A New Catalytic Activity of Antimony(III) Chloride in Palladium(0)-Catalyzed Conjugate Addition of Aromatics to α,β-Unsaturated Ketones and Aldehydes with Sodium Tetraphenylborate and Arylboronic Acids

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A remarkable catalytic effect of antimony(III) chloride is disclosed in palladium(0)-catalyzed conjugate addition of aromatics to α,β-unsaturated ketones and aldehydes with sodium tetraphenylborate and arylboronic acids in acetic acid at 25 °C. Several other metal chlorides such as $AlCl_3$, $SnCl_4$, $AsCl_3$, $TiCl_4$, $FeCl_3$, $MoCl_5$, and $CeCl_3$ are also effective in some cases, but $SbCl_3$ is the salt of choice. Two key steps are proposed for this reaction: one is the oxidative addition of a C–B bond to Pd(0) forming an arylpalladium species, and the other is the formation of an antimony enolate derived from the initial coordination of $SbCl_3$ to the carbonyl oxygen of an organopalladium intermediate.

Introduction

The chemistry of organic and inorganic antimony compounds has recently received considerable attention,[1] in which several organic transformations using antimony(III) chloride as a catalyst have been developed.[2] However, so far only a few examples have been reported for carbon–carbon bond-forming reactions using the chloride: Friedel–Crafts acylation,[3] Barbier-type allylation, reduction, and acetalization of aldehydes,[4] and Mukaiyama aldol and Michael reactions.[5] We found recently that arylboron compounds reacted with alkenes to give the corresponding arylated alkenes (Heck-type products) in the presence of $Pd(OAc)_2$ (cat.) and NaOAc[6] and that triarylstibines worked as reagents for conjugate addition of aromatics to enones and enals in the presence of $Pd(OAc)_2$ (cat.) and AgOAc.[7] Consideration of the role of antimony in the latter reaction led us to attempt the former reaction in the presence of an inorganic antimony(III) salt. Eventually, it was disclosed that the addition of only a catalytic amount of $SbCl_3$ resulted in formation of the corresponding conjugate addition products in high yields from enones and enals by use of a variety of arylboron compounds. This is in sharp contrast to Heck-type arylation of the substrate observed in the reactions without the addition of $SbCl_3$. We will report here the detailed results of this reaction from both synthetic and mechanistic viewpoints.[8]

Results and Discussion

Conjugate Addition of Benzene to Enones and Enals with Sodium Tetraphenylborate. Treatment of equimolar amounts of sodium tetraphenylborate and benzalacetone (**1a**) in acetic acid in the presence of a catalytic amount of palladium(II) acetate (10 mol %) and sodium acetate (2 mol equiv to **1a**) at 25 °C for 24 h afforded 4,4-diphenyl-2-butanone (**2a**) (the conjugate addition product[9]) and 4,4-diphenyl-3-buten-2-one (**3a**) (the Heck-type product[10]) in 87% yield (**2a/3a** = 24/76) together with biphenyl (4%). Although it is well-known that organoboranes, R_3B (R = alkyl, alkenyl, alkynyl), react with enones and enals to afford 1,4-addition products even in the absence of palladium catalyst,[11] the above reaction with $NaBPh_4$ did not proceed at all without the palladium catalyst, only benzene being formed. Interestingly, when a catalytic amount of antimony(III) chloride (10 mol %) was further added, the conjugate addition product **2a** was obtained nearly as a sole product (92% yield, **2a/3a** = 98/2) (Scheme 1). This reaction condition was eventually revealed to be the best for obtaining **2a** (Table 1). Both lower and higher reaction temperatures resulted in lower yields of **2a**. The reaction proceeded using other palladium(II) salts such as $PdCl_2$, Na_2PdCl_4, $PdCl_2(PhCN)_2$, and $Pd(NO_3)_2$ in place

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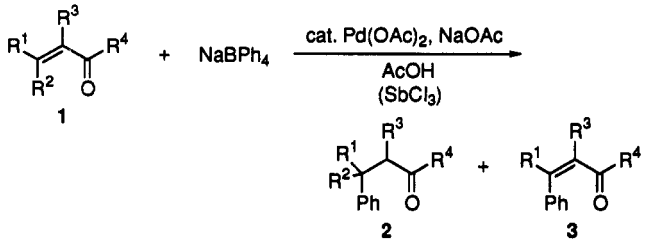
Scheme 1



a: R^1=Ph; R^2,R^3=H; R^4=Me
b: R^1,R^4=Me; R^2,R^3=H
c: R^1=n-C_5H_{11}; R^2,R^3=H; R^4=Me
d: R^1,R^2,R^3=H; R^4=Me
e: R^1,R^2,R^4=Me; R^3=H
f: R^1,R^4=Ph; R^2,R^3=H
g: R^1,R^4=$(CH_2)_3$; R^2,R^3=H
h: R^1,R^4=$(CH_2)_2$; R^2,R^3=H
i: R^1=Me; R^2,R^3,R^4=H
j: R^1=n-C_3H_7; R^2,R^3,R^4=H
k: R^1,R^2,R^3,R^4=H
l: R^1,R^2,R^4=H; R^3=Me
m: R^1=$(Me)_2C$=CH; R^2,R^3=H; R^4=Me

