JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

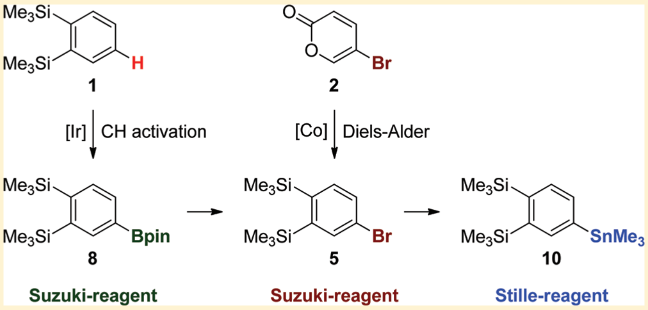
# Synthesis of Bromo-, Boryl-, and Stannyl-Functionalized 1,2-Bis(trimethylsilyl)benzenes via Diels−Alder or C−H Activation Reactions

Christian Reus, Nai-Wei Liu, Michael Bolte, Hans-Wolfram Lerner, and Matthias Wagner*

Institut für Anorganische und Analytische Chemie, J. W. Goethe-Universität Frankfurt, Max-von-Laue-Strasse 7, D-60438 Frankfurt (Main), Germany

Supporting Information

**ABSTRACT:** 1,2-Bis(trimethylsilyl)benzenes are key starting materials for the synthesis of benzyne precursors, Lewis acid catalysts, and certain luminophores. We have developed efficient, high-yield routes to functionalized 4-R-1,2-bis(trimethylsilyl)benzenes, starting from either 1,2-bis(trimethylsilyl)acetylene/5-bromopyran-2-one (**2**) or 1,2-bis(trimethylsilyl)benzene (**1**)/bis(pinacolato)diborane. In the first reaction, **5** (R = Br) is obtained through a cobalt-catalyzed Diels−Alder cycloaddition. The second reaction proceeds via iridium-mediated C−H activation and provides **8** (R = Bpin). Besides its use as a Suzuki reagent, compound **8** can be converted into **5** with $CuBr_2$ in *i*-PrOH/MeOH/$H_2O$. Lithium−bromine exchange on **5**, followed by the addition of $Me_3SnCl$, gives **10** (R = $SnMe_3$), which we have applied for Stille coupling reactions. A Pd-catalyzed C−C coupling reaction between **5** and **8** leads to the corresponding tetrasilylbiphenyl derivative. The bromo derivative **5** cleanly undergoes Suzuki reactions with electron-rich as well as electron-poor phenylboronic acids.

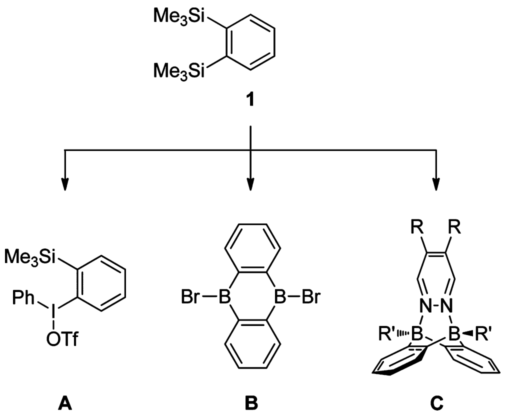


## INTRODUCTION

Polysubstituted arenes constitute versatile fine chemicals for organic synthesis.[1] This is exceptionally true if the individual functional groups are selected such that stepwise orthogonal derivatization is possible.

Our group is particularly interested in 1,2-bis(trimethylsilyl)benzenes because their broad application potential ranges from organic synthesis to materials chemistry and molecular recognition (Scheme 1). For example, the parent compound **1** serves as the key starting material for the synthesis of (i) (phenyl)[2-(trimethylsilyl)phenyl]iodonium triflate (**A**), one of the most efficient benzyne precursors available to date;[2] (ii) 9,10-dibromo-9,10-dihydro-9,10-diboraanthracene (**B**), an important building block of luminescent boron-doped $\pi$-conjugated materials;[3] and (iii) various other 9,10-dihydro-9,10-diboraanthracenes, which have been used as fluoride detectors,[4] for the complexation of mono- and ditopic Lewis bases (e.g., **C**; R′ = H, R = H or R^R = $C_6H_4$),[5] and as Lewis acidic phthalazine activation catalysts (**C**; R′ = methyl, R^R = $C_6H_4$).[6]

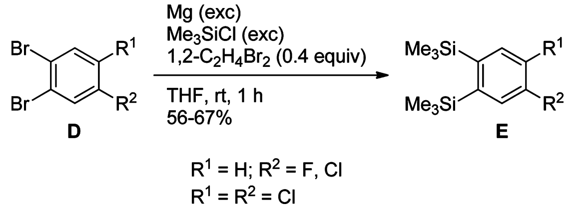
**Scheme 1**



Most synthesis protocols of **1** suffer from one or more of the following disadvantages: use of toxic and cancerogenic solvents, expensive chemicals, inconvenient reaction conditions (e.g., very low or rather high temperatures; extended reaction times), low yields.[7] Very recently, we have shown that **1** is readily accessible from 1,2-dibromobenzene, $Me_3SiCl$, and Mg turnings in the presence of 1,2-dibromoethane as an entrainer (THF, rt, 30 min; 62%).[8] However, as a shortcoming, also this new method requires strongly reducing conditions and is therefore compatible with only a very limited number of functional groups. Apart from **1**, we have so far only been able to synthesize the three fluoro- or chloro-bearing derivatives **E**, which turned out to be rather inert toward further C−X activation (X = F, Cl; Scheme 2). Surprisingly, when alkyl-substituted 1,2-dibromobenzenes **D** were employed ($R^1 = R^2 =$

**Received:** February 14, 2012
**Published:** March 13, 2012

**Scheme 2. Derivatives of 1 Accessible via the Entrainment Approach**



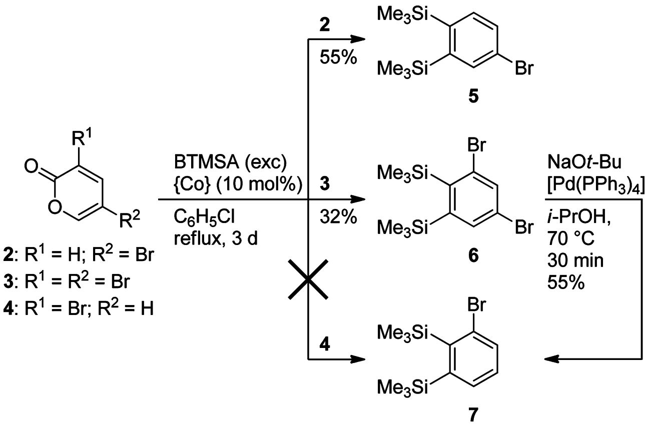
methyl; $R^1$ = H, $R^2$ = *tert*-butyl), the double silylation reaction almost completely failed, whereas the phenyl-substituted starting material gave the corresponding derivative **E** ($R^1$ = H, $R^2$ = phenyl) in 60% yield (see below).

