Simple, Highly Active Palladium Catalysts for Ketone and Malonate Arylation: Dissecting the Importance of Chelation and Steric Hindrance

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Abstract: A remarkably active catalyst system for α-arylation of ketones and malonates was developed by proposing that sterically hindered alkylphosphines would accelerate the catalytic reaction rates. We initially tested the bisphosphine ligand D^{t}BPF (1,1′-*bis*-(di-*tert*-butylphosphino)ferrocene) for this palladium-catalyzed chemistry. This catalyst system led to fast reaction rates for reactions of aryl bromides with ketones, including room temperature chemistry in many cases. In some cases turnover numbers were 20 000. The catalyst also gave mild reactions with aryl chlorides with yields that were similar to the chemistry with aryl bromides. Independent synthesis of the arylpalladium enolate complexes with isobutyrophenone enolate showed that only one phosphorus of the bisphosphine ligand D^{t}BPF was coordinated in the enolate complex. Thus, we tested sterically hindered alkylphosphine ligands for the ketone and malonate arylation process and found that P(*t*-Bu)$_3$ gave exceptionally fast rates and high turnover numbers for these reactions. These results demonstrate several principles for the catalytic chemistry that we did not anticipate: palladium complexes of monophosphine ligands can activate aryl chlorides under mild conditions, and palladium enolates coordinated by certain monophosphines can undergo C−C bond-forming reductive elimination much faster than β-hydrogen elimination.

Introduction

The coupling of enolates with aryl halides, a transformation as fundamental as enolate alkylation, has historically been difficult to conduct.[1−3] Previously, this reaction was reported with use of tin enolates of methyl ketones in modest yields and in low yields with higher homologs.[1,4] In addition this reaction was conducted with use of silyl enol ethers in the presence of tin fluoride,[2] which also uses a stoichiometric amount of tin and presumably generates the same tin enolate. Direct intramolecular reactions of ketones with aryl halides in modest yields was reported many years ago with stoichiometric or high catalyst loadings of Ni(COD)$_2$.[3,5] Intramolecular ketone arylation has been recently conducted more successfully with palladium complexes.[6] Other methods involve the use of electrophilic and often toxic main group aryl reagents.[7,8] The coupling of malonates with aryl halides is even less common. In some cases these reactions can be conducted with stoichiometric amounts of copper[9,10] or with catalytic amounts of copper[11] most commonly with *o*-halobenzoic acids.[12,13] However, these malonate arylations require aryl iodides. Similarly, palladium-catalyzed reactions of malononitriles[14] occur in lower yields with bromoarenes and require harsher conditions for hydrolysis than malonic esters.

Recently our group,[15] Buchwald and Palucki,[16] and Satoh et al.[17] showed that palladium complexes catalyzed a simple ketone arylation process. The use of resolved rather than racemic BINAP and substrates that form quaternary carbons allowed this reaction to be conducted asymmetrically.[18] We have sought an understanding of the catalyst properties that are important to develop more active systems for the arylation of carbonyl compounds. We began this effort with several hypotheses that were untested for the ketone arylation. First, oxidative addition of the aryl halides and reductive elimination of product both involve a low-coordinate Pd(0) reactive intermediate. Therefore, steric effects should increase the energy of the more stable high coordinate species, decreasing the relative energy of the reactive intermediate and increasing reaction rates.[19,20] Second, alkyl-

(1) Kosugi, M.; Hagiwara, I.; Sumiya, T.; Migita, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 242−246.
(2) Kuwajima, I.; Urabe, H. *J. Am. Chem. Soc.* **1982**, *104*, 6831−6833.
(3) Semmelhack, M. F.; Chong, B. P.; Stauffer, R. D.; Rogerson, T. D.; Chong, A.; Jones, L. D. *J. Am. Chem. Soc.* **1975**, *97*, 2507−2516.
(4) Kosugi, M.; Suzuki, M.; Hagiwara, I.; Goto, K.; Saitoh, K.; Migita, T. *Chem. Lett.* **1982**, 939−940.
(5) Millard, A. A.; Rathke, M. W. *J. Org. Chem.* **1977**, *99*, 4833−4835.
(6) Muratake, H.; Natsume, M. *Tetrahedron Lett.* **1997**, *38*, 7581−7582.
(7) Barton, D. H. R.; Finet, J. P.; Khamsi, J.; Pichon, C. *Tetrahedron Lett.* **1986**, *27*, 3619−3522.
(8) Barton, D. H. R.; Donnelly, D. M. X.; Finet, J.-P.; Guiry, P. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1365−1375.
(9) Osuka, A.; Kobayashi, S.; Suzuki, H. *SYNTHESIS* **1983**, 67−68.
(10) Setsune, J.-i.; Matsukawa, K.; Wakemoto, H.; Kitao, T. *Chem. Lett.* **1981**, 367−370.
(11) Okuro, K.; Furuune, M.; Miura, M.; Nomura, M. *J. Org. Chem.* **1993**, *58*, 7606−7607.
(12) Bruggink, A.; McKillop, A. *Tetrahedron* **1975**, *31*, 2607−2619.
(13) McKillop, A.; Rao, D. P. *Synthesis* **1977**, 759.
(14) Malononitrile has been shown to react with aryl iodides with palladium catalysts to form the less readily hydrolyzed aryl malononitriles: Uno, M.; Seto, K.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 932−933.
(15) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 12382−12383.
(16) Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 11108−11109.
(17) Satoh, T.; Kawamura, Y.; Miura, M.; Nomura, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1740−1742.
(18) Åhman, J.; Wolfe, J. P.; Troutman, M. V.; Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 1918−1919.
(19) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 7369−7370.

