

Improved Synthesis of 1,2-Bis(trimethylsilyl)benzenes using Rieke-Magnesium or the Entrainment Method

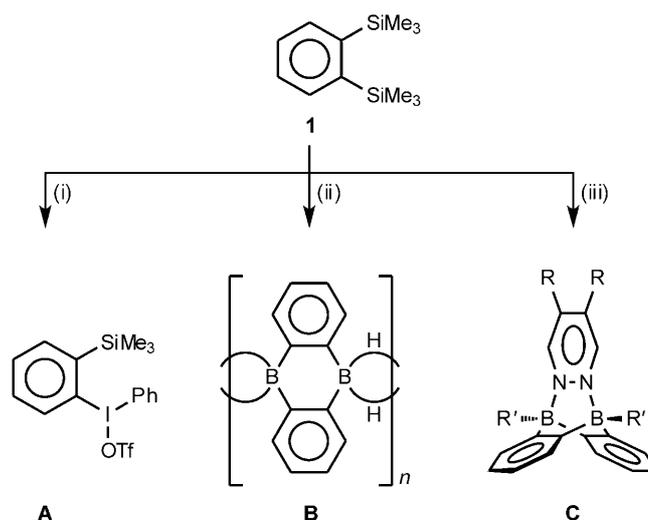
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Abstract: 1,2-Bis(trimethylsilyl)benzene is the key starting material for the synthesis of efficient benzyne precursors and certain luminescent π -conjugated materials. We now report that it can be conveniently prepared in tetrahydrofuran from 1,2-dibromobenzene, chlorotrimethylsilane, and either Rieke-magnesium (Mg^R) or magnesium turnings in the presence of 1,2-dibromoethane as an entrainer (Mg^c). The most important advantages of these new protocols over the currently best-established procedure (1,2-dichlorobenzene, chlorotrimethylsilane, magnesium turnings, hexamethylphosphoramide) lie in the milder reaction conditions (Mg^R : 0 °C, 2 h; Mg^c : room temperature, 30 min vs. 100 °C, 2 days) and in the fact that the cancerogenic solvent hexamethylphosphoramide is avoided. Moreover, the improved protocols are also applicable for the high-yield synthesis of 1,2,4,5-tetrakis(trimethylsilyl)benzene, 4-fluoro-1,2-bis(trimethylsilyl)benzene, 4-chloro-1,2-bis(trimethylsilyl)benzene, and 4,5-dichloro-1,2-bis(trimethylsilyl)benzene.

Keywords: arenes; entrainment method; Grignard reaction; Rieke-magnesium; silanes; silylation

ides with triethoxysilane or triorganosilanes.^[3] However, especially the synthesis of sterically encumbered arylsilanes still poses considerable challenges as illustrated by the case of 1,2-bis(trimethylsilyl)benzene (**1**; Scheme 1), which is only accessible *via* pathways requiring either highly toxic or very costly chemicals.



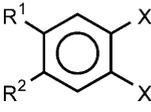
Scheme 1. 1,2-Bis(trimethylsilyl)benzene (**1**) is a key starting material for the preparation of the benzyne precursor **A**, the polymer building block **B**, and Lewis-acid catalysts **C**. (i) *cf.* Ref.^[5]; (ii) *cf.* Refs.^[6,7]; (iii) *cf.* Ref.^[8]

Introduction

Arylsilanes and their hypervalent derivatives are valuable intermediates in organic synthesis, for example, in borylation^[1] or Pd-catalyzed Hiyama cross-coupling reactions.^[2] Accordingly, various different methods for the preparation of (functionalized) arylsilanes have been worked out, ranging from the arylation of halosilanes with organolithium or Grignard reagents to the transition metal-mediated silylation of aryl hal-

Compound **1** is the key starting material for the synthesis of (i) (phenyl)[2-(trimethylsilyl)phenyl]iodonium triflate (**A**; Scheme 1), one of the most efficient benzyne precursors available to date,^[4,5] (ii) 9,10-dihydro-9,10-diboraanthracene (**B**; Scheme 1), a versatile building block of luminescent boron-doped π -conjugated polymers,^[6,7] and (iii) 9,10-dimethyl-9,10-dihydro-9,10-diboraanthracene, a powerful ditopic Lewis-

Table 1. Comparison of the yields of 1,2-bis(trimethylsilyl)benzenes obtained with different Grignard methods.