Thus, if we want to exploit the full potential of 1,2-bis(trimethylsilyl)benzenes in the areas outlined above (cf. Scheme 1), additional methods allowing the synthesis of more sophisticated **E**-type compounds are in demand. In this paper, we are focusing on a substitution pattern $R^1$ = H and $R^2$ = Br, Bpin, or $SnMe_3$, which are the key functional groups for further Pd-mediated C−C cross-coupling reactions (HBpin: pinacolborane). We will show how these substituents can be introduced starting either from 1,2-bis(trimethylsilyl)acetylene (BTMSA) via the assembly of the benzene ring through a Diels−Alder reaction or by the Ir-catalyzed C−H activation of parent **1**.

## ■ RESULTS AND DISCUSSION

**Bromo-Substituted 1,2-Bis(trimethylsilyl)benzenes via Diels−Alder Reactions.** Seyferth and Kitamura employed the Diels−Alder reaction of 5-R-pyran-2-ones with 1,2-bis(trimethylsilyl)acetylene (BTMSA) to prepare a selection of 4-R-1,2-bis(trimethylsilyl)benzenes (R = H, $CO_2Me$, C(O)-Me, C(O)*t*-Bu, C(O)$C_6H_5$, C(O)$C_6H_4$Me).[9] Following a similar approach, we first treated the literature-known bromo-substituted pyran-2-ones **2**−**4**[10,11] with BTMSA in $C_6H_5Cl$ at reflux temperature for 7 days (Scheme 3; cf. the Supporting Information for X-ray crystal structure analyses of **2**−**4**). 4-Bromo-1,2-bis(trimethylsilyl)benzene (**5**) was obtained in 40% yield, whereas **6** and **7** did not form in significant amounts. This result contradicts the previous finding that **3** is more reactive than **2** in Diels−Alder cycloadditions.[12] In the presence of the catalyst system Zn/$ZnI_2$/[$CoBr_2$(dppe)($OH_2$)(THF)],[13] the reactions **2** → **5** and **3** → **6** proceeded with yields of 55 and 32%, respectively, already after a reaction time of 3 days (dppe: 1,2-bis(diphenylphosphino)ethane). In the case of **6**, it is essential to stop the reaction at this stage because prolonged heating results in protodesilylation at the 2-position of the benzene ring. For the transformation **4** → **7**, also the cobalt-catalyzed protocol does not work. However, we found that **7** is accessible in yields of 55% by catalytic dehalogenation of **6** ([Pd($PPh_3$)$_4$], *i*-PrOH/NaO*t*-Bu; Scheme 3).[14] For a selective monodehalogenation at the 5-position, it is mandatory not to exceed a reaction time of 30 min and an oil bath temperature of 70 °C.

**Scheme 3. Syntheses of Bromo-Substituted 1,2-Bis(trimethylsilyl)benzenes**[a]

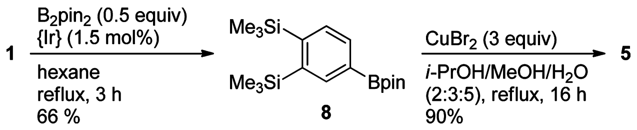


[a]{Co} = (Zn/$ZnI_2$/[$CoBr_2$(dppe)($OH_2$)(THF)], 2:2:1).

The NMR data of **5** are unexceptional and therefore do not merit further discussion. One of the two $SiMe_3$ $^1H$ NMR resonances in both **6** (0.38 and 0.50 ppm) and **7** (0.37 and 0.52 ppm) is significantly deshielded compared to the corresponding signals of **5** (0.35 and 0.37 ppm). We attribute this effect to the presence of the *ortho*-Br substituent in **6** and **7**.

**Bpin-Substituted 1,2-Bis(trimethylsilyl)benzenes via a C−H Activation Reaction.** Parent 1,2-bis(trimethylsilyl)-benzene **1** undergoes selective borylation at the 4-position (cf. **8**; Scheme 4) with 0.5 equiv of $B_2pin_2$ in the presence of an in situ generated iridium catalyst ([Ir(cyclooctene)$_2$Cl]$_2$/4,4′-dimethyl-2,2′-bipyridine/NaOMe[15]).

**Scheme 4.** [a]



[a]{Ir} = ([Ir(cyclooctene)$_2$Cl]$_2$/4,4′-dimethyl-2,2′-bipyridine/NaOMe, 1:2:6).

After 3 h at reflux temperature in hexane, the yield of **8** amounts to 50% (NMR spectroscopic control) and does not improve upon increasing the reaction time and/or addition of further catalyst or any of the starting materials. Since no significant amounts of side products were detectable, one might argue that borylation comes to a halt because the intermediate HBpin (**1** + $B_2pin_2$ → **8** + HBpin) is not an active reagent in this special case, so that the subsequent conversion **1** + HBpin → **8** + $H_2$ does not occur. However, $H_2$ evolution is visible after an induction period of 30 min to 1 h, which contradicts this assumption. When working on a preparative scale, separation of the catalyst is conveniently achieved by flash chromatography. Since solid **8** is easily separable from liquid **1** by crystallization, the unreacted starting material can be recycled and directly reused. Typical combined yields of **8** after two consecutive runs are about 65%.

The $^1H$ NMR spectrum of **8** is characterized by one Bpin resonance, two $SiMe_3$ signals, and three aryl-H resonances. These features testify to the formation of only one isomer. The proton integral values are consistent with one Bpin substituent and two $SiMe_3$ groups per molecule.

The structure of **8** has finally been proven by X-ray diffraction. The compound crystallizes with two crystallographically independent molecules, **8** and **8**$_A$, in the asymmetric unit. Since most key metrical parameters are similar for **8** and **8**$_A$, only a plot of **8** is shown in Figure 1. Considerable steric strain between the *ortho*-$SiMe_3$ groups is obvious from the elongated Si−$C_{ipso}$ distances, which possess an even larger average value (1.901(4) Å) than the average Si−$CH_3$ bond

