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Bromine as the Ortho-Directing Group in the Aromatic Metalation/Silylation of Substituted Bromobenzenes

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The one-pot metalation/disilylation of selected bromobenzenes bearing electron-withdrawing substituents *p*-, *m*-, *o*-XC_6H_4Br (X = F, Cl, I, CN, CF_3) using 2 equiv of lithium diisopropylamide (LDA) and 2 equiv of chlorotrimethylsilane (TMSCl) was investigated. The best results of disilylation were obtained for para-substituted bromobenzenes, but the regioselectivity of the reaction is strongly influenced by the ortho-directing power of the substituent. On the contrary, the disilylation of meta-substituted bromobenzenes was not efficient or even failed in some cases and hence monosilylated derivatives were isolated as major or sole products. Diverse reactivity was observed for ortho-substituted bromobenzenes, e.g., 2-bromobenzonitrile and 2-bromochlorobenzene, were converted into corresponding disilylated derivatives in a high and moderate yield, respectively, whereas 1-bromo-2-(trifluoromethyl)benzene underwent only monosilylation.

Introduction

The ortho-directed metalation of substituted arenes can be regarded nowadays as the classical synthetic method used for the functionalization of these compounds.[1] Among halogen substituents, fluorine possesses the strongest ortho-directing ability, and this property has been extensively studied and has also found many applications to organic synthesis.[2,3] The metalation of brominated arenes is not so straightforward since the ortho-directing ability of bromine is relatively weak.[4] An important limitation is the competitive bromine−lithium exchange that occurs preferentially to the ortho-metalation if alkyllithium reagents are employed. Hence, only non-carbon-based strong bases such as lithium amides, e.g., LDA or lithium 2,2,6,6-tetramethylpiperidide (LTMP), can be considered as effective deprotonating agents. Until now, only a few reports concerning the metalation of oligobromobenzenes[5−7] and brominated heteroarenes[8,9] have been published. On the other hand, *ortho*-bromoaryllithium intermediates are significantly less thermally stable than their fluorine and chlorine analogues[10,11] and may decompose under metalation conditions to form arynes[6,12−14] or are susceptible to isomerization, via the well-known Bunnett's "halogen dance" process.[5] These undesired reactions could be successfully avoided by trapping the organolithium species in situ using the appropriate electrophile (TMSCl) as was proved recently for the metalation of 1,2- and 1,4-dibromobenzene.[7] In this paper, we present the significant extension of our previous work, providing new and interesting results concerning the metalation/silylation of substituted monobromobenzenes.

Results and Discussion

It was found earlier that fluorinated bromobenzenes are metalated preferentially in the position ortho to the fluorine due to the stronger ortho-directing ability of fluorine with respect to bromine.[3,4] In fact, the disilylation of 1-bromo-4-fluorobenzene proceeds smoothly in positions 3 and 5 adjacent to the fluorine as demonstrated by the high-yield isolation of 1-bromo-4-fluoro-3,5-bis(trimethylsilyl)benzene (**1a**) as shown in Scheme 1.

A different regioselectivity of disilylation was observed for 1-bromo-4-chlorobenzene since 1-bromo-4-chloro-2,5-bis(trimethylsilyl)benzene (**2a**) was isolated as the product in a good yield, which resembles the behavior of 1,4-dibromobenzene.[7] Apparently, the introduction of the TMS group reduces the ortho-directing power of the neighboring halogen atom depending on the first position metalated, i.e., ortho to chlorine or bromine (Scheme 1). Hence, the second metalation occurs predominantly in