Product	Starting Material		Entrainment Approach ^[a] X = Br	 R ¹ X R ² X Riecke-Mg Approach ^[a] X = Br	Fe-Catalyzed Approach ^[b] X = Br	HMPA Approach X = Cl
	R ¹	R ²				
1	H	H	62%	65% ^[c]	41%	75% ^[d]
2	X	X	54%	80%	38%	49% ^[e]
4	Cl	Cl	67%	70%	–	–
5	F	H	56%	53%	–	–
8	Cl	H	59%	60% ^[f]	–	–
11	Me	Me	< 10% ^[g]	10–40% ^[h]	19%	50% ^[i]
12	<i>t</i> -Bu	H	< 10% ^[g]	0%	14%	–

^[a] This work.

^[b] Mg powder/Me₃SiCl/DIBAL-H, TMEDA, FeCl₃/THF, –10 °C to 0 °C, 1 day; *cf.* Ref.^[15]

^[c] Isolated yield after redistillation of several combined forerunnings.

^[d] Mg turnings/Me₃SiCl/HMPA, 100 °C, 2 days; *cf.* Ref.^[9]

^[e] Mg powder/Me₃SiCl/HMPA-THF, 100 °C, 2 days; *cf.* Ref.^[26]

^[f] X = I.

^[g] Yields were estimated from the ¹H NMR spectra of the crude product mixtures.

^[h] Yields suffer from poor reproducibility.

^[i] Mg/Me₃SiCl/HMPA-THF; *cf.* Ref.^[24]

acid catalyst (*cf.* **C** for the activation of 1,2-diazines; Scheme 1).^[8]

The currently best-established synthesis protocol for compound **1**, which starts from 1,2-dichlorobenzene, Mg turnings, and Me₃SiCl, suffers from two major disadvantages: (i) the use of the toxic and carcinogenic solvent hexamethylphosphoramide (HMPA) is necessary, and (ii) the transformation requires high temperature (100 °C) and a long reaction time (2 days).^[9] To avoid the use of HMPA, **1** can alternatively be prepared from 1,2-dibromobenzene, *tert*-butyllithium (4 equiv.), and an excess of Me₃SiOTf (OTf = triflate; Et₂O-THF, –120 °C).^[10] Here, the use of Me₃SiCl does not give **1** in appreciable amounts, which, together with the fact that *tert*-butyllithium is employed instead of Mg, renders this methodology rather expensive. Given this background, [2-(hydroxydimethylsilyl)phenyl]-(phenyl)iodonium triflate has been suggested as a substitute for **A**,^[11] because the synthesis of this new benzyne precursor proceeds *via* 1,2-bis(dimethylsilyl)benzene, which is sterically less encumbered than **1** and accessible from 1,2-dibromobenzene/Mg/Me₂(H)SiCl in THF.^[12] For the synthesis of **B**, the silyl derivative **1** could, in principle, be replaced by 1,2-bis(trimethylstannyl)benzene.^[13] However, in this case 4 equivalents of Me₃SnCl are generated as a side product of the assembly of the 9,10-dihydro-9,10-diboraanthracene scaffold with BCl₃. Me₃SnCl is not only toxic but also difficult to remove quantitatively from the resulting 9,10-dichloro-9,10-dihydro-9,10-diboraanthracene intermediate.

The synthesis protocols for **1** reviewed thus far demonstrate that substantial efforts have already been spent on optimizing the reagents and the reaction conditions. However, in the case of the Grignard approaches, only one study is known which focuses on the arguably most influential parameter, i.e., the activity of the magnesium employed: Wegner et al. applied the diisobutylaluminum hydride (DIBAL-H) activation procedure^[14] to magnesium powder and showed that a subsequent Grignard reaction with Me₃SiCl in THF provided **1** in 37% yield (reflux, 45 min).^[15] They have also shown that a catalytic amount of anhydrous FeCl₃ (3 mol%)^[16] allows one to conduct the silylation at –10 °C (1 day; yield of **1**: 41%) and thereby to prepare a number of alkyl-, alkoxy- or fluorine-substituted 1,2-bis(trimethylsilyl)benzenes.

