Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2010

SUPPORTING INFORMATION

Preparation and Characterization of $[CF_3SO_3(SiMe_3)_2]^+[B(C_6F_5)_4]^-$

Axel Schulz and Alexander Villinger**

This file includes:

1. Experimental

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Trifluoromethylsulfonatotrimethylsilane $Me_3Si–CF_3SO_3$ (99%, Sigma-Aldrich) was recondensed prior to use. Benzene and diethyl ether were dried over Na/benzophenone and freshly distilled prior to use Trimethylsilicenium tetrakis(pentafluorophenyl)borate $[Me_3Si][B(C_6F_5)_4]$ was prepared as previously reported.[1] Diethyl(trimethylsilyl)oxonium tetrakis(pentafluorophenyl)borate $[Et_2OSiMe_3][B(C_6F_5)_4]$ (**2**) has been reported previously, but was prepared according to a modified procedure. [2]

NMR: ^{29}Si INEPT, ^{19}F{^{1}H}, ^{13}C{^{1}H}, ^{13}C DEPT, ^{11}B{^{1}H}, and ^{1}H NMR spectra were obtained on a Bruker AVANCE 250, or 300 spectrometer and were referenced internally to the deuterated solvent (^{13}C, C_6D_6: $\delta_{\text{reference}}$ = 128 ppm) or to protic impurities in the deuterated solvent (^{1}H, C_6D_5H: $\delta_{\text{reference}}$ = 7.16 ppm). Measurement in neat trifluoromethylsulfonatotrimethylsilane was perfomed with C_6D_6 as external reference (denoted as $C_6D_{6(\text{ext.})}$; $\delta_{\text{reference}}$ see above), which was added in a sealed glass capillary. C_6D_6 was dried over Na/benzophenone and freshly distilled prior to use**.**

IR: Nicolet 6700 FT-IR spectrometer with a Smart Endurance ATR device was used.

Raman: Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064 nm) was used.

CHN analyses: Analysator Flash EA 1112 from Thermo Quest was used. V_2O_5 was added.

Melting points are uncorrected (EZ-Melt, Stanford Research Systems). Heating-rate 20 °C/min (clearing-points are reported).

2. Structure elucidation

X-ray Structure Determination: X-ray quality crystals of $[(SiMe_3)_2CF_3SO_3][B(C_6F_5)_4]$ (**1**) and diethyl(trimethylsilyl)oxonium tetrakis(pentafluorophenyl)borate $[Et_2OSiMe_3][B(C_6F_5)_4]$ (**2**) were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures. The samples were cooled to 173(2) K during measurement. The data was collected on a Bruker Apex Kappa-II CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$). The structures were solved by direct methods (*SHELXS-97*)[3] and refined by full-matrix least squares procedures (*SHELXL-97*).[4] Semi-empirical absorption corrections were applied (*SADABS*).[5] All non hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model. The structure of **2** is known in literature. [2]

Table S1. Crystallographic Details of **1** and **2**.

	1	**2**
Chem. Formula	$C_{31}H_{18}BF_{23}O_3SSi_2$	$C_{34}H_{22}BF_{20}O\ Si$
Form. Wght. [g mol^{-1}]	974.50	865.42
Colour	Colourless	Colourless
Cryst. system	Triclinic	Monoclinic
Space group	*P*-1	*P*2$_1$/c
a [Å]	10.319(6)	10.0769(4)
b [Å]	13.300(7)	21.4560(8)
c [Å]	15.086(9)	16.9696(6)
α [°]	68.287(10)	90.00
β [°]	82.484(12)	105.6467(19)
γ [°]	76.86(2)	90.00
V [Å^3]	1870.7(19)	3533.0(2)
Z	2	4
$\rho_{calc.}$ [g cm^{-3}]	1.730	1.627
μ [mm^{-1}]	0.300	0.202
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073
T [K]	173(2)	173(2)
Measured reflections	38916	34014
Independent reflections	10715	8099
Reflections with $I > 2\sigma(I)$	8535	5515
$R_{int.}$	0.0259	0.0404
$F(000)$	968	1732
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0360	0.0460
wR_2 (all data, F^2)	0.1035	0.1332
GooF	1.053	1.060
Parameters	556	534
CCDC #	766935	770479

Scheme S1. Numbering scheme of **1**.

