Supporting Information

Reactions of Silyl-Stabilized Sulfur Ylides with Organoboranes: Enantioselectivity, Mechanism and Understanding

Dean Howells,[†] *Raphaël Robiette,*[‡] *Guang Y. Fang,*[†] *Luke S. Knowles,*[†] *Michael D. Woodrow,*[§] *Jeremy N. Harvey,*[†]* *Varinder K. Aggarwal*[†,]*

School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK; Unité de Chimie organique et médicinale, Université catholique de Louvain; Pl. L. Pasteur 1, B-1348 Louvain-la-Neuve, Belgium; Medicinal Chemistry II, GlaxoSmithKline R&D, Stevenage, SG1 2NY, UK

V.Aggarwal@bristol.ac.uk

---

† University of Bristol

‡ Université catholique de Louvain

§ Medicinal Chemistry II, GlaxoSmithKline R&D, Stevenage

General information

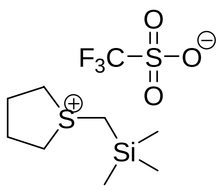
All air and water sensitive reactions were carried out in oven dried glassware under argon atmosphere. Solvents were dried by standard method.[1] NMR spectra were recorded on Jeol 270 MHz or Jeol 400 MHz spectrometers using tetramethylsilane as the internal standard (0.00 ppm). $CDCl_3$ was used as the internal standard for ^{13}C NMR spectra. CI mass spectra were obtained using a VG Platform mass spectrometer. IR spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer. Flash chromatography was performed using silica gel (Merck Kieselgel 60). Melting points were determined with a Kofler hot stage apparatus and were not corrected.

Triethylborane, tributylborane and triphenylborane were bought from Aldrich and used without further purification. Sulfide **7**[2] and Sulfonium salts **8**[2] and **10**[3] were made according to literature procedures.

General procedure for preparation of sulfonium salts from trimethylsilylmethyl triflate and corresponding sulfides

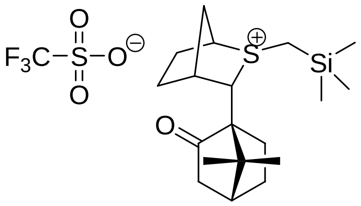
Trimethylsilylmethyl trifluoromethane sulfonate (5.0 mmol) was added dropwise to the solution of the corresponding sulfide (2.0 equivalents when tetrahydrothiophene was used; and 1.1 equivalents while chiral sulfides were used) in dry DCM (1 mL) under nitrogen atmosphere. After addition the reaction was stirred for four hours. To the mixture was then added diethyl ether (8 mL), and the sulfonium salt was precipitated as a white solid. The supernatant was taken out and the solid was washed with ether (2 × 5 mL), and dried under reduced pressure.

1-(Trimethylsilyl-methyl)-tetrahydro-thiophenium trifluoro-methanesulfonate



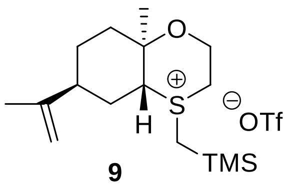
The sulfonium salt **5** was obtained in 92% yield as white needles, mp 85-86 °C (from DCM); ν_{max} (film)/cm^{-1} 2966 1246; δ_H (270 MHz, $CDCl_3$) 3.74 (2H, dt, J 12.9, 7.3 Hz), 3.37 (2H, dt, J 12.9, 7.3 Hz), 2.66 (2H, s), 2.54-2.44 (2H, m), 2.40-2.30 (2H, m), 0.29 (9H, s, Me); δ_C (100 MHz, $CDCl_3$) 46.9, 28.5, 27.9, -1.3; *m/z* (ESI+) 175 (100%, M^+); Found: C, 33.4; H 5.60. $C_9H_{19}SiS_2O_3F_3$ requires: C, 33.3; H, 5.60.

3-(7,7-Dimethyl-2-oxo-bicyclo[2.2.1]hept-1-yl)-2-trimethylsilanylmethyl-2-thionia-bicyclo[2.2.1]heptane; trifluoro-methanesulfonate