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(1) (a) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879. (b) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306.
(2) Bridges, A. J.; Lee, A.; Maduakor, E. C.; Schwartz, C. E. *Tetrahedron Lett.* **1992**, *33*, 7495. Bridges, A. J.; Lee, A.; Maduakor, E. C.; Schwartz, C. E. *Tetrahedron Lett.* **1992**, *33*, 7499.
(3) Moyroud, J.; Guesnet, J.-L.; Bennetau, B.; Mortier, J. *Tetrahedron Lett.* **1995**, *36*, 885.
(4) Mongin, F.; Schlosser, M. *Tetrahedron Lett.* **1996**, *37*, 6551.
(5) Mongin, F.; Marzi, E.; Schlosser, M. *Eur. J. Org. Chem.* **2001**, *14*, 2771.
(6) Leroux, F.; Schlosser, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4272.
(7) Luliński, S.; Serwatowski, J. *J. Org. Chem.* **2003**, *68*, 5384.
(8) Van, P. C.; Macomber, R. C.; Mark, H. B., Jr.; Zimmer, H. *J. Org. Chem.* **1984**, *49*, 5250.
(9) Effenberger, F.; Daub, W. *Chem. Ber.* **1991**, *124*, 2119.
(10) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc*, **1956**, *78*, 2217.
(11) Chen, L. S.; Chen, G. J.; Tamborski, C. *J. Organomet. Chem.* **1980**, *193*, 283.
(12) Gilman, H.; Gaj, B. J. *J. Org. Chem.* **1957**, *22*, 447.
(13) Dougherty, T. K.; Lau, K. S. Y.; Hedberg, F. L. *J. Org. Chem.* **1983**, *48*, 5273.
(14) Pellissier, H.; Santelli, M. *Tetrahedron* **2003**, *59*, 701 and references therein.

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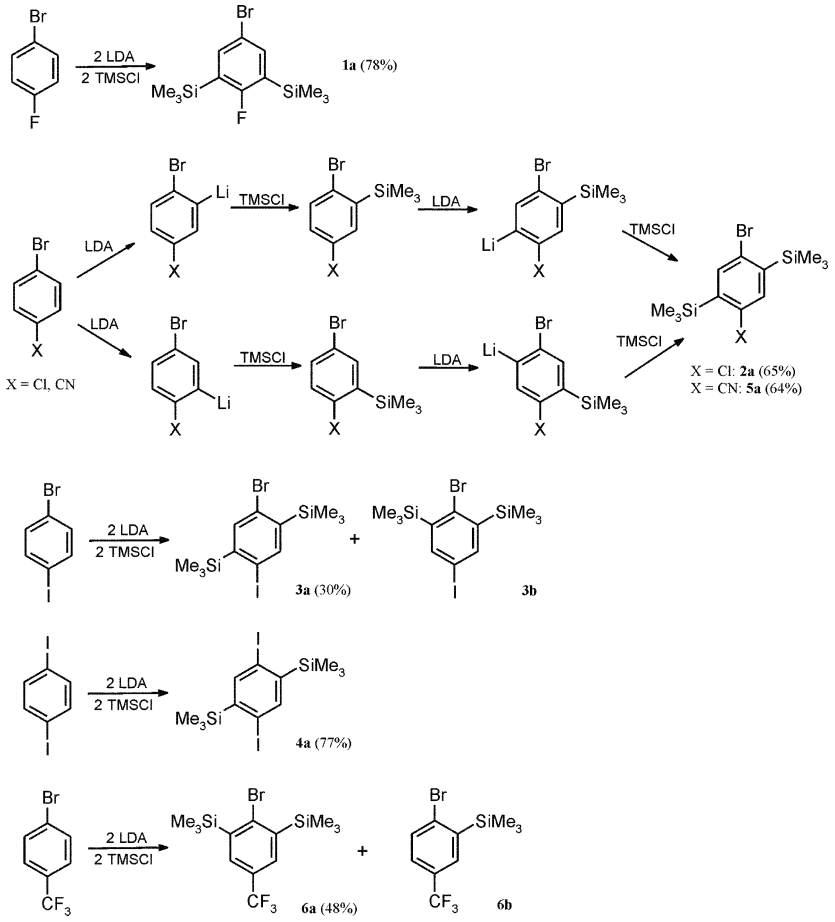
SCHEME 1 [16]



the position para to the first introduced TMS group, which reflects a small difference of acidifying properties of chlorine and bromine.[15]

