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1,4-Addition of Arylboronic Acids and Arylsiloxanes to α,*β*-Unsaturated Carbonyl Compounds via Transmetalation to Dicationic Palladium(II) Complexes

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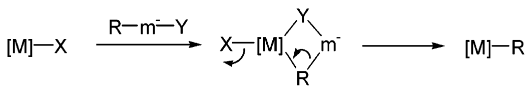
A high reactivity of dicationic palladium(II) complexes for transmetalation of organoboron and -silicon compounds was demonstrated in the 1,4-addition of arylboronic acids or arylsiloxanes to acyclic and cyclic enones. [Pd(dppe)(PhCN)$_2$](SbF$_6$)$_2$ and nitrile-free catalysts prepared in situ from Pd(acac)$_2$, dppben, and Cu(BF$_4$)$_2$·6H$_2$O or oxidation of Pd(dba)$_2$ with Cu(BF$_4$)$_2$·6H$_2$O in the presence of dppe or dppben effectively catalyzed the reactions of arylboronic acids at room temperature and arylsiloxanes at 75 °C. A catalytic cycle involving transmetalation between Ar−[m] (m = B(OH)$_2$, Si(OMe$_3$)) and [Pd]$^{2+}$ to give an Ar−[Pd]$^+$ intermediate, insertion of an enone into the C−Pd bond, giving a palladium enolate, and finally hydrolysis with water to regenerate [Pd]$^{2+}$ species was proposed. The reaction between [Pd(dppe)(PhCN)$_2$](BF$_4$)$_2$ (**4a**) and PhB(OH)$_2$ in the presence of PPh$_3$ allowed the first isolation of the transmetalation intermediate [Pd(Ph)(dppe)(PPh$_3$)](BF$_4$) and characterization by X-ray analysis. The reaction of a series of para-substituted arylboronic acids with **4a** showed a slightly negative ρ value (−0.54), demonstrating an electronic effect that was accelerated by the donating substituents.

Introduction

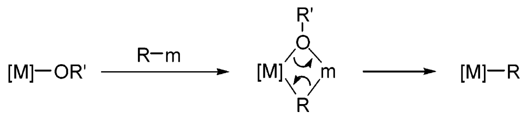
Transmetalation between organometallic reagents and transition metals is a fundamental process involved in metal-catalyzed C−C bond-forming reactions. It is the first step in the metal-catalyzed conjugate addition of organic electrophiles to α,*β*-unsaturated carbonyl compounds[1] and the second step in the palladium- or nickel-catalyzed cross-coupling reactions of carbon nucleophiles.[2−4] Although boron and silicon compounds are attractive reagents in organic syntheses, due to their high thermal stability and air stability for isolation or handling and due to their compatibility with a wide range of functional groups, transmetalation to transition metals is very slow, due to the low nucleophilicity of the organic group on these nonmetal elements. Organoboron and -silicon compounds are inert to palladium(II) or nickel(II) halides, but they transfer the organic groups to palladium(II) or other transition metals by one of the following three processes. The addition of bases such as alkoxy, hydroxy, and fluoride anions exerts a remarkable accelerating effect on the cross-coupling reactions of organoboron[3,5] and -silicon[4,6] compounds (eq 1). Thereby, the coordination of a negatively



(1)

[M]=Pd(II), Ni(II), Rh(I); X=halogen; Y=HO$^-$, RO$^-$, F$^-$

charged base enhances the nucleophilicity of the organic group so that ligand exchange between R−Pd−X (X = halogen) and an organometallic reagent proceeds smoothly via an S$_E$2 (cyclic) transition state. The second process is transmetalation to [M]−OR (M = Pd, Rh, Re; RO = OAc, OMe, OH) complexes (eq 2). Due to the high



(2)

[M]=Pd(II), Rh(I), Re(I); R'=H, Me

oxophilicity of boron and silicon compounds and high

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basicity of [M]−OR complexes,[7] transmetalation takes place without any assistance of bases for Pd,[3] Rh,[8] and Re[9] complexes. Thus, cross-coupling reactions of these compounds often proceed under neutral conditions for organic electrophiles, directly yielding RO−Pd complexes via oxidative addition. Indeed, the cross-coupling reactions of boron or silicon compounds with allylic acetates,[10] allylic carbonates,[11] 1,3-butadiene monoxide,[12] propargyl carbonates,[13] acetic anhydrides,[14] and phenyl trifluoroacetate[15] have been carried out in the absence of bases. Such (alkoxo)palladium(II) complexes are also considered to be an intermediate of cross-coupling reactions of organoboron compounds in basic media, since they are obtained in situ by ligand exchange between R−Pd−X and a base.[16] The third process is transmetalation to cationic transition-metal complexes (eq 3). Cross-coupling reactions of boron and

$$[\mathrm{M}]^+ \xrightarrow{\mathrm{R-m}} [\mathrm{M}]\mathrm{-R} \qquad (3)$$

$$[\mathrm{M}]^+ = \mathrm{Pd}^{2+},\ \mathrm{RPd}^+,\ \mathrm{Pt}^{2+}$$

silicon compounds with Ph_2IBF_4[17] and ArN_2BF_4,[18] which afford an Ar−$[Pd]^+$ intermediate via oxidative addition, have been carried out in the absence of bases. Another example reported in this category is a stoichiometric reaction between $[Pt(S)_2(PEt_3)_2][CF_3SO_3]_2$ (S = MeOH, H_2O) and $[Ph_4B]Na$, Ph_3B, or $PhB(OH)_2$, giving $[Pt(Ph)(S)(PEt_3)_2]^{2+}$.[19]

