Supplementary Material (ESI) for Chemical Communications

Is phenyl a good migrating group in the rearrangement of organoborates generated from sulfur ylides?

Raphaël Robiette, Guang Yu Fang, Jeremy N. Harvey,* and Varinder K. Aggarwal,*

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.

E-mail: jeremy.harvey@bristol.ac.uk; v.aggarwal@bristol.ac.uk

Supporting information

I. Experimental procedures and analysis data

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IV. Cartesian coordinates and energies (a.u.) of the considered structures

I. Experimental procedures and analysis data

General information

All air and water sensitive reactions were carried out in oven dried glassware under an argon atmosphere. Solvents were dried by standard methods.[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 (0.0 ppm). 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.

Synthesis of Dihexylphenylborane

After extensive study, we found that dihexylphenylborane could be conveniently synthesised through the reaction of PhMgCl with methyl dihexylborinic ester rather than chlorodihexylborane which had been used previously.[2] The selection of reaction solvent is important. Reactions carried out in pentane as indicated in literature led to formation of a mixture of boranes,[2] while the reactions in diethyl ether gave the desired compound in high purity and good yield. We also found that the concentration of the methyl borinic ester in certain cases (e.g. synthesis of dihexylphenylborane) was important as well. The reaction using 1 M solution of methyl dihexylborinic ester in diethyl ether as indicated in the literature[2] gave a mixture of boranes, while the reaction using 0.5 M solution of methyl dihexylborinic ester in diethyl ether furnished the desired compound in high yield and purity.

Synthesis of chlorodihexylborane

We synthesised chlorodihexylborane from 1-hexene and boron trichloride following Matteson's procedure.[3]

To a vigorously stirred boron trichloride solution (1 M in heptane, 35 mL) was added a mixture of 1-hexene (2.94 g, 35 mmol) and diethylsilane (3.08 g, 35 mmol) at -78 ºC. After addition, the mixture

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[1] A. B. Pangborn, M. A. Giardello,R. M. Grubbs, R. K. Rosen, F. T. Timmers, *Organometallics*, 1996, **15**, 1518.

[2] W. K. Gary, H. C. Brown, *J. Organomet. Chem*. 1974, **73**, 1

[3] R. Soundararajan, D. S. Matteson,. *J. Org. Chem*., 1990, **55**, 2274.

was stirred for 30 mins at -78 ºC and for another 30 mins at room temperature. After the solvent was removed under vacuum a crude product was obtained as a colourless oil, which, according to the ^{11}B NMR and ^{1}H NMR, was in high purity and was used without further purification in the next transformation. ^{1}H NMR (300 MHz, $CDCl_3$) 0.86-0.90 (6H, m), 1.26-1.38 (16H, m), 1.48-1.50 (4H, m). ^{11}B NMR (96 MHz, $CDCl_3$) 77.

Synthesis of methyl dihexylborinic ester

The crude chlorodihexylborane (2.9 g, 14.0 mmol) obtained above was dissolved in hexane (20 mL). To the solution was added slowly pre-degassed methanol (0.7 mL, 16.8 mmol) at -78 ºC. After addition, the reaction mixture was allowed to warm to room temperature under reduced pressure. As the temperature increased hydrochloride, hexane and the excess methanol were removed, and the residue was the crude product, which, examined by ^{1}H NMR and ^{11}B NMR, was in high purity and was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) 0.81-0.90 (10H, m), 1.25-1.37 (16H, m), 3.68 (3H, s). ^{11}B NMR (96 MHz, $CDCl_3$) 54.

Synthesis of Dihexylphenylborane

A pre-dried 100 mL Schlenk flask was charged with methyl dihexylborinic ester (1.0 M in diethyl ether, 20 mL, 20 mmol). The solution was diluted to 0.5 M by addition of anhydrous diethyl ether (20 mL). Phenyl magnesium chloride (2 M in THF, 20 mmol) was added dropwise to the solution at -78 ˚C. After addition, the reactants were allowed to worm to room temperature and stirred for 3 hours. The solvent was removed under reduced pressure a white solid, which presumably is the ate complex of the borane, was obtained. Hexane (60 mL) was introduced to crack the ate complex. The mixture was vigorously stirred for 5 hours and was then the slurry mixture was allowed to settle. The supernatent was transferred into a Schlenk flask by cannular. The solid was extracted with hexane (60 mL) again. The hexane solutions were combined. After removing the solvent the crude product (4.18g, 81%) was obtained as a colourless oil, which was used in next transformation without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) 0.88 (6H, t, J=7.0 Hz), 1.26-1.58 (16H, m), 1.59 (4H, t, J=7.3 Hz), 7.35-7.45 (3H, m), 7.80-7.84 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) 14.3, 22.8, 25.3, 32.0, 33.1, 127.9, 131.7, 134.1. ^{11}B NMR (96 MHz, $CDCl_3$) 78.

Synthesis of *B*-phenyl-9-borabicyclo(3,3,1)nonane[4]

B-Methoxy-9-BBN (1 M solution in hexane, Aldrich, 20 mL, 20 mmol) was introduced into a Schlenk flask. The hexane was removed under reduced pressure and the borinic ester was redissolved in anhydrous diethyl ether (40 mL). To the solution of the borinic ester in diethyl ether was added phenyl magnesium chloride (2 M in THF, 10 mL, 20 mmol) at -78 ºC. The reaction mixture was then stirred at room temperature for 3 hours. The same workup procedure as the one which was applied in the synthesis of dihexylphenylborane was followed to give a colourless oil (2.81g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) 1.29-1.40 (m, 4H), 1.78-1.93 (m, 4H), 2.00-2.08 (m, 4H), 2.31-2.37 (m, 2H), 7.48-7.52 (m, 2H), 7.56-7.63 (m, 1H), 8.01 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) 23.7, 34.4, 128.3, 133.0, 134.9. ^{11}B NMR (96 MHz, $CDCl_3$) 80.

Synthesis of diethylphenylborane

Methyl diethylborinic ester (2.6 mL, 20.0 mmol) was dissolved in diethyl ether (40 mL). To the solution was added phenyl magnesiumchloride (2 M in THF, 10 mL, 20 mmol) at -78 ºC. The reaction mixture was then allowed to room temperature and stirred for 3 hours. The same workup procedure as the one which was applied in the synthesis of dihexylphenylborane was followed which result in a colourless oil in (1.9 g, 65% yield). ^{1}H NMR (300 MHz, $CDCl_3$) 1.06 (6H, t, J = 7.5 Hz), 1.61 (4H, q, J = 7.5 Hz), 7.35-7.45 (3H, m), 7.80-7.84 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) 7.5, 126.7, 133.0, 134.6. ^{11}B NMR (96 MHz, $CDCl_3$) 77.

General Procedure for Borane-Ylide Reactions

To the mixture of sulfonium salt (0.50 mmol) in THF (4 mL) was added LHMDS (1 M in THF, 0.55 mL) at – 78 ˚C. The mixture was stirred for 2 hours before being cooled to the temperature around – 100-110 ˚C. The borane (1M in THF, 0.55 mL) was added within 10 mins. Half an hour later after addition, the cooling bath was removed, and the reaction temperature was allowed to rise to 0 ˚C. Aqueous NaOH solution (2 M, 2 mL) and H_2O_2 solution (30%, 1 mL) were added subsequently. The mixture was stirred at room temperature for 8 hours. Then, the reaction mixture was diluted with NaOH (2 M, 4 mL) and water (10 mL) and extracted with diethyl ether twice (2 × 30 mL). The ethereal solutions were combined and dried over anhydrous $MgSO_4$. After filtration and removal of the solvent under reduced pressure, the residue was further purified by chromatography or directly analysed by GC.

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[4] E. Kalbarczk, S. Pasynkiewicz, *J. Organomet. Chem*., 1985, **292**, 119.