The disilylation of 1-bromo-4-iodobenzene was also efficacious but not so regioselective. A mixture of 1-bromo-4-iodo-2,5-bis(trimethylsilyl)benzene (**3a**, 57%) and 1-bromo-4-iodo-2,6-bis(trimethylsilyl)benzene (**3b**, 19%) was obtained. The main product could be isolated from the mixture by fractional crystallization from ethanol in ca. 30% yield. The synthesis of compound **3a** is the first example of the successful trapping of the *ortho*-iodoaryllithium species that is not stabilized by the adjacent electronegative substituents such as fluorine.[2] On the other hand, it should be noted that the formation of a significant amount of **3b** gives evidence for distinctly weaker ortho-directing properties of iodine with respect to bromine. Nevertheless, 1,4-diiodobenzene could also be disilylated without difficulty under standard conditions to produce 1,4-diiodo-2,5-bis(trimethylsilyl)benzene (**4a**) in 77% yield.

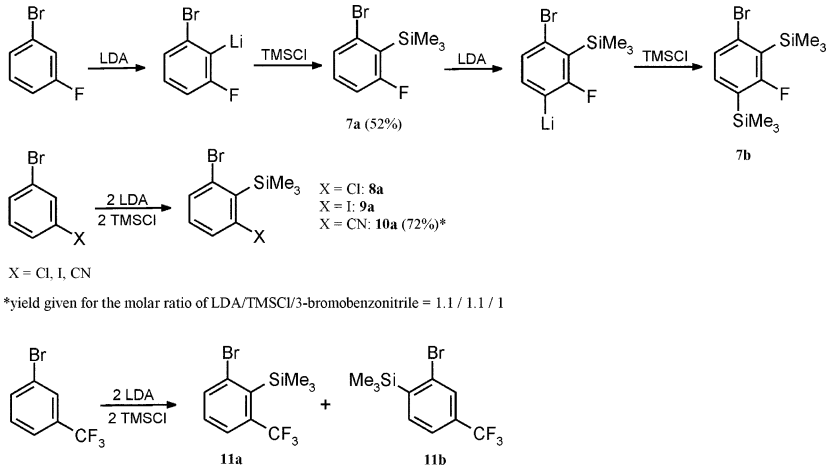
Results obtained for halogen-substituted bromobenzenes have prompted us to investigate the reactivity of their analogues bearing carbon-based electronegative functions, i.e., the nitrile and trifluoromethyl groups. It was found earlier that these substituents are good ortho directors for aromatic lithiation.[17,18] On the basis of literature reports,[17] we have might suppose the disilylation of 4-bromobenzonitrile to occur predominantly in positions 2 and 6 adjacent to the nitrile group due to the stronger acidifying effect of this group with respect to bromine. However, this was apparently not the case since 4-bromo-2,5-bis(trimethylsilyl)benzonitrile (**5a**) was isolated as the only product in a good yield. Such a reaction course provides evidence for a similar ortho-directing power of the nitrile group when compared to bromine and chlorine.

On the contrary, the metalation and subsequent silylation of 1-bromo-4-(trifluoromethyl)benzene was controlled exclusively by bromine. 1-Bromo-4-(trifluoromethyl)-2,6-bis(trimethylsilyl)benzene (**6a**) was isolated as the major product (48%), but the small amount (ca. 15%) of the monosilylated compound, i.e., 1-bromo-4-(trifluoromethyl)-2-(trimethylsilyl)benzene (**6b**), was also detected in the reaction mixture. Presumably, the relatively weak ortho-directing properties of the CF_3 group may be atrributed to a considerable extent to the steric repulsions with the bulky base. This explanation is strongly supported by the diverse regioselectivity of the metalation of 1,3-bis(trifluoromethyl)benzene, which is strongly dependent on the size of the base used.[19]

