Supporting Information for
Unexpected New Chemistry of the Bis(thioimidazoly)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 δ_{H} 7.27, δ_{C} 77.23 for CDCl_3 ; δ_{H} 2.05, δ_{C} 29.8 for acetone- d_6 ; δ_{H} 1.94, δ_{C} 1.39 for CD_3CN ; and δ_{H} 4.92, δ_{C} 48.0 for CD_3OD . 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 K α 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 4787 reflections with $I > 5\sigma(I)$ from the data set. Analysis of the data showed negligible crystal decay during collection. An empirical absorption correction was applied with SADABS.¹ Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL.²

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 than sulfur, does indicate the correct orientation of the polar axis.

(1) SMART Version 5.625, SAINT+ Version 6.22 and SADABS Version 2.05. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2001.

(2) Sheldrick, G. M. SHELXTL Version 6.1; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.

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 CH₂(N-tim)₂ (**1**).

Identification code	CH ₂ (N-tim) ₂ (1)	
Empirical formula	C ₉ H ₁₂ N ₄ S ₂	
Formula weight	240.35	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Fdd2	
Unit cell dimensions	a = 13.5218(10) Å	α = 90°.
	b = 36.256(3) Å	β = 90°.
	c = 4.4236(3) Å	γ = 90°.
Volume	2168.6(3) Å ³	
Z	8	
Density (calculated)	1.472 Mg/m ³	
Absorption coefficient	0.462 mm ⁻¹	
F(000)	1008	
Crystal size	0.70 x 0.20 x 0.12 mm ³	
Theta range for data collection	2.25 to 26.35°.	
Index ranges	-16 ≤ h ≤ 16, -44 ≤ k ≤ 44, -5 ≤ l ≤ 5	
Reflections collected	5709	
Independent reflections	1115 [R(int) = 0.0270]	
Completeness to theta = 26.35°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8065	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1115 / 1 / 76	
Goodness-of-fit on F ²	1.094	
Final R indices [I > 2σ(I)]	R1 = 0.0291, wR2 = 0.0741	
R indices (all data)	R1 = 0.0294, wR2 = 0.0743	
Absolute structure parameter	0.12(10)	
Largest diff. peak and hole	0.292 and -0.175 e.Å ⁻³	

Table 3. Bond lengths [Å] and angles [°] for CH₂(N-tim)₂ (**1**).

S(1)-C(1)	1.685(2)
C(1)-N(2)	1.356(3)
C(1)-N(1)	1.366(2)
C(2)-C(3)	1.336(3)
C(2)-N(1)	1.389(2)
C(2)-H(2)	0.9500
C(3)-N(2)	1.390(3)
C(3)-H(3)	0.9500
C(4)-N(2)	1.455(3)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-N(1)#1	1.456(2)
C(5)-N(1)	1.456(2)
C(5)-H(5)	0.9900
N(2)-C(1)-N(1)	105.31(17)
N(2)-C(1)-S(1)	127.34(15)
N(1)-C(1)-S(1)	127.35(15)
C(3)-C(2)-N(1)	107.34(17)
C(3)-C(2)-H(2)	126.3
N(1)-C(2)-H(2)	126.3
C(2)-C(3)-N(2)	107.32(17)
C(2)-C(3)-H(3)	126.3
N(2)-C(3)-H(3)	126.3
N(2)-C(4)-H(4A)	109.5
N(2)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
N(2)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
N(1)#1-C(5)-N(1)	112.6(2)
N(1)#1-C(5)-H(5)	109.1
N(1)-C(5)-H(5)	109.1
C(1)-N(1)-C(2)	109.87(16)
C(1)-N(1)-C(5)	125.45(14)
C(2)-N(1)-C(5)	124.66(14)
C(1)-N(2)-C(3)	110.14(17)
C(1)-N(2)-C(4)	124.81(17)
C(3)-N(2)-C(4)	125.03(18)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+3/2,z

X-Ray Structure Determination, $\text{CH}_2(\mu\text{-C}_4\text{H}_5\text{N}_2\text{S})_2\text{CH}_2](\text{PF}_6)_2 \cdot (5 \cdot \text{CH}_3\text{CN})$

X-ray intensity data from a colorless bar were measured at 150(1) K using Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$.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

$(\text{C}_{10}\text{H}_{14}\text{N}_4\text{S}_2)(\text{PF}_6)_2 \cdot \text{CH}_3\text{CN}$ 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 $\text{C}_{10}\text{H}_{14}\text{N}_4\text{S}_2^{2+}$ 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.