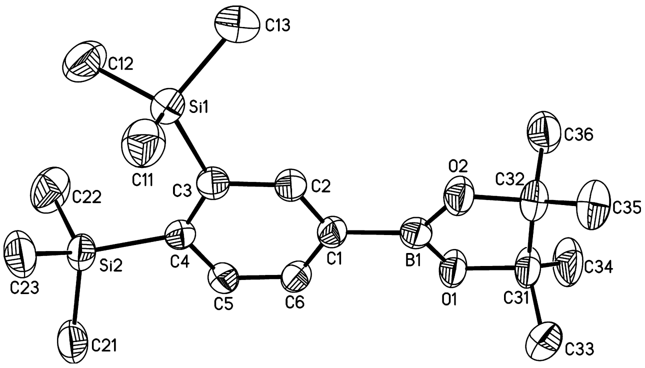


**Figure 1.** Molecular structure and numbering scheme of compound **8** (displacement ellipsoids are drawn at the 50% probability level; H atoms are omitted for clarity). The compound crystallizes with two crystallographically independent molecules, **8** and $\mathbf{8_A}$, in the asymmetric unit. Since most key metrical parameters are similar for **8** and $\mathbf{8_A}$, only a plot of **8** is shown and selected bond lengths (Å), bond angles (deg), and torsion angles (deg) of **8** are listed: Si(1)−C(3) = 1.894(4), Si(2)−C(4) = 1.898(3), B(1)−O(1) = 1.364(5), B(1)−O(2) = 1.367(5), B(1)−C(1) = 1.564(5); Si(1)−C(3)−C(4) = 129.8(2), Si(2)−C(4)−C(3) = 127.7(3); Si(1)−C(3)−C(4)−Si(2) = −4.7(4), C(2)−C(1)−B(1)−O(2) = 8.9(5), C(6)−C(1)−B(1)−O(1) = 10.9(5).

length (1.867(4) Å). Moreover, the average Si−$C_{ipso}$−$C'_{ipso}$ bond angles are expanded to 128.5(3)°. As has already been deduced from the NMR spectra, a Bpin substituent occupies the 4-position of the benzene ring. The identity of the single crystal with the bulk material was proven by high-resolution X-ray powder diffraction.

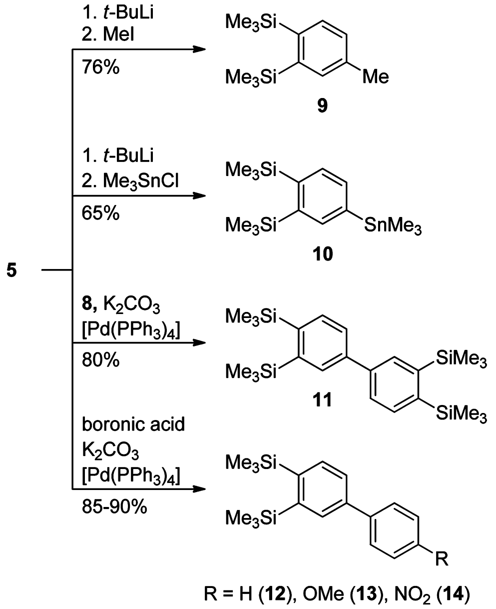
Hartwig et al. recently reported that arylboronic esters can be converted to aryl bromides upon treatment with 3 equiv of $CuBr_2$ in MeOH/$H_2O$ (1:1).[16] For the transformation of **8** into **5**, we adapted the synthesis protocol by adding *i*-PrOH to the solvent mixture in order to increase the solubility of **8**. NMR spectroscopic monitoring of the reaction progress revealed 50% conversion after a reaction time of 6 h at reflux temperature (*i*-PrOH/MeOH/$H_2O$ = 2:3:5); after 16 h, **5** had formed in essentially quantitative yield (Scheme 4).

**Further Derivatizations of 5 and 8.** Lithium−bromine exchange between **5** and *t*-BuLi in $Et_2O$ or THF at −78 °C and subsequent treatment of the phenyl lithium intermediate with MeI or $Me_3SnCl$ provides in good yields the 4-methylated or 4-stannylated 1,2-bis(trimethylsilyl)benzenes **9** and **10**, respectively (Scheme 5).

The synthesis of **9**, which has previously been prepared by titanium-catalyzed Diels−Alder cycloaddition of 2-methyl-1,3-butadiene with BTMSA, followed by aromatization of the primary cyclohexa-1,4-diene,[17] just served as a proof-of-principle in the present case. Compound **10**, however, has application potential in further Stille-type[18] C−C coupling reactions (see below).

Aryl bromides together with arylboronic esters constitute the two most widely used components in Suzuki-type[19] cross-coupling reactions. In order to test the utility of **5** and **8** in this context at the same time, we performed a Suzuki reaction[20] between these two compounds and obtained the tetrasilylbiphenyl **11** in 80% yield (Scheme 5; cf. the Supporting Information for an X-ray crystal structure analysis of **11**). The reactivity of **5** was further explored by conducting C−C coupling reactions with *p*-R-phenylboronic acids bearing substituents with greatly different mesomeric effects (i.e., R = H, OMe, $NO_2$). According to NMR spectroscopy, the formation of all three biphenyl products (**12**−**14**) was essentially quantitative (isolated yields: 85−90%), which underlines the broad application scope of our new building block. X-ray crystal structure analyses of **13** and **14** reveal similarly elongated Si−$C_{ipso}$ bond lengths and widened Si−$C_{ipso}$−$C'_{ipso}$ bond angles as in molecule **8** (cf. the Supporting Information for more details).

**Scheme 5. Derivatizations of 5 via Li−Br Exchange Reactions (5 → 9,10) or Suzuki-Type Coupling Reactions (5 → 11−14)**



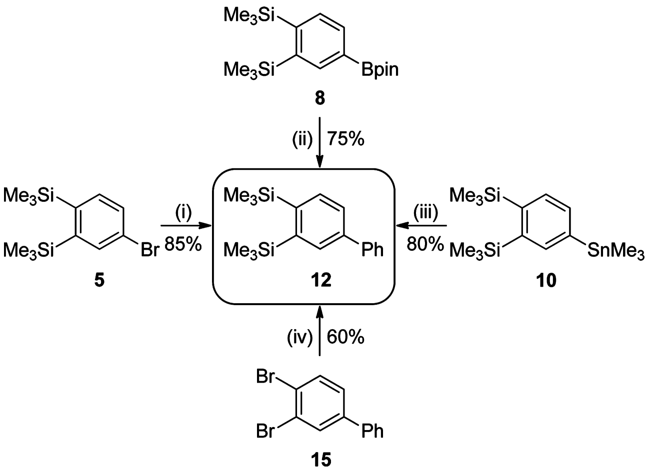
**Comparison of Different Access Routes to 4-Phenyl-1,2-bis(trimethylsilyl)benzene (12).** In the preceding paragraph, we have shown that 4-bromo-1,2-bis(trimethylsilyl)-benzene **5** readily undergoes Suzuki reactions with electron-rich as well as electron-poor phenylboronic acids. For an evaluation of the performance of **5**, **8**, and **10** in Pd-mediated C−C coupling reactions, we selected 4-phenyl-1,2-bis(trimethylsilyl)-benzene (**12**) as the target molecule (Scheme 6). Under comparable reaction conditions, all three species gave comparably high yields of **12** (i.e., 75−85%), which shows that one is free to choose between arylboronic acids or bromoarenes as coupling partners and basic or base-free reaction media.

