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# PREPARATION OF 2-ARYL-3-SILYL- AND 2-ARYL-3-GERMYL-1,3-BUTADIENES VIA ARYLNICKELATION AND ZINCIOMETHYLATION

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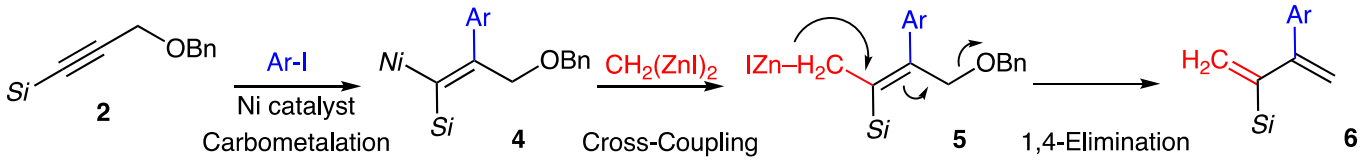
**Abstract** – Benzyl 3-silyl(or germyl)propargyl ether, aryl iodide, and bis(iodozincio)methane were assembled in the presence of a nickel catalyst to efficiently give 2-aryl-3-silyl(germyl)-1,3-butadienes via arylnickelation, zinciomethylation, and 1,4-elimination of zinc benzyloxide. As a ligand, an electron-deficient phosphine such as tris(2-furyl)phosphine was effective.

## INTRODUCTION

Catalyst design based on biological transformations has enabled organic syntheses to achieve high performance.[1] A transition-metal catalyst forms and breaks bonds in molecules by repeating oxidation/reduction processes around a specific metal atom using a specific Lewis acidity. In addition, the ligand of the metal atom can further enhance the potential of the metal atom and also control the stereochemistry by using the steric environment of the ligand itself. By utilizing these abilities to assemble multiple molecules at the same time and perform complex bond recombinations concurrently, the transition-metal catalyst has become the most powerful tool in modern synthetic organic chemistry. For example, a carbometalation of an organic halide with an alkyne under the existence of a transition metal catalyst is a highly selective method in which the organic moiety of the organic halide is added to the alkyne[2] and the three components are assembled by cross-coupling with different nucleophiles via the resulting alkenyl transition metal. It is still used for the selective alkene synthesis.[3] We have shown

Dedicated with respect to Prof. Dr. Yasuyuki Kita on the occasion of his 77th birthday

several approaches to zinciomethylation using bis(iodozincio)methane (**1**).[4] In one approach, it was used as the nucleophilic component, along with aryl iodide and alkyne, to produce allyl zinc.[5] In this instance, when propargyl ether is used as the alkyne with a leaving group, 1,3-butadiene can be obtained by a three-component assembling reaction via elimination.[6,7] The 2,3-disubstituted-1,3-butadienes obtained by this reaction have a cross-diene structure and this is included in the structures of various useful substances.[8] These dienes were also prepared by several reactions including Wittig reactions of 1,2-diketones,[9] transition metal-catalyzed cross-coupling reactions,[10] and oxidative coupling of *N*-tosylhydrazones.[11] Cross-coupling reactions of organoborane or -stannanes with 2-butyne-1,4-diol derivatives also directly produced 2,3-disubstituted-1,3-butadienes.[12] Our method starts the treatment of benzyl 3-trialkylsilylpropargyl ether **2** with aryl iodide **3** and bis(iodozincio)methane (**1**) in the presence of a nickel-catalyst.[7] Regioselective arylnickelation of **3** to silylalkyne **2** gave **4**, which reacts with **1** via cross-coupling, and 1,3-diene **6** via 1,4-elimination (Scheme 1).



