Highly Regio- and Stereoselective Acylboration, Acylsilation, and Acylstannation of Allenes Catalyzed by Phosphine-Free Palladium Complexes: An Efficient Route to a New Class of 2-Acylallylmetal Reagents

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Abstract: A new method for the synthesis of substituted 2-acylallylmetal reagents in a highly regio- and stereoselective fashion involving a three-component assembly of allenes, acyl chlorides, and bimetallic reagents (B—B, Si—Si, and Sn—Sn) catalyzed by phosphine-free palladium complexes is described. Treatment of various allenes ($CR^2R^3=C=CH_2$) with acyl chlorides (R^1COCl) and bispinacolatodiboron in the presence of $PdCl_2(CH_3CN)_2$ in toluene at 80 °C gave 2-acylallylboronates $CR^2R^3=C(COR^1)CH_2B$-$(OCMe_2CMe_2O)$ in moderate to good yields. The acylsilation of allenes with acid chlorides and hexamethyldisilane (**5**) proceeded successfully in the presence of $Pd(dba)_2$ in CH_3CN affording the corresponding allylsilanes ($CR^2R^3=C(COR^1)CH_2SiMe_3$) in good to moderate yields. Several chloroformates (R^4OCOCl) also react with 1,1-dimethylallene (**2a**) and **5** to afford allylsilanes ($CR^2R^3=C(COOR^4)CH_2$-$SiMe_3$) in 66—70% yields. Acylstannation of allenes could also be achieved by slow addition of hexabutylditin (**10**) to the reaction mixture of acyl chloride (or chloroformate**)** and allene **2a** in CH_3CN in the presence of $Pd(dba)_2$ at 60 °C; the corresponding 2-substituted allylstannanes were isolated in moderate to good yields. The above catalytic reactions are completely regioselective and highly stereoselective. A mechanism is proposed to account for the catalytic reactions and the stereochemistry.

1. Introduction

The transition metal-catalyzed addition of an electrophile and a nucleophile to an unsaturated carbon-linkage is a powerful method in organic synthesis for the construction of two carbon—carbon bonds from three different components.[1] In the design of these three-component assembling reactions, the control of both regio- and stereoselectivity is an important consideration. In addition, it is necessary to suppress competitive reactions such as direct coupling of the electrophile and nucleophile, β-hydride elimination, and polymerization of the alkene. It is a great challenge for synthetic chemists to develop new three-component assembling reactions in a highly regio- and stereo-selective fashion.

The metal-mediated allene chemistry has been the subject of intense interest for the past two decades.[2] In particular,

palladium-catalyzed coupling reactions of allenes are highly useful providing the opportunity to generate complex molecular frameworks in an efficient manner.[3] Recent efforts from our laboratories revealed that allenes are useful substrates for three-component assembling reactions.[4] Phosphine-free palladium complexes are efficient catalysts for this type of reaction. This process presumably involves an oxidative addition of organic electrophile to the Pd(0) catalyst to give an organopalladium-(II) intermediate. Insertion of allene into the metal—carbon bond of organopalladium intermediate generates a π-allylpalladium complexes that is relatively stable to β-hydride elimination. Attack of the π-allyl species by a nucleophile leads to the three-component assembling product. Other groups have developed phosphine palladium-catalyzed three-component assembling reactions of allenes.[5,6] Shimizu and Tsuji reported a phosphine palladium-catalyzed coupling of allenes with aryl iodides and

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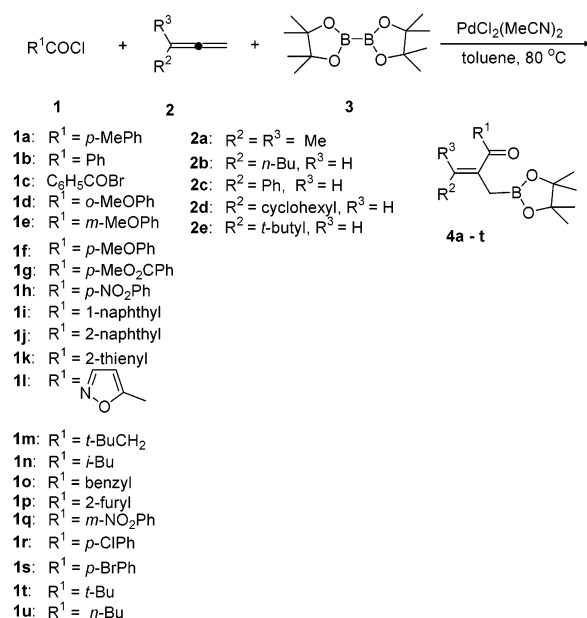
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amines.[5] Cazes and co-workers have demonstrated the reaction of allenes with malonates and vinyl halides or vinyl triflates catalyzed by palladium phosphine complexes.[6] However, these phosphine palladium-catalyzed reactions suffer from the drawback of low regio- and stereoselectivity.[5,6] Although several types of electrophiles such as aryl iodides, vinyl iodides, and viny triflates have been used,[4-6] acyl halides as electrophiles have not been explored in the three-component assembling reactions of allenes.

Allylboranes form an important class of organometallic compounds that have been proven to be versatile synthetic intermediates in organic synthesis. The addition of allylboranes to aldehydes is an attractive method for the preparation of homoallylic alcohols;[7] the reaction has been extensively used for the synthesis of natural products.[8] In addition, the coupling of allylboranes with aryl halides in Suzuki coupling reactions is well-known.[9] A common method for preparing allylboranes involves a palladium-catalyzed coupling of allylic electrophiles with tetraalkoxydiboron[10] and triethylborane.[11] But, this method generally gave very poor regio- and stereoselectivity. Other methods for the preparation include regio- and stereoselective platinum-catalyzed coupling of allyl halides with pinacolborane[12] and platinum-catalyzed diboration of allenes.[13] Recently, we discovered an efficient regio- and stereoselective route to 2-borylallylboronates via diboration of allenes catalyzed by palladium complexes and organic iodides.[14]

