



III.2.11 Palladium-Catalyzed Cross-Coupling Involving Alkylmetals or Alkyl Electrophiles

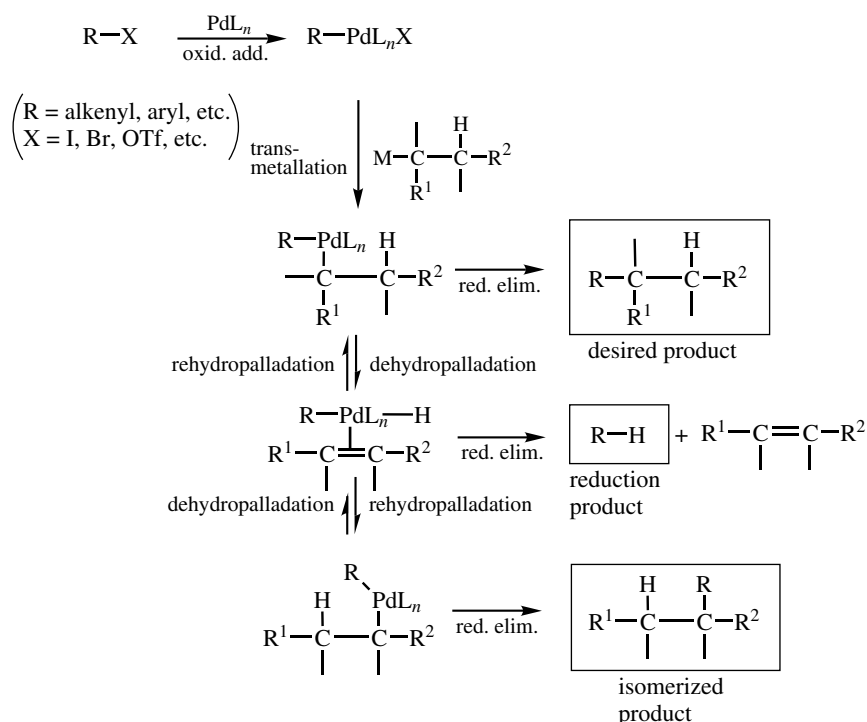
III.2.11.1 Palladium-Catalyzed Cross-Coupling Involving Saturated Alkylmetals

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A. INTRODUCTION

In **Sects. III.2.9** and **III.2.10**, Pd-catalyzed cross-coupling reactions involving allylic, benzylic, and propargylic organometals and organic electrophiles are discussed. Pd complexes readily undergo oxidative addition with organic electrophiles containing β,γ -unsaturated alkyl groups, allowing their Pd-catalyzed cross-coupling to proceed readily. In sharp contrast with these β,γ -unsaturated alkyl electrophiles, alkyl electrophiles either without an unsaturated carbon–carbon bond or with only a γ,δ - or more remote unsaturated group are much more reluctant to undergo oxidative addition with Pd (**Sect. I.2**). Furthermore, even if alkylpalladium derivatives are formed by oxidative addition, those that contain one or more β -H atoms are prone to β -dehydropalladation to give alkenes and H–Pd derivatives. These two factors make it generally difficult to achieve Pd-catalyzed cross-coupling with alkyl electrophiles without β,γ -unsaturation. Although the Pd-catalyzed cross coupling reaction of MeMgX was reported as early as 1975,^[1] the use of alkylmetals containing β -H atoms was not reported until 1978.^[2] Although the initial attempts to use alkyllithiums were unsuccessful,^[1] a later investigation reported moderately satisfactory results for the Pd-catalyzed reaction of β -bromostyrene with $n\text{-BuLi}$.^[3] The fact that the reaction can take place via Li–Br exchange without a catalyst makes the interpretation of the observed results difficult, and further clarification of this point may be desirable. In fact, there have been very few studies reporting successful uses of organolithiums in Pd-catalyzed cross-coupling. A few independent reports published in the following couple of years^{[4]–[6]} have established that higher primary normal alkyl- and isoalkyl-containing Grignard reagents and alkylzincs readily participate in Pd-catalyzed cross-coupling reactions with alkenyl and aryl halides containing I and Br. Even secondary and tertiary alkylmetals containing Mg and Zn^{[4]–[6]} can be used, although

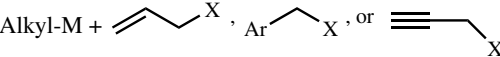
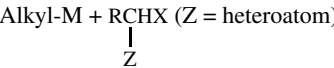
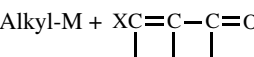
alkyl group isomerization, that is, *s*-alkyl to *n*-alkyl and *t*-alkyl to isoalkyl, and reduction of organic electrophiles are two serious side reactions associated with Pd-catalyzed alkylation. The mechanistic courses of these two side reactions and their relationships with the desired cross-coupling reaction can readily be rationalized by **Scheme 1**.^[6] Although it is generally no more than a reasonable working hypothesis, it does suggest that the extent of reduction of organic electrophiles, that is, dehalogenation and related processes, and of the alkyl group isomerization should critically depend on the relative rates of three processes—reductive elimination, dehydropalladation, and rehydropalladation. If this analysis is indeed reasonable, it would be desirable to slow down dehydropalladation relative to the desired reductive elimination. This mechanism also suggests that, after the putative oxidative addition and transmetalation steps, the metal counteranions may not exert significant influences. In reality, however, the mechanism of the reaction most probably is much more complicated by other processes involving some resting states.



Scheme 1

In this section, those Pd-catalyzed alkylation reactions that involve the use of either saturated or remotely unsaturated (i.e., δ -, ϵ -, and beyond) alkylmetals will be reviewed, with focus on their reactions with alkenyl and aryl electrophiles. For other Pd-catalyzed reactions of alkylmetals, readers are referred to the sections indicated below. Pd-catalyzed alkylation reactions of homoallyl-, homopropargyl-, or homobenzylmetals with alkenyl and aryl electrophiles possess a special synthetic significance in that they offer alternative

and generally superior and highly satisfactory routes to 1,5-dienes, 1,5-enynes, and related compounds of natural origin and/or of medicinal significance that are difficult to access. For this reason, these reactions are discussed separately in **Sect. III.2.11.2**.

Related Topics	Section Number
Alkyl-M + heteroaryl-X	III.2.7
Alkyl-M + alkynyl-X	III.2.8.2
Alkyl-M + 	III.2.9
Alkyl-M + RCOX	III.2.12.1
Alkyl-M +  (Z = heteroatom)	III.2.12.2
Use of β -heterosubstituted electrophiles	III.2.14.2
Alkyl-M + 	III.2.15
Asymmetric cross-coupling	III.2.16
Synthesis of natural products	III.2.18

B. Pd-CATALYZED ALKYLATION WITH ALKYL METALS CONTAINING Li, Al, AND Sn

As in some other cases of Pd-catalyzed cross-coupling, nearly ten or a dozen metals including Li, Cu, Mg, Zn, B, Al, and Sn have been used as the metal counterions, and trends similar to several other cases have been observed.

1. **Li.** Despite some early successful results with alkyllithiums,^[3] they have scarcely been used in Pd-catalyzed alkylation. This must, in part, be due to their inability to tolerate many conventional polar functional groups. As discussed earlier, however, the high intrinsic reactivity of alkyllithiums appears to be responsible for some of the difficulties observed with alkyllithiums. In any event, it may be stated that the current scope of Pd-catalyzed alkylation with alkyllithiums is rather limited. In cases where alkylmetals containing other metals are prepared via alkyllithiums, however, it would be desirable and advisable to examine the reaction of alkyllithiums themselves to justify the use of other metals. Some of the favorable results observed with alkyllithiums^[3] are summarized in **Scheme 2**.

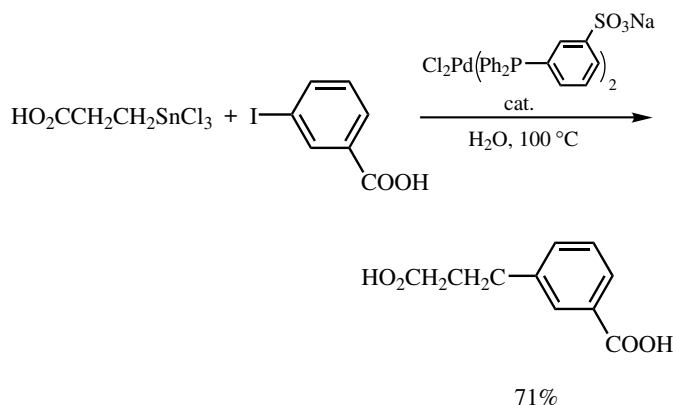
2. **Cu and Zr.** Little is known about the use of Si, Zr, and even Cu in Pd-catalyzed alkylation with alkylmetals. It should be recalled, however, that Cu-promoted or -catalyzed alkylation without the involvement of Pd or other transition metal complexes is a widely applicable and generally satisfactory synthetic methodology.