The reaction of 4-methylbenzyl sulfonium tetrafluoroborate and diethylphenylborane[5]

1-(4-Methylphenyl)-1-propanol and 1-(4-methylphenyl)-1-phenylmethanol were obtained. 1-(4-Methylphenyl)-1-propanol was obtained as a colourless oil in 65% yield: ^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t, *J* = 7.6 Hz), 1.67-1.84 (2H, dq, J = 7.6, 7.2 Hz), 2.33 (3H, s), 4.52 (1H, t, *J*=7.2 Hz). 7.13-7.15 (2H, d, *J* = 7.8 Hz), 7.20-7.23 (2H, d, *J* = 7.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 10.1, 21.0, 31.7, 75.7, 125.9, 129.0, 137.0, 141.5. 1-(4-Methylphenyl)-1-phenylmethanol was obtained as a white crystalline solid in 28% yield: m.p. 62-3 ^{o}C (ethyl acetate-petrol). ^{1}H NMR (400 MHz, $CDCl_3$) 2.30 (s, 3H), 5.72 (s, 1H), 7.08-7.34 (m, 9H).

The reaction of benzyl sulfonium tetrafluoroborate and dihexylphenylborane

Both 1-phenylheptan-1-ol and diphenylmethane were obtained. 1-Phenylheptan-1-ol was obtained as colourless oil in 63% isolated yield, and diphenylmethane was obtained as colourless oil in 29% yield. Data obtained for 1-phenylheptan-1-ol: ^{1}H NMR[6] (400 MHz, $CDCl_3$) 0.86 (3H, t, *J*=6.8 Hz), 1.21-1.43 (8H, m), 1.64-1.73 (1H, m), 1.74-1.82 (1H, m), 4.63 (1H, dt, *J*=3.0, 6.2 Hz), 7.24-7.34 (5H, m). ^{13}C NMR (101 MHz, $CDCl_3$) 14.2, 22.7, 25.9, 29.3, 31.9, 39.2, 74.8, 126.0, 127.5, 128.3, 145.0. Data obtained for diphenylmethane: ^{1}H NMR[7] (400 MHz, $CDCl_3$) 3.91 (2H, s), 7.10-7.22 (10H, m). ^{13}C NMR (101 MHz, $CDCl_3$) 42.0, 126.2, 128.5, 129.0, 141.2.

The reaction of 4-methylbenzyl sulfonium tetrafluoroborate and *B*-phenyl-9-borabicyclo(3,3,1)nonane

1-(4-Methylphenyl)-1-phenylmethanol[8] and *cis*-5-(Hydroxy-4-tolylmethyl)cyclooctanol were obtained in a 5/2 ratio (crude). *cis*-5-(Hydroxy-*p*-tolylmethyl)cyclooctanol was obtained as a white crystalline solid in 24% yield. M.p 108-110 ˚C; ν_{max}/cm^{-1} (neat) 3273, 2919, 2852. ^{1}H NMR (400 MHz, $CDCl_3$) 1.15-1.24 (1H, m), 1.29-1.48 (5H, m), 1.54-1.66 (2H, m), 1.72-1.92 (7H, m), 2.34 (3H, s), 3.91-3.97 (1H, m), 4.36 (1H, d, *J*=7.3 Hz), 7.14 (2H, d, *J*=7.8 Hz), 7.20 (2H, d, *J*=7.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 21.2, 22.9, 23.3, 28.8, 30.5, 36.2, 44.3, 51.1, 72.2, 79.4, 126.6, 129.1, 137.2, 140.8. *m/z* (ESI) 271 (M + Na^+); HRMS found 271.1673, $C_{16}H_{18}NaO_2$ required 271.1667. 1-(4-Methylphenyl)-1-

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[5] Y.-J. Chen, R.-X. Lin, C. Chen, *Tetrahedron Asymmetry*, 2004, **15**, 3561.

[6] G. Kabalka, W. George, Z. Wu, Y. Ju, *Tetrhedron*, 2001, **57**, 1663.

[7] T. Nishino, Y. Nishiyama, N. Sonoda, *Bull. Chem. Soc.* 2003, **76**, 635.

[8] C. Krug.J. F. Hartwig, *J. Am. Chem. Soc*., 2002, **124**, 1674.

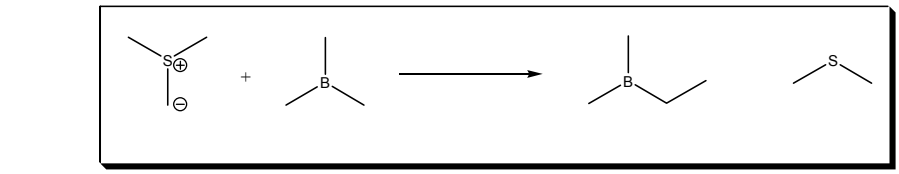
phenylmethanol was obtained as a white crystalline solid in 65% yield. M.p. 62-3 ^{o}C (ethyl acetate-petrol). ^{1}H NMR (400 MHz, $CDCl_3$) 2.30 (s, 3H), 5.72 (s, 1H), 7.08-7.34 (m, 9H).

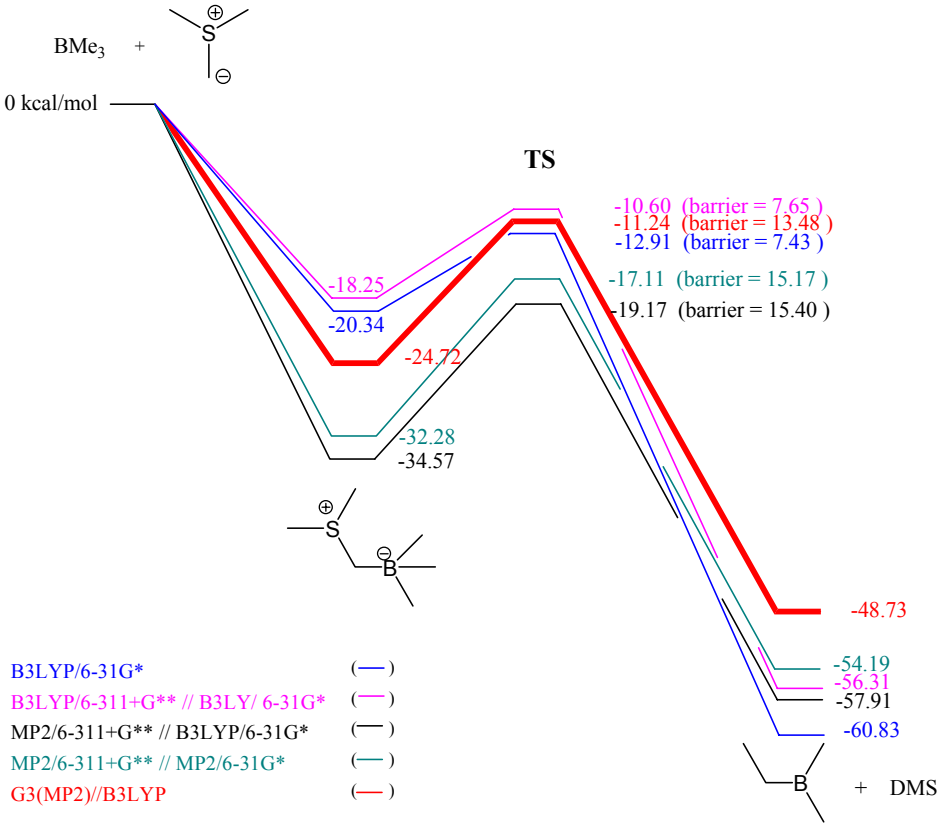
II. Computational details

All species have been fully geometry optimized using the Jaguar 4.0 pseudospectral program package, except transition states for which the Gaussian 03 program package was used. Geometry optimization was carried out using the well established B3LYP hybrid density functional and the standard split valence polarized 6-31G* basis set (optimization of the model reaction, BMe_3 + CH_2SMe_2, at MP2/6-31G* level using the Gaussian 03 program package did not lead to significant structure change).

Frequency calculations have been carried out on every transition state structures using the Gaussian 03 program package in order to check the correct nature of the point on the potential energy surface.