The chiral sulfonium salt **6** was obtained in 96% as white needles; mp 129-131 °C (from DCM); ν_{max} (film)/cm^{-1} 2960, 1732, 1256; δ_H (400 MHz, $CDCl_3$) 4.37 (1H, br), 3.95 (1H, d, *J* 5.1 Hz), 3.13 (1H, br), 2.89 (1H, d, *J* 15.0 Hz), 2.79 (1H, d, *J* 12.5 Hz), 2.59 (1H, dt, *J* 18.7, 3.7 Hz), 2.43-2.36 (1H, m, *J* 3.7 Hz), 2.40 (1H, d, *J* 15.0 Hz), 2.27-2.11 (3H, m), 2.23 (1H, d, *J* 11.4 Hz), 2.16 (1H, t, *J* 4.39 Hz), 1.98 (1H, d, *J* 18.7 Hz), 1.72-1.62 (2H, m), 1.57-1.51 (1H, m), 1.47-1.40 (1H, m), 1.22 (3H, s), 1.12 (3H, s), 0.26 (9H, s); δ_C (100 MHz, $CDCl_3$) 215.8, 73.3, 60.8, 58.7, 50.0, 45.0, 44.2, 43.0, 40.9, 33.2, 29.4, 27.2, 27.0, 24.3, 22.0, 19.6, -1.3; *m/z* (ESI): 337 (100%, M^+); accurate mass found: 337.2016, $C_{19}H_{33}SOSi$ requires: 337.2028.

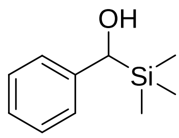
Synthesis of sulfonium salt 9



9

The sulfonium salt **9** was obtained as a brown oil (0.24 g, 1.1 mmol, 100% crude) which then was left under high vacuum for about 2 hours and dried over P_4O_{10} for a week prior to use. ν_{max} (film)/cm^{-1} 2964, 2845, 1223. δ_H (400 MHz; $CDCl_3$) 5.10 (1H, s), 4.91 (1H, s), 4.27 (1H, m), 4.14 (1H, m), 3.62 (1H, m), 3.54 (1H, m), 3.35 (1H, dd, *J* 13.5, 4.0 Hz), 3.02 (1H, ddd, *J* 13.5, 4.0, 2.0 Hz), 2.79 (1H, d, *J* 13.5 Hz), 2.72 (1H, m Hz), 2.57 (1H, d, *J* 13.0 Hz), 1.97-1.74 (2H, m), 1.74-1.65 (2H, m), 1.69 (3H, s), 1.52 (3H, s), 0.32 (9H, s); δ_C (100 MHz, $CDCl_3$) 128.1, 123.8, 75.4, 62.8, 57.5, 41.0, 39.5, 27.2, 25.9, 23.7, 20.4, 15.7, 0.0; *m/z* (ESI): 299 (M^+, 100%) found 299.1859 for $C_{16}H_{31}OSSi$ required 299.1860.

Phenyl-trimethylsilyl-methanol[4] from sulfonium salt 5



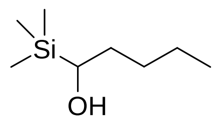
To a solution of dry sulfonium triflate **5** (0.16 g, 0.50 mmol) in dry THF (4 mL) at –78 °C was added 1.0 M LiHMDS in THF (0.60 mL, 0.60 mmol). After 5 min the reaction was cooled to –98

°C and 0.25 M triphenylborane in THF (2.4 mL, 0.60 mmol) was added. The reaction was then allowed to warm to rt and stirred overnight. Thereafter, the reaction mixture was cooled to 0 °C and a solution of premixed 30% H_2O_2 in water (2.5 mL) and 2.0 M NaOH (2.5 mL) was added dropwise. The resulting reaction mixture was stirred at room temperature overnight; after which it was extracted with diethyl ether (2 x 20 mL), organic phase were combined and washed with 1.0 M NaOH (2 x 10 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (2% ethyl acetate in petrol, R_f = 0.26) to give the title compound in 61% yield as a colorless oil; ν_{max} (film)/cm^{-1} 3419, 3061, 1246; δ_H (400 MHz, $CDCl_3$) 7.31 (2H, d, *J* 7.7 Hz), 7.20-7.16 (3H, m), 4.53 (1H, s), 1.73 (1H, br), 0.01 (9H, s); δ_C (100 MHz, $CDCl_3$) 144.4, 128.3, 125.9, 125.0, 70.7, -4.0.

Phenyl-trimethylsilyl-methanol from sulfonium 6 or 9

To a solution of dry chiral sulfonium triflate **6/9** (0.50 mmol) in dry THF (8 mL) at –78 °C was added 1.0 M LiHMDS in THF (0.60 mL, 0.60 mmol). After 5 min the reaction was cooled to –98 °C and 0.25 M triphenylborane in THF (2.40 mL, 0.60 mmol) was added. The reaction was then allowed to warm to rt and stirred overnight. Thereafter, the reaction mixture was cooled to 0 °C and a solution of premixed 30% H_2O_2 in water (2.5 mL) and 2.0 M NaOH (2.5 mL) was added dropwise. The resulting reaction mixture was stirred at room temperature overnight; after which it was extracted with diethyl ether (2 x 20 mL), organic phase were combined and washed with 1.0 M NaOH (2 x 10 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (2% ethyl acetate in petrol, R_f = 0.26) to give the title compound in 66% yield (41% yield when salt **9** was used) as a colorless oil.