In view of the great synthetic utility of allylboranes, the development of a novel and efficient method for the synthesis of these reagents in a regio- and stereoselective fashion would be highly valuable. Our continuing interest in the metal-mediated allene chemistry[4,15] prompted us to explore the possibility of using acyl chlorides as electrophiles in three-component assembling reactions of allenes. In a preliminary communication, we reported a palladium-catalyzed highly regio- and stereoselective three-component assembly of allenes, acyl chlorides, and diboron leading to 2-acylallylboronates.[16] Herein, we wish to report the full details of this acylboration reaction and the extension of this methodology to acylsilation and acylstannation of allenes. These catalytic reactions provide a convenient

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Scheme 1

1a: R^1 = *p*-MePh   **2a:** R^2 = R^3 = Me
1b: R^1 = Ph   **2b:** R^2 = *n*-Bu, R^3 = H
1c: C$_6$H$_5$COBr   **2c:** R^2 = Ph, R^3 = H
1d: R^1 = *o*-MeOPh **2d:** R^2 = cyclohexyl, R^3 = H
1e: R^1 = *m*-MeOPh **2e:** R^2 = *t*-butyl, R^3 = H
1f: R^1 = *p*-MeOPh
1g: R^1 = *p*-MeO$_2$CPh
1h: R^1 = *p*-NO$_2$Ph
1i: R^1 = 1-naphthyl
1j: R^1 = 2-naphthyl
1k: R^1 = 2-thienyl
1l: R^1 =

1m: R^1 = *t*-BuCH$_2$
1n: R^1 = *i*-Bu
1o: R^1 = benzyl
1p: R^1 = 2-furyl
1q: R^1 = *m*-NO$_2$Ph
1r: R^1 = *p*-ClPh
1s: R^1 = *p*-BrPh
1t: R^1 = *t*-Bu
1u: R^1 = *n*-Bu

synthetic method for a wide range of 2-acylallylmetal reagents from easily available starting materials that are difficult to prepare by other methods.

2. Results and Discussion

2.1. Palladium-Catalyzed Acylboration of Allenes. The reaction of toluoyl chloride (**1a**) with 1,1-dimethylallene (**2a**) and bis(pinacolato)diboron (**3**) at 60 °C for 10 h in the presence of PdCl$_2$(MeCN)$_2$ (5.0 mol %) in toluene gave 2-acylallyl-boronate **4a** in 81% yield (Scheme 1). No other regioisomer was detected as evidenced by the ^{1}H NMR spectrum of the crude reaction mixture. This catalytic three-component assembling reaction is completely regioselective with the toluoyl and the boryl group adding to the middle and unsubstituted terminal carbons of the allene moiety. The presence of a carbonyl group in **4a** is revealed by the observation of a resonance at 201.2 ppm in the ^{13}C NMR spectrum and a strong absorption at 1655 cm^{-1} in the IR spectrum of this product. Control experiments indicated that, in the absence of palladium catalyst, no three-component assembling product **4a** was observed.

To understand the nature of the catalytic reaction, the catalytic activities of various palladium complexes for the reaction of **1a** with **2a** and **3** in toluene were studied. At 60 °C, Pd(dba)$_2$ and Pd(OAc)$_2$ were effective catalysts affording **4a** in 79 and 77%, respectively, but PdCl$_2$(PPh$_3$)$_2$ was completely ineffective for the reaction. The use of PdCl$_2$(MeCN)$_2$ at 80 °C afforded **4a** in 82% yield. The addition of 1 equiv of PPh$_3$ relative to the PdCl$_2$(CH$_3$CN)$_2$ solution strongly retarded the catalytic reaction. An examination of the effect of solvent on the yield of **4a** using PdCl$_2$(CH$_3$CN)$_2$ as the catalyst reveals that toluene was the solvent of choice. Other solvents such as THF and CH$_3$-CN were also effective affording **4a** in 75 and 77% yields, respectively. The absence of phosphine ligand in the palladium complex is crucial for the three-component assembling reaction to proceed smoothly. The above optimization studies led us to employ the following standard procedure for the acylboration of various allenes: acyl chloride (0.55 mmol), allene (1.0 mmol), diboron (0.50 mmol), and 5.0 mol % of PdCl$_2$(MeCN)$_2$ in toluene at 80 °C.

Table 1. Results of Palladium-Catalyzed Three-Component Assembly of Acid Chlorides **1**, Allenes **2**, and Diboron **3**[a]

Entry	R[1]COCl			Product	E/Z	Yield (%)[b,c]
1	**1a**	**2a**	**4a**	R[1] = *p*-MePh		72(82)
2	**1b**	**2a**	**4b**	R[1] = Ph		68(74)
3	**1c**	**2a**	**4b**	R[1] = Ph		67(74)
4	**1d**	**2a**	**4c**	R[1] = *o*-MeOPh		57(72)
5	**1e**	**2a**	**4d**	R[1] = *m*-MeOPh		75(85)
6	**1f**	**2a**	**4e**	R[1] = *p*-MeOPh		61(76)
7	**1g**	**2a**	**4f**	R[1] = *p*-MeO₂CPh		67(81)
8	**1h**	**2a**	**4g**	R[1] = *p*-NO₂Ph		77(88)
9	**1i**	**2a**	**4h**	R[1] = 1-naphthyl		92(99)
10	**1j**	**2a**	**4i**	R[1] = 2-naphthyl		57
11	**1k**	**2a**	**4j**	R[1] = 2-thienyl		71(85)
12	**1l**	**2a**	**4k**	R[1] = 5-isooxazolyl		62(83)
13	**1m**	**2a**	**4l**	R[1] = *t*-BuCH₂		80(88)
14	**1n**	**2a**	**4m**	R[1] = *i*-Bu		63
15	**1o**	**2a**	**4n**	R[1] = Bz		57(72)
16	**1m**	**2b**	**4o**	R[1] = *t*-BuCH₂	99/1	91
17	**1f**	**2b**	**4p**	R[1] = *p*-MeOPh	98/2	70(93)
18	**1i**	**2b**	**4q**	R[1] = 1-naphthyl	99/1	71(96)
19	**1m**	**2c**	**4r**		93/7	77
20	**1m**	**2d**	**4s**		93/7	88
21	**1a**	**2e**	**4t**		98/2	50

[a] All reactions were carried out using acyl chloride (0.55 mmol), bis(pinacolato)diboron (0.50 mmol), allene (1.00 mmol), PdCl₂(CH₃CN)₂ (0.025 mmol), and toluene (2.0 mL) at 80 °C. [b] Isolated yield. [c] Yields determined by the ¹H NMR integration method using mesitylene as an internal standard are shown in parentheses.