Table 1. Palladium-Catalyzed Reaction of $NaBPh_4$ with 1a under Various Conditions[a]

palladium salt	base	condns °C	condns h	convn[b] (%) of **1a**	products and yield[c] (%) **2a**	**3a**
$Pd(OAc)_2$	NaOAc	25	24	94	90	2
$Pd(OAc)_2$	NaOAc	10	24	50	39	2
$Pd(OAc)_2$	NaOAc	50	20	54	35	9
$Pd(OAc)_2$		25	24	46	34	1
$Pd(OAc)_2$	KOAc	25	24	94	85	3
$Pd(OAc)_2$	K_2CO_3	25	24	95	84	4
$Pd(OAc)_2$	KOH	25	28	86	78	2
$Pd(OAc)_2$	Et_3N	25	24	99	83	7
$PdCl_2$	NaOAc	25	24	100	84	6
Na_2PdCl_2	NaOAc	25	24	93	83	4
$PdCl_2(PhCN)_2$	NaOAc	25	24	70	59	3
$Pd(NO_3)_2$	NaOAc	25	24	43	34	1
$PdCl_2(PPh_3)_2$	NaOAc	25	24	19	0	0
$Pd(OAc)_2/PPh_3$[d]	NaOAc	25	24	12	0	0

[a] All reactions were carried out with **1a** (1 mmol), $NaBPh_4$ (1 mmol), palladium salt (0.1 mmol), $SbCl_3$ (0.1 mmol), and base (2 mmol) in AcOH (20 mL). [b] By GLC. [c] GLC yield based on **1a**. [d] PPh_3 (0.2 mmol) was added.

of $Pd(OAc)_2$, but the yield of **2a** was generally lower than that by the use of $Pd(OAc)_2$. The presence of phosphine, namely the use of $PdCl_2(PPh_3)_2$ and $Pd(OAc)_2/PPh_3$, stopped the reaction almost completely. A variety of bases, organic and inorganic, can also be used in place of sodium acetate. The use of 0.5 equiv and 0.25 equiv of $NaBPh_4$ to 1 equiv of **1a** afforded the phenylated products in 75% (based on **1a**; **2a/3a** = 93/7) and 43% (**2a/3a** = 79/21) yields, respectively, together with biphenyl (4–7% yield). The result indicates that at least two phenyl groups out of four in the borate are available for phenyl transfer and also the ratio of **2a/3a** increases with the increase of the amount of the borate used.

This conjugate addition could be applied to many α,β-unsaturated ketones and aldehydes, typical results of which are summarized in Table 2. The product yield was very dependent on the nature of the substrate. In all cases, biphenyl was formed in less than 10% yield as a side product, while a large amount of benzene was always formed. With methyl vinyl ketone (**1d**) and acrolein (**1k**) the reaction was accompanied by the formation of an appreciable amount of the Heck-type product, but in other cases the Heck-type product was scarcely formed. In many cases, the increase of the amount of $SbCl_3$ shortened the reaction time and afforded the conjugate addition product in a higher yield as exemplified in the cases of **1i**, **1j**, **1l**, and **1m**.

Table 2. Palladium-Catalyzed Reactions of $NaBPh_4$ with Various Enones and Enals[a]

enone or enal **1**	$SbCl_3$ (mmol)	reaction time (h)	yield[b] (%) of **2**
1b	0.1	24	65
1c	0.1	24	47
1d	0.1	24	32[c,d]
1e	0.1	24	39
1f	0.1	24	84
1g	0.1	24	91
1h	0.1	24	42
1i	0.1	24	31
1i	0.5	5	63
1j	0.3	6	60
1k	0.1	20	31[c,e]
1l	0.3	5	14
1l	0.3	24	41
1m	0.1	24	17
1m	0.3	24	53

[a] All reactions were carried out with enone or enal (1mmol), $NaBPh_4$ (1 mmol), $Pd(OAc)_2$ (0.1 mmol), and NaOAc (2 mmol) in AcOH (20 mL) at 25 °C. [b] Isolated hydroarylation products based on enones and enals unless otherwise stated. [c] GLC yield. [d] Other product: (*E*)-4-phenyl-3-buten-2-one (20%). [e] Other product: (*E*)-cinnamaldehyde (8%).

Since it is known that $NaBPh_4$ reacts with acetic acid to give triphenylboron (Ph_3B), benzene, and sodium acetate,[12] it might be conceivable that Ph_3B is the main phenylating species. In fact, we observed in a separate experiment that the reaction of triphenylboron (1 mmol) with an equimolar amount of 2-cyclohexen-1-one (**1g**) under the above reaction conditions in the presence of 10 mol % $SbCl_3$ afforded 3-phenylcyclohexanone (**2g**) and 3-phenyl-2-cyclohexenone (**3g**)[13] in 93% and 5% yields, respectively, together with benzene (0.91 mmol). On the other hand, treatment of $NaBPh_4$ (1 mmol) in place of Ph_3B afforded similar yields of both phenylated products (97% yield, **2g/3g** = 98/2) together with more benzene (2.21 mmol). Similarly, Ph_3B also reacted with **1a** in place of **1g** to afford the conjugate addition compound **2a** as a major phenylation product.[14] These results support the assumption that triphenylboron is the actual phenylating reagent. Here, benzene is surely derived from the reaction of either triphenylboron or $NaBPh_4$ with acetic acid.