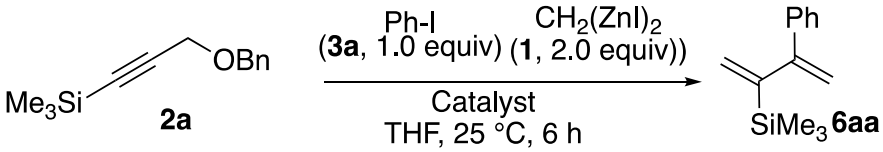

**Scheme 1**

## RESULTS AND DISCUSSION

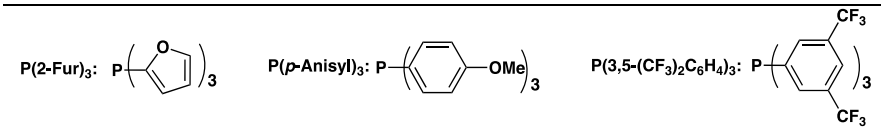
As shown in Table 1, treatment of 3-trimethylsilyl-1-bezyloxy-2-propyne (**2a**) with bis(iodozincio)methane (**1**) and iodobenzene (**3a**) in the presence of a palladium catalyst that was prepared from $Pd_2dba_3$•$CHCl_3$ and phosphine ligands resulted in quantitative recovery of alkyne **2a** (entries 1 and 2). Use of a Ni (II) catalyst gave the desired 2-aryl-3-silyl-1,3-butadiene **6aa**. Optimization of the yield by tuning the nickel catalyst was examined. The catalyst prepared from 2 mol% of $Ni(cod)_2$ and 3 mol% of $P(2\text{-furyl})_3$ improved the yield of **4a** to 99%.

As we reported previously,[7] 2-aryl-3-silyl-1,3-butadienes are prepared using this Ni-catalyzed reaction. As shown in Table 2, substrates with various organosilyl groups (**2b-d**) were examined in the transformation and gave the corresponding dienes **6** in good yields. Importantly, it has already been reported that benzyl[13] and 2,6-dimethoxyphenyl[14] groups on silane are easily substituted with a F atom; the F group on the Si group facilitates the Hiyama-coupling (Scheme 2).[15] This provides mild conditions for F-replacement of the 2,6-dimethoxyphenyl group on the Si atom while keeping the acid-sensitive diene skeleton intact. A variety of aryl iodides were applied to this transformation (entries 5–9) and were efficiently introduced on the 2-position of the 1,3-butadiene **6**. Aryl diiodides **3g–i** gave bis(dienyl)arenes **6ag-ai** efficiently and regioselectively (entries 10–12).

**Table 1.** Screening of Ni- and Pd-catalysts for 2-aryl-3-silyl-1,3-butadiene **6aa**

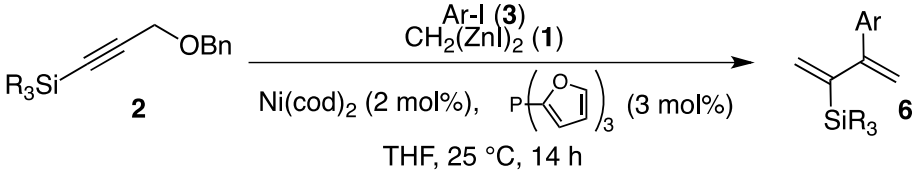



| entry | Catalyst | **6aa**/%[a] |
|---|---|---|
| 1 | $Pd_2dba_3$•$CHCl_3$ (0.05), P(*p*-Tol)$_3$ (0.2) | <1[b] |
| 2 | $Pd_2dba_3$•$CHCl_3$ (0.05), P(2-Fur)$_3$ (0.2) | <1[b] |
| 3 | $NiCl_2$(dppe) (0.1) | 39 |
| 4 | $NiCl_2$(P(*p*-Anisyl)$_3$)$_2$ (0.1) | 16 |
| 5 | Ni(cod)$_2$ (0.1), P(3,5-$(CF_3)_2C_6H_4$)$_3$ (0.2) | 72 |
| 6 | Ni(cod)$_2$ (0.1), P(2-Fur)$_3$ (0.2) | 84 |
| 7 | Ni(cod)$_2$ (0.02), P(2-Fur)$_3$ (0.03) | 99 |

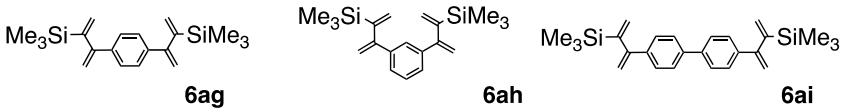



[a]Yields were determined by $^1$H-NMR using bromoform as an internal standard. [b]Recovery of **2a** (> 90%).

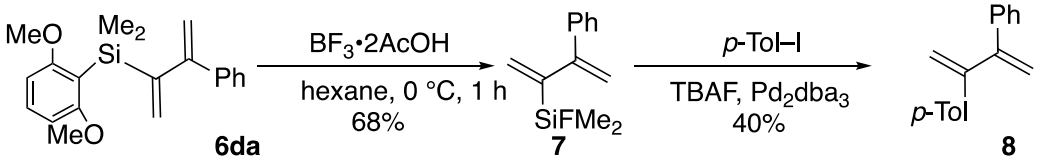
**Table 2.** Preparation of 2-aryl-3-silyl-1,3-butadienes **6**