In addition to **1a**, a wide range of acyl chlorides **1b**−**o** also react readily with allene **2a** and diboron **3** in the presence of PdCl₂(MeCN)₂. Table 1 summarizes the results of these reactions. Treatment of benzoyl chloride (**1b**) with **2a** and **3** afforded **4b** in 68% yield (entry 2). The same product was obtained in 67% yield for the reaction of benzoyl bromide (**1c**) with **2a** and **3** (entry 3). Aroyl chlorides **1d**−**f** bearing an electron-donating methoxy group at the ortho, meta, and para position react smoothly with **2a** and **3** to give **4c**−**e** in 57, 75, and 61% yields, respectively (entries 4−6). Aroyl chlorides **1g**−**h** with electron-withdrawing groups −CO₂Me and −NO₂ group also undergo three-component reaction efficiently to give **4f** and **4g** in 67 and 77% yields, respectively (entries 7 and 8). The presence of ortho substituent in the aroyl chloride does not significantly affect the product yield (entry 4). As expected, aroyl chlorides with electron-withdrawing groups give higher yield than those with the electron-donating substituents (entries

Scheme 2
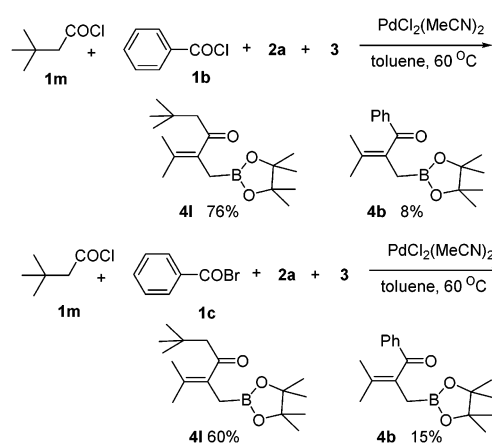
4−8). The reaction with 1-naphthonyl chloride (**1i**) proceeded quantitatively, but the reaction with 2-naphthonyl chloride (**1j**) gave only a moderate yield of 57% (entries 9 and 10). Heteroaromatic acyl chlorides, 2-thiophenecarbonyl chloride (**1k**), and isooxazole-5-carbonyl chloride (**1l**) also participated in the reaction giving **4j** and **4k** in 71 and 62% yields, respectively (entries 11 and 12).

Under similar conditions, alkanoyl chlorides including *tert*-butylacetyl chloride (**1m**), isovaleryl chloride (**1n**), and phenyl-acetyl chloride (**1o**) undergo three-component reaction effectively with **2a** and **3** to afford **4l**−**n** in 80, 63, and 57% yields, respectively (entries 13−15). To our surprise, alkanoyl chlorides react much faster than aroyl chlorides under the standard reaction conditions. The reaction time required for alkanoyl chloride is 2 h, while for aroyl chloride it is 10 h. The difference in reactivity was further demonstrated by the following crossover experiments (Scheme 2). The reaction of the same amounts of acid chlorides benzoyl chloride (**1b**) and *tert*-butylacetyl chloride (**1m**) with **2a** and **3** in the presence of PdCl₂(CH₃CN)₂ in toluene at 60 °C for 10 h afforded the corresponding allylboronates **4b** and **4l** in 8 and 76% yields, respectively. Under similar reaction conditions, benzoyl bromide and *tert*-butylacetyl chloride compete with **2a** and **3** to furnish the corresponding **4b** and **4l** in 15 and 60% yields, respectively. The above results strongly suggest that *tert*-butylacetyl chloride is more reactive than benzoyl chloride and benzoyl bromide in the present acylboration of allene. Although the exact reason for the reactivity difference is not clear, it seems that the insertion of allene into the alkanoyl-Pd bond is faster than into the aroyl-Pd bond.[17]

The present three-component assembling reaction can be further extended to monosubstituted allenes. Thus, the reaction of *n*-butylallene (**2b**) with **1m** and **3** in the presence of PdCl₂(CH₃CN)₂ is highly regio- and stereoselective affording **4o** in a high yield of 91% (entry 16). The stereochemistry of (*E*)-allylboronate **4o** was established by the typical ¹H NMR NOE experiments. The acylboration of *n*-butylallene also proceeded smoothly with acyl chlorides **1f** and **1i** to give products **4p** and **4q**, respectively, with complete regio- and extremely high stereoselectivity (entries 17 and 18). Similarly, the reactions of phenylallene (**2c**) and cyclohexylallene (**2d**) with **1m** and **3** and also *tert*-butylallene (**2e**) with **1a** and **3** provided the corresponding allylboronates **4r**, **4s**, and **4t** in 77, 88, and
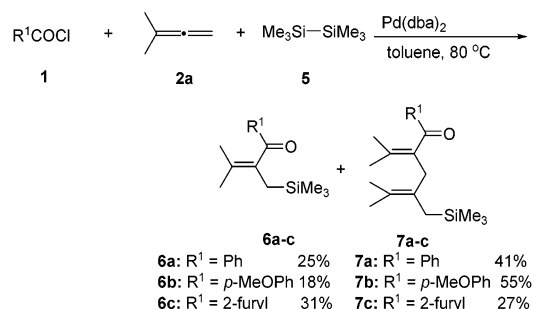
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50% yields with high *E* stereoselectivity (entries 19−21). In all cases, a single or predominately *E* isomer was obtained with an *E/Z* ratio falling in the narrow range 93/7 to 99/1. The stereoselectivity of products appears little affected by the substituent on allenes. However, under similar conditions, the reaction of **1** and **3** with 1,3-substituted allenes PhCHCCHMe or Me$_2$CCCMe$_2$ is extremely slow, and no desired product was observed.
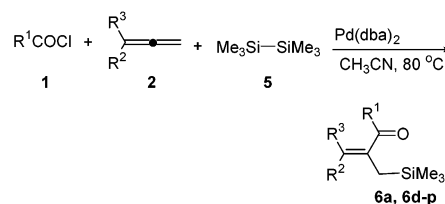
There are several interesting features of the present catalytic reaction. First, all of the phosphine-free palladium-catalyzed acylboration of allenes are completely regioselective and highly stereoselective affording the corresponding 2-acylallylboronates in good to moderate yields. Second, unlike most transition metal-mediated addition reactions of acid chlorides, acyl group regioselectively adds to the allene moiety without decarbonylation.[18] Finally, the catalytic acylboration proceeds smoothly in the absence of base, in contrast to most transmetalation processes of diboron that required the assistance of base.[19]