3. **Al and Sn.** Both trialkylalanes^{[7]–[14]} and tetraalkyltins^{[15]–[31]} have been used successfully in Pd-catalyzed alkylation. Even so, the current scope with respect to

$\text{PhCH=CHBr} + \text{LiR} \xrightarrow{\text{cat. PdL}_n} \text{PhCH=CHR}$			
<i>E</i> or <i>Z</i>	R	PdL_n	Yield (%)
<i>Z</i>	Me	$\text{Pd(PPh}_3)_4$	90
<i>Z</i>	Me	$\text{Cl}_2\text{Pd(PPh}_3)_2$	95
<i>E</i>	Me	$\text{Pd(PPh}_3)_4$	88
<i>Z</i>	Bu	$\text{Ph(PPh}_3)_4$	62
<i>Z</i>	Bu	$\text{Cl}_2\text{Pd(PPh}_3)_2$	73
<i>Z</i>	Bu	$\text{Cl}_2\text{Pd(PBu}_3)_2$	14
<i>E</i>	Bu	$\text{Pd(PPh}_3)_4$	46

Scheme 2

alkylalanes is mostly limited to Me_3Al , Et_3Al , Pr_3Al , and $(i\text{-Bu})_3\text{Al}$, the only exception being $\text{Me}_3\text{SiCH}_2\text{AlR}_2$, where R is Me_3SiCH_2 or Me.^[9] One practical difficulty is that only one of the three alkyl groups in R_3Al can be used in this reaction, which can be a serious limitation in cases where more elaborate and expensive alkyl groups are involved. Alkyltins are generally even less reactive. In many cases, Me_4Sn appears to be satisfactory. On the other hand, $(n\text{-Bu})_4\text{Sn}$ appears to be significantly less reactive. In general, the scope with respect to alkyltins is almost as limited as in the cases of alkylalanes. Typically, only one out of four alkyl groups is utilized in the reaction. More recently, however, the use of R_3SnX , where X is a halogen, in Pd-catalyzed alkylation has been reported.^{[30],[31]} The use of $\text{HO}_2\text{CCH}_2\text{CH}_2\text{SnCl}_3$ to achieve alkylation in 71% yield is noteworthy and promising^[30] (Scheme 3). In most cases, however, Pd-catalyzed alkylation with alkylmetals containing Al and Sn may also be achieved with those containing Mg, Zn, and B. Collectively, these three metals provide satisfactory procedures of significantly wider scope. Consequently, the use of other metals, such as Al and Sn, will have to be well justified. Some representative results observed with alkylalanes^{[7]–[14]} and alkylstannanes^{[15]–[29]} are shown in Tables 1 and 2, respectively.



Scheme 3

TABLE 1. Pd-Catalyzed Cross-Coupling Reactions of Alkylaluminums with Alkenyl and Aryl Electrophiles

RM	R'X	Catalyst	Solvent	Yield (%)	Reference
Me ₃ Al		Pd(PPh ₃) ₄	DCE	91	[7]
Me ₃ Al		Pd(PPh ₃) ₄	DCE	72	[7]
Me ₃ Al		Pd(PPh ₃) ₄	Benzene	83	[8]
Me ₃ Al		Cl ₂ Pd(PPh ₃) ₂ -DIBAH	THF	53	[11]
Me ₃ Al	2-MePhOTf	Pd(PPh ₃) ₄	THF	53	[10]
Me ₃ Al	4-ClPhOTf	Pd(PPh ₃) ₄	THF	97	[10]
Me ₃ Al		PdCl ₂ -PPh ₃	THF	95	[12]
Me ₃ Al		Pd(PPh ₃) ₄	THF	71–86	[13]
Et ₃ Al		Pd(PPh ₃) ₄	DCE	80	[7]
Et ₃ Al		Pd(PPh ₃) ₄	Benzene	82	[8]
Et ₃ Al		Pd(PPh ₃) ₄	Benzene	55	[8]
Et ₃ Al		Pd(PPh ₃) ₄	THF	24	[14]
Pr ₃ Al	PhOTf	Pd(PPh ₃) ₄	THF	97	[10]
Pr ₃ Al	(1)	PdCl ₂ -PPh ₃	THF	53	[12]
<i>i</i> -Bu ₃ Al	(1)	PdCl ₂ -PPh ₃	THF	13	[12]
<i>i</i> -Bu ₃ Al	PhOTf	Pd(PPh ₃) ₄	THF	52	[10]

TABLE 2. Pd-Catalyzed Cross-Coupling Reactions of Alkyltins with Alkenyl and Aryl Electrophiles

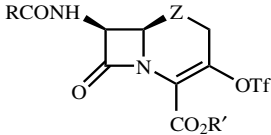
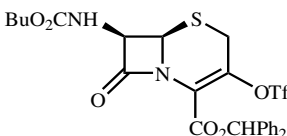
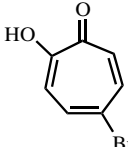
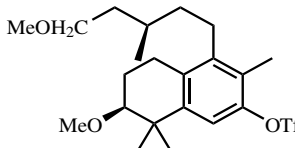
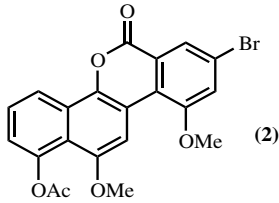
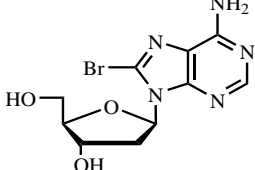
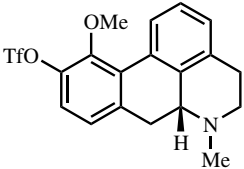
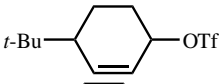
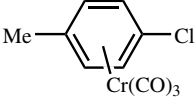
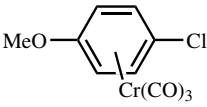
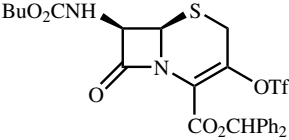
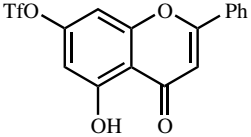
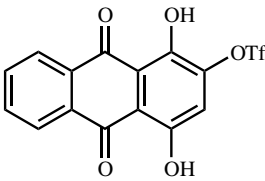
RM	R'X	Catalyst	Solvent	Yield (%)	Reference
Me ₄ Sn		Cl ₂ Pd(CH ₃ CN) ₂ LiCl	DMF	70	[22]
Me ₄ Sn		Pd ₂ (dba) ₃ -TFP	NMP	85	[25]
Me ₄ Sn	PhBr	PhCH ₂ Pd(PPh ₃) ₂ Cl	HMPA	89	[15]
Me ₄ Sn	4-MeC ₆ H ₄ Br	PhCH ₂ Pd(PPh ₃) ₂ Cl	HMPA	84	[15]
Me ₄ Sn	4-FC ₆ H ₄ Br	PhCH ₂ Pd(PPh ₃) ₂ Cl	HMPA	89	[15]
Me ₄ Sn	4-MeCOC ₆ H ₄ Br	PhCH ₂ Pd(PPh ₃) ₂ Cl	HMPA	99	[15]
MeSnBr ₃	3-HO ₂ CC ₆ H ₄ I	PdCl ₂	KOH-H ₂ O	98	[30]
MeSnCl ₃	4-HO ₂ CC ₆ H ₄ I	PdCl ₂	KOH-H ₂ O	82	[31]
Me ₄ Sn	4-MeCOC ₆ H ₄ OTf	Pd(PPh ₃) ₄	Dioxane	75	[20]
Me ₄ Sn	2,6-(MeO) ₂ C ₆ H ₃ OTf	PdCl ₂ (PPh ₃) ₂ -LiCl	DMF	92	[24]
Me ₄ Sn	4-ClC ₆ H ₄ N ₂ BF ₄	Pd(OAc) ₂	CH ₃ CN	88	[16]
Me ₄ Sn	4-NO ₂ C ₆ H ₄ N ₂ PF ₆	Pd(OAc) ₂	CH ₃ CN	95	[16]
Me ₄ Sn		Pd(PPh ₃) ₄	Dioxane	80	[23]
Me ₄ Sn		Cl ₂ Pd(PPh ₃) ₂	DMF	75	[29]
Me ₄ Sn	 <p>(2)</p>	Pd(PPh ₃) ₄	THF	61	[19]
Me ₄ Sn		Pd(PPh ₃) ₄	NMP	92	[28]

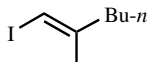
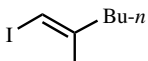
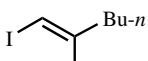
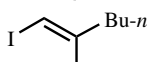
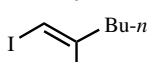
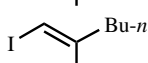
TABLE 2. (Continued)

