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1,4-Carbosilylation of 1,3-Dienes via Palladium Catalyzed Three-Component Coupling Reaction

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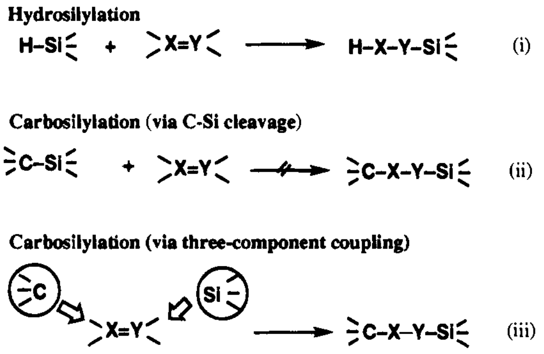
Abstract: Three-component coupling reaction of acid chlorides, organodisilanes, and 1,3-dienes achieves 1,4-carbosilylation of the 1,3-dienes to afford allylic silanes as the product. Bis(dibenzylideneacetone)palladium, a naked Pd(0) complex without donating ligand, showed high catalytic activity. A carbon and a silicon substituent are introduced at 1- and 4-positions of the 1,3-dienes regio- and stereoselectively with concomitant decarbonylation of the acid chlorides. A wide variety of allylic silanes are synthesized in high yields from these easily accessible substrates. On the other hand, a bulky acid chloride such as adamantane-1-carboxylic acid chloride did not undergo the decarbonylation reaction but afforded allylic silanes containing acyl functionality. In all these reactions, transmetalation of the disilanes with η^3-allylchloropalladium intermediates might be a critical step in the catalytic cycle. As a model reaction for the transmetalation, reaction of di-μ-chlorobis[(1,2,3-η)-4-phenyl-2-butenyl]dipalladium with disilanes was carried out. Although intermediate η^3-allylsilylpalladium species could not be detected, the corresponding allylic silanes, silyl chlorides, and Pd(0) metal were formed during the reaction. Furthermore, a similar three-component coupling reaction using aryl iodides, organosilylstannanes, and dienes also proceeded. However, the selectivity and the yield decreased considerably.

Introduction

Addition of organosilanes (H−Si) to unsaturated compounds (*hydrosilylation*)[1] is a most useful reaction for synthesis of a wide variety of organosilicon compounds [Scheme 1(i)]. On the other hand, if a carbon and a silicon unit, instead of a hydrogen and a silicon, are introduced simultaneously into unsaturates (*carbosilylation*), the reaction might be far more beneficial as synthetic method. However, while some carbon−metal bonds[2] such as C−Al and C−Cu are reactive enough to undergo so-called carbometalation reaction, most C−Si bonds are inert under usual reaction conditions. Therefore, it seems extremely difficult to activate C−Si bonds directly[3] toward insertion of unsaturates into these bonds [Scheme 1(ii)]. In order to resolve this dilemma, we explored three-component coupling reaction,[4] in which a carbon and a silicon substituents are introduced from different sources into unsaturated substrates [Scheme 1(iii)]. We adopted 1,3-dienes as the unsaturated substrates, since selective introduction of the carbon and the silicon units at 1- and 4-positions of the 1,3-dienes gives synthetically important allylic silanes. Allylic silanes[5] are highly versatile synthetic intermediates due to their regioselective reactions with various electrophiles.[6] Therefore, much attention has been paid to preparation method[7] of allylic silanes including allylic Grignard reactions,[7a,b] hydrosilylation of 1,3-dienes,[7c−e] and Wittig reactions with β-silylethylidenephosphorane.[7f,g]

Scheme 1



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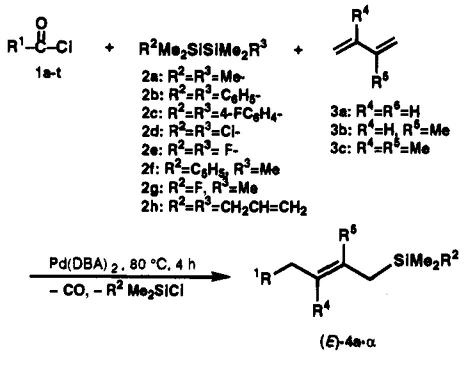
In this paper, we describe a palladium catalyzed three-component coupling reaction of organodisilanes (Si−Si),[8] 1,3-dienes, and acid chlorides to realize the overall carbosilylation reaction. The reaction is highly regio- and stereoselective providing a useful synthetic method of allylic silanes from these easily accessible starting materials. We also developed similar three-component coupling reaction with 1,3-dienes, where organosilylstannanes (Si−Sn)[9] are employed as the silicon source and aryl iodides as the carbon source.

Results and Discussion

Carbosilylation of 1,3-Dienes Using Acid Chlorides and Organodisilanes. It is well-known that acid chlorides react with low valent transition metal complexes by oxidative addition[10] and generate carbon−transition metal bonds. On the other hand, organodisilanes[8] are very useful silylating reagents in the presence of a transition metal catalyst. First we employed acid chlorides as a carbon source and organodisilanes as a silicon source in the three-component coupling reaction with 1,3-dienes (eq 1).[11] The results are summarized in Table 1. Benzoyl chloride (**1a**) reacts with hexamethyldisilane (**2a**) and 1,3-butadiene (**3a**) in the presence of a catalytic amount (5 mol %) of Pd(DBA)$_2$[12,13] (DBA = dibenzylideneacetone) to afford the coupling product (**4a**) in high yield (entry 1). The phenyl and the silyl substituents are introduced regio- and stereoselectively at the 1- and 4-positions of **3a** providing only the (*E*) isomer. Decarbonylation from the acid chloride[14] proceeded completely and coupling products containing carbonyl functionalities were not detected.



(1)