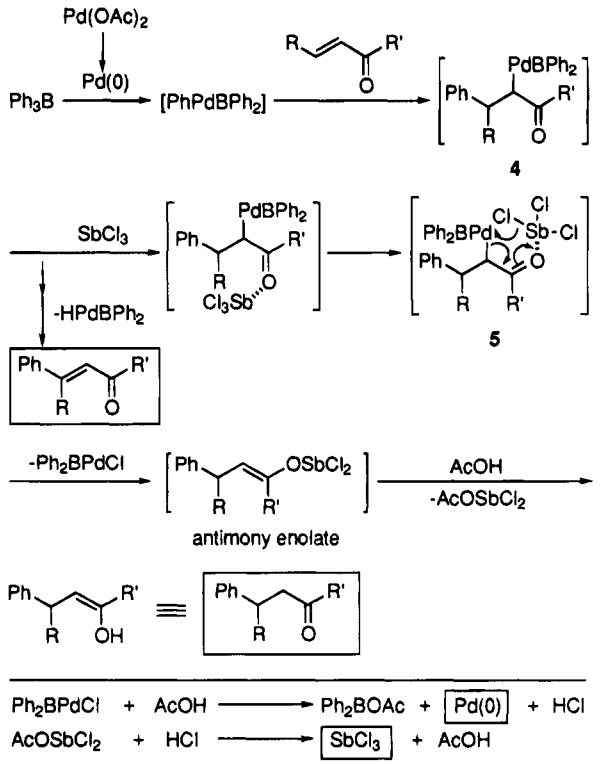
Although the details of the reaction scheme are not certain, a plausible pathway is presented in Scheme 2. Phenylpalladium borane [$PhPdBPh_2$], initially formed *in situ* by oxidative addition of a carbon–boron bond to palladium(0), adds to enones or enals to produce an alkylpalladium(II) species **4**. Antimony(III) chloride, as a weak Lewis acid, may coordinate to the carbonyl oxygen of this species, and subsequent C–C bond rotation is expected to give the species **5**, from which the concerted elimination of Ph_2BPdCl occurs to give presumably an antimony enolate. The presence of phosphines might prevent such an elimination by blocking a vacant site of palladium. The protonolysis of the enolate then leads to the conjugate addition product. Palladium(0) may be

(12) See, for example: Negishi, E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 7, p 270.

(13) For the formation of this compound, see: Genet, J. P.; Blart, E.; Savignac, M. *Synlett* **1992**, 715.

(14) The reaction of triphenylboron (1 mmol) with an equivalent amount of **1a** in the presence of 10 mol % $SbCl_3$ in acetic acid (20 mL) at 25 °C for 24 h afforded **2a** and **3a** in 49% and 13% yields, respectively, together with benzene (1.36 mmol).

Scheme 2



regenerated by reductive elimination of Ph_2BCl from Ph_2BPdCl. The oxidative addition of a carbon–boron bond to Pd(0) forming an organopalladium intermediate has so far been proposed in several cases.[6,15] The formation of a palladium enolate from **4** is probably not possible as **4** is quite labile in acetic acid and also does not allow for the noted effect of $SbCl_3$.

The effect of a wide range of Lewis acids other than $SbCl_3$ upon this conjugate adddition was examined using either benzalacetone (**1a**) or 2-cyclohexen-1-one (**1g**) as a substrate, the results of which are summarized in Table 3. As shown in Table 3, all salts examined were almost ineffective for the formation of **2** except for arsenic(III) chloride in the case of **1a** and **1g** and titanium(IV) salts in the case of **1g**. In general, the reactions using the cyclic enone **1g** showed a higher selectivity for the formation of the conjugate addition product than those using the linear enone **1a** probably because the bond rotation is not necessary in the course of **4** to **5** due to *s-trans* conformation of **1g** and the retardation of β-hydride *syn*-elimination leading to the Heck-type product **3g** due to the requirement of isomerization in **4** after *cis* addition of both a phenyl moiety and a palladium moiety.

Conjugate Addition of Aromatics to Cyclic Enones with Arylboronic Acids. In place of sodium tetraphenylborate, arylboronic acids could also be used for this conjugate addition under the same conditions, but the reaction was quite substrate selective. Thus, treatment of **1a** (1 mmol) with benzeneboronic acid (**6n**) (1.2 mmol) in acetic acid at 25 °C for 20 h in the presence of $Pd(OAc)_2$ (0.1 mmol), NaOAc (2 mmol), and $SbCl_3$ (0.1 mmol) afforded the conjugate addition product **2a** in 12% yield together with the Heck-type product **3a** (15% yield). The use of a larger amount of $SbCl_3$ (2–10 times) did not give satisfactory results. Other enones such as 3-penten-2-one (**1b**) and 3-buten-2-one (**1d**) afforded only the corresponding Heck-type products in low yields. In contrast, with 2-cyclohexen-1-one (**1g**) the conjugate addition product **2g** was obtained in a high yield together with a small amount of the Heck-type product **3g** in 97% yield (**2g/3g** = 92/8). However, the reaction did not proceed effectively in the absence of $SbCl_3$ (29% yield, **2g/3g** = 86/14). With other easily available arylboronic acids **6o-6s** the corresponding conjugate addition products were also formed highly selectively and in high yields (Scheme 3). The reaction also proceeded with 2-cyclopenten-1-one (**1h**). In the case of 2-methyl-5-isopropyl-2-cyclohexen-1-one, neither the conjugate addition product nor the Heck-type product was formed. Typical results are summarized in Table 4.

In contrast to the reaction using tetraphenylborate anion, a variety of metallic chlorides were effective for this hydroarylation reaction. Thus, in the reactions of 2-cyclohexen-1-one (**1g**) with benzeneboronic acid (**6n**) under the catalytic conditions shown in Table 4, titanium(IV) chloride and arsenic(III) chloride exhibited nearly the same catalytic activity as $SbCl_3$, and other Lewis acids such as $BiCl_3$, $AlCl_3$, $TiCl_2(O\text{-}i\text{-}Pr)_2$, $SnCl_4$, $MoCl_5$, and $CeCl_3$ were moderately effective (66–77% yield of **2g** + **3g** with **2g/3g** = 88–92/8–12), while Lewis acids such as $BF_3{\cdot}OEt_2$, $Al(O\text{-}i\text{-}Pr)_3$, $Ti(O\text{-}i\text{-}Pr)_4$, and $Yb(OTf)_3$ were less effective (53–62% yield of **2g** + **3g** with **2g/3g** = 83–86/14–17).