RM	R'X	Catalyst	Solvent	Yield (%)	Reference
Me ₄ Sn		Pd(PPh ₃) ₄ , LiCl	DMF	77	[27]
Et ₄ Sn	PhN ₂ BF ₄	Pd(OAc) ₂	CH ₃ CN	7	[16]
Et ₄ Sn	(2)	Pd(PPh ₃) ₄	THF	44	[19]
Me ₂ CHSnCl ₃	4-HO ₂ CC ₆ H ₄ I	PdCl ₂	KOH-H ₂ O	25	[31]
HO ₂ C(CH ₂) ₂ SnCl ₃	4-HOC ₆ H ₄ I	PdCl ₂	KOH-H ₂ O	<10	[30]
HO ₂ C(CH ₂) ₂ SnCl ₃	3-HO ₂ CC ₆ H ₄ I	PdCl ₂	KOH-H ₂ O	71	[30]
Bu ₄ Sn		Pd(PPh ₃) ₄ , LiCl	THF	80	[17] [18]
Bu ₄ Sn		Pd(PPh ₃) ₄	THF	75	[21]
Bu ₄ Sn		Pd(PPh ₃) ₄	THF	82	[21]
BuSnCl ₃	4-HO ₂ CC ₆ H ₄ I	PdCl ₂	KOH-H ₂ O	74	[31]
Bu ₄ Sn		Pd ₂ (dba) ₃ , TFP	NMP	16	[25]
Bu ₄ Sn	4-MeCOC ₆ H ₄ OTf	Pd(PPh ₃) ₄	Dioxane	82	[20]
Bu ₄ Sn		PdCl ₂ (PPh ₃) ₂ , LiCl	DMF	92	[20]
Bu ₄ Sn		PdCl ₂ (PPh ₃) ₂	DMF	74	[26]
(Me ₃ SiCH ₂) ₄ Sn	4-NO ₂ C ₆ H ₄ OTf	Pd(PPh ₃) ₄	Dioxane	N.R.	[20]

C. Pd-CATALYZED ALKYLATION WITH ALKYLMETALS CONTAINING Mg AND Zn

As in many other cases of Pd-catalyzed cross-coupling, Mg and Zn, in particular, have exhibited the highest reactivity under the influence of Pd catalysts and the widest scope with respect to the alkylmetal structure. Earlier studies have established that those alkylmagnesiums and alkylzincs containing not only Me, *n*-alkyl, and isoalkyl groups^{[1],[2],[6]} but also sterically more hindered secondary and even tertiary alkyl groups^{[4]–[6]} can be employed successfully, as indicated in **Table 3**. Particularly noteworthy is that homoallyl-, homopropargyl, and homobenzylnmetals containing Mg and Zn can be employed successfully despite the presence of relatively acidic β -H atoms.^[6] This has provided the basis for developing the synthetic methodology discussed in **Sect. III.11.2**.

TABLE 3. Scope of Pd-Catalyzed Alkylation with Alkylmetals Containing Mg and Zn

Alkylmetal	Organic Electrophile	Catalyst ^a	Yield (%)	Ref- erence
MeMgBr		A	100	[1]
EtMgBr	(<i>Z</i>)-BrCH=CHPh	A	87	[2]
	(<i>E</i>)-ICH=CHPh			
<i>n</i> -BuZnCl		A	76	[6]
<i>n</i> -BuMgBr		A	25	[6]
H ₂ C=CH(CH ₂) ₂ ZnCl		A	81	[6]
H ₂ C=CH(CH ₂) ₂ MgBr		A	21	[6]
Me ₃ SiC≡C(CH ₂) ₂ ZnCl		A	91	[6]
<i>s</i> -BuZnCl		A	68 ^b	[6]
<i>s</i> -BuMgCl	PhBr	A	4	[4]
<i>s</i> -BuMgCl	PhBr	B	5	[4]
<i>s</i> -BuMgCl	PhBr	C	43	[4]
<i>s</i> -BuMgCl	PhBr	D	51	[4]
<i>s</i> -BuMgCl	PhBr	E	95 ^c	[4]
<i>s</i> -BuMgCl	(<i>E</i>)-BrCH=CHPh	E	97 ^c	[4]
<i>s</i> -BuMgCl	Br(Me)C=CH ₂	E	80 ^c	[4]
<i>t</i> -BuMgCl	(<i>E</i>)-BrCH=CHPh	E	60 ^d	[5]

^aA = Pd(PPh₃)₄; B = Cl₂Pd(PPh₃)₂; C = Cl₂Pd(dppp); D = Cl₂Pd(dppb); E = Cl₂Pd(dppf).

^bA 60:40 mixture of *s*-Bu and *n*-Bu isomers.

^cNo regioisomerization took place.

^dAdditionally, the isobutylated product was formed in 16% yield.

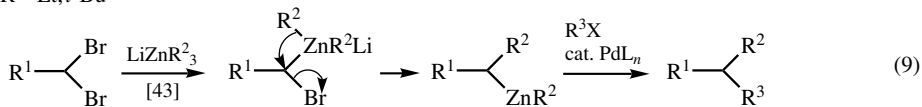
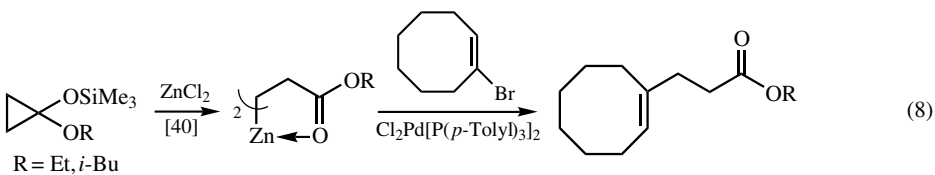
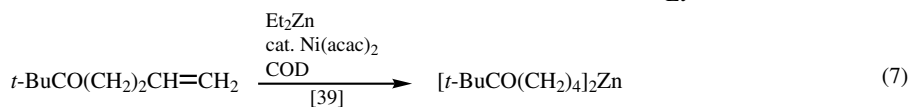
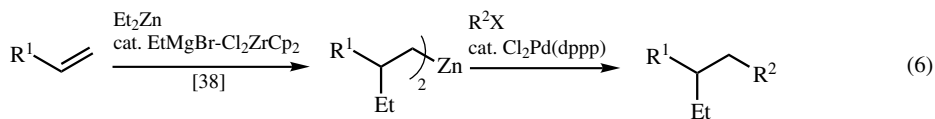
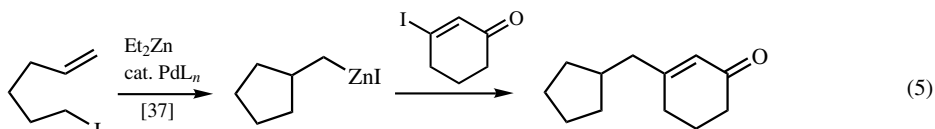
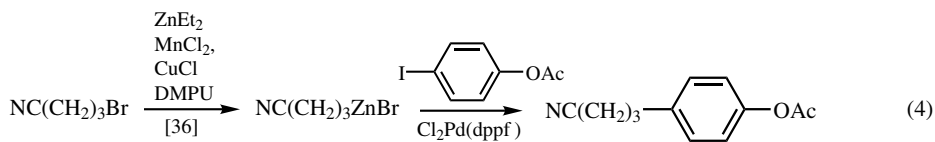
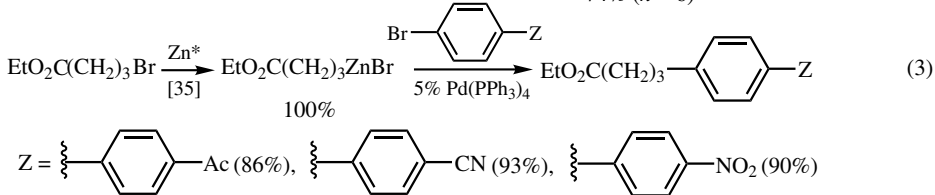
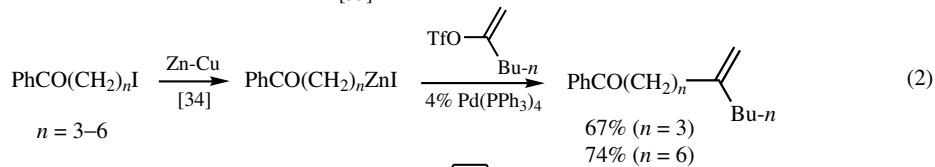
All alkyl groups present in alkylmagnesiums and alkylzincs can be utilized. The main limitation associated with Mg and Zn stems from their intrinsically high reactivity limiting the range of functional groups that can be tolerated. It should be noted, however, that Zn can tolerate most of the carbonyl groups except acyl halides, anhydrides, and aldehydes. Thus, esters, amides, carboxylic acids, and ketones as well as cyano, nitro, and many saturated heterofunctionalities, such as halo groups including iodides, can be tolerated even in the organozinc reagents themselves. So, the overall chemoselectivity associated with Zn is generally high and significantly higher than that with Mg. Coupled with the generally higher catalytic reactivity of Zn even relative to Mg, alkylzincs are, in many cases, superior to Grignard reagents. Even so, the use of Zn must be justified by carefully comparing the relative merits and demerits of Zn and Mg, particularly in those cases where alkylzincs are generated from the corresponding alkylmagnesiums.

