 

# Accounts

## Transition Metal-Catalyzed Carbostannylation of Alkynes and Dienes

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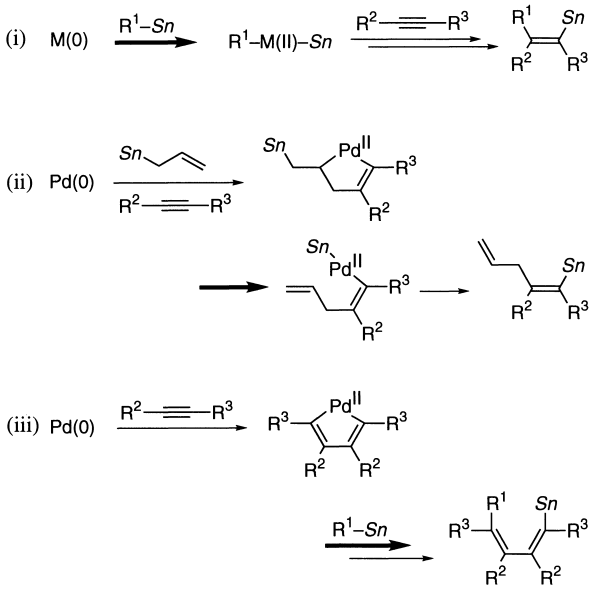
(Received December 14, 2001)

Carbon–tin bonds in alkynyl-, allyl-, acyl-, alkenyl-, and arylstannanes were found to add to carbon–carbon unsaturated bonds of alkynes, 1,3-dienes and 1,2-dienes in the presence of a catalytic amount of palladium or nickel complexes to give alkenyl- or allylstannanes having various functional groups. Mechanisms are proposed that start with oxidative addition of a carbon–tin bond, or palladacycle formation followed by $\beta$-tin elimination or by the reaction with an organostannane.

Organostannanes are widely used synthetic precursors that react with various organic electrophiles in the presence of appropriate activators.[1] Due to the modest nucleophilicity of organostannanes, the palladium-catalyzed cross-coupling reaction of organostannanes proceeds with tolerance toward various functional groups, being called the Kosugi–Migita–Stille reaction, and has become one of the most important carbon–carbon bond forming reactions.[1,2] Easy handling and high chemoselectivity of allylstannanes are utilized for the reaction with Lewis acid-activated carbonyl groups.[1,3] Organostannanes are usually prepared by a method involving the reaction of trialkyltin halides with other organometallic reagents. This works well particularly for syntheses of simple ones. However, organostannanes having an electrophilic functional group like a carbonyl or hydroxy group cannot be obtained by the method without troublesome protection and deprotection steps. By appropriate activation of carbon–tin bonds, carbostannylation of unsaturated bonds would be possible, we considered, giving organostannanes of much more complex structures with labile functional groups. When we started our study on the carbostannylation of alkynes, however, there were only two precedents:[4,5,6] both were limited to allylstannanes and afforded *anti*-adducts without any late transition metal catalyst. For example, Yamamoto and his co-workers reported the Lewis acid-catalyzed allylstannylation of alkynes, using Lewis acids to activate carbon–carbon triple bonds.[7] On the other hand, Hosomi's group disclosed the radical reaction of allylstannanes with alkynes or alkenes initiated by AIBN and obtained the corresponding *anti*-allylstannylation products.[8]

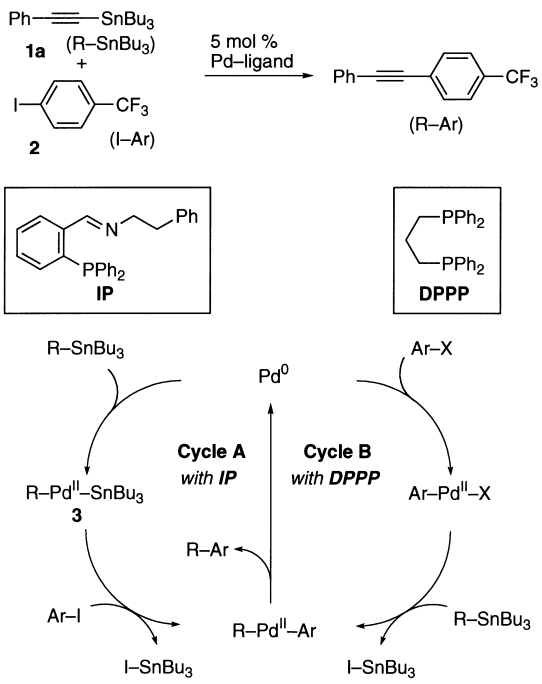
In this account, we briefly summarize a novel synthetic methodology through the palladium- or nickel-catalyzed carbostannylations of unsaturated carbon–carbon bonds of alkynes, 1,3-dienes, and 1,2-dienes. The synthetic transformations have been accomplished on the basis of a new concept for cleavage of carbon–tin bonds by transition metal complexes and are considered to work through (Scheme 1): (i) oxidative addition of carbon–tin bonds to a palladium(0) or nickel(0) complex, (ii) $\beta$-tin elimination from palladacyclopent-2-enes generated by oxidative cyclization of allylstannanes and alkynes with a palladium(0) complex, or (iii) reaction of organostannanes with palladacyclopentadienes derived from two molecules of alkynes and a palladium(0) complex.




Scheme 1.

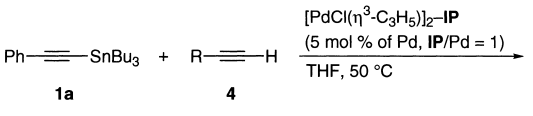
## 1. Carbostannylation of Alkynes

Before our discovery of the carbostannylation of carbon–carbon unsaturated bonds, we had been studying the cross-coupling reaction of alkynylstannane **1a** with aryl iodide **2** using a palladium(0) complex and *N*-(2-diphenylphosphinobenzylidene)-2-phenylethylamine (**IP**)[9] ligand and had observed that the reaction proceeded through oxidative addition of the alkynylstannane to a palladium(0)–**IP** complex (Cycle A in Scheme 2).[10,11,12] The mechanism contrasts sharply to the well-accepted catalytic cycle of the cross-coupling reaction with organostannanes as well as with other organometallic compounds, a reaction documented to start with oxidative addition of an aryl halide (Cycle B in Scheme 2).[2,13] A palladium complex with 1,3-bis(diphenylphosphino)propane (**DPPP**) also was found to undergo the oxidative addition with **1a**, but the resulting oxidative adduct in this case did not participate in the reaction; the reaction actually proceeds via Cycle B! This observation was the first demonstration that a carbon–tin bond could add oxidatively to a palladium(0) complex,[14] whereas oxidative addition of carbon–tin bonds to platinum(0) complexes had some precedents.[15] We envisaged that oxidative adduct **3** might react with alkynes to give alkynylstannylation products. Gratifyingly, the expected alkynylstannylation reaction of alkynes did proceed highly effectively. Subsequently, allyl- and acylstannylations of alkynes were disclosed.




Scheme 2.

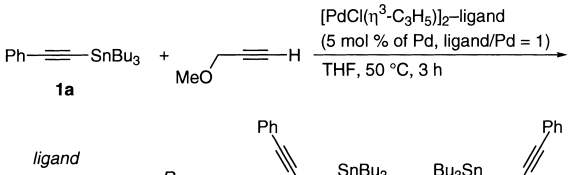
**1-1. Alkynylstannylation.**[16] We first examined the reaction of **1a** under an acetylenic atmosphere (1 atm) in THF (50 °C, 2 h) in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$–**IP** (5 mol% of Pd, Pd/**IP** = 1) to find that alkynylstannylation product tributyl[(*Z*)-2-(phenylethynyl)ethenyl]tin was obtained in 81% yield (Eq. 1). Use of triphenylphosphine or **DPPP** as a ligand lowered the yield even after a prolonged reaction period. The Pd–**IP** catalyst was applicable also to the stereoselective alkynylstannylation with arylacetylenes, conjugated ynoates, propargyl (2-propynyl) amides and propargyl ethers, and the corresponding products were isolable in high yields as mixtures (**5** and **6**) of regioisomers.

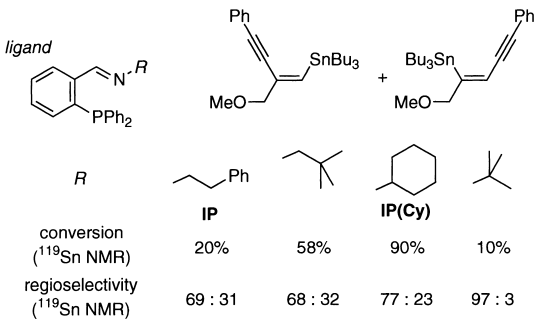



(1)

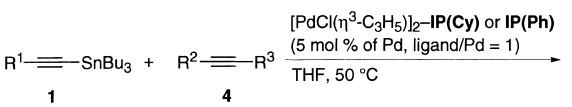
| R | time | yield | **5** : **6** |
|---|---|---|---|
| H | 2 h | 81% | – |
| Ph | 21 h | 81% | 92 : 8 |
| $MeOCH_2$ | 96 h | 67% | 67 : 33 |
| $CO_2Et$ | 3 h | 78% | 20 : 80 |

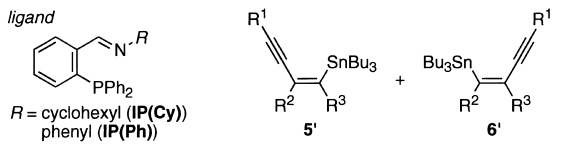
Substituent *R* on nitrogen of the iminophosphine ligands markedly affected the regioselectivity and reaction rate. A ligand with bulkier *R* accelerated the reaction of methyl propargyl ether with **1a** and increased the regioselectivity as shown in Eq. 2, although *t*-butyl turned out to be too bulky and retarded the reaction. Iminophosphine **IP(Cy)** derived from cyclohexylamine (*R* = *c*-Hex) turned out to be a well-balanced ligand in view of activity and selectivity, and was effective also for the reaction of propargyl amides and arylacetylenes. However, the reaction of ethyl propiolate with **1a**, giving regioisomeric ratios opposite to those of propargyl ethers and arylacetylenes, proceeded faster with a palladium complex of phenyl-substituted iminophosphine **IP(Ph)**. Selected results of alkynylstannylation of various alkynes using Pd–**IP(Cy)** or Pd–**IP(Ph)** are summarized in Eq. 3 and Table 1.