Such transmetalation of B, Si, and Sn compounds to palladium(II) or rhodium(I) complexes has recently been demonstrated in their addition reactions to alkenes and alkynes.[1] Rhodium(I) complexes were found to be excellent catalysts for 1,4-addition of aryl- or-1-alkenylboron,[8,20] -silicon,[21] -tin,[22] and titanium[23] compounds to α,β-unsaturated carbonyl compounds and to other activated or unactivated C−C, C−O, and C−N double bonds or triple bonds.[24] Various addition reactions analogous to copper-catalyzed reactions of lithium and magnesium reagents have been achieved by a catalytic cycle starting from transmetalation to yield an aryl- or 1-alkenylrhodium(I) intermediate. The corresponding addition reactions catalyzed by palladium complexes are rare; however, there are some reports that palladium(II) complexes catalyze 1,4-addition to enones. The Heck reaction of aryl halides with enones often predominated the formation of Michael-type products over alkene products derived by an insertion−elimination process.[25] The 1,4-addition of ArHgCl,[26] $SnAr_4$,[26] $ArB(OH)_2$,[27] and $ArSi(OMe)_3$[28] to enones was carried out by using neutral palladium(II) catalysts in acidic media in the presence of Bu_4NCl or a Lewis acid such as $SbCl_3$. We have recently reported that arylboronic acids easily transmetalate to $[Pd(dppe)]^{2+}$, in which 1,4-addition to enones was carried out in an aqueous medium at room temperature for arylboronic acids[29] and at 75 °C for arylsiloxanes[30] (Scheme 1). These reactions take place under neutral conditions by a process analogous to that shown

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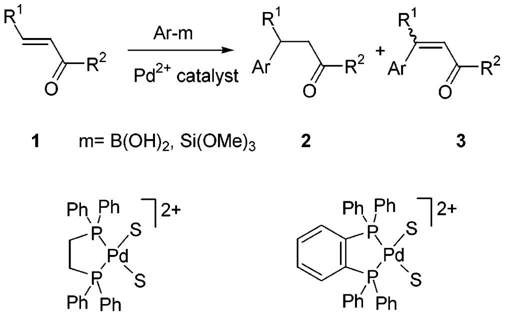
Scheme 1. 1,4-Addition of Arylboron and -silicon Compounds to Enones



4a: $[Pd(dppe)(PhCN)_2](BF_4)_2$ **5** $[Pd(dppben)(solvent)_2]^{2+}$
4b: $[Pd(dppe)(PhCN)_2](SbF_6)_2$
4c: $[Pd(dppe)(solvent)_2](BF_4)_2$

Table 1. 1,4-Addition of $PhB(OH)_2$ or $PhSi(OMe)_3$ to 2-Cyclohexenone: In Situ Preparation of Nitrile-Free Palladium(2+) Catalysts[a]

entry	M of Ph−[M]	Pd precursor	additive	yield/% (**2**/**3**)[b]
1	$B(OH)_2$	$[Pd(dppe)(PhCN)_2](SbF_6)_2$	none	87 (**2** >99)
2[c]	$B(OH)_2$	$PdCl_2(PhCN)_2$/dppe	$AgSbF_6$	61 (**2** >99)
3[c]	$B(OH)_2$	$PdCl_2$(dppe)	$AgSbF_6$	82 (**2** >99)
4[d]	$B(OH)_2$	$PdCl_2$(dppe)	$Cu(BF_4)_2$	60 (**2** >99)
5	$B(OH)_2$	$Pd(acac)_2$/dppe	$Cu(BF_4)_2$	83 (**2** >99)
6	$B(OH)_2$	$Pd(acac)_2$/dppben	$Cu(BF_4)_2$	92 (**2** >99)
7[e]	$B(OH)_2$	$Pd(acac)_2$/dppben	$Cu(BF_4)_2$	98 (**2** >99)
8	$B(OH)_2$	$Pd(dba)_2$/dppe	$Cu(BF_4)_2$	77 (**2** >99)
9[f]	$B(OH)_2$	$Pd(acac)_2$/bisphosphine	$Cu(BF_4)_2$	0−21
10	$Si(OMe)_3$	$[Pd(dppe)(PhCN)_2](BF_4)_2$	none	0 (−)
11	$Si(OMe)_3$	$PdCl_2$(dppe)	$AgBF_4$	44 (88/12)
12	$Si(OMe)_3$	$Pd(acac)_2$/dppe	$Cu(BF_4)_2$	<1 (−)
13	$Si(OMe)_3$	$Pd(dba)_2$/dppe	$Cu(BF_4)_2$	80 (88/12)
14	$Si(OMe)_3$	$Pd(dba)_2$/dppben	$Cu(BF_4)_2$	77 (92/8)
15	$Si(OMe)_3$	$Pd(dba)_2$/dppe	HBF_4	73 (94/6)
16	$Si(OMe)_3$	$Pd(dba)_2$/dcpe	$Cu(BF_4)_2$	33 (98/2)

[a] A mixture of 2-cyclohexenone (1 mmol), phenylboronic acid (1.5 mmol) in $THF-H_2O$ (10/1, 6.6 mL) was stirred at room temperature for 23 h in the presence of a palladium precursor (5 mol %) and an additive (if used, 0.2 mmol). All reactions of $PhSi(OMe)_3$ (2.5 mmol) with 2-cyclohexenone (1 mmol) were carried out at 75 °C for 23 h in dioxane−H_2O (2/1, 9 mL) in the presence of a palladium precursor (5 mol %) and an additive (0.2 mmol, 20 mol %). [b] Isolated yields by column chromatography. [c] In $THF-H_2O$ (6/1). [d] In anhydrous THF, since no reaction was observed in aqueous THF. [e] In DME−H_2O (10/1). [f] Dppm (trace), dppp (trace), dppb (trace), dppf (trace), and dcpe (21%).

in eq 3. In this paper, we report the effect of catalysts, including in situ preparation of dicationic palladium(II) complexes and reaction scope as well as mechanism and including the first isolation of the transmetalation intermediate.