Herein, we will show that the reaction time of the iron-catalyzed approach and the associated yield of **1** can be improved further by using (i) Rieke-Mg (Mg^R)^[17] or (ii) Mg turnings in the presence of 1,2-dibromoethane as an entrainer for continuous activation (Mg^e;^[18] Table 1). Both protocols also provide convenient high-yield routes to 1,2,4,5-tetrakis(trimethylsilyl)benzene and first time access to 4-fluoro-1,2-bis(trimethylsilyl)benzene, 4-chloro-1,2-bis(trimethylsilyl)benzene as well as 4,5-dichloro-1,2-bis(trimethylsilyl)benzene. Especially the latter two compounds are relevant, because they offer the possibility of extensive functionalization *via* transition metal-mediated C–C coupling reactions.^[19] In those cases where the substitution pattern on the phenylene ring is not

an issue (e.g., numerous applications of **B**; Scheme 1), the readily available 1,2-dibromo-4,5-dimethylbenzene^[20] could be an economically attractive alternative to the parent 1,2-dibromobenzene as a starting material. Thus, we also investigated the reaction between Mg^R/Mg^e , Me_3SiCl , and 1,2-dibromo-4,5-dimethylbenzene.

Results and Discussion

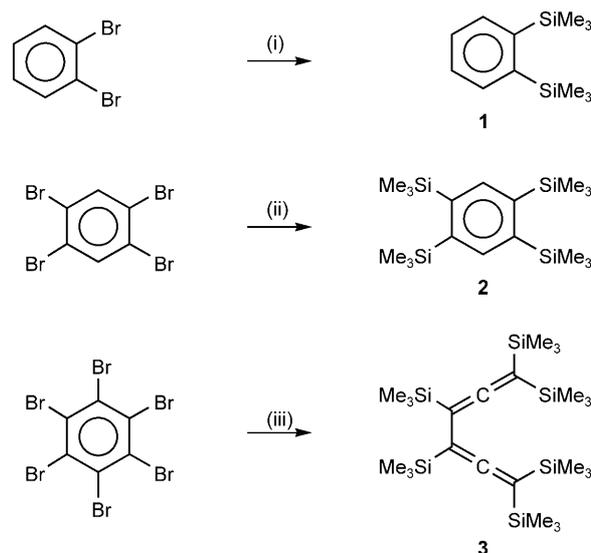
The slurry of Mg^R in THF used in our investigations was prepared from $MgCl_2$ and 1.5 equivalents of **K**; excess $MgCl_2$ as well as the generated **KCl** were not removed (*cf.* the Experimental Section). In a previous report, the presence of **KI** in the Mg^R -forming step has been described to produce a particularly reactive metal powder.^[21] For the synthesis of the compounds discussed here, such a beneficial effect could not be confirmed.

In the entrainment approach, continuous activation at room temperature was achieved by dropwise addition of 1,2-dibromoethane to a mixture of **Mg** turnings, the respective 1,2-dibromobenzene derivative, and excess Me_3SiCl in THF. An amount of 0.2–0.8 equivalents of the entrainer was sufficient for quantitative conversion. In contrast to the Rieke-**Mg** protocol, which requires carefully dried solvent and the strict maintenance of inert conditions, the THF (*p.a.* grade) employed in the entrainment method was used as received from the commercial supplier and the glassware was just briefly flushed with N_2 .

The reaction of Mg^R/Mg^e with 1,2-dibromobenzene and excess Me_3SiCl in THF at 0°C/20°C gave 1,2-bis(trimethylsilyl)benzene (**1**) in 65%/62% yield (Scheme 2; Table 1).^[22] In terms of solvent toxicity as well as the required reaction temperatures and times, both protocols offer major advantages over the established method^[9] while comparable product yields are achieved (Table 1).