| entry | $R_3Si$ | Ar-I | **6** / % |
|---|---|---|---|
| 1[a] | $Me_3Si$- (**2a**) | Ph-I (**3a**) | 99 (**6aa**)[c] |
| 2[a] | $PhMe_2Si$- (**2b**) | Ph-I (**3a**) | 76 (**6ba**)[c] |
| 3[a] | $BnMe_2Si$- (**2c**) | Ph-I (**3a**) | 97 (**6ca**)[c] |
| 4[a] | (2,6-$(MeO)_2C_6H_3$)$Me_2Si$- (**2d**) | Ph-I (**3a**) | 92 (**6da**)[c] |
| 5[a] | $Me_3Si$- (**2a**) | *p*-Tol-I (**3b**) | 100 (**6ab**)[c] |
| 6[a] | $Me_3Si$- (**2a**) | *p*-$MeOC_6H_4$-I (**3c**) | 96 (**6ac**)[c] |
| 7[a] | $Me_3Si$- (**2a**) | *p*-$CF_3C_6H_4$-I (**3d**) | 83 (**6ad**)[c] |
| 8[a] | $Me_3Si$- (**2a**) | *p*-$BrC_6H_4$-I (**3e**) | 96 (**6ae**)[c] |
| 9[a] | $Me_3Si$- (**2a**) | *p*-$NCC_6H_4$-I (**3f**) | 32 (**6af**)[c] |
| 10[b] | $Me_3Si$- (**2a**) | *p*-$IC_6H_4$-I (**3g**) | 64 (**6ag**)[d] |
| 11[b] | $Me_3Si$- (**2a**) | *m*-$IC_6H_4$-I (**3h**) | 66 (**6ah**)[d] |
| 12[b] | $Me_3Si$- (**2a**) | 4,4'-diiodobiphenyl (**3i**) | 99 (**6ai**)[d] |



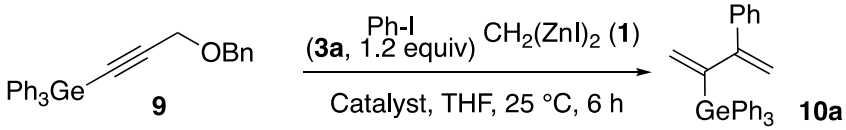

[a]**1** (1.2 mmol), **2** (1.0 mmol), and **3** (1.2 mmol) were added to a catalyst THF solution prepared from Ni(cod)$_2$ (0.02 mmol) and P(2-Fur)$_3$ (0.03 mmol). [b]**1** (1.2 mmol), **2** (1.0 mmol), and **3** (0.4 mmol) were added to a catalyst THF solution prepared from Ni(cod)$_2$ (0.04 mmol) and P(2-Fur)$_3$ (0.06 mmol). [c]Isolated yields based on **2**. [d]Isolated yields based on **3**.




**Scheme 2**

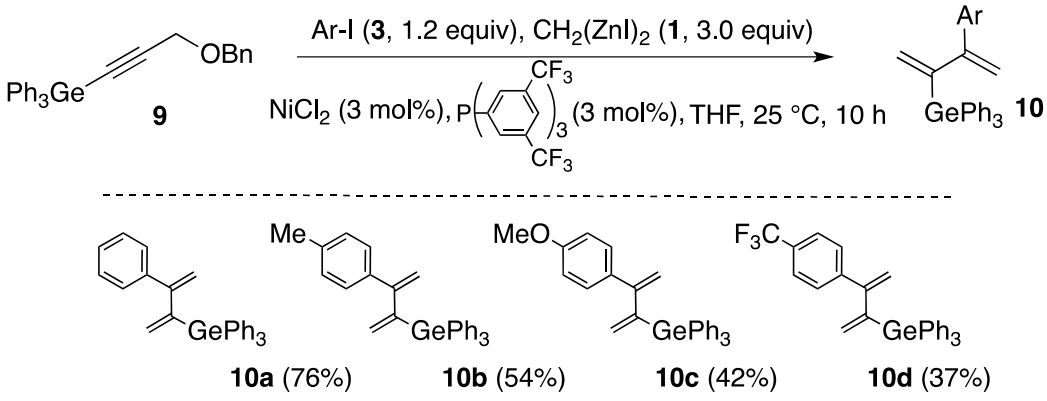
The protocol to prepare 2-aryl-3-silyl-1,3-butadiene **6** from propargyl ether **2** was extended to germyl substituted propargyl ether **9** to obtain **10**. The diene **10** may have a chance to introduce an aryl group via Germyl-Stille coupling,[16] and would also be a useful precursor to prepare various organogermyl compounds. As shown in Table 3, the catalyst prepared from 3.0 mol% of nickel chloride and 3.0 mol% of $P(3,5\text{-}(CF_3)_2C_6H_4)_3$ was effective for this transformation. In Scheme 3, various aryl iodides were examined to obtain 2-aryl-3-germyl-1,3-butadiene **10**. The transformation did not proceed efficiently compare to the silyl case. The diene **10** was obtained in reasonable yields.