Results and Discussion

Reaction Conditions. Addition of phenylboronic acid (1.5 equiv) to 2-cyclohexenone in $THF-H_2O$ (10/1) was carried out at room temperature to optimize the catalyst system (Table 1). A dicationic benzonitrile complex (**4b**) was an excellent catalyst, giving 87% yield at room temperature (entry 1), whereas neutral palladium complexes such as $PdCl_2$(dppe) and $Pd(acac)_2$/dppe were not effective.[29] The SbF_6 salt gave the best yields among a series of dicationic palladium-dppe complexes of ClO_4, OTf, BF_4, and PF_6. Although the benzonitrile complex (**4a**,**b**)[31] was a bench-stable catalyst that required no further activation, the corresponding nitrile-free complexes (**4c** and **5**) would provide much more active catalysts for transmetalation and insertion due to their high electrophilicity. The use of a traditional method for in situ preparation of **4c** (S = H_2O, solvent) from $PdCl_2$(dppe) and $AgSbF_6$ or $AgBF_4$[31] gave a result comparable to that obtained by a benzonitrile complex (**4a**) (entry 3). $Cu(BF_4)_2$ was less effective for the palladium chloride complex (entry 4), but it worked nicely for $Pd(acac)_2$ (entries 5−7). Electrochemical oxidation of palladium(0) complexes has been reported for in situ preparation of such dicationic complexes from $Pd(PPh_3)_4$.[32] Alternatively, chemical oxidation of $Pd(dba)_2$ with $Cu(BF_4)_2$ in the presence of dppe or dppben was found to be convenient for preparation of an analogously active catalyst (entry 8). Among these representative procedures for in situ preparation of dicationic palladium catalysts, a combination of $Pd(acac)_2$, dppben, and $Cu(BF_4)_2$ in aqueous DME resulted in a quantitative yield (entry 7). The catalyst efficiency was greatly dependent on the phosphine ligand and is highly characteristic for bis(diphenylphosphino) ligands bridged by two carbon atoms. Dppe and dppben gave 83−98% yields (entries 5−7), whereas the corresponding catalysts prepared from dppm, dppp, dppb, dppf, binap, and PPh_3 resulted in almost no reactions (entry 9). The corresponding alkylphosphine derivatives such as dcpe were also less effective, due to their bulkiness and strong σ-donation to the palladium(II) metal center. The addition of a base exerts a large accelerating effect for related rhodium-catalyzed 1,4-addition.[20a,24a] The presence of an inorganic base such as K_2CO_3 also accelerated the reaction, but addition of such a base always resulted in the formation of a Heck product (**3**; 4−11%), whereas such a side reaction was negligible in the absence of a base. The reaction proceeded smoothly in less polar solvents such as THF, DME, 1,4-dioxane, and acetone and was very slow in donating solvents such as DMF and MeCN. In contrast to the excellent reactivity of arylboronic acids and boroxines $(ArBO)_3$, all attempts at using boronic esters were unsuccessful. The corresponding reactions of 1,2-ethanediol and 1,3-propanediol esters of phenylboronic acid resulted in very low yields in either the presence or absence of water.

The use of cationic nitrile-free catalysts was critical for phenylsiloxane, because of its slow transmetalation compared to that of arylboronic acids.[30] Thus, **4a**,**b** stabilized by two benzonitriles did not catalyze the reaction at all, even at 75 °C (entry 10). In situ preparation of a nitrile-free catalyst from $PdCl_2$(dppe) and $AgBF_4$ (entry 11) or $Pd(acac)_2$, dppe, and $Cu(BF_4)_2$ unexpectedly resulted in low catalyst efficiency (entry 12). The best catalyst for arylsiloxanes was obtained by chemical oxidation of $Pd(dba)_2$ with $Cu(BF_4)_2$ in the presence of 1 equiv of dppe or dppben (entries 13 and 14). It is interesting that treatment of $Pd(dba)_2$ with HBF_4 provided an analogously efficient catalyst, which gave a result comparable to that obtained by the chemical oxidation method (entry 15). The addition of phenylsiloxane to cyclic enones suffered from a formal trans elimination, giving Heck products[33] (**3**). The Heck product (**3**) was decreased by decreasing the reaction

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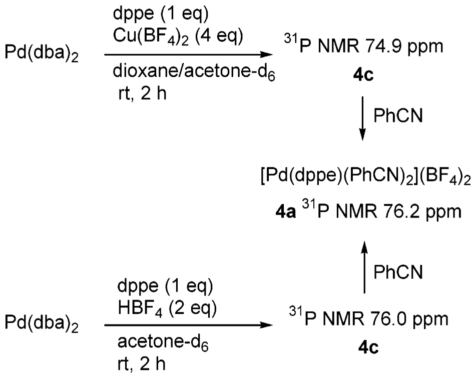
Table 2. 1,4-Addition of $ArB(OH)_2$ and $ArSi(OMe)_3$ to α,*β*-Unsaturated Ketones and Aldehydes