(2)




(3)

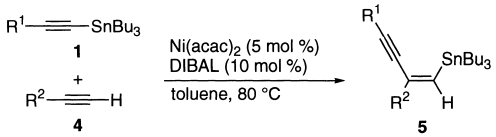
A nickel(0) complex prepared in situ from $Ni(acac)_2$ and hydridodiisobutylaluminum (1:2) also catalyzes the *syn*-selective addition of alkynylstannanes to terminal alkynes (Eq. 4 and

Table 1. Alkynylstannylation of Alkynes[a)]

| Entry | $R^1$ | $R^2$ | $R^3$ | Ligand | Time/h | Yield/%[b)] | **5′**:**6′**[c)] |
|---|---|---|---|---|---|---|---|
| 1 | Ph | $MeOCH_2$ | H | **IP(Cy)** | 5 | 81 | 79 : 21 |
| 2[d)] | | H | H | **IP(Cy)** | 1 | 70 | — |
| 3 | | $AcNHCH_2$ | H | **IP(Cy)** | 3 | 71 | 88 : 12 |
| 4 | | $(CH_2CO)_2NCH_2$ | H | **IP(Cy)** | 3 | 77 | 90 : 10 |
| 5 | | Ph | H | **IP(Cy)** | 5 | 73 | > 99 : 1 |
| 6 | | 4-$MeC_6H_4$ | H | **IP(Cy)** | 6 | 70 | 97 : 3 |
| 7[e)] | | EtO | H | **IP(Cy)** | 5 | 58 | > 99 : 1 |
| 8[f)] | | EtOCO | Me | **IP(Cy)** | 93 | 29 | 1 :> 99 |
| 9 | | EtOCO | H | **IP(Ph)** | 1 | 71 | 7 : 93 |
| 10 | | Ac | H | **IP(Cy)** | 1 | 83 | 13 : 87 |
| 11[d)] | Bu | H | H | **IP(Cy)** | 2 | 88 | — |
| 12 | | Ph | H | **IP(Cy)** | 12 | 86 | > 99 : 1 |
| 13 | | EtOCO | H | **IP(Ph)** | 24 | 62 | 7 : 93 |

a) The reaction was carried out in THF (3 mL) at 50 °C using an alkynylstannane (0.34 mmol) and an alkyne (1.0 mmol) in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (8.2 μmol), and **IP(Cy)** or **IP(Ph)** (0.016 mmol). b) Isolated yields based on the alkynylstannane. c) Determined by $^1H$ or $^{119}Sn$ NMR. d) The reaction was carried out under an acetylene atmosphere (1 atm). e) Ethoxyacetylene (0.34 mmol) was used. f) Solvent = dioxane, temperature = 90 °C.

Table 2). The most characteristic feature of the nickel catalyst is high regioselectivity, where the stannyl group of alkynylstannanes exclusively attacks the terminal acetylenic carbon. Although the nickel complex cannot catalyze the addition to electron-deficient alkynes, the palladium catalyst discussed above can complement the reaction with such substrates.



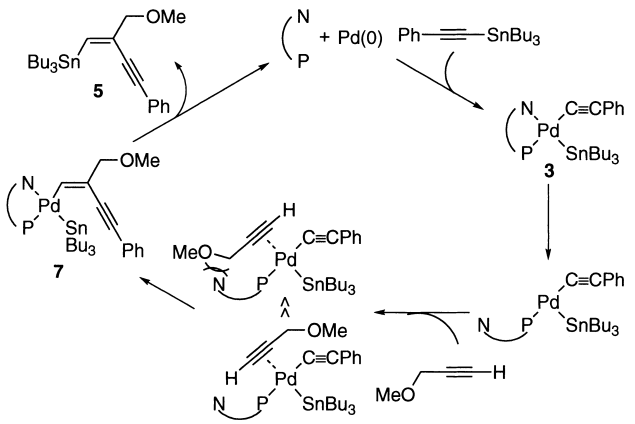

(4)

Table 2. Alkynylstannylation of Alkynes[a)]

| Entry | $R^1$ | $R^2$ | Time/h | Yield/% |
|---|---|---|---|---|
| 1 | Ph | Hex | 24 | 72 |
| 2 | 2-$CF_3$-$C_6H_4$ | Hex | 4 | 82 |
| 3 | 4-$CF_3$-$C_6H_4$ | Hex | 10 | 70 |
| 4 | 4-MeO-$C_6H_4$ | Hex | 36 | 56 |
| 5 | 4-$CF_3$-$C_6H_4$ | Cyclohexen-1-yl | 5 | 79 |

a) The reaction was carried out in toluene (0.5 mL) at 80 °C using an alkynylstannane (0.76 mmol) and an alkyne (2.3 mmol) in the presence of a Ni(0) catalyst prepared in situ from $Ni(acac)_2$ (38 μmol) and a 1.5 M toluene solution of hydridodiisobutylaluminum (76 μmol). b) Isolated yield based on the alkynylstannane.

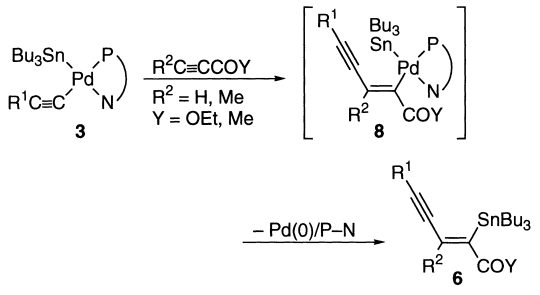
Since alkynylstannanes can oxidatively add to palladium–iminophosphine complexes with ease, it seems pertinent to assume that the catalytic cycle of the palladium-catalyzed alkynylstannylation is initiated by this process, though the following steps may differ depending on the structure of the alkynes. On the basis of ligand effects on reaction rate and regioselectivity, we have proposed a catalytic cycle in Scheme 3 for the palladium-catalyzed reaction of such alkynes as propargyl ethers and arylacetylenes. Oxidative addition of phenylethynylstannane **1a** to a palladium(0) complex gives palladium(II)




Scheme 3.

complex **3**, with the phenylethynyl group being located *cis* to the imino moiety as we reported before.[10] Subsequently, an alkyne, methyl propargyl ether here, would coordinate to a vacant coordination site generated by dissociation of the imino group from palladium,[17] insert into the C–Pd bond (carbopalladation) of **3**, and then undergoes reductive elimination to afford the alkynylstannylation products, regenerating the palladium(0) complex. Such a bulky substituent as a cyclohexyl group in **IP(Cy)** is assumed to facilitate dissociation from the palladium center and to accelerate alkyne insertion. Although the dissociation might be easier with the *t*-butyl-substituted iminophosphine, excessive bulkiness of *t*-Bu appears to inhibit the coordination of an alkyne and to retard the reaction. The bulkiness is definitely attributed also to the high regioselectivity. Thus, the steric repulsion between a methoxymethyl group of the alkyne and the nitrogen substituent in iminophosphines unfavorably influences the reaction efficiency but favorably influences the regioselectivity.

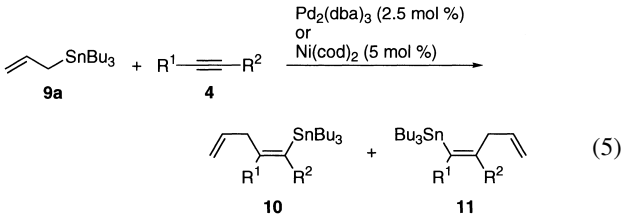
Electron-deficient alkynes are likely to undergo Michael-type addition of an alkynyl group (Scheme 4), giving **6** predominantly through alkenylpalladium complex **8**. At present,




Scheme 4.

it is not clear why higher regioselectivity was observed with **IP(Ph)** than with any other iminophosphine ligands. We do not have any indications to clarify the reaction mechanism of the nickel-catalyzed alkynylstannylation; the catalytic cycle should at least include oxidative addition of an alkynylstannane to a nickel(0) complex.

**1-2. Allylstannylation.**[18,16b] Allylstannylation of alkynes also can be catalyzed by a palladium or nickel complex. Results summarized in Eq. 5 and Table 3 show that zero-valent




(5)

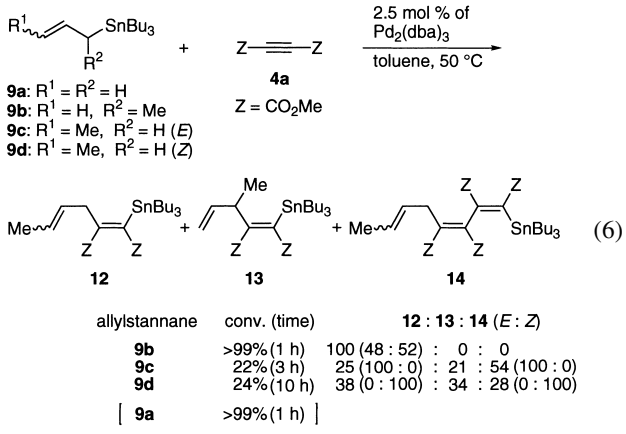
metals of nickel ($Ni(cod)_2$) and palladium ($Pd_2(dba)_3$) without any ligand do catalyze but again complement each other about the scope of alkynes. The nickel catalyst allows most types of alkynes to participate in the reaction, whereas the palladium catalyst is effective only for highly electron-deficient alkynes. $Ni(cod)_2$ is more sensitive to the electronic character of $R^1$ or $R^2$ (Eq. 5) than $Pd_2(dba)_3$, which favors the formation of Michael-type products. Representative examples with ethyl 2-butynoate can be seen in entries 4, 12, and 13.

The reaction of substituted allylstannanes has provided us with an important clue to the mechanism of the palladium-catalyzed allylstannylation of alkynes. Dimethyl acetylenedicarboxylate (**4a**) reacted with three isomers **9b**, **9c**, and **9d** of butenyl(tributyl)tins in the presence of 2.5 mol% of $Pd_2(dba)_3$. Results are summarized in Eq. 6. $\alpha$-Methylallylstannane **9b** adds to **4a**, forming a bond exclusively at its $\gamma$-position. Regioisomers of **9b**, (*E*)-2-buten-1-yl(tributyl)tin (**9c**) and (*Z*)-2-buten-1-yl(tributyl)tin (**9d**), reacted with **4a** in different manners, giving roughly equal amounts of $\alpha$- and $\gamma$-adducts (**12** and **13**) in addition to dimerization–carbostannylation product **14**. The configuration of the crotyl (2-butenyl) group in **9c** or **9d** was retained in **12**, in contrast to the fact that **12** derived from **9b** consisted of a mixture of stereoisomers. $\alpha$-Methylallylstannane **9b** and non-substituted allylstannane **9a**, both lacking the $\gamma$-methyl group, reacted much faster than **9c** or **9d**. All these observations are explained rationally by the two catalytic cycles depicted in Scheme 5, though results for the intermediates remain to be studied. Thus, $\alpha$-methylallylstannane **9b** and **4a** might first undergo oxidative cyclization with the palladium(0) complex to afford palladacyclopentene **15** (Cycle C). Oxidative cyclization of a terminal alkene and **4a** with a palladium(0) complex has a precedent.[19] $\beta$-Tin elimination from **15** would give **16**, whose reductive elimination affords allylstannylation product **12** as a mixture of stereoisomers. Cycle C explains well the carbon–carbon bond formation at the $\gamma$-carbon of allylstannanes. Steric repulsion between the $\gamma$-methyl of crotylstannane **9c** (or **9d**) and the ester moiety on **4a** should prevent the formation of palladacyclopentene **15′**, and