The reaction also proceeds with substituted benzoyl chlorides in good to high yields. Thus, chloro (**1c**), bromo (**1d**), nitro (**1e**), and keto (**1f** and **1g**) functionalities were tolerated in the reaction (entries 3−7). Usually direct synthesis of these functionalized allylic silanes are highly difficult by the conventional procedures.[7] 2- and 1-Naphthoyl chlorides (**1h** and **1i**) also afforded the corresponding products in excellent yields (entries 8 and 9). 2-Furoyl chloride (**1j**), 5-bromo-2-furoyl chloride (**1k**), and 2-thiophenecarbonyl chloride (**1l**) also afforded the (*E*)-1,4-adducts in good yields (entry 10−12). Terephthaloyl chloride (**1m**) afforded the corresponding compound having two allylic silane side chains (entry 13). However, *o*-phthaloyl chloride and 2-(*p*-toluoyl)benzoyl chloride were not consumed in the reaction, suggesting steric congestion with these substrates affects the reaction. Various (*E*)-alkenoyl chlorides (**1n−r**) can be employed in the present coupling reaction and provided the corresponding (*E*)-1,4 adducts regio- and stereoselectively (entries 14−18). Alkynoyl chlorides (**1s** and **1t**) also afforded the corresponding products in high yields (entries 19 and 20). As 1,3-dienes, isoprene (**3b**) and 2,3-dimethyl-1,3-diene (**3c**) can be employed. The reaction gave the products (**4u−w**) regioselectively (entries 21−23); with isoprene (**3b**) the trimethylsilyl group is introduced on the methylene carbon closer to the methyl substituent. In these cases, however, stereoselectivity was often modest. Symmetrically substituted disilanes such as 1,1′-diphenyl- (**2b**), 1,1′-di-(4-fluorophenyl)- (**2c**), 1,1′-dichloro- (**2d**), and 1,1′-difluorotetramethyldisilanes (**2e**) afforded the corresponding carbosilylation products (**4x-α**) with high regio- and stereoselectivity (entries 24−27). As for monosubstituted unsymmetrical disilanes, phenylpentamethyldisilane (**2f**) afforded the dimethylphenylsilyl derivative (**4x**) exclusively (entry 28), whereas fluoropentamethyldisilane (**2g**) gave fluorodimethyl isomer (**4α**) as a major product (entry 29).

Effects of some reaction conditions and selected catalyst precursors were examined in the coupling reaction using **1a**, **2a**, and **3a**. As a solvent, aromatic hydrocarbon such as toluene gave the best results (entry 1); the reaction in tetrahydrofuran (THF) and dimethylformamide (DMF) lowered the yields considerably (15% and 5%, respectively). The reaction proceeds smoothly at 80 °C, while lower (50 °C) or higher (130 °C) reaction temperature reduced the yield considerably (19% and 36%, respectively). As a catalyst precursor, Pd(DBA)$_2$,[12,13] a naked Pd(0) complex without donating ligand, is most effective. An addition of AsPh$_3$ (As/Pd = 4) or P(OEt)$_3$ (P/Pd = 4) to Pd(DBA)$_2$ reduced the yield of **4a** to 41% or 13%, respectively.

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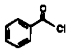
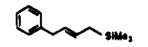
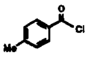
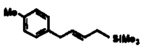
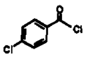
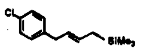
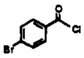
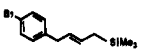
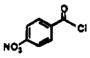
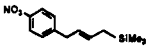
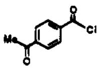
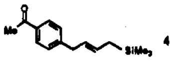
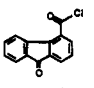
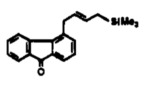
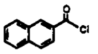
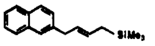
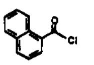
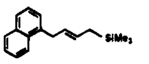
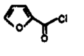
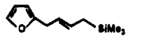
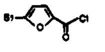
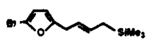
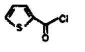
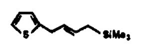
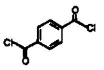
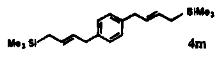
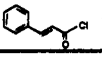
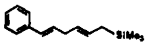
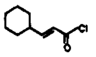
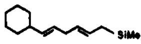
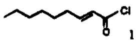
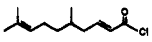
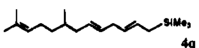
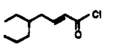
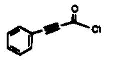
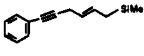
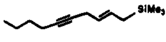
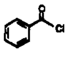
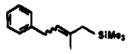
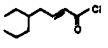
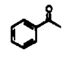
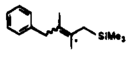
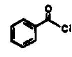
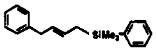
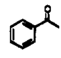
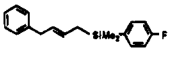
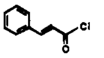
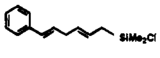
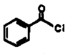
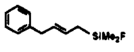
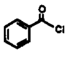
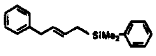
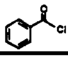
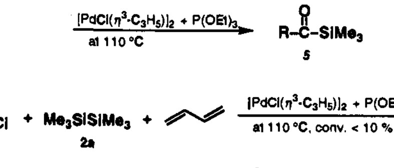
Table 1. 1,4-Carbosilylation of 1,3-Dienes Using Acid Chlorides and Organodisilanes[a]

entry	acid chloride	disilane	diene	product	yield / %[b]
1	 **1a**	**2a**	**3a**	 **4a**	86(93)
2	 **1b**	**2a**	**3a**	 **4b**	77
3	 **1c**	**2a**	**3a**	 **4c**	80
4	 **1d**	**2a**	**3a**	 **4d**	90
5	 **1e**	**2a**	**3a**	 **4e**	51
6	 **1f**	**2a**	**3a**	 **4f**	92
7	 **1g**	**2a**	**3a**	 **4g**	74
8	 **1h**	**2a**	**3a**	 **4h**	95
9	 **1i**	**2a**	**3a**	 **4i**	92
10	 **1j**	**2a**	**3a**	 **4j**	61
11	 **1k**	**2a**	**3a**	 **4k**	63
12	 **1l**	**2a**	**3a**	 **4l**	64
13	 **1m**	**2a**[c]	**3a**	 **4m**	70
14	 **1n**	**2a**	**3a**	 **4n**	94
15	 **1o**	**2a**	**3a**	 **4o**	78
16	 **1p**	**2a**	**3a**	 **4p**	72
17	 **1q**	**2a**	**3a**	 **4q**	57
18	 **1r**	**2a**	**3a**	 **4r**	81
19	 **1s**	**2a**	**3a**	 **4s**	85
20	 **1t**	**2a**	**3a**	 **4t**	75
21	 **1a**	**2a**	**3b**	 **4u**[d]	82(91)
22	 **1r**	**2a**	**3b**	 **4v**[e]	80
23	 **1a**	**2a**	**3c**	 **4w**[f]	47
24	 **1a**	**2b**	**3a**	 **4x**	68
25	 **1a**	**2c**	**3a**	 **4y**	71
26	 **1n**	**2d**	**3a**	 **4z**	61
27	 **1a**	**2e**	**3a**	 **4α**	40
28	 **1a**	**2f**	**3a**	 **4x**	89
29	 **1a**	**2g**	**3a**	**4α** + **4a** 70 % 9 %	

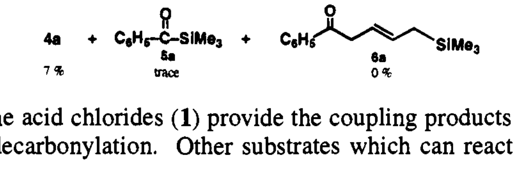
[a] Conditions: acid chloride (**1**: 0.50 mmol), disilane (**2**: 0.50 mmol), 1,3-diene (**3**: 1.5 mmol), Pd(DBA)$_2$ (0.025 mmol; 5 mol %), and toluene (2.0 mL) at 80 °C for 4 h. [b] Isolated yields. Numbers in parentheses show GC yields determined by the internal standard method. [c] The disilane (1.0 mmol). [d] *E*/*Z* = 75/25. [e] *E*/*Z* = 91/9. [f] *E*/*Z* = 65/35.