			yield/%[a] (**2**/**3**)		
entry	Ar of Ar−[M]	enone	[M] = $B(OH)_2$[b]	[M] = $B(OH)_2$[c]	[M] = $Si(OMe)_3$[d]
1	Ph	2-cyclopentenone	78 (**2** >99)	86 (**2** >99)	60 (43/57)
2	Ph	2-cyclohexenone	87 (**2** >99)	98 (**2** >99)	78 (92/ 8)
3	$4\text{-}MeOC_6H_4$	2-cyclohexenone	80 (**2** >99)	95 (**2** >99)	61 (59/41)
4	$2\text{-}MeOC_6H_4$	2-cyclohexenone	95 (**2** >99)	91 (**2** >99)	
5	$4\text{-}MeC_6H_4$	2-cyclohexenone	95 (**2** >99)	92 (**2** >99)	62 (81/19)
6	$4\text{-}FC_6H_4$	2-cyclohexenone	90 (**2** >99)	88 (**2** >99)	
7	$4\text{-}CH_3COC_6H_4$	2-cyclohexenone	96 (**2** >99)[e]	96 (**2** >99)[e]	
8	$4\text{-}CF_3C_6H_4$	2-cyclohexenone	94 (**2** >99)[e]	91 (**2** >99)[e]	
9	Ph	2-cycloheptenone	87 (**2** >99)	79 (**2** >99)	86 (**2** >99)
10	Ph	(E)-$C_5H_{11}CH{=}CHCOCH_3$	99 (**2** >99)	95 (**2** >99)	84 (**2** >99)
11	$4\text{-}MeOC_6H_4$	(E)-$C_5H_{11}CH{=}CHCOCH_3$			77 (**2** >99)[f]
12	$2\text{-}MeOC_6H_4$	(E)-$C_5H_{11}CH{=}CHCOCH_3$			74 (**2** >99)
13	$4\text{-}CH_3COC_6H_4$	(E)-$C_5H_{11}CH{=}CHCOCH_3$			85 (**2** >99)[f]
14	$4\text{-}CF_3C_6H_4$	(E)-$C_5H_{11}CH{=}CHCOCH_3$	-	-	90 (**2** >99)[g]
15	Ph	(E)-$i\text{-}C_3H_7CH{=}CHCOCH_3$	82 (**2** >99)	80 (**2** >99)	60 (**2** >99)
16	Ph	(E)-$PhCH{=}CHCOCH_3$	83 (**2** >99)	86 (**2** >99)	90 (**2** >99)
17	Ph	(E)-$PhCH{=}CHCOPh$	90 (**2** >99)	70 (**2** >99)	80 (**2** >99)
18	Ph	(E)-$C_3H_7CH{=}CHCHO$	76 (**2** >99)[h]	70 (**2** >99)	72 (**2** >99)[j]
19	Ph	(E)-$PhCH{=}CHCHO$	43 (**2** >99)[i]	73 (**2** >99)	74 (**2** >99)[j]

[a] Isolated yields by chromatography. [b] At room temperature for 23 h using an enone (1 mmol), $ArB(OH)_2$ (1.5 mmol), and $[Pd(dppe)(PhCN)_2](SbF_6)_2$ (5 mol %) in $THF-H_2O$ (10/1, 6.6 mL). [c] At room temperature for 23 h using enone (1 mmol), $ArB(OH)_2$ (1.5 mmol), $Pd(acac)_2$ (5 mol %), dppben (5 mol %), and $Cu(BF_4)_2{\cdot}6H_2O$ (0.2 mmol) in $DME-H_2O$ (10/1, 6.6 mL). [d] At 75 °C for 23 h using an enone (1 mmol), $ArSi(OMe)_3$ (2.5 mmol), $Pd(dba)_2$ (5 mol %), dppben (5 mol %), and $Cu(BF_4)_2{\cdot}6H_2O$ (0.2 mmol, 20 mol %) in dioxane$-H_2O$ (2/1, 9 mL), unless otherwise noted. [e] Reaction was conducted in the absence of water. [f] Dioxane$-H_2O$ (6/1). [g] Dioxane$-H_2O$ (12/1). [h] 1,3-Diphenylhexan-1-one (1.6%) was also produced. [i] Reaction accompanied by 1,3,3-triphenylpropan-1-one (4%). [j] At 95 °C for 9 h.

Scheme 2. In Situ Preparation of Nitrile-Free Cationic Palladium(II) Catalyst



temperature. For example, the selectivity of **2**/**3** = 88/12 (entry 13) increased to **2**/**3** = 96/4 (48% yield) when addition to 2-cyclohexenone was carried out at 50 °C. The formation of **3** was also decreased even at 75 °C when the catalyst was prepared from dppben (**5**) (entry 14). Other complexes of bidentate ligands such as dppm, dppp, dppb, dppf, and binap again did not catalyze the reaction. Although CsF and $Bu_4NF{\cdot}nH_2O$ are excellent reagents that accelerate the transmetalation of organosilicon compounds,[4,6] the presence of these bases strongly retarded the reaction.

A quantitative formation of a dicationic palladium(II) species by chemical oxidation of a palladium(0) complex was shown by a ^{31}P NMR study (Scheme 2). The phosphorus signal of dppe at −12.3 ppm completely shifted to 74.9 ppm after 2 h, when a mixture of $Pd(dba)_2$ and dppe was treated with $Cu(BF_4)_2$ at room temperature. The cationic palladium(II) species thus obtained was tentatively assigned to be $[Pd(dppe)(S)_2](BF_4)_2$ (**4c**; S = H_2O, solvent), since it was converted into **4a** (76.2 ppm in acetone-d_6) upon treatment with benzonitrile. All attempts at isolation of **4a** failed because of difficulty in removing the copper salts, but ^{31}P and ^{13}C NMR spectra of crude product exhibited signals characteristic of **4a**. Other oxidizing reagents such as $Cu(ClO_4)_2$ and $Cu(OTf)_2$ were less effective. The reaction of $Pd(dba)_2$ with HBF_4 at room temperature in the presence of dppe also gave a single signal of a dicationic palladium(II) species (**4c**). The palladium(0) complex can be oxidized to a palladium(II) species ($HPdBF_4$) via oxidative addition of an acid to a palladium(0) complex that can be led to a dicationic palladium(II) species via metathesis between HBF_4 and $HPdBF_4$ with elimination of hydrogen. However, such a signal was negligible in the corresponding reaction of CH_3CO_2H, CF_3CO_2H, TsOH, CF_3SO_3H, HCl, or $HClO_4$, though an analogous reaction of $Pd(PPh_3)_4$ and TfOH was reported to provide a dicationic palladium(II) catalyst.[34]