2.2. Palladium-Catalyzed Acylsilation of Allenes. Transition-metal-catalyzed reactions involving organosilanes are useful for the construction of carbon−carbon bonds in organic synthesis.[20] In particular, allylsilane compounds are extensively used in carbonyl addition reactions[21] and coupling reactions.[22] Recently, allylsilanes were employed as key intermediates for the total syntheses of peduncularine,[23a] citreoviral,[23b] allomuscarine,[23c] epimuscarine,[23c] and serotonin antagonist LY426965.[23d] The synthetic utility of allylsilanes was further demonstrated in the metal-catalyzed reaction with dienes[24] and alkynes.[25] Several methods for the synthesis of allylsilanes catalyzed by transition metal complexes are known. A palladium-catalyzed synthesis of allylsilanes via the coupling of allylic acetates with hexamethyldisilane was reported by Tsuji and co-workers.[26] However, the reaction requires a higher temperature and longer reaction period. The same group also described a palladium-catalyzed decarbonylative coupling of acid chlorides, allenes, and disilanes to give the corresponding allylsilanes.[17] We have recently developed a highly regio- and stereoselective synthesis of allylsilanes by the palladium-catalyzed three-component assembly of allenes, aryl iodides, and silylstannanes.[4a] The

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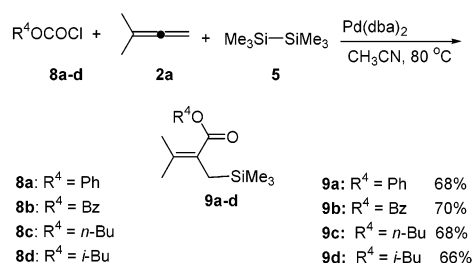**Scheme 3**

6a: R^1 = Ph   25%   **7a:** R^1 = Ph   41%
6b: R^1 = *p*-MeOPh 18%   **7b:** R^1 = *p*-MeOPh 55%
6c: R^1 = 2-furyl   31%   **7c:** R^1 = 2-furyl   27%

Scheme 4

observed acylboration of allenes prompted us to examine the feasibility of acylsilation of allenes. The investigation led successfully to the synthesis of a new class of 2-acylallylsilanes. The results are shown below.

Treatment of **1b** with **2a** and hexamethyldisilane (**5**) in the presence of Pd(dba)$_2$ (5.0 mol %) in toluene at 80 °C for 5 h gave a mixture of products **6a** and **7a** in 25 and 41% yields, respectively (Scheme 3). The spectral data of these products reveal that **6a** is a three-component assembling product of allene, acyl chloride, and disilane, while **7a** is a double-allene insertion product consisting of two molecules of allene, an acyl, and a silyl group. Similarly, reactions with acyl chlorides **1f** and **1p** afforded the corresponding double-allene insertion products **7b** and **7c**, respectively, in addition to the normal three-component assembling products **6b** and **6c**. These results are greatly different from the foregoing acylboration of allenes in which no double-allene insertion occurred.

To improve the selectivity of acylsilation reaction, the effect of solvent and ligand on the reaction of **1b** with **2a** and **5** using Pd(dba)$_2$ as the catalyst was investigated. To our delight, the reaction in CH$_3$CN gave only acylsilation product **6a** in 80% yield with no double-allene insertion product **7a** detected. THF is also a suitable solvent for the acylsilation of allenes, affording **6a** exclusively in 76% yield. However, no catalytic reaction occurred in DMF. At 60 °C, the yield of **6a** is lower (63%) than that obtained at 80 °C. Similar to acylboration of allenes, the presence of phosphine ligands such as 4 equiv of PPh$_3$, 1 equiv of dppe, or 1 equiv of dppf relative to the catalyst strongly retarded the catalytic acylsilation of allenes. On the basis of the above results, it appears that CH$_3$CN and palladium complexes without any phosphine ligand are the solvent and the catalyst of choice, respectively, for three-component assembling of **1b** with **2a** and **5**. Thus, the following reaction conditions, allene (1.00 mmol), acyl chloride (1.00 mmol), disilane (1.20 mmol), Pd(dba)$_2$ (5.0 mol %), CH$_3$CN (2.0 mL), reaction temperature 80 °C, and reaction time 5 h (Scheme 4), were chosen as the general reaction conditions for the acylsilation of allenes.