Furthermore, the addition of PBu$_3$ (P/Pd = 4) or bidentate ligands such as DPPE [1,2-bis(diphenylphosphino)ethane], DPPP [1,2-bis(diphenylphosphino)propane], and DPPF [1,1′-bis(diphenylphosphino)ferrocene] (for these bidentate phosphines, ligand/Pd = 2) totally suppressed the conversion of **1a**. Other selected transition metal precursors (5 mol %) such as Pd(PPh$_3$)$_4$, PdCl$_2$(PPh$_3$)$_2$, Pt(DBA)$_2$, and Pt(CO)$_2$(PPh$_3$)$_2$ were not active as the catalyst and the acid chlorides remained intact. Thus, palladium(0) complex without coordinating ligands is essential as the catalyst precursor for the present three-component coupling reaction.

In the reactions listed in Table 1, the decarbonylation[14,15] from the acid chlorides (**1**) took place completely. Usually, *catalytic* decarbonylation of acid chlorides or aldehydes are sluggish,[16] especially at lower reaction temperatures. In the present coupling reaction, highly unsaturated nature of the palladium catalyst center might facilitate such fast and complete decarbonylation of the acid chlorides. After the reaction, comparable amount of carbon monoxide was detected in the gas phase by GC analysis (on Molecular Sieve 13X-S, oven temperature at 50 °C). When the reaction was carried out under carbon monoxide pressure (10 kg/cm^2), consumption of the acid chlorides was low (<10%), and **4** was not obtained at all. Yamamoto and co-workers reported that palladium catalyzed reaction of acid chlorides (**1**) with Me$_3$SiSiMe$_3$ (**2a**) affords acyl silanes (**5**) by suppressing the decarbonylation of **1** (eq 2).[17] The key to the suppression was added triethyl phosphite [P(OEt)$_3$] ligand to [PdCl(η^3-C$_3$H$_5$)]$_2$. We attempted the same catalyst system under the reaction conditions of entry 1. However, conversion of the acid chloride (**1a**) was quite low (<10%), and the yield of the coupling product (**4a**) was only 7% with concomitant formation of a trace of PhCOSiMe$_3$ (**5a**) (eq 3). Allylic silanes having carbonyl functionality such as **6a** were not obtained at all. Other ligands such as P(OPh)$_3$, P(OPr^i)$_3$, and P(OCH$_2$)$_3$CEt added to Pd(DBA)$_2$ or [PdCl(η^3-C$_3$H$_5$)]$_2$ could not suppress the decarbonylation; usually these added ligands lowered the conversion of the acid chlorides considerably.

 (2)[17]

$$\underset{\mathbf{1}}{\mathrm{R}\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{Cl}} + \underset{\mathbf{2a}}{\mathrm{Me_3SiSiMe_3}} \xrightarrow[\text{at }110\,^\circ\mathrm{C}]{[\mathrm{PdCl}(\eta^3\text{-}\mathrm{C_3H_5})]_2\ +\ \mathrm{P(OEt)_3}} \underset{\mathbf{5}}{\mathrm{R}\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{SiMe_3}} \qquad (2)$$

 (3)

The acid chlorides (**1**) provide the coupling products (**4**) via the decarbonylation. Other substrates which can react with a

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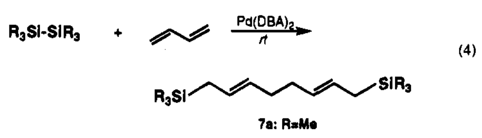
(15) (a) Rich, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5886. (b) Krafft, T. E.; Rich, J. D.; McDermott, P. J. *J. Org. Chem.* **1990**, *55*, 5430.

(16) (a) Tsuji, J. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P. Eds.; John Wiley & Sons: New York, 1977; Vol. 2, pp 595–654. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 775.

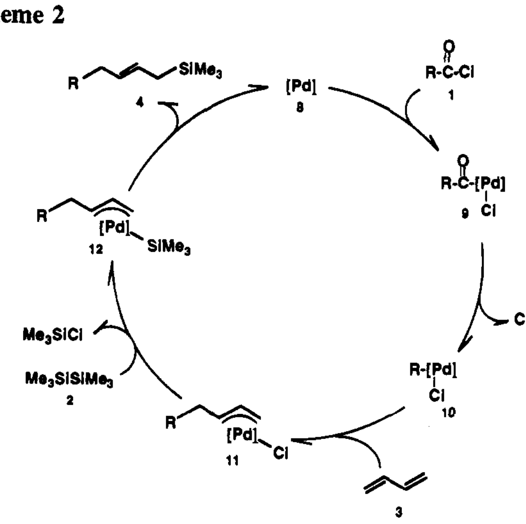
low valent metal center by oxidative addition might work as the carbon source in an analogous three-component coupling reaction. Thus, several candidates for the carbon source are examined. Benzoyl bromide[14b] and benzoyl fluoride[18] did not afforded the coupling product (**4a**) at all; with benzoyl bromide the reaction was complicated, while benzoyl fluoride did not convert. Heptanoyl chloride did not afford the carbosilylation products at all presumably due to β-hydrogen elimination of hexyl palladium intermediate generated by the oxidative addition of the acid chloride followed by the decarbonylation. As for an aryl halide, bromobenzene afforded **4a** in 40% yield. However, with iodobenzene, its conversion was low (40%), and the yield of **4a** was only 8%. Chlorobenzene did not convert at all. β-Bromostyrene afforded the corresponding coupling product (**4n**) in lower yield (32%) than the corresponding cinnamoyl chloride (entry 14). With 4-bromobenzoyl chloride (**1d**) as mentioned above (entry 4), the reaction occurred at the acid chloride site rather than the aromatic bromide site, suggesting the reaction at the former site seems to be faster than the latter. This rate difference was confirmed in a competitive reaction between 4-methylbenzoyl chloride (**1b**; 1.0 equiv) and bromobenzene (1.0 equiv) in the presence of $Me_3SiSiMe_3$ (**2a**; 0.50 equiv) and 1,3-butadiene (**3a**; 3.0 equiv) under standard reaction conditions [at 80 °C, for 2 h, with 5 mol % of $Pd(DBA)_2$ based on **2a**]. In the reaction, most of the bromobenzene was recovered and the coupling product came almost from the acid chloride: yield of **4b**, 78%; **4a**, trace. The same result was observed with benzoyl chloride (**1a**; 1.0 equiv), 4-bromotoluene (1.0 equiv), **2a** (0.50 equiv), and **3a** (3.0 equiv) indicating the *p*-methyl substituents have virtually no effects on the reactivity: yield of **4a**, 89%; **4b**, trace. Moreover, esters having good leaving groups such as phenyl trifluoromethanesulfonate (C_6H_5OTf) and diethyl phenyl phosphate [$C_6H_5OP(O)(OC_2H_5)_2$] have no reactivities in the reaction. We have recently reported dimerization–double silylation of 1,3-dienes using **2a** catalyzed by $Pd(DBA)_2$, in which the reaction smoothly proceeds at room temperature and provides the product (**7**) in high yield regio- and stereoselectively (eq 4).[8a] When the substrates of the carbon source were apparently inert [with C_6H_5COF, C_6H_5Cl, C_6H_5OTf, and $C_6H_5OP(O)(OC_2H_5)_2$], **7a** was formed in high yields (>80%).