Presumably, the reaction proceeds in a similar way as the tetraphenylborate anion case and involves an oxidative addition of a C–B bond of arylboronic acid to palladium(0). Thus, the initial oxidative addition of a C–B bond of **6** to palladium(0), formed *in situ* by reduction of palladium(II) acetate, gives an arylpalladium(II) species [$ArPdB(OH)_2$] which adds to the enone in 1,2-fashion to produce a cyclohexylpalladium species **7**. Metal chloride coordinates to the carbonyl oxygen of **7** to give the species **8**. This is followed by an elimination of $ClPdB(OH)_2$ to give the metal enolate **9** which is labile to acetic acid (Scheme 4).

On the other hand, a similar reaction between the boronic acid **6n** and the enone **1g** in the presence of triphenylphosphine (0.2 mmol) did not give any phenylated products as in the cases of reactions using $NaBPh_4$.

In summary, a new catalytic activity of $SbCl_3$ was disclosed in the Pd(0)-catalyzed arylation of enones and enals. The presence of $SbCl_3$ dramatically changed the major reaction products from Heck-type substitution compounds to Michael-type conjugate addition compounds.

Experimental Section

General Procedure. GLC analyses were carried out on a CBP 10-S25-050 column (Shimadzu, fused silica capillary column, 0.33 mm × 25 m, 5.0 μm film thickness) using helium as carrier gas. GLC yields were determined using suitable hydrocarbons as internal standards. The isolation of a pure product was carried out with column chromatography (Wakogel C-200, 100–200 mesh, Wako Pure Chemical Ind. Ltd.) or thin-layer chromatography (silica gel 60 HF_{254}, Merck).

Materials. Commercially available organic and inorganic compounds were used without further purification. Sodium tetraphenylborate, benzeneboronic acid (**6n**), and 3-nitrobenzeneboronic acid (**6r**) were commercial products. Other boronic acids such as 4-methylbenzeneboronic acid (**6o**), 4-methoxybenzeneboronic acid (**6p**), 4-chlorobenzeneboronic acid (**6q**), and 1-naphthaleneboronic acid (**6s**) were prepared by the

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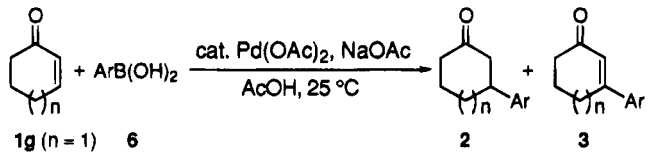
Table 3. Effect of Lewis Acids on Pd-Catalyzed Reactions of $NaBPh_4$ with 1a and 1g[a]

Lewis acid	convn[b] (%) of **1a**	yield[c] (%) **2a** + **3a**	ratio **2a/3a**	convn[b] (%) of **1g**	yield[c] (%) **2g** + **3g**	ratio **2g/3g**
$SbCl_3$	94	92	98/2	100	97	98/2
$AsCl_3$	70	66	97/3	98	92	96/4
$BiCl_3$	10	3	100/0	40	5	100/0
$BF_3{\bullet}OEt_2$	100	91	19/81	67	36	89/11
$AlCl_3$	17	11	50/50	74	50	92/8
$Al(O\text{-}i\text{-}Pr)_3$	100	92	21/79	72	43	88/12
$TiCl_4$	20	19	68/32	91	81	94/6
$Ti(O\text{-}i\text{-}Pr)_4$	100	83	40/60	76	48	92/8
$TiCl_2(O\text{-}i\text{-}Pr)_2$	16	12	50/50	91	79	91/9
$SnCl_2$	29	25	52/48	57	29	90/10
$SnCl_4$	24	18	44/56			
$ZnCl_2$	15	10	40/60	59	29	90/10
$FeCl_3$	34	22	73/27	71	48	94/6
$MoCl_5$	20	12	75/25	60	39	92/8
$Yb(OTf)_3$	100	96	17/83	58	24	88/12

[a] All reactions were carried out with **1a** or **1g** (1mmol), $NaBPh_4$ (1 mmol), $Pd(OAc)_2$ (0.1 mmol), NaOAc (2 mmol), and Lewis acid (0.1 mmol) in AcOH (20 mL) at 25 °C for 20 h. [b] By GLC. [c] GLC yield based on **1a** or **1g**.

Scheme 3



1g (n = 1) **6** **2** **3**

1h (n = 0) **n**: Ar = phenyl
o: Ar = 4-methylphenyl
p: Ar = 4-methoxyphenyl
q: Ar = 4-chlorophenyl
r: Ar = 3-nitrophenyl
s: Ar = 1-naphthyl

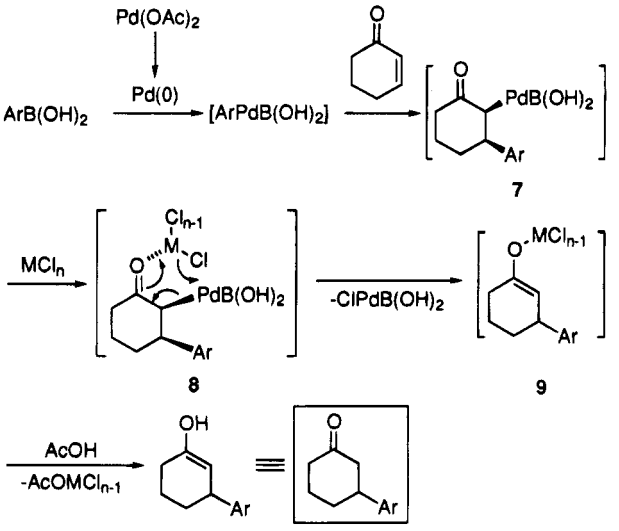
Table 4. Palladium-Catalyzed Conjugate Addition of Aromatics to Enones with Arylboronic Acids[a]