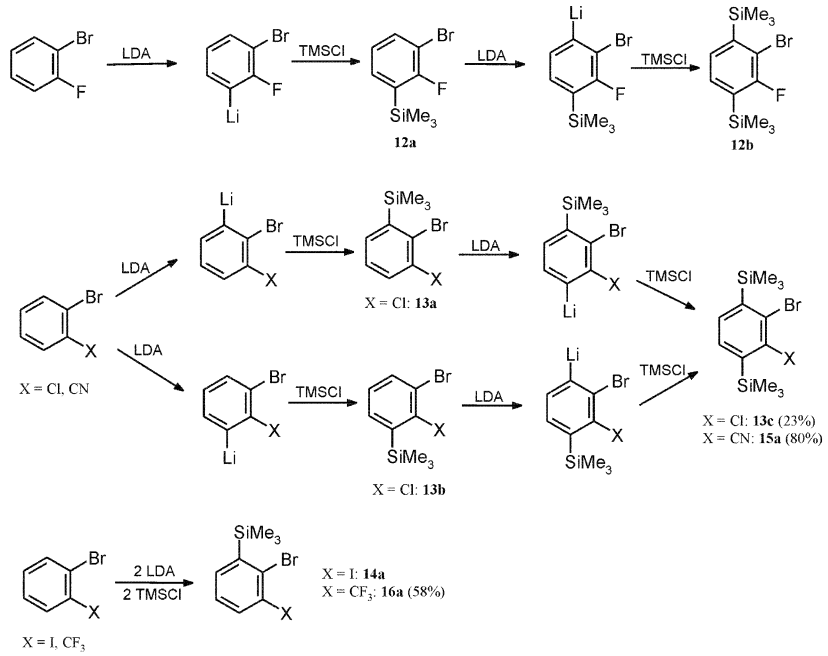
Meta-substituted bromobenzenes were generally susceptible to metalation and subsequent monosilylation in

(15) Mongin, F.; Schlosser, M. *Tetrahedron Lett.* **1997**, *38*, 1559.
(16) Yields of isolated pure products are given in parentheses.
(17) Krizan, T. D.; Martin J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6155.
(18) Bigwood, M. P.; Corran, P. J.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7643.
(19) Schlosser, M.; Katsoulos, G.; Takagishi, S. *Synlett* **1990**, 747.

SCHEME 2



SCHEME 3



the most activated position 2, i.e., between bromine and the electronegative substituent. However, the introduction of the second TMS group was not straightforward in most cases (Scheme 2). The attempted disilylation of 1-bromo-3-fluorobenzene resulted in the formation of the mixture containing mainly the monosilylated product, i.e., 1-bromo-3-fluoro-2-(trimethylsilyl)benzene (**7a**). The yield of 1-bromo-3-fluoro-2,4-bis(trimethylsilyl)benzene was rather poor, and this compound could not be satisfactorily purified (**7b**). 1-Bromo-3-chlorobenzene[20] and 1-bromo-3-iodobenzene were converted exclusively into expected monosilylated products, which were found to be resistant against further metalation and silylation. Clearly, the activation of remaining hydrogen atoms by the adjacent heavier halogen substituents is not sufficient to enable deprotonation. A different behavior was found for 3-bromobenzonitrile, as the disilylation of this compound was observed. Unfortunately, a mixture of products was formed and it was not possible to isolate them in a pure state. However, when 3-bromobenzonitrile was treated with only 1.1 equiv of LDA and 1.1 equiv of TMSCl, then the pure 3-bromo-2-(trimethylsilyl)benzonitrile (**10a**) was prepared in a good yield. Finally, 1-bromo-3-(trifluoromethyl)benzene was converted into the mixture of monosilylated derivatives. Contrary to previous examples, the product expected for electronic reasons, i.e., 1-bromo-3-(trifluoromethyl)-2-(trimethylsilyl)benzene (**11a**), was formed in a rather low yield (ca. 30%), whereas 2-bromo-4-(trifluoromethyl)-1-(trimethylsilyl)benzene (**11b**, ca. 70%) was the major product. The preferred formation of **11b** points again to the importance of steric factors in the metalation of CF_3-substituted arenes.[19]

