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^e). 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^e: 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 highyield synthesis of 1,2,4,5-tetrakis(trimethylsilyl)ben-4-fluoro-1,2-bis(trimethylsilyl)benzene, zene, 4chloro-1,2-bis(trimethylsilyl)benzene, and 4,5-dichloro-1,2-bis(trimethylsilyl)benzene.

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

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 halides 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*. Refs.^[8]

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-

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

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

^[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 cancerogenic 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 tertbutyllithium 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/ $Me_2(H)SiCl$ in THF.^[12] For the synthesis of **B**, the silvl derivative 1 could, in principle, be replaced by 1,2bis(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 diisobutylaluminium 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 silvlation 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(trime-thylsilyl)benzene and first time access to 4-fluoro-1,2-bis(trimethylsilyl)benzene, 4-chloro-1,2-bis(trimethyl-silyl)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, Me₃SiCl, 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 Me₃SiCl 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 N₂.

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-Br₄C₆H₂/Me₃SiCl/THF, reflux, 2 days: 20%;^[25] Mg/1,2,4,5-Cl₄C₆H₂/Me₃SiCl/HMPA-THF, 100 °C, 2 days: 49%;^[23,24,26] Mg/1,2,4,5-Br₄C₆H₂/Me₃SiCl/DIBAL-H, TMEDA, FeCl₃/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 Me₃SiCl.^[27] The target compound, hexakis(trimethyl-silyl)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 Me₃SiCl and Mg^R in THF. (i) Mg^R: +5Me₃SiCl, +2.5Mg^R, 0°C, 1.5 h, 65%; Mg^e: +8Me₃SiCl, +3Mg, +0.21,2-C₂H₄Br₂, room temperature, 30 min, 62%. (ii) Mg^R: +11Me₃SiCl, +9Mg^R, 0°C→room temperature, 3.5 h, 80%; Mg^e: +12Me₃SiCl, +8Mg, +1.51,2-C₂H₄Br₂, room temperature, 2 h, 54%. (iii) Mg^R: +30Me₃SiCl, +15Mg^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/Me₃SiCl/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)-1,2,4,5hexatetraene (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/ SiMe₃ 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



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product distribution [%]: 50

(¹H NMR)

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} : +10Me₃SiCl, +3Mg^R, -40 °C \rightarrow room temperature, 2 h, 70%; Mg^e: +8Me₃SiCl, +4Mg, +0.41,2-C₂H₄Br₂, room temperature, 45 min, 67%. (ii) Mg^R: +7Me₃SiCl, +3Mg^R, room temperature \rightarrow 40°C, 1 h, 53%; Mg^e: +8Me₃SiCl, +4Mg, +0.41, 2-C₂H₄Br₂, room temperature, 45 min, 56%. (iii) Mg^{R} : +5 Me₃SiCl, +1.1 Mg^{R} room temperature $\rightarrow 40$ °C, 1 h. (iv) Mg^R: +9 Me₃SiCl, $+2.5 \text{ Mg}^{\text{R}}$, $-40 \,^{\circ}\text{C} \rightarrow \text{room}$ temperature, 2 h, 60%; Mg^e: +10Me₃SiCl, +15Mg, +101,2-C₂H₄Br₂, room temperature, 4 h, 70%. (v) Mg^R: +5 Me₃SiCl, +1.1 Mg^R, -40 °C \rightarrow room temperature, 2.5 h.

1,2-dibromo-4-chlorobenzene, than requiring 15 equivalents of Mg and 10 equivalents of entrainer for full conversion. At the same time, the chemoselectivity of the halogen/SiMe₃ exchange was comparable to that of 1,2-dibromo-4-chlorobenzene. Attempts at the synthesis of 4-bromo-1,2-bis(trimethylsilyl)benzene starting from 4-bromo-1,2-diiodobenzene and Mg^R failed due to pronounced Br/SiMe₃ 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^e), 1,2-dibromo-4-fluorobenzene \rightarrow 5 (Mg^{R}, Mg^{e}) , 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 Si-C_{ipso} distances, which possess an even larger value [1.907(5) Å] than the average Si-CH₃ bond length [1.872(6) Å]. Moreover, the Si(1)–C(1)–C(2) and Si(2)-C(2)-C(1) bond angles are expanded to 126.7(4)° and 129.2(4)°, respectively, and the torsion angle Si(1)-C(1)-C(2)-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 onequarter (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 (Å), bond angles (deg), and torsion angle (deg): Si(1)-C(1)=1.908(5), Si(2)-C(2)=1.905(5); Si(1)-C(1)-C(2) = 126.7(4),Si(2)-C(2)-C(1) = 129.2(4);Si(1)-C(1)-C(2)-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 4chloro-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-²⁹Si-HETCOR NMR experiments and will be explained for 1-bromo-4fluoro-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 ${}^{3}J_{\rm F,H} =$ 8.6 Hz and ${}^{4}J_{\rm F,H} =$ 4.8 Hz are evident from the major ¹⁹F NMR signal. Since a ${}^{4}J_{\rm H,F}$ = 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 SiMe₃ resonance in the ¹H-¹H-ROESY and in the ¹H-²⁹Si-HETCOR NMR spectrum. We therefore conclude that the SiMe₃ group of the major isomer occupies the 2-position of the benzene ring (cf. 6). Consistent with that, the SiMe₃ resonance of the minor isomer 7 shows cross-peaks exclusively to the signal of the H-6 proton.

1,2-Dibromo-4,5-dimethylbenzene with reacts Me₃SiCl 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 hardto-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 1,2dibromo-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-dime-thylbenzene 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 Me₃SiCl 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. Me₃SiCl was stored over CaH₂ 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 N₂. THF (*p.a.* grade, stabilized with 0.025% BHT) was purchased from *Acros Organics* (Geel, Belgium) and stored over KOH. Me₃SiCl 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 $(5 \times 40 \text{ mL})$, 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 1,2dibromoethane (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 $(2 \times$ 20 mL). The combined organic layers were washed with water $(4 \times 20 \text{ mL})$, 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]

Supporting Information

Synthesis details and NMR spectroscopic characterization of 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12, ¹H NMR spectrum of the crude product 1 (Mg^e), ¹H-¹H-COSY, ¹H-¹H-ROESY, and ¹H-²⁹Si-HETCOR NMR spectra of product mixtures obtained in the experiments with substoichiometric amounts of Mg^R as well as details of the X-ray crystal structure analyses and key crystallographic data of 4-chloro-1,2-diiodobenzene, 4-bromo-1,2-diiodobenzene, and 4 are available in the Supporting Information.

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