(1) SMART Version 5.625, SAINT+ Version 6.22. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2001.

(2) Sheldrick, G. M. SHELXTL Version 6.1; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.

Table 1. Crystal data and structure refinement for marq08a. [$\text{CH}_2(\mu\text{-C}_4\text{H}_5\text{N}_2\text{S})_2\text{CH}_2$](PF_6)₂ (**5**· CH_3CN)

Identification code	$\text{CH}_2(\mu\text{-C}_4\text{H}_5\text{N}_2\text{S})_2\text{CH}_2$](PF_6) ₂ (5 · CH_3CN)	
Empirical formula	$\text{C}_{12}\text{H}_{17}\text{F}_{12}\text{N}_5\text{P}_2\text{S}_2$	
Formula weight	585.37	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$\text{P2}_1/\text{c}$	
Unit cell dimensions	$a = 16.1527(8)$ Å	$\alpha = 90^\circ$.
	$b = 10.0182(5)$ Å	$\beta = 103.5910(10)^\circ$.
	$c = 13.8856(7)$ Å	$\gamma = 90^\circ$.
Volume	$2184.06(19)$ Å ³	
Z	4	
Density (calculated)	1.780 Mg/m ³	
Absorption coefficient	0.503 mm ⁻¹	
F(000)	1176	
Crystal size	$0.38 \times 0.16 \times 0.10$ mm ³	
Theta range for data collection	1.30 to 26.40° .	
Index ranges	$-20 \leq h \leq 20$, $-12 \leq k \leq 12$, $-17 \leq l \leq 17$	
Reflections collected	22440	
Independent reflections	4483 [$R(\text{int}) = 0.0398$]	
Completeness to $\theta = 26.40^\circ$	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4483 / 21 / 329	
Goodness-of-fit on F^2	1.063	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0385$, $wR_2 = 0.1028$	
R indices (all data)	$R_1 = 0.0432$, $wR_2 = 0.1059$	
Largest diff. peak and hole	0.476 and -0.376 e.Å ⁻³	

Table 2. Bond lengths [Å] and angles [°] for $\text{CH}_2(\mu\text{-C}_4\text{H}_5\text{N}_2\text{S})_2\text{CH}_2(\text{PF}_6)_2$ (**5**·CH₃CN)

S(1)-C(11)	1.7371(19)
S(1)-C(2)	1.810(2)
S(2)-C(21)	1.740(2)
S(2)-C(2)	1.822(2)
C(1)-N(11)	1.457(3)
C(1)-N(21)	1.459(3)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(11)-N(12)	1.332(3)
C(11)-N(11)	1.351(2)
C(12)-C(13)	1.345(3)
C(12)-N(11)	1.376(3)
C(12)-H(12)	0.9500
C(13)-N(12)	1.376(3)
C(13)-H(13)	0.9500
C(14)-N(12)	1.468(3)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(21)-N(22)	1.334(3)
C(21)-N(21)	1.342(3)
C(22)-C(23)	1.349(3)
C(22)-N(21)	1.374(3)
C(22)-H(22)	0.9500
C(23)-N(22)	1.377(3)
C(23)-H(23)	0.9500
C(24)-N(22)	1.469(3)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
N(31)-C(31)	1.134(3)
C(31)-C(32)	1.451(3)
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
P(1)-F(4)	1.5815(15)
P(1)-F(6)	1.5849(14)
P(1)-F(1)	1.5866(15)
P(1)-F(3)	1.5919(15)
P(1)-F(5)	1.6003(13)
P(1)-F(2)	1.6059(14)
P(2A)-F(9A)	1.584(2)