**Table 3.** Screening of Ni-catalysts for preparation of 2-aryl-3-germyl-1,3-butadiene **10a**[a]




| entry | Catalyst | **1** /equiv | **10a**/ %[b] |
|---|---|---|---|
| 1 | $NiCl_2$ (2.0 mol%)/ $P(2\text{-Fur})_3P$ (3.0 mol%) | 2.4 | 22 |
| 2 | $NiCl_2$ (2.0 mol%)/ $P(2\text{-Fur})_3P$ (6.0 mol%) | 3.0 | 30 |
| 3 | $NiCl_2$ (3.0 mol%)/ $P(3,5\text{-}(CF_3)_2C_6H_4)_3$ (6.0 mol%) | 2.4 | 50 |
| 4 | $NiCl_2$ (3.0 mol%)/ $P(3,5\text{-}(CF_3)_2C_6H_4)_3$ (6.0 mol%) | 3.0 | 61 |
| 5 | $NiCl_2$ (3.0 mol%)/ $P(3,5\text{-}(CF_3)_2C_6H_4)_3$ (3.0 mol%) | 3.0 | 76 |

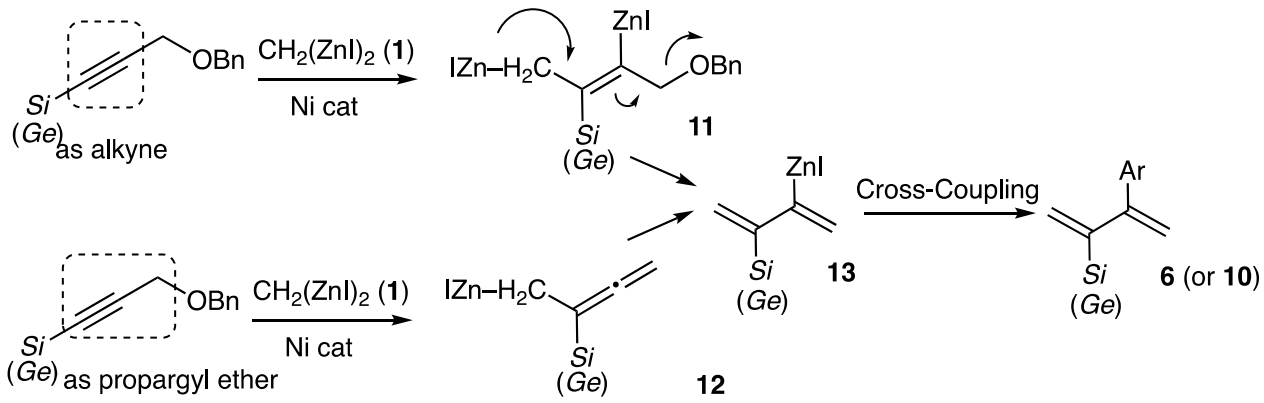
[a]**9** (1.0 mmol) and **3a** (1.2 mmol) were added to a catalyst THF solution prepared from $NiCl_2$ (0.02 mmol) and $PAr_3$. [b]Isolated yields.