enone	arylboronic acid	$SbCl_3$ (mmol)	reaction time (h)	convn[b] (%) of enone	GLC yield[c] (%) **2**[d]	GLC yield[c] (%) **3**[e]
1a	**6n**	0.1	20	33	12	15
1a	**6n**	0.2	24	46	25	12
1a	**6n**	1	24	53	33	14
1b	**6n**	0.1	24	13	trace	<10
1d	**6n**	0.1	20	*f*	trace	15
1g	**6n**	0.2	5	76	66	3
1g	**6n**[g]	0.1	20	93	82	7
1g	**6n**	0.1	20	100	(89)	(8)
1g	**6o**	0.1	20	100	(87)	(8)
1g	**6p**	0.1	20	100	(87)	(9)
1g	**6q**	0.1	24	100	(80)	(13)
1g	**6r**	0.1	24	72	(59)	*h*
1g	**6s**	0.1	24	96	(90)	*h*
1h	**6n**	0.1	24	97	(78)	(15)
1h	**6o**	0.1	24	99<	(82)	(14)

[a] All reactions were carried out with enone (1mmol), arylboronic acid **6** (1.2 mmol), $Pd(OAc)_2$ (0.1 mmol), and NaOAc (2 mmol) in AcOH (20 mL) at 25 °C unless otherwise stated. [b] By GLC. [c] GLC yield based on enone. Isolated yield is shown in parentheses. [d] Michael-type product. [e] Heck-type product. [f] Not determined. [g] 1 mmol was used. [h] Trace, if any.

reported method.[16] All enones and enals were commercial products except for 3-nonen-2-one (**1c**)[17] and 2-methyl-5-isopropyl-2-cyclohexen-1-one,[18] which were synthesized by the known methods. 4,4-Diphenyl-3-buten-2-one (**3a**) was also prepared separately by the known method[19] and used as an authentic sample for GLC determination: ^1H NMR δ 1.88 (s, 3H), 6.58 (s, 1H), 7.20–7.42 (m, 10H); ^{13}C NMR δ 30.32, 127.68, 128.39, 128.42, 128.78, 129.45, 129.59, 138.95, 140.75, 200.17. 4-Phenylbutan-2-one (**2d**) and 3-phenylpropanal (**2k**) used as authentic samples for GLC determination were commercial products. All Lewis acids were commercial products except for $TiCl_2(O\text{-}i\text{-}Pr)_2$[20] and $Yb(OTf)_3$,[21] which were prepared by the known methods. Transition metal salts such as $Pd(OAc)_2$, $PdCl_2$, Na_2PdCl_4, and $Pd(NO_3)_2$ were commercial products. $PdCl_2(PhCN)_2$[22] and $PdCl_2(PPh_3)_2$[23] were synthesized as reported previously.

Scheme 4



General Procedure for Pd(0)-Catalyzed Conjugate Addition of Benzene to Enones and Enals with Sodium Tetraphenylborate. A mixture of sodium tetraphenylborate (0.342 g, 1 mmol), enone or enal (1 mmol), palladium(II) acetate (0.023 g, 0.1 mmol), sodium acetate (0.164 g, 2 mmol), and antimony(III) chloride (0.1–0.5 mmol) was stirred in acetic acid (20 mL) at 25 °C for an appropriate time. The precipitated

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black solid was filtered off, and the filtrate was poured into brine (100 mL), extracted with dichloromethane (30 mL × 2), and washed with a saturated aqueous $NaHCO_3$. The organic phase was washed with water and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure left a pale yellow oil or solid which was separated by column chromatography or TLC using an ethyl acetate–hexane mixture as an eluent to give the hydroarylation products. For GLC determination, similar reactions were carried out in the presence of an appropriate amount of 1,2-diphenylethane as an internal standard. The hydrophenylation products prepared by the above procedure were characterized spectroscopically as shown below, and all reactions were carried out using 0.1 mmol (0.023 g) of $SbCl_3$ unless otherwise mentioned. Compound **2c** is new.

4,4-Diphenylbutan-2-one (2a): 88% yield; oil; IR (neat) 3080, 3060, 3025, 3000, 1720, 1600, 1490, 1445, 1355, 1155, 740, 730, 695, 540 cm^{-1}; ^1H NMR δ 2.06 (s, 3H), 3.17 (d, J = 7.7 Hz, 2H), 4.58 (t, J = 7.7 Hz, 1H), 7.13–7.30 (m, 10H); ^{13}C NMR δ 30.62, 46.01, 49.64, 126.43, 127.68, 128.56, 148.83, 206.83; MS *m/z* (relative intensity) 224 (M^+, 38), 181 (29), 167 (100), 152 (20), 103 (41), 91 (6), 77 (20).

4-Phenylpentan-2-one (2b): 65% yield; oil; IR (neat) 3070, 3040, 2960, 1720, 1600, 1495, 1450, 1360, 1160, 1025, 755, 695, 530 cm^{-1}; ^1H NMR δ 1.26 (d, J = 7.0 Hz, 3H), 2.05 (s, 3H), 2.60–2.79 (m, 2H), 3.23–3.37 (m, 1H), 7.15–7.32 (m, 5H); ^{13}C NMR δ 21.99, 30.53, 35.44, 51.97, 126.31, 126.75, 128.53, 146.16, 207.81; MS *m/z* (relative intensity) 162 (M^+, 34), 147 (65), 119 (15), 105 (100), 91 (52), 77 (35), 51 (21).

4-Phenylnonan-2-one (2c): 47% yield; oil; IR (neat) 3020, 2920, 2850, 1720, 1600, 1495, 1450, 1360, 1155, 750, 695 cm^{-1}; ^1H NMR δ 0.82 (t, J = 6.6 Hz, 3H), 1.12–1.23 (m, 6H), 1.52–1.63 (m, 2H), 1.99 (s, 3H), 2.70 (d, J = 7.3 Hz, 2H), 3.05–3.16 (m, 1H), 7.13–7.32 (m, 5H); ^{13}C NMR δ 14.03, 22.49, 27.04, 30.60, 31.73, 36.43, 41.30, 50.92, 126.29, 127.46, 128.43, 144.62, 207.98; MS *m/z* (relative intensity) 218 (M^+, 3), 160 (94), 147 (77), 117 (42), 104 (76), 91 (100), 77 (14), 55 (15). Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.40; H, 10.15.