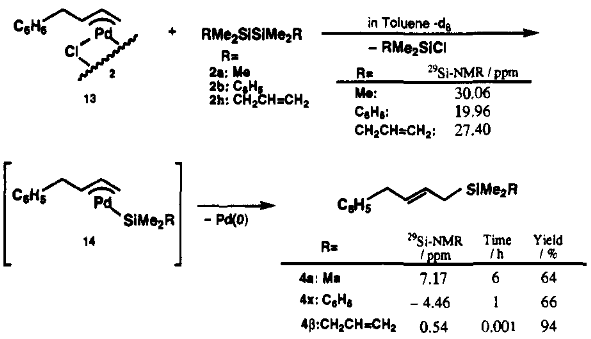
(4)

In the present reaction, one of the silyl moieties of the disilanes (**2**) is incorporated in the allylic silane (**4**) as the product. Fate of the other silyl moiety of **2** was examined in the reaction using $Me_3SiSiMe_3$ (**2a**) by measuring ^{29}Si-NMR spectra of the resulting reaction mixture. After the reaction was carried out under the same reaction conditions as entry 1, the expected amount of Me_3SiCl (30.31 ppm; lit.[19a] 30.27 ppm) was found along with excess **2a** (−20.51 ppm; lit.[19b] −20.51 ppm), indicating that one of the silyl moieties of the disilane (**2**) is trapped as the silyl chloride. Strong Si−Cl bond (Si−Cl bond energy of Me_3SiCl:[20] 113 kcal mol^{-1}) may be a driving force of the reaction.

Scheme 2



Scheme 3



R=	^{29}Si-NMR / ppm
Me:	30.06
C_6H_5:	19.96
$CH_2CH{=}CH_2$:	27.40

R=	^{29}Si-NMR / ppm	Time / h	Yield / %
4a: Me	7.17	6	64
4x: C_6H_5	− 4.46	1	66
4β: $CH_2CH{=}CH_2$	0.54	0.001	94

A possible catalytic cycle for the present reaction via the decarbonylation (Table 1) is shown in Scheme 2. Oxidative addition of acid chloride (**1**) to the Pd(0) active catalyst species (**8**) initiates the catalytic cycle and gives acyl palladium species (**9**). After the decarbonylation to **10**, 1,3-diene (**3**) inserts into the resulting C−Pd bond providing allylchloropalladium intermediate (**11**). Transmetalation of disilane (**2**) with **11** may provide allylsilyl species (**12**) with a concomitant formation of the silyl chloride. Finally, reductive elimination of **12** affords the allylic silane (**4**) as the product and regenerates the Pd(0) active catalyst (**8**).

With regard to the catalytic cycle, oxidative addition of acid chlorides[10] (**1**) to a low valent metal complex ($\mathbf{8} + \mathbf{1} \rightarrow \mathbf{9}$) and decarbonylation of acyl metal complexes[14] ($\mathbf{9} \rightarrow CO + \mathbf{10}$) are well-known. Furthermore, insertion of 1,3-diene (**3**) into carbon−metal bond ($\mathbf{10} + \mathbf{3} \rightarrow \mathbf{11}$) has been also observed in several transition metal reactions.[21] However, there is no precedent for explicit transmetalation of disilanes to form silyl-metal species ($\mathbf{11} + \mathbf{2} \rightarrow \mathbf{12}$). Thus, we examined a model reaction of the transmetalation step. In the carbosilylation reaction of 1,3-butadiene (**3a**) using benzoyl chloride (**1a**) and $Me_3SiSiMe_3$ (**2a**) (entry 1), chloro[(1,2,3-η)-4-phenyl-2-butenyl]-palladium intermediate (**11a**: R = C_6H_5) might be involved in the catalytic cycle. As a model complex for **11a**, di-μ-chlorobis-[(1,2,3-η)-4-phenyl-2-butenyl]dipalladium (**13**) was prepared from the corresponding chloride and Na_2PdCl_4.[33c,35] Then, a stoichiometric reaction of **13** with $Me_3SiSiMe_3$ (**2a**; 2 equiv) was carried out at room temperature in toluene-d_8 (Scheme 3). In the reaction, a clear yellow solution gradually turned brown, and finally palladium mirror and a small amount of palladium powder appeared in 6 h. ^{29}Si-NMR spectrum of the colorless

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(17) Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics* **1987**, *6*, 974.

(18) Olah, G. A.; Kreinenbuhl, P. *J. Org. Chem.* **1967**, *32*, 1614.

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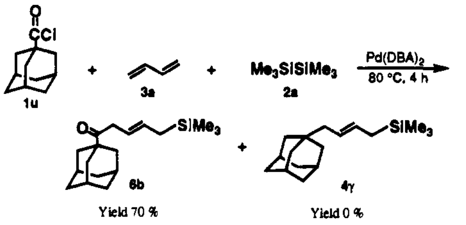
(20) Corey, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, 1989; p 6.

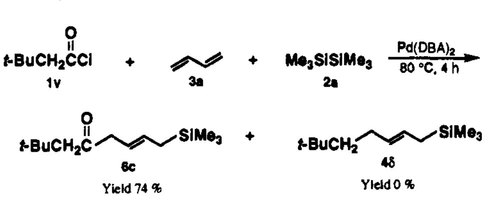
(21) Kemmitt, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 5, pp 53−55, 219−220.

filtrate showed that Me_3SiCl (30.06 ppm) and **4a** (7.17 ppm) were formed in equal amounts; yield of the latter was 64% which was determined with ^{1}H-NMR spectrum using mesitylene as an internal standard. The transmetalation would proceed via intermediate allylsilyl metal species (**14**) with a concomitant formation of silyl chloride. We attempted to isolate the intermediate **14** by adding PPh_3 or PMe_3 (2 equiv) to the reaction mixture. However, the added ligand apparently hindered the transmetalation, and any silyl species such as **14** could not be detected with ^{29}Si-, ^{1}H-, and ^{13}C-NMR spectra. 1,1′-Diphenyltetramethyldisilane (**2b**) also reacted with **13** under the same reaction conditions. The reaction was faster than that of **2a**; in 1 h, the palladium mirror appeared. With 1,1′-diallyltetramethyldisilane (**2h**), the reaction was much faster; within 5 s black powders precipitated. In these reaction mixtures, comparable amount of the corresponding silyl chloride [$C_6H_5Me_2SiCl$[22] or $(CH_2{=}CHCH_2)Me_2SiCl$] and allylic silane (**4x** or **4β**) were detected by ^{29}Si-NMR. The yields of **4x** and **4β** were determined with ^{1}H-NMR spectra using mesitylene as the internal standard. Precoordination through the unsaturated substituents of **2b** and **2h** might accelerate the transmetalation reaction. In these cases, the postulated intermediate **14** could not be detected, either. As soon as **14** is formed, fast reductive elimination of these highly unsaturated (14e) species may afford **4** and Pd(0) very quickly.