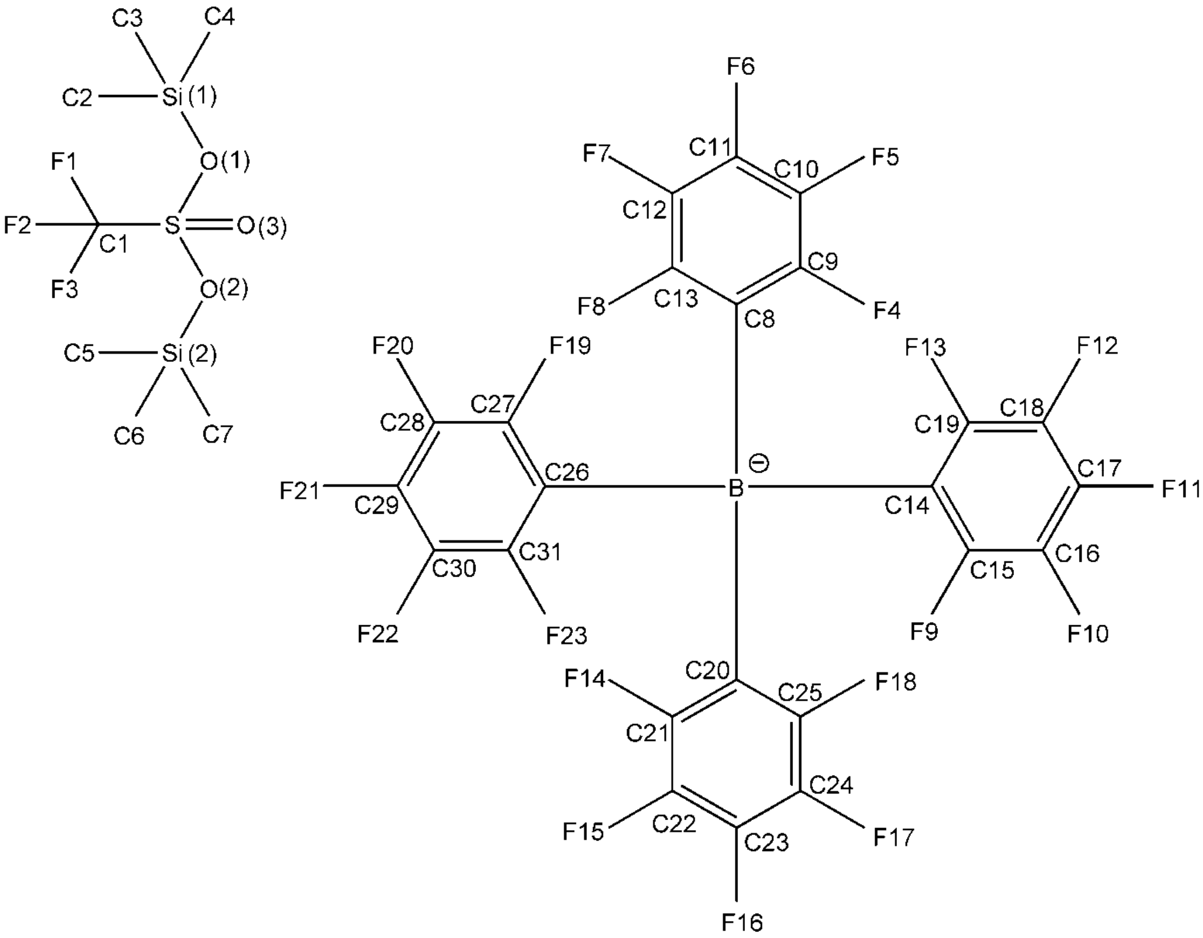


Table S2. Selected bond lenghts (Å), angles and torsion angles (°) of **1**.

