Supplementary Information for

High-yielding and Facile Synthesis of Organosilicon Compounds containing m-Carboranylmethyl Group

Xiao-Jie Han, Hua-Feng Fei, Bo-Zheng Liu, Yong-Xia Tan, Xue-Zhong Zhang, Ze-Min Xie, and Zhi-Jie Zhang*

Laboratory of Advanced Polymer Materials, Institute of Chemistry Chinese Academy of Sciences Zhongguancun North First Street 2,100190 Beijing (China)

College of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, No.19A Yuquan Road, Beijing 100049 (China)

Table of contents

1. General..........................................................................................................................S2
2. Experimental section .....................................................................................................S3
3. references ......................................................................................................................S7
4. NMR Spectra ...............................................................................................................S8
1. General

All moisture sensitive reactions were carried out in flame-dried glassware under nitrogen atmosphere. The solvents used were purified by distillation over the drying agents indicated and were transferred under nitrogen: Et₂O (Na), THF (Na), THP (Na), CH₂Cl₂ (CaH₂). All reactions were monitored by thin-layer chromatography (TLC) on gel F₂54 plates using UV light as visualizing agent (if applicable), and a solution of Palladium chloride (0.01 g/L) in 5% aqueous hydrochloric acid (followed by heating as developing agents).

¹H NMR and ¹³C NMR were recorded in CDCl₃ solution on a AVANCE 400 spectrometer, ²⁹Si NMR and ¹¹B NMR spectra were recorded in CDCl₃ solution on a Bruker AVIII 500WB respectively. Chemical shifts were denoted in ppm (δ), and calibrated by using residual undeuterated solvent (CHCl₃ (7.26 ppm), DMSO-d₅ (2.50 ppm)) as internal reference for ¹H NMR and the deuterated solvent (CDCl₃ (77.00 ppm) or DMSO-d₆ (39.51 ppm)) ¹³C NMR, to external BF₃·OEt₂ (0.00 ppm) for boron chemical shifts and to external Si(Me)₄ for silicon chemical shifts. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, br = broad, m = multiplet. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker ApexII mass spectrometer by means of the FAB technique or Waters GCT by means of the EI technique or Bruker solariX XR by means of the ESI technique. IR spectra were recorded on a Bruker TENSOR-27 FT-IR spectrometer. The X-ray single-crystal determination was performed on a Rigaku RAXIS RAPID IP X-ray single crystal diffractometer. GC was carried out on a SHIMADZU GC-2010. Melting point was afforded by EXSTAR6000 DSC6220.

Compounds (chloromethyl)(4-methoxyphenyl)dimethylsilane and (chloromethyl)dimethyl(phenyl)dimethylsilane were prepared according to literature method. All other chemicals were purchased from Beijing J&K Scientific.
2. Experimental section

2.1 Preparation of 1,7-bis(phenyl(dimethyl)silylmethyl)-m-carborane 1

To a solution of n-BuLi (2.5 M solution in n-hexane, 4.4 mL, 11 mmol) in dry solvent* (10 mL) was added a solution of m-carborane (0.72 g, 5 mmol) in solvent (10 mL). The mixture was stirred at room temperature under nitrogen for 6 h. Following (chloromethyl)dimethyl(phenyl)silane (2.03 g, 11 mmol) was added in one portion, the mixture was refluxed for 10 h. The reaction was quenched with water and the mixture was extracted with ether, the combined extracts were washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure, and the yields were identified by GC.

*Solvent: THF, DE, Dioxane, DME, PhOMe, THP.

![Scheme 1: Preparation of 1,7-bis(phenyl(dimethyl)silylmethyl)-m-carborane 1](image)

2.2 Preparation of 1,7-bis(4-methoxyphenyl(dimethyl)silylmethyl)-m-carborane 3

To a solution of n-BuLi (2.5 M solution in n-hexane, 8.8 mL, 22 mmol) in dry THP (20 mL) was added a solution of m-carborane (1.44 g, 10 mmol) in THP (20 mL). The mixture was vigorously stirred at room temperature under nitrogen atmosphere for 1 h (screen was listed in Table S2). Following (chloromethyl)(4-methoxyphenyl)dimethylsilane (4.40 g, 20.5 mmol) was added in one portion, the mixture was refluxed for 10 h. The reaction was quenched with water and the mixture was extracted with ether. The combined extracts were washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure, and the residue was purified by recrystallization (from n-hexane) to afford white solid 1,7-bis(4-methoxyphenyl(dimethyl)silylmethyl)-m-carborane 3 (2.50 g, 50% isolated yield).