For the model reaction (BMe_3 + CH_2SMe_2), single point calculations using MP2/6-311+G** (Gaussian 03) and B3LYP/6-311+G** (Jaguar 4.0) methods, and G3(MP2)//B3LYP calculations (Gaussian 03) were carried out. A comparison of the different methods is given in the figure below.



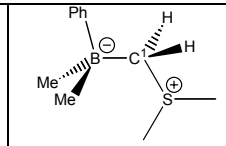
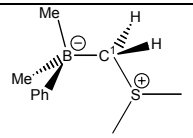
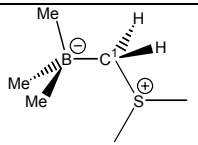
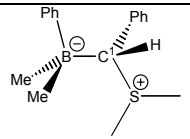
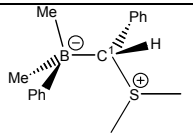
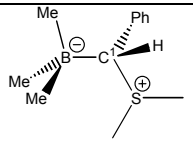


No significant difference in structure was observed between B3LYP/6-31G* and MP2/6-31G* optimized structures. One can notice however a systematic energetic underestimation of the migration barrier obtained at B3LYP level compared to the value obtained using G3(MP2)//B3LYP method. Accordingly, energies reported in this study were obtained after single point calculations at the MP2/6-311+G** level of theory on every optimized B3LYP/6-31G* structures.

Several local minima and saddle points corresponding to each intermediate or transition state were frequently found. This is due to the possibility of multiple conformations of phenyl substituent and around the C1-B and C1-S bonds. We have systematically varied the relevant diehedral angles, and optimized several different local minima and saddle points (up to ten different calculations for each species). The date presented refer to the lowest energy form unless mentioned otherwise.

III. NBO analysis

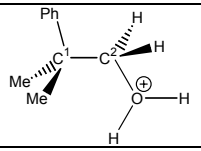
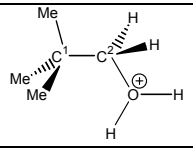
NBO analysis has been performed on every transition structure at the B3LYP/6-31G* level of theory using Jaguar 5.0 pseudospectral program package.

												
barrier[a]	13.19 kcal/mol		19.27 kcal/mol		15.40 kcal/mol		14.72 kcal/mol		16.36 kcal/mol		12.47 kcal/mol	
NPA Charge (a.u.)												
	ate complex	TS	ate complex	TS	ate complex	TS	ate complex	TS	ate complex	TS	ate complex	TS
R	-0.3324	-0.1588	-0.2725	-0.1929	-0.2940	-0.1305	-0.3320	-0.2424	-0.2640	-0.3187	-0.2878	-0.2090
B	0.4377	0.4061	0.4319	0.3840	0.4482	0.4104	0.4547	0.4136	0.4470	0.4326	0.4610	0.4160
C^1	-0.8122	-0.5314	-0.8188	-0.5841	-0.8251	-0.5310	-0.5531	-0.2901	-0.5629	-0.2956	-0.5694	-0.2882
S	0.8959	0.4714	0.9055	0.6100	0.9024	0.4662	0.8615	0.5407	0.8766	0.4443	0.8827	0.5376
Stabilization (kcal/mol)												
$\pi_{Ph} \rightarrow \sigma^*_{CS}$	1.23	**18.00**	-	-	-	-	0.82	**7.10**	-	-	-	-
$\sigma_{B-R} \rightarrow \sigma^*_{CS}$	5.34	32.88	3.75	17.98	4.37	40.28	4.69	16.34	3.97	53.57[b]	3.66	15.90
						$\pi_{Ph'} \rightarrow \sigma^*_{CS}$	5.38	20.92	4.88	10.39	5.02	21.45

[a] obtained at MP2/6-311+G**//B3LYP/6-31G* level of theory

[b] this point appears to be out of line compared to other values. This could be due to the need in that precise case to force the NBO analysis to consider a structure with a σ_{C2-S} bond for the TS.

Wagner-Meerwein rearrangement

				
barrier[a]	3.58 kcal/mol		11.27 kcal/mol	
NPA Charge (a.u.)				
	ion	TS	ion	TS
R	0.1060	0.2198	0.0948	0.2416
C^1	-0.1149	-0.1081	-0.1206	-0.0152
C^2	-0.0802	-0.0741	-0.0765	-0.1023
O	-0.7068	-0.8122	-0.6898	-0.9282
Stabilization (kcal/mol)				
$\pi_{Ph} \rightarrow \sigma^*_{CO}$	3.55	**22.88**	-	-
$\sigma_{C1-R} \rightarrow \sigma^*_{CO}$	7.85	19.05	6.77	102.66

[a] obtained at MP2/6-311+G**//B3LYP/6-31G* level of theory

IV. Cartesian coordinates (in Å) and energies (a.u.) of the considered structures

A. Model reaction: BMe_3 + CH_2SMe_2

BMe_3 (B3LYP 6-31G*)

E(B3LYP 6-31G*) = -144.60852
E(B3LYP 6-311+G**) = -144.65648
E(MP2 6-311+G**) = -144.13564
E(G3(MP2)) = -144.29865

B 0.00468 .01980 .00000
C 1.58647 -.02570 .00000
H 2.07487 .95468 .00000
H 1.95379 -.58774 .87204
H 1.95379 -.58774 -.87204
C -.79653 1.38017 .00000
H -.18479 2.28865 .00000
H -1.46906 1.41791 -.87099
H -1.46906 1.41791 .87099
C -.79093 -1.35060 .00000
H -1.88220 -1.24964 .00000
H -.50834 -1.95818 -.87272
H -.50834 -1.95818 .87272

BMe_3 (MP2 6-31G*)

E(MP2 6-31G*) = -144.01029
E(MP2 6-311+G**) = -144.13564

B 0.00000 0.02841 0.00000
C 1.55945 0.28099 0.00000
H 1.84818 1.33476 0.00000
H 2.01863 -0.20106 0.87248
H 2.01863 -0.20106 -0.87248
C -1.05182 1.20271 0.00000
H -0.62319 2.20757 0.00000
H -1.71205 1.10502 -0.87171
H -1.71205 1.10502 0.87171
C -0.50985 -1.46873 0.00000
H -1.59777 -1.57648 0.00000
H -0.11350 -2.00285 -0.87280
H -0.11350 -2.00285 0.87280

CH_2SMe_2 (B3LYP 6-31G*)

E(B3LYP 6-31G*) = -517.228444
E(B3LYP 6-311+G**) = -517.29857
E(MP2 6-311+G**) = -516.33055
E(G3(MP2)) = -516.56482

H 2.31962 1.57603 -.02079
C 2.66753 2.60119 .02968
H 2.00559 3.41440 .28820
S 4.22434 3.02760 -.28623
C 4.80358 2.36410 -1.92800
H 5.86718 2.58221 -2.06899
H 4.62969 1.28482 -1.97669
H 4.20900 2.86905 -2.69164
C 5.43086 2.02333 .71637
H 6.45757 2.26145 .42000
H 5.26533 2.29517 1.76055
H 5.23528 .95583 .57602

CH_2SMe_2 (MP2 6-31G*)

E(MP2 6-31G*) = -144.01029
E(MP2 6-311+G**) = -144.13564

H -1.74224 -0.00864 1.38926
C -1.64397 -0.00706 0.31189
H -2.50168 -0.01865 -0.34024
S -0.18838 -0.00146 -0.43458
C 0.89407 -1.34575 0.18478
H 1.89463 -1.26557 -0.24947
H 0.95418 -1.29971 1.27580
H 0.42692 -2.28454 -0.11524
C 0.87754 1.35533 0.18408
H 1.87951 1.28558 -0.24866
H 0.40027 2.28837 -0.11785
H 0.93663 1.31144 1.27523

Ate complex (B3LYP 6-31G*)