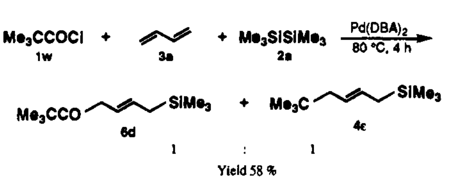
Coupling Reaction without Decarbonylation of Acid Chlorides. The acid chlorides such as listed in Table 1 undergo the complete decarbonylation reaction (vide supra). In contrast, adamantane-1-carboxylic acid chloride (**1u**) did not undergo the decarbonylation, but selectively afforded **6b** containing the acyl functionality in 70% yield (eq 5). Notably, the coupling product via the decarbonylation (**4γ**) was not afforded at all. Similar result was obtained with *tert*-butylacetyl chloride (**1v**), affording **6c** in 74% yield without formation of **4δ** (eq 6). With these sterically demanding acid chlorides, equilibrium between acyl and alkylcarbonyl species might lie far toward the former.[23] On the other hand, pivaloyl chloride (**1w**) afforded a mixture of two allylic silanes formed with and without the decarbonylation (**6d** and **4ε** in 58% yield; **6d**/**4ε** = 1/1) (eq 7). Thus, difference between the reaction with and without the decarbonylation seems to be very subtle. A competitive reaction between **1u** and **1a** was carried out (eq 8). In the reaction, only **4a** derived from **1a** via the decarbonylation was afforded exclusively; **6b**, **6a**, and **4γ** were not obtained at all. The similar reactivity was observed in the competitive reaction between **1u** and **1o**, affording only **4o** derived from **1o**; **6b**, **6e**, and **4γ** were not obtained (eq 9). Insertion of the diene into aryl– or alkenyl–Pd bond (**10** + **3** → **11**: in Scheme 2) might be much faster than the insertion into acyl–Pd bonds (**9** + **3** → **15**: in Scheme 4, cycle A). From benzoylformyl chloride (**1x**), the main product is the double decarbonylation product (**4a**), while **6a** was obtained only in low yield (eq 10). Moreover, phenylacetyl chloride (**1y**) did not afford the corresponding allylic silane, but afforded only acylsilane (**5b**) in high yield (eq 11). In this case, the oxidative addition of **1y** to the Pd(0) affords a phenylacetylpalladium intermediate. This particular metal species is well-known to be easily enolized: $C_6H_5CH_2(C{=}O)M \leftrightarrow C_6H_5CH{=}CH(OH)M$.[24] The enolization might affect the reaction and prevent the insertion of the 1,3-diene (Scheme 4, cycle B).



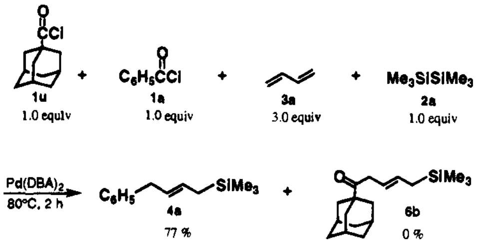
(5)



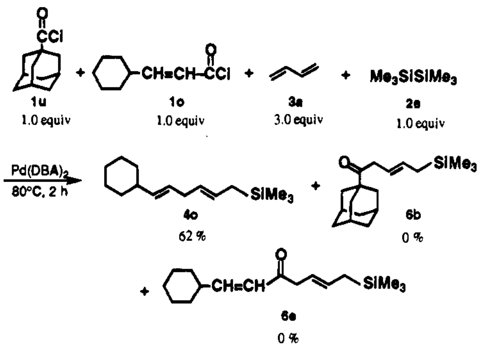
(6)



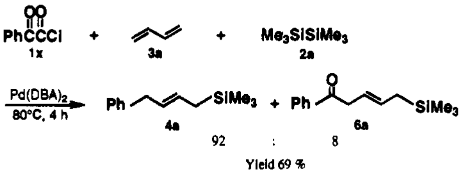
(7)



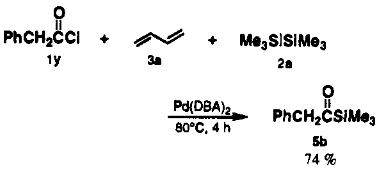
(8)



(9)



(10)



(11)

Carbosilylation of 1,3-Dienes Using Aryl Iodides and Organosilylstannanes. In the carbosilylation of 1,3-dienes (**3**) using disilanes (**2**) (eq 1), the transmetalation of **2** is a key step in the catalytic cycle (Scheme 2). On the other hand, organo-

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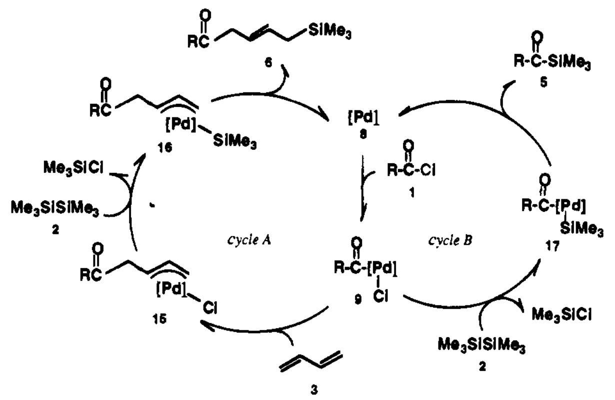
[22] ^{29}Si-NMR: Nguyen, D. C.; Chvalovsky, V.; Schraml, J.; Magi, M.; Lippmaa, E. *Collect. Czech. Chem. Commun.* **1975**, *40*, 875.

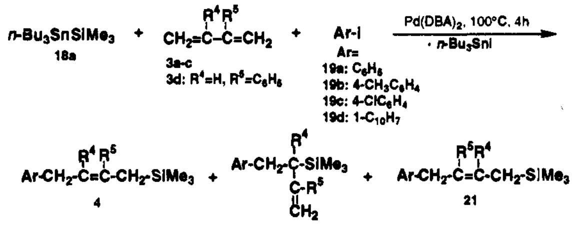
[23] Alexander, J. J. In *The Chemistry of the Metal-Carbon Bonds*; Hartley, F. R., Patai, S., Eds.; John Wiley & Sons: Chichester, 1985; Vol. 2, pp 346–347.