Scope and Limitation. Representative results obtained by 1,4-addition of arylboronic acids or arylsiloxanes to enones and enals are summarized in Table 2. Representative arylboronic acids possessing an electron-donating or -withdrawing group were added to cyclic and acyclic enones at room temperature in the presence of $[Pd(dppe)(PhCN)_2](BF_4)_2$ (fourth column) or a nitrile-free catalyst prepared in situ from $Pd(acac)_2$, dppben, and $Cu(BF_4)_2$ (fifth column). Reactions of arylboronic acids proceeded in the presence of water, as did the analogous rhodium-catalyzed reactions of arylboronic acids.[8,20] For example, p-tolylboronic acid (boronic acid/boroxine = 87/13) and tris(p-tolyl)boroxine resulted in 77% and 43% yields, respectively, in the absence of water, and both yields improved to about 95% with the addition of water to the boronic acid or to the boroxine. Thus, most reactions were carried out in $THF-H_2O$ or $DME-H_2O$ (10/1), but (4-acetylphenyl)- and (4-(trifluo-

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romethyl)phenyl)boronic acid unexpectedly resulted in very low yields in aqueous solution (entries 7 and 8). A 31% yield using 4-(trifluoromethyl)phenylboronic acid (boronic acid/boroxine = 100/0) in aqueous THF was improved to 94% in anhydrous THF (entry 8, fourth and fifth columns). The reaction has broad scope for cyclic enones having no substituents at the α- and *β*-carbons and for acyclic α,*β*-unsaturated ketones or aldehydes having one substituent on the *β*-carbon, but all attempts at the addition to α,*β*- and *β*,*β*-disubstituted enones were unsuccessful. A very slow addition to ethyl acrylate resulted in a mixture of ethyl 3-phenylpropiolate (5%) and ethyl cinnamate (31%). No reaction was observed for *N*-benzyl crotonamide.

The addition of arylsiloxanes gives results comparable to those of arylboronic acids when a nitrile-free catalyst was used at 75 °C. The catalyst was prepared in situ from Pd(dba)$_2$, dppe, and Cu(BF$_4$)$_2$ (sixth column). Among the substrates screened, 2-cyclopentenone (entry 1) and 2-cyclohexenone (entries 2−5) have a strong tendency to yield an alkene product (**3**), though such a side reaction was negligible for 2-cycloheptenone (entry 9), acyclic enones (entries 10−17), and enals (entries 18 and 19). It was very interesting that the formation of **3** was more serious in cyclic enones than that in acyclic enones, since the syn addition of Ar−[Pd]$^+$ to a cyclic enone affords a C-bound palladium intermediate that has a *β*-hydrogen trans to the C−Pd bond. Thus, the *β*-hydride elimination to give **3** may proceed through epimerization of the C−Pd bond cis to the *β*-hydrogen via equilibration between *C*-palladium enolate and *O*-palladium enolate.[33] Representative arylsiloxanes added to enones in high yields in dioxane−H$_2$O (1/1), but those possessing a 4-MeO, 4-MeCO, and 4-CF$_3$ group resulted in moderate yields, as was observed in analogous arylboronic acids. These yields were improved significantly when the water content in 1,4-dioxane was decreased to 6:1 or 12:1 (entries 11, 13, and 14). Enals required a higher temperature than did enones because they form hemiacetals in aqueous media (entries 18 and 19).

Transmetalation to Pd^{2+} Complexes. Transmetalation between **4** and ArB(OH)$_2$ may provide the monocationic arylpalladium(II) complex of water, solvent, or benzonitrile [Pd(Ar)(dppe)(S)]$^+$. Isolation of the intermediate failed, due to the thermal instability of the cationic organopalladium(II) species.[35,36] To stabilize the intermediate with a phosphine ligand, the reaction of [Pd(dppe)(PhCN)$_2$](BF$_4$)$_2$ (**4a**) with PhB(OH)$_2$ (2.4 equiv) was carried out in the presence of PPh$_3$ (1 equiv) (Scheme 3). ^{1}H and ^{31}P NMR studies showed the formation of **6** in 72% yield. The ^{31}P signals exhibited at 21 ppm (dd, *J* = 23.5 and 360 Hz), 42 ppm (dd, *J* = 23.5 and 29.5 Hz), and 50 ppm (dd, *J* = 29.5 and 360 Hz) were identical with an authentic material obtained from *trans*-[Pd(Ph)(Br)(PPh$_3$)$_2$], dppe, and AgBF$_4$ at −20 °C. The formation of **6** was also observed by ^{31}P NMR when **4a** was treated with PhSi(OMe)$_3$ (6 equiv) and PPh$_3$ (1 equiv) in dioxane/acetone-d_6/D$_2$O for 11 h at room temperature. Finally, **6** was isolated and crystallized from CH$_2$Cl$_2$/benzene/hexane at temperatures ranging from −30 °C to room temperature to give a single crystal for X-ray analysis.

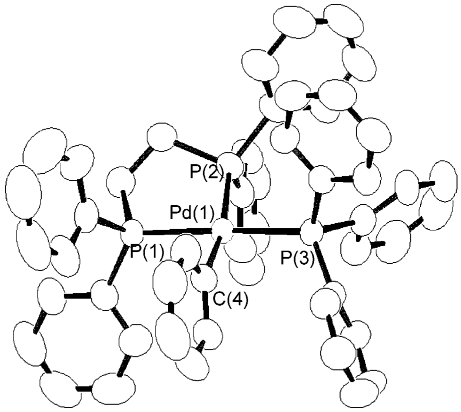

Figure 1. X-ray structure of **6** (^{31}P NMR: 21 ppm (dd, *J* = 23.5 and 360 Hz), 42 ppm (dd, *J* = 23.5 and 29.5 Hz) and 50 ppm (dd, *J* = 29.5 and 360 Hz)).