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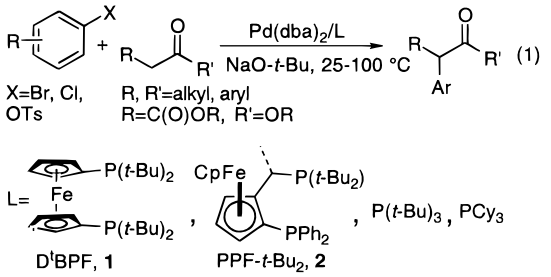
phosphines should be more resistant toward P−C cleavage processes than arylphosphines, and should provide higher turnover numbers.[21,22] Third, chelation would prevent the enolate intermediates from undergoing β-hydrogen elimination,[23,24] which would prevent formation of α-aryl ketone products. Consistent with this third hypothesis, our pervious catalysts containing either DPPF or a more sterically hindered *o*-tolyl version of this ligand and the catalyst systems reported by Buchwald involved either bisphosphine ligands or ligands with both phosphorus and nitrogen donor atoms that can chelate to the metal and/or act as hemilabile ligands.[16,18,25]

For these reasons, we initiated our studies by using palladium complexes of the sterically hindered bisphosphine ligand 1,1′-bis(di-*tert*-butylphosphino)ferrocene (D^{t}BPF, **1**).[19,26] The high activity of these catalysts confirmed some of our hypotheses, but preliminary mechanistic data disproved the importance of chelation and led us to select simple, sterically hindered alkyl monophosphines as remarkably active catalysts for arylation of both ketones and malonates. These synthetic studies and preliminary mechanistic results are reported here.

Results and Discussion

Synthetic Studies with D^{t}BPF. The overall ketone arylation reaction is shown in eq 1. As shown in Table 1, reactions

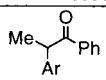
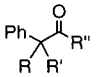
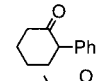
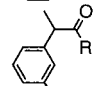
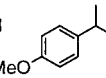
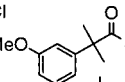
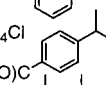
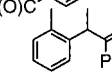
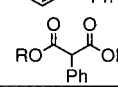


employing D^{t}BPF as ligand provided mild arylation of ketones with bromoarenes. Turnover numbers of 20 000 were observed in some cases. Monoarylation of acetophenone was accomplished with 2 equiv of base. Heterocyclic bromides that might displace a hindered phosphine were also suitable substrates. Reactions employing D^{t}BPF as ligand coupled dialkyl ketones with bromoarenes (Entries 11 and 13). Reactions with cyclohexanone selectively gave the monoarylation product. 4-Methyl-3-pentanone reacted with 3-bromoanisole to provide the products from a single α-arylation in 84% yield, with the product formed from arylation of the less hindered alkyl group dominating. The ratio of α-arylation products was 89:11 in the crude reaction mixture (GC analysis).

The catalyst containing D^{t}BPF provided clean chemistry with chloroarenes at only 70 °C. Electron neutral and even electron rich chloroarenes gave the coupled product in high yield, and sterically hindered aryl chlorides were suitable substrates despite the size of the ligand. The use of 2 mol % of Pd(dba)$_2$ led to complete reaction, and 1 mol % ligand was optimal.[27] Reactions of chloroarenes with acyclic dialkyl ketones showed similar selectivity to those with bromoarenes. Typical palladium chemistry of aryl chlorides occurs at high temperatures or with electron-poor chloroarenes. These results and others reported recently[25] demonstrate that lower temperatures are possible for many coupling processes with palladium complexes.

Ketones did not react with aryl tosylates when using D^{t}BPF as ligand, but a related chelating phosphine with *tert*-butyl substituents 1-diphenylphosphino-2-(di-*tert*-butylphosphino)-ethylferrocene (PPF-*t*-Bu$_2$, **2**)[28−30] gave good yields when using 5 mol % catalyst at 70 °C. Little palladium-catalyzed chemistry with aryl tosylates has been reported previously and only one example of cross-coupling.[19] Although **2** is a homochiral ligand in its commercially available form and the product contains a new stereocenter, the basic conditions lead to the formation of racemic product.

Table 1. Reaction of Ketones and Malonates with ArBr, ArCl, and ArOTs

Entry	ArX	Product	mol% Pd[a]/L	Conditions[b]	Yield[c]
1.	PhBr		2 % A /**1**	25 °C, 2 h	99%
2.			0.005% A /**1**	60 °C, 36 h	99%
3.			0.5% B/PBu$^t_3$	25 °C, 2 h	97%
4.			0.005% "	60 °C, <24 h	98%
5.	3-bromopyridine		2 % A/**1**	50 °C, 5 h	87%
6.	4-MeC$_6$H$_4$OTs		5% B /**2**	70 °C, 12 h	60%
7.	PhBr	 R=R'=H,	2 % A/**1**	25 °C, 12 h	90%
8.		R"=Ph	1% B/PBu$^t_3$	25 °C, 6 h	96%
9.		R=R'=Me,	2 % A/**1**	50 °C, 6 h	87%
10.		R"=Ph	1% B/PBu$^t_3$	50 °C ,12 h	92%
11.	3-MeOC$_6$H$_4$Br	R=H, R'=Me,	2 % A/**1**	70 °C, 12 h	92%[d]
12.		R"=*i*-Pr	1% B/PBu$^t_3$	50 °C, 12h	83%[e]
13.	PhBr		2 % A/**1**	70 °C, 12 h	70%
14.			1% B/PBu$^t_3$	50 °C, 3 h	73%
15.	PhCl	 R=Ph	2 % A/**1**	70 °C, 3 h	86%
16.			2% B/PBu$^t_3$	70 °C, 4 h	90%
17.			2% B/PCy$_3$	50 °C, 12 h	93%
18.	3-MeOC$_6$H$_4$Cl	R=*i*-Pr	2 % A/**1**	70 °C, 12 h	78%[f]
19.			2% B/PBu$^t_3$	70 °C, 12 h	69%[g]
20.	4-MeOC$_6$H$_4$Cl		2 % A/**1**	70 °C, 12 h	91%
21.			2% B/PBu$^t_3$	70 °C, 12 h	91%
22.			2% B/PCy$_3$	70 °C, 12 h	93%
23.	3-MeOC$_6$H$_4$Cl		2 % A/**1**	70 °C, 12 h	78%
24.			2% B/PBu$^t_3$	70 °C, 12 h	82%
25.	4-PhC(O)C$_6$H$_4$Cl		2% B/PBu$^t_3$	70 °C, 24 h	95%
26.	2-MeC$_6$H$_4$Cl		2 % A/**1**	70 °C, 12 h	80%
27.	PhCl	 R=*t*-Bu	2 % A/**1**	100 °C, 12 h[h]	78%
28.	PhBr	R=Et	2% B/PBu$^t_3$	70 °C, 3 h[h]	80%