1-Trimethylsilyl-pentan-1-ol[5] from sulfonium 5



To a solution of dry sulfonium triflate **5** (164 mg, 0.5 mmol) in dry THF (5 mL) at –78 °C was added 1.0 M LiHMDS in THF (0.60 mL, 0.60 mmol). After 5 min the reaction was cooled to –98 °C and 1.0 M tributylborane in THF (0.60 mL, 0.60 mmol) was added. The reaction was allowed to warm to room temperature and stirred overnight. To the reaction mixture was added a premixed 30% H_2O_2 in water (2.5 mL) and 2.0 M NaOH (2.5 mL) dropwise at 0 °C and stirred at room temperature for 4 hours. The mixture was extracted with diethyl ether (2 x 20 mL), organic phases were combined and washed with brine (20 mL), dried over anhydrous $MgSO_4$, concentrated *in vacuo* to give clear oil, which was then purified by column chromatography (5% diethyl ether in pentane, R_f = 0.15) gave the alcohol as an colorless oil in 63% yield; δ_H (400 MHz, $CDCl_3$) 3.27

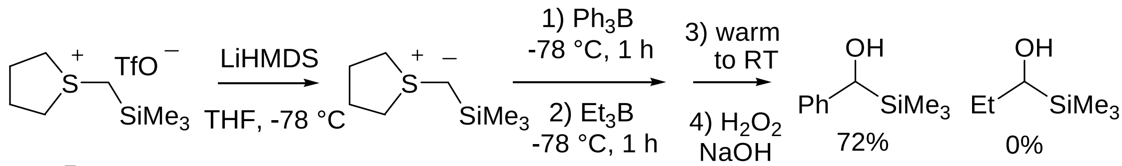
(1H, td, *J* 8.3, 5.4 Hz), 1.56-1.45 (3H, m), 1.42-1.11 (3H, m), 1.17 (1H, br), 0.89 (3H, t, *J* 7.3 Hz), 0.02 (9H, s); δ_C (100 MHz, $CDCl_3$) 66.3, 33.3, 29.1, 22.8, 14.2, -3.8.

1-Trimethylsilyl-pentan-1-ol from sulfonium 6

To a solution of dry sulfonium triflate **6** (0.23 g, 0.5 mmol) in dry DCM (2 mL) at –78 °C was added 1.0 M LiHMDS in THF (0.60 mL, 0.60 mmol). After 5 min the reaction was cooled to –98 °C and 1.0 M tributylborane in THF (0.60 mL, 0.60 mmol) was added. The reaction was allowed to warm to room temperature and stirred overnight. To the reaction mixture was added a premixed 30% H_2O_2 in water (2.5 mL) and 2.0 M NaOH (2.5 mL) dropwise at 0 °C; and the reaction mixture was then stirred at room temperature for 4 hours; thereafter the mixture was extracted with diethyl ether (2 x 20 mL), organic phases were combined and washed with brine (20 mL), dried over anhydrous $MgSO_4$, concentrated *in vacuo* to give clear oil, which was then purified by column chromatography (5% diethyl ether in pentane, R_f = 0.15) to give the alcohol as an colorless oil in 72% yield.

The Cross-over experiment with silyl-stabilized sulfonium ylide:

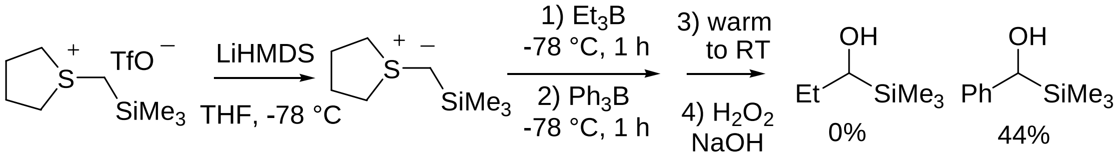
1) Adding triphenylborane to ylide 5 first then adding triethylborane:



5

To a solution of dry sulfonium triflate **5** (163mg, 0.50 mmol) in dry THF (5 mL) was added 1.0 M LiHMDS in THF (0.55 mL, 0.55 mmol) at -78 °C under nitrogen atmosphere. After 20 mins 0.25 M triphenylborane in THF (3.0 mL, 0.75 mmol) was added over a 1 min period and reaction was stirred at -78 °C for 30 min followed by addition of 1.0 M triethylborane in THF (0.75 mL, 0.75 mmol). The reaction mixture was stirred at -78 °C for another 30 mins before being warmed to room temperature over 1 hour period. After the reaction mixture was stirred at room temperature for 2 hours the premixed aqueous solution of 1.0 M NaOH (1.5 mL) and H_2O_2 (0.5 mL) was added at 0 °C, and stirred overnight at room temperature. The mixture was extracted with ether (2 x 10 mL), washed with 1.0 M NaOH (2 x 5 mL), brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo* . The crude product was further purified by column chromatography (2% diethyl ether in pentane) to gave Phenyl-trimethylsilyl-methanol in 72% yield.