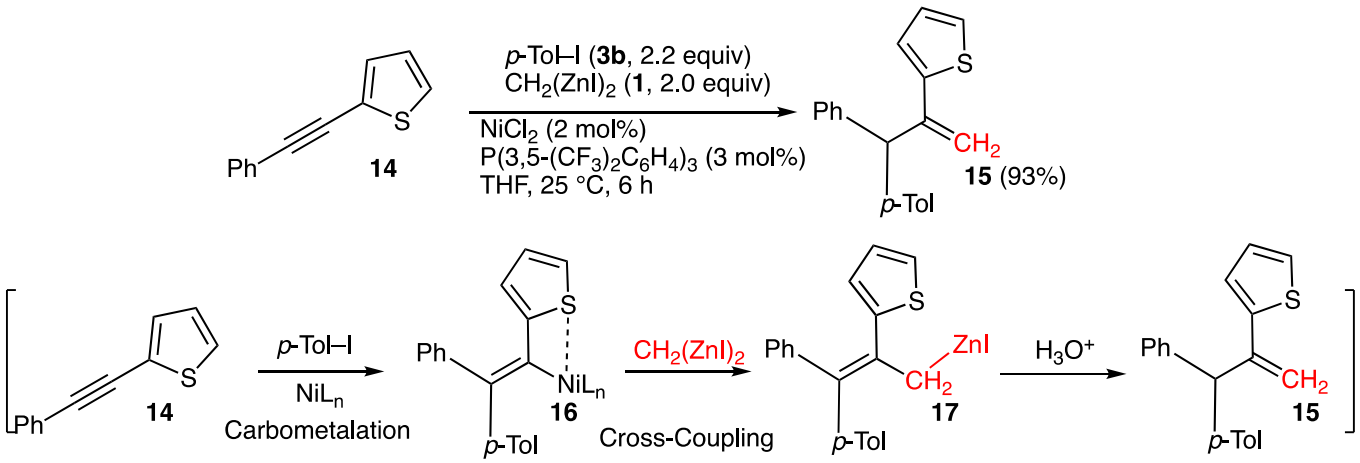

**Scheme 3**

As shown previously in Scheme 1, these transformations were supposed to start from arylnickelation followed by a cross-coupling between alkenyl nickel and bis(iodozincio)methane (**1**). Alternatively, a

direct reaction of **1** with propargyl ether under a nickel-catalyst may give dienyl zinc **13** via **11** or **12**, which can afford the product **6** or **10** via a cross-coupling with aryl iodide (Scheme 4). Although the pathway in Scheme 4 is reasonable, treatment of propargyl ether **2a** with **1** and catalytic amount of $Ni(cod)_2/P(2\text{-}Fur)_3$ in the absence of aryl iodide resulted in the complete recovery of **2a**. In addition, as shown in Scheme 5, the diarylalkyne without benzyl ether group **14** was converted into **15** via the allylzinc **17**.[5] The oxidative insertion of the nickel catalyst into C–O bond of propargylic ether is not crucial. Thus, the pathway shown in Scheme 1, in which arylnickelation to alkyne initiates the transformation may be more plausible.




**Scheme 4**




**Scheme 5**

In conclusion, we can show the products of the coupling of propargyl ether, aryl iodide, and bis(iodozincio)methane catalyzed by Ni; 2-aryl-3-silyl(or germyl)-1,3-butadienes were efficiently produced. Those dienes can be a nucleophilic component for cross-coupling, or the synthetically useful 1,3-diene unit could be substituted with a silyl or germyl group. These products would be important precursors for organo-silyl or -germyl compounds.[17]

## EXPERIMENTAL

Nuclear magnetic resonance spectra were taken on Varian UNITY INOVA 500 ($^1$H, 500 MHz; $^{13}$C, 125.7 MHz) spectrometer using chloroform for $^1$H NMR as an internal standard (δ = 7.26 ppm), $CDCl_3$ for $^{13}$C NMR as an internal standard (δ = 77.0 ppm). $^1$H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. TLC analyses were performed by means of Merck Kieselgel 60 F254 (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and an aqueous vanillin solution followed by heating. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–100 μm). Unless otherwise noted, commercially available reagents were used without purification. Tetrahydrofuran, dehydrated stabilizer free ―Super― was purchased from Kanto Chemical Co., stored under argon, and used as it is. Zinc powder was used after washing with 10% HCl according to the reported procedure.[18]

### Procedure for preparation of bis(iodozincio)methane (1)[4]

A mixture of pure zinc dust (150 mmol), diiodomethane (1.0 mmol), and $PbCl_2$ (0.005 mmol) in THF (5.0 mL) was sonicated for 1 h in an ultrasonic cleaner bath under Ar. When pyrometallurgy zinc dust was used instead of pure zinc, it is not necessary to add $PbCl_2$. Both of pure zinc and pyrometallurgy zinc are commercially available. To the mixture, diiodomethane (50 mmol) in THF (45 mL) was added dropwise over 30 min at 0 °C with vigorous stirring. The mixture was stirred for 4 h at 25 °C. After the stirring was stopped, the reaction vessel was allowed to stand undisturbed for several hours. Excess zinc was separated by sedimentation. $^1$H NMR spectra of the obtained supernatant showed a broad singlet at –1.2 ppm at 0 °C, which corresponded to the methylene proton of **1**. The supernatant was used for the further reaction as a solution of **1** in THF (0.1–0.5 M). Bis(iodozincio)methane in THF can be kept unchanged at least for a month in a sealed reaction vessel.