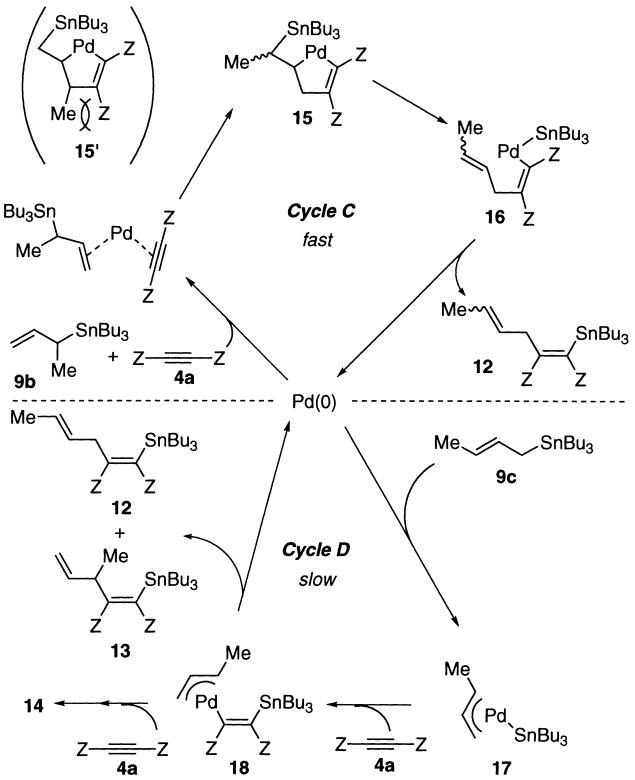
Table 3. Allylstannylation of Alkynes[a)]

| Entry | $R^1$ | $R^2$ | Catalyst | Temp/°C | Time/h | Yield/%[b)] | **10**:**11**[c)] |
|---|---|---|---|---|---|---|---|
| 1 | Hex | H | $Ni(cod)_2$ | 80 | 5 | 93 | 64:36 |
| 2 | H | H | $Ni(cod)_2$ | 80 | 14 | 80 | — |
| 3 | Pr | Pr | $Ni(cod)_2$ | 80 | 0.5 | 77 | — |
| 4 | Me | $CO_2Et$ | $Ni(cod)_2$ | 100 | 12 | 78 | 65:35 |
| 5 | Me | Ph | $Ni(cod)_2$ | 100 | 12 | 77 | > 99:1 |
| 6 | $Me_3Si$ | Ph | $Ni(cod)_2$ | 100 | 14 | 76 | > 99:1 |
| 7 | $Me_3Si$ | $CO_2Et$ | $Ni(cod)_2$ | 100 | 40 | 78 | > 99:1 |
| 8 | Bu | C≡CBu | $Ni(cod)_2$ | 100 | 14 | 64 | > 99:1 |
| 9 | $Me_3Si$ | C≡CSiMe$_3$ | $Ni(cod)_2$ | 100 | 8 | 70 | > 99:1 |
| 10 | Bu | CN | $Pd_2(dba)_3$ | 90 | 72 | 63 | > 99:1 |
| 11 | Ph | $SO_2$(*p*-tol) | $Pd_2(dba)_3$ | 50 | 1 | 73 | 92:8 |
| 12 | Me | $CO_2Et$ | $Pd_2(dba)_3$ | 50 | 50 | 37 | 86:14 |
| 13[d)] | Me | $CO_2Et$ | $Pd_2(dba)_3$ | 50 | 62 | 55 | 91:9 |
| 14 | Ph | $CO_2Et$ | $Pd_2(dba)_3$ | 50 | 43 | 100 | 79:21 |
| 15 | Ph | $CF_3$ | $Pd_2(dba)_3$ | 50 | 14 | 98 | 72:28 |
| 16[e)] | MeOCO | $CO_2Me$ | $Pd_2(dba)_3$ | 50 | 0.5 | 80 | — |

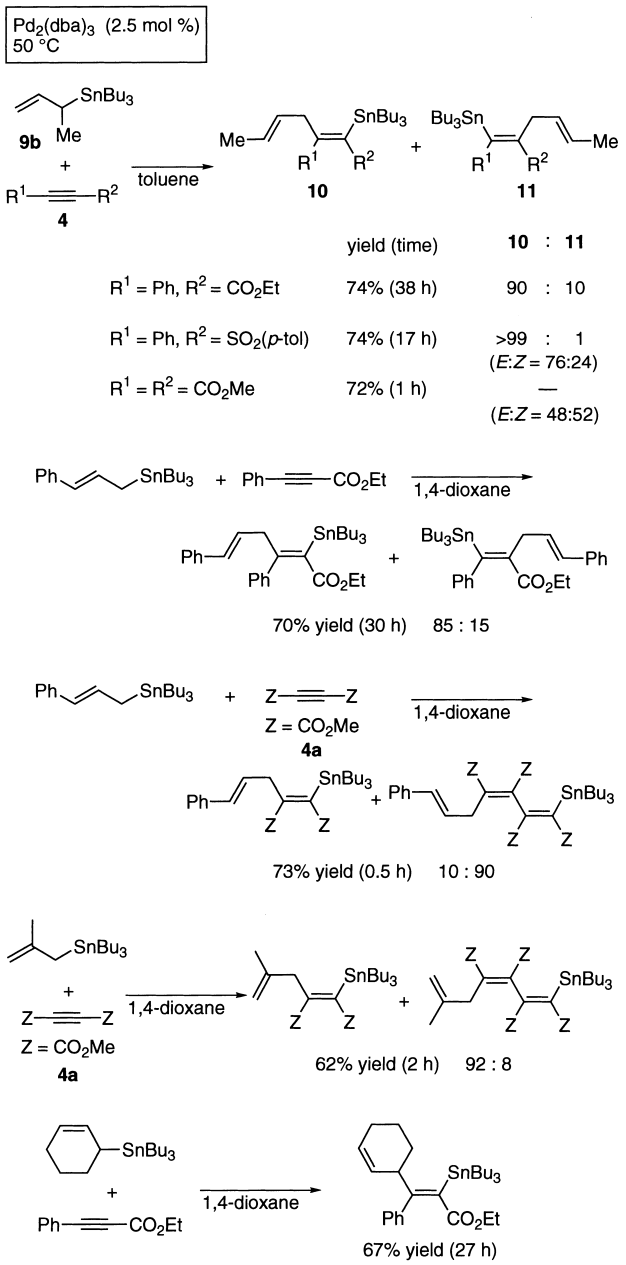
a) Entries 1–9: the reaction was carried out in toluene (0.3 mL) using allyl(tributyl)tin (0.46 mmol) and an alkyne (1.38 mmol) in the presence of $Ni(cod)_2$ (23 μmol); entries 10–16: the reaction was carried out in 1,4-dioxane (3.0 mL) at 50 °C using allyl(tributyl)tin (0.33 mmol), an alkyne (0.99 mmol) and $Pd_2(dba)_3$ (8.2 μmol). b) Isolated yield based on the allylstannane. c) Determined by $^{119}$Sn NMR. d) $[PhN{=}C(Me)]_2$ (16.4 μmol) was used. e) A 1:2 adduct of the allylstannane and the alkyne was also obtained in 8% yield.



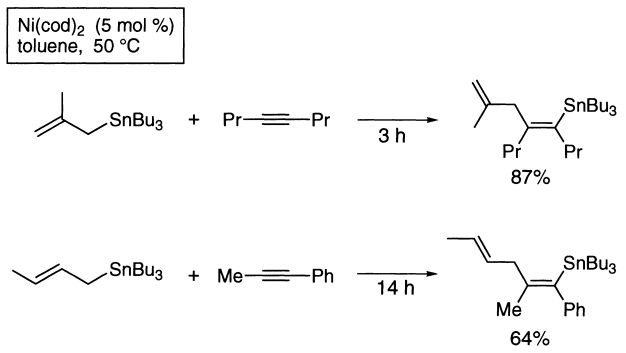

(6)




Scheme 5.




Scheme 6.




Scheme 7.

an alternative pathway, Cycle D, becomes plausible. Oxidative addition of **9c** to a palladium(0) complex should give **17**, which undergoes insertion of alkyne **4a** to produce π-allylpalladium(II) complex **18**. Reductive elimination from **18** would provide dienylstannanes (*E*)-**12** and **13**, whereas trienylstannane **14** is obtained by insertion of another molecule of **4a** to **18** and the consequent reductive elimination.

The reactions of variously substituted allylstannanes with electron-deficient alkynes proceeded in the presence of 2.5 mol% of $Pd_2(dba)_3$ (Scheme 6). α-Methylallylstannane **9b** added also to alkynes other than **4a** to give γ-adducts exclusively, whereas a γ-substituted allylstannane, tributyl(cinnamyl)tin, afforded α-adducts as the sole products.

The nickel-catalyzed reaction using substituted allylstannanes also provided allylstannylation products (Scheme 7). (*E*)-Crotylstannane **9c** forms a bond exclusively at its α-position, where the regioselectivity concerning an alkyne is per-

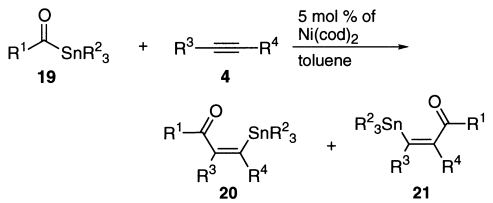
Table 4. Acylstannylation of Alkynes[a)]

| Entry | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Temp/°C | Time/h | Yield/%[b)] | **20**:**21**[c)] |
|---|---|---|---|---|---|---|---|---|
| 1 | Ph | Me | Pr | Pr | 100 | 2 | 65 | — |
| 2 | Ph | Me | Me | Ph | 100 | 1.5 | 61 | 83:17 |
| 3 | $(CH_2)_5N$ | Bu | Pr | Pr | 100 | 1.5 | 66 | — |
| 4 | $(CH_2)_5N$ | Bu | Me | Ph | 100 | 2 | 81 | 64:36 |
| 5 | Ph | Me | $CH_3(CH_2)_4$ | $CO_2Me$ | 30 | 2.5 | 66 | 88:12 |
| 6 | Ph | Me | $Me_3Si$ | $CO_2Et$ | 30 | 3 | 85 | 98:2 |
| 7 | Ph | Me | Me | $CO_2Me$ | 30 | 1.5 | 56 | 91:9 |
| 8 | Ph | Me | Ph | $CO_2Et$ | 30 | 24 | 58 | 66:34 |
| 9 | Et | Bu | $CH_3(CH_2)_4$ | $CO_2Me$ | 30 | 24 | 47 | 79:21 |

a) The reaction was carried out in toluene (0.3 mL in entries 1–4, 0.4 mL in entries 5–9) using an acylstannane (0.46 mmol in entries 1–4, 0.30 mmol in entries 5–9), an alkyne (0.69 mmol in entries 1–4, 0.90 mmol in entries 5–9) and $Ni(cod)_2$ (0.23 μmol in entries 1–4, 0.15 μmol in entries 5–9). b) Isolated yield based on the acylstannane. c) Determined by $^{119}Sn$ NMR.