In addition to **1b**, a series of aroyl chlorides **1** (**1a**, **1h**, **1j**, **1k**, and **1q**) including electron-donating, electron-withdrawing,

Table 2. Results of Palladium-Catalyzed Three-Component Assembly of Acid Chlorides **1**, Allenes **2**, and Disilane **5** in CH$_3$CN[a]

Entry	R^{1}COCl	Allene		Product	E/Z	Yield (%)[b,c]
1	**1b**	**2a**	**6a**	R^1 = Ph		80
2	**1a**	**2a**	**6d**	R^1 = p-MePh		88
3	**1h**	**2a**	**6e**	R^1 = p-NO$_2$Ph		78
4	**1q**	**2a**	**6f**	R^1 = m-NO$_2$Ph		76
5	**1j**	**2a**	**6g**	R^1 = 2-naphthyl		74
6	**1k**	**2a**	**6h**	R^1 = 2-thienyl		77
7	**1r**	**2a**	**6i**	R^1 = p-ClPh		88(97)
8	**1s**	**2a**	**6j**	R^1 = p-BrPh		87(95)
9	**1m**	**2a**	**6k**	R^1 = t-BuCH$_2$		57
10	**1t**	**2a**	**6l**	R^1 = t-Bu		43
11	**1u**	**2a**	**6m**	R^1 = n-Bu		47
12	**1a**	**2b**	**6n**		1/99	88(95)
13	**1a**	**2d**	**6o**		1/99	87(95)
14	**1a**	**2c**	**6p**		30/37	67

[a] All reactions were carried out using acyl chloride (1.00 mmol), allene (1.00 mmol), disilane (1.20 mmol), Pd(dba)$_2$ (0.05 mmol), and CH$_3$CN (2.0 mL) at 80 °C. [b] Isolated yield. [c] Yields determined by the ^{1}H NMR integration method using mesitylene as an internal standard are shown in parentheses.

and heteroaromatic chlorides all undergo three-component assembling reactions with **2a** and **5** in the presence of Pd(dba)$_2$ in CH$_3$CN affording the corresponding 2-acylallylsilanes **6d**−**h** in good to moderate yields (Table 2, entries 2−6). The catalytic acylsilation reaction is highly chemoselective as evidenced by the results in entries 7 and 8. Under similar reaction conditions, 4-chlorobenzoyl chloride (**1r**) as well as 4-bromobenzoyl chloride (**1s**) react chemoselectively with **2a** and **5** to afford the corresponding 2-acylallylsilanes **6i** and **6j** in 88 and 87% yields, respectively. These observations clearly suggest that the oxidative addition of the ArCO−Cl bond is faster than that of the Ar−Cl or Ar−Br bond to Pd(0). In addition to aroyl chlorides, alkanoyl chlorides including *tert*-butylacetyl chloride (**1m**), *tert*-butylcarbonyl chloride (**1t**), and *n*-butylcarbonyl chloride (**1u**) undergo three-component assembling with **2a** and **5** to afford the corresponding allylsilane products **6k**−**m**, albeit in lower yields than those from aroyl chlorides (entries 9−11).

The catalytic reaction is also successfully applied to mono-substituted allenes. Thus, *n*-butylallene (**2b**) reacted with **1a** and disilane **5** to furnish the three-component assembly product **6n** in 88% yield (Table 2, entry 12). The catalytic reaction is highly regio- and stereoselective; no other isomer was detected in the ^{1}H NMR spectrum of the crude reaction mixture. The Z stereochemistry of allylsilane **6n** was established by ^{1}H NMR NOE techniques. The reaction with cyclohexylallene (entry 13) is also highly stereoselective giving (Z)-**6o** as the sole product, but the reaction with phenylallene is less stereoselective affording **6p** with an E/Z ratio of 30:37 (entry 14).

Scheme 5

8a: R^4 = Ph
8b: R^4 = Bz
8c: R^4 = n-Bu
8d: R^4 = i-Bu

9a: R^4 = Ph   68%
9b: R^4 = Bz   70%
**9c**: R^4 = n-Bu 68%
9d: R^4 = i-Bu 66%

Similar to acyl chlorides, chloroformates can also be used as the electrophiles in the catalytic three-component assembling of allenes (Scheme 5). Various chloroformates including phenyl chloroformate (**8a**), benzyl chloroformate (**8b**), *n*-butyl chloroformate (**8c**), and isobutyl chloroformate (**8d**) reacted with **2a** and **5** in the presence of Pd(dba)$_2$ in CH$_3$CN to furnish the corresponding allylsilanes **9a**−**d** in 68, 70, 68, and 66% yields, respectively. In all cases, the R^{4}OCO− and silyl groups are added to the middle and to the terminal carbons, respectively, of allene **2a**, indicating that the catalytic reaction is completely regioselective. It is noteworthy that this is the first time chloroformates are employed as electrophiles in the three-component assembling reaction of allenes.

In addition to the observed high regio- and stereoselectivity, two intriguing features merit comment for the present acyl-silation of allenes. First, there is no decarbonylation product observed in all reactions. For comparison, in the previous palladium-catalyzed three-component reaction of acyl chlorides, disilanes, and 1,3-dienes reported by Tsuji et al., decarbonylative coupling products were formed.[17] Second, no direct coupling product between disilane and acid chloride was found under the reaction conditions. It is to be noted that direct coupling of disilanes with acid chlorides catalyzed by palladium complexes occurs readily as reported in the literature.[27]

2.3. Palladium-Catalyzed Acylstannation of Allenes. Allylstannanes are versatile synthetic reagents[28] that have been used as key intermediates in the total syntheses of pseudopterolide[29a,b] and epothilones B and D.[29b] In addition, allylstannanes are extensively employed in coupling reactions[30] and allylation reactions with aldehydes.[21,31] A traditional route to allylstannanes involves palladium-catalyzed couplings of allylic acetates with Et$_2$AlSnBu$_3$,[32] ditin,[33] and Bu$_3$SnCl.[34] However, the utility of these reactions is limited by the poor regio- and stereoselectivity. Another palladium-catalyzed synthesis of allylstannanes is the coupling of allylic phosphates with

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Table 3. Results of Palladium-Catalyzed Three-Component Assembly of Acid Chlorides **1**, Dimethylallene (**2a**), and Ditin **10**[a]