In a series of ortho-substituted bromobenzenes, a diverse reactivity was observed (Scheme 3). 1-Bromo-2-fluorobenzene could be easily monosilylated in the expected position ortho to the fluorine to give 1-bromo-2-fluoro-3-trimethylsilylbenzene (**12a**) as the major product in 60% yield.[3] The subsequent silylation of this compound

(20) Effenberger, F.; Daub, W. *Chem. Ber.* **1991**, *124*, 2113.

was rather slow, and only a low yield (ca 20%) of impure 2-bromo-3-fluoro-1,4-bis(trimethylsilyl)benzene (**12b**) was isolated.

In the case of 1-bromo-2-chlorobenzene, a mixture of 2-bromo-3-chloro-1-trimethylsilylbenzene (**13a**, 20%), 1-bromo-2-chloro-3-trimethylsilylbenzene (**13b**, 22%), and 2-bromo-3-chloro-1,4-bis(trimethylsilyl)benzene (**13c**, 40%) was obtained, showing again that there is no significant difference of acidifying properties of chlorine and bromine.[15] The latter compound could be isolated from this mixture, albeit in a quite low yield (23%). The higher-yield formation of **13c** with respect to **12b** should be noted, suggesting that chlorine or bromine in the meta position activate the hydrogen atom in compounds **13a** and **13b**, respectively, more strongly than the fluorine does in **12a**.[21]

Interestingly, a much better result was achieved when 2-bromobenzonitrile was subjected to disilylation, as 2-bromo-3,6-bis(trimethylsilyl)benzonitrile (**15a**) was synthesized in a good yield (80%). On the other hand, 1-bromo-2-(trifluoromethyl)benzene gave only the monosilylated product, namely, 2-bromo-3-(trifluoromethyl)-benzene-1-trimethylsilylbenzene (**16a**), which provides the next piece of clear evidence for the better acidifying properties of bromine when compared to the CF_3 group.

In conclusion, the activity of bromine as the ortho-directing group in the aromatic lithiation was found to be comparable to the activity of chlorine and the nitrile group and stronger with respect to the CF_3 group. It should be noted that the application of the metalation/silylation sequence to the functionalization of bromobenzenes was proved in many cases, which is important especially from the synthetic point of view. This approach may be a suitable method for further transformations of these compounds, e.g., due to the reactivity of the TMS groups and/or bromine.

Experimental Section

1-Bromo-4-fluoro-3,5-bis(trimethylsilyl)benzene (1a). LDA (2 M, 55 mL, 110 mmol) was added dropwise to a solution of 1-bromo-4-fluorobenzene (7.8 g, 50 mmol) in THF (70 mL) containing TMSCl (12.0 g, 14 mL) at −70 °C. The resultant solution was stirred for 30 min at −75 °C and hydrolyzed with dilute aqueous H_2SO_4. The yellow organic phase was separated, and the water phase was extracted with ether. Evaporation of the combined organic solutions left a pale yellow oil. The oil was distilled in vacuo to give a crude product as a colorless oil. Methanol (10 mL) was added, and the solution was left to stand overnight in a −20 °C freezer. Crystals that separated from the solution were filtered, washed with cold methanol, and dried to give **1a** as a white crystalline material, mp 48−50 °C. Yield: 12.5 g (78%). ^{1}H NMR: δ 7.46 (d, 2H, $^3J_{HF}$ = 4.8 Hz), 0.32 (d, 18H, $^5J_{HF}$ = 1.0 Hz). ^{13}C{^{1}H} NMR: δ 170.9 (d, $^1J_{CF}$ = 236.4 Hz), 139.0 (d, $^3J_{CF}$ = 12 Hz), 128.9 ($^2J_{CF}$ = 38.2 Hz), 117.8 (d, $^4J_{CF}$ = 3 Hz), −0.9. Anal. Calcd for $C_{12}H_{20}BrFSi_2$: C, 45.13; H, 6.31. Found: C, 44.85; H, 6.13.