In less demanding cases, relatively economical Pd catalysts, such as $\text{Pd}(\text{PPh}_3)_4$ and $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$, used in conjunction with THF and other relatively inexpensive solvents are generally satisfactory. In more demanding cases, however, the use of bidentate ligands, especially dppf and dppp,^{[4],[5]} in conjunction with more polar solvents, in particular DMF, has proved to be desirable or even necessary.

It is worth noting that there are various other inherently more chemoselective methods for the preparation of alkylzinc reagents.^[32] In addition to alkyllithiums and Grignard reagents, alkylmetals containing various other metals, such as B, Al, and Sn, can serve as precursors to alkylzincs,^[32] as exemplified in Eq. 1^[33] in **Scheme 4**. This example also points to the superior reactivity of Zn relative to Sn. Direct oxidative zincation of alkyl iodides and even bromides with Zn can be performed in many different ways including the use of the Zn–Cu couple^[34] (Eq. 2), addition of 1,2-dibromoethane and Me_3SiCl ,^[32] reduction of ZnX_2 ($\text{X} = \text{Cl}$ or Br) with Li and naphthalene (Rieke's zinc)^[35] (Eq. 3), and I–Zn exchange with Et_2Zn ^[36] often in the presence of added catalysts, such as MnCl_2 and CuCl (Eq. 4) (**Scheme 4**).

Carbozincation and hydrozincation of alkenes also provide chemoselective routes to alkylzincs. Palladium complexes, such as $\text{Cl}_2\text{Pd}(\text{dppf})$, have been shown to catalyze not only Zn–I exchange between alkyl iodides and dialkylzincs but also intramolecular carbozincation to produce cyclopentenylmethylzincs^[37] (Eq. 5). It has recently been reported that monosubstituted alkenes can be ethylzincated with 0.5 molar equiv of Et_2Zn in the presence of 10 mol % of Cp_2ZrCl_2 and 20 mol % of EtMgBr to give bis(2-ethylalkyl)zincs in good yields.^[38] Furthermore, the alkylzincs thus generated *in situ* can undergo, in the same reaction vessel, Pd-catalyzed cross-coupling with various organic electrophiles including PhI and vinyl bromide in good yields^[38] (Eq. 6). Hydrozincation of monosubstituted alkenes can be achieved with Et_2Zn in the presence of Ni catalysts^[39] (Eq. 7).

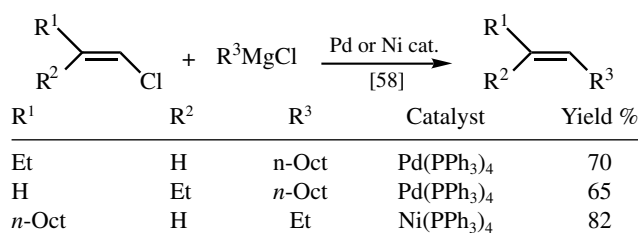
There are some other chemoselective routes to heterofunctional alkylzinc derivatives via rearrangements and migratory insertion. Zinc homoenolates can be generated by treating 1-siloxy-1-alkoxycyclopropanes with ZnCl_2 .^{[40]–[42]} The resultant zinc homoenolates readily react with alkenyl and aryl bromides and iodides under the influence of $\text{Cl}_2\text{Pd}[\text{P}(o\text{-Tol})_3]_2$ to give the corresponding cross-coupling products generally in good to excellent yields (Eq. 8). The same zinc homoenolates can also be prepared from the corresponding iodides by direct zincation with the Zn–Cu couple^[34] (Eq. 2). Finally, treatment of 1,1-dibromoalkanes with lithium trialkylzincates induces a cascade involving Br–Zn exchange followed by an alkyl migration from Zn to the $\alpha\text{-C}$ atom to generate secondary alkylzincs^[43] (Eq. 9).



Scheme 4

The versatility and chemoselectivity of Pd-catalyzed alkylation with alkylzincs are amply indicated by additional examples summarized in **Tables 4** and **5**. In **Table 4**, additional representative examples of the use of hetero-substituted alkylzincs are shown, while those involving the use of hetero-substituted organic electrophiles are summarized

in **Table 5**. The following noteworthy features are seen in **Table 4**. Fluorine atoms can be present in essentially any positions including α and β .^{[44],[45]} β -Zinco- α -amino acid derivatives are noteworthy examples of zinc homoenolates.^{[46]–[50]} Some relatively electronegative metals, such as Si and B, can be present in various positions including α ,^{[51]–[54]} γ ,^[55] and δ .^[6] The superior intrinsic reactivity of Zn relative to Si and B is evident from these examples. In **Table 5**, some representative examples of the use of heterosubstituted organic electrophiles are shown. Less reactive halogens, that is, F, Cl, and even Br in some cases, can be accommodated in alkenyl^[56] and aryl halides.^[57] It is noteworthy that Pd-catalyzed alkylation can be achieved even with alkenyl chlorides^[58] and that one of the two or more Cl atoms in a molecule can selectively be utilized in the reaction (**Scheme 5**). Although proximal heterofunctional groups can interfere with Pd-catalyzed cross-coupling through chelation, various oxyfunctional groups^{[59]–[62]} in organic electrophiles can be tolerated. The use of (*Z*)-3-iodo-2-buten-1-ol protected as the chlorozinc or bromozinc derivatives is noteworthy, as it provides an efficient and selective route to many (*Z*)-terpenoids (**Sect. III.2.11.2**). Also noteworthy is that alkenyl sulfides^[63] can be tolerated, whereas alkenyl sulfones^[64] undergo hydrogenolysis involving the S group. Boryl groups (e.g., BR_3) can also be tolerated,^[65] indicating that the BR_2 groups in either the starting compound or the product are far less reactive than the alkylzinc reagent under the conditions used.



Scheme 5

Pd-catalyzed alkylation with alkylzincs and alkylmagnesiums has been applied to the synthesis of natural products and related compounds of biochemical interest, as exemplified in Scheme 6.

D. Pd-CATALYZED ALKYLATION WITH ALKYLBORONS

D.i. Background

Despite the low intrinsic reactivity of alkylboranes, Pd-catalyzed alkylation with alkylboron compounds holds considerable promise as a unique and chemoselective alkylation method. It is unique in part because hydroboration of alkenes is by far the most general and dependable method for stoichiometrically converting alkenes into organometals and in part because alkylboron compounds thus generated can satisfactorily participate in Pd-catalyzed alkylation under basic conditions. In this connection, it should be noted that the current scopes of hydroalumination and hydrozirconation of alkenes are much more limited than

TABLE 4. Pd-Catalyzed Alkylation with Hetero-Substituted Alkylzincs and Alkylmagnesiums

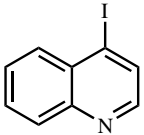
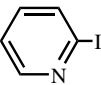
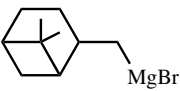

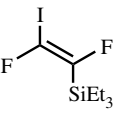
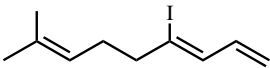
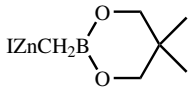
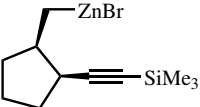

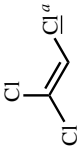
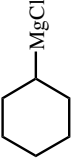
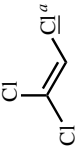
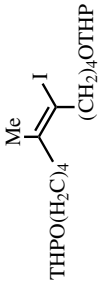
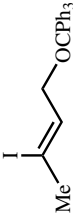