When applied to 1,2,4,5-tetrabromobenzene, both procedures also work faithfully for the preparation of 1,2,4,5-tetrakis(trimethylsilyl)benzene (**2**; Scheme 2), a versatile building block for linear polycyclic aromatic compounds.^[23,24] The obtained yields of **2** (Mg^R : 80%, Mg^e : 54%; Table 1) are substantially higher than the yields of alternative synthesis methods ($Mg/1,2,4,5-Br_4C_6H_2/Me_3SiCl/THF$, reflux, 2 days: 20%;^[25] $Mg/1,2,4,5-Cl_4C_6H_2/Me_3SiCl/HMPA-THF$, 100°C, 2 days: 49%;^[23,24,26] $Mg/1,2,4,5-Br_4C_6H_2/Me_3SiCl/DIBAL-H, TMEDA, FeCl_3/THF$, –10°C to 0°C, 1 day: 38%^[15]).

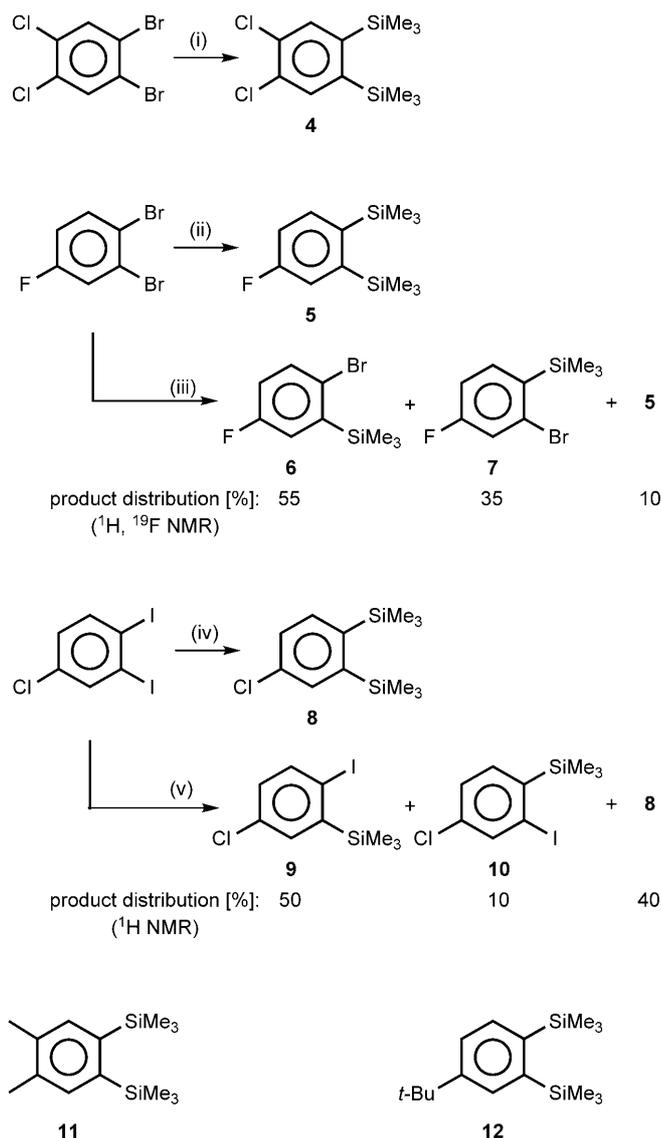
Encouraged by these positive results, we next tested whether the use of Mg^R also provides a route for the six-fold silylation of hexabromobenzene with Me_3SiCl .^[27] The target compound, hexakis(trimethylsilyl)benzene, has already been described by Sakurai



Scheme 2. Synthesis of the 1,2-bis(trimethylsilyl)benzenes **1** and **2** in THF; reaction of hexabromobenzene with Me_3SiCl and Mg^R in THF. (i) Mg^R : +5 Me_3SiCl , +2.5 Mg^R , 0°C, 1.5 h, 65%; Mg^e : +8 Me_3SiCl , +3 **Mg**, +0.2 1,2- $C_2H_4Br_2$, room temperature, 30 min, 62%. (ii) Mg^R : +11 Me_3SiCl , +9 Mg^R , 0°C→room temperature, 3.5 h, 80%; Mg^e : +12 Me_3SiCl , +8 **Mg**, +1.5 1,2- $C_2H_4Br_2$, room temperature, 2 h, 54%. (iii) Mg^R : +30 Me_3SiCl , +15 Mg^R , 0°C→room temperature, 1.5 h; **3** could be detected as one of several components in the product mixture.