Scheme 3. B-Pd and Si−Pd Transmetalation

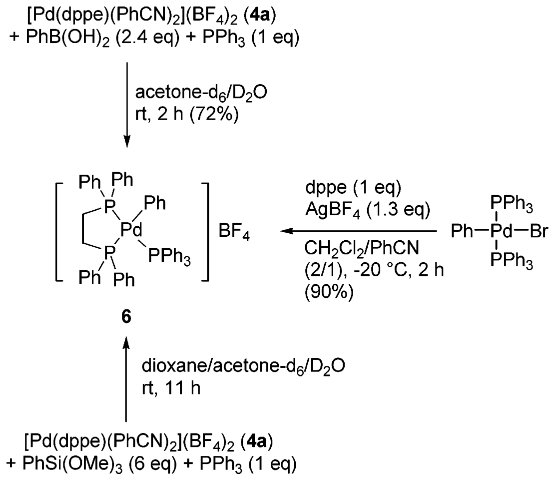

Table 3. Crystallographic Data for 6

empirical formula	C$_{57}$H$_{52}$BF$_4$P$_3$PdCl$_2$
solvent	1 benzene, 1 CH$_2$Cl$_2$
fw	1094.07
cryst color, habit	colorless, platelet
crysta dimens, mm	1.40 × 0.40 × 0.10
cryst syst	monoclinic
a, Å	11.323(6)
b, Å	23.58(1)
c, Å	20.078(8)
β, deg	101.39(4)
V, Å^3	5254.7(5)
space group	*P*2$_1$/*n* (No. 14)
Z	4
D_{calcd}, g/cm^3	1.383
temp, °C	23.0
total no. of rflns	47 751
no. of unique data	11 935
R_{int}	0.052
R1 ($I > 2.00\sigma(I)$)	0.056
wR2 ($I > -10.00\sigma(I)$)	0.169
goodness of fit indicator	0.98

An ORTEP plot of **6** is shown in Figure 1; crystal data and refinement details are given in Table 3. The molecular structure consists of a distorted-square-planar coordination geometry for a Pd atom containing a phenyl group, two diphenylphosphino groups of dppe, and one triphenylphosphine. The sum of the angles around Pd is 359.7°, the significant bond angles being ∠P(1)−Pd−P(2) (84.9°), ∠P(3)−Pd−C(4) (86.3°), ∠P(1)−

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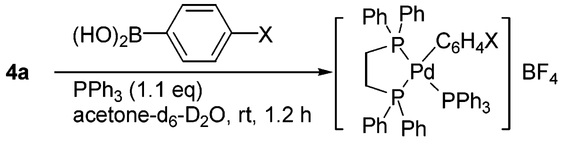

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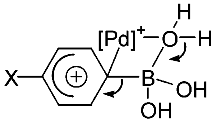

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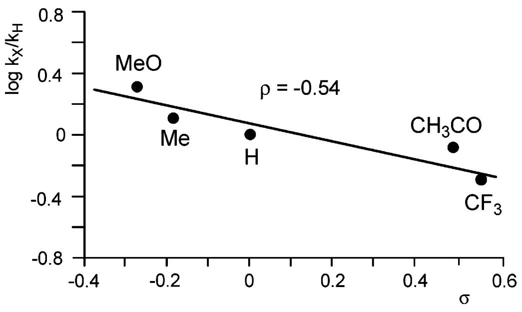
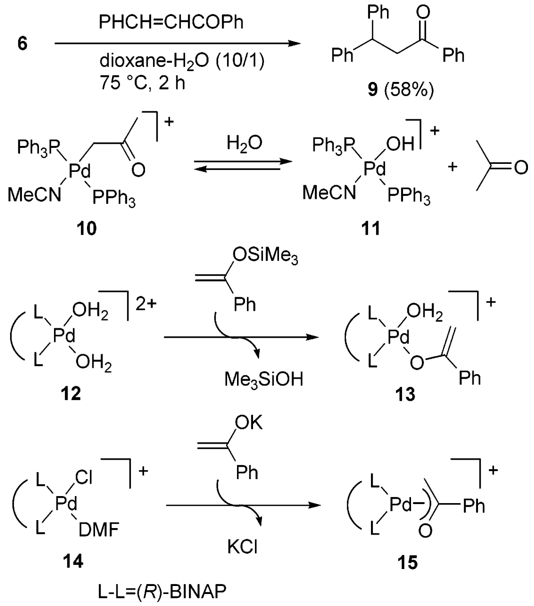


Figure 2. Electronic effect on transmetalation.

Pd−C(4) (87.8°), and ∠P(2)−Pd−P(3) (100.7°). The phenyl group bound to palladium describes a 86.3° dihedral angle with the plane defined by P(3), Pd, and C(4) with a bond length of 2.05 Å. The P(1)−Pd−P(2) angle (84.9°) is slightly smaller, but it is similar to the angles of neutral $PdCl_2(dppe)$ (85.8°),[37] $Pd(CH_2CH_2Ph)_2$(dppe) (85.5°),[38] and Pd(*o*-An)(I)(dppe) (86.32°).[39] The P(2)−Pd bond length (2.36 Å), which is trans to the phenyl ligand, is slightly longer than that of P(1)−Pd (2.31 Å), as was observed in [Pd(Ph)(binap)(RNH_2)]OTf (2.40 Å).[36]

Electronic Effect on Transmetalation. Transmetalation is a critical process involved in various metal-catalyzed bond-forming reactions,[3,4] but the mechanistic features, including its kinetics, still remain unexplored due to instability of the intermediates. The electronic effect on transmetalation of para-substituted arylboronic acids is shown by the Hammett plot[40] in Figure 2. A series of reactions of para-substituted arylboronic acids with **4a** was carried out at 20 °C for 1.2 h in the presence of PPh_3 (1.1 equiv). The reaction rates, which were calculated by ^1H NMR spectra on the basis of relative signals of **7** and an internal standard (triphenylmethane), gave a negative ρ value (−0.54), demonstrating that the donating substituents slightly accelerate the reaction. Aromatic C−B or C−Si bond cleavage with water, halogens, or metal salts occurs by electrophilic substitution.[41] Thus, transmetalation to a dicationic aqua complex[42,43] may proceed through a chelated Wheland intermediate (**8**), which is analogous to cleavage of aromatic main metal−carbon bonds with cationic palladium or platinum complexes.[19,44] Although the effects of such substituents can be best interpreted by assuming **8**, the observed effect was very small compared to that reported in protonolysis or halogenolysis of aromatic C−B and C−Si bonds via an analogous transition state.[41]