S—O3	1.4109 (13)	**C5—Si2—C7**	114.32 (12)
S—O1	1.4769 (12)	**O2—Si2—C7**	104.26 (11)
S—O2	1.4774 (13)	**S—O1—Si1**	132.16 (7)
S—C1	1.830 (2)	**S—O2—Si2**	135.01 (8)
Si1—O1	1.8131 (15)	**F2—C1—F1**	110.10 (18)
Si1—C3	1.8249 (17)	**F2—C1—F3**	111.15 (17)
Si1—C4	1.833 (2)	**F1—C1—F3**	109.74 (15)
Si1—C2	1.835 (2)	**F2—C1—S**	110.41 (13)
Si2—C6	1.818 (2)	**F1—C1—S**	108.30 (14)
Si2—C5	1.8204 (18)	**F3—C1—S**	107.06 (15)

Si2—O2	1.8240 (14)	**O3—S—O1—Si1**	3.63 (14)
Si2—C7	1.834 (3)	**O2—S—O1—Si1**	−128.98 (11)
F1—C1	1.311 (2)	**C1—S—O1—Si1**	123.41 (11)
F2—C1	1.298 (2)	**C3—Si1—O1—S**	−176.83 (10)
F3—C1	1.313 (2)	**C4—Si1—O1—S**	63.76 (13)
O3—S—O1	116.77 (8)	**C2—Si1—O1—S**	−57.13 (13)
O3—S—O2	116.76 (8)	**O3—S—O2—Si2**	6.19 (15)
O1—S—O2	106.64 (8)	**O1—S—O2—Si2**	138.81 (11)
O3—S—C1	109.95 (9)	**C1—S—O2—Si2**	−114.36 (13)
O1—S—C1	101.89 (8)	**C6—Si2—O2—S**	48.10 (16)
O2—S—C1	102.98 (9)	**C5—Si2—O2—S**	169.29 (13)
O1—Si1—C3	99.67 (6)	**C7—Si2—O2—S**	−73.03 (15)
O1—Si1—C4	102.33 (7)	**O3—S—C1—F2**	−177.53 (14)
C3—Si1—C4	115.91 (9)	**O1—S—C1—F2**	57.99 (16)
O1—Si1—C2	104.08 (7)	**O2—S—C1—F2**	−52.42 (16)
C3—Si1—C2	115.65 (9)	**O3—S—C1—F1**	61.86 (13)
C4—Si1—C2	115.76 (10)	**O1—S—C1—F1**	−62.61 (13)
C6—Si2—C5	117.16 (11)	**O2—S—C1—F1**	−173.02 (11)
C6—Si2—O2	105.66 (8)	**O3—S—C1—F3**	−56.41 (15)
C5—Si2—O2	97.95 (8)	**O1—S—C1—F3**	179.12 (12)
C6—Si2—C7	114.58 (13)	**O2—S—C1—F3**	68.71 (14)

Scheme S2. Numbering scheme of **2**.

