Supporting Information for

Unexpected New Chemistry of the Bis(thioimidazolyl)methanes

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**Experimental. General Methods.** Potassium hexafluorophosphate, tetrabutylammonium bromide and hexafluorophosphate and 2-mercapto-3-methylimidazole and most solvents were used as received. Acetonitrile used for voltammetric studies was dried over CaH$_2$ and distilled under nitrogen prior to use. Silica gel (0.040-0.063 mm, 230-400 mesh) and neutral alumina (avg. particle size 50-200 µm) were used for chromatographic separations as indicated. Chemical shifts were referenced to solvent resonances at either $\delta_H$ 7.27, $\delta_C$ 77.23 for CDCl$_3$; $\delta_H$ 2.05, $\delta_C$ 29.8 for acetone-d$_6$; $\delta_H$ 1.94, $\delta_C$ 1.39 for CD$_3$CN; and $\delta_H$ 4.92, $\delta_C$ 48.0 for CD$_3$OD. Melting point determinations were made on samples contained in glass capillaries and are uncorrected.
X-Ray Structure Determination, CH₂(N-tim)₂ (1)

X-ray intensity data from a colorless needle were measured at 150(1) K using Mo Kα radiation, λ = 0.71073 Å. Raw data frame integration and Lp corrections were performed with SAINT+. Final unit cell parameters were determined by least-squares refinement of 4787 reflections with I > 5σ(I) from the data set. Analysis of the data showed negligible crystal decay during collection. An empirical absorption correction was applied with SADABS. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F² were performed with SHELXTL.

C₉H₁₂N₄S₂ crystallizes in the orthorhombic space group Fdd2 as determined uniquely by the pattern of systematic absences in the intensity data. The asymmetric unit contains half a molecule located on a two-fold axis of rotation. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms with refined isotropic displacement parameters. The final absolute structure (Flack) parameter is 0.1(1), which, though somewhat ambiguous owing the absence of any atoms heavier that sulfur, does indicate the correct orientation of the polar axis.


Figure S1.

Molecule on two-fold axis. View down two-fold. Displacement ellipsoids drawn at the 50% probability level.
Table 1. Crystal data and structure refinement for CH$_2$(N-tim)$_2$ (1).

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<th>Value</th>
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<td>Identification code</td>
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<tr>
<td>Temperature</td>
<td>150(1) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
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<td>Fdd2</td>
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<td>Unit cell dimensions</td>
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<tr>
<td></td>
<td>b = 36.256(3) Å    β = 90°</td>
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<tr>
<td></td>
<td>c = 4.4236(3) Å    γ = 90°</td>
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<td>Z</td>
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<td>Density (calculated)</td>
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<td>Absorption coefficient</td>
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<tr>
<td>F(000)</td>
<td>1008</td>
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<td>Crystal size</td>
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<td>Index ranges</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Max. and min. transmission</td>
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<tr>
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<td>Full-matrix least-squares on F$^2$</td>
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<td>Goodness-of-fit on F$^2$</td>
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<td>Final R indices [l$&gt;$2sigma(l)]</td>
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<td>R indices (all data)</td>
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<tr>
<td>Absolute structure parameter</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.292 and -0.175 e.Å$^{-3}$</td>
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Table 3. Bond lengths [Å] and angles [°] for CH$_2$(N-tim)$_2$ (1).

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<th>Bond</th>
<th>Distance</th>
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<td>S(1)-C(1)</td>
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<tr>
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<tr>
<td>C(4)-H(4C)</td>
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<td>C(5)-N(1)</td>
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<td>N(1)-C(1)-S(1)</td>
<td>127.35(15)</td>
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<td>C(3)-C(2)-N(1)</td>
<td>107.34(17)</td>
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<td>C(3)-C(2)-H(2)</td>
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<td>107.32(17)</td>
</tr>
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<td>C(2)-C(3)-H(3)</td>
<td>126.3</td>
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<tr>
<td>N(2)-C(3)-H(3)</td>
<td>126.3</td>
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<td>N(2)-C(4)-H(4A)</td>
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<td>N(2)-C(4)-H(4B)</td>
<td>109.5</td>
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<tr>
<td>H(4A)-C(4)-H(4B)</td>
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<td>N(2)-C(4)-H(4C)</td>
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<td>H(4A)-C(4)-H(4C)</td>
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<td>H(4B)-C(4)-H(4C)</td>
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</tr>
<tr>
<td>N(1)#1-C(5)-N(1)</td>
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Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+3/2,z
X-Ray Structure Determination, CH$_2$(µ-C$_4$H$_7$N$_2$S)$_2$CH$_2$)(PF$_6$)$_2$ (5·CH$_3$CN)

X-ray intensity data from a colorless bar were measured at 150(1) K using Mo Kα radiation, $\lambda = 0.71073$ Å.$^1$ Raw data frame integration and Lp corrections were performed with SAINT+.$^1$ Final unit cell parameters were determined by least-squares refinement of 7272 reflections with $I > 5\sigma(I)$ from the data set. Analysis of the data showed negligible crystal decay during collection. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against $F^2$ were performed with SHELXTL.$^2$

(C$_{10}$H$_{14}$N$_4$S$_2$)(PF$_6$)$_2$·CH$_3$CN crystallizes in the space group P2$_1$/c as determined uniquely by the pattern of systematic absences in the intensity data. The asymmetric unit contains one C$_{10}$H$_{14}$N$_4$S$_2^{2+}$ cation, two PF$_6$~ counterions and an acetonitrile molecule of crystallization. One PF$_6$~ anion (P2, F7-F12) is disordered over two close orientations (A/B) in the ratio A/B = 0.887(4) / 0.113(4). A total of 21 restraints were employed to restrain the geometry of the minor disorder component to be similar to that of the major component (one SHELX SAME instruction). All non-hydrogen atoms were refined with anisotropic displacement parameters except the F atoms of the minor disorder component (isotropic). Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms.