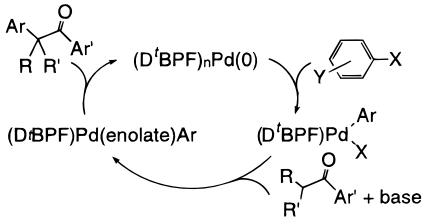
[a] A = Pd(dba)$_2$; B = Pd(OAc)$_2$. [b] 1:1.25 ratio of Pd/L for reactions of aryl bromides or for aryl chlorides using monophosphines; 1:0.5 ratio of Pd/L for reactions of aryl chlorides using ligand 1; 1.5 equiv of NaO-*t*-Bu for all reactions except those for acetophenone that used 2.2 equiv of base, 1.1 equiv of ketone, THF solvent. [c] Yields are an average of two runs on 1 or 2 mmol scale. [d] 89:11 ratio of isomers in crude reaction. [e] 74:26 ratio of isomers in crude reaction. [f] 87:13 ratio of isomers in crude reaction. [g] 76:24 ratio of isomers in crude reaction. [h] Reaction conducted in dioxane solvent using 1.1 equiv of NaO-*t*-Bu.

(20) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 3694−3703.
(21) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441−12453.
(22) Morita, D. K.; Stille, J. K.; Norton, J. R. *J. Am. Chem. Soc.* **1995**, *117*, 8576−8581.
(23) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217−7218.
(24) Hayashi, T.; Knoishi, M.; Kumada, M. *Tetrahedron Lett.* **1979**, *21*, 1871−1874.
(25) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722−9723.
(26) Butler, I. R.; Cullen, W. R.; Kim, T. J.; Rettig, S. J.; Trotter, J. *Organometallics* **1985**, *4*, 972−80.

(27) Pd(dba)$_2$ did not catalyze the ketone arylation and slowly gave biaryl product. One can understand the activity of this Pd/bisphosphine ratio in terms of the mechanistic data and results with the 1:1 Pd/monophosphine ratio described below.

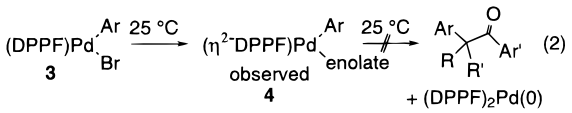
(28) This ligand is commercially available from Strem.
(29) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062−4066.
(30) Togni, A.; Breutel, C.; Soares, M. C.; Zanetti, N.; Gerfin, T.; Gramlich, V.; Spindler, F.; Rihs, G. *Inorg. Chim. Acta* **1994**, *222*, 213−24.

Scheme 1



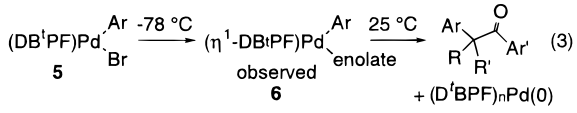
Qualitative Mechanistic Studies. Scheme 1 shows a general mechanism for the ketone arylation. Considering the success of chelating phosphine ligands in previous palladium-catalyzed arylation of ketone enolates that could undergo β-hydrogen elimination, it seemed likely that this ligand property was important to favor reductive elimination over β-hydrogen elimination.[23,24,31]

Preliminary mechanistic data with D^{t}BPF as ligand cast doubt upon the requirements for chelation. Arylpalladium enolate complexes were generated with both DPPF and D^{t}BPF ligands to evaluate structure/reactivity relationships. Reaction of (DPPF)Pd(*p*-Tol)(Br) (**3**)[15] with the enolate of isobutyrophenone gave a single set of doublets (δ 29.83, 10.37, J = 34.2 Hz) corresponding to an arylpalladium enolate complex **4** (eq 2).



This enolate was identified as an O-bound enolate due to the two different enolate methyl groups observed in the ^{1}H NMR spectrum near 2 ppm. This species reacted at room temperature in the presence or absence of added PPh_3 to trap the Pd(0) product, but gave <10% yield of α-aryl ketone. Biaryls, presumably from disproportionation of the arylpalladium enolate and from P−C cleavage, were the major products.

In contrast, addition of isobutyrophenone enolate to (D^{t}BPF)Pd(Ph)(Br) (**5**)[32] at −78 °C (eq 3) generated a single arylpalladium enolate product **6** that underwent reductive elimination in quantitative yield at room temperature (^{1}H NMR spectroscopy with internal standard). Moreover, the ^{31}P{^{1}H} NMR spectrum of the enolate complex displayed two singlets at 24.8 and 57.2 ppm in a 1:1 ratio. One singlet lay in the region of coordinated ligand and the other in the region near, but not identical with that of free D^{t}BPF (24.6 ppm). We have not yet rigorously determined the geometry and hapticity of the enolate ligand, due to its reactivity at room temperature, its temperature-dependent ^{1}H NMR spectra, and the overlap of enolate methyl resonances with the *tert*-butyl groups of the ligand. However, the absence of resonances near 2 ppm suggest a different binding mode than for the DPPF complex **4**. Further studies on complex **6** and related palladium enolates will be conducted in the future. For now, it is important to realize that this complex clearly contains a D^{t}BPF ligand that is bound to the metal by only one phosphorus atom as determined by ^{31}P{^{1}H} NMR spectroscopy.



From these initial studies, we concluded that sterically hindered monophosphines may be appropriate for this type of cross coupling.