### Preparation of 2-trimethylsilyl-3-phenyl-1,3-butadiene (6aa: General procedure for 6aa–af)

Under Ar, $Ni(cod)_2$ (0.02 mmol) and $P(2\text{-furyl})_3$ (0.03 mmol) were stirred in THF (0.3 mL) for 10 min at 0 °C. Then bis(iodozincio)methane (**1**) (0.45 M in THF, 1.2 mmol) and a solution of 3-trimethylsilyl-1-benzyloxy-2-propyne (**2a**) (1.0 mmol) and iodobenzene (**3a**, 1.2 mmol) in THF (1.5 mL) were subsequently added and the mixture was stirred for 14 h at 25 °C. After the mixture was cooled to 0 °C, hexane/AcOEt (5/1, 20 mL) was added. After the addition of sat. $NH_4Cl$aq, the mixture was extracted with hexane/AcOEt (5/1). The combined organic layers were washed with brine, dried over $Na_2SO_4$, and concentrated in vacuo. Purification on a neutral silica-gel column chromatography gave 2-trimethlsilyl-3-phenyl-1,3-butadiene (**6aa**) as colorless oil in 99% yield (0.20 g).

**Preparation of 4,4'-bis(3-trimethylsilyl-1,3-butadien-2-yl)biphenyl (6ai: General procedure for 6ag–ai)**

Under Ar, $Ni(cod)_2$ (0.04 mmol) and $P(2\text{-furyl})_3$ (0.06 mmol) were stirred in THF (0.6 mL) for 10 min at 0 °C Then bis(iodozincio)methane (**1**) (0.45 M in THF, 1.2 mmol) and a solution of 3-trimethylsilyl-1-benzyloxy-2-propyne (**2a**) (1.0 mmol) and iodobenzene (**3a**, 0.4 mmol) in THF (2.0 mL) were subsequently added and the mixture was stirred for 14 h at 25 °C. After the mixture was cooled to 0 °C, hexane/AcOEt (5/1, 20 mL) was added. After the addition of sat. $NH_4Cl$aq, the mixture was extracted with hexane/AcOEt (5/1). The combined organic layers were washed with brine, dried over $Na_2SO_4$, and concentrated in vacuo. Purification on a neutral silica-gel column chromatography gave 4,4'-bis(3-trimethylsilyl-1,3-butadien-2-yl)biphenyl (**6ai**) as colorless oil in 99% yield (0.40 g).

**Preparation of 2-triphenylgermyl-3-phenyl-1,3-butadiene (10a: General procedure for 10a–d)**

Under Ar, $NiCl_2$ (0.03 mmol, 3 mol%) and $P(3,5\text{-}(CF_3)_2C_6H_3)_3$ (0.03 mmol, 3 mol%) were stirred in THF (0.3 mL) for 10 min at 0 °C. Then bis(iodozincio)methane (**1**) (0.45 M in THF, 3.0 mmol), and a solution of 3-triphenylgermyl-1-benzyloxy-2-propyne (**9**) (1.0 mmol) and iodobenzene (**3a**, 1.2 mmol) in THF (1.5 mL) were subsequently added and the mixture was stirred for 10 h at 25 °C. After the mixture was cooled to 0 °C, hexane/AcOEt (5/1, 20 mL) was added. After the addition of sat. $NH_4Cl$aq, the mixture was extracted with hexane/AcOEt (5/1). The combined organic layers were washed with brine, dried over $Na_2SO_4$, and concentrated in vacuo. Purification on a neutral silica-gel column chromatography gave 2-triphenylgermyl-3-phenyl-1,3-butadiene (**10**) as a white solid in 76% yield (0.33 g).

**Compounds 6aa-ai and Compound 8 were known molecules:**

**6aa** (190441-04-4); **6ab** (869218-11-1), **6ac** (869218-12-2), **6ad** (869218-13-3), **6ae** (869218-14-4), **6af** (869218-15-5), **6ba** (869218-16-6), **6ca** ( 869218-17-7), **6da** (869218-18-8), **6ag** (869218-21-3), **6ah** (869218-22-4), **6ai** (869218-23-5), **8** (69218-20-2). All spectra were shown in ref 7.