Figure S2.

Asymmetric unit.


<table>
<thead>
<tr>
<th>Identification code</th>
<th>CH₂(µ-C₄H₅N₂S)₂CH₂][PF₆]₂ (5·CH₃CN)</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₂H₁₇F₁₂N₅P₂S₂</td>
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<td>Wavelength</td>
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<td>Crystal system</td>
<td>Monoclinic</td>
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<td>Space group</td>
<td>P2₁/c</td>
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<tr>
<td>Unit cell dimensions</td>
<td>a = 16.1527(8) Å, α = 90°, b = 10.0182(5) Å, β = 103.5910(10)°, c = 13.8856(7) Å, γ = 90°.</td>
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<td>Volume</td>
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<td>Z</td>
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<td>Density (calculated)</td>
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<td>Largest diff. peak and hole</td>
<td>0.476 and -0.376 e.Å⁻³</td>
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Table 2.  Bond lengths [Å] and angles [°] for CH$_2$(µ-C$_4$H$_5$N$_2$S)$_2$CH$_2$)(PF$_6$)$_2$ (5·CH$_3$CN)

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<th>Bond</th>
<th>Length/Angle</th>
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<td>S(1)-C(11)</td>
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<td>P(2A)-F(9A)</td>
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P(2A)-F(8A)  1.588(2)
P(2A)-F(11A)  1.591(2)
P(2A)-F(10A)  1.597(2)
P(2A)-F(12A)  1.598(2)
P(2B)-F(11B)  1.562(14)
P(2B)-F(10B)  1.573(14)
P(2B)-F(7B)  1.575(15)
P(2B)-F(9B)  1.589(15)
P(2B)-F(12B)  1.595(14)
P(2B)-F(8B)  1.611(14)

C(11)-S(1)-C(2)  102.79(9)
C(21)-S(2)-C(2)  101.12(9)
N(11)-C(1)-N(21)  111.13(16)
N(11)-C(1)-H(1A)  109.4
N(21)-C(1)-H(1A)  109.4
N(11)-C(1)-H(1B)  109.4
N(21)-C(1)-H(1B)  109.4
H(1A)-C(1)-H(1B)  108.0
S(1)-C(2)-S(2)  115.02(11)
S(1)-C(2)-H(2A)  108.5
S(2)-C(2)-H(2A)  108.5
S(1)-C(2)-H(2B)  108.5
S(2)-C(2)-H(2B)  108.5
H(2A)-C(2)-H(2B)  107.5
N(12)-C(11)-N(11)  107.55(17)
N(12)-C(11)-S(1)  124.26(15)
N(11)-C(11)-S(1)  127.80(15)
C(13)-C(12)-N(11)  106.81(18)
C(12)-C(13)-N(12)  107.50(18)
C(12)-C(13)-H(13)  126.2
N(12)-C(13)-H(13)  126.2
N(12)-C(14)-H(14A)  109.5
N(12)-C(14)-H(14B)  109.5
H(14A)-C(14)-H(14B)  109.5
N(12)-C(14)-H(14C)  109.5
H(14A)-C(14)-H(14C)  109.5
H(14B)-C(14)-H(14C)  109.5
N(22)-C(21)-N(21)  107.74(16)
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N(21)-C(21)-S(2)  127.27(15)
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Symmetry transformations used to generate equivalent atoms:
Figure S3. $^1$H NMR Spectrum (300 MHz, CDCl$_3$) of CH$_2$(N-tim)$_2$ (1)
Figure S4. $^1$H NMR Spectrum (CDCl$_3$) of CH$_2$(S-tim)$_2$ (2)
Figure S5. NMR Spectrum of a sample of CH$_2$(S-tim)$_2$ after heating at 150$^\circ$C for 16 hours. The solvent resonance is marked by an asterisk. The resonances for CH$_2$(S-tim)$_2$ are marked with triangles, those for CH$_2$(N-tim)$_2$ are marked with circles, while those for a species assigned as CH$_2$(S-tim)(N-tim) are marked with open squares. Inset: Magnification of the downfield portion of the spectrum.
Figure S6. $^1$H NMR Spectrum (CDCl$_3$) of ClCH$_2$(S-tim) (3)
Figure S7. $^1$H NMR Spectrum (300 MHz, CD$_3$OD) of [CH$_2$(μ-C$_6$H$_3$N$_2$S)$_2$CH$_2$](Cl)$_2$ (5)

The solvent resonance is marked by an asterisk.
Figure S8. $^1$H NMR Spectrum (300 MHz, CD$_3$CN) of [CH$_2$(μ-C$_4$H$_4$N$_2$S)$_2$CH$_2$](PF$_6$)$_2$ (5)
Figure S9. Cyclic and Square Wave Voltammogram for an equimolar mixture of ferrocene and CH₂(S-tim)₂ (2).
Figure S10. Cyclic and Square Wave Voltammogram for ClCH$_2$(S-tim) (3).
Figure S11. Cyclic and Square Wave Voltammagram for $[\text{CH}_2(\mu-\text{C}_4\text{H}_5\text{N}_2\text{S})_2\text{CH}_2]\text{(PF}_6\text{)}_2$ (5).