Synthetic Studies Involving Sterically Hindered Alkylmonophosphines. Considering our mechanistic conclusions concerning the coordination number of D^{t}BPF in the arylpalladium enolate intermediate, we evaluated $PhP(t\text{-}Bu)_2$ as a model for monodentate D^{t}BPF in the ketone arylation. We also evaluated the simple, commercially available monophosphines $P(t\text{-}Bu)_3$[33,34] and PCy_3. The reactions of aryl bromides with ketones occurred in high yields with these ligands. Reactions with $P(t\text{-}Bu)_3$ were faster than those with $PhP(t\text{-}Bu)_2$, and further chemistry with $PhP(t\text{-}Bu)_2$ was not pursued. Cyclohexanone, 3-methyl-2-propanone, acetophenone, propiophenone, and isobutyrophenone reacted with electron rich, electron neutral, electron poor, sterically hindered, or sterically unhindered aryl bromides and aryl chlorides in high yield when using $P(t\text{-}Bu)_3$ as ligand (Table 1) Turnover numbers for reaction of propiophenone with phenyl bromide were as high as 20 000. Reaction of propiophenone with aryl chlorides also occurred in high yield when using PCy_3 as ligand.

We were able to find conditions that led to monoarylation of all ketones except methyl alkyl ketones. These conditions were developed by considering the acid/base equilibria that result from a more acidic and less nucleophilic reaction product. Reactions of methyl aryl ketones occurred with high selectivity for monoarylation by using 2 equiv of base. If 1 equiv of base is used, the enolate ion of the product is formed in preference to the enolate of the starting ketone and the enolate of the product ketone is an active reagent for the arylation process. Two equivalents of alkoxide base ensures that all ketones exist in their enolate form. The reaction of dialkyl ketones occurred with high selectivity for monoarylation when using 1 equiv of base. In this case, we propose that neither product nor starting ketone is quantitatively deprotonated by the alkoxide base. Further, the enolate of the product is deprotonated at the more acidic tertiary benzylic position, which is sterically hindered and less reactive than the more nucleophilic and less hindered enolate of the starting ketone. Qualitative studies showed that methyl alkyl ketones do undergo formation of diarylation products in good yield, but these reactions were not pursued in detail.

The selectivity for arylation of dialkyl ketones with two enolizable positions is perplexing at this point. Overall, it appears that bisphosphine ligands provide better selectivity than do the ligands in this work that are either monophosphines or bind in a monodentate fashion when the enolate is coordinated. The higher selectivity may, in fact, indicate that the bisphosphines with the smaller aryl substituents generate more sterically demanding enolate complexes. More detailed mechanistic analysis concerning the structures, exchanges, and reductive elimination rates of different enolate complexes are necessary to provide an unambiguous reason for the observed selectivity and a means to combine the high selectivity with high activity in a simple ligand system.

Arylation of Malonates. The alkylation of malonates is one of the fundamental reactions of organic chemistry and allows the synthesis of various carboxylic acids. Arylation of malonates is synthetically challenging as discussed in the introduction. However, the use of either D^{t}BPF or $P(t\text{-}Bu)_3$ in combination with palladium catalyst precursors led to mild arylation of simple malonates. Reaction of phenyl chloride with di-*tert*-butylma-

(31) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232−8245.

(32) This complex was prepared by addition of DB^{t}PF to {Pd[P(*o*-tolyl)$_3$](Ph)Br}$_2$ in toluene and precipitation by addition of pentane. Mann, G.; Hartwig, J.F. To be submitted for publication.

(33) Nishiyama, M.; Yamamoto, T.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 617−620.

(34) Yamamoto, T.; Nishiyama, M.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 2367−2370.

lonate in the presence of NaO-*t*-Bu and a combination of D^t-BPF and Pd(dba)$_2$ as catalyst led to the formation of aryl malonate product in high yield at 100 °C. Reactions with this catalyst system did not form useful yields of aryl malonates from diethylmalonate in dioxane solvent. However, reactions between the inexpensive diethyl malonate and phenyl bromide with Pd(OAc)$_2$ and P(*t*-Bu)$_3$ as catalyst did cleanly produce the desired aryl malonate product.

Intermolecular reactions of malonates with aryl halides using transition metal catalysts are rare if not unprecedented,[14] and have been conducted intramolecularly only at high temperatures.[35] These malonate arylations did not occur in reasonable rates when using DPPF, BINAP, PPh_3, or P(*o*-tolyl)$_3$ as ligand. In most cases, it is likely that the anions of β-dicarbonyl compounds will form complexes that are stable to reductive elimination. Of course, acetylacetonate complexes are common and are often remarkably stable. In the case of the complexes containing *tert*-butylphosphine ligands, these β-dicarbonylate complexes are more reactive than expected and lead to the formation of aryl malonates. This chemistry is certainly valuable synthetically as a route to α-aryl carboxylic acid derivatives that are a common building block for pharmaceutical materials.

Conclusions

The results presented here suggest several important principles for the palladium-catalyzed arylation of ketones. First, the selectivity for reductive elimination from the enolate intermediate, rather than β-hydrogen elimination, does not require chelation or arylphosphine ligands and is driven toward reductive elimination by steric hindrance. Second, high selectivity for reaction with the less hindered side of a dialkyl ketone may benefit from chelation, and palladium complexes of the simple monophosphines here and complexes of bidentate phosphines[15,16,18] serve as complementary catalysts. Third, activation of chloroarenes under mild conditions does not require chelation, as one might expect from previous palladium chemistry with chloroarenes.[36−38] Finally, arylation of simple malonates occurs with catalyst systems containing sterically hindered alkylphosphines, providing a convenient route to α-aryl carboxylic acids. A detailed mechanistic basis for these conclusions will be one subject of future studies in our lab.

Experimental Section

General Methods. Reactions were conducted with standard Schlenk and drybox techniques. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AM 500 MHz spectrometer with TMS (^{1}H) or residual protiated (^{13}C) solvent used as a reference. ^{31}P{^{1}H} NMR spectra were recorded on an Omega 300 MHz spectrometer with shifts reported relative to an external 85% H_3PO_4 standard; resonances downfield of the standard are reported as positive. Low resolution mass spectra were obtained on a Hewlett Packard 5890 series II gas chromatograph interfaced with a Hewlett Packard 5989 A mass spectrometer. Tetrahydrofuran was distilled from sodium and benzophenone and was stored in the drybox. 1,1′-Bis(di-*tert*-butylphosphino)ferrocene[39] was prepared by literature procedures and was recrystallized under nitrogen. "[Pd(DBA)$_2$]" is predominantly a mixture of Pd(dba)$_3$ and Pd$_2$(dba)$_3$ and was obtained by the synthesis reported for [Pd$_2$(DBA)$_3$] without recrystallizing the crude precipitate.[40] The potassium enolate of isobutyrophenone was prepared by addition of isobutyrophenone to a toluene/pentane solution of potassium hexamethyldisilazide and was recrystallized from THF/ether after isolation by filtration. All other solvents and compounds were used as received.