E(B3LYP 6-31G*) = -661.86941
E(B3LYP 6-311+G**) = -661.98423
E(MP2 6-311+G**) = -660.52132
E(G3(MP2)) = -660.90290

B -1.84656 -1.86169 0.60192
C -0.15476 -1.92806 0.43155
H 0.39977 -1.54914 1.30048
C -2.15882 -0.26785 0.33873
H -3.23547 -0.07205 0.45405
H -1.64772 0.40679 1.04494
H -1.88804 0.06881 -0.67519
S 0.51204 -3.58504 0.06807
H 0.15060 -1.36550 -0.46023
C -2.56999 -2.79444 -0.54070
H -3.66007 -2.65133 -0.50912
H -2.25894 -2.54836 -1.56929
H -2.41766 -3.88372 -0.42445
C -2.30602 -2.26722 2.12915
H -3.34856 -1.95290 2.28700
H -2.29094 -3.34117 2.37735
H -1.71804 -1.75694 2.91079
C 0.03666 -4.60687 1.49372
H -1.03834 -4.76510 1.42362
H 0.57088 -5.55730 1.42114
H 0.27293 -4.08949 2.42591
C 2.31703 -3.49410 0.34347
H 2.75115 -4.49101 0.22808
H 2.72755 -2.82676 -0.4175
H 2.52650 -3.09585 1.3397

Ate complex (MP2 6-31G*)

E(MP2 6-31G*) = -660.24588
E(MP2 6-311+G**) = -660.522746

B -1.81746 -1.87094 0.61182
C -0.14070 -1.93211 0.45293
H 0.40079 -1.57278 1.33801
C -2.15028 -0.29655 0.33741
H -3.22670 -0.10964 0.44943
H -1.64275 0.38243 1.03871
H -1.87890 0.02925 -0.67766
S 0.48305 -3.56249 0.06411
H 0.16153 -1.33976 -0.41942
C -2.52902 -2.80870 -0.52124
H -3.61600 -2.65816 -0.49089
H -2.21156 -2.56392 -1.54578
H -2.38050 -3.89506 -0.39929
C -2.28870 -2.25845 2.12873
H -3.34286 -1.97713 2.25296
H -2.23622 -3.32002 2.40717
H -1.73348 -1.70131 2.89878
C 0.01100 -4.57833 1.46748
H -1.05884 -4.75819 1.38961
H 0.56033 -5.51993 1.40485
H 0.23094 -4.05561 2.39970
C 2.26839 -3.49234 0.32870
H 2.69813 -4.48569 0.18199
H 2.68183 -2.80397 -0.41015
H 2.48315 -3.12689 1.33522

TS (B3LYP 6-31G*)

E(B3LYP 6-31G*) = -661.85734
E(B3LYP 6-311+G**) = -661.97203
E(MP2 6-311+G**) = -660.49676
E(G3(MP2)) = -660.881397

B -1.64350 0.03628 0.04089
C -0.38781 -0.82712 -0.30346
H 0.00491 -0.85187 -1.32478
C -2.55242 -1.15168 -0.85380
H -3.55482 -0.72697 -0.71266
H -2.36344 -1.19969 -1.93169
H -2.56778 -2.16914 -0.44862
S 1.66717 -0.06909 0.56259
H -0.25881 -1.79156 0.19350
C -2.10269 0.01964 1.59809
H -3.14109 0.36047 1.72158
H -2.03922 -0.97459 2.06607
H -1.48630 0.69532 2.21183
C -1.78584 1.47444 -0.70636
H -2.83763 1.79184 -0.75491
H -1.26077 2.28056 -0.17025

H -1.41087 1.48156 -1.74197
C 1.79947 1.53063 -0.29936
H 1.04352 2.18768 0.13254
H 2.79415 1.95635 -0.14288
H 1.59806 1.41294 -1.36741
C 2.93788 -1.02160 -0.33764
H 3.92471 -0.57273 -0.19257
H 2.94213 -2.03254 0.07699
H 2.70440 -1.06946 -1.40547

TS (MP2 6-31G*)

E(MP2 6-31G*) = -660.22459
E(MP2 6-311+G**) = -660.498554

B -1.33335 -2.01444 0.895673
C -0.16888 -2.19622 -0.106194
H 0.71213 -1.55402 -0.034950
C -1.54134 -0.51431 0.049544
H -2.45041 -0.20767 0.579392
H -0.77580 0.24542 0.225807
H -1.78113 -0.55048 -1.016411
S 1.19746 -4.07664 0.127702
H -0.39791 -2.43607 -1.146193
C -2.65842 -2.91089 0.667888
H -3.54500 -2.39863 1.063851
H -2.85927 -3.11400 -0.393025
H -2.61864 -3.88120 1.177662
C -0.97746 -1.67568 2.435055
H -1.80994 -1.14802 2.918324
H -0.80188 -2.57458 3.042326
H -0.09207 -1.03378 2.544688
C 0.04665 -5.14023 1.016069
H -0.67459 -5.52494 0.293660
H 0.58359 -5.97468 1.472389
H -0.48307 -4.56067 1.771832
C 2.17724 -3.46936 1.515227
H 2.65631 -4.30225 2.034043
H 2.95073 -2.81223 1.113137
H 1.54218 -2.90706 2.201863

BMe_2Et (B3LYP 6-31G*)

E(B3LYP 6-31G*) = -183.920035
E(B3LYP 6-311+G**) = -183.978090
E(MP2 6-311+G**) = -183.328722
E(G3(MP2)) = -183.532019

B -1.34093 -1.82764 .83056
C .16235 -2.26855 .60420
H .71085 -2.10830 1.54746
C -2.54090 -2.73969 .35586
H -2.41876 -3.78214 .68074
H -3.53345 -2.39220 .66397
H -2.53545 -2.78413 -.74546
C -1.63820 -.43739 1.52065
H -2.38408 .13991 .95600
H -2.10720 -.62556 2.49996
H -.76155 .19818 1.69176
C .44689 -3.67398 .05675
H 1.51926 -3.84962 -.09132
H .08062 -4.44996 .73996
H -.04832 -3.83628 -.90809
H .59810 -1.50844 -.06952

BMe_2Et (MP2 6-31G*)

E(MP2 6-31G*) = -183.17320
E(MP2 6-311+G**) = -183.32878

B 0.56177 -0.00185 -0.00292
C -0.78617 -0.82500 -0.04322
H -0.73759 -1.58496 0.75155
C 0.55316 1.57579 -0.00750
H -0.12162 1.97496 0.75850
H 1.53829 2.03215 0.11977
H 0.14219 1.92432 -0.96528
C 1.93605 -0.77692 0.02007
H 2.61390 -0.39328 -0.75195
H 2.43860 -0.57226 0.97544
H 1.85310 -1.86139 -0.09231
C -2.10815 -0.05992 0.03429
H -2.97040 -0.73070 -0.03264
H -2.19247 0.49013 0.97633
H -2.19303 0.66861 -0.77737
H -0.74917 -1.42195 -0.96921

SMe_2 (B3LYP 6-31G*)

E(B3LYP 6-31G*) = -478.01395
E(B3LYP 6-311+G**) = -478.06684
E(MP2 6-311+G**) = -477.22982
E(G3(MP2)) = -477.40917

S .00000 0.00000 -.59219
C .00000 1.39545 .58519
H .00000 2.31459 -.00670
H -.89456 1.38350 1.21609
H .89456 1.38350 1.21609
C .00000 -1.39545 .58519
H .00000 -2.31459 -.00670
H .89456 -1.38350 1.21609
H -.89456 -1.38350 1.21609

SMe_2 (MP2 6-31G*)

E(MP2 6-31G*) = -477.12111
E(MP2 6-311+G**) = -477.23035

S 0.00000 0.00000 0.66470
C 0.00000 1.36879 -0.51421
H 0.00000 2.29842 0.05800
H 0.89199 1.34818 -1.14516
H -0.89199 1.34818 -1.14516
C 0.00000 -1.36879 -0.51421
H 0.00000 -2.29842 0.05800
H -0.89199 -1.34818 -1.14516
H 0.89199 -1.34818 -1.14516