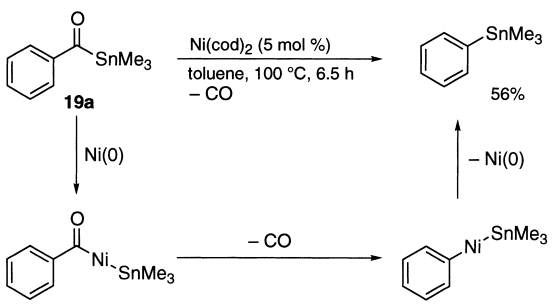
fect. The $\alpha$-selection should imply the possibility that the nickel-catalyzed allylstannylation proceeds through a catalytic cycle similar to Cycle D in Scheme 5, which is initiated by oxidative addition of an allylstannane to a palladium(0) complex.

**1-3. Acylstannylation.**[20,16b] $Ni(cod)_2$ was demonstrated to be effective also for acylstannylation of alkynes, which gives $\beta$-stannylenones and related compounds (Eq. 7 and Table 4). Use of a more polar solvent than toluene or a phosphine as a ligand caused decarbonylation from acylstannanes and the yields of the carbostannylation products decreased obviously.



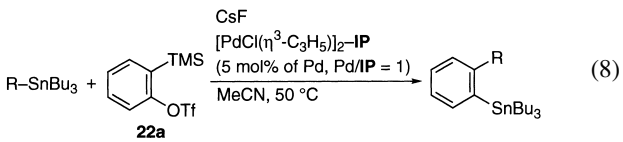

(7)

The first step of the catalytic cycle should be, we consider, oxidative addition of an acylstannane to the nickel(0) complex. Although we have not observed the formation of the oxidative adduct, the fact that trimethyl(phenyl)tin is generated through decarbonylation probably from the oxidative adduct in the nickel-catalyzed reaction of benzoyl(trimethyl)tin (**19a**) in the absence of an alkyne (Scheme 8) should demonstrate the ability of acylstannanes to oxidatively add to nickel(0) complexes. Then, insertion of an alkyne to the carbon–nickel or tin–nickel bond followed by reductive elimination should take place to give acylstannylation products.




Scheme 8.

**1-4. Carbostannylation of Arynes.**[21] The carbostannylation of benzyne (1,2-didehydrobenzene) prepared in situ from 2-(trimethylsilyl)phenyl triflate (trifluoromethanesulfonate) (**22a**) and CsF was found to be catalyzed by a palladium–iminophosphine complex as shown in Eq. 8 and Table 5. Iminophosphine **IP** having a 2-phenylethyl group on the nitrogen atom is more effective than other iminophosphines (**IP(Cy)**, **IP(Ph)**) or other phosphine ligands. In addition to alkynylstannanes, tributyl(vinyl)tin that was unreactive towards alkynes under similar conditions, successfully reacted with benzyne.



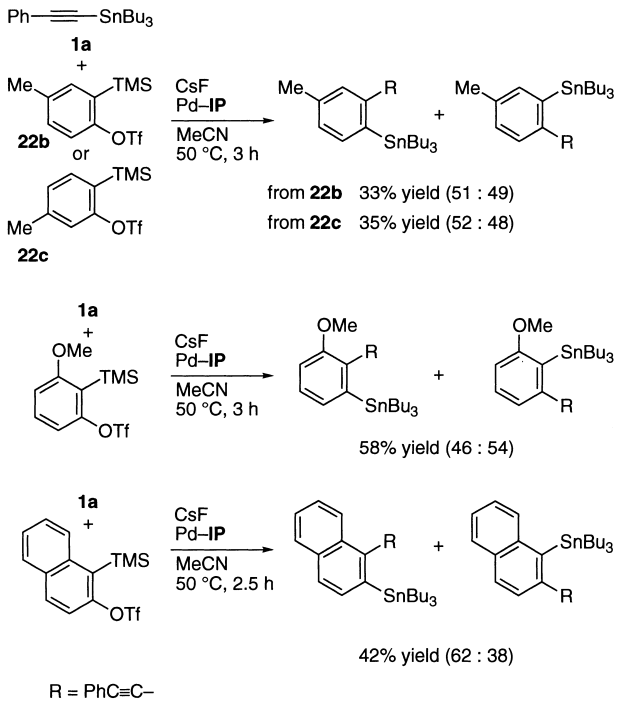

(8)

Table 5. Carbostannylation of Benzyne[a)]

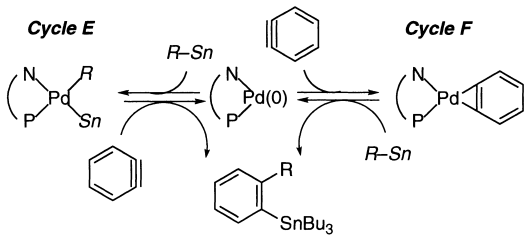
| Entry | R | Time/h | Yield/%[b)] |
|---|---|---|---|
| 1 | PhC≡C | 3 | 54 |
| 2 | *t*-BuC≡C | 8 | 53 |
| 3 | BuC≡C | 4 | 41 |
| 4 | MeC≡C | 0.5 | 30 |
| 5 | $MeOCH_2C{\equiv}C$ | 2.5 | 51 |
| 6 | $MeC(=CH_2)C{\equiv}C$ | 2 | 51 |
| 7 | 1-cyclohexenyl-C≡C | 1.5 | 35 |
| 8[c)] | $CH_2$=CH | 25 | 47 |

a) The reaction was carried out in MeCN (3 mL) at 50 °C using an organostannane (0.34 mmol), 2-(trimethylsilyl)phenyl triflate (0.69 mmol) and CsF (0.69 mmol) in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (8.2 μmol) and **IP** (16 μmol). b) Isolated yield based on the organostannane. c) An increased amount of benzyne precursors, 2-(trimethylsilyl)phenyl triflate (1.4 mmol) and CsF (1.4 mmol), was used.

The carbostannylation was also applicable to substituted benzynes (Scheme 9). The fact that both 4-methyl- and 5-methylbenzyne precursors (**22b** and **22c**) gave regioisomeric products in similar ratios and yields indicates that the common intermediate 4-methylbenzyne must be involved in both reactions.




Scheme 9.



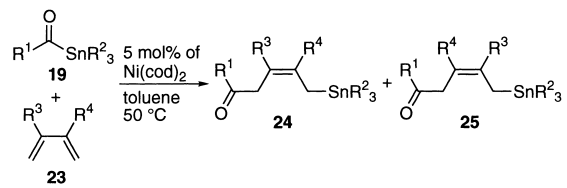

Scheme 10.

Two plausible catalytic cycles for this reaction are shown in Scheme 10. Cycle E, which is familiar to us, is possible but is rather improbable, because there have been no signs of oxidative addition of alkenylstannanes, which can participate in the present carbostannylation. Alternatively, the palladium(0)–**IP** complex might undergo oxidative cyclization with an aryne to form a palladacyclopropene (Cycle F),[22] which then reacts with an organostannane (Section 3).

## 2. Carbostannylation of Dienes

In contrast to the carbometalation of alkynes, the addition of carbon–metal bonds of organometallic compounds to dienes is extremely rare,[23,24] although it would provide synthetically useful alkenyl- or allylmetal reagents. Since we had discovered the carbostannylation of alkynes using organostannanes of adequate reactivity, we then studied the carbostannylation of dienes.[25,26] Our activation method (Type i in Scheme 1) that includes oxidative addition of a carbon–tin bond to a nickel(0) complex mentioned in the introductory section was found to be effective also for the carbostannylations of 1,3- and 1,2-dienes, whereas palladium complexes did not show sufficient catalytic activity in the addition of organostannanes to dienes.

**2-1. Acylstannylation of 1,3-Dienes.**[27] Acylstannylation of 1,3-dienes proceeded under the conditions for the acylstannylation of alkynes ($Ni(cod)_2$, no ligand, toluene, Section 1-3) but at lower temperatures (Eq. 9 and Table 6). Carbon–tin bonds in aromatic and aliphatic acylstannanes in addition to an aminocarbonylstannane reacted exclusively in a 1,4-manner with complete *syn*-selectivity except for the case of the aminocarbonylstannane. The reaction is applicable to various 2-substituted and 2,3-disubstituted 1,3-dienes but not to any 1-substituted ones. The regioselectivity in the reaction of unsymmetrical 1,3-dienes was at best 1:2 (entries 5–8).



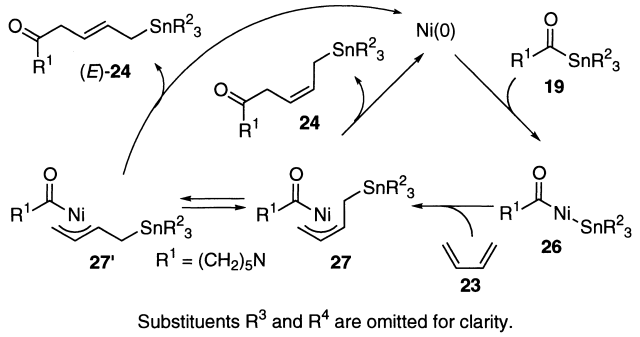

(9)

The catalytic cycle here also should be similar to the nickel-catalyzed acylstannylation of alkynes, starting with oxidative addition of an acylstannane to a nickel(0) complex. A 1,3-di-

Table 6. Acylstannylation of 1,3-Dienes[a)]

| Entry | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Time/h | Yield/%[b)] | **24**:**25**[c)] |
|---|---|---|---|---|---|---|---|
| 1 | Ph | Me | H | H | 0.2 | 72 | — |
| 2 | Ph | Me | Me | Me | 2 | 73 | — |
| 3[d)] | Ph | Me | Ph | Ph | 48 | 36 | — |
| 4[e)] | Ph | Me | $-(CH_2)_4-$ | | 24 | 45 | — |
| 5 | Ph | Me | Me | H | 2 | 74 | 33:67 |
| 6 | Ph | Me | Ph | H | 2 | 68 | 47:53 |
| 7 | Ph | Me | $SiMe_3$ | H | 2 | 84 | 44:56 |
| 8 | Ph | Me | $CH_2SiMe_3$ | H | 2 | 86 | 39:61 |
| 9[e)] | Et | Bu | Me | Me | 24 | 56 | — |
| 10[e)] | $Me_2C=CH$ | Bu | Me | Me | 2 | 52 | — |
| 11 | $(CH_2)_5N$ | Bu | Me | Me | 2 | 73[f)] | — |

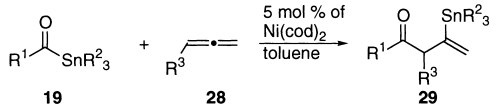
a) The reaction was carried out in toluene (0.3 mL) at 50 °C using an acylstannane (0.23 mmol), a 1,3-diene (0.69 mmol), and $Ni(cod)_2$ (11.5 μmol). b) Isolated yield based on the acylstannane. c) Determined by $^{119}Sn$ NMR. d) The reaction was carried out at 80 °C. e) The reaction was carried out at 70 °C. f) A 87:13 mixture of (*Z*)- and (*E*)-isomers was obtained.