General Procedure for the Reaction of Ketone with Arylbromide. The reaction conditions and results are shown in Table 1. A typical procedure is given for the reaction in Entry 1.

1,2-Diphenyl-1-propanone:[41] Pd(dba)$_2$ (23.0 mg, 0.040 mmol), D^t-BPF (23.7 mg, 0.050 mmol), and NaO^{t}Bu (288 mg, 3.00 mmol) were suspended in 2 mL of THF in a screw-capped vial. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. Bromobenzene (314 mg, 2.00 mmol) and propiophenone (289 mg, 2.20 mmol) were added to the reaction mixture by syringe. The reaction mixture was stirred at 25 °C and monitored by GC analysis. The crude reaction was diluted with ether and washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane/EtOAc = 95/5) to give 396 mg (94%) of 1,2-Diphenyl-1-propanone: ^{1}H NMR: (CDCl$_3$) δ 7.95 (d, J = 7.3 Hz, 2H), 7.48 (t, J = 7.3 Hz, 1H), 7.40−7.37 (m, 2H), 7.30−7.29 (m, 4H), 7.23−7.17 (m, 1H), 4.70 (q, J = 6.8 Hz, 1H), 1.54 (d, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 200.32, 141.55, 136.53, 132.83, 129.04, 128.82, 128.53, 127.82, 126.95, 47.91, 19.57.

2-Methyl-1,2-diphenyl-1-propanone:[42] Bromobenzene (157 mg, 1.00 mmol), isobutyrophenone (163 mg, 1.10 mmol), Pd(dba)$_2$ (11.5 mg, 0.020 mmol), D^{t}BPF (11.8 mg, 0.025 mmol), and NaO^{t}Bu (144 mg, 1.50 mmol) were used. Reaction at 50 °C for 6 h gave 196 mg (87%) of product after silica gel chromatography (hexane/EtOAc = 95/5). ^{1}H NMR (CDCl$_3$) δ 7.48 (d, J = 7.2 Hz, 2H), 7.38−7.33 (m, 5H), 7.29−7.26 (m, 1H), 7.21 (t, J = 7.9 Hz, 2H), 1.62 (s, 6H); ^{13}C-{^{1}H} NMR (CDCl$_3$) δ 203.67, 145.29, 136.25, 131.67, 129.72, 129.02, 127.95, 126.79, 125.72, 51.41, 27.87.

1-Phenyl-2-(3-pyridyl)-1-propanone:[43] 3-Bromopyridine (158 mg, 1.00 mmol), propiophenone (148 mg, 1.10 mmol), Pd(dba)$_2$ (11.5 mg, 0.020 mmol), D^{t}BPF (11.9 mg, 0.025 mmol), and NaO^{t}Bu (144 mg, 1.50 mmol) were used. Reaction at 55 °C for 12 h gave 183 mg (87%) of 1-phenyl-2-(3-pyridyl)-1-propanone after silica gel chromatography (hexane/EtOAc = 80/20). ^{1}H NMR (CDCl$_3$) δ 8.61 (s, 1H), 8.47 (d, J = 4.8 Hz, 1H), 7.94 (d, J = 7.5 Hz, 2H), 7.61 (d, J = 7.9 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.23 (dd, J = 4.8, 7.9 Hz, 1H), 4.75 (q, J = 6.9 Hz, 1H), 1.56 (d, J = 6.9 Hz, 3H); ^{13}C-{^{1}H} NMR (CDCl$_3$) δ 199.46, 149.32, 148.13, 136.85, 135.81, 135.04, 133.09, 128.57, 128.54, 123.69, 44.68, 19.20.

2-(3-Methoxyphenyl)-4-methyl-3-pentanone: 3-Bromoanisole (187 mg, 1.00 mmol), 2-methyl-3-pentanone (100 mg, 1.10 mmol), Pd(dba)$_2$ (11.5 mg, 0.020 mmol), D^{t}BPF (11.8 mg, 0.025 mmol), and NaO^{t}Bu (288 mg, 3.00 mmol) were used. Reaction at 50 °C for 12 h gave 189 mg (92%) of a mixture of 2-(3-methoxyphenyl)-4-methyl-3-pentanone and 2-(3-methoxyphenyl)-2-methyl-3-pentanone after silica gel chromatography (hexane/ether = 95/5). The ratio of isomers was determined by GC analysis in the crude reaction mixture. ^{1}H NMR: (CDCl$_3$) δ 7.24 (t, J = 7.9 Hz, 1H), 6.84−6.78 (m, 2H), 6.76 (s, 1H), 3.89 (q, J = 6.9 Hz, 1H), 3.80 (s, 3H), 2.70 (sept, 6.9 Hz, 1H), 1.37 (d, J = 6.9 Hz, 3H), 1.08 (d, J = 6.9 Hz, 3H), 0.93 (d, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 214.42, 159.93, 142.33, 129.76, 120.35, 113.61, 112.34, 55.16, 39.10, 25.17, 19.23, 18.28, 18.02. MS *m/e* (rel intensity) 206 (42), 135 (100), 120 (12), 105 (34), 91 (38), 77 (24), 71 (55), 51 (6). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.75: H, 8.71. Selected ^{1}H NMR of minor isomer: 0.97 (t, J = 7.3 Hz, 3H), 1.48 (s, 6H), 2.24 (q, J = 7.3 Hz, 2H), 3.81 (s, 3H), aromatic region overlaps with major isomer. MS *m/e* (rel intensity) 206 (41), 149 (100), 135 (9), 121 (56), 109 (31), 91 (28), 77 (12), 65 (6), 57 (6).