For completion, we also performed the synthesis of **12** via the entrainment route, starting from 3,4-dibromobiphenyl (**15**),[21] $Me_3SiCl$, and Mg turnings. The yields obtained were satisfactory (60%) but lower than those of the Pd-catalyzed protocols. The Grignard approach is also less versatile because it is not compatible with substituents that are sensitive to reducing conditions, strong nucleophiles, or radical intermediates. Nevertheless, from a fundamental point of view, the successful conversion **15** → **12** is remarkable given the fact that neither 4-*tert*-butyl- nor 4,5-dimethyl-1,2-bis(trimethylsilyl)-benzene is accessible by the entrainment method.[8]

## ■ CONCLUSION

1,2-Bis(trimethylsilyl)benzenes enjoy increasing interest for the preparation of benzyne precursors as well as 9,10-dihydro-9,10-diboraanthracenes. Certain derivatives of the latter class of

**Scheme 6. Four Different Approaches to 12**[a]



[a]Reagents and conditions: (i) $C_6H_5B(OH)_2$ (1.2 equiv), $K_2CO_3$ (3.6 equiv), $[Pd(PPh_3)_4]$ (7 mol %), toluene/EtOH/$H_2O$ (10:6:3), 80 °C, 1 day; (ii) $C_6H_5Br$ (1.1 equiv), $K_2CO_3$ (3.6 equiv), $[Pd(PPh_3)_4]$ (9 mol %), toluene/EtOH/$H_2O$ (10:6:3), 80 °C, 1 day; (iii) $C_6H_5Br$ (1.1 equiv), $[Pd(PPh_3)_4]$ (6 mol %), toluene, 100 °C, 1 day; (iv) $Me_3SiCl$ (exc), Mg (exc), 1,2-$C_2H_4Br_2$ (1.0 equiv), THF, rt, 1 day.

compounds have recently been introduced into the literature as catalysts for inverse electron-demand Diels–Alder reactions and as fluorophores in boron-doped $\pi$-conjugated materials. A decisive factor setting the pace of further developments in these emerging fields is the availability of appropriately functionalized 1,2-bis(trimethylsilyl)benzenes. In this paper, we describe brominated, borylated, and stannylated 1,2-bis(trimethylsilyl)benzenes, which serve as valuable reagents in Suzuki- and Stille-type C–C coupling reactions. The reaction protocols proved to be compatible with both electron-rich and electron-poor coupling partners, and they can be conducted in basic and base-free media. With these tools at hand, it should now be possible to access a broader variety of compounds through benzyne chemistry, to influence the Lewis acidity of 9,10-dihydro-9,10-diboraanthracene catalysts, and to tune the absorption/emission wavelengths as well as the redox potentials of corresponding boron-containing materials.

## ■ EXPERIMENTAL SECTION

**General Remarks.** All reactions were carried out in flame-dried glassware under a nitrogen or argon atmosphere using Schlenk techniques and carefully dried solvents. Chemical shifts are referenced to residual $CHCl_3$ signals ($^1H$: 7.260 ppm, $^{13}C\{^1H\}$: 77.16 ppm) external $BF_3{\cdot}Et_2O$ ($^{11}B\{^1H\}$: 0.00 ppm), external $SiMe_4$ ($^{29}Si$ INEPT: 0.00 ppm), or external $SnMe_4$ ($^{119}Sn$: 0.00 ppm). $^1H$ and $^{13}C$ NMR assignments were achieved using 2D NMR techniques including COSY, ROESY, HSQC, and HMBC. Abbreviations: s = singlet, d = doublet, dd = doublet of doublets, vt = virtual triplet, t = triplet, m = multiplet.

5-Bromopyran-2-one (**2**), 3,5-dibromopyran-2-one (**3**), and 3-bromopyran-2-one (**4**) were synthesized according to literature procedures.[10,11] Both routes lead to varying mixtures of these three compounds, which were separated by column chromatography (silica gel, hexane/EtOAc, 3:1). $[CoBr_2(dppe)(OH_2)(THF)]$[13] and 3,4-dibromobiphenyl (**15**)[21] were prepared according to literature procedures. All other chemicals are commercially available and were used as received.

*4-Bromo-1,2-bis(trimethylsilyl)benzene (**5**).* **Method A:** A mixture of **2** (1.29 g, 7.37 mmol), BTMSA (3.01 g, 17.7 mmol), Zn powder (0.11 g, 1.7 mmol), $ZnI_2$ (0.54 g, 1.7 mmol), and $[CoBr_2(dppe)(OH_2)(THF)]$ (0.62 g, 0.88 mmol) in $C_6H_5Cl$ (60 mL) was heated to reflux temperature for 3 days. The solution was cooled to rt, filtered, and all volatiles were removed from the filtrate in vacuo. Column chromatography (silica gel, hexane) gave **5** as a colorless liquid: yield 1.21 g (4.02 mmol, 55%). **Method B:** **8** (0.465 g, 1.33 mmol) was dissolved in a *i*-PrOH/MeOH mixture (2:3, 25 mL), and a solution of $CuBr_2$ (0.891 g, 3.99 mmol) in distilled $H_2O$ (25 mL) was added. The stirred reaction mixture was heated to reflux temperature for 16 h, cooled to rt, and extracted with $CHCl_3$ (3 × 15 mL). The organic phases were combined, washed with $H_2O$ (2 × 15 mL), dried over anhydrous $MgSO_4$, and filtered. All volatiles were removed from the filtrate in vacuo to give **5** as a colorless liquid: yield 0.359 g (1.19 mmol, 90%); $^1H$ NMR (250.1 MHz, $CDCl_3$) $\delta$ 0.35 (s, 9H; $SiMe_3$), 0.37 (s, 9H; $SiMe_3$), 7.44 (dd, 1H, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.0 Hz; H-5), 7.51 (d, 1H, $^3J_{HH}$ = 8.1 Hz; H-6), 7.74 (d, 1H, $^4J_{HH}$ = 2.0 Hz; H-3); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 1.9 ($SiMe_3$), 2.0 ($SiMe_3$), 124.0 (C-4), 130.8 (C-5), 137.1 (C-6), 137.8 (C-3), 144.7, 149.5 (C-1,2); $^{29}Si$ INEPT NMR (59.6 MHz, $CDCl_3$) $\delta$ −2.7, −2.6. Anal. Calcd for $C_{12}H_{21}BrSi_2$ [301.37]: C, 47.82; H, 7.02. Found: C, 47.45; H, 7.03.