2) Adding triethylborane to ylide 5 first then adding triphenylborane:

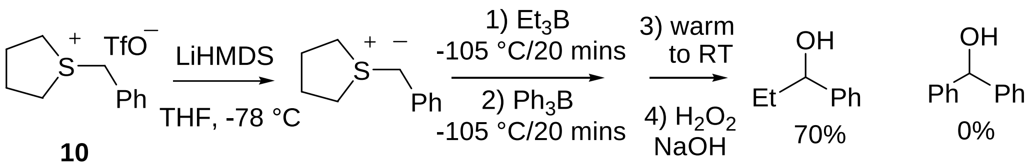


5

To a solution of dry sulfonium triflate **5** (0.16 g, 0.50 mmol) in dry THF (5 mL) was added 1.0 M LiHMDS in THF (0.55 mL, 0.55 mmol) at -78 °C under nitrogen atmosphere. After 20 mins 0.25 M triethylborane in THF (3.0 mL, 0.75 mmol) was added over a 1 min period and reaction was stirred at -78 °C for 30 min followed by addition of 1.0 M triphenylborane in THF (0.75 mL, 0.75 mmol). The reaction mixture was stirred at -78 °C for another 30 mins before being warmed to room temperature over 1 hour period. After the reaction mixture was stirred at room temperature for 2 hours the premixed aqueous solution of 1.0 M NaOH (1.5 mL) and H_2O_2 (0.5 mL) was added at 0 °C, and stirred overnight at room temperature. The mixture was extracted with ether (2 x 10 mL), washed with 1.0 M NaOH (2 x 5 mL), brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo* . The crude product was further purified by column chromatography (2% diethyl ether in pentane) to gave Phenyl-trimethylsilyl-methanol in 44% yield.

The Cross-over experiment with phenyl-stabilized sulfonium ylide

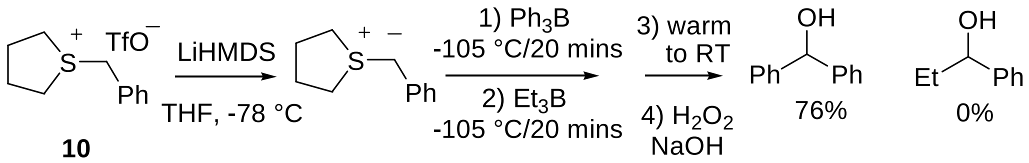
1) Addtion of triethylborane to ylide 10 followed by adding triphenylborane gave 1-Phenyl propan-1-ol[6]



10

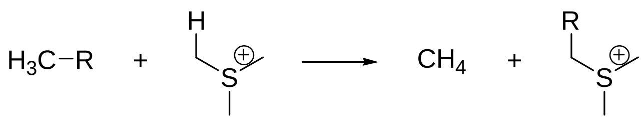
To a solution of dry sulfonium tetrafluoroborate **10** (133 mg, 0.5 mmol) in dry THF (5 mL) was added 1.0 M LiHMDS in THF (0.55 mL, 0.55 mmol) at –78 °C under nitrogen atmosphere. After 20 mins the reaction mixture was cooled to -105 °C and 1.0 M triethylborane in THF (0.75 mL, 0.75 mmol) was added over a 1 min period and reaction was stirred at -105 °C for 30 min. Then 0.25 M triphenylborane in THF (3.0 mL, 0.75 mmol) was added and the reaction was stirred at -105 °C for 30 min before warmed to room temperature over a 1 hour time, and was stirred at rt for 2 h. A premixed solution of 1.0 M NaOH (1.5 mL) and H_2O_2 (30% w/w, 0.5 mL) and added to the reaction at 0 °C, and the mixture was stirred overnight at rt. The reaction was extracted with diethyl ether (2 ×10 mL), washed with 1.0 M NaOH (2 x 5 mL) and brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo.* The crude product was purified by column chromatography (10% ethyl acetate in petrol, R_f = 0.18) to give the alcohol as a colourless oil in 70% yield; δ_H (400 MHz, $CDCl_3$) 7.35-7.22 (m, 5H), 4.57 (1H, t, J = 7.0 Hz), 1.85-1.66 (2H, m), 1.09-0.85 (3H, m); δ_C (100 MHz, $CDCl_3$) 140.0,128.6, 128.2, 126.0, 76.8, 32.7, 8.2.