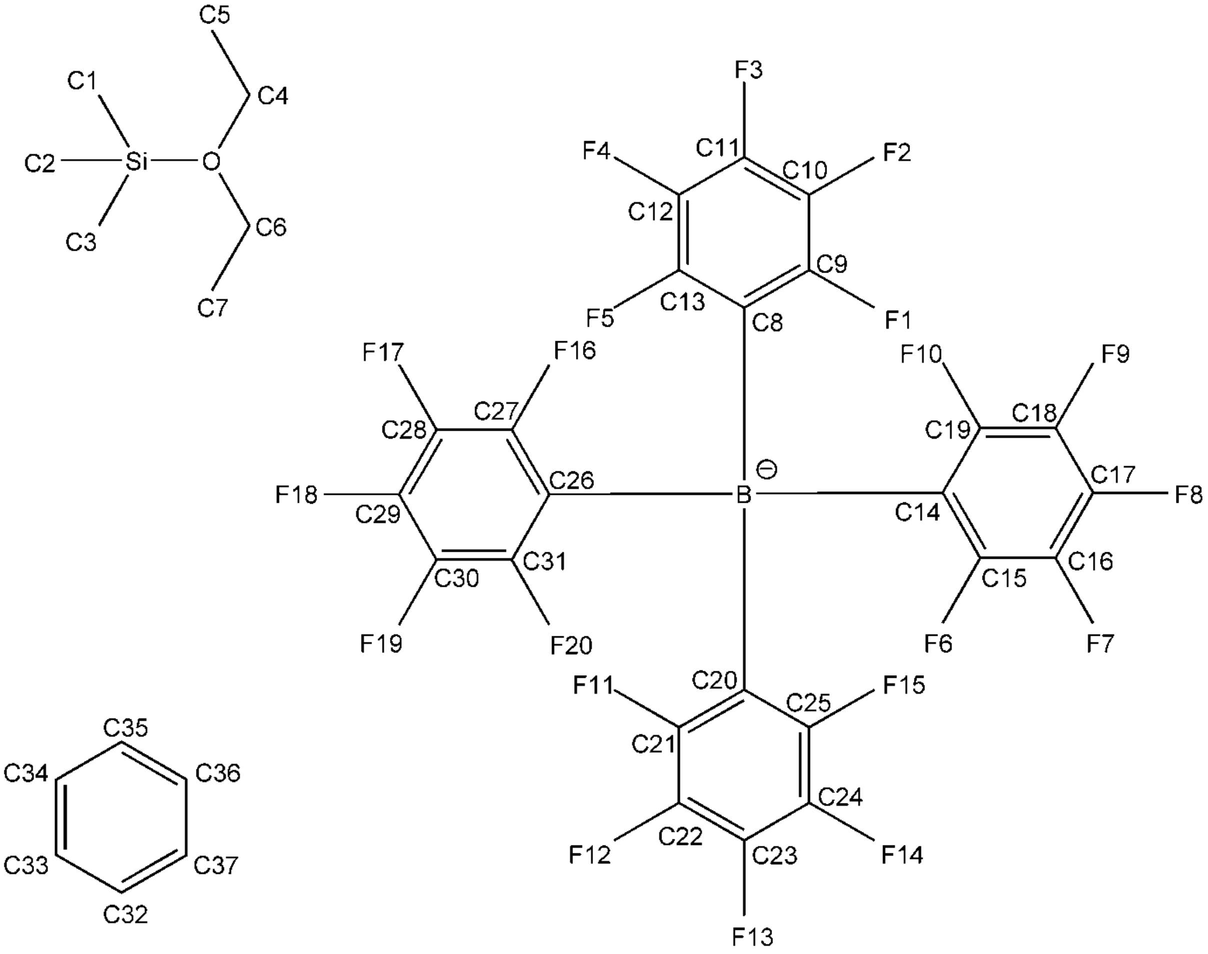


Table S3. Selected bond lenghts (Å), angles and torsion angles (°) of **2**.

Si—O	1.7906 (16)	**C6—O—Si**	120.97 (14)
Si—C1	1.826 (2)	**C4—O—Si**	123.49 (14)
Si—C2	1.834 (3)	**C5—C4—O**	111.0 (2)
Si—C3	1.842 (3)	**O—C6—C7**	110.7 (2)
O—C6	1.475 (3)	**C1—Si—O—C6**	169.65 (17)
O—C4	1.492 (3)	**C2—Si—O—C6**	51.55 (19)
C4—C5	1.485 (4)	**C3—Si—O—C6**	−69.97 (19)
C6—C7	1.491 (4)	**C1—Si—O—C4**	−25.6 (2)
O—Si—C1	104.37 (9)	**C2—Si—O—C4**	−143.73 (19)
O—Si—C2	104.15 (11)	**C3—Si—O—C4**	94.76 (19)

C1—Si—C2	112.45 (13)	**C6—O—C4—C5**	86.5 (3)
O—Si—C3	105.91 (11)	**Si—O—C4—C5**	−79.2 (2)
C1—Si—C3	113.77 (13)	**C4—O—C6—C7**	82.8 (3)
C2—Si—C3	114.87 (14)	**C1—Si—O—C6**	169.65 (17)
C6—O—C4	113.94 (17)		

3. Synthesis of bis(trimethylsilyl)trifluoromethylsulfonium tetrakis pentafluorophenyl-borate $[(SiMe_3)_2CF_3SO_3][B(C_6F_5)_4]$

$$[Me_3Si][B(C_6F_5)_4] \xrightarrow[\text{rt}]{\text{excess } Me_3Si\text{-}CF_3SO_3} [(Me_3Si)_2CF_3SO_3][B(C_6F_5)_4]$$