*3,5-Dibromo-1,2-bis(trimethylsilyl)benzene (**6**).* A mixture of **3** (0.54 g, 2.1 mmol), BTMSA (1.40 g, 8.22 mmol), Zn powder (0.03 g, 0.5 mmol), $ZnI_2$ (0.19 g, 0.60 mmol), and $[CoBr_2(dppe)(OH_2)(THF)]$ (0.22 g, 0.31 mmol) in $C_6H_5Cl$ (15 mL) was heated to reflux temperature for 3 days. The solution was cooled to rt, filtered, and all volatiles were removed from the filtrate in vacuo. Column chromatography (silica gel, hexane) gave **6** as a colorless liquid: yield 0.22 g (0.58 mmol, 28%). Some of the starting material **3** (0.081 g, 0.32 mmol, 15%) was recovered by eluting the column with $CHCl_3$ and could be directly used for further transformations to increase the overall yield to 32%. Analytically pure samples were obtained by HPLC using a RP C18 semipreparative column eluted with MeOH/*t*-BuOMe (3:1): $^1H$ NMR (300.0 MHz, $CDCl_3$) $\delta$ 0.38 (s, 9H; $SiMe_3$), 0.50 (s, 9H; $SiMe_3$), 7.65 (d, 1H, $^4J_{HH}$ = 2.0 Hz; Ar–H), 7.70 (d, 1H, $^4J_{HH}$ = 2.0 Hz; Ar–H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 3.0, 3.7, 123.2, 133.1, 135.8, 136.9, 146.1, 153.0; $^{29}Si$ INEPT NMR (59.6 MHz, $CDCl_3$) $\delta$ −0.7, −0.6. Anal. Calcd for $C_{12}H_{20}Br_2Si_2$ [380.27]: C, 37.90; H, 5.30. Found: C, 37.96; H, 5.19.

*3-Bromo-1,2-bis(trimethylsilyl)benzene (**7**).* **6** (0.1889 g, 0.4968 mmol), NaO*t*-Bu (0.0477 g, 0.496 mmol), and $[Pd(PPh_3)_4]$ (0.0082 g, 0.0071 mmol) were dissolved in *i*-PrOH (2 mL). The solution was heated to 70 °C (oil bath temperature) under vigorous stirring for 30 min, cooled to rt, and treated with a saturated aqueous solution of $NH_4Cl$ (5 mL). The mixture was extracted with hexane (3 × 10 mL). The organic phases were combined, washed with $H_2O$ (2 × 5 mL), dried over anhydrous $MgSO_4$, and filtered. All volatiles were removed from the filtrate in vacuo, and the residual crude material was purified by column chromatography (silica gel, hexane) to give a 10:1 mixture of **7** and **5** as a colorless liquid (NMR spectroscopic control): yield 0.082 g (0.272 mmol, 55%). An attempt to separate **7** from **5** by HPLC using a RP C18 semipreparative column eluted with MeOH/*t*-BuOMe (3:1) was not successful: $^1H$ NMR (250.1 MHz, $CDCl_3$) $\delta$ 0.37 (s, 9H; $SiMe_3$-1), 0.52 (s, 9H; $SiMe_3$-2), 7.10 (vt, 1H; H-5), 7.52 (dd, 1H, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.2 Hz; H-4), 7.58 (dd, 1H, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz; H-6); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 3.1 ($SiMe_3$), 3.8 ($SiMe_3$), 128.9 (C-5), 133.4 (C-3), 133.9 (C-4), 134.3 (C-6), 147.4 (C-2), 150.8 (C-1); $^{29}Si$ INEPT NMR (59.6 MHz, $CDCl_3$) $\delta$ −1.7, −1.4. Anal. Calcd for $C_{12}H_{21}BrSi_2$ [301.37]: C, 47.82; H, 7.02. Found: C, 47.39; H, 6.95.

*4-Pinacolatoboryl-1,2-bis(trimethylsilyl)benzene (**8**).* A mixture of **1** (5.05 g, 22.7 mmol), $B_2pin_2$ (2.89 g, 11.4 mmol), $[Ir(cyclooctene)_2Cl]_2$ (0.311 g, 0.347 mmol), NaOMe (0.108 g, 2.00 mmol), and 4,4′-dimethyl-2,2′-bipyridine (0.156 g, 0.847 mmol) in hexane (50 mL) was heated to reflux temperature for 3 h under vigorous stirring. The solution was cooled to rt, all volatiles were removed in vacuo, and the residual crude material was purified by flash column chromatography (silica gel, hexane/EtOAc, 15:1) to give a colorless solution of **8** in **1** after all volatiles had been removed from the eluate in vacuo. From this solution, **8** crystallized (rt, 12 h) almost quantitatively in the form of colorless plates that were suitable for X-ray structure analysis. The separation of the solid and the liquid phase provided 3.95 g

(11.3 mmol, 50%) of crystalline **8** as well as 1.65 g (7.42 mmol, 33%) of recovered starting material **1**. This was directly used for a second conversion so that, after two consecutive runs, the overall yield of **8** amounted to 5.23 g (15.0 mmol, 66%). Analytically pure samples were obtained by column chromatography (silica gel, hexane): $^1$H NMR (250.1 MHz, $CDCl_3$) $\delta$ 0.36 (s, 9H; $SiMe_3$), 0.38 (s, 9H; $SiMe_3$), 1.33 (s, 12H; Me), 7.67 (dd, 1H, $^3J_{HH} = 7.5$ Hz, $^5J_{HH} = 0.6$ Hz; H-6), 7.75 (dd, 1H, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.2$ Hz; H-5), 8.08 (m, 1H; H-3); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 2.0 ($SiMe_3$), 2.1 ($SiMe_3$), 25.0 ($CCH_3$), 83.8 ($CCH_3$), 127.9 (C-4), 134.1 (C-5), 134.6 (C-6), 141.2 (C-3), 145.1 (C-2), 149.9 (C-1); $^{11}$B NMR (96.3 MHz, $CDCl_3$) $\delta$ 30.7 ($h_{1/2}$ = 400 Hz); $^{29}$Si INEPT NMR (59.6 MHz, $CDCl_3$) $\delta$ −3.4, −3.2. Anal. Calcd for $C_{18}H_{33}BO_2Si_2$ [348.43]: C, 62.05; H, 9.55. Found: C, 61.64; H, 9.26.