2) Addtion of triphenylborane to ylide 10 followed by adding triethylborane gave diphenylmethanol[6]



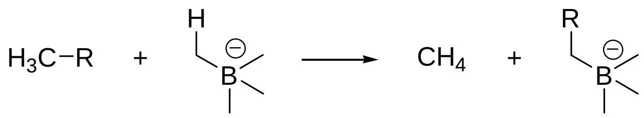
To a solution of dry sulfonium tetrafluoroborate **10** (0.13 g, 0.50 mmol) in dry THF (5 mL) was added 1.0 M LiHMDS in THF (0.55 mL, 0.55 mmol) at –78 °C under nitrogen atmosphere. After 20 mins the reaction mixture was cooled to -105 °C and 0.25 M triphenylborane in THF (3.0 mL, 0.75 mmol) was added over a 1 min period and reaction was stirred at -105 °C for 30 min. Then 1.0 M triethylborane in THF (0.75 mL, 0.75 mmol) was added and the reaction was stirred at -105 °C for 30 min before warmed to room temperature over a 1 hour time, and was stirred at rt for 2 h. A premixed solution of 1.0 M NaOH (1.5 mL) and H_2O_2 (30% w/w, 0.5 mL) was added to the reaction at 0 °C, and the resulting mixture was stirred overnight at rt. The reaction was extracted with diethyl ether (2 ×10 mL), washed with 1.0 M NaOH (2 x 5 mL) and brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo.* The crude product was purified by column chromatography (5% ethyl acetate in petrol, R_f = 0.22) to give the alcohol as a colourless oil in 76% yield. δ_H (400 MHz, $CDCl_3$) 7.40-7.27 (10H, m), 5.85 (1H, d, *J* = 2.0 Hz), 2.23 (1H, d, *J* = 2.0 Hz); δ_C (100 MHz, $CDCl_3$) 141.3, 129.1, 128.6, 126.2, 76.0.

Isodesmic reactions



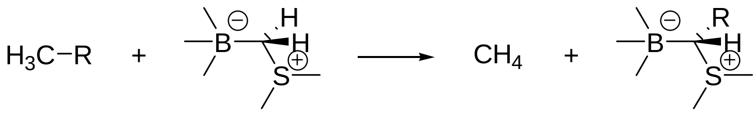
Eq. 1

R	ΔE (kcal/mol)
H	0.0
Ph	-11.3
TMS	-9.3



Eq. 2

R	ΔE (kcal/mol)
H	0.0
Ph	-12.7
TMS	-7.1



Eq. 3

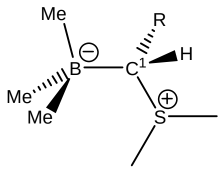
R	ΔE (kcal/mol)
H	0.0
Ph	-9.7
TMS	-2.3

Eq. 3 – Eq. 2 – Eq. 1 (informative of steric effects)

R	ΔE (kcal/mol)
H	0.0
Ph	14.3
TMS	14.1

NBO analysis

NBO analysis has been performed on every transition structure at the B3LYP/6-31G* level of theory using Jaguar 6.0 pseudospectral program package.



NPA charge at C^1 (a.u.)

R	**Ate complex**	**TS**	**δCharge**[a]
H	-0.825	-0.531	0.294
Ph	-0.569	-0.288	0.281
TMS	-1.118	-0.764	0.354

[a] δcharge = charge in TS – charge in ate complex

Energies and geometries

All geometries (cartesian coordinates in Å) were obtained after geometry optimization at the B3LYP/6-31G* level of theory. Energies (in a.u.) were obtained after single point calculations at the indicated level of theory.
For geometries and energies related to non-substituted and phenyl-substituted ylides reactions with BMe_3, see Supporting Information of *Chem. Comm.* **2006**, 741-743.

$TMSCH^{-}SMe_2$

E(B3LYP/6-31G*) =
-925.918120
E(MP2/6-311+G**) =
-924.182168

S	-3.45010	1.71240	0.04213
C	-5.05101	1.20004	-0.74574
H	-4.79222	0.51431	-1.55480
H	-5.67814	0.68563	-0.01119
H	-5.57212	2.07633	-1.14399
C	-4.23379	2.84104	1.29126
H	-4.89235	2.26597	1.94930
H	-3.41718	3.27346	1.87263
H	-4.79725	3.63077	0.78435
C	-2.72298	0.41589	0.79133
H	-3.34577	-0.14576	1.49077
Si	-0.96852	-0.04850	0.47128
C	0.07441	0.02827	2.06117
H	1.10270	-0.31532	1.88728
H	0.12373	1.05084	2.45460
H	-0.35345	-0.60453	2.84935
C	-0.83644	-1.83300	-0.17550
H	0.20993	-2.14115	-0.30083
H	-1.30626	-2.54339	0.51686
H	-1.33771	-1.94193	-1.14483
C	-0.18590	1.11386	-0.81101
H	0.85682	0.82409	-0.99207
H	-0.70908	1.07789	-1.77388
H	-0.18307	2.15744	-0.47468

