Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

New Catalytic Route to Borasiloxanes

Bogdan Marciniec,* Jędrzej Walkowiak

Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, E-mail: marcinb@amu.edu.pl

General methods

^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), $^{29}SiNMR$ (79 MHz) and ^{11}B NMR (96 MHz) spectra were recorded on Varian XL 300 MHz spectrometer in $CDCl_3$ or toluenen-d_8 ($C_6D_5CD_3$) solution. Chemical shifts are reported in (ppm) with reference to the residual solvent (CH_3Cl) peak for ^{1}H,^{13}C, to TMS for ^{29}Si and to BF_3-Et_2O for ^{11}B. Analytical gas chromatographic (GC) analyses were performed on a Varian Star 400CX with a DB-5 fused silica capillary column (30m · 0.15mm) and TCD. Mass spectra of the substrates and products were obtained by GC–MS analysis (VarianSaturn 2100T, equipped with a BD-5 capillary column (30m) and an ion trap detector. Elemental analyses were carried out by Vario EL III. The column chromatography was performed with silica gel 60 (70–230 mesh; Fluka). Toluene was dried by distillation from sodium and hexane from sodium hydride. Liquid substrates were also dried and degassed by bulb to bulb distillation. All the reactions were carried out under dry argon atmosphere.

Comment [J1]: All corrections were made in red colour

Materials

The chemicals were obtained from the following sources: toluene, dodecane, hexane, chlorodimethylphenylsilane were purchased from Fluka; $CDCl_3$ and $C_6D_5CD_3$ from Dr Glaser A.G. Basel., triethylsilanol, tri(*iso*-propyl)silanol, *tert*-butyldimethylsilanol were purchased from Gelest, tris(*tert*-butoxy)silanol and triphenylsilanol from Aldrich. Dimethylphenylsilanol was prepared by hydrolysis of chlorodimethylphenylsilane. 2-vinyl-[1,3,2]-dioxaborolane and 2-vinyl-[1,3,2]-dioxaborinane were synthesized according to the literature procedure with some modifications.[1-2] The ruthenium complexes $[RuHCl(CO)(PCy_3)_2]$ (**I**), $[RuHCl(CO)(PPh_3)_3]$ (**II**), $[Ru(BO_2C_6H_4)Cl(CO)(PCy_3)_2]$ **(III)** were prepared according to literature procedures.[3-6]

Representative experimental procedure for *O*-borylation of silanols by vinylboronates

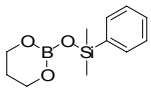
The glass reactor was charged under argon with dry and deoxygenated silanol ($5x10^{-4}$mol), vinylborane ($1x10^{-3}$ – $1.5x10^{-3}$mol), toluene (1mL) and [Ru]-H: [$RuHClCO(PCy_3)_2$] or [$RuHClCO(PPh_3)_3$)] ($5x10^{-6}$-$1x10^{-5}$ mol) and dodecane as an internal standard (5% by volume of all components) under the conditions given in Table 1 and 2. The reactions with 2-vinyl-[1,3,2]-dioxaborolane were carried out in a closed system in 100-130^{o}C in sealed tubes, in any other cases in an open system. Reaction mixture was heated at (60-130^{o}C) for 6–24h. Silanol conversion was determined by GC, and after its disappearance, solvent and excess of borane were removed under vacuum and the crude product was purified by column chromatography (silica gel/hexane) or bulb to bulb distillation giving the corresponding borasiloxane.

Experimental procedure for stoichiometric experiments

In an NMR tube 0.01g of [$Ru(BO_2C_6H_4)Cl(CO)(PCy_3)_2$] ($1.2x10^{-5}$mol) and 0.0024g of dimethyl*tert*-butylsilanol ($1.8x10^{-5}$mol) and toluene-d_8 (0.6mL) were placed under argon. The reaction was carried out in 100^{o}C and the course of the reaction was monitored by ^{1}H NMR.