*4-Methyl-1,2-bis(trimethylsilyl)benzene (**9**).* A solution of **5** (0.205 g, 0.681 mmol) in $Et_2O$ (10 mL) was cooled to −78 °C and *t*-BuLi in pentane (1.6 M, 0.70 mL, 1.1 mmol) was added dropwise with stirring. After 45 min, the reaction mixture was slowly warmed from −78 °C to rt and stirred for further 1 h. To the resulting pale yellow solution was added MeI (0.070 mL, 0.16 g, 1.1 mmol), and after stirring for 12 h at rt, the reaction mixture was quenched by the addition of a saturated aqueous solution of $NH_4Cl$ (5 mL). The organic phase was separated with a separation funnel, and the aqueous phase was extracted with hexane (3 × 10 mL). The organic phases were combined, washed with $H_2O$ (2 × 10 mL), dried over anhydrous $MgSO_4$, and filtered. All volatiles were removed from the filtrate in vacuo, and the residual crude material was purified by column chromatography (silica gel, hexane) to give **9** as a colorless liquid: yield 0.122 g (0.516 mmol, 76%). Analytically pure samples were obtained by HPLC using a RP C18 semipreparative column eluted with MeOH/*t*-BuOMe (3:1): $^1$H NMR (400.1 MHz, $CDCl_3$) $\delta$ 0.36 (s, 9H; $SiMe_3$), 0.37 (s, 9H; $SiMe_3$), 2.35 (s, 3H; Me), 7.15−7.18 (m, 1H; H-5), 7.49−7.50 (m, 1H; H-3), 7.58 (d, 1H, $^3J_{HH} = 7.7$ Hz; H-6); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 2.1 ($SiMe_3$), 2.1 ($SiMe_3$), 21.6 (Me), 128.7 (C-5), 135.6 (C-6), 136.3 (C-3), 137.4 (C-4), 142.4 (C-1), 146.2 (C-2); $^{29}$Si INEPT NMR (59.6 MHz, $CDCl_3$) $\delta$ −3.7, −3.5.

*4-Trimethylstannyl-1,2-bis(trimethylsilyl)benzene (**10**).* A solution of **5** (0.133 g, 0.441 mmol) in THF (20 mL) was cooled to −78 °C and *t*-BuLi in pentane (1.6 M, 0.65 mL, 1.0 mmol) was added dropwise with stirring. After 15 min, a solution of $Me_3SnCl$ (0.113 g, 0.567 mmol) in THF (5 mL) was added over a period of 5 min. The reaction mixture was slowly warmed from −78 °C to rt, stirred for further 60 min, and quenched by the addition of a saturated aqueous solution of $NH_4Cl$ (5 mL). The mixture was extracted with hexane (3 × 10 mL), and the combined organic phases were washed with $H_2O$ (2 × 10 mL), dried over anhydrous $MgSO_4$, and filtered. All volatiles were removed from the filtrate in vacuo, and the residual crude material was purified by column chromatography (silica gel, hexane) to give **10** as a colorless liquid: yield 0.110 g (0.286 mmol, 65%); $^1$H NMR (300.0 MHz, $CDCl_3$) $\delta$ 0.30 (s, 9H; $SnMe_3$), 0.37 (s, 9H; $SiMe_3$), 0.39 (s, 9H; $SiMe_3$), 7.49 (dd, 1H, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.1$ Hz; H-5), 7.64 (dd, 1H, $^3J_{HH} = 7.3$ Hz, $^5J_{HH} = 0.7$ Hz; H-6), 7.81 (dd, 1H, $^4J_{HH} = 1.1$ Hz, $^5J_{HH} = 0.7$ Hz; H-3); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ −9.5 ($SnMe_3$), 2.0 ($SiMe_3$), 2.1 ($SiMe_3$), 134.8 (C-6), 135.7 (C-5), 142.0 (C-4), 142.7 (C-3), 145.4 (C-2), 146.0 (C-1); $^{29}$Si INEPT NMR (59.6 MHz, $CDCl_3$) $\delta$ −3.5, −3.3; $^{119}$Sn NMR (111.9 MHz, $CDCl_3$) $\delta$ −28.1. Anal. Calcd for $C_{15}H_{30}Si_2Sn$ [385.28]: C, 46.76; H, 7.85. Found: C, 46.39; H, 7.98.

**General Procedure for Suzuki-Type Coupling Reactions (5 → 11−14).** *4-(3′,4′-Bis(trimethylsilyl)phenyl)-1,2-bis(trimethylsilyl)benzene (**11**).* **5** (0.4280 g, 1.420 mmol), **8** (0.4942 g, 1.418 mmol), $K_2CO_3$ (0.6889 g, 4.984 mmol), and [$Pd(PPh_3)_4$] (0.0805 g, 0.0697 mmol) were dissolved in a degassed toluene/EtOH/$H_2O$ mixture (10:6:3, 60 mL). The solution was heated to 80 °C (oil bath temperature) under vigorous stirring for 1 day, cooled to rt, treated with $H_2O$ (20 mL), and the organic phase was separated with a separation funnel. The aqueous phase was extracted with $CHCl_3$ (3 × 20 mL), and the organic phases were combined, washed with $H_2O$ (2 × 20 mL), dried over anhydrous $MgSO_4$, and filtered. All volatiles were removed from the filtrate in vacuo, and the residual crude material was purified by column chromatography (silica gel, hexane) to obtain **11** as a colorless solid: yield 0.495 g (1.12 mmol, 80%). Compound **11** crystallized from a solution in MeOH/*t*-BuOMe (3:1) upon evaporation in the form of thin colorless needles that were suitable for X-ray structure analysis: $^1$H NMR (250.1 MHz, $CDCl_3$) $\delta$ 0.41 (s, 18H; $SiMe_3$), 0.42 (s, 18H; $SiMe_3$), 7.56 (dd, 2H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 2.0$ Hz; H-5), 7.77 (dd, 2H, $^3J_{HH} = 7.8$ Hz, $^5J_{HH} = 0.5$ Hz; H-6), 7.92 (dd, 2H, $^4J_{HH} = 2.0$ Hz, $^5J_{HH} = 0.5$ Hz; H-3); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 2.1 ($SiMe_3$), 2.1 ($SiMe_3$), 126.5 (C-5), 134.4 (C-3), 135.9 (C-6), 140.4 (C-4), 145.0 (C-1), 146.8 (C-2); $^{29}$Si INEPT NMR (59.6 MHz, $CDCl_3$) $\delta$ −3.2, −2.9. Anal. Calcd for $C_{24}H_{42}Si_4$ [442.94]: C, 65.08; H, 9.56. Found: C, 64.78; H, 9.50.