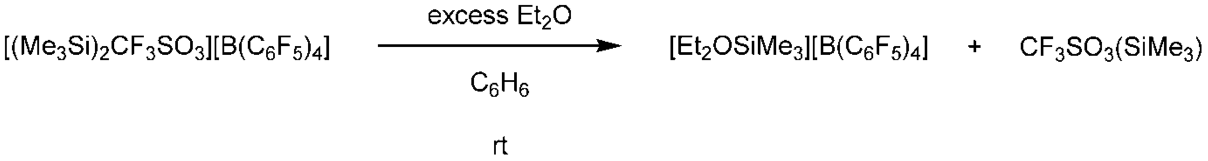
To neat trimethylsilicenium tetrakis(pentafluorophenyl)borate $[Me_3Si][B(C_6F_5)_4]$ (0.752 g, 1.0 mmol), a minimum of trifluoromethylsulfonato trimethylsilane (10 to 20 fold molar excess) was added dropwise at ambient temperatures with stirring, followed by gently heating to 60 °C. The resulting clear colourless solution was concentrated to incipient crystallisation. Storage at 5 °C for ten hours resulted in the deposition of colourless crystals. Removal of the supernatant by decantation, washing with 2 mL of neat trifluoromethylsulfonate and drying *in vacuo* yielded 0.811 g (0.832mmol, 83%) bis(trimethylsilyl)trifluoromethylsulfonium tetrakis pentafluorophenylborate $[(SiMe_3)_2CF_3SO_3][B(C_6F_5)_4]$ (**1**) as colourless crystals.

Crystals suitable for X-ray crystallographic analysis were obtained directly from the above reaction solution.

$[(Me_3Si)_2CF_3SO_3][B(C_6F_5)_4]$ (1)

Mp 127 °C (dec.). Anal. calc. % (found): C, 38.21 (40.71); H, 1.86 (1.80); ^{1}H NMR (25 °C, C_6D_6, 250.13 MHz): δ = -0.06 (s, 18H, $[((CH_3)_3Si)_2CF_3SO_3]^+$). ^{11}B NMR (25 °C, C_6D_6, 96.3 MHz): δ = -15.9. $^{13}C\{^{1}H\}$ NMR (25 °C, C_6D_6, 75.5 MHz): δ = -0.92 (s, $[((CH_3)_3Si)_2CF_3SO_3]^+$), 117.7 (q, $[((CH_3)_3Si)_2CF_3SO_3]^+$, $^{1}J(^{13}C\text{-}^{19}F)$ = 321 Hz), 125 (br, *ipso-C*), 136.9 (dm, *m*-*C*F, $^{1}J(^{13}C\text{-}^{19}F)$ = 246 Hz), 138.8 (dm, *p*-*C*F, $^{1}J(^{13}C\text{-}^{19}F)$ = 246 Hz), 149.0 (dm, *o*-*C*F, $^{1}J(^{13}C\text{-}^{19}F)$ = 242 Hz). $^{19}F\{^{1}H\}$ NMR (25 °C, C_6D_6, 282.4 MHz): δ = -167.1 (m, 8F, *m*-C*F*), -163.2 (m, 4F, *p*-C*F*), -132.1 (m, 8F, *o*-C*F*), -74.1 (s, 3F, $[((CH_3)_3Si)_2CF_3SO_3]^+$). $^{29}Si\{^{1}H\}$ NMR (25 °C, C_6D_6, 59.6 MHz): δ = -75.4 (s, $[((CH_3)_3Si)_2CF_3SO_3]^+$). ^{1}H NMR (25 °C, $C_6D_{6(ext.)}$, 250.13 MHz): δ = 0.77 (s, $(CH_3)_3Si\text{–}CF_3SO_3$), $^{1}J(^{1}H\text{-}^{13}C)$ = 121.3 Hz). $^{13}C\{^{1}H\}$ NMR (25 °C, $C_6D_{6(ext.)}$, 62.9 MHz): δ = -0.49 (s, $(CH_3)_3Si\text{–}CF_3SO_3$, $^{1}J(^{13}C\text{-}^{29}Si)$ = 60.2 Hz), 119.0 (s, $(CH_3)_3Si\text{–}CF_3SO_3$, $^{1}J(^{13}C\text{-}^{19}F)$ = 317 Hz). ^{11}B NMR (25 °C, $C_6D_{6(ext.)}$, 80.3 MHz): δ = -16.2. $^{29}Si\{^{1}H\}$ NMR (25 °C, $C_6D_{6(ext.)}$, 49.7 MHz): δ = 45.2 ($(CH_3)_3Si\text{–}CF_3SO_3$). $^{19}F\{^{1}H\}$ NMR (25 °C, $C_6D_{6(ext.)}$, 282.4 MHz): δ = -167.9 (m, 8F, *m*-C*F*), -164.4 (m, 4F, *p*-C*F*), -132.2 (m, 8F, *o*-C*F*), -78.0 (($(CH_3)_3Si–CF_3SO_3$). IR (ATR, 16 scans): 2979 (w), 2917 (w), 1644 (m), 1513 (s), 1460 (s), 1413 (m), 1383 (m), 1373 (m), 1367 (m), 1354 (m), 1268 (m), 1245 (s), 1200 (m), 1115 (m), 1107 (m), 1085 (s), 1008 (m), 974 (s), 912 (w), 907 (w), 867 (s), 834 (m), 814 (s), 773 (s), 770 (s), 756 (s), 727 (w), 684 (m), 662 (s), 623 (s), 612 (m), 604 (m), 574 (m), 542 (m). Raman (300 mW, 25 °C, 10000 scans, cm^{-1}, rel. intensity > 1): = 2984 (5), 2917 (10), 2754 (3), 1647 (5), 1430 (2), 1389 (3), 1375 (3), 1300 (2), 1285 (2), 1096 (2), 1084 (2), 1072 (2), 1013 (2), 987 (2), 924 (2), 878 (2), 822 (4), 784 (3), 726 (2), 647 (2), 621 (5), 585 (8), 492 (6), 476 (6), 450 (7), 422 (6), 396 (6), 343 (2), 300 (2), 245 (4), 184 (3), 160 (4).