[24] (a) Alper, H. *Adv. Organomet. Chem.* **1981**, *19*, 183. (b) Francalanci, F.; Gardano, A.; Abis, L.; Fiorani, T.; Foà, M. *J. Organomet. Chem.* **1983**, *243*, 87.

Scheme 4



stannanes are well-known to undergo the transmetalation efficiently.[25] Thus, we tried to utilize organosilylstannanes (**18**) in place of **2** as the silicon source. When **18** was used in place of **2** in eq 1, conversion of **18** was low and the corresponding carbosilylation products (**4**) were obtained only in low yields (<5%). After examination of several possible carbon source, we found that aryl iodides (**19**) are suitable in the carbosilylation reaction using **18** (eq 12). The results are listed in Table 2. Iodobenzene (**19a**) reacted with n-$Bu_3SnSiMe_3$ (**18a**) and 1,3-butadiene (**3a**) to afford the corresponding carbosilylation products (entry 30). Unlike the reaction using disilanes (**2**) as the silicon source, the reaction provided only a mixture of 1,4- (**4a**: *E*/*Z* mixture) and 1,2-adduct (**20a**) in 50% yield. Similar selectivity and yields were obtained when **19b**, **19c**, or 1-iodonaphthalene (**19d**) was used as the aryl iodide (entries 31−33). Aryl bromides and chlorides did not provide the corresponding carbosilylation products at all. Isoprene (**3b**; entries 34−36), 2,3-dimethyl-1,3-butadiene (**3c**; entry 37), and 2-phenyl-1,3-butadiene (**3d**; entries 38 and 39) also provided the corresponding coupling products. However, selectivity of the reaction was also moderate; a mixture of 1,4- and 4,1-adducts were obtained when the unsymmetrical dienes (**3b** and **3d**) were employed.



$$\underset{\mathbf{18a}}{n\text{-}\mathrm{Bu_3SnSiMe_3}} + \underset{\substack{\mathbf{3a\text{-}c}\\ \mathbf{3d}:\ \mathrm{R^4{=}H,\ R^5{=}C_6H_5}}}{\mathrm{CH_2{=}\overset{R^4}{\overset{|}{C}}{-}\overset{R^5}{\overset{|}{C}}{=}CH_2}} + \underset{\substack{\mathrm{Ar=}\\ \mathbf{19a}:\ \mathrm{C_6H_5}\\ \mathbf{19b}:\ \mathrm{4\text{-}CH_3C_6H_4}\\ \mathbf{19c}:\ \mathrm{4\text{-}ClC_6H_4}\\ \mathbf{19d}:\ \mathrm{1\text{-}C_{10}H_7}}}{\mathrm{Ar\text{-}I}} \xrightarrow[-\,n\text{-}\mathrm{Bu_3SnI}]{\mathrm{Pd(DBA)_2,\ 100^\circ C,\ 4h}}$$

$$\underset{\mathbf{4}}{\mathrm{Ar\text{-}CH_2\text{-}\overset{R^4}{\overset{|}{C}}{=}\overset{R^5}{\overset{|}{C}}\text{-}CH_2\text{-}SiMe_3}} + \underset{\mathbf{20}}{\mathrm{Ar\text{-}CH_2\text{-}\overset{R^4}{\overset{|}{C}}\text{-}SiMe_3}\atop \mathrm{\underset{CH_2}{\overset{\|}{C\text{-}R^5}}}} + \underset{\mathbf{21}}{\mathrm{Ar\text{-}CH_2\text{-}\overset{R^5}{\overset{|}{C}}{=}\overset{R^4}{\overset{|}{C}}\text{-}CH_2\text{-}SiMe_3}} \qquad (12)$$

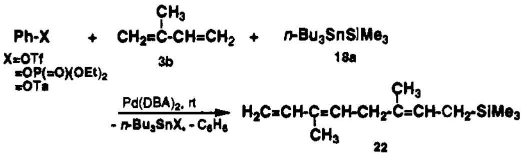
Effect of the catalyst precursor was examined in the reaction using **18a**, **3b**, and **19a**. Among the complexes examined, $Pd(DBA)_2$ shows the best result (entry 34); the yield is 39% with $PdMe_2(COD)$, 40% with $Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$, 40% with $PdBr_2(COD)_2$, 32% with $PdCl_2(COD)_2$, 20% with $Pd(PPh_3)_4$, and 16% with $Pd(OAc)_2$. Naked palladium complex without donating ligands seems most favorable, which is reminiscent of the carbosilylation using the organodisilanes (**2**) and the acid chlorides (**1**) (eq 1). Other selected catalyst precursors such as $RhCl(PPh_3)_3$, $[Rh(COD)_2]BF_4$, and $Pt(CO)_2(PPh_3)_2$ did not show any catalytic activity. As for the organosilylstannane, n-$Bu_3SnSiMe_3$ (**18a**) was the most suitable. Other silylstannanes such as $Me_3SnSiMe_3$, $Me_3SnSiMe_2(t\text{-}Bu)$, $Me_3SnSiMe_2Ph$, $Ph_3SnSiMe_3$, and n-$Bu_3SnSiMe_2SiMe_3$ were totally ineffective and did not afford any carbosilylation products.

Table 2. Carbosilylation Using n-$Bu_3SnSiMe_3$ (**18a**)[a]

		product		
entry	diene	Ar−I	yield,[b] %	distribution[c]
30	**3a**	**19a**	(50) 42	**4a**:**20a**:**21a** = 84(88):16:−
31	**3a**	**19b**	40	**4b**:**20b**:**21b** = 85(88):15:−
32	**3a**	**19c**	56	**4c**:**20c**:**21c** = 88(87):12:−
33	**3a**	**19d**	61	**4i**:**20i**:**21i** = 85(87):15:−
34	**3b**	**19a**	(57) 48	**4u**:**20u**:**21u** = 75(55):13:12
35[d]	**3b**	**19a**	(39)	**4u**:**20u**:**21u** = 71(55):13:16
36	**3b**	**19d**	62	**4**ζ:**20**ζ:**21**ζ = 75(64):13:12
37	**3c**	**19a**	44	**4w**:**20w**:**21w** = 100(68):0:−
38	**3d**	**19a**	67	**4**η:**20**η:**21**η = 88(67):6:6
39	**3d**	**19d**	85	**4**θ:**20**θ:**21**θ = 84(70):8:8

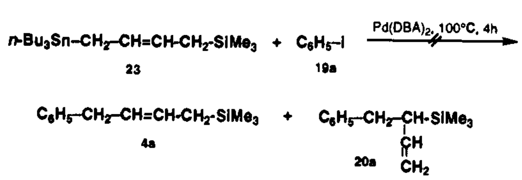
[a] n-$Bu_3SnSiMe_3$ (**18a**: 0.50 mmol), **3** (1.5 mmol), **19** (0.50 mmol), $Pd(DBA)_2$ (0.025 mmol), toluene (2.0 mL), at 100 °C for 4 h. [b] Isolated yield. Numbers in parentheses show GC yields determined by the internal standard method. [c] Percentages of the *E*-isomers of **4** are shown in the parentheses. [d] $PdMe_2(COD)$ (0.025 mmol) is used in place of $Pd(DBA)_2$.