Spectroscopic data of several borasiloxanes

[1,3,2]-dioxaborinan-2-yl)dimethylphenylsiloxane



^{1}H NMR ($CDCl_3$; δ (ppm)): 0.41 (s, 6H, $Si(C\underline{H}_3)_2Ph$), 1.90 (br, 2H, $BOCH_2C\underline{H}_2CH_2O$), 4.04 (br, $BOC\underline{H}_2CH_2C\underline{H}_2O$) 7.35-7.39 (m, 3H, m,p-$C_6\underline{H}_5$), 7.59-7.62 (m, 2H, o-$C_6\underline{H}_5$)

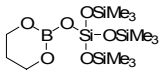
^{13}C NMR ($CDCl_3$; δ (ppm)): -0.03 ($Si(\underline{C}H_3)_2$), 27.1 ($BOCH_2\underline{C}H_2CH_2O$), 62.8 ($BOCH_2\underline{C}H_2CH_2O$), 127.5 ($\underline{C}_6H_5$), 129.2 ($\underline{C}_6H_5$), 133.0 ($\underline{C}_6H_5$), 138.6 ($\underline{C}_6H_5$)

^{11}B NMR ($CDCl_3$, δ (ppm)): 26.9

^{29}Si NMR ($CDCl_3$, δ (ppm)): 2.9

MS (EI) [*m/z* (rel. int. (%))]: 221 ((M^+-15), (100)), 193 (15), 179 (8), 159 (6), 143 (11), 117 (13), 91 (18), 77(8)

[1,3,2]-dioxaborinan-2-yl)tris(trimethylsiloxy)siloxane



^{1}H NMR ($CDCl_3$; δ (ppm)): 0.09 (s, 27H, $Si(OSi(C\underline{H}_3)_3)_3$), 1.89 (m, 2H, $B\overline{OCH_2C\underline{H}_2CH_2O}$), 4.015 (br, $B\overline{OC\underline{H}_2CH_2C\underline{H}_2O}$)

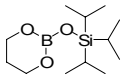
^{13}C NMR ($CDCl_3$; δ (ppm)): 1.6 ($Si(OSi(\underline{C}H_3)_3$), 27.2 ($B\overline{OCH_2\underline{C}H_2CH_2O}$), 62.6 ($B\overline{O\underline{C}H_2CH_2\underline{C}H_2O}$) **^{11}B NMR ($CDCl_3$, δ (ppm)):** 28.7

^{29}Si NMR ($CDCl_3$, δ (ppm)): 9.2

MS (EI) [*m/z* (rel. int. (%))]: 381 ((M^+-15 (100)), 323 (25), 309 (55), 281 (41), 267 (40), 251 (10), 193 (2)

Anal Calcu. for $C_{12}H_{33}BO_6Si_4C$: C, 36.35; H, 8.39 found C, 36.76, H 8.60

[1,3,2]-dioxaborinan-2-yl) tri(*iso*-propyl)siloxane



^{1}H NMR ($CDCl_3$; δ (ppm)): 1.03 (21H, $Si(C_3\underline{H}_7)_3$) 1.89 (br, 2H, $B\overline{OCH_2C\underline{H}_2CH_2O}$), 4.02 (t, 4H $B\overline{OC\underline{H}_2CH_2C\underline{H}_2O}$)

^{13}C NMR ($CDCl_3$; δ (ppm)): 12.5 ($Si(\underline{C}H(CH_3)_2)_3$), 17.8 ($Si(CH(\underline{C}H_3)_2)_3$, 27.3 ($B\overline{OCH_2\underline{C}H_2CH_2O}$), 62.8 ($B\overline{O\underline{C}H_2CH_2\underline{C}H_2O}$)

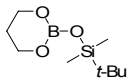
^{11}B NMR ($CDCl_3$, δ (ppm)): 26.6

^{29}Si NMR ($CDCl_3$, δ (ppm)): 10.4

MS (EI) [*m/z* (rel. int. (%))]: 215 (M^+-43 (100)), 187 (60), 173 (10), 159 (42), 145 (20), 131 (11), 117(15), 101 (14)

