The Thioether-Methyleneborane

$(PhSCH_2B(C_6F_5)_2)_2$: Synthesis and Reactivity with

Donors and Alkynes

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Thermodynamic Calculations for **1**

From the VT NMR of compound **1**, one can calculate the change in enthalpy (ΔH), change in entropy (ΔS), and change in Gibbs free energy (ΔG) of the system. By measuring the integral of the peak corresponding to the CH_2 protons of the dimer of **1** that exists at -60°C and compare that to the new CH_2 peak that grows in as temperatures increase to 55°C, one can obtain a ratio and calculate the equilibrium constant K_{eq}. At room temperature the ^1H resonances were referenced internally to the residual protonated solvent resonance (δ 2.09 for d_8-toluene) and at every other temperature the ^1H resonances were referenced externally to the aryl protons of trimethoxyborane (δ 6.14). A Van't Hoff plot was then constructed by plotting the natural logarithm of K_{eq} against the inversion of the temperature (Figure S.2). The data used to construct the Van't Hoff plot are tabulated in Table S.1. A stacked plot of the methylene resonances is shown in Figure S.1.
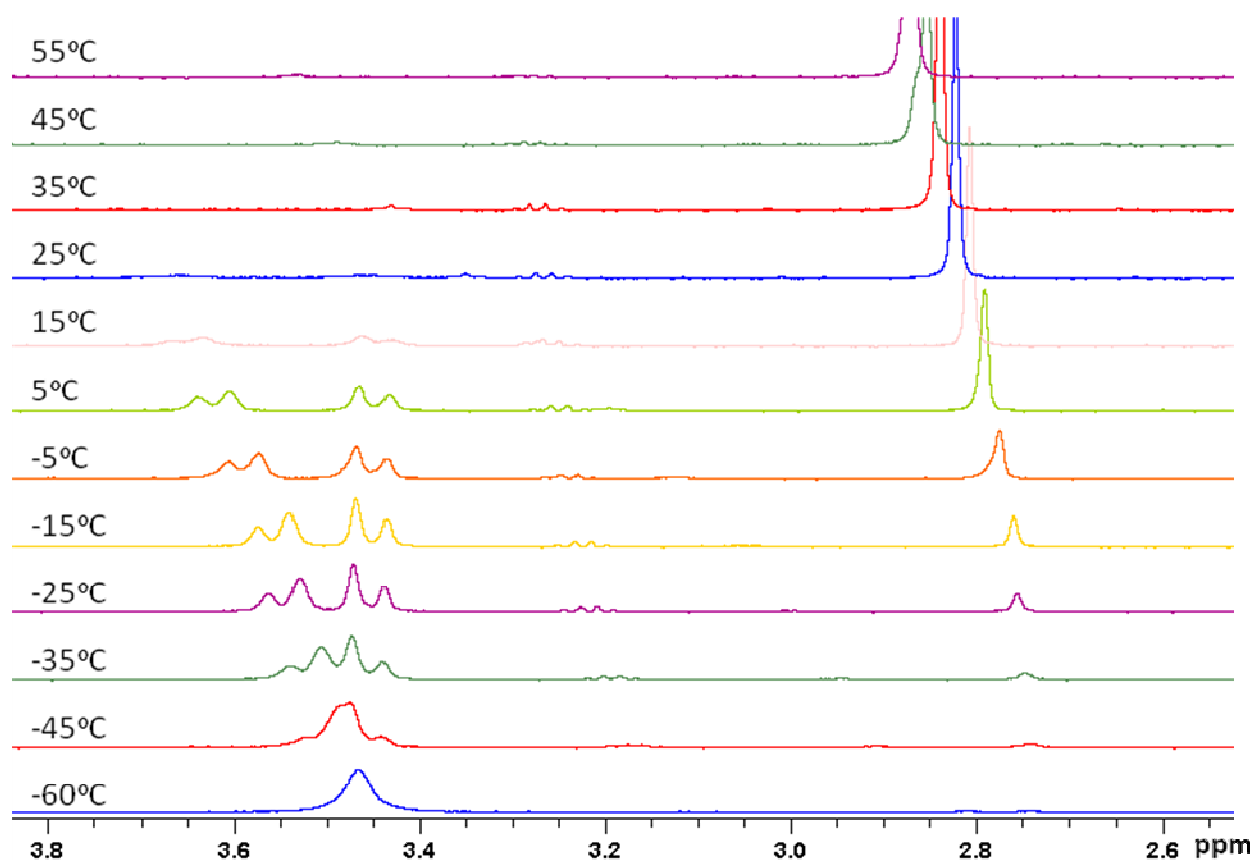
Figure S.1 VT of ^{1}H NMR tracking the methylene shift of **1**