$TMSCH(SMe_2)BMe_3$

E(B3LYP/6-31G*) =
-1070.53370
E(MP2/6-311+G**) =
-1068.356486

C	-11.86148	1.41258	1.35297
H	-12.67278	2.15270	1.28947
B	-10.74610	2.01489	2.57703
Si	-11.12905	1.16199	-0.42245
C	-13.17038	-0.10581	3.59240
H	-13.78748	0.76911	3.79876
H	-13.72191	-1.03216	3.77674
H	-12.26388	-0.07568	4.19192
C	-14.35952	-0.11428	1.13055
H	-14.86418	0.80669	1.43455
H	-14.28020	-0.16125	0.04596
H	-14.90521	-0.98690	1.49972
C	-9.85111	3.20573	1.87532
H	-10.45308	4.04064	1.48357
H	-9.20351	3.64171	2.65091
H	-9.17399	2.89131	1.06834
C	-11.61608	2.74179	3.78004
H	-12.39492	3.42447	3.39975
H	-12.10526	2.09009	4.51813

H -10.93385 3.37304 4.36930
C -9.75423 0.83691 3.15437
H -9.09262 1.27137 3.91899
H -10.24276 -0.01904 3.65293
H -9.09021 0.39806 2.39634
C -9.43158 0.33089 -0.41263
H -9.47056 -0.65731 0.06041
H -9.08758 0.18837 -1.44527
H -8.68195 0.92188 0.11877
C -11.08881 2.84152 -1.29335
H -10.40670 3.54631 -0.81293
H -10.76591 2.70655 -2.33369
H -12.08506 3.30033 -1.31670
C -12.21478 0.05245 -1.54157
H -11.70241 -0.05914 -2.50614
H -12.36744 -0.96187 -1.15167
H -13.19614 0.49308 -1.75836
S -12.67135 -0.14462 1.83469

TS

E(B3LYP/6-31G*) =
-1070.525340
E(MP2/6-311+G**) =
-1068.331199

S -2.28480 0.66542 1.74035
C -2.55472 1.26699 3.44033
H -2.71290 0.38772 4.06967
H -1.68339 1.82024 3.79297
H -3.45053 1.89368 3.47141
C -2.03866 2.23707 0.85346
H -1.15890 2.75344 1.23584
H -1.88645 1.99026 -0.19881
H -2.93407 2.85642 0.95642
B 1.09194 0.96200 1.98593
C -0.01062 -0.17795 1.95835
H -0.30632 -0.52093 2.95857
Si -0.24333 -1.56361 0.63729
C -0.85874 -0.83441 -1.00165
H -0.84336 -1.60924 -1.77859
H -1.88858 -0.46266 -0.94251
H -0.21495 -0.01491 -1.33882
C 1.36950 -2.48900 0.27494
H 1.16884 -3.27112 -0.46924
H 2.13931 -1.82709 -0.13414
H 1.78215 -2.97681 1.16441
C -1.49969 -2.83679 1.27343
H -1.62651 -3.64657 0.54379
H -1.16189 -3.29452 2.21169
H -2.48850 -2.39852 1.45082
C 1.61156 1.53034 0.54547
H 1.84311 0.74437 -0.18945
H 0.89633 2.20976 0.05636
H 2.53697 2.11273 0.66758
C 2.25817 -0.13747 2.62305
H 2.59007 -0.94764 1.97138
H 3.10943 0.54426 2.75473
H 2.01972 -0.55452 3.60877
C 0.91691 2.13019 3.12424
H 1.87373 2.64899 3.28349
H 0.20027 2.92367 2.86019
H 0.61263 1.74340 4.11039

$Me_2BCH(Me)TMS$

E(B3LYP/6-31G*) =
-592.593897
E(MP2/6-311+G**) =
-591.169815

B -1.69967 -1.93411 0.02142
C -0.13182 -1.95080 0.00968
H 0.21268 -2.05791 -1.03279
C -2.50967 -2.46728 1.27716
H -2.05188 -2.20626 2.23983
H -3.56115 -2.15745 1.29687
H -2.50563 -3.56960 1.24343
C -2.51978 -1.42712 -1.23636
H -3.25180 -0.65497 -0.95820
H -1.91940 -1.04887 -2.07129
H -3.12540 -2.26513 -1.61796
Si 0.52579 -0.19619 0.47176
C 2.42208 -0.21476 0.39247
H 2.86141 -0.89372 1.13194
H 2.77989 -0.52372 -0.59727
H 2.82136 0.78813 0.58953
C -0.00638 0.28714 2.22699
H 0.31783 -0.45143 2.96991
H 0.43330 1.25100 2.51190
H -1.09523 0.38434 2.31082
C -0.10129 1.11294 -0.74710
H 0.34447 2.08904 -0.51791
H 0.16770 0.86366 -1.78061
H -1.19002 1.22961 -0.70926
C 0.54447 -3.03092 0.88829
H 1.63773 -3.00965 0.80980
H 0.29151 -2.91100 1.94817
H 0.22288 -4.03978 0.59901