Scheme 4. Insertion and Hydrolysis Step



Steps for Insertion and Hydrolysis. The reaction between chalcone and **6** was carried out at 75 °C in aqueous 1,4-dioxane to give an addition product (**9**) in 58% yield (Scheme 4). A catalytic reaction between chalcone and phenylboronic acid (1.5 equiv) in the presence of PPh_3 (5 mol %) and **4a** (5 mol %) resulted in no reaction at room temperature, but an analogous reaction at 75 °C gave **9** in 85% yield. Thus, the presence of PPh_3 acts to retard the reaction, as does benzonitrile, but the formation of **9** in both catalytic and stoichiometric reactions suggested the mechanism involving the phenylpalladium(II) species as a key intermediate. This reaction involves cis insertion of the double bond into the Pd−Ph bond of **6** to give a monocationic palladium(II) enolate and its hydrolysis with water. Observation of a palladium enolate intermediate failed, because **6** stabilized by triphenylphosphine did not react with chalcone and other enones at temperatures lower than 75 °C or in the absence of water. Thus, no relevant information is now available for a palladium−enolate intermediate. Several coordination modes are possible for isolated palladium enolate camplexes[45,46] that are in equilibrium in solution, depending upon the substituents on enolate and the ligands on palladium.[46a] Espinet synthesized a C-bound enolate of a cationic

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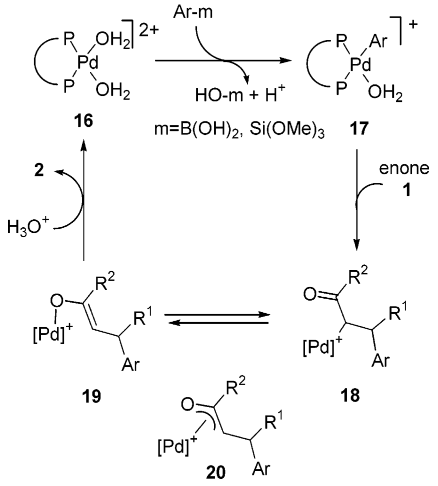
Scheme 5. Catalytic Cycle



palladium complex (**10**) from *trans*-[Pd(CH_2COCH_3)(Cl)-(PPh_3)$_2$] with $AgBF_4$.[45a] NMR spectroscopic studies by Sodeoka found that O-bound enolate (**13**)[46b] and oxa-π-allyl enolate (**15**)[46b,e] are produced on treatment of a cationic palladium complex (**12** or **14**) with a silyl or potassium enolate. Among these three species, **10** and **13** are reported to be highly susceptible to hydrolytic cleavage, whereas **15** is relatively inert to water.

Catalytic Cycle. The proposed catalytic cycle based on these observations is shown in Scheme 5. Dicationic palladium(II) complexes (**16**) are excellent catalysts that enable smooth transmetalation of arylboronic acids, arylsiloxanes, and presumably also other main-group-metal reagents under neutral conditions.[47] The reaction selectively provides a monocationic arylpalladium(II) species (**17**). The addition of **17** to enones yields a C-bound palladium(II) enolate (**18**), which would be in equilibrium with *O*-enolate (**19**) or oxa-π-allyl species (**20**). The resulting *C*-enolate (**18**) or *O*-enolate (**19**) is then hydrolyzed with water to regenerate a dicationic aqua complex (**16**).[42,43] Very smooth insertion of a C−C or C−N double bond into a C−[Pd]$^+$ bond due to high Lewis acidity of the metal center is a great advantage of cationic palladium(II) catalysts that has been demonstrated in palladium-catalyzed Heck reactions,[48] Mannich reactions,[46b,e] aldol reactions,[49] and polymerizations of alkenes.[50] The high susceptibility of cationic palladium(II) enolates to hydrolytic cleavage is also an advantage of the cationic catalysts in preventing the formation of Heck coupling products via β-hydride elimination from **18** and precipitation of palladium black.

Because of the simple experimental procedures under neutral conditions, palladium-catalyzed asymmetric addition will be a topic of further reports from this laboratory.[47]

Experimental Section

Reagents. [Pd(dppe)(PhCN)$_2$]X$_2$ (X = BF_4, SbF_6, OTf, ClO_4) were prepared by published procedures.[31] Arylsiloxanes possessing a 4-methoxy, 2-methoxy, 4-methyl, 4-acetylphenyl, or 4-trifluoromethyl group were synthesized by the reported method.[51] All arylboronic acids were commercially available and used without further purification. The ratios of boronic acid to boroxine were as follows: PhB(OH)$_2$ (68/32), 4-MeOPhB(OH)$_2$ (68/32), 2-MeOPhB(OH)$_2$ (100/0), 4-MePhB(OH)$_2$ (87/13), 4-MeCOPhB(OH)$_2$ (100/0), and 4-CF_3PhB(OH)$_2$ (100/0). The following abbreviations are used for phosphine ligands: dppm ($Ph_2PCH_2PPh_2$), dppe ($Ph_2PCH_2CH_2PPh_2$), dppp ($Ph_2PCH_2CH_2CH_2PPh_2$), dppb ($Ph_2PCH_2CH_2CH_2CH_2PPh_2$), dppben (1,2-bis(diphenylphosphino)benzene), dcpe (1,2-bis(dicyclohexylphosphino)ethane), and dppf (1,1′-bis(diphenylphosphino)ferrocene).

1,4-Addition of Arylboronic Acids to Enones (Table 2). A flask charged with [Pd(dppe)(PhCN)$_2$](BF_4)$_2$ (0.05 mmol) and arylboronic acid (1.5 mmol) was flushed with argon. THF (6 mL), an enone (1.0 mmol), and water (0.6 mL) were added successively. After being stirred for 23 h at room temperature, the product was extracted with ether and washed with 0.5 M K_2CO_3. Chromatography on silica gel gave the pure product.