Table S.1 Data used in Van't Hoff plot for $PhSCH_2B(C_6F_5)_2$

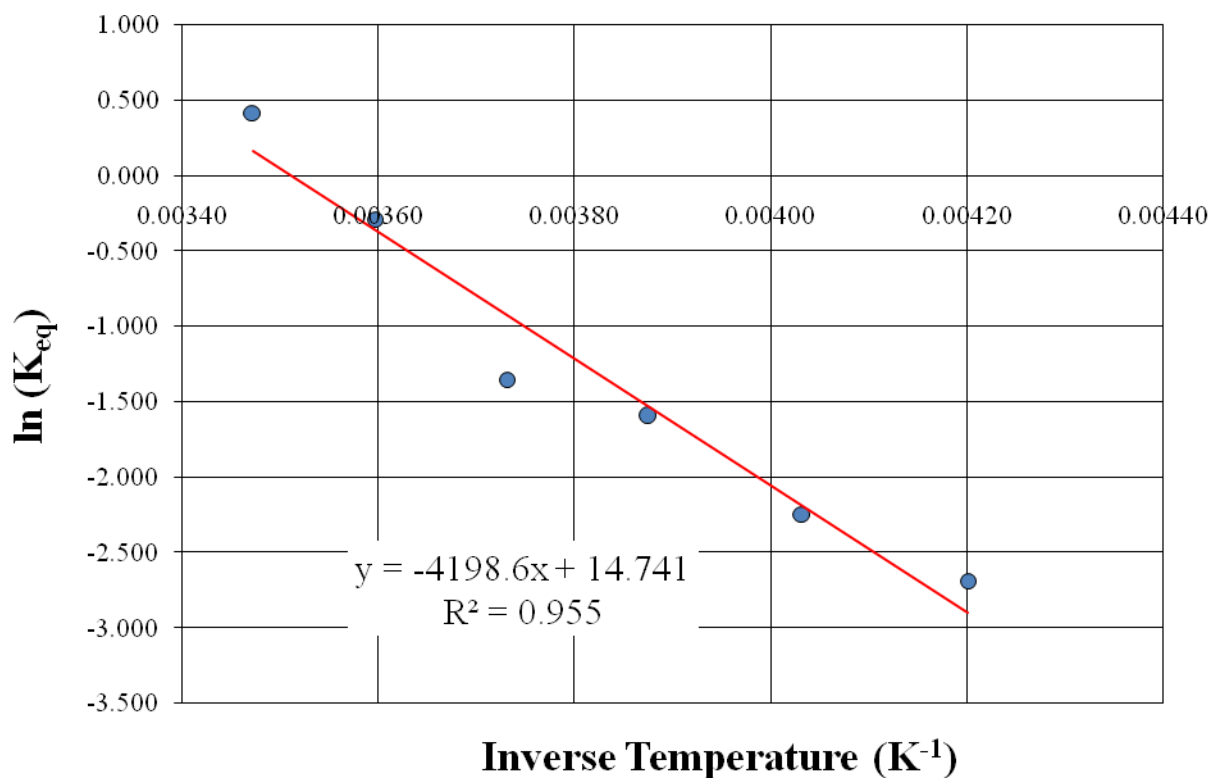| T (°C)	T (K)	1/T (K^{-1})	∫ monomer	∫ dimer	K_{eq} = ∫ monomer/ ∫ dimer	ln(K_{eq})
15	288	0.00347	1756.29	1157.66	1.517	0.417
5	278	0.00360	1155.72	1542.29	0.749	-0.289
-5	268	0.00373	806.69	3118.70	0.259	-1.352
-15	258	0.00388	431.39	2118.89	0.204	-1.592
-25	248	0.00403	267.36	2523.94	0.106	-2.245
-35	238	0.00420	187.43	2747.12	0.068	-2.685

Figure S.2 Van't Hoff plot showing the relationship between the dimer and monomer of compound **1**

$\Delta G = \Delta H - T\Delta S = -RT\ln(K_{eq})$

$\ln(K_{eq}) = -\Delta H/(RT) + \Delta S/R$

$\Delta H^{\circ} = -mR = -(-4198.6 \text{ K})(8.314 \text{ J/(mol·K)}) = 34.9 \text{ kJ/mol}$

$\Delta S^{\circ} = bR = (14.741)(8.314 \text{ J/(mol·K)}) = 122.6 \text{ J/(mol·K)}$

$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = (34.9 \text{ kJ/mol}) - (298.15 \text{ K})(122.6 \text{ J/(mol·K)}) = -1.63 \text{ kJ/mol}$