B. BMe_3 + $PhCHSMe_2$

$PhCHSMe_2$

E(B3LYP 6-31G*) = -748.29197
E(MP2 6-311+G**) = -746.75294

C 2.60933 .08803 -.28422
C 1.98349 1.31912 .02277
C .60275 1.26389 .33855
C -.09801 .06402 .34618
C .54181 -1.14144 .03907
C 1.90099 -1.11216 -.27495
H 3.66615 .05998 -.53344
C 2.63943 2.60783 .03705
H .08489 2.18962 .58057
H -1.15708 .06882 .59471
H -.00671 -2.07902 .04497
H 2.42229 -2.03580 -.51745
H 2.06802 3.49413 .28502
S 4.22639 3.00478 -.28970
C 4.81055 2.37892 -1.94479
H 5.86038 2.66057 -2.06877
H 4.69244 1.29768 -2.02998
H 4.19533 2.88133 -2.69331
C 5.44671 2.03509 .73139
H 6.45690 2.34184 .44454
H 5.25291 2.30414 1.77125
H 5.32081 .95995 .59493

Ate complex

E(B3LYP 6-31G*) = -892.91730
E(MP2 6-311+G**) = =-890.94140

B -1.82879 -1.83520 .56598
C -.11210 -1.87682 .39738
H .34283 -1.61426 1.36188
C -2.23339 -.26141 .32409
H -3.31121 -.13744 .50813
H -1.72344 .43678 1.00754
H -2.04461 .10103 -.69636
S .52070 -3.60098 .06622
C 1.66477 .62263 -2.66445
C 1.92400 .85720 -1.31369
C 1.36794 .02703 -.33905
C .52243 -1.03782 -.68916
C .26558 -1.25851 -2.05391
C .83586 -.44096 -3.02871
H 2.10103 1.26347 -3.42586
H 2.56282 1.68451 -1.01518
H 1.57384 .21835 .71192
H -.40009 -2.06310 -2.35043
H .62147 -.62878 -4.07758
C -2.58981 -2.80618 -.52120
H -3.67559 -2.74168 -.35735
H -2.42941 -2.52308 -1.57285
H -2.35212 -3.88408 -.45271

C -2.21932 -2.23966 2.11768
H -3.25769 -1.93172 2.31022
H -2.18706 -3.30884 2.37962
H -1.60903 -1.71330 2.87156
C -.01656 -4.62398 1.46998
H -1.08296 -4.80361 1.34631
H .53842 -5.56450 1.42429
H .16513 -4.10405 2.41238
C 2.31287 -3.52408 .41233
H 2.74970 -4.51343 .25479
H 2.74187 -2.80932 -.29234
H 2.48374 -3.18558 1.43770

TS

E(B3LYP 6-31G*) = -892.91327
E(MP2 6-311+G**) = -890.92152

B -1.48692 -1.53141 0.00109
C -0.49890 -0.34625 -0.46035
H -0.75880 0.05714 -1.44670
C -0.95967 -2.68207 -1.11490
H -1.60850 -3.55533 -0.95713
H -1.06873 -2.39038 -2.16913
H 0.07602 -3.01174 -0.96383
S -1.23724 1.60587 0.59121
C -1.32157 -2.10098 1.52515
H -2.08648 -2.86729 1.71852
H -0.35567 -2.58391 1.73368
H -1.46973 -1.32782 2.29743
C -3.05025 -1.15135 -0.32897
H -3.68386 -2.04708 -0.26113
H -3.48186 -0.43259 0.38880
H -3.21037 -0.73971 -1.33977
C -2.36492 2.29366 -0.66619
H -3.22084 1.62023 -0.72545
H -2.69482 3.29062 -0.36167
H -1.87117 2.34282 -1.64101
C 0.14527 2.78525 0.44489
H -0.19670 3.78898 0.71182
H 0.91907 2.46609 1.14569
H 0.55897 2.77987 -0.56736
C 3.76425 -0.15273 0.06711
C 3.19054 0.14532 -1.16990
C 1.80473 0.10560 -1.31936
C 0.96476 -0.26031 -0.24943
C 1.56304 -0.56177 0.99038
C 2.94575 -0.49962 1.14656
H 4.84332 -0.11598 0.19105
H 3.82008 0.41288 -2.01436
H 1.36020 0.33673 -2.28498
H 0.93333 -0.84152 1.82653
H 3.38955 -0.73247 2.11087

PhCHB(Me)$_2$Me

E(B3LYP 6-31G*) = -414.96820
E(MP2 6-311+G**) = -413.74332

B -1.34346 -1.81679 .73233
C .18022 -2.23090 .48364
H .79339 -1.82042 1.29801
C -2.55543 -2.62545 .11952
H -2.32546 -3.62077 -.27456
H -3.37020 -2.72321 .85039
H -2.98168 -2.03405 -.70588
C -1.64937 -.53507 1.60285
H -2.61182 -.05918 1.37949
H -1.70619 -.86671 2.65405
H -.86057 .22565 1.56609
C .46644 -3.74016 .38200
H 1.52768 -3.93102 .18148
H .20464 -4.24687 1.31883
H -.11150 -4.21913 -.41463
C 1.21780 .02781 -3.09082
C 1.63616 .46173 -1.83154
C 1.30776 -.27238 -.69181
C .55843 -1.45671 -.77871
C .13914 -1.87544 -2.05280
C .46762 -1.14462 -3.19514
H 1.47471 .59601 -3.98081
H 2.22392 1.37120 -1.73511
H 1.64547 .07012 .28391
H -.44824 -2.78380 -2.15571
H .13564 -1.49379 -4.16970

C. BPhMe$_2$ + CH$_2$SMe$_2$

BPhMe$_2$

E(B3LYP 6-31G*) = -336.34926
E(MP2 6-311+G**) = -335.35198

B -1.34339 -1.86315 .79336
C .15775 -2.32405 .56013
H .71452 -2.36635 1.50736
C -2.48788 -2.83445 .29957
H -2.36294 -3.81523 .78346
H -3.52317 -2.51459 .45331
H -2.35331 -3.03363 -.77456
H .24472 -3.30536 .08065
H .69989 -1.60071 -.06647
C -2.15196 1.99814 2.74668
C -3.21316 1.17631 2.36061
C -2.95441 -.04580 1.74110
C -1.63940 -.48912 1.48841
C -.59118 .36618 1.89273
C -.83607 1.59059 2.51092
H -2.34870 2.95221 3.22936
H -4.23801 1.48963 2.54243
H -3.79306 -.67068 1.44804
H .43805 .06434 1.71784
H -.00695 2.22699 2.80960

Ate complex (Me anti)

E(B3LYP 6-31G*) = -853.61505
E(MP2 6-311+G**) = -851.75073

B -1.82945 -1.79131 .52717
C -.14264 -1.83885 .39936
H .29744 -1.06733 1.04385
C -2.18477 -.21420 .21753
H -3.27273 -.06086 .25169
H -1.74633 .47171 .95961
H -1.85559 .13319 -.77393
S .60800 -3.36708 1.06271
H .24768 -1.71891 -.61890
C -2.26958 -2.19555 2.05446
H -3.34572 -2.03379 2.21091
H -2.08118 -3.24512 2.34207
H -1.75717 -1.57491 2.80613
C 2.35342 -3.33531 .52435
H 2.83868 -2.50234 1.03784
H 2.83471 -4.27372 .81253
H 2.40952 -3.19102 -.55778
C -.01377 -4.70860 .00248
H .53951 -5.61439 .26291
H -1.07726 -4.82695 .21110
H .11420 -4.44930 -1.05031
C -3.62634 -4.40672 -2.66194
C -4.01511 -4.55290 -1.32979
C -3.45518 -3.73768 -.33911
C -2.49215 -2.74984 -.62517
C -2.13864 -2.62144 -1.98534
C -2.68380 -3.42693 -2.98728
H -4.05668 -5.03733 -3.43638
H -4.75840 -5.30098 -1.06005
H -3.78372 -3.87126 .68960
H -1.42211 -1.85243 -2.27579
H -2.38094 -3.28750 -4.02363

Ate complex (Ph anti)

