_6H_4$)]$_2$I (1ee). An identical procedure employing $Pd_2(dba)_3{\cdot}C_6H_6$ (**2**) (0.100 g, 0.101 mmol), **5** (0.155 g, 0.390 mmol), and 4-iodobenzotrifluoride (0.056 g, 0.206 mmol) yielded 0.227 g of complex **1ee** (0.199 mmol, 98%). A portion of this material was recrystallized from aqueous THF to yield pale yellow-green crystals as a mono-THF solvate. Lyophilization of the solvate from 90:10 water:methanol gave a solvate-free powder in 83% recovery based on the crude material: ^{1}H NMR (CD_3OD) δ 6.44 (d, J = 8.1 Hz, 1H), 6.77 (d, J = 8.1 Hz, 1H), 7.27 (m, 4H), 7.38 (m, 2H), 7.44 (m, 4H), 7.66 (m, 2H), 7.77 (d, J = 8.1 Hz, 2H); ^{13}C NMR (CD_3OD) δ 124.6 (m), 125.8 (q, $^1J_{C-F}$ = 269.9 Hz), 126.2 (apparent t, J_{app} = 5.2 Hz), 129.1 (apparent t, J_{app} = 5.2 Hz), 131.5, 131.7 (q, $^2J_{C-F}$ = 23.6 Hz), 135.6 (apparent t, J_{app} = 6.2 Hz), 136.0 (apparent t, J_{app} = 6.5 Hz), 136.8 (br), 147.2, additional resonances not resolved; ^{19}F NMR (CD_3OD) δ −61.35; ^{31}P NMR (CD_3OD) δ 23.8. Anal. Calcd for $C_{43}H_{32}F_3IK_2O_6P_2PdS_2$: C, 45.33; H, 2.83. Calcd for the monohydrate: C, 44.63; H, 2.96. Found: C, 44.89; H, 3.16.

Ligand Synthesis. P(C_6H_5)$_2$(4-$SO_3KC_6H_4$) (5). To an oven-dried, argon-flushed 250 mL Schlenk flask equipped with a stir bar were added 50 mL of THF and 1.00 g of potassium (25.3 mmol). A solution containing 2.20 g of chlorodiphenylphosphine (10.0 mmol) in 20 mL of THF was added dropwise over the course of 10 min *via* an addition funnel. Following a brief induction period, the bright orange-red phosphide anion was generated rapidly. The solution was stirred for 1 h. Excess potassium was removed under an argon back-flush. The flask was equipped with an oven-dried condenser, and potassium 4-fluorobenzenesulfonate (2.21 g, 10.5 mmol) was added. The solution was heated at reflux under argon until colorless, *ca*. 5 h. Workup proceeded by pouring the cooled reaction mixture into 150 mL of water. The resulting aqueous solution was washed twice with 50 mL of ether and then concentrated to yield a white solid. Crystallization from degassed water yielded 2.64 g of **5** as a stable hydrate (6.63 mmol, 66%): ^{1}H NMR (DMSO-d_6) δ 7.22 (m, 3 H), 7.37 (m, 3 H), 7.62 (m, 1 H); ^{13}C NMR (DMSO-d_6) δ 125.8 (d, $^2J_{C-P}$ = 7.0 Hz), 128.8 (d, $^2J_{C-P}$ = 7.2 Hz), 129.0 (s), 132.7 (d, $^1J_{C-P}$ = 19.7 Hz), 133.2 (d, $^1J_{C-P}$ = 19.5 Hz), 136.5 (d, $^3J_{CP}$ = 11.4 Hz), 137.1 (d, $^3J_{CP}$ = 11.6 Hz), 148.7 (s); ^{31}P NMR (DMSO-d_6) δ −6.03; MS (FAB) (*m*/*z*) 380 (MH^+), 419 (MK^+). Anal. Calcd for $C_{18}H_{16}KPO_4S$: C, 54.32; H, 4.05. Found: C, 54.41; H, 4.04.

As(C_6H_5)$_2$(4-$SO_3KC_6H_4$) (6). To an oven-dried, argon-flushed 250 mL Schlenk flask equipped with a glass-coated stir bar was added 1.380 g of potassium (35.4 mmol) and 50 mL of DME. A solution containing 3.38 g of As(C_6H_5)$_3$ (11.0 mmol) in 50 mL of DME was added *via* an addition funnel, and the mixture was stirred at room temperature for *ca*. 10 h. Excess potassium was removed under an argon back-flush. The flask was fitted with an addition funnel charged with 4-fluorobenzenesulfonic acid in toluene (29 mL of a 0.373 M stock). Upon cooling of the reaction to −78 °C, the acid solution was added dropwise over 15 min. Following addition, the reaction flask was allowed to warm to room temperature, equipped with an oven-dried condenser, and heated to reflux under argon until colorless, *ca*. 4 h. Workup proceeded exactly as for **11** to yield 2.904 g of **12** (6.84 mmol, 62%): ^{1}H NMR (DMSO-d_6) δ 7.24 (d, J = 8.2 Hz, 1 H), 7.27 (m, 2 H), 7.37 (m, 3 H), 7.62 (d, J = 8.2 Hz, 1 H); ^{13}C NMR (DMSO-d_6) δ 125.9, 128.7, 128.9, 132.7, 133.2, 138.8, 139.4, 148.5; MS (FAB) (*m*/*z*) 425 (MH^+), 463 (MK^+). Anal. Calcd for $C_{18}H_{14}AsKO_3S$: C, 50.94; H, 3.33. Found: C, 50.59; H, 3.38.

Acknowledgment. We gratefully thank the National Science Foundation (U.S.), the Office of Naval Research, and Lawrence Berkeley Laboratories for funding this research. T.I.W. thanks the U.S. Department of Education, Dow Chemical, and IBM for fellowship support. Similarly, F.E.G. thanks the U.S. Department of Education for a graduate fellowship.

OM9602567