Alkenyl iodides such as 1-iodo-1-octene and 1-iodo-1-cyclohexene reduced the yields appreciably (<20%), and the selectivities of the reaction were still moderate. The reaction path changed dramatically, when phenyl trifluoromethanesulfonate (Ph-OTf), diethyl phenyl phosphate ($PhOP({=}O)(OEt)_2$), or phenyl p-toluenesulfonate (Ph-OTs) was employed as the carbon source (eq 13). The reaction proceeded even at room temperature. However, no carbosilylation products were obtained, but an equimolar mixture of all four stereoisomers of **22** were isolated in 75−85% yields. The phenyl group was not incorporated in the products. As for the fate of the phenyl functionality, comparable formation of benzene was confirmed by GC analysis (on Chromosorb 103 at 200 °C). The mechanism of this reaction is not clear at the present stage.



$$\underset{\substack{\mathrm{X{=}OTf}\\ \mathrm{{=}OP({=}O)(OEt)_2}\\ \mathrm{{=}OTs}}}{\mathrm{Ph\text{-}X}} + \underset{\mathbf{3b}}{\mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}\text{-}CH{=}CH_2}} + \underset{\mathbf{18a}}{n\text{-}\mathrm{Bu_3SnSiMe_3}} \xrightarrow[-\,n\text{-}\mathrm{Bu_3SnX},\ -\,\mathrm{C_6H_6}]{\mathrm{Pd(DBA)_2,\ rt}} \underset{\mathbf{22}}{\mathrm{H_2C{=}CH\text{-}\underset{CH_3}{\underset{|}{C}}{=}CH\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{C}}{=}CH\text{-}CH_2\text{-}SiMe_3}} \qquad (13)$$

We have recently reported 1,4-silylstannation of 1,3-dienes (**3**) using **18** catalyzed by $Pt(CO)_2(PPh_3)_2$, which affords **23** selectively.[9a] There might be some possibility that the 1,4-silylstannation of the 1,3-dienes occurred first, and its product (**23**) was an intermediate for following Stille coupling reaction[25] to give **4a** and/or **20a**. However, in the reaction of **23** with iodobenzene (eq 14), no reactions occurred, and both **23** and **19a** were recovered unchanged.[26] Therefore, intermediacy of the 1,4-silylstannation products (**23**) is unlikely.



$$\underset{\mathbf{23}}{n\text{-}\mathrm{Bu_3Sn{-}CH_2{-}CH{=}CH\text{-}CH_2\text{-}SiMe_3}} + \underset{\mathbf{19a}}{\mathrm{C_6H_5{-}I}} \xrightarrow{\mathrm{Pd(DBA)_2,\ 100^\circ C,\ 4h}}\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!/\qquad \underset{\mathbf{4a}}{\mathrm{C_6H_5{-}CH_2{-}CH{=}CH\text{-}CH_2\text{-}SiMe_3}} + \underset{\mathbf{20a}}{\mathrm{C_6H_5{-}CH_2{-}\underset{\underset{CH_2}{\overset{\|}{CH}}}{\underset{|}{C}}H\text{-}SiMe_3}} \qquad (14)$$

A possible catalytic cycle for the carbosilylation using **18a** is illustrated in Scheme 5. Oxidative addition of aryl iodide (**19**) to palladium(0) species (step a) initiates the catalytic cycle.

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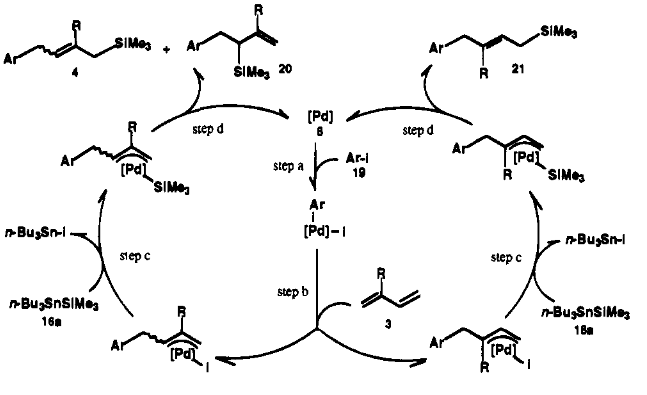
[25] (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Kosugi, M.; Migita, T. *Yuki Gosei Kagaku Kyokaishi* **1980**, *38*, 1142; *Chem. Abstr.* **1981**, *95*, 81044d. (c) Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47. (d) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771. (e) Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551. (f) Hassner, A.; Stumer, C. *Organic Syntheses Based on Name Reactions and Unnamed Reactions*; Pergamon, Elsevier: Oxford, 1994; pp 367−368.

[26] We recently found this type of reaction proceeds in good yields when $Pd(DBA)_2$−$AsPh_3$−LiCl catalyst system is employed. See: Obora, Y.; Tsuji, Y.; Kobayashi, M.; Kawamura, T. *J. Org. Chem.* **1995**, *60*, 4647.

Scheme 5



Insertion of 1,3-diene (**3**) into the resulting Pd−C bond (step b) affords η^3-allyl palladium intermediate. Then, transmetalation with **18a** (step c) provides allylsilyl palladium species and tributyltin iodide. Formation of the latter was confirmed by GC analysis (OV-17). Finally, reductive elimination of allylic silanes (step d) affords the products and regenerates the active catalyst species. The regiochemistry of the reaction is determined by steps b and d, while the stereochemistry would be governed by relative stability between syn and anti η^3-allyliodopalladium intermediates.

Conclusion

Carbosilylation of 1,3-dienes has been achieved by a three-component coupling reaction of the 1,3-dienes, organodisilanes, and acid chlorides. The reaction proceeds highly regio- and stereoselectively to afford various allylic silanes as the product. In the catalytic cycle, transmetalation of the disilanes with η^3-allylchloropalladium intermediate might be a critical step. Similar three-component coupling reaction proceeds using organosilylstannanes, aryl iodides, and 1,3-dienes, although the selectivity and the yield were considerably low.