CH_4

E(MP2/6-311+G**) =
-40.379501

H -9.96454 0.16951 -0.12392
H -11.54798 0.33388 -0.93250
H -10.40204 1.70308 -0.92671
C -10.78449 0.85662 -0.34994
H -11.22318 1.22003 0.58318

Me-Ph

E(MP2/6-311+G**) =
-270.784091

H -12.183448 0.57491 1.74834
H -12.421734 2.22306 1.14135
C -9.694846 0.35876 -2.40297
C -10.193376 1.64940 -2.22119
C -10.841946 1.99004 -1.03351
C -11.001724 1.05354 -0.00415
C -10.501152 -0.23974 -0.20204
C -9.851846 -0.58576 -1.38763
H -9.190887 0.09085 -3.32790
H -10.081188 2.39310 -3.00629
H -11.229136 2.99894 -0.90292
H -10.620311 -0.98465 0.58266
H -9.471532 -1.59584 -1.51866
C -11.677597 1.43359 1.29317
H -10.950771 1.80849 2.02575

$SiMe_4$

E(MP2/6-311+G**) =
-448.211006

Si -10.77537 0.85702 -0.37437
H -12.15180 0.62826 1.71568
H -12.19272 2.29434 1.12250
C -9.73916 2.26589 -1.10568
H -10.35142 3.15593 -1.29590
H -8.92999 2.56171 -0.42658
H -9.27973 1.97236 -2.05762
C -9.66553 -0.64878 -0.06710
H -8.85560 -0.41228 0.63390
H -10.23418 -1.48559 0.35686
H -9.20348 -1.00202 -0.99721
C -12.15299 0.38946 -1.58971
H -11.74299 0.05547 -2.55082
H -12.77476 -0.42406 -1.19618
H -12.81413 1.24121 -1.79168
C -11.54332 1.42161 1.26441
H -10.77187 1.70035 1.99269

S^+Me_3

E(MP2/6-311+G**) =
-516.766491

H -12.20278 -2.10452 2.84861
H -10.74758 -1.62603 1.93541
C -13.87505 0.44344 2.55274
H -13.39593 0.93319 3.40360
H -14.48051 1.15206 1.98256
H -14.50317 -0.38773 2.88208
S -12.62214 -0.23858 1.41651
H -12.13806 1.91827 0.50962
H -11.20876 1.64556 2.02772
C -11.55201 1.20194 1.09031
H -10.70850 0.85202 0.49045
C -11.59222 -1.25882 2.52327
H -11.24873 -0.67158 3.37796

$Me_2S^+CH_2Ph$

E(MP2/6-311+G**) =
-747.189107

H -13.37913 -1.85264 2.72960
H -11.61300 -1.98548 2.52535
C -13.98264 0.69788 1.29377
H -13.78008 1.34634 2.14884
H -14.13186 1.28489 0.38473
H -14.86134 0.07285 1.46967
S -12.57514 -0.41901 1.00042
H -10.23942 0.04137 0.90192
H -11.19175 1.28206 0.06691
C -11.07083 0.74389 1.01171
C -12.45245 -1.28995 2.59449
H -12.30203 -0.57457 3.40571
C -10.68050 3.33744 4.41052
C -11.38874 3.76433 3.28520
C -11.52162 2.92140 2.18350
C -10.94682 1.63931 2.19888
C -10.22446 1.22428 3.33043
C -10.09451 2.07005 4.43027
H -10.57329 3.99758 5.26609
H -11.82640 4.75772 3.26071
H -12.04851 3.27176 1.29864
H -9.73919 0.25079 3.34054
H -9.52536 1.74578 5.29621

$Me_2S^+CH_2TMS$

E(MP2/6-311+G**) =

-924.612782

H -14.74278 -0.94370 1.00356
H -14.32746 0.62738 1.74173
C -12.15394 -1.62249 -0.38037
H -12.38299 -1.02982 -1.26909
H -11.11459 -1.95816 -0.39567
H -12.81523 -2.48965 -0.30674
S -12.37921 -0.61929 1.12852
H -10.39831 0.51113 0.57700
H -11.80339 1.38050 -0.06544
C -11.39913 0.88557 0.82492
C -14.10275 -0.06178 0.92677
H -14.23014 0.42862 -0.04125
Si -11.17695 2.11427 2.33880
C -10.28182 1.16275 3.69170
H -10.09456 1.82021 4.54917
H -10.86147 0.30953 4.06384
H -9.30837 0.78889 3.35366
C -12.85616 2.73988 2.92402
H -12.70004 3.54631 3.65117
H -13.45945 3.16032 2.11096
H -13.44617 1.97202 3.43923
C -10.13483 3.49629 1.60475
H -9.90727 4.23943 2.37861
H -9.17807 3.13034 1.21509
H -10.65401 4.01958 0.79374