*4-Phenyl-1,2-bis(trimethylsilyl)benzene (**12**).* **Method A:** via the Suzuki-type coupling reaction of **5** and $C_6H_5B(OH)_2$. This compound was obtained according to the general procedure for Suzuki-type coupling reactions (cf. **11**). Subsequent purification by HPLC using a RP C18 semipreparative column eluted with MeOH/*t*-BuOMe (3:1) gave **12** as a colorless liquid: yield 85%. **Method B:** via the Suzuki-type coupling reaction of **8** and $C_6H_5Br$. This compound was obtained according to the general procedure for Suzuki-type coupling reactions (cf. **11**). Subsequent column chromatography (silica gel, hexane) gave **12** as a colorless liquid: yield 75%. **Method C:** via the Stille-type coupling reaction of **10** and $C_6H_5Br$. **10** (0.018 g, 0.047 mmol), $C_6H_5Br$ (0.005 mL, 0.008 g, 0.05 mmol), and [$Pd(PPh_3)_4$] (0.004 g, 0.003 mmol) were dissolved in toluene (5 mL). The solution was heated to 100 °C (oil bath temperature) under vigorous stirring for 1 day, cooled to rt, and all volatiles were removed in vacuo. The residual crude material was purified by column chromatography (silica gel, hexane) to obtain **12** as a colorless liquid: yield 0.011 g (0.037 mmol, 80%). **Method D:** via the entrainment method. Mg turnings (0.23 g, 9.5 mmol) were covered with THF (30 mL) and treated at rt with neat $Me_3SiCl$ (0.8 mL, 0.7 g, 6 mmol) and **15** (0.21 g, 0.67 mmol). A temperature of approximately 20 °C was maintained by means of a water bath throughout the reaction time. A solution of 1,2-$C_2H_4Br_2$ (0.060 mL, 0.13 g, 0.70 mmol) in THF (10 mL) was added dropwise to the vigorously stirred slurry over 30 min. After further stirring for 1 day at rt, the slurry was filtered, the filtrate treated with $H_2O$ (10 mL), and the organic phase separated with a separation funnel. The aqueous phase was extracted with $CHCl_3$ (3 × 10 mL), the organic phases were combined, washed with $H_2O$ (2 × 10 mL), dried over anhydrous $MgSO_4$, and filtered. All volatiles were removed from the filtrate in vacuo, and the residual crude material was purified by HPLC using a RP C18 semipreparative column eluted with MeOH/*t*-BuOMe (3:1) to obtain **12** as a colorless liquid: yield 0.120 g (0.402 mmol, 60%); $^1$H NMR (400.1 MHz, $CDCl_3$) $\delta$ 0.42 (s, 9H; $SiMe_3$), 0.43 (s, 9H; $SiMe_3$), 7.37 (t, 1H, $^3J_{HH} = 7.5$ Hz; $C_6H_5$), 7.46 (vt, 2H, $^3J_{HH} = 7.5$ Hz; $C_6H_5$), 7.56 (dd, 1H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.8$ Hz; H-5), 7.61 (d, 2H, $^3J_{HH} = 7.5$ Hz; $C_6H_5$), 7.77 (d, 1H, $^3J_{HH} = 7.8$ Hz, H-6), 7.91 (d, 1H, $^4J_{HH} = 1.8$ Hz; H-3); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 2.1 ($SiMe_3$), 2.1 ($SiMe_3$), 126.5 (C-5), 127.4 ($C_6H_5$), 127.5 ($C_6H_5$), 128.9 ($C_6H_5$), 134.2 (C-3), 135.9 (C-6), 140.3 (C-4), 141.5 ($C_6H_5$), 144.9 (C-1), 146.8 (C-2); $^{29}$Si INEPT NMR (59.6 MHz, $CDCl_3$) $\delta$ −3.3, −2.9. Anal. Calcd for $C_{18}H_{26}Si_2$ [298.57]: C, 72.41; H, 8.78. Found: C, 72.39; H, 8.55.

*4-(4′-Methoxyphenyl)-1,2-bis(trimethylsilyl)benzene (**13**).* This compound was obtained according to the general procedure for Suzuki-type coupling reactions (cf. **11**). Subsequent column chromatography (silica gel, $CHCl_3$) gave **13** as a pale yellow solid: yield 86%. Compound **13** crystallized from a solution in hexane upon evaporation in the form of colorless plates that were suitable for X-ray structure analysis: $^1$H NMR (300.0 MHz, $CDCl_3$) $\delta$ 0.41 (s, 9H; $SiMe_3$), 0.43 (s, 9H; $SiMe_3$), 3.87 (s, 3H; OMe), 6.98−7.04 (m, 2H; H-3′,5′), 7.50−7.58 (m, 3H; H-5, H-2′,6′), 7.75 (dd, 1H, $^3J_{HH} = 7.8$ Hz, $^5J_{HH} = 0.5$ Hz; H-6), 7.88 (dd, 1H, $^4J_{HH} = 2.0$ Hz, $^5J_{HH} = 0.5$ Hz; H-3); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 2.1 ($SiMe_3$), 2.1 ($SiMe_3$), 55.5 (OMe), 114.4 (C-3′,5′), 126.1 (C-5), 128.4 (C-2′,6′), 133.8 (C-3), 134.0 (C-1′), 135.9 (C-6), 139.9 (C-4), 144.1 (C-1), 146.7 (C-2), 159.4 (C-4′); $^{29}$Si INEPT NMR (59.6 MHz, $CDCl_3$) $\delta$ −3.4, −3.0.

Anal. Calcd for $C_{19}H_{28}OSi_2$ [328.60]: C, 69.45; H, 8.59. Found: C, 69.51; H, 8.64.

*Synthesis of 4-(4′-Nitrophenyl)-1,2-bis(trimethylsilyl)benzene (**14**).* This compound was obtained according to the general procedure for Suzuki-type coupling reactions (cf. **11**). Subsequent column chromatography (silica gel, $CHCl_3$) gave **14** as a yellow solid: yield 90%. Compound **14** crystallized upon diffusion of $CHCl_3$ into a solution of **14** in hexane in the form of colorless needles that were suitable for X-ray structure analysis: $^1$H NMR (400.1 MHz, $CDCl_3$) $\delta$ 0.41 (s, 9H; $SiMe_3$), 0.42 (s, 9H; $SiMe_3$), 7.57 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.9 Hz; H-5), 7.69−7.76 (m, 2H; H-2′,6′), 7.80 (d, 1H, $^3J_{HH}$ = 7.8 Hz; H-6), 7.89 (d, 1H, $^4J_{HH}$ = 1.9 Hz; H-3), 8.17−8.41 (m, 2H; H-3′,5′); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 2.0 ($SiMe_3$), 2.0 ($SiMe_3$), 124.3 (C-3′,5′), 126.6 (C-5), 127.9 (C-2′,6′), 134.1 (C-3), 136.1 (C-6), 137.8 (C-4), 147.3 (C-4′), 147.4, 147.6 (C-1,2), 148.0 (C-1′); $^{29}$Si INEPT NMR (59.6 MHz, $CDCl_3$) $\delta$ −2.8, −2.5. Anal. Calcd for $C_{18}H_{25}NO_2Si_2$ [343.57]: C, 62.93; H, 7.33; N, 4.08. Found: C, 62.89; H, 7.33; N, 3.84.