Scheme 11.

ene would then insert into the carbon–nickel bond (carbonickelation) or the tin–nickel bond (stannylnickelation) of the resulting oxidative adduct (**26**) to give a π-allylnickel complex **27**;[28] the following reductive elimination could give acylstannylation product **24** and regenerate the nickel(0) complex. Worthy to note is that the stereochemical outcome depends on the $R^1$ moiety of acylstannanes, namely benzoylstannane affords *syn*-adduct as a sole product and aminocarbonylstannane gives a mixture of *syn*- and *anti*-adducts. This fact may imply that the stannylnickelation pathway shown in Scheme 11 is more plausible than the carbonickelation pathway, and isomerization of *anti*-π-allylnickel **27** ($R^1 = (CH_2)_5N$) to *syn*-isomer **27′** before reductive elimination may be responsible for the coproduction of (*E*)-isomer of **24**. The aminocarbonyl group appears to retard the reductive elimination leading to **24**.

**2-2. Acylstannylation of 1,2-Dienes.**[29] The methodology can be extended to acylstannylation of 1,2-dienes, which gives α-(acylmethyl)vinylstannanes as the major products through the addition of carbon–tin bonds to internal double bonds of 1,2-dienes (Eq. 10). This type of alkenylstannanes[30] having an exomethylene group is inaccessible by the standard carbostannylation of alkynes. Under the conditions similar to the acylstannylation of 1,3-dienes, various alkyl-, aryl-, and methoxyallenes undergo acylstannylation with aromatic and aliphatic acylstannanes as summarized in Table 7.




(10)

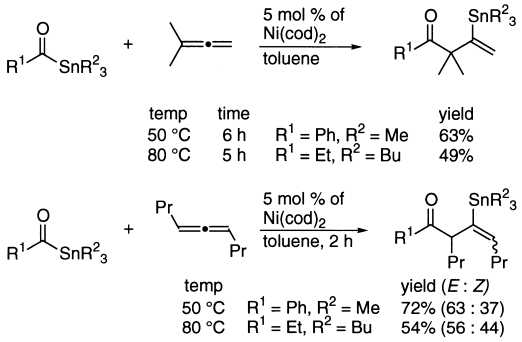
Disubstituted allenes also participated in the acylstannylation. Addition of carbon–tin bonds takes place preferentially at the internal double bond of the 1,1-disubstituted allene in Eq. 11 as is the case with the reaction of monosubstituted allenes. The fact that the reaction of the 1,3-disubstituted allene in Eq. 12 with acylstannanes gave mixtures of stereoisomers gives us a key to solve the reaction mechanism. Oxidative addition of an acylstannane to the nickel(0) complex must initiate the catalytic cycle, which should be followed by either stannylnickelation or acylnickelation. The catalytic cycles exemplified by the reaction of 4,5-nonadiene are shown in Scheme 12. If acylnickelation would take proceed with Cycle H, (*E*)-alkenylstannanes should be obtained at least as major products (discrimination between H and Pr) through stereo-retained reductive elimination from (*E*)-alkenylnickel complexes **31**.[31] As the isomeric ratios are close to 1:1, Cycle G appears to be

Table 7. Acylstannylation of 1,2-Dienes[a)]

| Entry | $R^1$ | $R^2$ | $R^3$ | Time/h | Yield/%[b)] |
|---|---|---|---|---|---|
| 1[c)] | Ph | Me | H | 1.5 | 64 |
| 2 | Ph | Me | Bu | 1.5 | 79 |
| 3 | Ph | Me | *t*-Bu | 1.5 | 59 |
| 4 | Ph | Me | 4-$MeOC_6H_4$ | 2 | 50 |
| 5 | Ph | Me | Ph | 2 | 53 |
| 6 | Ph | Me | 4-$CF_3C_6H_4$ | 2 | 35 |
| 7 | Ph | Me | MeO | 2 | 26 |
| 8[c)] | Ph | Bu | H | 4 | 48 |
| 9[c)] | Et | Bu | H | 1.5 | 67 |
| 10[d)] | Et | Bu | Bu | 2 | 53 |
| 11[d)] | Et | Bu | Ph | 3.5 | 43 |
| 12[d)] | Et | Bu | MeO | 2.5 | 48 |
| 13[c),e)] | $(CH_2)_5N$ | Me | H | 2 | 25 |

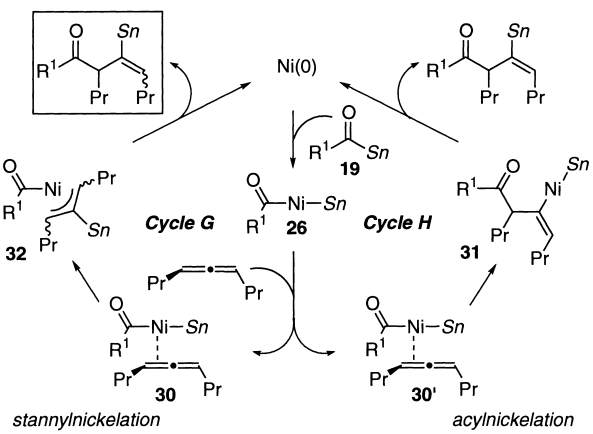
a) The reaction was carried out in toluene (0.4 mL) at 50 °C using an acylstannane (0.30 mmol), a 1,2-diene (0.90 mmol), and $Ni(cod)_2$ (15 μmol). b) Isolated yield based on the acylstannane. c) The reaction was carried out under an allene atmosphere (1 atm). d) The reaction was carried out at 80 °C. e) The reaction was carried out at 100 °C in the presence of 60 μmol of $Ni(cod)_2$.

plausible. Namely, stannylnickelation might proceed in preference to acylnickelation.




(11)

(12)




Scheme 12.

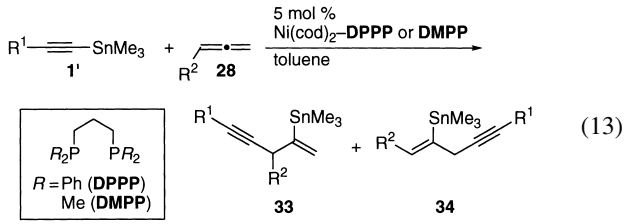
**2-3. Alkynylstannylation of 1,2-Dienes.**[32] The reaction conditions of the acylstannylation of 1,3- and 1,2-dienes turned out to be futile for the corresponding alkynylstannylation as they stand. After a thorough search for better reaction conditions, we found that alkynylstannylation of 1,2-dienes

Table 8. Alkynylstannylation of 1,2-Dienes[a)]

| Entry | Ligand | $R^1$ | $R^2$ | Temp/°C | Time/h | Yield/%[b)] | **33**:**34**[c)] |
|---|---|---|---|---|---|---|---|
| 1 | **DPPP** | Ph | Bu | 30 | 10 | 72 | 85:15 |
| 2[d)] | | Ph | Bu | 60 | 40 | 70 | 87:13 |
| 3 | | Ph | H | 30 | 10 | 63 | — |
| 4 | | Ph | *t*-Bu | 50 | 70 | 57 | 98:2 |
| 5 | | Ph | MeO | 0 | 23 | 53 | 28:72 |
| 6 | | 4-$CF_3C_6H_4$ | Bu | 30 | 5 | 92 | 87:13 |
| 7 | | 4-$MeOC_6H_4$ | Bu | 30 | 72 | 52 | 77:23 |
| 8 | | $Me_3Si$ | H | 50 | 7 | 91 | — |
| 9 | | $Et_3Si$ | H | 50 | 24 | 90 | — |
| 10 | **DMPP** | Ph | Bu | 30 | 10 | 82 | 32:68 |
| 11[d)] | | Ph | Bu | 60 | 46 | 70[e)] | 37:63 |
| 12 | | Ph | *t*-Bu | 50 | 49 | 67 | 14:86 |
| 13 | | $Me_3Si$ | Bu | 50 | 26 | 81[e)] | 37:63 |

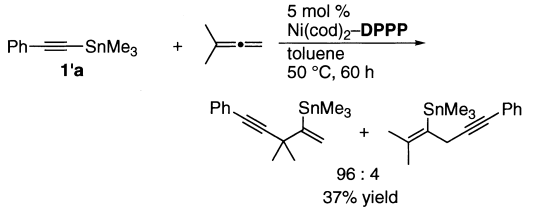
a) The reaction was carried out in toluene (0.3 mL) using an alkynylstannane (0.20 mmol), a 1,2-diene (0.60 mmol in entries 1–9, 0.30 mmol in entries 10–13) in the presence of $Ni(cod)_2$ (10 μmol) and a bisphosphine ligand (10 μmol). b) Isolated yield based on the alkynylstannane. c) Determined by $^{119}Sn$ NMR. d) Tributyl(phenylethynyl)tin was used instead of the trimethylstannyl analogue. e) Determined by $^{119}Sn$ NMR using $Bu_4Sn$ (entry 11) or $Me_4Sn$ (entry 13) as an internal standard.

took place in the presence of a catalytic amount of a nickel(0) complex coordinated by a 1,3-diphosphinopropane ligand. Other mono- and bisphosphine ligands such as triphenylphosphine, 1,4-bis(diphenylphosphino)butane, and **IP** gave only complex mixtures of products. The substituents on phosphorous of the bisphosphine ligands affected markedly the selection of allene double bonds: a Ni–**DPPP** catalyst favored the internal double bond of allene to give addition products **33** predominantly, whereas 1,3-bis(dimethylphosphino)propane (**DMPP**) preferred to react at the terminal double bonds and **34** were obtained as major products (Eq. 13). Results using aryl- and silylethynylstannanes, various mono- or nonsubstituted allenes, and **DPPP** or **DMPP** ligand are summarized in Table 8. All of alkenylstannanes **34** in Table 8 have (*Z*)-configuration.