1-Bromo-4-chloro-2,5-bis(trimethylsilyl)benzene (2a). This compound was prepared using the procedure described for **1a** starting from 1-bromo-4-chlorobenzene (9.6 g, 50 mmol). A crude solid product was filtered, washed with water and cold methanol, and dried to give colorless crystals of **2a**, mp 85−87 °C. Yield: 11.0 g (65%). ^{1}H NMR: δ 7.54 (s, 1H), 7.34 (s, 1H), 0.39 (s, 9H), 0.37 (s, 9H). ^{13}C{^{1}H} NMR: δ 144.5, 142.4, 140.0, 139.6, 136.7, 128.8, −0.6, −0.8. Anal. Calcd for $C_{12}H_{20}BrClSi_2$: C, 42.92; H, 6.00. Found: C, 42.53; H, 5.75.

1-Bromo-4-iodo-2,5-bis(trimethylsilyl)benzene (3a). LDA (2 M, 33 mL, 66 mmol) was added dropwise to a solution of 1-bromo-4-iodobenzene (8.5 g, 30 mmol) in THF (70 mL) containing TMSCl (7.2 g, 8.5 mL) at −70 °C. The resultant solution was stirred for 30 min at −75 °C and hydrolyzed with dilute aqueous H_2SO_4. The reddish organic phase was separated, and the water phase was extracted with ether. Evaporation of the combined organic solutions left a crude solid that was filtered, washed with water and cold methanol (3 × 10 mL), and dried to give a mixture of **3a** and **3b** in ca. 57 and 19% yields, respectively (9.7 g, combined yield = 76%). Fractional crystallization from ethanol (80 mL, 35 °C) afforded pure **3a**, mp 93−95 °C. Yield: 3.8 g (30%). ^{1}H NMR: δ 7.81 (s, 1H), 7.48 (s, 1H), 0.41 (s, 9H), 0.38 (s, 9H). ^{13}C{^{1}H} NMR: δ 149.3, 147.2, 145.1, 140.3, 131.0, 103.1, −0.5, −0.7. Anal. Calcd for $C_{12}H_{20}BrISi_2$: C, 33.70; H, 4.72. Found: C, 33.81; H, 4.83.

1,4-Diiodo-2,5-bis(trimethylsilyl)benzene (4a). This compound was prepared using the procedure described for **3a** starting from 1,4-diiodobenzene (9.9 g, 30 mmol. A crude solid product was filtered, washed with water and methanol, and dried to give **4a** as white crystals, mp 132−134 °C. Yield: 10.9 g (77%). ^{1}H NMR: δ 7.77 (s, 2H), 0.41 (s, 18H). ^{13}C{^{1}H} NMR: δ 149.5, 147.4, 104.6, −0.6. Anal. Calcd for $C_{12}H_{20}I_2Si_2$: C, 30.39; H, 4.25. Found: C, 30.34; H, 4.20.

4-Bromo-2,5-bis(trimethylsilyl)benzonitrile (5a). This compound was prepared using the procedure described for **1a** starting from 4-bromobenzonitrile (9.1 g, 50 mmol). A crude solid product was filtered, washed with water and cold methanol (3 × 10 mL), and dried to give colorless crystals of **5a**, mp 107−110 °C. Yield: 10.5 g (64%). ^{1}H NMR: δ 7.70 (s, 1H), 7.68 (s, 1H), 0.42 (s, 9H), 0.40 (s, 9H). ^{13}C{^{1}H} NMR: δ 147.9, 143.4, 140.8, 138.7, 135.7, 120.0, 115.8, −0.7, −1.40. Anal. Calcd for $C_{13}H_{20}BrNSi_2$: C, 47.84; H, 6.18; N, 4.29. Found: C, 47.85; H, 5.95; N, 4.26.