$K_{eq} = e^{-\Delta G^{\circ}/RT} = e^{-(-1.63 \text{ kJ/mol})/(8.314 \text{ J/(mol·K)}\times298.15 \text{ K})} = 1.93$

Thermodynamics of $B(C_6F_5)_3 \cdot SMe_2$

VT NMR was performed in order to determine the change in enthalpy (ΔH), change in entropy (ΔS), and change in Gibbs free energy (ΔG) of the system described in Scheme S.1. At room temperature the ^1H resonances were referenced internally to the residual protonated solvent resonance (δ 6.94 for C_6D_5Br) and at every other temperature the ^1H resonances were referenced externally to the methyl protons of trimethoxyborane (δ 3.51). The adduct $B(C_6F_5)_3 \cdot SMe_2$ and free $B(C_6F_5)_3$ and SMe_2 were monitored by the two peaks in the ^1H NMR corresponding to the methyl protons. At room temperature there is only one peak occurring at δ 1.60 for the dimethylsulfide adduct (δ_{adduct}). At 140°C there is no more adduct and there is only free $B(C_6F_5)_3$ and SMe_2 species in which the methyl protons occur at δ 1.84 (δ_{free}). At temperatures between 25−140°C, this peak shift (δ_{peak}) was monitored, as displayed in Figure S.3.

$$B(C_6F_5)_3 \cdot SMe_2 \underset{rt}{\overset{140°C}{\rightleftharpoons}} B(C_6F_5)_3 + SMe_2$$
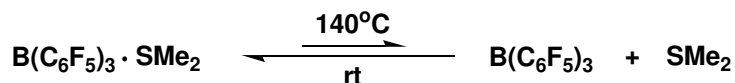
Scheme S.1 Relationship studied of the adduct $B(C_6F_5)_3 \cdot SMe_2$ and free $B(C_6F_5)_3$ and SMe_2
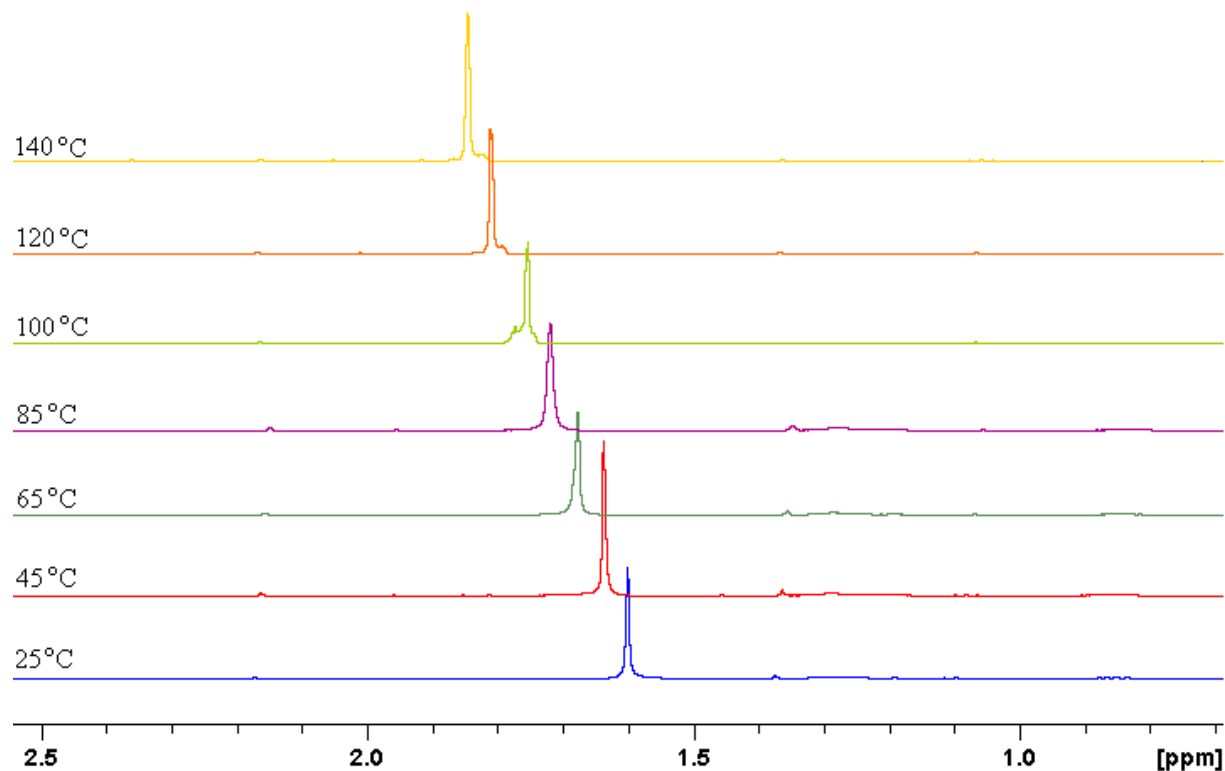
Figure S.3 VT of ^{1}H NMR tracking the methyl shift from adduct to free dimethylsulfide