**X-ray Crystal Structure Analyses of 2, 3, 4, 8, 11, 13, and 14.** Data were collected on a two-circle diffractometer with graphite-monochromated Mo K$\alpha$ radiation. Empirical absorption corrections were performed using the MULABS[22] option in PLATON.[23] The structures were solved by direct methods using the program SHELXS[24] and refined against $F^2$ with full matrix least-squares techniques using the program SHELXL-97.[25] **8** crystallizes with two and **11** with four crystallographically independent molecules in the asymmetric unit. The absolute structure has been determined for **4** and **13** (Flack *x*-parameter = 0.06(7) and 0.1(2), respectively). For **11**, the absolute structure could not be determined reliably (Flack *x*-parameter = 0.3(4)). CCDC reference numbers: 865765 (**2**), 865766 (**3**), 865767 (**4**), 865768 (**8**), 865769 (**11**), 865770 (**13**), and 865771 (**14**).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Details of the X-ray crystal structure analyses and key crystallographic data of **2**, **3**, **4**, **8**, **11**, **13**, and **14**. $^1$H and $^{13}$C NMR spectra of the new compounds. Crystallographic data of **2**, **3**, **4**, **8**, **11**, **13**, and **14** in the crystallographic information file (CIF) format. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: matthias.wagner@chemie.uni-frankfurt.de.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors acknowledge financial support by the Beilstein Institut, Frankfurt/Main, Germany, within the research collaboration NanoBiC.

## ■ REFERENCES

(1) (a) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879−933. (b) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901−2915. (c) Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E. Jr.; Smith, M. R. III. *Science* **2002**, *295*, 305−308. (d) Snieckus, V. *Beilstein J. Org. Chem.* **2011**, *7*, 1215−1218. (e) Hartwig, J. F. *Acc. Chem. Res.* **2011**, DOI: 10.1021/ar200206a.

(2) (a) Kitamura, T.; Yamane, M. *J. Chem. Soc., Chem. Commun.* **1995**, 983−984. (b) Kitamura, T.; Yamane, M.; Inoue, K.; Todaka, M.; Fukatsu, N.; Meng, Z.; Fujiwara, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11674−11679. Aryne chemistry has been extensively reviewed: (c) Pellissier, H.; Santelli, M. *Tetrahedron* **2003**, *59*, 701−730. (d) Wenk, H. H.; Winkler, M.; Sander, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 502−528. (e) Sanz, R. *Org. Prep. Proced. Int.* **2008**, *40*, 215−291.

(3) (a) Lorbach, A.; Bolte, M.; Li, H.; Lerner, H.-W.; Holthausen, M. C.; Jäkle, F.; Wagner, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4584−4588. (b) Chai, J.; Wang, C.; Jia, L.; Pang, Y.; Graham, M.; Cheng, S. Z. D. *Synth. Met.* **2009**, *159*, 1443−1449. (c) Lorbach, A.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2010**, *29*, 5762−5765. (d) Januszewski, E.; Lorbach, A.; Grewal, R.; Bolte, M.; Bats, J. W.; Lerner, H.-W.; Wagner, M. *Chem.—Eur. J.* **2011**, *17*, 12696−12705.

(4) Agou, T.; Sekine, M.; Kawashima, T. *Tetrahedron Lett.* **2010**, *51*, 5013−5015.

(5) Lorbach, A.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Chem. Commun.* **2010**, *46*, 3592−3594.

(6) (a) Kessler, S. N.; Wegner, H. A. *Org. Lett.* **2010**, *12*, 4062−4065. (b) Kessler, S. N.; Neuburger, M.; Wegner, H. A. *Eur. J. Org. Chem.* **2011**, 3238−3245. (c) Wegner, H. A.; Kessler, S. N. *Synlett* **2012**, 699−705.

(7) (a) Kitamura, T.; Todaka, M.; Fujiwara, Y. *Org. Synth.* **2002**, *78*, 104−108. (b) Bettinger, H. F.; Filthaus, M. *J. Org. Chem.* **2007**, *72*, 9750−9752. (c) Bader, S. L.; Kessler, S. N.; Wegner, H. A. *Synthesis* **2010**, 2759−2762.

(8) Lorbach, A.; Reus, C.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Adv. Synth. Catal.* **2010**, *352*, 3443−3449.

(9) (a) Seyferth, D.; White, D. L. *J. Organomet. Chem.* **1972**, *34*, 119−128. (b) Kitamura, T.; Wasai, K.; Todaka, M.; Fujiwara, Y. *Synlett* **1999**, 731−732. (c) Kitamura, T.; Aoki, Y.; Isshiki, S.; Wasai, K.; Fujiwara, Y. *Tetrahedron Lett.* **2006**, *47*, 1709−1712.

(10) Afarinkia, K.; Posner, G. H. *Tetrahedron Lett.* **1992**, *33*, 7839−7842.

(11) Cho, C.-G.; Park, J.-S.; Jung, I.-H.; Lee, H. *Tetrahedron Lett.* **2001**, *42*, 1065−1067.

(12) Cho, C.-G.; Kim, Y.-W.; Lim, Y.-K.; Park, J.-S.; Lee, H.; Koo, S. *J. Org. Chem.* **2002**, *67*, 290−293.

(13) (a) Hilt, G.; Lüers, S. *Synthesis* **2002**, 609−618. (b) Hess, W.; Treutwein, J.; Hilt, G. *Synthesis* **2008**, 3537−3562. The complex $[Ru(OAc)_2(PPh_3)_2]$, which is an efficient click reaction catalyst (Zhang, L.; Chen, X.; Xue, P.; Sun, H. H. Y.; Williams, I. D.; Sharpless, K. B.; Fokin, V. V.; Jia, G. *J. Am. Chem. Soc.* **2005**, *127*, 15998−15999) did not accelerate any of our [4 + 2] cycloaddition reactions.

(14) Navarro, O.; Kaur, H.; Mahjoor, P.; Nolan, S. P. *J. Org. Chem.* **2004**, *69*, 3173−3180. In this paper, the catalytic dehalogenation of aryl chlorides using (NHC)Pd(allyl)Cl complexes and NaO*t*-Bu as hydride transfer reagent is described. We achieved the selective monodehalogenation of the aryl bromide **6** with the catalyst $[Pd(PPh_3)_4]$.

(15) (a) Ishiyama, T.; Takagi, J.; Hartwig, J. F.; Miyaura, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 3056−3058. (b) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890−931. The related catalyst system $[Ir(1,4\text{-cyclooctadiene})OMe]_2$/4,4′-dimethyl-2,2′-bipyridine provided significantly lower yields of **8**.

(16) Murphy, J. M.; Liao, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 15434−15435.

(17) Mach, K.; Antropiusová, H.; Petrusová, L.; Tureček, F.; Hanuš, V. *J. Organomet. Chem.* **1985**, *289*, 331−339.

(18) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508−524. (b) Espinet, P.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4704−4734.

(19) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483.

(20) A Suzuki coupling reaction involving 4-bromotrimethylsilylbenzene has been reported in the patent literature and was adapted for the present cases: Whitehouse, D.; Hu, S.; Fang, H.; van Zandt, M. PCT Int. Appl. WO 2004/099170, 2004.

(21) Diemer, V.; Leroux, F. R.; Colobert, F. *Eur. J. Org. Chem.* **2011**, 327−340.

(22) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38.

(23) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.

(24) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

(25) Sheldrick, G. M. *SHELXL-97*. A Program for the Refinement of Crystal Structures; Universität Göttingen, Göttingen, Germany, 1997.