et al., who started from hexabromobenzene and developed a three-step synthesis sequence *via* hexakis(dimethylsilyl)benzene.^[28] Previous attempts of Gilman et al. at the direct trimethylsilylation of hexabromobenzene ($Mg/Me_3SiCl/THF$, reflux, 12 h) have failed.^[29,30] The only well-defined product that could be isolated in small amounts from the reaction mixtures, was 1,1,3,4,6,6-hexakis(trimethylsilyl)-1,2,4,5-hexatetraene (**3**; Scheme 2).^[29,30] Since hexakis(trimethylsilyl)benzene is known to undergo a rearrangement reaction to afford **3** upon thermal treatment,^[28] we reckoned that the lower reaction temperature required for the Rieke-**Mg** protocols might offer an opportunity to prepare hexakis(trimethylsilyl)benzene in one step. However, the reaction with Mg^R took a similar course as the Gilman experiments and **3** was obtained as one of several products (Scheme 2).

Apart from the parent 1,2-bis(trimethylsilyl)benzene (**1**), the halogenated derivatives **4**, **5**, and **8** were also readily prepared from the corresponding 1,2-dibromo- and 1,2-diiodobenzenes (Scheme 3; Table 1). The use of 1,2-dibromo-4-chlorobenzene in the synthesis of **8** with Mg^R led to an undesired partial $Cl/SiMe_3$ exchange even though the reaction temperature was lowered to –40°C. This problem was solved by using 4-chloro-1,2-diiodobenzene instead. With the Mg^e method, we were surprised to find that 4-chloro-1,2-diiodobenzene turned out to be far less reactive



Scheme 3. Synthesis of the halogenated 1,2-bis(trimethylsilyl)benzenes **4**, **5**, and **8** in THF; product distribution of the corresponding reactions with 1.1 equivalents of Mg^{R} in THF; drawings of **11** and **12**. (i) Mg^{R} : $+10\text{Me}_3\text{SiCl}$, $+3\text{Mg}^{\text{R}}$, $-40^\circ\text{C}\rightarrow\text{room temperature}$, 2 h, 70%; Mg^{c} : $+8\text{Me}_3\text{SiCl}$, $+4\text{Mg}$, $+0.41,2\text{-C}_2\text{H}_4\text{Br}_2$, room temperature, 45 min, 67%. (ii) Mg^{R} : $+7\text{Me}_3\text{SiCl}$, $+3\text{Mg}^{\text{R}}$, room temperature $\rightarrow 40^\circ\text{C}$, 1 h, 53%; Mg^{c} : $+8\text{Me}_3\text{SiCl}$, $+4\text{Mg}$, $+0.41,2\text{-C}_2\text{H}_4\text{Br}_2$, room temperature, 45 min, 56%. (iii) Mg^{R} : $+5\text{Me}_3\text{SiCl}$, $+1.1\text{Mg}^{\text{R}}$, room temperature $\rightarrow 40^\circ\text{C}$, 1 h. (iv) Mg^{R} : $+9\text{Me}_3\text{SiCl}$, $+2.5\text{Mg}^{\text{R}}$, $-40^\circ\text{C}\rightarrow\text{room temperature}$, 2 h, 60%; Mg^{c} : $+10\text{Me}_3\text{SiCl}$, $+15\text{Mg}$, $+101,2\text{-C}_2\text{H}_4\text{Br}_2$, room temperature, 4 h, 70%. (v) Mg^{R} : $+5\text{Me}_3\text{SiCl}$, $+1.1\text{Mg}^{\text{R}}$, $-40^\circ\text{C}\rightarrow\text{room temperature}$, 2.5 h.

than 1,2-dibromo-4-chlorobenzene, requiring 15 equivalents of Mg and 10 equivalents of entrainer for full conversion. At the same time, the chemoselectivity of the halogen/ SiMe_3 exchange was comparable to that of 1,2-dibromo-4-chlorobenzene. Attempts at the synthesis of 4-bromo-1,2-bis(trimethylsilyl)ben-

zene starting from 4-bromo-1,2-diiodobenzene and Mg^{R} failed due to pronounced Br/ SiMe_3 exchange.