$B^{-}Me_4$

E(MP2/6-311+G**) =
-183.957876

B -10.52291 2.02147 2.20686
C -10.06696 3.50063 1.60701
H -10.92830 4.16117 1.39485
H -9.41684 4.06332 2.30275
H -9.50248 3.42378 0.65899
C -11.36257 2.23352 3.62288
H -12.27809 2.84017 3.49166
H -11.69274 1.27849 4.07240
H -10.76745 2.74605 4.40158
C -9.17197 1.10188 2.49792
H -8.48753 1.56637 3.23220
H -9.41355 0.10001 2.89944
H -8.56795 0.92690 1.58814
H -11.82544 0.25313 1.44551
H -12.41217 1.81567 0.86890
C -11.49069 1.24958 1.10105
H -10.98555 1.08127 0.13150

$Me_3B^{-}CH_2Ph$

E(MP2/6-311+G**) =
-414.382770

B -10.62763 2.04492 2.52164
C -9.88230 3.42615 2.00778
H -10.59524 4.22027 1.71843
H -9.24791 3.86346 2.79925
H -9.22209 3.27274 1.13760
C -11.60104 2.38009 3.81755
H -12.37824 3.13240 3.59123
H -12.13492 1.49062 4.19853
H -11.02673 2.78113 4.67162
C -9.50803 0.90607 2.94203
H -8.86098 1.25843 3.76499
H -9.96295 -0.03693 3.29767
H -8.82967 0.62935 2.11748
C -11.65607 1.44163 1.30424
H -12.18007 0.56508 1.71759
H -12.42387 2.20740 1.10998
C -9.69640 0.35313 -2.41656
C -10.19378 1.64422 -2.22321
C -10.83597 1.98623 -1.03414
C -11.00868 1.06052 0.01544
C -10.49719 -0.23500 -0.20539
C -9.85432 -0.58360 -1.39208
H -9.19589 0.08302 -3.34495
H -10.08186 2.39216 -3.00808
H -11.21406 2.99775 -0.89974
H -10.60796 -0.97643 0.58339
H -9.47373 -1.59694 -1.51964

$Me_3B^{-}CH_2TMS$

E(MP2/6-311+G**) =
-591.80071

B -10.65897 2.18521 2.53708
C -10.39091 3.76554 2.12075
H -11.32641 4.31351 1.90518
H -9.89550 4.32236 2.93656
H -9.74852 3.89706 1.23328
C -11.58382 2.15001 3.91325
H -12.57029 2.63027 3.77943
H -11.78957 1.12326 4.26725
H -11.10124 2.67424 4.75827
C -9.21700 1.42847 2.84169
H -8.69362 1.88334 3.70180
H -9.33308 0.35802 3.09008
H -8.50134 1.47307 2.00053
Si -10.77913 0.88568 -0.30159
C -11.54367 1.39747 1.32575
H -11.96544 0.46469 1.74859
H -12.42924 2.01728 1.09021
C -9.70617 2.21878 -1.14810
H -10.27065 3.14731 -1.29987
H -8.83828 2.46866 -0.52760
H -9.34168 1.88121 -2.12876
C -9.68155 -0.67040 -0.12996
H -8.86531 -0.48996 0.57816
H -10.26173 -1.52174 0.25086
H -9.24240 -0.97145 -1.09167
C -12.11727 0.41643 -1.60112
H -11.67670 0.07902 -2.55050
H -12.76170 -0.39166 -1.22911
H -12.76852 1.27236 -1.82470

[1] A. B. Pangborn, M. A. Giardello, R. M. Grubbs, R. K. Rosen and F. T. Timmers, *Organometallics*, **1996**, *15*, 1518.
[2] D. M. Badine, C. Hebach and V. K. Aggarwal, *Chem. Asian, J*. **2006**, *1*, 438.
[3] V. K. Aggarwal, G. Y. Fang and A. T. Schmidt, *J. Am. Chem. Soc.* **2005**, *127*, 1642.
[4] J. Cossrow and S. D. Rychnovsky, *Org. Lett.* **2002**, *4*, 147.
[5] R. J. Linderman and Y. Suhr,*J. Org. Chem.* **1988**, *53*, 1569.
[6] C.-J. Li and Y. Meng, *J. Am. Chem. Soc*. **2000**, *122*, 9538.