To the solution of the crude product after recrystallization dissolved in dry THP (20 mL) was added a solution of n-BuLi (2.5 M solution in n-hexane, 1 mL, 2.5 mmol). The mixture was vigorously stirred at room temperature under nitrogen atmosphere for 1 h. Following (chloromethyl)(4-methoxyphenyl)dimethylsilane (0.54 g, 2.5 mmol) was added in one portion. After refluxing for 10 h, the reaction was quenched with water and the mixture was extracted with ether. The combined extracts were washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure, and the residue was purified by recrystallization (from n-hexane) to afford 3 2.1 g. The overall yield of 3 was 88%.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.42-7.40 (d, J=8Hz, 2H, C6H4), 6.96-6.94 (d, J=8Hz, 2H), 3.85 (s, 6H), 3.5-1.3 (br, 10H), 1.67 (s, 4H), 0.36 ppm (s, 12H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ 74.2, 25.3, -3.8 ppm. $^{29}$Si NMR (500MHz, CDCl$_3$): -4.52 ppm. $^{11}$B NMR (500 MHz, CDCl$_3$): δ -7.05, -10.03, -10.76 ppm. IR: ν =2608, 1595, 1502, 1278, 1250, 1112, 1029, 829, cm$^{-1}$. HRMS (FAB): m/z calcd for C$_{22}$H$_{40}$B$_2$Si$_2$O$_2$ [M+1$^+$]: 500.3556. Found: 500.3578. Mp 78.9°C.
2.3 Preparation of 1,7-bis(hydroxy(dimethyl)silyl)methyl)-m-carborane 6

To a solution of 3 (1 g, 2 mmol) in dry CH₂Cl₂ (30 mL) was added dropwise a solution of bromine (0.8 g, 5 mmol) in dry CH₂Cl₂ (30 mL) (10 mL). The reaction mixture was stirred at 0 °C for 30 min; then warmed to room temperature for 10 h. Intermediate 5 was obtained after removing CH₂Cl₂ under reduced pressure. Subsequently, the obtained orange oily liquid 5 was dissolved in anhydrous ether (20 mL) under nitrogen atmosphere. After that, the orange solution was injected to a solution of H₂O (0.144 mL, 8 mmol) and Et₃N (2.8 mL, 20 mmol) in ether (100 mL) by nitrogen through double-tipped needle at -15 °C with vigorous stirring. At the moment, mass of white solid was precipitated immediately. Following the mixture was stirred for another 10 min and filtrated, the filtrate was condensed and recrystallized to afford the expected hydrolysed product 1,7-bis(hydroxy(dimethyl)silyl)methyl)-m-carborane 6 (0.64 g, quantitative) as white solid.

5: ²⁹Si NMR (300MHz, CH₂Cl₂): 21.36 ppm.

6: ¹H NMR (400 MHz, D₆-DMSO): δ 5.62 (s, 2H), 3.75-1.25 (br, 10H), 1.51 (s, 4H), 0.10 ppm (s, 12H). ¹³C NMR (400 MHz, CDCl₃): δ 74.0, 28.7, -0.9 ppm. ²⁹Si NMR (500MHz, CDCl₃): 9.51 ppm. ¹¹B NMR (500 MHz, CDCl₃): δ -1.06, -2.03, -3.97, -5.00, -5.93, -6.40ppm. IR: ν =3331, 2605, 1259, 1216, 1026, 871, 837, 779 cm⁻¹. HRMS (ESI): m/z calcd for C₈H₂₈B₁₀O₂Si₂ [M+Na]+: 343.2529. Found: 343.2532. Mp 133.5 °C.

* 5 was very sensitive to moisture, ¹H and ¹³C NMR were afforded with difficulty.

Scheme 3: Preparation of 1,7-bis(hydroxy(dimethyl)silyl)methyl)-m-carborane 6

double tipped needle

Fig. 1: The sketch of hydrolysis 5
2.4 Preparation of 1,7-bis(dimethylsilylmethyl)-m-carborane 7

To a solution of 3 (1 g, 2 mmol) in dry CH₂Cl₂ (30 mL) was added dropwise a solution of bromine (0.8 g, 5 mmol) in dry CH₂Cl₂ (10 mL). The reaction mixture was stirred at 0 °C for 30 min; then warmed to room temperature for 10 h. Intermediate 5 was obtained after removing CH₂Cl₂ under reduced pressure. Subsequently, the obtained orange oily liquid 5 was dissolved in THF (20 mL) under nitrogen atmosphere. The LiAlH₄ (2.4 M solution in THF, 2 mL, 4.8 mmol) was dropped to the orange solution at 0 °C with vigorous stirring. Following the mixture was stirred for another 10 min, the reaction was quenched by dropwise adding HCl (0.5 M, 20 mL). The mixture was extracted with Et₂O and the combined extract was condensed under reduced pressure, the orange residue was purified by filtration with column chromatography. The expected reduction product 1,7-bis(dimethylsilylmethyl)-m-carborane 7 (0.57 g, quantitative) was afforded as colourless liquid.

1H NMR (400 MHz, CDCl₃): δ 3.99-3.90 (m, 2H), 3.50-1.20 (br, 10H), 1.52-1.51 (d, J=4Hz, 4H), 0.13-0.12 ppm (d, J=4Hz, 12H).

13C NMR (400 MHz, CDCl₃): δ 74.2, 25.4, -3.8 ppm.