**Triphenyl(3-phenylbuta-1,3-dien-2-yl)germane (10a)**

Prepared following the general procedure using 1.0 mmol of **9**: Yield 76% (0.33 g). A white solid (mp 97–98 °C); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.52 – 7.50 (m, 6H), 7.37 – 7.27 (m, 10H), 7.22 – 7.20 (m, 4H), 5.97 (d, *J* = 2.4 Hz, 1H), 5.62 (d, *J* = 2.2 Hz, 1H), 5.18 (d, *J* = 1.2 Hz, 1H), 5.16 (d, *J* = 1.2 Hz, 1H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ 151.8, 148.0, 141.0, 136.4, 135.2, 132.1, 128.9, 128.1, 128.0, 127.9, 127.3, 116.2; HRMS ($EI^+$): Found 434.1088, Calcd for $C_{28}H_{24}Ge$ 434.1089; IR (KBr): 3067, 2331, 1090, 735, 698, 668 $cm^{-1}$.

**Triphenyl(3-(*p*-tolyl)buta-1,3-dien-2-yl)germane (10b)**

Prepared following the general procedure using 1.0 mmol of **9**: Yield 54% (0.24 g). A white solid (mp 126–127 °C); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.53 – 7.51 (m, 6H), 7.38 – 7.32 (m, 9H), 7.17 (d, *J* = 6.3

Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 5.98 (d, *J* = 2.4 Hz, 1H), 5.60 (d, *J* = 2.4 Hz, 1H), 5.16 (d, *J* = 1.0 Hz, 1H), 5.12 (d, *J* = 1.0 Hz, 1H), 2.31 (s, 3H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ 151.6, 148.1, 138.2, 136.9, 136.5, 135.2, 131.9, 128.8, 128.6, 128.1, 128.0, 115.7, 21.1; HRMS ($EI^+$): Found 448.1247, Calcd for $C_{29}H_{26}Ge$ 448.1246; IR (KBr): 3068, 2919, 2360, 1090, 827, 736, 698, 668 $cm^{-1}$.

**(3-(*p*-Anisyl)buta-1,3-dien-2-yl)triphenylgermane (10c)**

Prepared following the general procedure using 0.5 mmol of **9**: Yield 42% (0.19 g). A brown solid (mp 94–95 °C); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.51 – 7.49 (m, 6H), 7.36 – 7.31 (m, 9H), 7.19 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.00 (d, *J* = 2.4 Hz, 1H), 5.61 (d, *J* = 2.4 Hz, 1H), 5.13 (d, *J* = 1.2 Hz, 1H), 5.08 (d, *J* = 1.2 Hz, 1H), 3.78 (s, 3H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ 158.9, 151.4, 148.4, 136.5, 135.2, 133.4, 131.6, 129.2, 128.9, 128.1, 114.6, 113.2, 55.2; HRMS ($EI^+$): Found 464.1192, Calcd for $C_{29}H_{26}OGe$ 464.1195; IR (KBr): 3068, 3051, 2331, 1510, 1430, 1248, 1178, 1090, 1034, 835, 736, 698 $cm^{-1}$.

**Triphenyl(3-(4-(trifluoromethyl)phenyl)buta-1,3-dien-2-yl)germane (10d)**

Prepared following the general procedure using 0.5 mmol of **9**: Yield 37% (0.19 g). A yellow solid. (mp 81–82 °C); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.50 – 7.48 (m, 6H), 7.42 – 7.31 (m, 13H), 5.98 (d, *J* = 2.2 Hz, 1H), 5.66 (d, *J* = 2.2 Hz, 1H), 5.25 (d, *J* = 0.7 Hz, 1H), 5.22 (d, *J* = 0.7 Hz, 1H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ 151.0, 147.9, 144.5, 136.0, 135.2, 134.5, 132.3, 129.0, 128.9, 128.2, 124.8 (t), 124.8, 117.1; HRMS ($EI^+$): Found 502.0962, Calcd for $C_{29}H_{23}F_3Ge$ 502.0963; IR (KBr): 3068, 3051, 2360, 1432, 1325, 1167, 1126, 1091, 1065, 849, 736, 698, 668 $cm^{-1}$.

**3-Phenyl-2-(2-thienyl)-3-(*p*-tolyl)propene (15)**

Under Ar, $NiCl_2$ (0.02 mmol, 2.6 mg) and $P(3,5\text{-}(CF_3)_2C_6H_3)_3$ (0.03 mmol, 21 mg) were added to THF (0.2 mL) and stirred at room temperature for 10 min. To this mixture, bis(iodozincio)methane (**1**, 0.45 M in THF, 2.2 mmol), 2-(phenylethynyl)thiophene (**14**, 1.0 mmol) and *p*-iodotoluene (**3b**, 2.0 mmol) were added and stired at room tempreture for 8 h. 1M HClaq was added to the reaction mixture. The resulting mixture was extracted with AcOEt. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated in vacuo. After a purification by a flash silica gel column chromatography, the pure product **15** was isolated in 93% yield (185 mg, orange oil).