Experimental Section

Materials. The reagents and the solvents were dried and purified before use by usual procedures.[27] Hexamethyldisilane (**2a**) was purchased from Aldrich. 1,2-Difluorotetramethyldisilane,[28a] fluoropentamethyldisilane,[28a] 1,2-dichlorotetramethyldisilane,[28b] and chloropentamethyldisilane[28b] were prepared by the methods reported by Kumada. Other disilanes were prepared from chloropentamethyldisilane or dichlorotetramethyldisilane by the reactions with corresponding organolithium (for **2b**, **2c**, and **2f**) or organomagnesium (**2h**) reagents. 2-Phenyl-1,3-butadiene was prepared by the known method.[29] Some acid chlorides were prepared from the corresponding carboxylic acids with thionyl chloride[30a] (for **1i**−**j**, **1p**−**q**) or with oxalyl chloride[30b] (for **1f**). Phenyl trifluoromethanesulfonate[31a] and diethyl phenyl phosphate[31b] were prepared by the reported procedures. Organosilylstannanes (**18**) were prepared by the methods by Chenard.[32] The following catalyst precursors were prepared by the published methods: $Pd(PPh_3)_4$,[33a] $PdCl_2(PhCN)_2$,[33b] $[PdCl(\eta^3\text{-}C_3H_5)]_2$,[33c] $PdCl_2(PPh_3)_2$,[33d] $PdMe_2(COD)$,[33e] $Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$,[33c] $PdBr_2(COD)$,[33f] $PdCl_2(COD)$,[33f] $Pt(DBA)_2$,[33g] $Pt(CO)_2(PPh_3)_2$,[33h] $Ru(COD)(COT)$,[33i] $[Rh(COD)_2]BF_4$.[33j]

Analytical Procedure. The NMR spectra (in $CDCl_3$) were recorded with JEOL α-400 and GX-270 spectrometers. The mass spectra were measured on Shimadzu QP-1000 (EI) and Shimadzu 9020-DF (HRMS) equipped with a PAC 1100S computer system. The GC analysis was made on a Shimadzu GC-8APF equipped with an integrater (C-R6A) with a column (3 mm i.d. × 3m) packed with Silicon OV-17 (2% on Uniport HP, 60/80 mesh) or Apiezon Grease L (5% on Uniport HP, 60/80 mesh). Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Coupling of Acid Chlorides (1), Organodisilanes (2), and 1,3-Dienes (3) (Eq 1). A typical procedure is described for the synthesis of **4a**. A mixture of 1,3-butadiene (**3a**; 1.5 mmol, 0.94 mL of 1.6 M stock solution in toluene), Pd $(DBA)_2$ (14 mg, 0.025 mmol), benzoyl chloride (**1a**; 70 mg, 0.50 mmol), hexamethyldisilane (**2a**; 73 mg, 0.50 mmol), toluene (2.0 mL), and a magnetic stirring bar were placed under argon flow in a 30 mL stainless steel autoclave containing an inserted glass liner. An air purge was confirmed by three pressurization (20 atm)−depressurization sequences with argon. The autoclave was heated to 80 °C in 10 min and held at this temperature for 4 h. The reaction was terminated by rapid cooling, and the autoclave was discharged. The resulting reaction mixture was passed through a short Florisil column (8 mm i.d. × 50 mm). GC analysis (OV-17) with phenanthrene as an internal standard showed the product (**4a**) was formed in 93% yield. The product (**4a**) was isolated in 86% yield (88 mg) by medium-pressure column chromatography (silica gel: Wakogel 300, 45−75 mm; hexane as an eluent) followed by Kugelrohr distillation (Büchi; pot temperature 80 °C/0.3 mmHg).

Coupling of Aryl Iodides (19), Organosilylstannanes (18), and 1,3-Dienes (3) (Eq 12). A typical reaction procedure is described for the synthesis of **4a**. A mixture of 1,3-butadiene (**3a**; 1.5 mmol, 0.94 mL of 1.6 M stock solution in toluene), $Pd(DBA)_2$ (14 mg, 0.025 mmol), **19a** (102 mg, 0.5 mmol), **18a** (181 mg, 0.5 mmol), toluene (2.0 mL), and a magnetic stirring bar were placed under argon flow in a 30 mL stainless autoclave containing an inserted glass liner. An air purge was confirmed by three pressurization (20-atm)−depressurization sequences with argon. After the reaction, the reaction mixture was treated with saturated ammonium fluoride solution to remove tributyltin iodide as insoluble tributyltin fluoride. The product was isolated in 42% yield (43 mg) by medium-pressure chromatography (silica gel/hexane) followed by Kugelrohr distillation.

Preparation of Di-μ-chlorobis[(1,2,3-η-4-phenyl-2-butenyl]dipalladium (13). 1-Chloro-4-phenyl-2-butene was prepared by the reaction of 1,4-dichloro-2-butene with phenyllithium in the presence of nickel catalyst.[34] Then, according to the published procedure,[33c,35] di-μ-chlorobis[(1,2,3-η-4-phenyl-2-butenyl]dipalladium (**13**) was prepared as a yellow solid (1.06 g, 78%) from 1-chloro-4-phenyl-2-butene and Na_2PdCl_4 with bubbling carbon monoxide: ^{1}H-NMR ($CDCl_3$) δ 3.04 (d, J = 12 Hz, 2H), 3.12−3.22 (m, 4H), 4.04 (d, J = 6 Hz, 2H), 4.19 (m, 2H), 5.35 (dt, J = 6 Hz, 12 Hz, 2H), 7.22−7.35 (m, 10H); ^{13}C-NMR δ 38.05 (t), 59.32 (d), 84.87 (d), 110.20 (t), 126.66 (d), 128.67 (d), 128.85 (d), 137.82 (s).

Reaction of Di-μ-chlorobis[(1,2,3-η)-4-phenyl-2-butenyl]dipalladium (13) with Disilanes (2a, 2f, 2h) (Scheme 3). The reaction using **2a** is typical. In a 5 mmϕ NMR tube, **13** (15 mg, 0.03 mmol) was dissolved in an argon-degassed toluene-d_8 (0.5 mL). Hexamethyldi-

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silane (**2a**) (9 mg 0.06 mmol) was added into the solution at 0 °C. Then, the mixture was left at room temperature. In 6 h, palladium mirror appeared on the wall of the NMR tube. The liquid part was transferred through a short Celite plug to another NMR tube. The formation of **4a** was confirmed by ^{1}H- and ^{13}C-NMR spectra. On the ^{1}H-NMR spectrum, the yield of **4a** was determined (64%) using mesitylene as an internal standard. Furthermore, the ^{29}Si-NMR spectrum is most diagnostic of comparable formation of trimethylsilyl chloride (30.06 ppm; lit.[19a] 30.27 ppm); also two other resonances appeared at −19.86 ppm (for excess **2a**; lit.[19b] −20.51 ppm) and 7.17 ppm (for **4a**).

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Supporting Information Available: Spectral (^{1}H and ^{13}C NMR and MS) and some elemental analysis data for **4a−z**, **4α,β**, **4ϵ−θ**, **5b**, **6b−d**, **20a−c**, **20i**, **20u**, **20ζ−θ**, **21u**, **21ζ−θ**, and **22** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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