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2-Phenyl-1-cyclohexanone:[44] Bromobenzene (157 mg, 1.00 mmol), cyclohexanone (108 mg, 1.10 mmol), $Pd(dba)_2$ (11.5 mg, 0.020 mmol), D^{t}BPF (11.8 mg, 0.025 mmol), and NaO^{t}Bu (144 mg, 1.50 mmol) were used. Reaction at 55 °C for 3 h gave 122 mg (70%) of 2-phenyl-1-cyclohexanone after silica gel chromatography (hexane/ether = 90/10). ^{1}H NMR ($CDCl_3$) δ 7.35 (t, J = 7.2 Hz, 2H), 7.27 (t, J = 7.2 Hz, 1H), 7.16 (d, J = 7.2 Hz, 2H), 3.62 (dd, J = 12.3, 5.4 Hz, 1H), 2.57−2.44 (m, 2H), 2.31−2.27 (m, 1H), 2.18−2.15 (m, 1H), 2.09−1.99 (m, 2H), 1.87−1.59 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 210.14, 138.88, 128.557, 128.34, 126.86, 57.34, 42.22, 42.18, 35.13, 27.83, 25.31.

General Procedure for the Reaction of Ketone with Arylchloride. The reaction conditions and results are shown in Table 1. A typical procedure is given for the reaction of Entry 15.

1,2-Diphenyl-1-propanone:[41] $Pd(dba)_2$ (36.6 mg, 0.064 mmol), D^t-BPF (23.8 mg, 0.050 mmol), and NaO^{t}Bu (288 mg, 3.00 mmol) were suspended in 2 mL of THF in a screw-capped vial. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. Chlorobenzene (225 mg, 2.00 mmol) and propiophenone (295 mg, 2.20 mmol) were added to the reaction mixture by syringe. The vial was heated at 70 °C and monitored by GC analysis. The crude reaction was diluted with ether and washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane/EtOAc = 95/5) to give 365 mg (87%) of 1,2-diphenyl-1-propanone.

2-(3-Methoxyphenyl)-1-phenyl-1-propanone: 3-Chloroanisole (285 mg, 2.00 mmol), propiophenone (295 mg, 2.20 mmol), $Pd(dba)_2$ (36.6 mg, 0.064 mmol), D^{t}BPF (23.8 mg, 0.050 mmol), and NaO^{t}Bu (288 mg, 3.00 mmol) were used. Reaction at 70 °C for 2 h gave 477 mg (99%) of 2-(3-methoxyphenyl)-1-phenyl-1-propanone after silica gel chromatography (hexane/EtOAc = 95/5). ^{1}H NMR ($CDCl_3$) δ 7.96 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.21 (t, J = 7.8 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.83 (s, 1H), 6.74 (d, J = 7.8 Hz, 1H), 4.65 (q, J = 7.0 Hz, 1H), 3.77 (s, 3H), 1.53 (d, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 200.13, 160.02, 143.05, 136.50, 132.80, 129.99, 128.76, 128.49, 120.20, 113.53, 112.15, 55.15, 47.91, 19.45. MS *m/e* (rel intensity) 240(11), 135 (14), 105 (100), 91 (11), 77 (40), 51 (9). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.74: H, 6.65.

2-(3-Methoxyphenyl)-2-methyl-1-phenyl-1-propanone: 3-Chloroanisole (143 mg, 1.00 mmol), isobutyrophenone (163 mg, 1.10 mmol), $Pd(dba)_2$ (18.3 mg, 0.032 mmol), D^{t}BPF (12.0 mg, 0.025 mmol), and NaO^{t}Bu (144 mg, 1.50 mmol) were used. Reaction at 70 °C for 12 h gave 201 mg (79%) of 2-(3-methoxyphenyl)-1-phenyl-1-propanone after silica gel chromatography (hexane/EtOAc = 95/5). ^{1}H NMR ($CDCl_3$) δ 7.51 (d, J = 8.3 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.29−7.22 (m, 3H), 6.91 (d, J = 7.4 Hz, 1H), 6.88 (t, J = 2.3 Hz, 1H), 6.81 (dd, J = 8.3, 2.3 Hz, 1H), 3.79 (s, 3H), 1.58 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 203.51, 160.06, 146.95, 136.24, 131.70, 130.00, 129.66, 127.96, 118.24, 111.90, 111.67, 55.17, 51.38, 27.79. MS *m/e* (rel intensity) 254 (14), 149 (100), 121 (48), 105 (99), 91 (27), 77 (67), 65 (7), 51 (18). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.29; H, 7.13. Found: C, 80.50: H, 7.14.

2-(4-Methoxyphenyl)-1-phenyl-1-propanone:[45] 4-Chloroanisole (284 mg, 2.00 mmol), propiophenone (295 mg, 2.20 mmol), $Pd(dba)_2$ (36.6 mg, 0.064 mmol), D^{t}BPF (23.8 mg, 0.050 mmol), and NaO^{t}Bu (288 mg, 3.00 mmol) were used. Reaction at 70 °C for 12 h gave 192 mg (92%) of 2-(4-methoxyphenyl)-1-phenyl-1-propanone after silica gel chromatography (hexane/EtOAc = 95/5). ^{1}H NMR ($CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 4.65 (q, J = 6.8 Hz, 1H), 3.76 (s, 3H), 1.51 (d, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 200.55, 158.51, 136.53, 133.50, 132.73, 128.80, 128.76, 128.49, 114.40, 55.15, 46.95, 19.55.