In summary, selectivity was not an issue in the case of the transformations 1,2-dibromo-4,5-dichlorobenzene \rightarrow **4** (Mg^{R} , Mg^{c}), 1,2-dibromo-4-fluorobenzene \rightarrow **5** (Mg^{R} , Mg^{c}), and 4-chloro-1,2-diiodobenzene \rightarrow **8** (Mg^{R}).

Compounds **4**, **5**, and **8** have been characterized by (heteronuclear) NMR spectroscopy and combustion analysis (*cf.* the Supporting Information). Moreover, in the case of **4** an X-ray crystal structure analysis was performed (Figure 1). Considerable steric strain within this molecule can be inferred from the elongated $\text{Si}-\text{C}_{\text{ipso}}$ distances, which possess an even larger value [$1.907(5)\text{ \AA}$] than the average $\text{Si}-\text{CH}_3$ bond length [$1.872(6)\text{ \AA}$]. Moreover, the $\text{Si}(1)-\text{C}(1)-\text{C}(2)$ and $\text{Si}(2)-\text{C}(2)-\text{C}(1)$ bond angles are expanded to $126.7(4)^\circ$ and $129.2(4)^\circ$, respectively, and the torsion angle $\text{Si}(1)-\text{C}(1)-\text{C}(2)-\text{Si}(2)$ of $-10.4(8)^\circ$ deviates from the ideal value of 0° .

In order to find out whether the behavior of the bromo (iodo) substituent in the *para* position to the fluorine (chlorine) atom is different from the one in the *meta* position, we repeated the reaction of 1,2-dibromo-4-fluorobenzene (4-chloro-1,2-diiodobenzene) with only 1.1 equivalents of Mg. In this case, only the Rieke-Mg approach was applied, because it allows easy control of the actual amount of active metal even on a very small scale (Scheme 3). About one-quarter (one-half) of the organic starting material remained unreacted. Consequently, significant amounts of the halogenated 1,2-bis(trimethylsilyl)benzene **5**

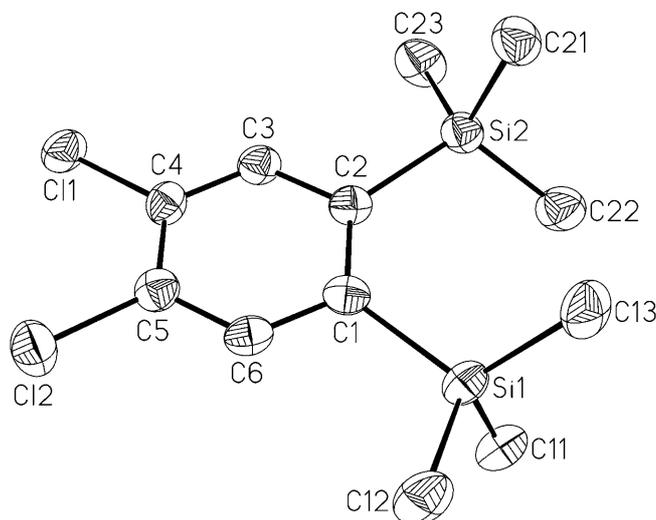


Figure 1. Molecular structure and numbering scheme of compound **4**. Displacement ellipsoids are drawn at the 50% probability level. H-atoms have been omitted for clarity. Selected bond lengths (\AA), bond angles (deg), and torsion angle (deg): $\text{Si}(1)-\text{C}(1)=1.908(5)$, $\text{Si}(2)-\text{C}(2)=1.905(5)$; $\text{Si}(1)-\text{C}(1)-\text{C}(2)=126.7(4)$, $\text{Si}(2)-\text{C}(2)-\text{C}(1)=129.2(4)$; $\text{Si}(1)-\text{C}(1)-\text{C}(2)-\text{Si}(2)=-10.4(8)$.

(8) were formed in both cases; the product distribution of both reactions was determined by NMR spectroscopy and is shown in Scheme 3. Compared to 4-chloro-1,2-diiodobenzene, 1,2-dibromo-4-fluorobenzene thus shows (i) a higher degree of overall conversion, (ii) a lower degree of 1,2-disilylation, and (iii) a considerably lower selectivity between the two monosilylated isomers.