$^1$H NMR ($CDCl_3$) δ 7.36-7.1 (m, 10H), 6.98- 6.96 (m, 1H), 6.9-6.85 (m, 1H), 5.79 (s, 1H), 5.35 (s, 1H), 4.66 (s, 1H), 2.34 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 145.5, 144.1, 142.3, 139.0, 136.0, 129.3, 129.2, 129.0, 128.3, 127.2, 126.4, 124.3, 124.0, 115.5, 56.1, 21.4; HRMS ($EI^+$) found 290.1127, Calcd for $C_{20}H_{18}S$: 290.1129; IR (neat): 3058.3, 3024.5, 2919.4, 2869.2, 1896.1, 1802.6, 1614.5, 1600.0, 1511.3, 1493.0, 1450.5, 1438.0, 1239.3, 1185.3, 1112.0, 1076.3, 1061.9, 1022.3, 896.9, 852.6, 782.2, 752.3 $cm^{-1}$.

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## REFERENCES

1. (a) B. M. Trost, *Acc. Chem. Res.*, 1980, **13**, 385; (b) B. M. Trost and D. L. VanVranken, *Chem. Rev.*, 1996, **96**, 395; (c) B. M. Trost, *Angew. Chem. Int. Ed.*, 1995, **34**, 259; (d) B. M. Trost and M. L. Crawley, *Chem. Rev.*, 2003, **103**, 2921.
2. (a) T. Takahashi, D. Kuroda, T. Kuwano, Y. Yoshida, T. Kurahashi, and S. Matsubara, *Chem. Commun.*, 2018, **54**, 12750; (b) C. M. Le, P. J. C. Menzies, D. A. Petrone, and M. Lautens, *Angew. Chem. Int. Ed.*, 2015, **54**, 254.
3. (a) E. Negishi, Z. H. Huang, G. W. Wang, S. Mohan, and C. Wang, *Acc. Chem. Res.*, 2008, **41**, 1474; (b) N. Asao and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1071; (c) D. S. Müller and I. Marek, *Chem. Soc. Rev.*, 2016, **45**, 4552.
4. S. Matsubara, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 82.
5. Y.Shimada, Z. Ikeda, and S. Matsubara, *Org. Lett.*, 2017, **19**, 3335.
6. S. Matsubara, K. Ukai, N. Toda, K. Utimoto, and K. Oshima, *Synlett*, 2000, 1202.
7. Z. Ikeda, K. Oshima, and S. Matsubara, *Org. Lett.*, 2005, **7**, 4859.
8. M. De Paolis, I. Chataigner, and J. Maddaluno, *Top. Curr. Chem.*, 2012, **327**, 87.
9. B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, 1989, **89**, 863.
10. (a) M. Shimizu, T. Kurahashi, K. Shimono, K. Tanaka, I. Nagao, S. Kiyomoto, and T. Hiyama, *Chem. Asian J.*, 2007, **2**, 1400; (b) K. C. Nicolaou, P. G. Bulger, and D. Sarlah, *Angew. Chem. Int. Ed.*, 2005, **44**, 4442.
11. H. Jiang, L. He, X. Li, H. Chen, W. Wu, and W. Fu, *Chem. Commun.*, 2013, **49**, 9218.
12. (a) J. Böhmer and R. Grigg, *Tetrahedron*, 1999, **55**, 13463; (b) N. J. Green, A. C. Willis, and M. S. Sherburn, *Angew. Chem. Int. Ed.*, 2016, **55**, 9244.
13. B. M. Trost, M. R. Machacek, and Z. T. Ball, *Org. Lett.*, 2003, **5**, 1895.
14. K. Utimoto, Y. Otake, H. Yoshino, E. Kuwahara, K. Oshima, and S. Matsubara, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 753.
15. T. Hiyama and Y. Hatanaka, *Pure Appl. Chem.*, 1994, **66**, 1471.
16. T. Nakamura, H. Kinoshita, H. Shinokubo, and K. Oshima, *Org. Lett.*, 2002, **2**, 3165.
17. F. Zhao, S. G. Zhang, and Z. F. Xi, *Chem. Commun.*, 2011, **47**, 4348.
18. L. F. Fieser and M. Fieser, '*Reagents for Organic Synthesis, Vol 1*', *Wiley*, *New York*, 1967, p 1276.