E(B3LYP 6-31G*) = -853.60925
E(MP2 6-311+G**) = -851.74264

B -2.04851 -2.04793 .66002
C -.35842 -1.99486 .53289
H .16919 -1.61602 1.41844
C -2.55678 -3.01455 1.88821
H -3.61348 -2.81363 2.11390
H -2.52031 -4.08810 1.63508
H -2.01604 -2.88871 2.84093
S .42555 -3.61103 .14473
H -.07820 -1.37950 -.33132
C -2.67604 -2.55343 -.76884
H -3.77313 -2.48788 -.75661
H -2.34374 -1.97114 -1.64262
H -2.43899 -3.60726 -.99301
C .48093 -4.44721 1.75922
H -.54959 -4.63948 2.05588
H 1.02992 -5.38434 1.64202
H .96559 -3.79975 2.49444
C 2.20937 -3.27919 -.08220
H 2.74361 -4.22952 -.16687
H 2.31847 -2.71549 -1.01134

H 2.59332 -2.69329 .75701
C -2.83512 2.30833 1.45328
C -2.89246 1.37948 2.49324
C -2.65380 .02578 2.24068
C -2.35561 -.46025 .95328
C -2.30309 .50610 -.07129
C -2.53802 1.86232 .16369
H -3.02252 3.36286 1.64311
H -3.12707 1.70903 3.50399
H -2.71240 -.67382 3.07184
H -2.08459 .18872 -1.09014
H -2.49494 2.57209 -.66070

TS Me migration

E(B3LYP 6-31G*) = -853.60452
E(MP2 6-311+G**) = -851.71999

B -1.31652 -1.88821 0.82768
C -0.12143 -2.11912 -0.13980
H 0.76452 -1.48575 -0.06392
C -1.58383 -0.44116 -0.13454
H -2.47161 -0.08097 0.39920
H -0.81319 0.33238 -0.06347
H -1.86317 -0.58199 -1.18237
S 1.25345 -4.08269 0.22948
H -0.28435 -2.43802 -1.16973
C -0.95192 -1.42879 2.34266
H -1.77188 -0.86674 2.81143
H -0.75041 -2.27796 3.01357
H -0.06758 -0.77616 2.38233
C 0.00104 -5.22164 0.90621
H -0.59769 -5.57869 0.06590
H 0.49705 -6.06735 1.39006
H -0.65617 -4.69785 1.60216
C 2.10484 -3.57411 1.76084
H 2.54707 -4.44672 2.24924
H 2.90228 -2.88363 1.47528
H 1.40898 -3.06963 2.43440
C -4.82951 -4.61889 0.36926
C -4.46852 -4.12915 1.62417
C -3.37036 -3.27373 1.75543
C -2.59043 -2.87456 0.65378
C -2.98908 -3.38341 -0.59908
C -4.08230 -4.23787 -0.74800
H -5.68285 -5.28402 0.26049
H -5.04284 -4.41120 2.50431
H -3.11566 -2.90614 2.74684
H -2.43609 -3.09852 -1.49373
H -4.35459 -4.60466 -1.73568

TS Ph migration

E(B3LYP 6-31G*) = -853.60030
E(MP2 6-311+G**) = -851.72160

B -1.07578 -1.60204 0.63931
C 0.10183 -1.53613 -0.42486
H 0.92980 -0.83708 -0.28270
S 1.65195 -3.31232 -0.51512
C 0.67436 -4.71601 0.11099
H -0.02965 -4.99614 -0.67516
H 1.33657 -5.55899 0.32590
H 0.11713 -4.42006 1.00057
C 2.64330 -2.91504 0.96333
H 3.26266 -3.77297 1.23809
H 3.29242 -2.07579 0.70205
H 1.99023 -2.62989 1.79065
C -2.28388 2.50458 -0.84342
C -1.35448 2.37621 0.19122
C -0.94185 1.10984 0.60591
C -1.46124 -0.06718 0.03017
C -2.37177 0.09533 -1.03315
C -2.79029 1.35690 -1.45713
H -2.60680 3.48967 -1.17135
H -0.95061 3.26365 0.67351
H -0.21824 1.03315 1.41345
H -2.78024 -0.78506 -1.52206
H -3.51062 1.44556 -2.26736
H -0.12340 -1.63940 -1.48851
C -2.26176 -2.68135 0.33524
H -3.21948 -2.34439 0.75581
H -2.44201 -2.88035 -0.73217
H -2.05910 -3.65751 0.79963
C -0.63384 -1.55711 2.20855
H -1.46240 -1.22106 2.84732
H -0.36106 -2.55860 2.57840
H 0.21998 -0.90073 2.43519

EtBMePh

E(B3LYP 6-31G*) = -375.65890
E(MP2 6-311+G**) = -374.54363

B -1.33732 -1.86972 .80676
C .17352 -2.32954 .60600
H .69865 -2.24375 1.57090
C -2.49382 -2.81640 .29279
H -2.40836 -3.80360 .77098
H -3.52036 -2.46508 .43320
H -2.35462 -3.01545 -.78051
C .42976 -3.72282 .01161
H 1.50168 -3.92969 -.09226
H .00449 -4.51289 .64211
H -.02112 -3.82715 -.98225
H .66600 -1.57111 -.02681
C -2.15623 2.00622 2.73846
C -3.21288 1.16922 2.37434
C -2.94895 -.05472 1.76002
C -1.63321 -.48826 1.49397
C -.58967 .38202 1.87885
C -.83972 1.60998 2.48769
H -2.35656 2.96242 3.21541
H -4.23887 1.47182 2.56777
H -3.78598 -.68946 1.48434
H .44125 .09189 1.69518
H -.01319 2.25770 2.76865

$PhCH_2BMe_2$

E(B3LYP 6-31G*) = -375.65831
E(MP2 6-311+G**) = -374.54692

B -1.30770 -1.90185 .86971
C .20586 -2.21680 .48308
H .81805 -1.97590 1.36737
H .49985 -1.45341 -.25653
C 1.07805 -6.20331 -.97289
C .72848 -5.18786 -1.86485
C .46223 -3.90108 -1.39485
C .53762 -3.59770 -.02745
C .89221 -4.62836 .85532
C 1.15934 -5.91693 .39100
H 1.28837 -7.20544 -1.33688
H .66718 -5.39552 -2.93033
H .19820 -3.11558 -2.10082
H .96514 -4.41536 1.92038
H 1.43627 -6.69699 1.09591
C -2.43357 -2.98967 .69472
H -3.43792 -2.66834 .99124
H -2.47009 -3.32572 -.35203
H -2.17456 -3.89546 1.26221
C -1.66012 -.46855 1.43137
H -2.44727 -.00650 .81704
H -2.10572 -.56553 2.43312
H -.82111 .23337 1.49893

D. $BPhMe_2$ + $PhCHSMe_2$

Ate complex (Me anti)

E(B3LYP 6-31G*) = -1084.66200
E(MP2 6-311+G**) = -1082.17197

B -1.85251 -1.85078 .41480
C -.19212 -2.20468 .16687
H .31662 -2.24486 1.13756
C -2.75931 -2.22390 -.89951
H -3.81203 -1.96532 -.71634
H -2.46758 -1.65187 -1.79111
H -2.76213 -3.28781 -1.19703
S .05737 -3.92906 -.51951
C -1.90079 -.23376 .71015
H -2.92856 .05662 .97049
H -1.26813 .08781 1.55200
H -1.60793 .37127 -.15950
C -.58882 -5.08333 .73046
H -1.67590 -5.01419 .71987
H -.25869 -6.08525 .44321
H -.22450 -4.81193 1.72314
C 1.84611 -4.24250 -.32567
H 2.06530 -5.25760 -.66595
H 2.36956 -3.51672 -.95039
H 2.13743 -4.11563 .72032
C -3.18603 -3.99049 4.14814
C -3.91014 -4.11986 2.96244
C -3.48872 -3.45969 1.80304