The assignment of the structures **6** and **9** to the major monosilylated isomers is based on ^1H - ^1H -COSY, ^1H - ^1H -ROESY, and ^1H - ^{29}Si -HETCOR NMR experiments and will be explained for 1-bromo-4-fluoro-2-trimethylsilylbenzene/2-bromo-4-fluoro-1-trimethylsilylbenzene (**6/7**), but similar arguments apply to **9/10** (for plots of the spectra see the Supporting Information). Both isomers **6/7** give rise to three signals in the aromatic region of the ^1H NMR spectrum. The major isomer shows: (i) one multiplet at 6.90 ppm, (ii) one doublet of doublets at 7.13 ppm, and (iii) one doublet of doublets at 7.47 ppm. Values of $^3J_{\text{FH}} = 8.6$ Hz and $^4J_{\text{FH}} = 4.8$ Hz are evident from the major ^{19}F NMR signal. Since a $^4J_{\text{HF}} = 4.8$ Hz coupling only appears in the 7.47 ppm ^1H NMR resonance, we assign this signal to the H-6 proton. The ^1H - ^1H -COSY spectrum, in turn, allows us to assign the 6.90 ppm and the 7.13 ppm resonances to H-5 and H-3, respectively. The H-3 signal shows a cross peak to the major SiMe_3 resonance in the ^1H - ^1H -ROESY and in the ^1H - ^{29}Si -HETCOR NMR spectrum. We therefore conclude that the SiMe_3 group of the major isomer occupies the 2-position of the benzene ring (*cf.* **6**). Consistent with that, the SiMe_3 resonance of the minor isomer **7** shows cross-peaks exclusively to the signal of the H-6 proton.

1,2-Dibromo-4,5-dimethylbenzene reacts with Me_3SiCl and Mg^{R} at room temperature in THF to give 1,2-bis(trimethylsilyl)-4,5-dimethylbenzene (**11**; Scheme 3) in amounts of 10%–40%. The following features of this transformation are remarkable: (i) The yields of **11** are low, even though the related compound 1,2,4,5-tetrakis(trimethylsilyl)benzene is formed in 80% yield under similar reaction conditions. (ii) The yields of **11** suffer from poor reproducibility, which is most likely due to different and hard-to-control surface structures of the Mg^{R} employed (this is not an issue in the cases discussed before). (iii) We do not observe major by-products, but after a period of clean formation of **11**, the reaction comes to a halt. Application of the Rieke-Mg protocol to 1,2-dibromo-4-*tert*-butylbenzene did not lead to the target compound **11**, even at elevated temperatures.

The entrainment method, in contrast, results in a quantitative consumption of 1,2-dibromo-4,5-dimethylbenzene as well as 1,2-dibromo-4-*tert*-butylbenzene already at room temperature. In both cases, complex product mixtures are formed, the major constituents being **11** (<10%)/2,3,6,7-tetramethylbiphe-

nylene (5%) and 4-*tert*-butyl-1,2-bis(trimethylsilyl)benzene (**12**; <10%)/di-*tert*-butylbiphenylenes (5%), respectively (Scheme 3; Table 1).

Conclusions

1,2-Bis(trimethylsilyl)benzene and 1,2,4,5-tetrakis(trimethylsilyl)benzene have been conveniently prepared from the corresponding bromobenzenes and Me_3SiCl in Grignard-type reactions, i.e., *via* the Rieke-Mg method (Mg^{R}) and the entrainment method (Mg^{e} ; entrainer: 1,2-dibromoethane). One important improvement with respect to the currently best-established synthesis protocol for 1,2-bis(trimethylsilyl)benzene lies in the fact that the syntheses can be carried out in THF rather than in the cancerogenic solvent HMPA. Moreover, the reactions readily proceed at room temperature or below, as opposed to 100 °C in the HMPA method, and the reaction times are reduced from 2 days to 1.5 hours (Mg^{R}) to 30 minutes (Mg^{e}). The yields obtained are comparable for all three protocols. We are aware that bromobenzenes are more costly than the chlorobenzenes employed in the HMPA route, however, this argument is more than outweighed by the gain in safety and time efficiency.