4-Methyl-4-phenylpentan-2-one (2e): 39% yield; oil; IR (neat) 3050, 3020, 2950, 2870, 1700, 1590, 1490, 1435, 1355, 1130, 1095, 1070, 1025, 755, 695, 530 cm^{-1}; ^1H NMR δ 1.43 (s, 6H), 1.79 (s, 3H), 2.74 (s, 2H), 7.20–7.38 (m, 5H); ^{13}C NMR δ 28.94, 31.82, 37.33, 57.02, 125.52, 126.02, 128.31, 148.10, 208.16; MS *m/z* (relative intensity) 176 (M^+,12), 119 (100), 91 (68), 77 (14), 51 (10).

1,3,3-Triphenyl-1-propanone (2f): 84% yield; a white solid; mp 90–92 °C (lit.[24] mp 95 °C); IR (KBr) 3040, 3000, 2900, 1660, 1580, 1480, 1435, 1365, 1255, 1200, 1170, 1020, 740, 690, 555 cm^{-1}; ^1H NMR δ 3.71 (d, J = 7.3 Hz, 2H), 4.82 (t, J = 7.3 Hz, 1H), 7.13–7.52 (m, 13H), 7.89–7.92 (m, 2H); ^{13}C NMR δ 44.67, 45.89, 126.33, 127.81, 128.00, 128.52, 128.55, 133.03, 137.01, 144.12, 197.92; MS *m/z* (relative intensity) 286 (M^+, 10), 167 (35), 105 (100), 91 (2), 77 (36), 51 (10).

3-Phenylcyclohexanone (2g): 91% yield; oil; IR (neat) 3065, 3030, 2950, 2870, 1710, 1600, 1495, 1445, 1255, 1225, 1030, 755, 695 cm^{-1}; ^1H NMR δ 1.69–1.87 (m, 2H), 2.05–2.18 (m, 2H), 2.30–2.63 (m, 4H), 2.94–3.06 (m, 1H), 7.20–7.35 (m, 5H); ^{13}C NMR δ 25.52, 32.75, 41.16, 44.72, 48.91, 126.53, 126.66, 128.66, 144.34, 210.96; MS *m/z* (relative intensity) 174 (M^+, 82), 131 (72), 117 (100), 104 (70), 91 (35), 77 (26), 51 (23).

3-Phenylcyclopentanone (2h): 42% yield; oil; IR (neat) 3010, 2940, 2870, 1725, 1585, 1480, 1440, 1390, 1270, 1220, 1130, 1020, 750, 690, 530 cm^{-1}; ^1H NMR δ 1.90–2.06 (m, 1H), 2.21–2.50 (m, 4H), 2.61–2.70 (m, 1H), 3.34–3.47 (m, 1H), 7.21–7.37 (m, 5H); ^{13}C NMR δ 31.16, 38.82, 42.17, 45.74, 126.70, 128.65, 143.05, 218.26; MS *m/z* (relative intensity) 160 (M^+, 74), 117 (42), 104 (100), 91 (21), 77 (22), 65 (12), 51 (30).

3-Phenylbutanal (2i). Using 0.5 mmol (0.114 g) of $SbCl_3$: 63% yield; oil; IR (neat) 3095, 3070, 3040, 2975, 2940, 2890, 2830, 2725, 1730, 1600, 1495, 1450, 1075, 1050, 1025, 760, 700 cm^{-1}; ^1H NMR δ 1.31 (d, J = 7.0 Hz, 3H), 2.59–2.79 (m, 2H), 3.29–3.42 (m, 1H), 7.17–7.34 (m, 5H), 9.69 (t, J = 2.2 Hz, 1H); ^{13}C NMR δ 22.16, 34.29, 51.72, 126.53, 126.75, 128.67, 145.46, 201.80; MS *m/z* (relative intensity) 148 (M^+, 39), 133 (34), 105 (100), 91 (63), 77 (51), 51 (33).

3-Phenylhexanal (2j). Using 0.3 mmol (0.068 g) of $SbCl_3$: 60% yield; oil; IR (neat) 3100, 3075, 3050, 2975, 2950, 2890, 2830, 2725, 1730, 1605, 1500, 1455, 760, 700 cm^{-1}; ^1H NMR δ 0.86 (t, J = 7.3 Hz, 3H), 1.12–1.26 (m, 2H), 1.58–1.66 (m, 2H), 2.69–2.72 (m, 2H), 3.13–3.24 (m, 1H), 7.16–7.33 (m, 5H), 9.66 (t, J = 2.2 Hz, 1H); ^{13}C NMR δ 13.92, 20.43, 38.81, 39.86, 50.59, 126.55, 127.46, 128.61, 143.91, 202.08; MS *m/z* (relative intensity) 176 (M^+, 27), 133 (78), 117 (13), 105 (70), 91 (100), 77 (35), 65 (11), 51 (16).

2-Methyl-3-phenylpropanal (2l). Using 0.3 mmol (0.068 g) of $SbCl_3$: 41% yield; oil; IR (neat) 3100, 3075, 3040, 2980, 2945, 2885, 2870, 2825, 2720, 1730, 1605, 1500, 1455, 1280, 1030, 740, 700 cm^{-1}; ^1H NMR δ 1.09 (d, J = 7.0 Hz, 3H), 2.56–2.71 (m, 2H), 3.06–3.12 (m, 1H), 7.15–7.33 (m, 5H); ^{13}C NMR δ 16.48, 39.28, 41.21, 126.42, 128.42, 129.00, 139.03, 201.03; MS *m/z* 148 (M^+, 25), 105 (16), 91 (100), 77 (13), 65 (17), 51 (12).