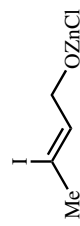
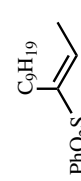
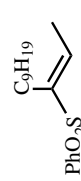
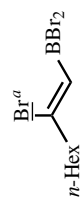
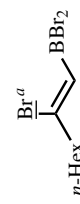
RM	R'X	Catalyst	Solvent	Yield (%)	Reference
CF ₃ ZnI	(<i>E</i>)-PhCH=CHBr	Pd(PPh ₃) ₄	THF	65	[44],[45]
<i>n</i> -C ₃ F ₇ ZnI	PhI	Cl ₂ Pd(PPh ₃) ₂	THF	78	[44],[45]
<i>i</i> -C ₃ F ₇ ZnI	4-MeC ₆ H ₄ I	Cl ₂ Pd(PPh ₃) ₂	THF	81	[44],[45]
CF ₃ ZnI	(<i>E</i>)-PhCH=CHCH ₂ Br	Pd(OAc) ₂	THF	51	[45]
IZn-CH ₂ -CH(NHBoc)-CO ₂ Bn (1)	PhI	Cl ₂ Pd[P(<i>o</i> -Tol) ₃] ₂	THF	55	[46]
(1)	1-Naph-I	Cl ₂ Pd[P(<i>o</i> -Tol) ₃] ₂	THF	64	[46]
(1)	4-NO ₂ C ₆ H ₄ I	Cl ₂ Pd[P(<i>o</i> -Tol) ₃] ₂	THF	61	[46]
(1)	2-MeOC ₆ H ₄ I	Cl ₂ Pd[P(<i>o</i> -Tol) ₃] ₂	THF	40	[46]
(1)	PhCOCl	Cl ₂ Pd(PPh ₃) ₂	THF	70	[47]
(1)	2-Furoyl-Cl	Cl ₂ Pd(PPh ₃) ₂	THF	90	[47]
(1)	4-(MeO) ₂ P(O)CH ₂ C ₆ H ₄ I	Cl ₂ Pd[P(<i>o</i> -Tol) ₃] ₂	THF	36	[48]
IZn-CH ₂ -CH(NHBoc)-CO ₂ Me		Cl ₂ Pd[P(<i>o</i> -Tol) ₃] ₂	THF	12	[49]
IZn-CH ₂ -CH(NHBoc)-CO ₂ Bn	(EtO) ₂ P(O)O- 	Cl ₂ Pd(PPh ₃) ₂	DMAC	86	[50]
BrMg(CH ₂) ₈ OTHP	(<i>Z</i>)- <i>n</i> -BuCH=CHI	Pd(PPh ₃) ₄	THF	65	[50]
 MgBr	(<i>E</i>)-PhCH=CHBr	Pd(PPh ₃) ₄	THF	78	[50]
Me ₃ SiCH ₂ ZnCl	<i>n</i> -Hex- 	Pd(PPh ₃) ₄	Et ₂ O-THF	80	[51]
Me ₃ SiCH ₂ MgCl	(<i>Z</i>)- <i>n</i> -PrCH=CHI	Pd(PPh ₃) ₄	Et ₂ O-THF	70	[51]
Me ₃ SiCH ₂ ZnBr		Pd(PPh ₃) ₄	THF	85	[52]
Me ₃ SiCH ₂ MgCl		Pd(PPh ₃) ₄	THF	97	[53]
IZnCH ₂ B- 	(<i>E</i>)-PhCH=CHI	Cl ₂ Pd(PPh ₃) ₂	THF	62	[54]
 ZnBr	Et- 	Pd(PPh ₃) ₄	THF	73	[55]

TABLE 5. Pd-Catalyzed Alkylation with Hetero-Substituted Organic Electrophiles

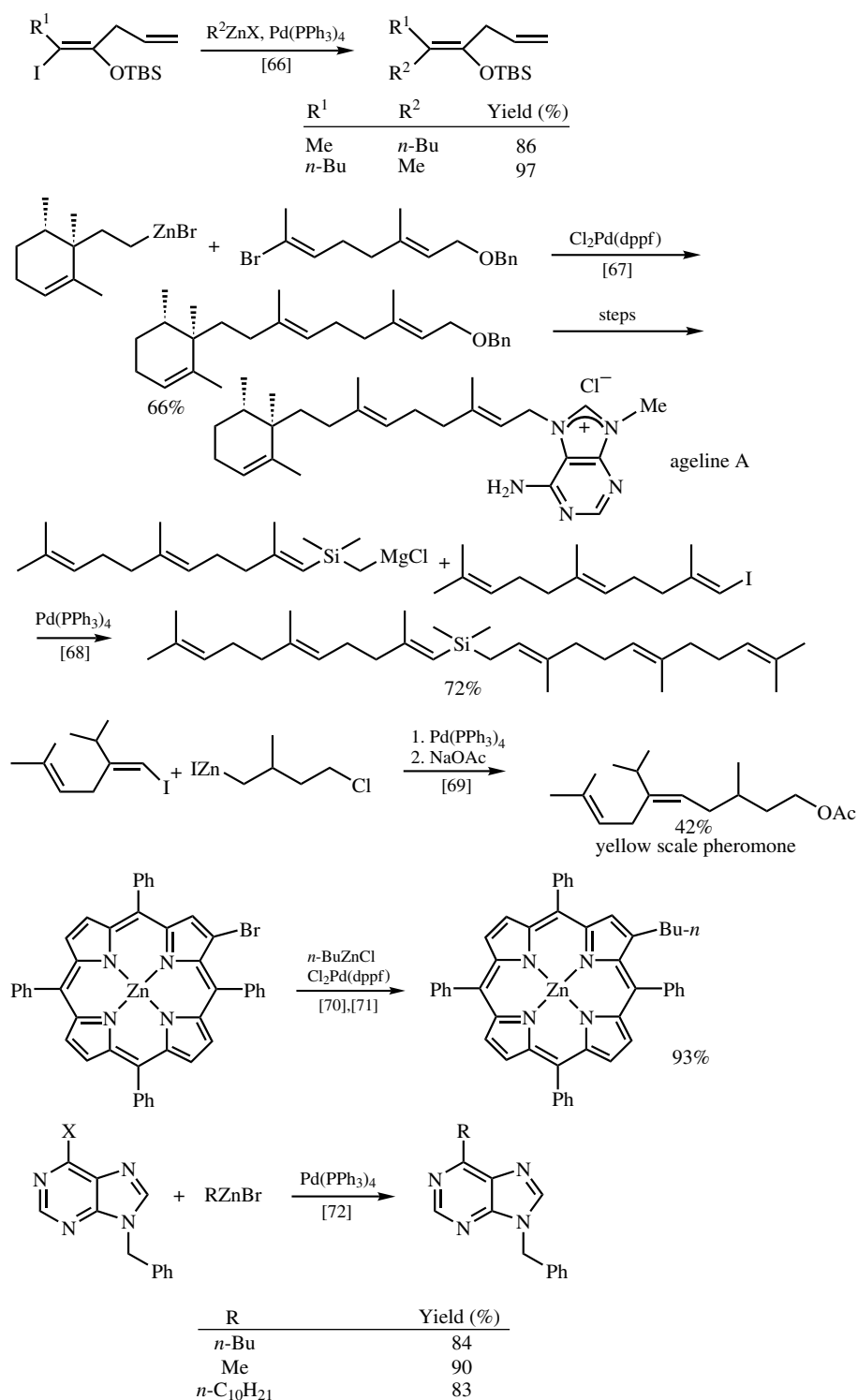
RM	R'X	Catalyst	Solvent	Yield (%)	Reference
<i>n</i> -OctMgCl		Pd(PPh ₃) ₄	Et ₂ O-benzene	65	[56]
		Pd(PPh ₃) ₄	Et ₂ O-benzene	81	[56]
MeMgCl	3-ClC ₆ H ₄ Cl	Cl ₂ Pd(dppf)	THF	93	[57]
PhMgCl	2-ClC ₆ H ₄ Cl	Cl ₂ Pd(dppf)	THF	79	[57]
<i>n</i> -PrMgCl	4-ClC ₆ H ₄ Cl	Cl ₂ Pd(dppf)	THF	80	[57]
<i>n</i> -BuMgCl	(<i>Z</i>)-ICH=CH(CH ₂) ₈ OTHP	Pd(PPh ₃) ₄	Et ₂ O-benzene	70	[59]
MeMgI		Pd(PPh ₃) ₄	benzene	80	[60]
<i>n</i> -BuZnCl		Cl ₂ Pd(PPh ₃) ₂ -BuLi	DMF	98	[61]

(Continued)

TABLE 5. (Continued)

RM	R'X	Catalyst	Solvent	Yield (%)	Reference
<i>n</i> -BuZnCl		Pd(PPh ₃) ₄	DMF	90	[61]
<i>n</i> -HexZnCl		Cl ₂ Pd(PPh ₃) ₂ -BuLi	DMF	80	[61]
Me ₂ C=CH(CH ₂) ₂ ZnCl	CH ₂ =C(I)CH ₂ CO ₂ H	Cl ₂ Pd(MeCN) ₂	DMF	65	[62]
<i>i</i> -PrZnBr	CH ₂ =C(I)CH ₂ CO ₂ H	Cl ₂ Pd(MeCN) ₂	DMF	78	[62]
THPO(CH ₂) ₆ MgCl	(Z)-BrCH=CHSPH	Cl ₂ Pd(PPh ₃) ₂	Et ₂ O-THF	75	[63]
<i>i</i> -PrMgCl		Pd(acac) ₂	THF	67	[64]
<i>n</i> -BuMgCl		Pd(acac) ₂ -2PBu ₃	THF	83	[64]
<i>n</i> -BuZnCl		Cl ₂ Pd(PPh ₃) ₂	THF	65	[65]
Me ₃ SiCH ₂ ZnCl		Cl ₂ Pd(PPh ₃) ₂	THF	59	[65]

^a The underlined atom reacts with the organozinc reagent.