As a result of the milder reaction conditions, functionalized 1,2-bis(trimethylsilyl)benzenes bearing fluoro or chloro substituents at their aromatic rings are also accessible with high selectivity and yields. Thus, a broad application of these 1,2-bis(trimethylsilyl)benzene derivatives in the field of benzyne chemistry, organic optoelectronic materials and catalysis can be envisaged.

Experimental Section

General Remarks

All reactions using Mg^{R} were carried out under a nitrogen atmosphere using Schlenk techniques and carefully dried solvents. Me_3SiCl was stored over CaH_2 and transferred by pipette into the reaction flask or dropping funnel. All reactions using Mg^{e} were carried out in glassware that had been briefly flushed with N_2 . THF (*p.a.* grade, stabilized with 0.025% BHT) was purchased from *Acros Organics* (Geel, Belgium) and stored over KOH. Me_3SiCl was obtained from *Apollo Scientific Ltd.* (Stockport, UK) and used as received. 1,2-Dibromo-4,5-dichlorobenzene,^[31] 4-chloro-1,2-diiodobenzene,^[32] and 4-bromo-1,2-diiodobenzene^[32] were synthesized according to literature procedures.

Preparation of Rieke-Magnesium (Mg^{R})

In a representative procedure, a stirred mixture of THF (800 mL), potassium (36.5 g, 934 mmol), and anhydrous MgCl_2 (61.0 g, 641 mmol) was carefully heated to reflux for

3 h. The resulting dark salt-containing Mg^R slurry was directly used for further transformations.

Synthesis of 1,2-Bis(trimethylsilyl)benzene (**1**) via Mg^R

A mixture of 1,2-dibromobenzene (24.5 mL, 48.0 g, 203 mmol), Me₃SiCl (135.0 mL, 115.6 g, 1064 mmol), and THF (150 mL) was added dropwise at 0°C over 1 h to a freshly prepared stirred suspension of Mg^R in THF (800 mL, 0.584 M, 467 mmol). The slurry was stirred for further 30 min at 0°C and then carefully quenched under nitrogen with a saturated aqueous solution of NaHCO₃ (300 mL). The formation of two phases was observed, which were separated with a separation funnel. The aqueous phase was extracted with hexane (5×40 mL), the THF phase and the extracts were combined, washed with water (5×40 mL), dried over anhydrous MgSO₄, and filtered. All volatiles were removed from the filtrate under vacuum to obtain a mixture of **1** (70%; NMR spectroscopic control) and PhSiMe₃ (30%) as a pale orange oil. Product **1** was isolated as a colorless liquid by fractional distillation under reduced pressure (60–65°C, 10⁻² Torr); yield: 23.53 g (52%). **Note:** The overall yield can be increased to approx. 65% when the combined forerunnings of several distillations are redistilled.

Synthesis of 1,2-Bis(trimethylsilyl)benzene (**1**) via Mg^e

Mg turnings (3.03 g, 125 mmol) were covered with THF (100 mL) and treated with neat Me₃SiCl (42.2 mL, 36.1 g, 332 mmol) and 1,2-dibromobenzene (5.00 mL, 9.78 g, 41.5 mmol). A temperature of approximately 20°C was maintained by means of a water bath throughout the reaction time, because otherwise the mixture warms perceptibly after an induction period of about 5 min. A solution of 1,2-dibromoethane (0.716 mL, 1.56 g, 8.30 mmol) in THF (10 mL) was added dropwise to the vigorously stirred slurry over 30 min. All volatiles were removed under vacuum and the remaining solid residue was treated at 0°C with hexane (60 mL) and water (60 mL). The two phases were separated and the aqueous phase was extracted with hexane (2×20 mL). The combined organic layers were washed with water (4×20 mL), dried over anhydrous MgSO₄, filtered, and all volatiles were removed from the filtrate under vacuum. The remaining orange oil was fractionally distilled under reduced pressure (60–65°C, 10⁻² Torr) to afford **1** as a colorless oil; yield: 5.69 g (62%).

¹H and ¹³C{¹H} NMR data were in accord with published values.^[10]

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