1-Bromo-4-(trifluoromethyl)-2,6-bis(trimethylsilyl)-benzene (6a). This compound was prepared using the procedure described for **1a** starting from 1-bromo-4-(trifluoromethyl)benzene (11.1 g, 50 mmol). A crude liquid product was distilled in vacuo to give a mixture of crystals and oil. Ethanol (10 mL) was added, and the solution was left to stand overnight in a −20 °C freezer. Crystals that separated from the solution were filtered, washed with cold ethanol (2 × 10 mL), and dried to give **6a** as colorless crystals, mp 78−80 °C. Yield: 8.7 g (48%). ^{1}H NMR: δ 7.61 (s, 2H), 0.43 (s, 18H). ^{13}C-{^{1}H} NMR: δ 143.5, 142.8, 133.8 (q, $^3J_{CF}$ = 3.8 Hz), 128.3 (q, $^2J_{CF}$ = 31.2 Hz), 124.7 (q, $^1J_{CF}$ = 272.6 Hz), −0.1. Anal. Calcd for $C_{13}H_{20}BrF_3Si_2$: C, 42.27; H, 5.46. Found: C, 42.45; H, 5.42.

1-Bromo-3-fluoro-2-(trimethylsilyl)benzene (7a). This compound was prepared using the procedure described for **1a** starting from 1-bromo-3-fluorobenzene (7.8 g, 50 mmol). A crude liquid product was distilled in vacuo to give **7a**, bp 97−100 °C (10 mmHg), as a colorless liquid. The residue contained **7b**, which could not be isolated in a pure form. Yield of **7a**: 6.4 g (52%). ^{1}H NMR: δ 7.35 (d, 1H), 7.16 (m, 1H), 6.94 (m, 1H), 0.47 (dd, 9H). ^{13}C{^{1}H} NMR: δ 167.3 (d, $^1J_{CF}$ = 246.5 Hz), 131.9 (d, $^3J_{CF}$ = 10.1 Hz), 130.3 (d, $^3J_{CF}$ = 12.1 Hz), 129.6 ($^4J_{CF}$ = 3.0 Hz), 127.6 (d, $^2J_{CF}$ =32 Hz), 114.5 (d, $^2J_{CF}$ = 28.3 Hz), 1.6 ($^4J_{CF}$ = 4.5 Hz). Anal. Calcd for $C_9H_{12}BrFSi$: C, 43.73; H, 4.89. Found: C, 43.70; H, 4.97.

3-Bromo-2-(trimethylsilyl)benzonitrile (10a). LDA (2 M, 27 mL, 54 mmol) was added dropwise to the solution of 3-bromobenzonitrile (9.1 g, 50 mmol) in THF (70 mL) containing TMSCl (6.0 g, 7 mL, 55 mmol) at −70 °C. The resultant solution was stirred 30 min at −75 °C and hydrolyzed with dilute aqueous H_2SO_4. The yellow organic phase was separated, and the water phase was extracted with ether. Evaporation of the combined organic solutions left a crude solid product. The product was filtered, washed with water and cold

(21) (a) Büker, H. H.; Nibbering, N. M. M.; Espinosa, D.; Mongin, F.; Schlosser, M. *Tetrahedron Lett.* **1997**, *38*, 8519 (b) Schlosser, M.; Marzi, E.; Cottet, F.; Büker, H. H.; Nibbering N. M. M. *Chem. Eur. J.* **2001**, *7*, 3511.