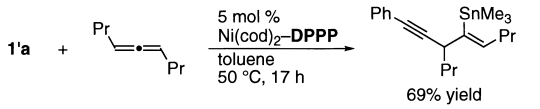


(13)

The preference of Ni–**DPPP** for the internal double bonds also was observed in the addition of a phenylethynylstannane to a 1,1-disubstituted allene (Eq. 14). In contrast to the acylstannylation mentioned above, the reaction of a 1,3-disubstituted allene gave a single alkynylstannylation product having (*Z*)-configuration (Eq. 15). On the basis of the stereochemistry observed here, we consider the reaction mechanism depicted in Scheme 13. Oxidative addition of an alkynylstannane to the nickel(0) complex and subsequent insertion of the terminal double bond of an allene through **36** into the tin–nickel bond provides $\beta$-stannyl-$\sigma$-allylnickel **37**. After isomerization of **37** to $\pi$-allylnickel complex **38** and then to **39**, reductive elimination at C-1 and/or C-3 of the allyl moiety should afford alkynylstannylation product **33** and/or **34**, respectively, although it is not clear how ligand **DPPP** or **DMPP** determines the course of the reaction. An alternative carbonickelation pathway appears improbable, because it should give **34′** at least as major products via alkenylnickel **40** as mentioned in the previous section.



(14)



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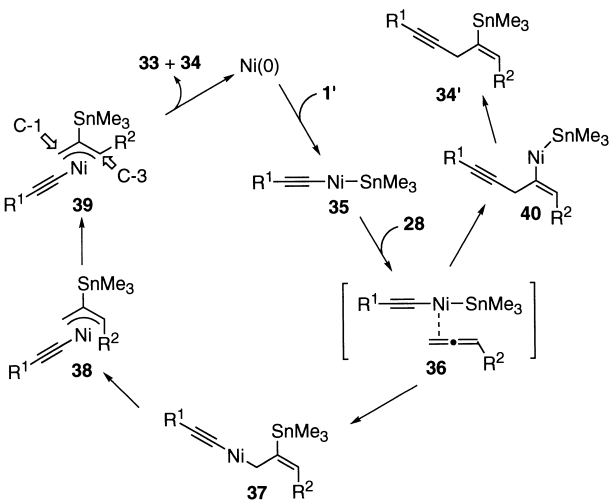



Scheme 13.

### 3. Dimerization–Carbostannylation of Alkynes[33]

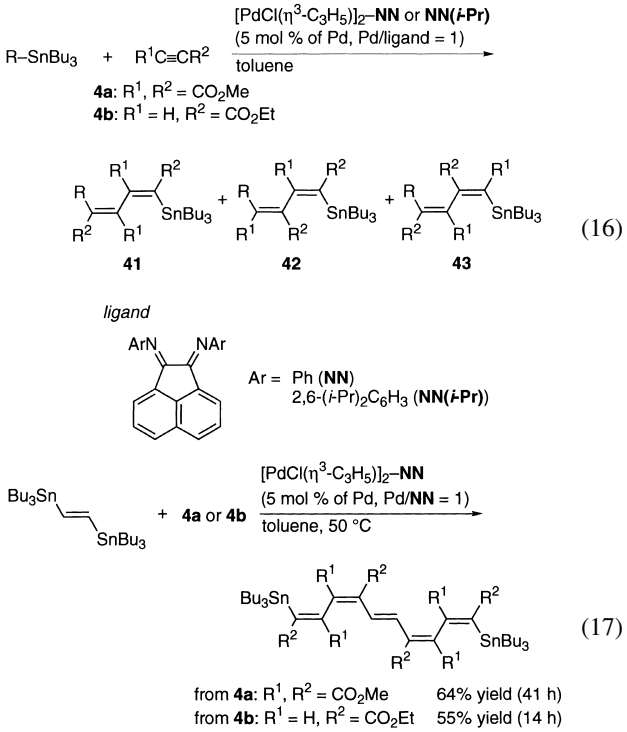
As we disclosed in Section 1-1, the reaction of tributyl(phen-

Table 9. Dimerization–Carbostannylation of Alkynes[a)]

| Entry | Alkyne | R | Ligand | Temp/°C | Time/h | Yield/%[b)] | **41**:**42**:**43**[c)] |
|---|---|---|---|---|---|---|---|
| 1 | **4b** | PhC≡C | **NN** | 50 | 0.7 | 77 | 100:0:0 |
| 2 | | BuC≡C | **NN** | 30 | 3 | 93 | 100:0:0 |
| 3 | | $Me_3SiC{\equiv}C$ | **NN** | 20 | 0.5 | 75 | 100:0:0 |
| 4 | | $CH_2$=CH | **NN** | 50 | 0.7 | 72 | 79:21:0 |
| 5 | | $CH_2$=CH | **NN(*i*-Pr)** | 50 | 1 | 78 | 100:0:0 |
| 6 | | (*E*)-PhCH=CH | **NN** | 50 | 14 | 76 | 89:11:0 |
| 7 | | (*E*)-HexCH=CH | **NN** | 50 | 40 | 78 | 71:29:0 |
| 8 | | 2-furyl | **NN** | 50 | 14 | 81 | 30:63:7 |
| 9 | | 2-furyl | **NN(*i*-Pr)** | 50 | 13 | 78 | 100:0:0 |
| 10 | | 2-thienyl | **NN** | 50 | 12 | 42 | 13:69:18 |
| 11 | | 2-thienyl | **NN(*i*-Pr)** | 50 | 22 | 68 | 100:0:0 |
| 12 | | 3-thienyl | **NN(*i*-Pr)** | 50 | 21 | 80 | 100:0:0 |
| 13 | | 2-benzofuryl | **NN(*i*-Pr)** | 50 | 23 | 79 | 100:0:0 |
| 14[d)] | | Ph | **NN(*i*-Pr)** | 50 | 27 | 42 | 100:0:0 |
| 15[d)] | | 4-$MeOC_6H_4$ | **NN(*i*-Pr)** | 50 | 19 | 64 | 100:0:0 |
| 16 | **4a** | PhC≡C | **NN** | 70 | 2 | 77 | — |
| 17 | | BuC≡C | **NN** | 90 | 19 | 32 | — |
| 18 | | $Me_3SiC{\equiv}C$ | **NN** | 90 | 2 | 52 | — |
| 19 | | $CH_2$=CH | **NN** | 50 | 2 | 76 | — |
| 20 | | (*E*)-PhCH=CH | **NN** | 50 | 1 | 75 | — |
| 21 | | (*E*)-HexCH=CH | **NN** | 50 | 8 | 75 | — |
| 22 | | 2-furyl | **NN** | 50 | 19 | 63 | — |
| 23 | | 2-benzofuryl | **NN** | 50 | 26 | 75 | — |
| 24 | | (*E*)-PhCH=$CHCH_2$ | **NN** | 20 | 1 | 86[e)] | — |

a) The reaction was carried out in toluene (3 mL) using an organostannane (0.34 mmol) and an alkyne (1.0 mmol) in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (8.2 μmol) and **NN** or **NN(*i*-Pr)** (16 μmol). b) Isolated yield based on the organostannane. c) Determined by $^{119}$Sn NMR. d) An aryl(trimethyl)tin was used instead of the tributylstannyl analogue. e) A 1:1 adduct was also obtained in 4% yield.

ylethynyl)tin (**1a**) with ethyl propiolate (**4b**) catalyzed by a palladium complex coordinated by **IP** or its derivative gives 1:1 adducts as a mixture of regioisomers. In contrast, use of 1,2-bis(phenylimino)acenaphthene (**NN**) as a ligand in lieu of the iminophosphine completely changed the reaction course; alkynylstannylation of **4b** was accompanied by dimerization of **4b** to afford (1*Z*,3*E*)-6-phenyl-1-tributylstannylhexa-1,3-dien-5-yne-1,4-dicarboxylate (**41a**) (Eq. 16). To the best of our knowledge, this is the first demonstration of dimerization–carbometalation of alkynes. Not only alkynylstannanes but also alkenyl-, allyl-, and arylstannanes are applicable to the reaction, giving conjugated alkynyldienylstannanes, trienylstannanes, and aryldienylstannanes, respectively (Table 9, entries 1–15). Although organostannanes other than alkynylstannanes gave dimerization–carbostannylation products as mixtures of regioisomers **41**, **42**, and **43** under the conditions, use of bulkier ligand **NN(*i*-Pr)** much improved the selectivity as was the case for the ligand effect in the palladium-catalyzed alkynylstannylation of alkynes described in Section 1-1, and **41** were produced as the sole products. We will discuss the ligand effect later in the context of reaction mechanism. Dimethyl acetylenedicarboxylate (**4a**) also reacts with organostannanes in the presence of the Pd–**NN** catalyst to give single isomers (Table 9, entries 16–24), although other alkynes such as phenylacetylene, 1-octyne, and 3-butyn-2-one cannot participate in the dimerization–carbostannylation. Noteworthy is that a highly conjugated π-system is readily constructed by the reaction of (*E*)-1,2-bis(tributylstannyl)ethene, six new covalent bonds being generated all at once to give α,ω-bisstannyldecapentaenes (Eq. 17).



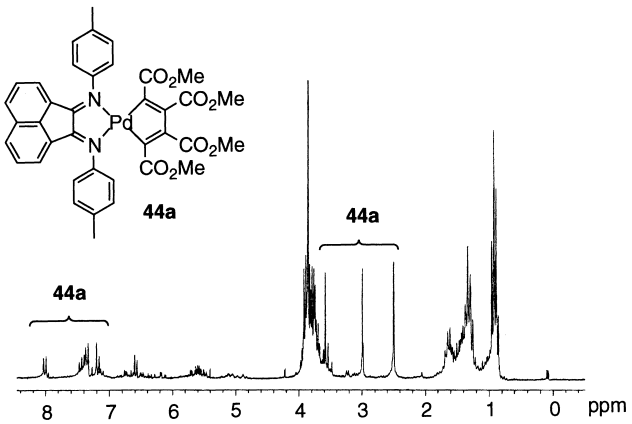
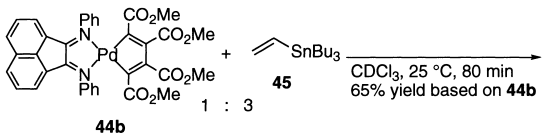
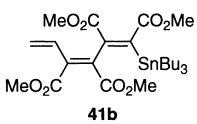


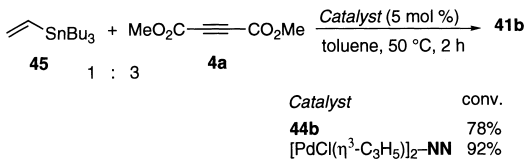

Fig. 1. $^1$H NMR (200 MHz) spectrum of the reaction mixture (at ca. 31% conversion) in the reaction of **45** with **4a** in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$–**NN(*p*-tol)** complex (20 mol% of Pd, Pd/**NN(*p*-tol)** = 1) in $CDCl_3$ at 25 °C.