4. Synthesis of diethyl(trimethylsilyl)oxonium tetrakis pentafluorophenylborate $[Et_2OSiMe_3][B(C_6F_5)_4]$ (2)



$$[(Me_3Si)_2CF_3SO_3][B(C_6F_5)_4] \xrightarrow[C_6H_6 \\ rt]{excess\ Et_2O} [Et_2OSiMe_3][B(C_6F_5)_4] + CF_3SO_3(SiMe_3)$$

To a stirred suspension of bis(trimethylsilyl)trifluoromethylsulfonium tetrakis pentafluorophenylborate $[(SiMe_3)_2CF_3SO_3][B(C_6F_5)_4]$ (**1**) (0.487g, 0.5mmol) in benzene (30mL), diethylether (1mL) was added dropwise at ambient temperature. The resulting clear colourless solution (two layers) was concentrated to incipient crystallisation. Storage at 5 °C for ten hours resulted in the deposition of colourless crystals. Removal of the supernatant by decantation, washing with benzene (1mL) and drying *in vacuo* yielded 0.382g (0.46mmol, 92%) diethyl(trimethylsilyl)oxonium tetrakis(pentafluorophenyl)borate $[Et_2OSiMe_3][B(C_6F_5)_4]$ (**2**) as a colourless solid. Mp 152 °C (dec., ca. 87°C loss of C_6H_6). IR (ATR, 16 scans): 2997 (w), 2914 (w), 1644 (m), 1512 (s), 1455 (s), 1382 (m), 1326 (w), 1269 (m), 1190 (w), 1147 (w), 1082 (s), 1029 (w), 970 (s), 906 (w), 883 (m), 865 (m), 846 (m), 826 (m), 796 (w), 769 (m), 755 (s), 683 (m), 660 (s), 644 (w), 611 (m), 602 (m), 573 (m), 550 (w). Crystals suitable for X-ray crystallographic analysis were obtained directly from the above reaction solution.