Anal Calcu. for $C_9H_{21}BO_3Si$: C, 55.81; H, 10.54 found C 56.14; H 10.73

([1,3,2]-dioxaborinan-2-yl)*tert*-butyldimethylsiloxane



^{1}H NMR ($CDCl_3$; δ (ppm)): 0.09 (6H, s, $Si(C\underline{H}_3)_2$(t-Bu)), 0.88 (9H, s, $Si(CH_3)_2(C(C\underline{H}_3)_3)$) 1.86 (q, 2H, $B\overline{OCH_2C\underline{H}_2CH_2O}$), 4.00 (t, 4H, $B\overline{OC\underline{H}_2CH_2C\underline{H}_2O}$)

^{13}C NMR ($CDCl_3$; δ (ppm)): -3.7 ($Si(C\underline{H}_3)_2$(t-Bu)), 18,0 ($Si(CH_3)_2(\underline{C}(CH_3)_3)$), 25.7 ($Si(CH_3)_2(C(\underline{C}H_3)_3)$, 27.2 ($B\overline{OCH_2\underline{C}H_2CH_2O}$), 62.8 ($B\overline{O\underline{C}H_2CH_2\underline{C}H_2O}$)

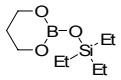
^{11}B NMR ($CDCl_3$, δ (ppm)): 26.8

^{29}Si NMR ($CDCl_3$, δ (ppm)):15.5

MS (EI) [*m/z* (rel. int. (%))]: 217 (M^++1 (6)), 159 (100), 131 (47), 117 (35), 101 (28)

Anal Calcu. for $C_{12}H_{27}BO_3Si$: C, 50.01; H, 9.79 found C, 50.14; H, 9.89

[1,3,2]-dioxaborinan-2-yl)triethylsiloxane



^{1}H NMR ($CDCl_3$; δ (ppm)): 0.62 (6H, q, $Si(C\underline{H}_2CH_3)_3$) 0.88 (9H, t, $Si(CH_2C\underline{H}_3)_3$) 1.87 (br, 2H, $BOCH_2C\underline{H}_2CH_2O$), 4.00 (t, 4H, $BOC\underline{H}_2CH_2C\underline{H}_2O$)

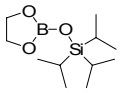
^{13}C NMR ($CDCl_3$; δ (ppm)): 5.6 ($Si(\underline{C}H_2CH_3)_3$, 6.7 ($Si(CH_2\underline{C}H_3)_3$), 27.3 ($BOCH_2\underline{C}H_2CH_2O$), 62.8 ($BO\underline{C}H_2CH_2\underline{C}H_2O$)

^{11}B NMR ($CDCl_3$, δ (ppm)): 26.9

^{29}Si NMR ($CDCl_3$, δ (ppm)): 15.8

MS (EI) [*m/z* (rel. int. (%))]: 187 (M^+-29 (100)), 159 (19), 131 (29), 103 (11), 73 (9)

[1,3,2]-dioxaborolan-2-yl) tri(*iso*-propyl)siloxane



^{1}H NMR ($CDCl_3$; δ (ppm)): 1.06 (br 21H, $Si(CH(CH_3)_2)_3$), 4.17 (s, 4H, $BO_2C_2\underline{H}_4$)

^{13}C NMR ($CDCl_3$; δ (ppm)): 12.4 ($Si(\underline{C}H(CH_3)_2)_3$), 17.7 ($Si(CH(\underline{C}H_3)_2)_3$, 64.6 ($BO_2\underline{C}_2H_4$)

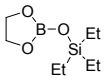
^{11}B NMR ($CDCl_3$, δ (ppm)): 31.6

^{29}Si NMR ($CDCl_3$, δ (ppm)): 12.8

MS (EI) [*m/z* (rel. int. (%))]:201 (M^+-43, (49)), 173 (57), 157 (8), 145 (100), 127 (23), 103 (45), 89 (5), 77 (19)

Anal Calcu. for $C_{11}H_{25}BO_3Si$: C, 54.10; H, 10.32 found C, 54.39; H 10.43

[1,3,2]-dioxaborolan-2-yl) triethylsiloxane



^{1}H NMR ($CDCl_3$; δ (ppm)): 0.65 (6H, qk, $Si(C\underline{H}_2CH_3)_3$), 0.96 (9H, t, $Si(CH_2C\underline{H}_3)_3$), 4.17 (s, 4H, $BO_2C_2\underline{H}_4$)