Using these chemical shifts, the ratio of adduct converted to free species can be calculated by the expression:

$$\text{Ratio converted} = |\delta_{\text{peak}} - \delta_{\text{adduct}}| / |\delta_{\text{adduct}} - \delta_{\text{free}}|$$

From this ratio, the concentrations of the adduct [B(C$_6$F$_5$)$_3$·SMe$_2$], and free species [B(C$_6$F$_5$)$_3$], [SMe$_2$], can be calculated by knowing the initial concentration of [B(C$_6$F$_5$)$_3$·SMe$_2$]$_i$ from the beginning.

The initial concentration of [B(C$_6$F$_5$)$_3$·SMe$_2$]$_i$ is calculated from the initial number of moles of adduct $N_{\text{B(C}_6\text{F}_5)_3\cdot\text{SMe}_2}$ and the volume of the sample V. The number of moles of adduct can be calculated from the number of moles of trimethoxyborane, TMB, (N_{TMB}), the integration of the methoxy protons of TMB ($\int_{\text{TMB}}$), the integration of the methyl protons of B(C$_6$F$_5$)$_3$·SMe$_2$

($\int_{B(C_6F_5)_3 \cdot SMe_2}$) and the number of protons associated with each integration (at 25°C). The expression is shown below:

$$N_{B(C_6F_5)_3 \cdot SMe_2} = N_{TMB} \times (9H/\int_{TMB}) \times (\int_{B(C_6F_5)_3 \cdot SMe_2}/6H)$$

There were 6 mg of TMB added to the sample (m_{TMB}) and thus $N_{B(C_6F_5)_3 \cdot SMe_2}$ can be determined:

$$N_{TMB} = m_{TMB}/M_{TMB} = (6.0 \times 10^{-3} \text{ g})/(168.19 \text{ g/mol}) = 3.57 \times 10^{-5} \text{ mol}$$

$$N_{B(C_6F_5)_3 \cdot SMe_2} = 3.57 \times 10^{-5} \text{ mol} \times (9H/10000) \times (1546.5/6H) = 8.28 \times 10^{-6} \text{ mol}$$

The volume of the sample can be calculated by the following formula:[1]

$$V = (0.1435 \times \text{solution height}) - 0.0249 = (0.1435 \times 6.8 \text{ mL}) - 0.0249 = 0.951 \text{ mL}$$

$$= 9.51 \times 10^{-3} \text{ L}$$

The initial concentration $[B(C_6F_5)_3 \cdot SMe_2]_i$ is:

$$[B(C_6F_5)_3 \cdot SMe_2]_i = N_{B(C_6F_5)_3 \cdot SMe_2}/V = 8.28 \times 10^{-6} \text{ mol}/9.51 \times 10^{-3} \text{ L} = 0.00870 \text{ mol/L}$$

This concentration was then multiplied by the ratio converted to determine the concentrations of $[B(C_6F_5)_3] = [SMe_2]$. The remaining concentrations of $[B(C_6F_5)_3 \cdot SMe_2]_r$ were simply the subtraction of $[B(C_6F_5)_3 \cdot SMe_2]_i - [B(C_6F_5)_3]$ or $[B(C_6F_5)_3 \cdot SMe_2]_i - [SMe_2]$, since $B(C_6F_5)_3$ and SMe_2 were present in a 1:1 ratio. The equilibrium constant K_{eq} was determined by:

$$K_{eq} = [B(C_6F_5)_3] \times [SMe_2] / [B(C_6F_5)_3 \cdot SMe_2]$$

A Van't Hoff plot was then constructed by plotting the natural logarithm of K_{eq} against the inverse of the temperature (Figure S.4). The data used to construct the Van't Hoff plot are tabulated in Table S.2.