methanol (3 × 10 mL), and dried to give colorless crystals of **10a**, mp 57−58 °C. Yield: 9.1 g (72%). ^{1}H NMR: δ 7.75 (dd, 1H), 7.65 (dd, 1H), 7.26 (t, 1H), 0.58 (s, 9H). ^{13}C{^{1}H} NMR: δ 144.2, 137.9, 134.2, 131.7, 130.5, 119.7, 119.6, 1.9. Anal. Calcd for $C_{10}H_{12}BrNSi$: C, 47.25; H, 4.76; N, 5.51. Found: C, 47.03; H, 4.53; N, 5.45.

2-Bromo-3-chloro-1,4-bis(trimethylsilyl)benzene (13c). This compound was prepared using the procedure described for **1a** starting from 1-bromo-2-chlorobenzene (9.6 g, 50 mmol). A crude liquid product was fractionally distilled in vacuo. The forerunner was a mixture of **13a** and **13b** (ca 1:1), bp 75−100 °C (2 Tr). The heavier fraction, bp 100−105 °C (2 mmHg), which contained mainly the product, was obtained as an oil that solidified while standing in a −20 °C freezer. The crude solid product was mixed with cold methanol (10 mL), filtered, and purified by recrystallization from methanol (15 mL). Colorless crystals of **13c**, mp 58−60 °C, were obtained. Yield: 4.0 g (23%). ^{1}H NMR: δ 7.37 (d, 1H), 7.29 (d, 1H), 0.40 (s, 9H), 0.37 (s, 9H). ^{13}C{^{1}H} NMR: δ 145.8, 142.7, 141.1, 133.8, 133.6, 131.1, −0.2, −0.5. Anal. Calcd for $C_{12}H_{20}BrClSi_2$: C, 42.92; H, 6.00. Found: C, 43.00; H, 6.13.

2-Bromo-3,6-bis(trimethylsilyl)benzonitrile (15a). This compound was prepared using the procedure described for **1a** starting from 2-bromobenzonitrile (9.1 g, 50 mmol). A crude solid product was filtered, washed with water and cold methanol (3 × 10 mL), and dried to give **15a** as a white solid, mp 87−89 °C. Yield: 13.0 g (80%). ^{1}H NMR: δ 7.56 (d, 1H), 7.49 (d, 1H), 0.43 (s, 9H), 0.41 (s, 9H). ^{13}C{^{1}H} NMR: δ 149.0, 144.1, 138.8, 134.5, 132.4, 121.0, 118.8, −0.5, −1.4. Anal. Calcd for $C_{13}H_{20}BrNSi_2$: C, 47.84; H, 6.18; N, 4.29. Found: C, 47.73; H, 5.95; N, 4.33.

2-Bromo-3-(trifluoromethyl)-1-(trimethylsilyl)benzene (16a). This compound was prepared using the procedure described for **1a** starting with 1-bromo-2-(trifluoromethyl)-benzene (11.1 g, 50 mmol). A crude product was distilled in vacuo to give **16a** as a colorless liquid, bp 101−104 °C (10 Tr). Yield: 8.5 g (58%). ^{1}H NMR: δ 7.68 (dd, 1H), 7.61 (m, 1H), 7.39 (m, 1H), 0.45 (s, 9H). ^{13}C{^{1}H} NMR: δ 145.5, 139.5, 130.5 (q, $^2J_{CF}$ = 30.2 Hz), 128.9 (q, $^3J_{CF}$ = 6 Hz), 127.9, 126.7, 123.6 (q, $^1J_{CF}$ = 273.6 Hz), 0.0. Anal. Calcd for $C_{10}H_{12}BrF_3Si$: C, 40.42; H, 4.07. Found: C, 40.50; H, 4.11.

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Supporting Information Available: Copies of the ^{13}C NMR spectra of compounds **1a**−**7a**, **10a**, **13c**, **15a**, and **16a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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