Entry	R[1]COCl		Product	Yield (%)[b]
1	**1a**	**11a**	R[1] = *p*-MePh	70
2	**1g**	**11b**	R[1] = *p*-MeO$_2$CPh	70
3	**1h**	**11c**	R[1] = *p*-NO$_2$Ph	65
4	**1q**	**11d**	R[1] = *m*-NO$_2$Ph	53
5	**1k**	**11e**	R[1] = 2-thienyl	18
6	**1r**	**11f**	R[1] = *p*-ClPh	80
7	**1s**	**11g**	R[1] = *p*-BrPh	75
8	**1j**	**11h**	R[1] = 2-naphthyl	45
9	**1m**	**11i**	R[1] = *t*-BuCH$_2$	55
10	**1t**	**11j**	R[1] = *t*-Bu	40

The product structure shows: R[1]-C(=O)-C(=CH$_2$... with CH$_3$ and CH$_2$SnBu$_3$ groups (2-acylallylstannane).
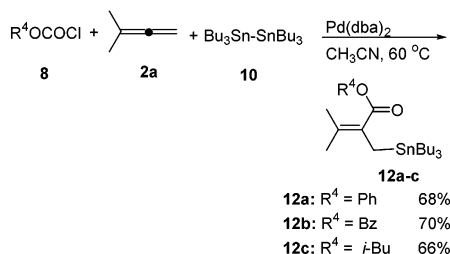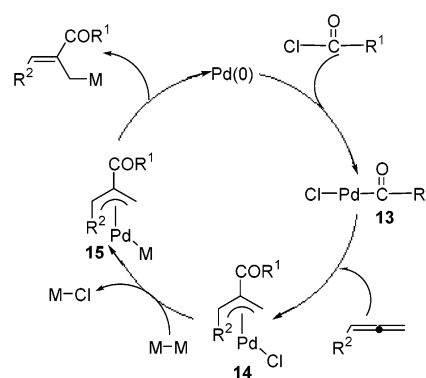
[a] All reactions were carried out using acyl chloride (1.00 mmol), allene (1.50 mmol), Pd(dba)$_2$ (0.05 mmol), CH$_3$CN (1.0 mL), and ditin (1.00 mmol) in CH$_3$CN (1.0 mL), which was added slowly by syringe pump over a period of 4 h at 60 °C. [b] Isolated yield.

Et$_2$AlSnBu$_3$ reported by Oshima and co-workers.[35] Recently, we developed a highly regio- and stereoselective method for the synthesis of allylic stannanes by the palladium-catalyzed addition of silylstannanes to allenes.[36]

The acylstannation of allenes catalyzed by nickel complexes is known in the literature.[37] The catalytic reaction involves addition of acylstannes to allenes to furnish α-(acylmethyl)-vinylstannanes. To the best of our knowledge, no example using palladium-catalyzed acylstannation of allenes has been reported. The present three-component reaction can be successfully extended to the synthesis of 2-acylallylstannanes. The results of this study are summarized in Table 3.

Under conditions similar to the acylboration and acylsilation of allenes, treating **1a** with **2a** and hexabutylditin (**10**) in the presence of Pd(dba)$_2$ in CH$_3$CN at 60 °C afforded only a trace amount of three-component assembling product, 2-acylallyl-stannane **11a**. Instead, the major product is tributyl(4-methyl-benzoyl)stannane formed by a direct coupling of acyl chloride **1a** with ditin **10**. The observation is surprising in view of the previously successful results of acylboration and acylsilation of allenes. The formation of direct coupling product (4-meth-ylbenzoyl)stannane suggests that the allene insertion step is relatively slow compared to the reaction of acyl group with ditin (vide infra). The competing direct coupling reaction was effectively suppressed by a slow addition of ditin **10** over a period of 4 h to the reaction mixture of **1a** and **2a** affording three-component acylstannation product **11a** in 70% yield (Scheme 6, Table 3, entry 1).

Several aroyl chlorides **1** (**1g**, **1h**, **1j**, **1k**, and **1q**−**s**) also react smoothly with **2a** and **10** to give the corresponding 2-acylallylstannanes **11b**−**h** in good to moderate yields (Table 3, entries 2−8). The catalytic acylstannation reaction tolerates a variety of functional groups such as ester, nitro, sulfur, chloro, and bromo on the aromatic ring of the aroyl chlorides (entries

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Scheme 6

Scheme 7

12a: R[4] = Ph   68%
12b: R[4] = Bz   70%
12c: R[4] = *i*-Bu   66%
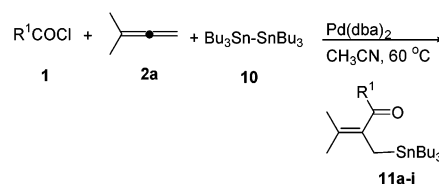
Scheme 8

2−7). Like acylsilation of allenes, the present acylstannation reaction is highly chemoselective (entries 6 and 7). Alkanoyl chlorides, **1m** and **1t** also react effectively with **2a** and **10** to give acylstannation products **11i** and **11j** in 55 and 40% yields, respectively (entries 9 and 10). In addition to 2-acylallylstan-nanes, the direct coupling product from acyl chloride and ditin was formed, but in less than 5% yield in all cases. There is no desired three-component product observed with monosubstituted allenes such as phenylallene and cyclohexylallene. The reaction was messy giving unidentified products as seen in the ^{1}H NMR spectrum of the crude reaction mixture.

In addition to acyl chlorides, chloroformates also have been successfully employed in the three-component stannation of allenes (Scheme 7). The reaction of **8a**, **8b**, and **8d** with **2a** and **10** in the presence of the Pd(dba)$_2$/CH$_3$CN system furnished the corresponding allylstannanes **12a**−**c** in 68, 70, and 66% yields, respectively.