29Si NMR (500MHz, CDCl₃): -14.54 ppm.

11B NMR (500 MHz, CDCl₃): δ -6.29, -7.26, -9.31, -9.86, -10.31, -10.77, -12.06 ppm. IR: ν =2959, 2597, 2138, 1254, 1027, 884, 841, 742 cm⁻¹.


Scheme 4: Preparation of 1,7-bis(dimethylsilylmethyl)-m-carborane 7

2.5 Preparation of 1,7-bis(vinyl(dimethyl)silylmethyl)-m-carborane 8

To a solution of 3 (1 g, 2 mmol) in dry CH₂Cl₂ (30 mL) was added dropwise a solution of bromine (0.8 g, 5 mmol) in dry CH₂Cl₂ (10 mL). The reaction mixture was stirred at 0 °C for 30 min; then warmed to room temperature for 10 h. Intermediate 5 was obtained after removing CH₂Cl₂ under reduced pressure. Subsequently, the obtained orange oily liquid 5 was dissolved in THF (20 mL) under nitrogen atmosphere. The BrMgvinyl (1 M solution in THF, 4.2 mL, 4.2 mmol) was dropped to the orange solution at 0 °C with vigorous stirring. Following the mixture was stirred for another 30 min, the reaction was quenched by water. The mixture was extracted with Et₂O and the combined extract was condensed under reduced pressure, the orange residue was purified by filtration with column chromatography. The expected reduction product 1,7-bis(vinyl(dimethyl)silylmethyl)-m-carborane 8 (0.59g, 88%) was afforded as colourless liquid.

1H NMR (300 MHz, CDCl₃): δ 6.20-5.96 (m, 4H), 5.73-5.65 (dd, J=3Hz, 21Hz), 3.50-1.20 (br, 10H),1.54 (s, 4H), 0.16 ppm (s, 12H). 13C NMR (300 MHz, CDCl₃): δ 137.6, 132.6, 74.1, 27.1, -2.6 ppm. 29Si NMR (500MHz, CDCl₃): -6.2 ppm. 11B NMR (500 MHz, CDCl₃): δ -6.01, -6.09, -9.12, -9.66, -10.14, -10.57, -11.72 ppm. IR: ν =2955, 2597, 1405, 1254, 1028, 952, 836, 779 cm⁻¹. HRMS (EI): m/z calcd for C₉H₂₆B₉Si₂ [M-1]⁺: 339.3046. Found: 339.2963. nD²⁵: 1.5218.

Scheme 5: Preparation of 1,7-bis(vinyl(dimethyl)silylmethyl)-m-carborane 8
2.6 Preparation of 1,7-bis(ethynyl(dimethyl)silylmethyl)-m-carborane 9

To a solution of 3 (1 g, 2 mmol) in dry CH$_2$Cl$_2$ (30 mL) was added dropwise a solution of bromine (0.8 g, 5 mmol) in dry CH$_2$Cl$_2$ (10 mL). The reaction mixture was stirred at 0 °C for 30 min; then warmed to room temperature for 10 h. Intermediate 5 was obtained after removing CH$_2$Cl$_2$ under reduced pressure. Subsequently, the obtained orange oily liquid 5 was dissolved in THF (20 mL) under nitrogen atmosphere. The BrMgethynyl (0.5 M solution in THF, 8.4 mL, 4.2 mmol) was dropped to the orange solution at 0 °C with vigorous stirring. Following the mixture was stirred for another 30 min, the reaction was quenched by water. The mixture was extracted with Et$_2$O and the combined extract was condensed under reduced pressure, the orange residue was purified by filtration with column chromatography. The expected reduction product 1,7-bis(ethynyl(dimethyl)silylmethyl)-m-carborane 9 (0.61 g, 91%) was afforded as colourless liquid.

$^1$H NMR (300 MHz, CDCl$_3$): δ 3.50-1.20 (br, 10H), 2.42 (s, 2H), 1.63 (s, 4H), 0.26 ppm (s, 12H). $^{13}$C NMR (300 MHz, CDCl$_3$): δ 94.8, 87.8, 73.5, 26.9, -1.1 ppm. $^{29}$Si NMR (500 MHz, CDCl$_3$): δ -17.51 ppm. $^{11}$B NMR (500 MHz, CDCl$_3$): δ -6.18, -7.15, -9.20, -9.81, -10.20, -10.64, -11.72 ppm. IR: ν = 3287, 2600, 2037, 1257, 1028, 844, 783, 680 cm$^{-1}$. HRMS (EI): m/z calcd for C$_{12}$H$_{28}$B$_{10}$Si$_2$ [M-1]$^+$: 335.2733. Found: 335.2643. n$_D^{25}$: 1.5710

Scheme 6: Preparation of 1,7-bis(ethynyl(dimethyl)silylmethyl)-m-carborane 9
3. references


4. NMR Spectra
H-Si

\[ \text{Si-H} \]

\( 7 \)