Scheme 6

that of hydroboration. Moreover, no generally satisfactory conditions for Pd-catalyzed alkylation of alkylaluminums and alkylzirconiums have as yet been developed. In cases where alkylboranes must be prepared by methods other than hydroboration, selection of B over Zn or Mg must be made through careful comparison of these metals in various respects.

D.ii. Scope

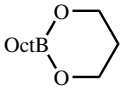
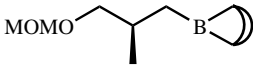
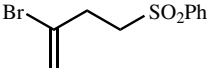
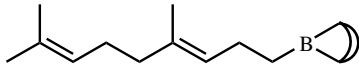
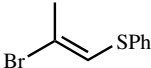
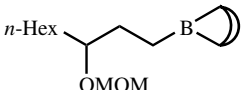


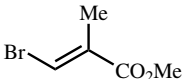

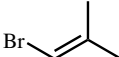


Alkylboranes themselves are rather inert under the more usual conditions of Pd-catalyzed cross-coupling. In the presence of suitable bases, such as NaOH and NaOMe, however, trialkylboranes can undergo relatively facile alkylation in the presence of Pd catalysts.^{[73],[74]} Only one of the three alkyl groups in a trialkylborane is usually utilized. 10-Alkyl-9-oxa-10-borabicyclo[3.3.2]decanes, which are examples of dialkylborinates, can readily and selectively transfer the 10-alkyl groups.^{[75],[76]} Selective utilization of one of the three alkyl groups of a trialkylborane is most conveniently performed through the use of *B*-alkyl-9-borabicyclo[3.3.1]nonanes (*B*-alkyl-9-BBN's), *B*-alkyldisiamylboranes, and *B*-alkyldicyclohexylboranes.^{[73],[74]} In contrast with arylation and alkenylation, Pd-catalyzed alkylation with alkylboronates, such as *B*-alkylcatecholboranes and alkylboronic acids, has not been very effective.^[74] In addition to organic iodides and bromides, organic triflates can serve as satisfactory electrophiles.^{[77],[78]} Alkylboranes containing methyl, *n*-alkyl, and isoalkyl groups including Me₃SiCH₂,^[76] homoallyl,^[74] and various heterofunctional alkyl groups have successfully been employed. Although some examples of the use of secondary alkylboranes are known,^[74] their reaction tends to be sluggish and low-yielding, and isomerization of secondary alkyl groups to primary alkyl groups is a serious concern. Indeed, tertiary alkyl groups, such as *t*-Bu, completely isomerize to isoalkyl groups.^[79]

Some representative examples of Pd-catalyzed alkylation with alkylboranes are shown in Table 6, and its notable applications are shown in **Scheme 7**.

E. SUMMARY

Pd-Catalyzed alkylation of alkenyl and aryl electrophiles with alkylzincs is a generally satisfactory and chemoselective method of alkylation. Together with the corresponding reaction of Grignard reagents, this reaction should be considered first. In cases where the required alkylmetals are readily accessible via hydroboration of suitable alkenes, B may become the metal of choice. However, the required boron reagents are generally more expensive than the alkylzinc reagents. Furthermore, they are intrinsically less reactive than organozincs, requiring more specialized and/or less desirable reagents, such as Ph₃As, as well as generally more rigorous conditions. In selecting the most satisfactory protocol for a given synthetic task, it is advisable to take all of these factors into consideration. Although the alkyltin reaction displays advantages over Zn, Mg, and B in a limited number of cases, Sn appears to be generally less favorable than Zn, Mg, and B in Pd-catalyzed alkylation. At present, other metals, such as Al, Si, Cu, and Zr, do not appear to be very useful in Pd-catalyzed alkylation.

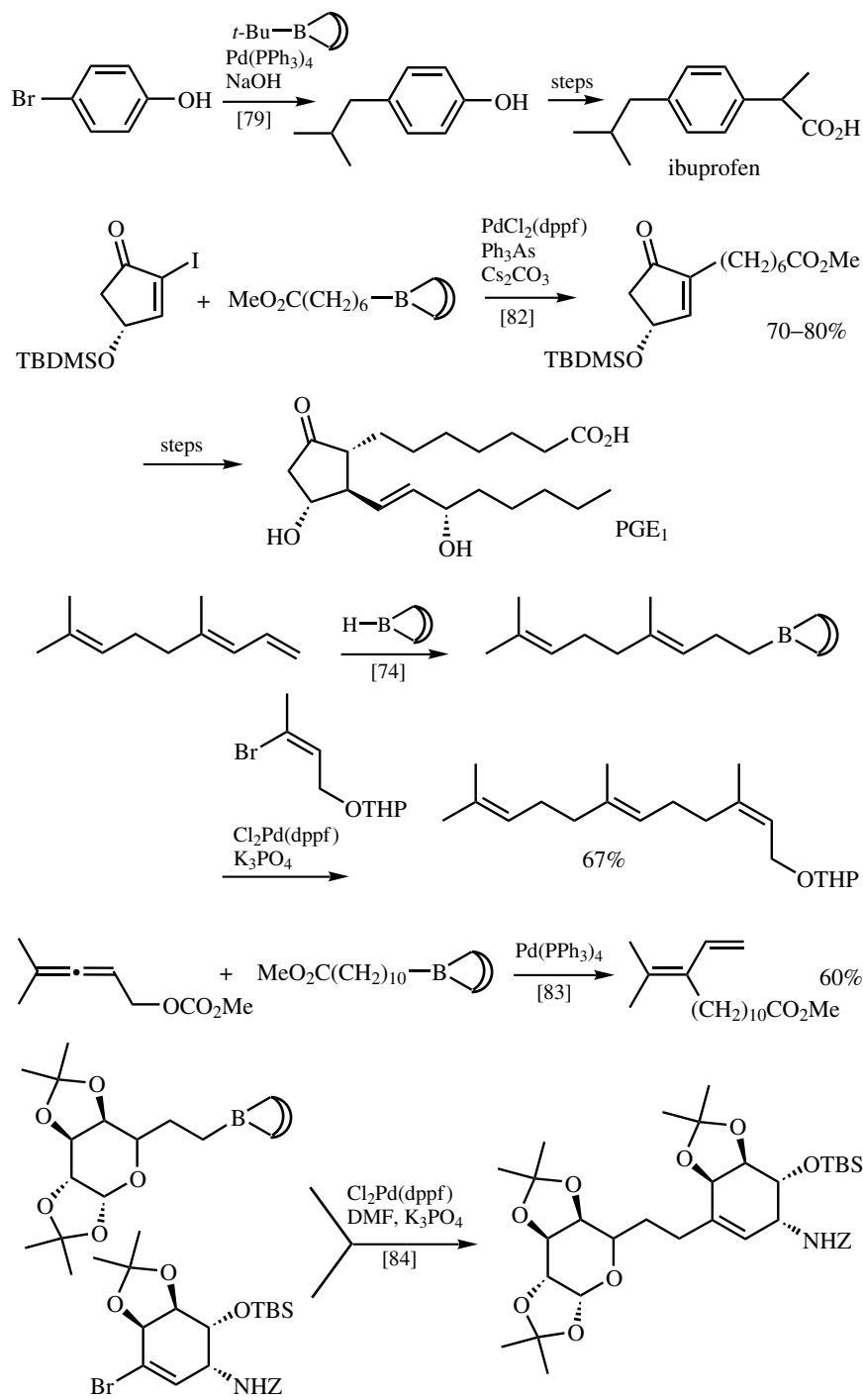
TABLE 6. Pd-Catalyzed Alkylation with Alkylborons in the Presence of Cl₂Pd(dppf)