6-Methyl-4-phenyl-5-hepten-2-one (2m). Using 0.3 mmol (0.068 g) of $SbCl_3$: 53% yield; oil; IR (neat) 3050, 3020, 2960, 2910, 1710, 1585, 1480, 1435, 1355, 1150, 1065, 745, 695, 540 cm^{-1}; ^1H NMR δ 1.68 (d, J = 1.5 Hz, 3H), 1.69 (d, J = 1.1 Hz, 3H), 2.05 (s, 3H), 2.67–2.83 (m, 2H), 4.02–4.11 (m, 1H), 5.22–5.26 (m, 1H), 7.12–7.34 (m, 5H); ^{13}C NMR δ 18.10, 25.82, 30.64, 39.97, 50.80, 126.17, 127.09, 127.11, 128.56, 132.57, 144.70, 207.47; MS *m/z* (relative intensity) 202 (M^+, 11), 187 (21), 145 (100), 129 (47), 117 (61), 105 (16), 91 (46), 77 (21), 51 (14).

Typical Procedure for Pd(0)-Catalyzed Conjugate Addition of Aromatics to Cyclic Enones with Arylboronic Acid. A solution of 2-cyclohexen-1-one (**1g**) (0.096 g, 1 mmol) in AcOH (10 mL) was added to the mixture of benzeneboronic acid (**6n**) (0.146 g, 1.2 mmol), $Pd(OAc)_2$ (0.023 g, 0.1 mmol), sodium acetate (0.164 g, 2 mmol), and antimony(III) chloride (0.023 g, 0.1 mmol). After the mixture was stirred at 25 °C for 20 h, the precipitated black solid was filtered off and the filtrate was poured into a brine (100 mL), extracted with dichloromethane (30 mL × 2), and washed with a saturated aqueous $NaHCO_3$. The organic phase was washed with water and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure left a pale yellow oil. TLC separation using ethyl acetate/hexane (1/10) as an eluent gave 3-phenylcyclohexanone (**2g**) (0.155 g, 89%) and 3-phenylcyclohexen-2-one (**3g**) (0.014 g, 8%). The products prepared by the above procedure were characterized spectroscopically as shown below. The compounds **2gr** and **2gs** are new.

3-Phenyl-2-cyclohexen-1-one (3gn = 3g): 8% yield; a pale yellow solid, mp 61–62 °C (lit.[25] mp 64.5–66 °C); ^1H NMR δ 2.14–2.21 (m, 2H), 2.47–2.52 (m, 2H), 2.76–2.80 (m, 2H), 6.43 (t, J = 1.5 Hz, 1H), 7.40–7.43 (m, 3H), 7.52–7.56 (m, 2H); ^{13}C NMR δ 22.81, 28.12, 37.26, 125.43, 126.10, 128.78, 130.02, 138.79, 159.93, 200.06; MS *m/z* (relative intensity) 172 (M^+, 59), 144 (100), 129 (13), 115 (87), 77 (13), 51 (16).

3-(4-Methylphenyl)cyclohexanone (2go): 87% yield; oil; ^1H NMR δ 1.69–1.87 (m, 2H), 2.01–2.14 (m, 2H), 2.28–2.59 (m, 4H), 2.31 (s, 3H), 2.89–3.02 (m, 1H), 7.07–7.14 (m, 4H); ^{13}C NMR δ 20.94, 25.51, 32.86, 41.12, 44.34, 49.00, 126.41, 129.31, 136.13, 141.42, 211.01; MS *m/z* (relative intensity) 188 (M^+, 52), 173 (5), 145 (27), 131 (100), 118 (36), 105 (19), 91 (28), 77 (10).

3-(4-Methylphenyl)-2-cyclohexen-1-one (3go): 8% yield; a pale yellow solid, mp 57–58 °C (lit.[26] mp 60 °C); ^1H NMR δ 2.10–2.19 (m, 2H), 2.38 (s, 3H), 2.45–2.50 (m, 2H), 2.74–2.79 (m, 2H), 6.42 (s, 1H), 7.20–7.23 (m, 2H), 7.43–7.46 (m, 2H); ^{13}C NMR δ 21.31, 22.80, 28.00, 37.26, 124.64, 126.04, 129.49, 135.80, 140.39, 159.80, 200.08; MS *m/z* (relative intensity) 186 (M^+, 74), 171 (39), 158 (100), 143 (14), 130 (54), 115 (86), 91 (13), 77 (18), 64 (21), 51 (15).

3-(4-Methoxyphenyl)cyclohexanone (2gp): 87% yield; oil; ^1H NMR δ 1.68–1.87 (m, 2H), 2.00–2.15 (m, 2H), 2.28–2.59 (m, 4H), 2.89–3.00 (m, 1H), 3.75 (s, 3H), 6.83–6.87 (m,

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2H), 7.10–7.13 (m, 2H); ^{13}C NMR δ 25.44, 32.96, 41.08, 43.90, 49.15, 55.16, 113.97, 127.46, 136.57, 158.24, 210.90; MS *m/z* (relative intensity) 204 (M^+, 52), 161 (23), 147 (100), 134 (28), 121 (20), 91 (24), 77 (11), 65 (13).