Since the present dimerization–carbostannylation of alkynes is not accompanied by 1:1 carbostannylation products nor by trimerization–carbostannylation products, the reaction is unlikely to proceed through a catalytic cycle similar to those of the carbostannylations of alkynes (Section 1): oxidative addition, insertion, and reductive elimination. Since it is well-documented that palladacyclopentadiene **44b** is formed through the oxidative cyclization of two molecules of **4a** with palladium–diimine complexes, is well-documented,[34] we considered that palladacyclopentadienes should be involved in the reaction. In fact, we monitored the reaction by $^1$H NMR using bis(*p*-tolylimine) **NN(*p*-tol)** ligand to find that the spectra of the reaction of tributyl(vinyl)tin (**45**) with **4a** showed, in addition to those of the substrates and the dimerization–carbostannylation products, no peaks other than those of palladacycle **44a** (Fig. 1). Furthermore, the reaction of palladacyclopentadiene **44b** with **45** gave dimerization–carbostannylation product **41b** in a reasonable yield (Eq. 18), and **44b** was shown to be an equally active catalyst (Eq. 19). All these observations suggest the involvement of the palladacyclopentadiene intermediates.



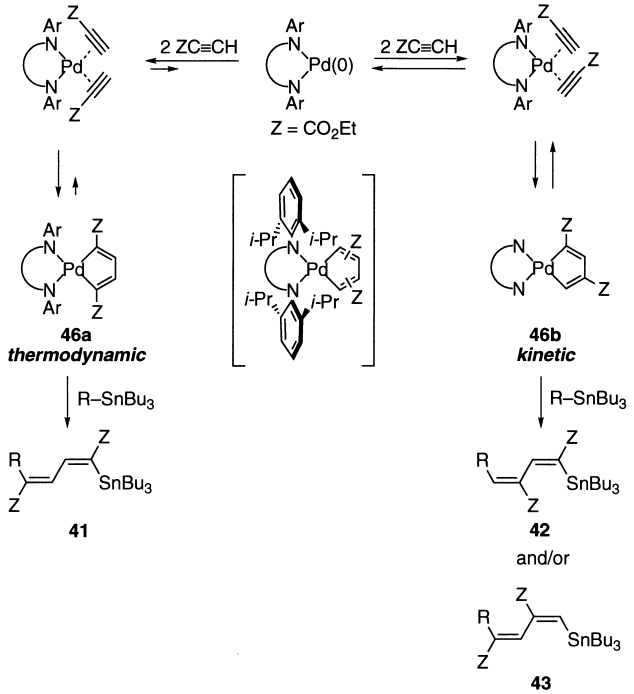




(18)




(19)

The perfect regioselectivity in the reaction of ethyl propiolate (**4b**) brought by introduction of a bulky substituent into the phenyl rings of diimine **NN** may be explained as follows (Scheme 14). There would be an equilibrium between palladacycle **46a** and **46b** through a palladium(0)–diimine complex,



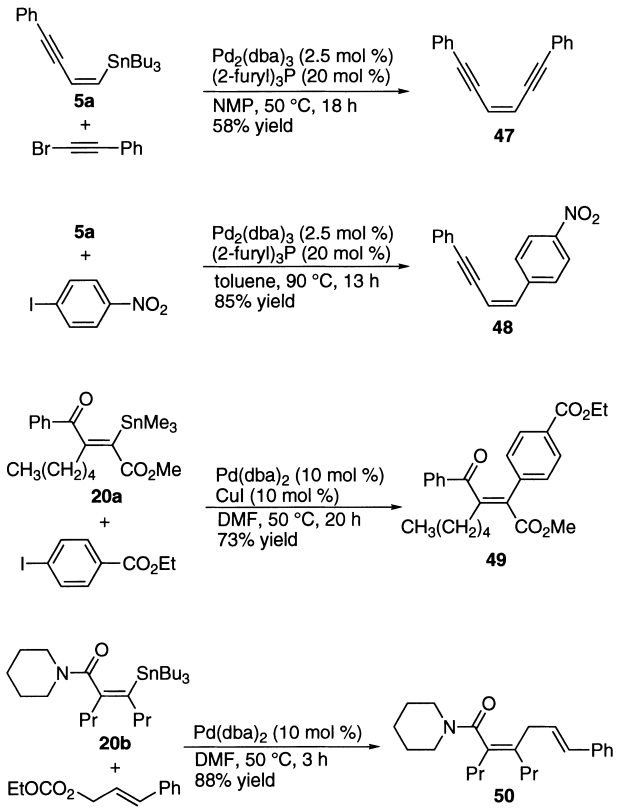

Scheme 14.

**46a** being thermodynamically stable and **46b** kinetically favored. Isopropyl groups on **NN(*i*-Pr)** block the apical position of palladium complex **46**[35] and thus retard the reaction with organostannanes to allow palladacyclopentadiene **46b** to isomerize to **46a**. This then reacts with organostannanes to give exclusively dimerization–carbostannylation product **41**.

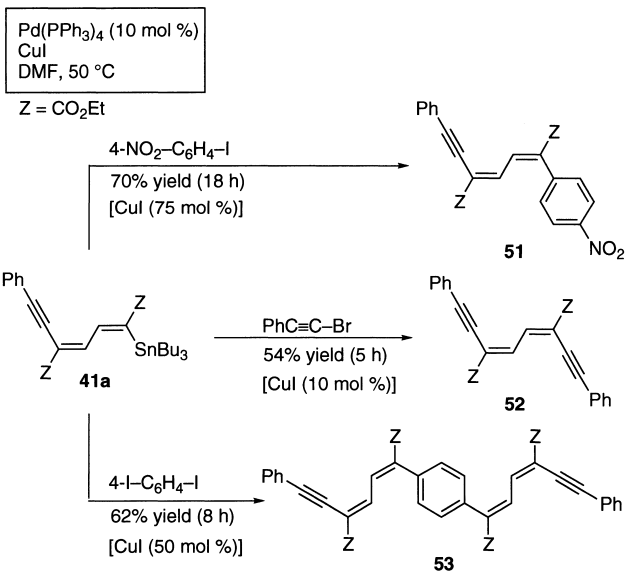
## 4. Synthetic Applications of the Carbostannylation Products

From the viewpoint of synthetic reagent, in sharp contrast to other organometallic compounds, organostannanes achieve an exquisite balance between stability and reactivity. They are storable at room temperature, usually being prepared and purified step by step prior to use. Meanwhile, the reagents have sufficient reactivity to attain carbon–carbon bond formation chemoselectively with the aid of an appropriate activator such as a palladium catalyst or a Lewis acid. The transformation methods are applicable also to the present carbostannylation products having certain functional groups. In this Section, we demonstrate the synthetic versatility by transformation to various compounds that possess complicated structures through cross-coupling reactions, homocoupling reactions and Lewis acid-mediated reactions with carbonyl and related compounds.

**4-1. Cross-Coupling Reaction.** The alkynyl- or acylstannylation of alkynes gives alkenylstannanes having a conjugated alkynyl or acyl group, respectively. Their π-conjugation can be easily extended by conversion of their stannyl group to an organic group having π-bonds through the cross-coupling reaction with organic electrophiles (Scheme 15). For example, alkynylstannylation product **5a** was transformed to enediyne **47** or arylenyne **48**,[13] whereas *β*-aryl enone **49** was obtained from *β*-stannyl enone **20a**. The reaction with an allylic electrophile also proceeded to give partially conjugated dienone **50**. Highly conjugated systems can be obtained simply from



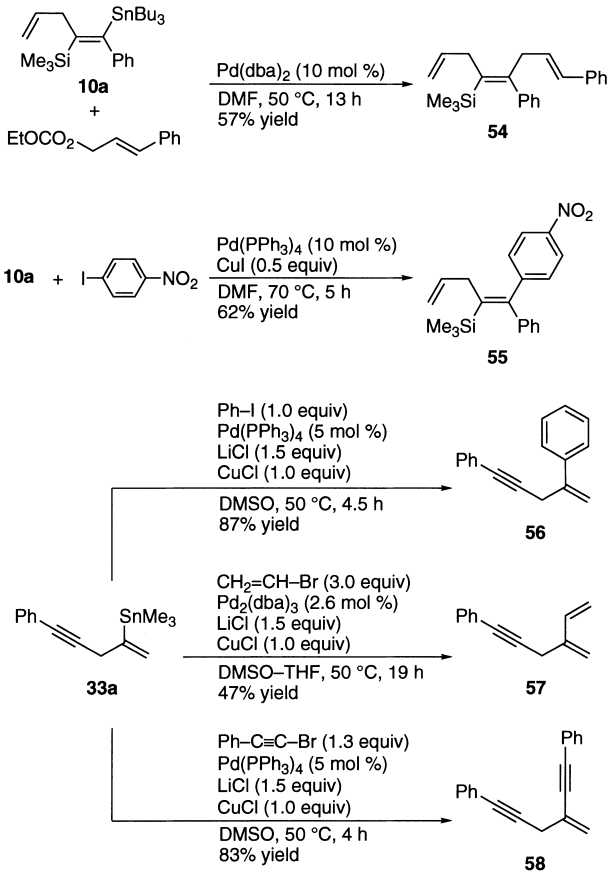

Scheme 15.




Scheme 16.

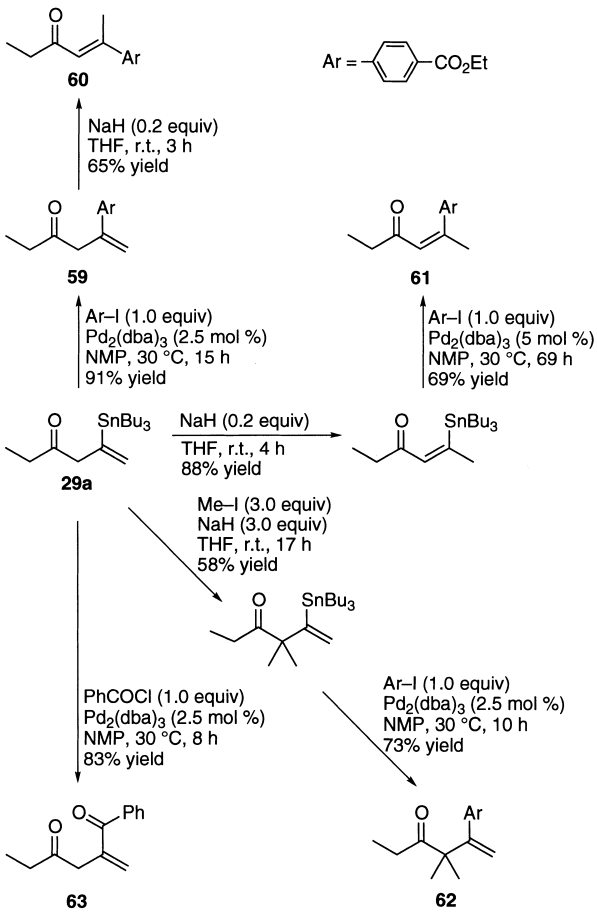
the dimerization–carbostannylation products. Thus, stannyl dienyne **41a** was coupled with 1-iodo-4-nitrobenzene, bromoacetylene, and 1,4-diiodobenzene to give **51**–**53** (Scheme 16).[36]

The cross-coupling reaction of allylstannylation product **10a** with an allyl carbonate provides triene **54**, whereas coupling of **10a** with an aryl iodide in the presence of 10 mol% of $Pd(PPh_3)_4$ gave partially conjugated aryldiene **55** (Scheme 17). Conjugated ethenes **56**–**58** can be obtained from alkynylstannylation product **33a** of allene. The cross-coupling reaction of allene-acylstannylation product **29a** with an aryl iodide also proceeded to give $\beta$-aryl-$\beta,\gamma$-unsaturated ketone **59**, which can be converted to conjugated $\beta$-aryl (*E*)-enone **60** through base-catalyzed isomerization of the carbon–carbon double bond (Scheme 18). Change of the order of the sequence (isomerization before cross-coupling) afforded the corresponding (*Z*)-isomer (**61**). Another $\beta$-aryl-$\beta,\gamma$-unsaturated ketone (**62**) is available through dimethylation of **29a** followed by cross-coupling with the aryl iodide. The cross-coupling of **29a** with benzoyl chloride provided exomethylene type enedione **63**.