2-(4-Methylphenyl)-1-phenyl-1-propanone:[46] 4-Chlorotoluene (253 mg, 2.00 mmol), propiophenone (295 mg, 2.20 mmol), $Pd(dba)_2$ (36.6 mg, 0.064 mmol), D^{t}BPF (23.8 mg, 0.050 mmol), and NaO^{t}Bu (288 mg, 3.00 mmol) were used. Reaction at 70 °C for 1 h gave 440 mg (99%) of 2-(4-methylphenyl)-1-phenyl-1-propanone after silica gel chromatography (hexane/EtOAc = 95/5). ^{1}H NMR ($CDCl_3$) δ 7.96 (d, J = 8.1 Hz, 2H), 7.47 (t, J = 8.1 Hz, 1H), 7.38 (t, J = 8.1 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 4.66 (q, J = 6.7 Hz, 1H), 2.29 (s, 3H), 1.52 (d, J = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 200.46, 138.55, 136.82, 136.51, 132.75, 129.74, 128.82, 128.50, 127.68, 47.52, 21.03, 19.58.

2-(2-Methylphenyl)-1-phenyl-1-propanone:[47] 2-Chlorotoluene (127 mg, 1.00 mmol), propiophenone (148 mg, 1.10 mmol), $Pd(dba)_2$ (18.3 mg, 0.032 mmol), D^{t}BPF (11.9 mg, 0.025 mmol), and NaO^{t}Bu (144 mg, 1.50 mmol) were used. Reaction at 70 °C for 12 h gave 189 mg (84%) of 2-(2-methylphenyl)-1-phenyl-1-propanone after silica gel chromatography (hexane/EtOAc = 95/5). ^{1}H NMR ($CDCl_3$) δ 7.38 (d, J = 7.3 Hz, 2H), 7.46 (t, J = 7.3 Hz, 1H), 7.36 (t, J = 7.3 Hz, 2H), 7.21 (d, J = 7.3 Hz, 1H), 7.12 (t, J = 7.3 Hz, 1H), 7.09 (t, J = 7.3 Hz, 1H), 7.04 (t, J = 7.3 Hz, 1H), 4.77 (q, J = 6.8 Hz, 1H), 2.51 (s, 3H), 1.48 (d, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 200.97, 140.19, 136.61, 134.57, 132.82, 132.69, 131.02, 128.52, 126.99, 126.90, 126.80, 44.61, 19.63, 18.06.

2-(2-Methylphenyl)-1-phenyl-1-ethanone:[48] 2-Chlorotoluene (127 mg, 1.00 mmol), acetophenone (132 mg, 1.10 mmol), $Pd(dba)_2$ (18.3 mg, 0.032 mmol), D^{t}BPF (11.9 mg, 0.025 mmol), and NaO^{t}Bu (144 mg, 1.50 mmol) were used. Reaction at 70 °C for 12 h gave 175 mg (83%) of 2-(2-methylphenyl)-1-phenyl-1-ethanone after recrystalization from n-hexane. ^{1}H NMR ($CDCl_3$) δ 8.04 (d, J = 7.3 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.3 Hz, 2H), 7.22−7.14 (m, 4H), 4.33 (s, 2H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 197.51, 136.95, 133.57, 133.23, 130.42, 133.15, 130.37, 128.73, 128.39. 127.29, 126.18, 43.53, 19.86.

Reactions with Tri-*tert*-butylphosphine as Ligand. The reaction conditions and results are shown in Table 1. A typical procedure is given for the reaction in Entry 8.

1,2-Diphenyl-1-ethanone:[49] $Pd(OAc)_2$ (2.3 mg, 0.010 mmol), tri-*tert*-butylphosphine (2.1 mg, 0.010 mmol), and NaO^{t}Bu (211 mg, 2.20 mmol) were suspended in 1 mL of THF in a screw-capped vial. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. Bromobenzene (157 mg, 1.00 mmol) and acetophenone (132 mg, 1.10 mmol) were added to the reaction mixture by syringe. The reaction mixture was stirred at 25 °C and monitored by GC analysis. The crude reaction was diluted with ether and washed with 1 N HCl, water, and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane/EtOAc = 95/5) to give 188 mg (96%) of 1,2-diphenyl-1-ethanone: ^{1}H NMR ($CDCl_3$) δ 8.02 (d, J = 7.1 Hz, 2H), 7.58−7.26 (m, 8H), 4.31 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 197.52, 136.79, 134.67, 133.09, 129.54, 129.50, 128.64, 128.62, 126.88, 45.50.

2-(4-Benzoylphenyl)-1-phenyl-1-propanone: $Pd(OAc)_2$ (4.5 mg, 0.020 mmol), tri-*t*-butylphosphine (4.1 mg, 0.020 mmol), NaO^{t}Bu (144 mg, 1.50 mmol), 4-bromobenzophenone (261 mg, 1.00 mmol), and propiophenone (148 mg, 1.10 mmol) were used. Reaction at 70 °C for 12 h gave 304 mg (97%) of 2-(4-benzoylphenyl)-1-phenyl-1-propanone after silica gel chromatography (hexane/EtOAc = 85/15). ^{1}H NMR ($CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 2H), 7.76−7.75 (m, 4H), 7.58 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.1 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.43−7.40 (m, 4H), 4.79 (q, J = 6.9 Hz, 1H), 1.59 (d, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 199.66, 196.14, 146.16, 137.51, 136.23, 133.10, 132.40, 130.82, 129.94, 129.80, 128.75, 128.63, 128.26, 127.79, 47.72, 19.37. MS *m/e* (rel intensity) 314 (10), 105 (100), 77 (38), 51 (13). Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.91: H, 5.88.

Reaction with 0.005 mol% catalyst: $Pd(OAc)_2$ (0.5 mg, 0.0023 mmol), tri-*tert*-butylphosphine (0.4 mg, 0.0020 mmol), and NaO^{t}Bu (5.80 g, 60.3 mmol) were suspended in 5 mL of THF in a screw-capped test tube. Bromobenzene (6.28 g, 40.0 mmol) and propiophenone (5.90 g, 44.0 mmol) were added to the reaction mixture in the drybox. The

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reaction tube was sealed with a cap and the mixture was stirred for 24 h at 60 °C. The reaction was diluted with ether and washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane/EtOAc = 95/5) to give 8.2 g (98%) of 1,2-diphenyl-1-propanone.