Table S.2 Data used in Van't Hoff plot for $B(C_6F_5)_3 \cdot SMe_2$

T (K)	1/T (K^{-1})	[B(C$_6$F$_5$)$_3$·SMe$_2$] (mol/L)	[B(C$_6$F$_5$)$_3$] = [SMe$_2$] (mol/L)	$K_{eq} = \dfrac{[B(C_6F_5)_3][SMe_2]}{[B(C_6F_5)_3 \cdot SMe_2]}$	ln(K$_{eq}$)
308	0.00325	0.00804	0.000661	5.43×10^{-5}	-9.82
318	0.00314	0.00740	0.00130	2.30×10^{-4}	-8.38
328	0.00305	0.00667	0.00203	6.17×10^{-4}	-7.39
338	0.00296	0.00601	0.00269	1.20×10^{-3}	-6.72
348	0.00287	0.00532	0.00338	2.15×10^{-3}	-6.14
358	0.00279	0.00448	0.00422	3.97×10^{-3}	-5.53

$$y = -9148.5x + 20.215$$
$$R^2 = 0.977$$
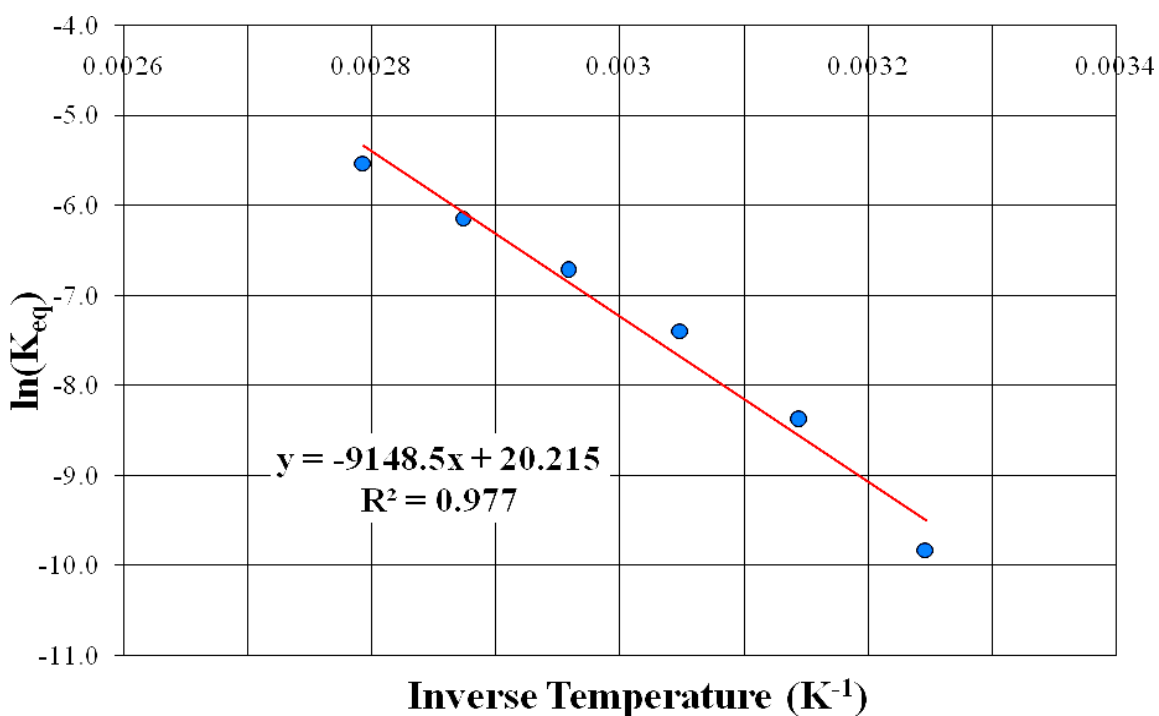
Figure S.4 Van't Hoff plot of $B(C_6F_5)_3 \cdot SMe_2$

The change in enthalpy (ΔH), change in entropy (ΔS), and change in Gibbs free energy (ΔG) of the system can be expressed in the following two equations:

$$\Delta G = \Delta H - T\Delta S = -RT\ln(K_{eq})$$

$$\ln(K_{eq}) = -\Delta H/(RT) + \Delta S/R$$

$$\Delta H^\circ = -mR = -(-9148.5 \text{ K})(8.314 \text{ J/(mol·K)}) = 76.1 \text{ kJ/mol}$$

$$\Delta S^\circ = bR = (20.215)(8.314 \text{ J/(mol·K)}) = 168.1 \text{ J/(mol·K)}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (76.1 \text{ kJ/mol}) - (298.15 \text{ K})(168.1 \text{ J/(mol·K)}) = 26.0 \text{ kJ/mol}$$

$$K_{eq} = e^{-\Delta G^\circ/RT} = e^{-(26.0 \text{ kJ/mol})/(8.314 \text{ J/(mol·K)} \times 298.15 \text{ K})} = 2.8 \times 10^{-5}$$

(1)   Heiden, Z. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2007**, *129*, 14303.