Alkylmetal	Organic Electrophile	Base	Yield(%)	Ref- erence
<i>B</i> -Me-9-BBN	(<i>Z</i>)-BrCH=CH(Hex- <i>n</i>)	NaOH ^a	100 (99% <i>Z</i>)	[75]
<i>B</i> -(<i>i</i> -Bu)-9-BBN	PhI	NaOMe	95	[73]
<i>B</i> -(<i>s</i> -Bu)-9-BBN	PhI	NaOMe	0	[73]
(<i>s</i> -Bu) ₃ B	PhI	KOH	40	[74]
<i>B</i> -Me ₃ SiCH ₂ -9-BBN	(<i>Z</i>)-BrCH=CH(Bu- <i>n</i>)	NaOH ^a	87 (98% <i>Z</i>)	[76]
(Cy) ₃ B	PhI	KOH	55	[74]
	PhI	NaOMe	1	[75]
<i>B</i> -Oct-9-BBN	PhI	NaOMe	98	[73]
<i>B</i> -Oct-9-BBN	2-MeOC ₆ H ₄ I	NaOH	90	[73]
<i>B</i> -Oct-9-BBN	4-MeO ₂ CC ₆ H ₄ I	NaOMe	82 ^b	[73]
<i>B</i> -Oct-9-BBN	4-NO ₂ C ₆ H ₄ OTf	K ₃ PO ₄	48 ^c	[77],[78]
<i>B</i> -Oct-9-BBN	BrCH=CMe ₂	NaOH	94	[73]
<i>B</i> -Oct-9-BBN	(<i>Z</i>)-Br(Me)CH=CHMe	NaOH	98	[73]
<i>B</i> -Oct-9-BBN	(<i>Z</i>)-BrCH=CHPh	NaOH	90	[73]
OctB(Sia) ₂	PhI	NaOH	82	[74]
OctB(Cy) ₂	PhI	NaOH	93	[74]
(Oct) ₃ B	PhI	NaOMe	96	[74]
		K ₂ CO ₃	84	[80]
		NaOH	78	[81]
		NaOH	64	[81]
NC(CH ₂) ₁₀ B 		K ₂ CO ₃	80	[74]
MeO ₂ C(CH ₂) ₁₀ B 		K ₃ PO ₄	92	[74]
MeO ₂ C(CH ₂) ₁₀ B 		K ₃ PO ₄	86	[77],[78]

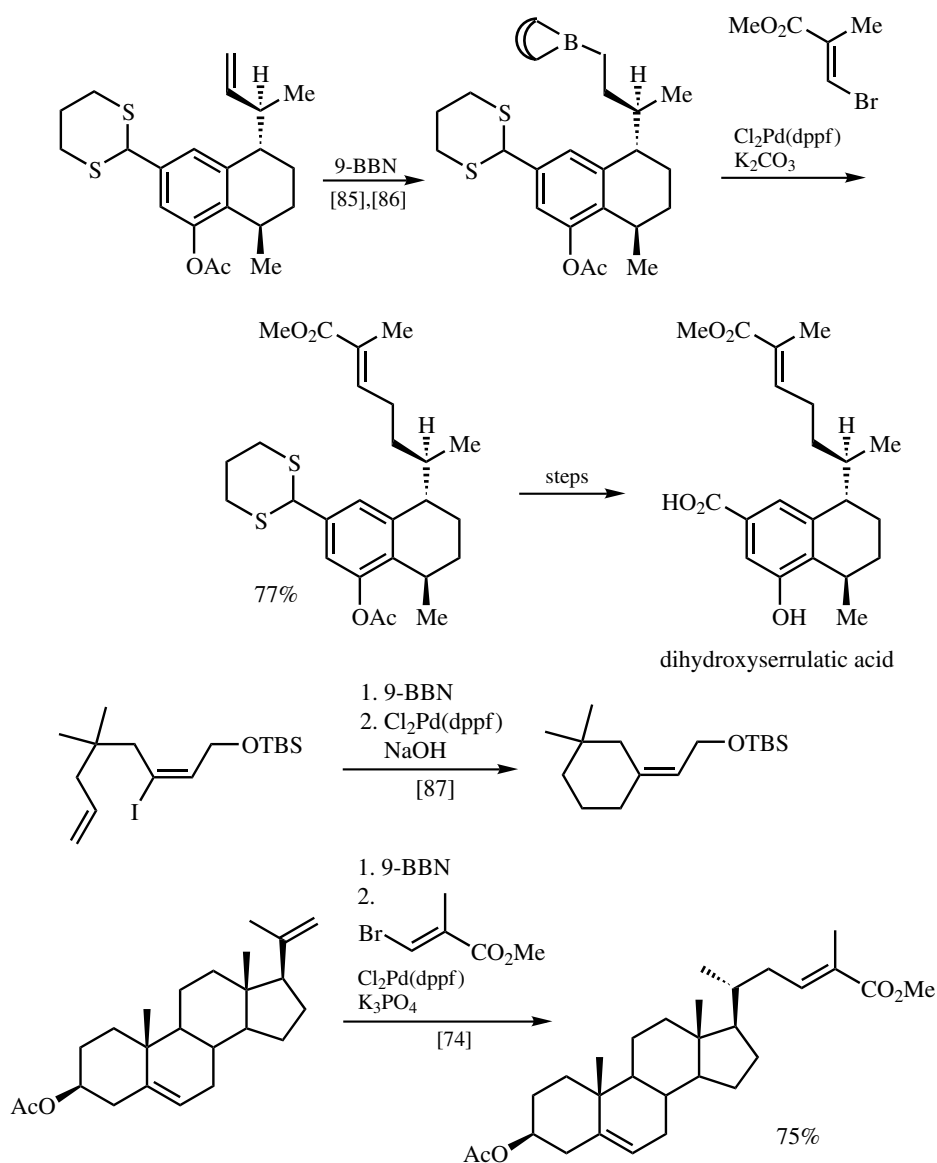
^a Pd(PPh₃)₄ was used as a catalyst.

^b After the cross-coupling reaction, the mixture was treated with acetic anhydride to prevent ester hydrolysis.

^c In addition, the corresponding aniline was produced in 30% yield.



Scheme 7



Scheme 7 (Continued)

REFERENCES

- [1] M. Yamamura, I. Moritani, and S. I. Murahashi, *J. Organomet. Chem.*, **1975**, 91, C39.
- [2] H. P. Dang and G. Linstrumelle, *Tetrahedron Lett.*, **1978**, 191.
- [3] S. I. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita, and K. Kondo, *J. Org. Chem.*, **1979**, 44, 2408.
- [4] T. Hayashi, M. Konishi, and M. Kumada, *Tetrahedron Lett.*, **1979**, 1871.
- [5] T. Hayashi, M. Konishi, K. Yokota, and M. Kumada, *Chem. Lett.*, **1980**, 767.

- [6] E. Negishi, L. F. Valente, and M. Kobayashi, *J. Am. Chem. Soc.*, **1980**, *102*, 3298.
- [7] K. Takai, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, **1980**, *21*, 2531.
- [8] M. Sato, K. Takai, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, **1981**, *22*, 1609.
- [9] M. G. Saulnier, J. F. Kadow, M. M. Tun, D. R. Langley, and D. M. Vyas, *J. Am. Chem. Soc.*, **1989**, *111*, 8320.
- [10] K. Hirota, Y. Isobe, and Y. Maki, *J. Chem. Soc. Perkin Trans. 1*, **1989**, 2513.
- [11] K. Asao, H. Iio, and T. Tokoroyama, *Synthesis*, **1990**, 382.
- [12] K. Hirota, Y. Kitade, Y. Kanbe, and Y. Maki, *J. Org. Chem.*, **1992**, *57*, 5268.
- [13] K. Hirota, Y. Kitade, Y. Kanbe, Y. Isobe, and Y. Maki, *Synthesis*, **1993**, 213.
- [14] F. Bracher and T. Papke, *Monatsh. Chem.*, **1995**, *126*, 805.
- [15] D. Milstein, and J. K. Stille, *J. Am. Chem. Soc.*, **1979**, *101*, 4992.
- [16] K. Kikukawa, K. Kono, G. Wada, and T. Matsuda, *J. Org. Chem.*, **1983**, *48*, 1333.
- [17] W. J. Scott, G. T. Crisp, and J. K. Stille, *J. Am. Chem. Soc.*, **1984**, *106*, 4630.
- [18] W. J. Scott and J. K. Stille, *J. Am. Chem. Soc.*, **1986**, *108*, 3033.
- [19] S. J. F. Macdonald, T. C. McKenzie, and W. D. Hassen, *J. Chem. Soc. Chem. Commun.*, **1987**, 1528.
- [20] A. M. Echavarren and J. K. Stille, *J. Am. Chem. Soc.*, **1987**, *109*, 5478.
- [21] W. J. Scott, *J. Chem. Soc. Chem. Commun.*, **1987**, 1755.
- [22] G. K. Cook, W. J. Hornback, C. L. Jordan, J. H. McDonald III, and J. E. Munroe, *J. Org. Chem.*, **1989**, *54*, 5828.
- [23] M. G. Banwell, M. P. Collis, G. T. Crisp, J. N. Lambert, M. E. Reum, and J. A. Scoble, *J. Chem. Soc. Chem. Commun.*, **1989**, 616.
- [24] G. Martorell, A. Garcia-Raso, and J. M. Saa, *Tetrahedron Lett.*, **1990**, *31*, 2357.
- [25] V. Farina, S. R. Baker, D. A. Benigni, S. I. Hauck, and C. Sapino, Jr., *J. Org. Chem.*, **1990**, *55*, 5833.
- [26] N. Tamayo, A. M. Echavarren, M. C. Paredes, F. Fariña, and P. Noheda, *Tetrahedron Lett.*, **1990**, *31*, 5189.
- [27] M. H. Hedberg, A. M. Johansson, and V. Hacksell, *J. Chem. Soc. Chem. Commun.*, **1992**, 845.
- [28] P. Mamos, A. A. Van Aerschot, N. J. Weyns, and P. A. Herdiwijn, *Tetrahedron Lett.*, **1992**, *33*, 2413.
- [29] J. G. Urones, I. S. Marcos, P. Basabe, N. M. Garrido, A. Jorge, R. F. Moro, and A. M. Lithgow, *Tetrahedron*, **1993**, *49*, 6079.
- [30] A. I. Roshchin, N. A. Bumagin, and I. P. Beletskaya, *Tetrahedron Lett.*, **1995**, *36*, 125.
- [31] R. Rai, K. B. Aubrecht, and D. B. Collum, *Tetrahedron Lett.*, **1995**, *36*, 3111.
- [32] P. Knochel and P. Jones, *Organozinc Reagents*, Oxford University Press, Oxford, **1999**, 354 pp.
- [33] E. Piers, M. Jean, and P. S. Marrs, *Tetrahedron Lett.*, **1987**, *28*, 5075.
- [34] Y. Tamaru, H. Ochiai, T. Nakamura, and Z. Yoshida, *Angew. Chem. Int. Ed. Engl.*, **1987**, *26*, 1157.
- [35] L. Zhu, R. M. Wehmeyer, and R. D. Rieke, *J. Org. Chem.*, **1991**, *56*, 1445.
- [36] I. Klement, P. Knochel, K. Chau, and G. Cahiez, *Tetrahedron Lett.*, **1994**, *35*, 1177.
- [37] H. Stadtmüller, R. Lentz, C. E. Tucker, T. Stüdemann, W. Dörner, and P. Knochel, *J. Am. Chem. Soc.*, **1993**, *115*, 7027.
- [38] S. Gagneur, J. L. Montchamp, and E. Negishi, *Organometallics*, **2000**, *19*, 2417.
- [39] S. Vettel, A. Vaupel, and P. Knochel, *Tetrahedron Lett.*, **1995**, *36*, 1023.
- [40] E. Nakamura and I. Kuwajima, *Tetrahedron Lett.*, **1986**, *27*, 83.