Reaction of propiophenone with *p*-tolyltosylate: $Pd(OAc)_2$ (9.0 mg, 0.040 mmol), ligand **2** (27.1 mg, 0.050 mmol), NaO^{t}Bu (144 mg, 1.50 mmol), and 4-methylphenyl-*p*-toluene sulfonate (262 mg, 1.00 mmol) were suspended in 1 mL of dioxane in a screw-capped vial. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. Propiophenone (132 mg, 1.10 mmol) was added to the reaction mixture by syringe. The reaction mixture was stirred at 100 °C and monitored by GC analysis. The crude reaction was diluted with ether and washed with 1 N HCl, water, and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane/EtOAc = 95/5) to give 135 mg (60%) of 2-(4-methoxyphenyl)-1-phenyl-1-propanone.

Reactions with Tricyclohexylphosphine as ligand. The reaction conditions and results are shown in Table 1. A typical procedure is given for the reaction of Entry 17.

1,2-Diphenyl-1-propanone:[48] $Pd(OAc)_2$ (4.5 mg, 0.020 mmol), Tricyclohexyphosphine (5.6 mg, 0.020 mmol), and NaO^{t}Bu (144 mg, 1.50 mmol) were suspended in 1 mL of THF in a screw-capped vial. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. Chlorobenzene (113 mg, 1.00 mmol) and propiophenone (144 mg, 1.10 mmol) were added to the reaction mixture by syringe. The reaction mixture was stirred at 50 °C and monitored by GC analysis. The crude reaction was diluted with ether and washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane/EtOAc = 95/5) to give 204 mg (97%) of 1,2-diphenyl-1-propanone[2]

Reaction of Malonates with Aryl Halides: Phenyl Di-*tert*-butylmalonate:[50] $Pd(OAc)_2$ (9.0 mg, 0.040 mmol), D^{t}BPF (23.8 mg, 0.050 mmol), and NaO^{t}Bu (288 mg, 3.00 mmol) were suspended in 2 mL of dioxane in a screw-capped vial. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. Chlorobenzene (225 mg, 2.00 mmol) and di-*tert*-butyl malonate (480 mg, 2.20 mmol) were added to the reaction mixture by a syringe. The reaction was heated at 100 °C and monitored by GC analysis. The reaction mixture was diluted with ether and was washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane/EtOAc = 80/20) to give 465 mg (80%) of phenyl di-*tert*-butylmalonate: ^{1}H NMR ($CDCl_3$) δ 7.40-7.33 (m, 5H), 4.44 (s, 1H), 1.47 (s, 18H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 167.44, 133.51, 129.30, 128.38, 127.83, 81.92, 60.10, 27.87.

Phenyl diethylmalonate:[51] $Pd(OAc)_2$ (4.5 mg, 0.020 mmol), P(^{t}Bu)$_3$ (4.1 mg, 0.020 mmol), and NaO^{t}Bu (100 mg, 1.04 mmol) were suspended in 2 mL of dioxane in a screw-capped vial. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. Bromobenzene (157 mg, 1.00 mmol) and diethyl malonate (176 mg, 1.10 mmol) were added to the reaction mixture by syringe. The reaction was heated at 70 °C and monitored by GC analysis. The reaction mixture was diluted with ether and washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane/EtOAc = 80/20) to give 205 mg (86%) of phenyl diethylbutylmalonate: ^{1}H NMR ($CDCl_3$) δ 7.42−7.33 (m, 5H), 4.62 (s, 1H), 4.23 (q, J = 7.3 Hz, 4H), 1.27 (t, J = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 168.13, 132.84, 129.25, 128.56, 128.16, 61.75, 57.98, 13.98.

Generation of {Pd(DPPF)(*p*-Tol)[OC(=CMe$_2$)Ph]}. Into a vial was weighed 8.3 mg (0.01 mmol) of {Pd(DPPF)(*p*-Tol)(Br)},[31] and into a second vial was weighed 2.6 mg (0.01 mmol) of KOC(=CMe$_2$)-Ph·THF. The palladium complex was suspended in 0.6 mL of benzene-d_6 and the suspension was added to the vial of enolate. The sample was transferred to an NMR sample tube and was shaken for 1−2 min until the palladium complex reacted with the enolate to make an orange solution with a white precipitate (KBr). The sample was then placed into the NMR probe and ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at room temperature. ^{1}H NMR (C_6D_6) δ 8.39 (t, 8.0 Hz, 4 H), 7.41 (t, 9 Hz, 4H), 7.2−7.0 (m, 11H), 6.89 (m, 4H), 6.80 (d, 6.6 Hz, 4H), 6.51 (m, 2H), 4.43 (s, 2H), 3.90 (s, 2H), 3.87 (s, 2H), 3.72 (s, 2H), 2.29 (s, 3H), 2.11 (s, 3H), 1.85 (s, 3H); ^{31}P{^{1}H} (C_6D_6) δ 29.83, 10.37 (J = 34.2 Hz).

Generation of {Pd(D^{t}BPF)(Ph)[OC(=CMe$_2$)Ph]}. Into a vial was weighed 7.4 mg (0.01 mmol) of {Pd(D^{t}BPF)(Ph)(Br)},[32] and into a second vial was weighed 2.6 mg (0.01 mmol) of KOC(=CMe$_2$)Ph·THF. The palladium complex was suspended in 0.6 mL of benzene-d_6 and the suspension was added to the vial of enolate. The sample was transferred to an NMR sample tube and was shaken for 1−2 min until the palladium complex reacted with the enolate to make an orange solution with a white precipitate (KBr). The sample was then placed into the NMR probe and ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at room temperature. ^{1}H NMR (toluene-d_8, 0 °C) δ 1.18 (d, 10.8 Hz, 18H), 1.23 (s, 3H), 1.24 (s, 3H), 1.32 (d, 14 Hz, 18H), 4.12 (s, 2H), 4.27 (s, 2H), 4.29 (s, 2H), 4.44 (m, 2H), 6.8−7.3 (m, 6H), 7.56 (d, 7.1 Hz, 2H), 7.86 (d, 6.8 Hz); ^{31}P{^{1}H} NMR (C_6D_6) δ 24.8 (s), 57.2 (s).

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