5. IR, Raman and NMR data of trifluoromethylsulfonato trimethylsilane $Me_3Si–CF_3SO_3$

^{1}H NMR (25 °C, C_6D_6, 300.13 MHz): δ = -0.07 (s, 9H, $^1J(^1H-^{13}C)$ = 121 Hz). $^{13}C\{^1H\}$ NMR (25 °C, C_6D_6, 75.5 MHz): δ = -0.43 (s, $(CH_3)_3Si–CF_3SO_3$, $^1J(^{13}C-^{29}Si)$ = 60.1 Hz), 119.1 (q, $(CH_3)_3Si–CF_3SO_3$, $^1J(^{13}C-^{19}F)$ = 317 Hz). $^{29}Si\{^1H\}$ NMR (25 °C, C_6D_6, 59.6 MHz): δ = 43.1. $^{19}F\{^1H\}$ NMR (25 °C, C_6D_6, 282.4 MHz): δ = -77.6.

^{1}H NMR (25 °C, $C_6D_{6(ext.)}$, 250.13 MHz): δ = 0.81 (s, 9H, $Si(CH_3)_3$, $^2J(^1H-^{29}Si)$ = 7.2 Hz, $^1J(^1H-^{13}C)$ = 121.4 Hz). $^{13}C\{^1H\}$ NMR (25 °C, $C_6D_{6(ext.)}$, 62.9 MHz): δ = -0.43 (s, $Si(CH_3)_3$, $^1J(^{13}C-^{29}Si)$ = 60.3 Hz), 119.0 (s, CF_3, $^1J(^{13}C-^{19}F)$ = 317 Hz). $^{29}Si\{^1H\}$ NMR (25 °C, $C_6D_{6(ext.)}$, 49.7 MHz): δ = 44.0. $^{19}F\{^1H\}$ NMR (25 °C, $C_6D_{6(ext.)}$, 282.4 MHz): δ = -78.1.

Raman (100 mW, 25 °C, 250 scans, cm^{-1}): = 2977 (4), 2912 (10), 1418 (1), 1396 (1), 1248 (2), 1156 (1), 967 (1), 772 (3), 616 (4), 545 (1), 516 (1), 422 (1), 346 (1), 330 (1), 315 (1), 264 (1), 228 (1), 197 (1), 158 (1).

IR (ATR, 16 scans): 2971 (w), 2911 (w), 1387 (s), 1315 (w), 1263 (m), 1246 (m), 1197 (s), 1152 (m), 1099 (w), 960 (s), 832 (s), 767 (s), 707 (w), 670 (w), 620 (s), 570 (s), 543 (s).

6. Computational Details

All calculations were carried out with the Gaussian 03 package of molecular orbital programs.[6] Structures were optimized within the DFT approach at the pbe1pbe level with an aug-cc-pVDZ.[7] Vibrational frequencies were also computed, to include zero-point vibrational energies in thermodynamic parameters and to characterize all structures as minima on the potential energy surface. A natural bond orbital analysis (NBO)[8] was performed at the same level, to study the charge distribution, bond polarization and hybridization effects.

7. References

---

[1] J. B. Lambert, S. Zhang, S. M. Ciro, *Organometallics* **1994,** *13*, 2430; M. Lehmann, A. Schulz, A. Villinger, *Angew. Chem.* **2009**, *121*, 7580.

[2] M. Driess, R. Barmeyer, C. Monse, K. Merz, *Angew. Chem. Int. Ed.* **2001**, 40(*12*), 2308.

[3] G. M. Sheldrick: SHELXS-97: Program for the Solution of Crystal Structures, University of Göttingen, Germany 1997.

[4] G. M. Sheldrick: SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, Germany 1997.

[5] G. M. Sheldrick: SADABS. Version 2. University of Göttingen, Germany 2004.

[6] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[7] a) T. H. Dunning, Jr. *J. Chem. Phys.* **1989**, *90*, 1007; b) D.E. Woon and T.H. Dunning, Jr. *J. Chem. Phys.* **1993**, *98*, 1358; c) K.A. Peterson and T.H. Dunning, Jr. *J. Chem. Phys.* **2002**, *117*, 10548.

---

[8] a) Glendening, E. D; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO Version 3.1*; b) Carpenter, J. E.; Weinhold, F. *J. Mol. Struc. (Theochem)* **1988**, *169*, 41; c) Weinhold, F.; Carpenter, J. E. *The Structure of Small Molecules and Ions*, Plenum Press, **1988**, 227; d) Weinhold, F.; Landis, C. *Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, **2005** and references therein.