C -2.33695 -2.64897 1.76872
C -1.64385 -2.52634 2.99133
C -2.04722 -3.18074 4.15741
H -3.50801 -4.50130 5.05263
H -4.80875 -4.73395 2.93919
H -4.08020 -3.57662 .89734
H -.76680 -1.88017 3.04379
H -1.48008 -3.05118 5.07772
C 2.04048 .48884 -2.39004
C 2.29237 .42850 -1.01861
C 1.58466 -.46581 -.21474
C .59305 -1.30026 -.75589
C .34841 -1.22684 -2.13847
C 1.06885 -.34602 -2.94513
H 2.59442 1.17978 -3.01964
H 3.04421 1.07406 -.57196
H 1.78766 -.50579 .85319
H -.41961 -1.85085 -2.58426
H .86119 -.30562 -4.01118

Ate complex (Ph anti)

E(B3LYP 6-31G*) = -1084.65629
E(MP2 6-311+G**) = -1082.16617

B -2.14036 -1.92920 .55709
C -.44385 -1.97137 .32202
H .06673 -1.67049 1.24544
C -2.59854 -2.94308 1.77496
H -3.65323 -2.75099 2.01403
H -2.55624 -4.01241 1.50338
H -2.05214 -2.81988 2.72423
S .16193 -3.75534 .10216
C -2.95331 -2.33198 -.80424
H -4.03590 -2.30677 -.61267
H -2.77996 -1.67507 -1.66751
H -2.73540 -3.35969 -1.14121
C .36511 -4.35598 1.81007
H -.62618 -4.42621 2.25386
H .83576 -5.34112 1.76643
H .98557 -3.65663 2.37653
C 1.92844 -3.65092 -.36242
H 2.34602 -4.66107 -.34890
H 1.97818 -3.23660 -1.36982
H 2.46399 -2.99931 .33259
C -2.74553 2.32799 1.86967
C -2.07571 1.41748 2.68985
C -1.89471 .09931 2.26640
C -2.36321 -.36976 1.02234
C -3.03092 .57501 .22197
C -3.22500 1.89697 .63190
H -2.89459 3.35586 2.19281
H -1.70111 1.73337 3.66212
H -1.38233 -.59067 2.93757
H -3.41678 .26996 -.74761
H -3.75287 2.59259 -.01806
C 1.12890 .42287 -2.92440
C 1.33759 .79159 -1.59479
C .84656 -.00404 -.55942
C .11413 -1.17059 -.82890
C -.10245 -1.52259 -2.17290
C .40950 -.73990 -3.20823
H 1.51813 1.03721 -3.73176
H 1.88725 1.69914 -1.35935
H 1.00589 .29571 .47318
H -.68951 -2.40494 -2.41134
H .23218 -1.03299 -4.23979

TS Me migration

E(B3LYP 6-31G*) = -1084.65550
E(MP2 6-311+G**) = -1082.14588

B 0.11520 1.58710 0.20168
C 1.22592 1.20327 -0.87709
C -0.32052 3.06042 -0.52953
H -1.18835 3.40590 0.04774
H 0.46823 3.81588 -0.44124
H -0.62767 3.01721 -1.58168
S 1.86471 -1.15091 -0.33996
H 0.80070 0.84860 -1.82165
C 0.58950 1.88380 1.73631
H -0.28409 2.08568 2.37176
H 1.12528 1.04498 2.20767
H 1.23622 2.76715 1.82914
C 3.41981 -1.40647 -1.25756
H 4.18899 -0.80453 -0.76924
H 3.70731 -2.46106 -1.21915
H 3.32308 -1.08223 -2.29786
C 0.73752 -2.17785 -1.34243
H 1.08741 -3.21434 -1.34005
H -0.24820 -2.11742 -0.87886
H 0.68095 -1.80560 -2.36917
C -3.17704 -1.45243 -0.13040
C -2.42604 -1.34165 1.04107
C -1.42026 -0.37452 1.14312
C -1.11539 0.51260 0.09182
C -1.89993 0.37547 -1.07167
C -2.91051 -0.58117 -1.18975
H -3.96426 -2.19815 -0.21377
H -2.62601 -2.00530 1.88020
H -0.85777 -0.30802 2.07130
H -1.72303 1.04257 -1.91427
H -3.49456 -0.64486 -2.10604
C 5.07657 2.94994 -1.59115
C 4.26533 2.56584 -2.66113
C 3.02624 1.97915 -2.41398
C 2.55776 1.78758 -1.09733
C 3.39107 2.18491 -0.03104
C 4.63839 2.75207 -0.27777
H 6.04728 3.40117 -1.77871
H 4.60018 2.71926 -3.68341
H 2.39495 1.67996 -3.24769
H 3.05210 2.03511 0.98648
H 5.27019 3.04820 0.55520

TS Ph migration

E(B3LYP 6-31G*) = -1084.65264
E(MP2 6-311+G**) = -1082.14261

B -0.06638 0.53105 0.73292
C -0.53469 -0.14495 -0.62619
H -0.43496 -1.22458 -0.76356
S -2.89064 -0.16762 -0.74620
C -3.31434 -1.67789 0.17986
H -3.14849 -1.46574 1.23799
H -4.36663 -1.92618 0.01747
H -2.66701 -2.50093 -0.12512
C -3.30293 -0.74911 -2.42499
H -4.35839 -1.02983 -2.47323
H -3.12390 0.08376 -3.10926
H -2.66636 -1.59271 -2.69956
C 4.16579 -0.45186 -0.54961
C 3.41918 -1.37950 0.18033
C 2.09708 -1.09644 0.52364
C 1.48550 0.12664 0.18206
C 2.25330 1.02782 -0.58246
C 3.57584 0.75453 -0.93274
H 5.19596 -0.66912 -0.82124
H 3.86761 -2.32401 0.48047
H 1.53470 -1.83234 1.09266
H 1.81404 1.97372 -0.88797
H 4.14659 1.48182 -1.50589
C -0.26130 2.14814 0.83767
H 0.49525 2.59495 1.49771
H -0.19487 2.68404 -0.12141
H -1.23425 2.41826 1.27358
C -0.46545 -0.25506 2.10501
H 0.19255 0.03351 2.93640
H -1.48637 -0.00028 2.43209
H -0.42564 -1.35315 2.04317
C 0.13415 1.89032 -4.36488
C 0.78669 0.67498 -4.10032
C 0.56868 0.01159 -2.88171
C -0.30186 0.56354 -1.92766
C -0.95441 1.77884 -2.19214
C -0.73639 2.44227 -3.41083
H 0.30542 2.41149 -5.32224
H 1.47061 0.24144 -4.84995
H 1.08132 -0.94316 -2.67390
H -1.63826 2.21235 -1.44262
H -1.24903 3.39703 -3.61865

Ph_2CHBMe_2

E(B3LYP 6-31G*) = -606.70272
E(MP2 6-311+G**) = -604.96171

B -1.03288 -1.86932 .99685
C .39726 -2.24129 .36436
H 1.13379 -2.12048 1.17183
C .73714 -6.37905 -.93444
C .56247 -5.37452 -1.88548
C .46107 -4.03637 -1.49502
C .52983 -3.67292 -.14400
C .71212 -4.69625 .80141

C .81414 -6.03157 .41631
H .81821 -7.41881 -1.23997
H .50985 -5.62782 -2.94156
H .34268 -3.27058 -2.25524
H .78267 -4.43725 1.85687
H .95839 -6.80075 1.17108
C -2.33270 -2.67439 .61241
H -3.26699 -2.12746 .78395
H -2.32701 -3.07827 -.40687
H -2.36043 -3.56073 1.26875
C -1.11965 -.69825 2.05211
H -1.85726 .05322 1.73730
H -1.50543 -1.09569 3.00406
H -.17440 -.18418 2.25859
C 1.23765 .95957 -2.46002
C 2.14857 .64651 -1.44884
C 1.87534 -.38761 -.55384
C .69207 -1.13628 -.64700
C -.21773 -.80415 -1.66593
C .05333 .22982 -2.56449
H 1.44922 1.76461 -3.15863
H 3.07550 1.20700 -1.35719
H 2.59262 -.62682 .22787
H -1.14649 -1.36065 -1.76275
H -.66607 .46601 -3.34435