Scheme 17.

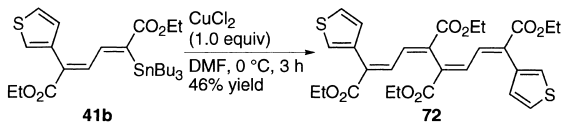
**4-2. Homocoupling Reaction followed by Annulations.** A wide variety of polycyclic compounds can be prepared from the alkynylstannylation products of 1,2-dienes through homocoupling as a key reaction. Examples are summarized in Scheme 19. $\alpha$-(Alkynylmethyl)vinylstannane **33b** homocoupled[37] in the presence of a palladium catalyst and copper(I)/(II) reagents to give symmetrical dienyldiyne **64**, which was desilylated with TBAF. The resulting dimethylenediyne **65** underwent two different modes of cyclization: annulation through the Diels–Alder reaction of the diene moiety and double annulation through nickel-catalyzed reaction of the diyne moiety with acetylene,[38] to give tricyclic compound **66**. Diels–Alder reaction of dienyldiyne **67**, the homocoupling product of **33a**, gave **68**, which was transformed to tetracyclic compound **69** through zirconocene-mediated reaction with *o*-diiodobenzene.[39] Alternatively, **67** was first converted by zirconocene-mediated cyclization to tetraene **70**, which underwent a double




Scheme 18.

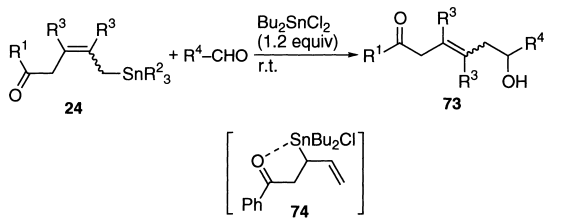
Diels–Alder reaction with diethyl acetylenedicarboxylate to afford tricyclic compound **71**.

Like the cross-coupling in the previous section, π-conjugation of dimerization–carbostannylation product **41b** can be extended to tetraene **72** by a copper(II)-mediated homocoupling reaction (Eq. 20).



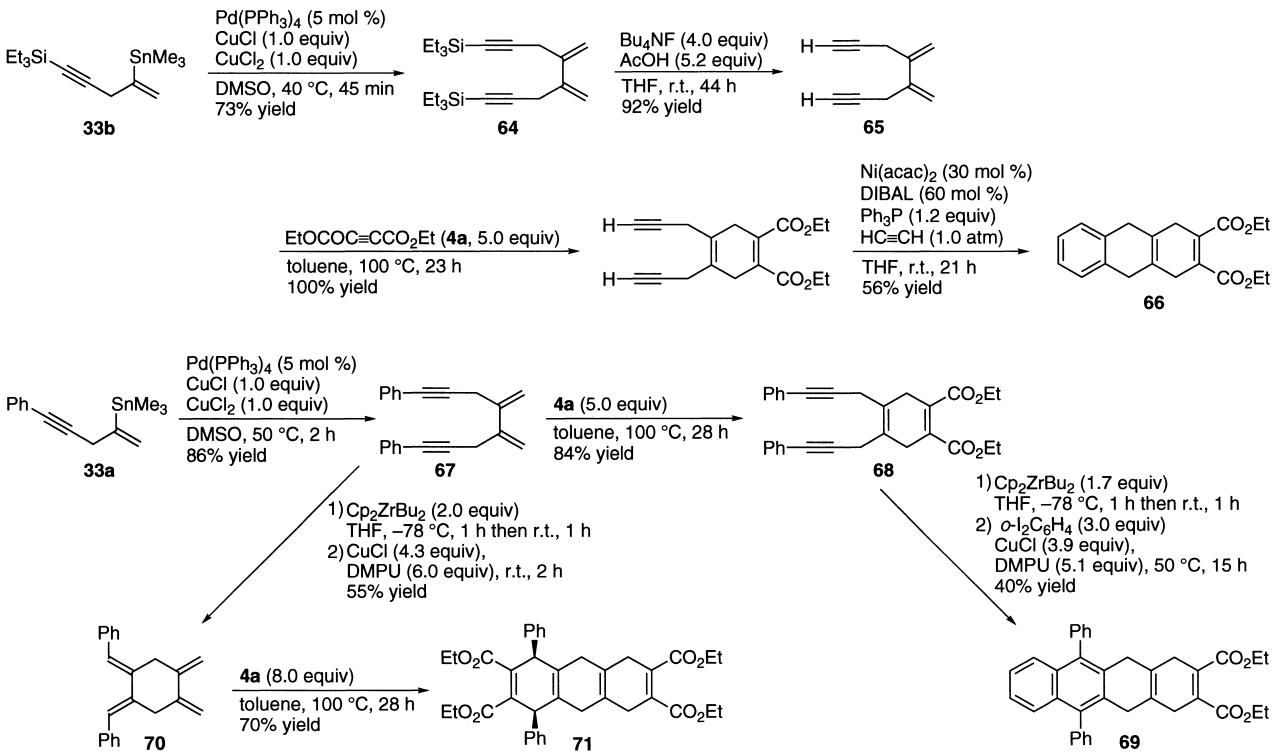

(20)

**4-3. Reaction with Carbonyl Groups.** As we disclosed in Section 2-1, the nickel-catalyzed acylstannylation of 1,3-dienes provides ε-oxo 2-alkenylstannanes, which are not easily available by other methods because of the reactive carbonyl functionality. The carbonyl group in the allylstannanes was found to assist regioselective addition to aldehydes (Eq. 21 and




(21)

Table 10). Allylstannane **24a** ($R^1$ = Ph) derived from benzoylstannane and 1,3-butadiene underwent the $Bu_2SnCl_2$-mediated reaction with aldehydes to give exclusively α-adduct **73** in sharp contrast to unfunctionalized tributyl(crotyl)stannane, which affords regioisomeric mixtures.[40] The exclusive α-selectivity should be ascribed to intramolecular coordination



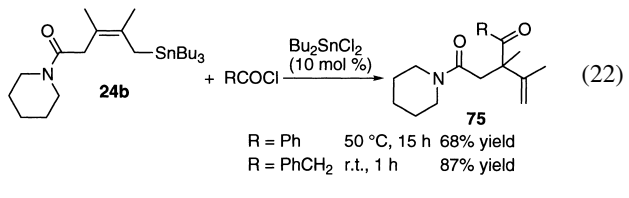

Scheme 19.

Table 10. Addition of Allylstannanes to Aldehydes Mediated by $Bu_2SnCl_2$[a)]

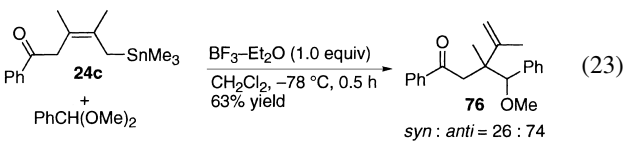
| Entry | $R^1$ | $R^2$ | $R^3$ | Config. of **24** | $R^4$ | Time/h | Yield/%[b)] | *E*:*Z* |
|---|---|---|---|---|---|---|---|---|
| 1 | Ph | Me | H | *Z* | *i*-Pr | 3.5 | 67 | 87:13 |
| 2 | Ph | Me | H | *Z* | Ph[c)] | 3.5 | 76 | 89:11 |
| 3 | $(CH_2)_5N$ | Bu | Me | *Z* | *i*-Pr | 2.0 | 98 | > 99:1 |
| 4 | $(CH_2)_5N$ | Bu | Me | *E* | *i*-Pr | 2.0 | 100 | > 99:1 |

a) The reaction was carried out at room temperature using an allylstannane (0.30 mmol), an aldehyde (0.60 mmol) and $Bu_2SnCl_2$ (0.36 mmol). b) Isolated yield based on the allylstannane. c) Benzaldehyde (0.36 mmol) was used.

(**74**) of the carbonyl group to the tin atom to induce the carbon–carbon bond formation at the terminal carbon. Perfect regioselectivity was observed also in the $Bu_2SnCl_2$-catalyzed reaction of allylstannane **24b** with acyl chlorides, the carbon–carbon bond being generated exclusively at the $\gamma$-carbon of the allylstannane (Eq. 22), whereas the corresponding reaction of tributyl(crotyl)tin is less efficient in both yield and regioselectivity.[41] Acetals also are good electrophiles for the acylstannylation products: allylstannane **24c** reacts with $BF_3$-activated benzaldehyde dimethyl acetal to give $\gamma$-adducts **76** as a mixture of diastereomers (Eq. 23).




(22)




(23)

## 5. Conclusion

It has been disclosed that the carbostannylation of alkynes, 1,3-dienes, and 1,2-dienes using alkynyl-, allyl-, acyl-, alkenyl-, and arylstannanes proceeds efficiently using a palladium or nickel catalyst with an appropriate ligand. In particular, bidentate ligands like iminophosphine, diimine, and bisphosphine ligands are demonstrated to play critical roles in many cases. Most of the carbostannylation reactions are based on the activation of carbon–tin bonds through the oxidative addition to a palladium(0) or nickel(0) complex. This novel activation concept will be applied not only to the present reaction using other organostannanes but also to carbometalations in general to assist us to design novel synthetic methodologies. The mechanistic insight into the reaction through palladacyclopentadienes (dimerization–carbostannylation of alkynes in Section 3) should provide us with a basis for the understanding of similar reactions of metallacycles and should definitely contribute to the development of new dimerization–carbometalation reactions of unsaturated compounds.

We are indebted to our collaborators for their devotion to our chemistry: Dr. H. Yoshida, K. Yamasaki, Y. Nakao, T. Kurahashi, and Y. Honda at Kyoto University, and Dr. T. Tsuchimoto and Y. Yamamoto at Japan Advanced Institute of Science and Technology. This research was supported by Grants-in-Aid for COE Research on Elements Science, No. 12CE2005 and Scientific Research, No.12750758 from the Ministry of Education, Science, Sports and Culture. E.S. thanks the Asahi Glass Foundation for financial support.

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