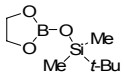
^{13}C NMR ($CDCl_3$; δ (ppm)): 5.3 ($Si(\underline{C}H_2CH_3)_3$), 6.4 ($Si(CH_2\underline{C}H_3)_3$), 64.5 ($BO_2\underline{C}_2H_4$)

^{11}B NMR ($CDCl_3$, δ (ppm)): 33.5

^{29}Si NMR ($CDCl_3$, δ (ppm)): 18.2

MS (EI) [*m/z* (rel. int. (%))]: 173 (M^+-29 (100)), 161 (36), 145 (53), 117 (43), 107 (28), 79(31), 63(13)

[1,3,2]-dioxaborolan-2-yl)*tert*-butyldimethylsiloxane



^{1}H NMR ($CDCl_3$; δ (ppm)): 0.13 (6H, s, $Si(C\underline{H}_3)_2$(t-Bu)), 0.90 (9H, s, $Si(CH_3)_2(C(C\underline{H}_3)_3)$) 4.17 (s, 4H, $BO_2C_2\underline{H}_4$)

^{13}C NMR ($CDCl_3$; δ (ppm)): -3.8 ($Si(C\underline{H}_3)_2$(t-Bu)), 18.0 ($Si(CH_3)_2(\underline{C}(CH_3)_3)$), 25.7 ($Si(CH_3)_2(C(\underline{C}H_3)_3)$), 64.5 ($BO_2\underline{C}_2H_4$)

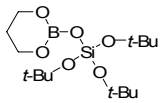
^{11}B NMR ($CDCl_3$, δ (ppm)): 31.7

^{29}Si NMR ($CDCl_3$, δ (ppm)): 18.4

MS (EI) [*m/z* (rel. int. (%))]: 145 (M^+-57 (100)), 127 (53), 119 (71), 103 (63), 77 (51), 61 (24)

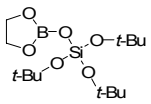
Anal Calcu. for $C_8H_{19}BO_3Si$: C, 47.54, H, 9.47; found C, 47.98, H, 9.61

[1,3,2]-dioxaborinan-2-yl)tris(*tert*-butoxy)siloxane



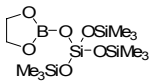
MS (EI) [*m/z* (rel. int. (%))]: 333 (M^+-15), 277 (52), 221 (100), 181 (8), 163 (14), 123 (12), 79 (12), 57 (11)

[1,3,2]-dioxaborolan-2-yl)tris(*tert*-butoxy)siloxane



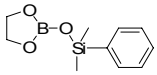
MS (EI) [*m/z* (rel. int. (%))]: 319 (M^+-15 (8)) 297 (5), 263 (24), 207 (100), 167 (5), 149 (5), 123 (19), 79 (8), 57 (11)

[1,3,2]-dioxaborolan-2-yl)tris(trimethylsiloxy)siloxane



MS (EI) [*m/z* (rel. int. (%))]: 367 (M^+-15 (96)), 323 (2), 309 (22), 281 (100), 267 (9), 251 (5), 235 (4), 207 (3), 193 (7), 73 (19)

[1,3,2]-dioxaborolan-2-yl)dimethylphenylsiloxane



MS (EI) [*m/z* (rel. int. (%))]: 207 (M^++1, (100)), 189 (18), 165 (31), 147 (60), 137 (39), 121 (28), 103 (34), 91 (27), 77(39)

References

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[2] H. C. Brown, D. Basavalah, N. G. Bhat, *Organometallics,* 1983, **2**, 1309.

[3] C. S. Yi, D. W. Lee, Y. Chen, *Organometallics*, 1999, **18**, 2043.

[4] J. J. Levison, S. D. Robinson, *J. Chem. Soc. A.,* 1970, 2947.

[5] B. Marciniec, M. Jankowska, C. Pietraszuk, *Chem. Commun*., 2005, 663.

[6] G. R. Clark, G. J. Irvine, W. R. Roper, L. J. Wright, *Organometallics,* 1997, **16**, 5499.

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