An alternative procedure using a nitrile-free catalyst: A flask charged with Pd(acac)$_2$ (0.05 mmol), dppben (0.05 mmol), Cu(BF_4)$_2$·6H_2O (0.2 mmol), and arylboronic acid (1.5 mmol) was flushed with argon. DME-H_2O (10/1, 6.6 mL) and an enone (1.0 mmol) were then added successively. After the mixture was stirred for 23 h at room temperature, chromatography on silica gel gave the pure product.

1,4-Addition of Arylsiloxanes to Enones (Table 2). Pd(dba)$_2$ (0.05 mmol), arylsiloxane (1.5 mmol), dppben (0.05 mmol), and Cu(BF_4)$_2$·6H_2O (0.20 mmol) were added to a flask containing a magnetic stirring bar and a septum inlet. The flask was then charged with argon. 1,4-Dioxane (6 mL), an enone (1.0 mmol), and water (3 mL) were added successively. After being stirred for 23 h at room temperature, the reaction mixture was filtered through a silica gel−$MgSO_4$ pad. The pad was repeatedly rinsed with hexane/AcOEt (1:1 or 3:1, ca. 70 mL). The product was isolated by chromatography on silica gel.

Synthesis of [Pd(Ph)(dppe)(PPh_3)](BF_4)$_2$ (6). A solution of $AgBF_4$ (0.6 mmol in acetone, 2.5 mL) was added to a mixture of *trans*-Pd(Br)(Ph)(PPh_3)$_2$ (0.5 mmol) and dppe (0.5 mmol) in CH_2Cl_2/PhCN (2/1, 7.5 mL) at −20 °C. After being stirred for 2 h at room temperature, the solids were removed by filtration through a Celite pad. Addition of hexane to the filtrate precipitated a crude product. The solid was dissolved in acetone, insoluble solid impurity was removed by filtration, and the solvent was then evaporated under reduced pressure at room temperature. The resulting solid was dissolved in a small amount of CH_2Cl_2, which was followed by filtration to obtain a clear brown solution. Benzene (in the same amount as that of CH_2Cl_2) and a small amount of hexane were successively added to the solution. The mixture was left to stand overnight in the refrigerator to give single crystals of **6**, which contains benzene and CH_2Cl_2 (1/1). ^{1}H NMR (acetone-

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d_6): δ 2.58−2.80 (m, 4H), 6.42 (m, 2H), 6.55 (m, 1H), 6.72 (m, 2H), 7.13−7.21 (m, 12 H), 7.34−7.57 (m, 23H). ^{11}B NMR (acetone-d_6): δ 0.952. ^{31}P NMR (acetone-d_6): δ 21.8 (dd, J = 23.5 and 360 Hz), 42.4 (dd, J = 23.5 and 29.5 Hz), 50.0 (dd, J = 29.5 and 360 Hz). ESI MS (acetone/methanol): $C_{50}H_{44}BF_4P_3Pd$, m/z 843 [$M^+ - BF_4$]. Anal. Calcd for $C_{50}H_{44}BF_4P_3Pd$: C, 64.50; H, 4.76. Found: C, 64.23; H, 5.28.

X-ray Crystallography (6). Data collection of a colorless platelet crystal of $C_{57}H_{52}BF_4P_3PdCl_2$ mounted on a glass fiber was performed on a Rigaku R-AXIS RAPID-F using graphite-monochromated Mo Kα radiation.

Synthesis of [Pd(Ph)(dppe)(PPh$_3$)](BF$_4$)$_2$ (6) via Transmetalation with Phenylboronic Acid (Scheme 3 and Figure 2). A mixture of [Pd(dppe)(PhCN)$_2$](BF$_4$)$_2$ (0.05 mmol), phenylboronic acid (0.12 mmol), and PPh$_3$ (0.05 mmol) in acetone-d_6 (1.0 mL) and D_2O (5.0 μL) was stirred for 2 h at room temperature. ^{1}H NMR and ^{31}P NMR spectra were identical with those of the authentic sample obtained by the above procedures.

The rate of transmetalation of para-substituted arylboronic acids (Figure 2) was determined as follows: a mixture of [Pd(dppe)(PhCN)$_2$](BF$_4$)$_2$ (0.05 mmol), PPh$_3$ (0.055 mmol), an arylboronic acid (0.05 mmol), and triphenylmethane (0.05 mmol, internal standard) in acetone-d_6 (1.0 mL) and D_2O (3.6 μL) was stirred at 20 °C. After being stirred for 1.2 h, the reaction mixture was filtered through a Celite pad. The yields of products (**7**) were estimated by integration of two hydrogens in *p*-methoxyphenyl (6.1 ppm), *p*-methylphenyl (6.2 ppm), phenyl (6.5 ppm), *p*-acetylphenyl (6.8 ppm), and *p*-(trifluoromethyl)phenyl (6.6 ppm) by ^{1}H NMR. The averages of two runs were plotted in Figure 2.

Synthesis of 9 (Scheme 4). [Pd(Ph)(dppe)(PPh$_3$)]BF$_4$ (**6**; 0.15 mmol) and chalcone (0.1 mmol) were dissolved in 1 mL of dioxane and 0.2 mL of water. After the mixture was stirred for 2 h at 75 °C, the product was extracted with two portions of ether. Chromatography on silica gel gave 1,3,3-triphenylpropan-1-one (**9**) in 58% yield. For catalytic reactions in the presence of PPh$_3$, a mixture of [Pd(dppe)(PhCN)$_2$](BF$_4$)$_2$ (0.05 mmol), PPh$_3$ (0.05 mmol), phenylboronic acid (1.5 mmol), and chalcone (1.0 mmol) in THF (6 mL) and water (0.6 mL) was stirred for 23 h at 75 °C to give **9** in 85% yield.

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Supporting Information Available: Text, tables, and figures describing experimental details, spectral and/or analytical data of the products, and X-ray data. This material is available free of charge via Internet at http://pubs.acs.org.

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