3. Mechanistic Consideration

On the basis of the known palladium chemistry and the foregoing results, a plausible mechanism is proposed in Scheme 8 to account for the present three-component assembling reactions. The catalytic reaction is likely initiated by the oxidative addition of acyl chloride to Pd(0) to give acyl Pd(II) intermediate **13**. Coordination followed by insertion of allene to the Pd-carbon bond produces π-allylpalladium(II) species **14**. Transmetalation of **14** with bimetallic reagents (B−B, Si−Si, and Sn−Sn) and subsequent reductive elimination of **15** yield the final product and regenerate the Pd(0) catalyst.
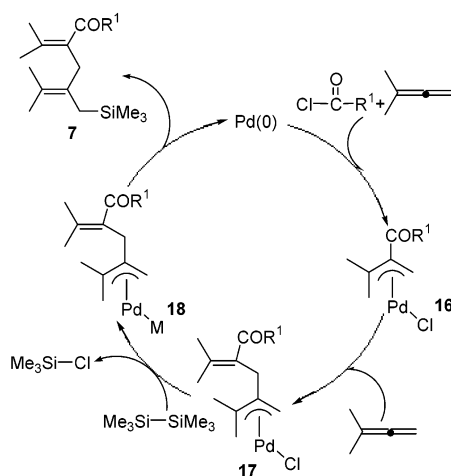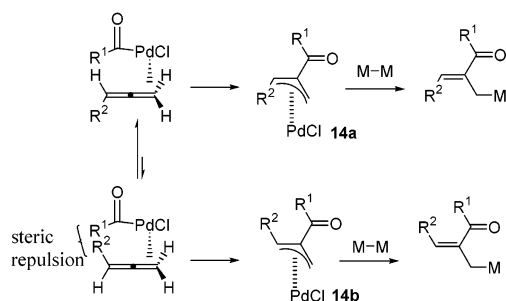
Scheme 9

Scheme 10

A modification of the mechanism shown in Scheme 8 can account for the formation of double-allene insertion product **7**. Intermediate **16** instead of undergoing transmetalation may further react with another allene molecule via coordination and then insertion to give a new π-allylpalladium complex **17** as depicted in Scheme 9. Transmetalation of **17** with disilane affords intermediate **18**. Subsequent reductive elimination of **18** gives double-insertion product **7** and regenerates the Pd(0) catalyst.

The highly stereoselective formation of either *E* or *Z* isomers from monosubstituted allenes is an attractive feature of the present methodology. It is to be noted that most carbopalladation reactions of monosubstituted allenes gave a mixture of *E* and *Z* isomeric products with a low degree of selectivity.[38] To account for the high stereoselectivity, a mechanism involving face-selective coordination of allenes to the palladium center is proposed (Scheme 10). The terminal double bond of allene is bonded to the palladium moiety at the face opposite to the substituents R^2 favorably to avoid steric congestion. On the other hand, coordination of the terminal double bond of allene to the palladium center at the other face with R^2 syn to the palladium center or coordination of the internal double bond of allene to the palladium center will lead to an increase of steric repulsion and is less likely. As shown in Scheme 10, the face-selective coordination results in a π-allylpalladium species **14a** with the R^2 group anti to the acyl moiety. Further reaction with bimetallic reagents (B−B, Si−Si, Sn−Sn) affords 2-acylallylmetal reagents

with high stereoselectivity. It is necessary that the latter step is faster than the syn−anti rearrangement of the π-allylpalladium species to obtain high stereoselectivity. The anti form of **14a** is responsible for the high stereoselectivity of the present catalytic reaction. In the reported phosphine-palladium-mediated three-component reaction of allenes,[5,6] the observed low stereoselectivity is probably due to the rapid syn−anti rearrangement of the π-allylpalladium species through a σ-allylpalladium intermediate assisted by the phosphine ligands.[39]

The same proposed mechanism in Scheme 8 satisfactorily accounts for the acylboration, acylsilation, and acylstannation of allenes, but the relative rate of each step in the catalytic cycle may be different for each of these three-component assembling reactions. For the acylboration, acylsilation, and acylstannation of allenes, the rates of oxidative addition of acyl chloride to Pd(0) to give **13** and the insertion of allene into the acyl-palladium(II) bond in **13** are expected to be the same for all these reactions, if the same catalyst and solvent were used for the catalytic reactions. On the other hand, the transmetalation step is different for different acylmetalation reactions of allene. Based on the foregoing observations that (i) only three-component acylboration of allene took place in toluene; (ii) double insertion of allene occurred for acylsilation of allene in toluene; and (iii) slow addition of ditin **10** is necessary to achieve successful acylstannation of allene, we can conclude that the relative rate of transmetalation is ditin **10** > diboron **3** > disilane **5**.

Although the reason for the exclusive formation of acylsilation product in CH$_3$CN or THF is not entirely clear, it is likely that these molecules are coordinated to the palladium center, for instance, to intermediate **14** in Scheme 8. The coordinating ability and the high concentration of these solvent molecules prevent further bonding of a second allene molecule to the palladium complex and completely inhibit the double-allene insertion process.

The facile formation of 2-acylallylic metal reagents without decarbonylation is an important characteristic feature of the present acylmetallation reactions. The results indicate that, in the present three-component assembling reactions, the addition of the acyl-palladium bond to allene is faster than decarbonylation of the acyl-palladium intermediate. However, in the palladium-catalyzed decarbonylative reaction of acid chlorides, disilanes, and 1,3-dienes reported by Tsuji, the acyl-palladium intermediate readily undergoes decarbonylation prior to addition to 1,3-dienes.[17] The facile insertion of allenes into an acyl-palladium(II) bond can be attributed to the highly energetic carbon−carbon double bonds of allenes (1,2-dienes) relative to those of 1,3-dienes.

4. Conclusions

We have successfully developed a new phosphine-free palladium-catalyzed three-component assembly of allenes, acyl chlorides, and bimetallic reagents (B−B, Si−Si, and Sn−Sn). This method leads to a new class of 2-acylallylmetal reagents in good to moderate yields. This is the first time that acyl chlorides are used as electrophiles in the three-component coupling reactions of allenes. In addition, chloroformtes are also used for the first time in these reactions. It is noteworthy that

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no decarbonylative coupling product was observed in all of these reactions. The acylboration of allenes proceeds smoothly in the absence of base. For acylsilation of allenes, CH_3CN appears to be the best solvent to achieve exclusive three-component acylsilation product, while, in toluene, acylsilation of allenes afforded a mixture of three-component acylsilation and double-allene insertion products. The successful acylstannation reaction was realized by the slow addition of ditin reagent to the reaction mixture of allene and acyl chloride. The presence of phosphine ligands strongly retarded the present 2-acylallylmetalation reaction. The methodology is compatible with a wide variety of functional groups tested. The catalytic reaction is completely regioselective in which the acyl group and metal add to the middle and unsubstituted terminal carbon of the allene moiety, respectively. In addition, the reaction is highly stereoselective in the case of monosubstituted allenes. The mechanism involving a face-selective coordination of allenes is proposed to account for the high stereoselectivity.