3-(4-Methoxyphenyl)-2-cyclohexen-1-one (3gp): 9% yield; a pale yellow solid; mp 82–83 °C (lit.[27] mp 84–85 °C); ^{1}H NMR δ 2.09–2.19 (m, 2H), 2.45–2.50 (m, 2H), 2.73–2.78 (m, 2H), 3.85 (s, 3H), 6.40 (t, J = 1.5 Hz, 1H), 6.90–6.96 (m, 2H), 7.49–7.54 (m, 2H); ^{13}C NMR δ 22.77, 27.86, 37.19, 55.39, 114.15, 123.68, 127.64, 130.80, 159.19, 161.24, 199.99; MS *m/z* (relative intensity) 202 (M^+, 92), 174 (100), 146 (53), 131 (38), 115 (18), 103 (32), 77 (30).

3-(4-Chlorophenyl)cyclohexanone (2gq): 80% yield; oil; ^{1}H NMR δ 1.68–1.88 (m, 2H), 2.01–2.18 (m, 2H), 2.30–2.60 (m, 4H), 2.92–3.02 (m, 1H), 7.12–7.17 (m, 2H), 7.26–7.31 (m, 2H); ^{13}C NMR δ 25.35, 32.64, 41.05, 44.04, 48.72, 127.96, 128.76, 132.27, 142.79, 210.50; MS *m/z* (relative intensiy) 210 (M^+ + 2, 25), 208 (M^+, 74), 165 (49), 151 (100), 138 (54), 115 (34), 103 (29), 77 (26), 51 (22).

3-(4-Chlorophenyl)-2-cyclohexen-1-one (3gq): 13% yield; a highly viscous oil (lit.[28] mp 54.5–55 °C); ^{1}H NMR δ 2.12–2.21 (m, 2H), 2.46–2.51 (m, 2H), 2.72–2.77 (m, 2H), 6.39 (t, J = 1.5 Hz, 1H), 7.36–7.50 (m, 2H); ^{13}C NMR δ 22.72, 28.00, 37.17, 125.64, 127.37, 129.01, 136.04, 137.19, 158.29, 199.67; MS *m/z* (relative intensity) 208 (M^+ + 2, 14), 206 (M^+, 38), 178 (83), 150 (24), 115 (100), 75 (14), 57 (16).

3-(3-Nitrophenyl)cyclohexanone (2gr): 64% yield; a yellow solid; mp 78–80 °C; ^{1}H NMR δ 1.76–2.02 (m, 2H), 2.12–2.26 (m, 2H), 2.37–2.66 (m, 4H), 3.11–3.22 (m, 1H), 7.50–7.62 (m, 2H), 8.08–8.14 (m, 2H); ^{13}C NMR δ 25.32, 32.46, 40.99, 44.25, 48.42, 121.52, 121.86, 129.73, 133.12, 146.32, 148.56, 209.66; MS *m/z* (relative intensity) 219 (M^+, 42), 189 (78), 176 (100), 146 (17), 132 (29), 120 (89), 103 (29), 91 (28), 77 (43), 65 (31), 55 (41). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.50; H, 6.02; N, 6.34.

3-(1-Naphthyl)cyclohexanone (2gs): 90% yield; a white solid; mp 72–73 °C; ^{1}H NMR δ 1.80–2.04 (m, 2H), 2.11–2.28 (m, 2H), 2.36–2.81 (m, 4H), 3.78–3.87 (m, 1H), 7.36–7.54 (m, 4H), 7.73 (d, J = 7.7 Hz, 1H), 7.83–7.87 (m, 1H), 8.02 (d, J = 8.1 Hz, 1H); ^{13}C NMR δ 25.53, 32.26, 39.34, 41.39, 48.53, 122.42, 122.68, 125.51, 125.60, 126.18, 127.23, 129.05, 130.89, 133.96, 140.03, 211.13; MS *m/z* (relative intensity) 224 (M^+, 83), 181 (20), 167 (100), 153 (50), 141 (26). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.60; H, 7.17.

3-Phenyl-2-cyclopenten-1-one (3hn = 3h): 15% yield; a pale yellow solid; mp 79–80 °C (lit.[29] mp 81.5–82.5 °C); ^{1}H NMR δ 2.57–2.61 (m, 2H), 3.03–3.07 (m, 2H), 6.58 (t, J = 1.8 Hz, 1H), 7.43–7.49 (m, 3H), 7.64–7.68 (m, 2H); ^{13}C NMR δ 28.64, 35.29, 126.82, 127.50, 128.93, 131.26, 134.08, 174.00, 209.37; MS *m/z* (relative intensity) 158 (M^+, 100), 129 (74), 115 (41), 102 (30), 77 (16), 64 (21), 51 (30).

3-(4-Methylphenyl)cyclopentanone (2hn): 82% yield; oil; ^{1}H NMR δ 1.85–2.01 (m, 1H), 2.18–2.47 (m, 4H), 2.32 (s, 3H), 2.56–2.66 (m, 1H), 3.28–3.41 (m, 1H), 7.13 (s, 4H); ^{13}C NMR δ 20.95, 31.24, 38.82, 41.80, 45.83, 126.58, 129.30, 136.20, 140.06, 218.37; MS *m/z* (relative intensity) 174 (M^+, 77), 159 (11), 145 (11), 131 (23), 118 (100), 105 (10), 91 (29), 77 (11), 56 (15).

3-(4-Methylphenyl)-2-cyclopenten-1-one (3hn): 14% yield; a pale yellow solid; mp 99–100 °C; ^{1}H NMR δ 2.41 (s, 3H), 2.55–2.59 (m, 2H), 3.01–3.05 (m, 2H), 6.53 (t, J = 1.7 Hz, 1H), 7.24–7.27 (m, 2H), 7.54–7.57 (m, 2H); ^{13}C NMR δ 21.55, 28.61, 35.25, 126.63, 126.82, 129.63, 131.34, 141.86, 174.09, 209.47; MS *m/z* (relative intensity) 172 (M^+, 92), 157 (100), 143 (15), 129 (53), 115 (43), 91 (8), 77 (7), 51 (13). Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.41; H, 7.01.

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