- [41] E. Nakamura, S. Aoki, K. Sekiya, H. Oshino, and I. Kuwajima, *J. Am. Chem. Soc.*, **1987**, *109*, 8056.
- [42] E. Nakamura, K. Sekiya, and I. Kuwajima, *Tetrahedron Lett.*, **1987**, *28*, 337.
- [43] T. Harada, Y. Kotani, T. Katsuhira, and A. Oku, *Tetrahedron Lett.*, **1991**, *32*, 1573.
- [44] T. Kitazume and N. Ishikawa, *Chem. Lett.*, **1982**, 137.
- [45] T. Kitazume and N. Ishikawa, *J. Am. Chem. Soc.*, **1985**, *107*, 5186.
- [46] R. F. W. Jackson, M. J. Wythes, and A. Wood, *Tetrahedron Lett.*, **1989**, *30*, 5941.
- [47] R. F. W. Jackson, K. James, M. J. Wythes, and A. Wood, *J. Chem. Soc. Chem. Commun.*, **1989**, 644.
- [48] R. L. Dow and B. M. Bechle, *Synlett*, **1994**, 293.
- [49] J. Matsubara, K. Otsubo, S. Morita, T. Ohtani, Y. Kawano, and M. Uchida, *Heterocycles*, **1996**, *43*, 133.
- [50] B. Ye, A. Otake, and T. R. Burke, Jr., *Synlett*, **1996**, 459.
- [51] E. Negishi, F. T. Luo, and C. L. Rand, *Tetrahedron Lett.*, **1982**, *23*, 27.
- [52] P. Martinet, R. Sauvetre, and J. F. Normant, *J. Organomet. Chem.*, **1989**, *367*, 1.
- [53] P. V. Fish, *Synth. Commun.*, **1996**, *26*, 433.
- [54] T. Watanabe, N. Miyauro, and A. Suzuki, *J. Organomet. Chem.*, **1993**, *444*, C1.
- [55] C. Meyer, I. Marek, G. Courtemanche, and J. F. Normant, *J. Org. Chem.*, **1995**, *60*, 863.
- [56] V. Ratovelomanana and G. Linstrumelle, *Tetrahedron Lett.*, **1985**, *26*, 2575.
- [57] T. Katayama and M. Umeno, *Chem. Lett.*, **1991**, 2073.
- [58] V. Ratovelomanana and G. Linstrumelle, *Synth. Commun.*, **1984**, *14*, 179.
- [59] D. Michelot, *Synthesis*, **1983**, 130.
- [60] M. Malacria and K. P. C. Vollhardt, *J. Org. Chem.*, **1984**, *49*, 5010.
- [61] E. Negishi, M. Ay, Y. V. Gulevich, and T. Noda, *Tetrahedron Lett.*, **1993**, *34*, 1437.
- [62] A. Duchêne, M. Abarbri, J. L. Parrain, M. Kitamura, and R. Noyori, *Synlett*, **1994**, 524.
- [63] V. Fiandanese, G. Marchese, F. Naso, and L. Ronzini, *J. Chem. Soc. Perkin Trans. I*, **1985**, 1115.
- [64] J. L. Fabre and M. Julia, *Tetrahedron Lett.*, **1983**, *24*, 4311.
- [65] Y. Satoh, H. Serizawa, N. Miyauro, S. Hara, and A. Suzuki, *Tetrahedron Lett.*, **1988**, *29*, 1811.
- [66] E. Negishi, Y. Zhang, F. E. Cederbaum, and M. B. Webb, *J. Org. Chem.*, **1986**, *51*, 4080.
- [67] K. Asao, H. Iio, and T. Tokoroyama, *Tetrahedron Lett.*, **1989**, *30*, 6401.
- [68] G. D. Prestwich and C. Wawrzenczyk, *Tetrahedron Lett.*, **1989**, *30*, 403.
- [69] J. G. Millar, *Tetrahedron Lett.*, **1989**, *30*, 4913.
- [70] S. G. DiMagno, V. S. Y. Liu, and M. J. Therien, *J. Am. Chem. Soc.*, **1993**, *115*, 2513.
- [71] S. G. DiMagno, V. S. Y. Liu, and M. J. Therien, *J. Org. Chem.*, **1993**, *115*, 2513.
- [72] L. L. Gundersen, A. K. Bakkestuen, A. J. Aasen, M. Overas, and F. Rise, *Tetrahedron*, **1994**, *50*, 9743.
- [73] N. Miyauro, T. Ishiyama, M. Ishikawa, and A. Suzuki, *Tetrahedron Lett.*, **1986**, *27*, 6369.
- [74] N. Miyauro, T. Ishiyama, H. Sasaki, M. Ishikawa, M. Satoh, and A. Suzuki, *J. Am. Chem. Soc.*, **1989**, *111*, 314.
- [75] J. A. Soderquist and B. Santiago, *Tetrahedron Lett.*, **1990**, *31*, 5541.
- [76] J. A. Soderquist, B. Santiago, and I. Rivera, *Tetrahedron Lett.*, **1990**, *31*, 4981.
- [77] T. Oh-e, N. Miyauro, and A. Suzuki, *Synlett*, **1990**, 221.
- [78] T. Oh-e, N. Miyauro, and A. Suzuki, *J. Org. Chem.*, **1993**, *58*, 2201.

- [79] I. Rivera, J. C. Colberg, and J. A. Soderquist, *Tetrahedron Lett.*, **1992**, 33, 6919.
- [80] S. J. O'Connor and P. G. Williard, *Tetrahedron Lett.*, **1989**, 30, 4637.
- [81] Y. Hoshino, T. Ishiyama, N. Miyaura, and A. Suzuki, *Tetrahedron Lett.*, **1988**, 29, 3983.
- [82] C. R. Johnson and M. P. Braun, *J. Am. Chem. Soc.*, **1993**, 115, 11014.
- [83] T. Moriya, T. Furuuchi, N. Miyaura, and A. Suzuki, *Tetrahedron*, **1994**, 50, 7961.
- [84] C. R. Johnson, M. W. Miller, A. Golebiowski, H. Sundram, and M. B. Ksetati, *Tetrahedron Lett.*, **1994**, 35, 8991.
- [85] M. Uemura, H. Nishimura, and Y. Hayashi, *Tetrahedron Lett.*, **1990**, 31, 2319.
- [86] M. Uemura, H. Nishimura, T. Minami, and Y. Hayashi, *J. Am. Chem. Soc.*, **1991**, 113, 5402.
- [87] N. Miyaura, M. Ishikawa, and A. Suzuki, *Tetrahedron Lett.*, **1992**, 33, 2571.