5. Experimental Section

General Considerations. All reactions were run under a nitrogen atmosphere on a dual-manifold Schlenk line, unless otherwise mentioned, and in oven-dried glassware. All solvents were dried according to known methods and distilled prior to use.[40] $PdCl_2(CH_3CN)_2$,[41] Pd-$(dba)_2$,[42] and allenes[43] were prepared by procedures previously reported. Reagents and chemicals were used as purchased without further purification. The purity of each product was checked by NMR analysis.

General Procedure for the Three-Component Assembly of Acyl Halide 1, Allene 2, and Diboron 3. To a 25-mL sidearm flask were added acyl chloride (0.55 mmol), $PdCl_2(CH_3CN)_2$ (0.025 mmol, 5.0 mol %), and bis(pinacolato)diboron (**3**) (0.50 mmol). The system was evacuated and purged with nitrogen 3 times. Allene (1.00 mmol) in toluene (2.0 mL) was added to the system, and the reaction mixture was stirred at 80 °C. After completion of the reaction (the time required for aroyl chloride is ~10 h, and for alkanoyl chloride, it is ~2 h), toluene (50 mL) was added to the reaction solution and the mixture was washed with brine (25 mL) 3 times. The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was distilled over Kugelrohr oven to give the desired product. Compounds **4a**−**t** were prepared according to this method. The product yield of each reaction is listed in Table 1.

Competitive Reaction of *tert*-Butylacetyl Chloride (1m) and Benzoyl Chloride (1b) or Benzoyl Bromide (1c) with Allene 2a and Diboron 3. To a 25-mL sidearm flask were added $PdCl_2(CH_3CN)_2$ (0.025 mmol, 5 mol %) and bis(pinacolato)diboron (**3**) (0.50 mmol). The system was evacuated and purged with nitrogen 3 times. *tert*-Butylacetyl chloride (0.25 mmol), benzoyl chloride (0.25 mmol) or benzoyl bromide (0.25 mmol), and 1,1-dimethylallene (1.00 mmol) in toluene (2.0 mL) were added to the system, and the reaction mixture

was stirred at 60 °C for 10 h. The crude reaction mixture was diluted with toluene (50 mL), and the mixture was washed with brine (25 mL) 3 times. The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The yields of **4b** and **4l** were determined by the ^{1}H NMR integration method using mesitylene as an internal standard.

General Procedure for the Reaction of Acyl Chloride 1 with Allene 2a, and Disilane 5 in Toluene. To a 25-mL sidearm flask was added $Pd(dba)_2$ (0.050 mmol). The system was evacuated and purged with nitrogen several times. Acyl chloride (1.00 mmol), dimethylallene (1.00 mmol), hexamethyldisilane (1.20 mmol), and toluene (2.0 mL) were added to the system, and the reaction mixture was stirred at 80 °C for 5 h. The crude reaction mixture was diluted with CH_2Cl_2 (50 mL), filtered through Celite and silica gel, and concentrated in vacuo. The residue was chromatographed on a silica gel column (hexane/EtOAc = 9/1) to give products **6** and **7**. Compounds **6a**−**c** and **7a**−**c** were prepared according to this method. The product yield of each reaction is listed in Scheme 3.

General Procedure for the Three-Component Assembly of Acyl Chloride 1 or Chloroformate 8, Allene 2, and Disilane 5 in CH_3CN. To a 25-mL sidearm flask was added $Pd(dba)_2$ (0.050 mmol). The system was evacuated and purged with nitrogen several times. Acyl chloride (1.00 mmol) or chloroformate (1.00 mmol), allene (1.00 mmol), hexamethyldisilane (1.20 mmol), and CH_3CN (2.0 mL) were added to the system, and the reaction mixture was stirred at 80 °C for 5 h. The crude reaction mixture was diluted with CH_2Cl_2 (50 mL), filtered through Celite and silica gel, and concentrated in vacuo. The residue was chromatographed on a silica gel column (hexane/EtOAc = 9/1) to give the desired product. Compounds **6a**, **6d**−**p**, and **9a**−**d** were prepared according to this method. The product yield of each reaction is listed in Table 2 and Scheme 5.

General Procedure for the Three-Component Assembly of Acyl Chloride 1 or Chloroformate 8, Allene 2a, and Ditin 10. To a 25-mL sidearm flask was added $Pd(dba)_2$ (0.050 mmol). The system was evacuated and purged with nitrogen several times. Acyl chloride (1.00 mmol) or chloroformate (1.00 mmol), allene (1.50 mmol), and CH_3-CN (1.0 mL) were added to the system, and the reaction mixture was stirred at 60 °C. Hexabutylditin (1.00 mmol) in CH_3CN (1.0 mL) was added slowly by syringe pump over a period of 4 h. After the injection was completed, the reaction was stirred for another 0.5 h. The crude reaction mixture was diluted with CH_2Cl_2 (50 mL), filtered through Celite and silica gel and concentrated in vacuo. The residue was chromatographed on a silica gel column (hexane/EtOAc = 9/1) to give the desired three-component assembly product. Compounds **11a**−**j** and **12a**−**c** were prepared according to this method. The product yield of each reaction is listed in Table 3 and Scheme 7. The spectral data of these allylmetal reagents are given in the Supporting Information.

Supporting Information Available: Spectral data for compounds **4a**−**t**, **6a**−**p**, **7a**−**c**, **9a**−**d**, **11a**−**j**, and **12a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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