PhCH(Me)BMePh

E(B3LYP 6-31G*) = -606.70719
E(MP2 6-311+G**) = -604.96072

B -1.01034 -2.32144 1.75886
C .52632 -2.70773 1.52371
H .62356 -3.48762 .75851
C 2.22102 .90316 -.21679
C 2.44793 .61002 1.12810
C 1.91735 -.54880 1.69901
C 1.15187 -1.44418 .93670
C .92950 -1.13208 -.41618
C 1.45789 .02392 -.98822
H 2.63598 1.80448 -.66000
H 3.04451 1.28321 1.73886
H 2.11570 -.76011 2.74539
H .33773 -1.81133 -1.02611
H 1.27512 .23689 -2.03853
C -1.38025 -1.34095 2.94831
H -1.99634 -.49835 2.60764
H -1.99085 -1.87182 3.69449
H -.51470 -.92090 3.47007
C 1.22286 -3.22786 2.79553
H 2.30067 -3.35667 2.63518
H 1.09183 -2.55649 3.65052
H .80893 -4.20079 3.08427
C -4.24390 -3.88674 -.79527
C -4.51299 -2.91589 .17308
C -3.48008 -2.42710 .97010
C -2.14930 -2.87994 .83247
C -1.91539 -3.86224 -.15324
C -2.94067 -4.36169 -.95596
H -5.04617 -4.27172 -1.41973
H -5.52551 -2.54265 .30368
H -3.70972 -1.67351 1.71805
H -.91140 -4.25195 -.29465
H -2.72584 -5.11988 -1.70458

E. Wagner-Meerwein

$Me_2(Ph)CCH_2OH_2^+$

E(B3LYP 6-31G*) = -465.02857
E(MP2 6-311+G**) = -463.76683

C -.46415 .31167 -.10278
C .41306 -.38609 .92061
H 1.10729 .25237 1.46370
H -.10894 -1.06931 1.58916
C -1.28863 -.72141 -.89578
H -.65412 -1.28252 -1.59550
H -1.80599 -1.43793 -.24948
H -2.04160 -.21655 -1.50681
C .37340 1.15693 -1.08705
H .97637 .52350 -1.75440
H -.29174 1.73877 -1.73073
H 1.04288 1.85879 -.58247
O 1.46220 -1.40903 .23535
H .99053 -2.10974 -.26380
H 2.04493 -.93698 -.39771
C -2.85047 2.80129 2.56849
C -3.42494 1.68695 1.95614
C -2.67014 .88488 1.09992
C -1.32833 1.19562 .82779
C -.75872 2.31665 1.45872
C -1.51336 3.11297 2.31830
H -3.44050 3.42325 3.23463
H -4.46549 1.43833 2.14130
H -3.14912 .03005 .63588
H .27619 2.59219 1.27523
H -1.05583 3.97835 2.78798

TS Ph migration

E(B3LYP 6-31G*) = -465.02559
E(MP2 6-311+G**) = -463.76112

C -1.03556 -1.86734 0.38669
C 0.30603 -2.01197 -0.20728
H 1.12861 -1.45703 0.23397
O 1.01511 -3.71254 0.36289
H 0.39139 -2.20687 -1.27239
H 1.98977 -3.74948 0.33196
H 0.69347 -4.45025 -0.18762
C -1.44238 2.08376 -1.45571
C -0.86763 1.95865 -0.18845
C -0.71715 0.70228 0.39050
C -1.16544 -0.45620 -0.28004
C -1.71532 -0.31506 -1.57265
C -1.86364 0.94406 -2.14573
H -1.55993 3.06533 -1.90476
H -0.53809 2.84083 0.35145
H -0.27717 0.63249 1.37879
H -2.05898 -1.18258 -2.12471
H -2.31050 1.03587 -3.13076
C -2.06134 -2.89027 -0.12810
H -3.07660 -2.54925 0.09293
H -1.99067 -3.06980 -1.20476
H -1.91577 -3.84748 0.38350
C -1.04042 -1.83331 1.92277
H -1.99649 -1.44550 2.28534
H -0.91075 -2.84690 2.31224
H -0.23957 -1.21818 2.34074

$Me_3CCH_2OH_2^+$

E(B3LYP 6-31G*) = -273.29431
E(MP2 6-311+G**) = -272.55230

C -.41559 .32650 -.04239
C .40393 -.52728 .90901
H 1.12544 .01861 1.51737
H -.17133 -1.22465 1.51855
C -1.33285 -.55507 -.91340
H -.77191 -1.18857 -1.61671
H -1.98065 -1.19603 -.30457
H -1.97962 .07523 -1.53035
C .50328 1.20346 -.91644
H 1.11016 .61502 -1.62102
H -.09959 1.87608 -1.53318
H 1.17325 1.82351 -.31002
C -1.27022 1.22065 .88974
H -1.89770 1.87510 .27712
H -1.93233 .62670 1.52881
H -.64711 1.85721 1.52701
O 1.35373 -1.51805 .14011
H .83679 -2.12995 -.42891
H 1.97774 -1.02694 -.43791

TS Me migration

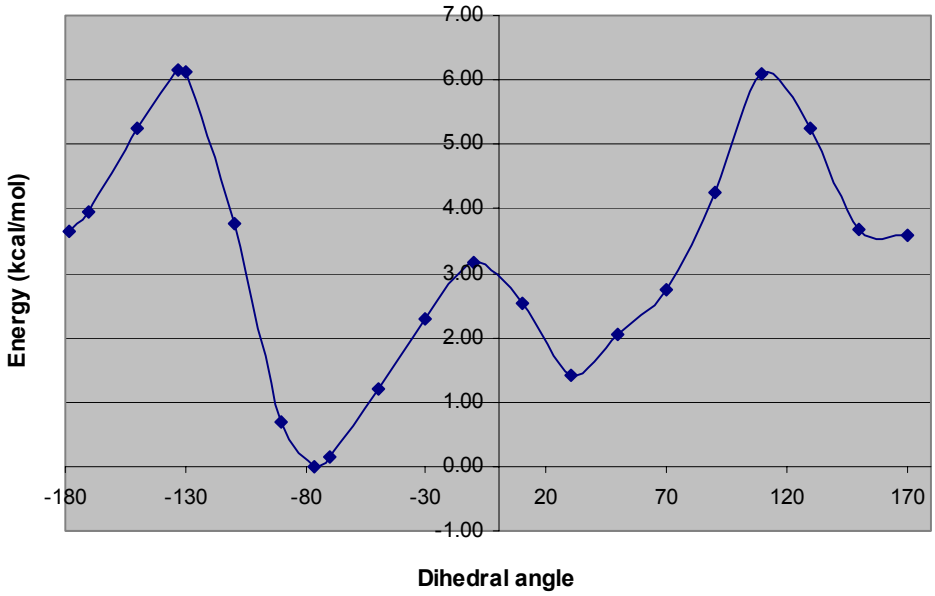
E(B3LYP 6-31G*) = -273.27352
E(MP2 6-311+G**) = -272.53432

C -1.33074 -1.98416 0.92549
C -0.28936 -2.06207 -0.01112
H 0.65938 -1.56474 0.15873
C -1.54446 -0.52785 0.00061
H -2.52534 -0.32225 0.44023
H -0.84865 0.26319 0.27304
H -1.68782 -0.60856 -1.07842
O 0.80510 -4.03279 0.57670
H -0.44042 -2.52356 -0.98071
C -2.53160 -2.89667 0.74307
H -3.40833 -2.50290 1.26481
H -2.78609 -3.04578 -0.31071
H -2.28881 -3.87179 1.17807
C -1.00333 -1.60092 2.35820

H -1.86796 -1.14995 2.85279
H -0.74184 -2.51492 2.90182
H -0.15780 -0.90990 2.42427
H 0.80323 -4.80959 -0.00638
H 1.69304 -4.01934 0.97004

F. Energy profiles

Torsional rotation around the B-C(1) profile, $Me_2PhBCH_2SMe_2$ (B3LYP 6-31G*)



Torsional rotation around the B-C(1) profile, $Me_2PhBCH_2SMe_2$ (B3LYP 6-31G*)