P(2A)-F(7A)	1.584(2)
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)	107.11(17)
C(13)-C(12)-H(12)	126.4
N(11)-C(12)-H(12)	126.4
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)
N(22)-C(21)-S(2)	124.73(15)
N(21)-C(21)-S(2)	127.27(15)
C(23)-C(22)-N(21)	106.81(18)
C(23)-C(22)-H(22)	126.6

N(21)-C(22)-H(22)	126.6
C(22)-C(23)-N(22)	107.51(18)
C(22)-C(23)-H(23)	126.2
N(22)-C(23)-H(23)	126.2
N(22)-C(24)-H(24A)	109.5
N(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
N(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
N(31)-C(31)-C(32)	179.9(3)
C(31)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(11)-N(11)-C(12)	108.74(16)
C(11)-N(11)-C(1)	125.33(16)
C(12)-N(11)-C(1)	125.87(16)
C(11)-N(12)-C(13)	109.08(17)
C(11)-N(12)-C(14)	126.08(17)
C(13)-N(12)-C(14)	124.82(18)
C(21)-N(21)-C(22)	109.12(17)
C(21)-N(21)-C(1)	125.21(16)
C(22)-N(21)-C(1)	125.66(17)
C(21)-N(22)-C(23)	108.82(17)
C(21)-N(22)-C(24)	125.62(17)
C(23)-N(22)-C(24)	125.52(17)
F(4)-P(1)-F(6)	91.12(11)
F(4)-P(1)-F(1)	178.83(11)
F(6)-P(1)-F(1)	89.97(10)
F(4)-P(1)-F(3)	89.57(11)
F(6)-P(1)-F(3)	179.29(11)
F(1)-P(1)-F(3)	89.34(10)
F(4)-P(1)-F(5)	90.55(9)
F(6)-P(1)-F(5)	90.27(8)
F(1)-P(1)-F(5)	89.88(9)
F(3)-P(1)-F(5)	89.88(8)
F(4)-P(1)-F(2)	89.83(9)
F(6)-P(1)-F(2)	89.05(8)
F(1)-P(1)-F(2)	89.75(9)
F(3)-P(1)-F(2)	90.80(8)
F(5)-P(1)-F(2)	179.22(8)
F(9A)-P(2A)-F(7A)	92.08(17)
F(9A)-P(2A)-F(8A)	89.11(13)

F(7A)-P(2A)-F(8A)	178.79(18)
F(9A)-P(2A)-F(11A)	178.12(18)
F(7A)-P(2A)-F(11A)	89.52(17)
F(8A)-P(2A)-F(11A)	89.29(14)
F(9A)-P(2A)-F(10A)	88.86(12)
F(7A)-P(2A)-F(10A)	89.11(15)
F(8A)-P(2A)-F(10A)	90.75(15)
F(11A)-P(2A)-F(10A)	90.18(16)
F(9A)-P(2A)-F(12A)	89.27(14)
F(7A)-P(2A)-F(12A)	91.18(15)
F(8A)-P(2A)-F(12A)	89.00(15)
F(11A)-P(2A)-F(12A)	91.67(17)
F(10A)-P(2A)-F(12A)	178.12(15)
F(11B)-P(2B)-F(10B)	97.7(10)
F(11B)-P(2B)-F(7B)	87.5(12)
F(10B)-P(2B)-F(7B)	93.4(12)
F(11B)-P(2B)-F(9B)	176.4(13)
F(10B)-P(2B)-F(9B)	85.2(11)
F(7B)-P(2B)-F(9B)	94.4(14)
F(11B)-P(2B)-F(12B)	90.9(10)
F(10B)-P(2B)-F(12B)	170.6(12)
F(7B)-P(2B)-F(12B)	90.8(11)
F(9B)-P(2B)-F(12B)	86.1(11)
F(11B)-P(2B)-F(8B)	87.4(10)
F(10B)-P(2B)-F(8B)	85.6(10)
F(7B)-P(2B)-F(8B)	174.7(13)
F(9B)-P(2B)-F(8B)	90.7(11)
F(12B)-P(2B)-F(8B)	90.9(10)

Symmetry transformations used to generate equivalent atoms:

Figure S3. ^1H NMR Spectrum (300 MHz, CDCl_3) of $\text{CH}_2(\text{N-tim})_2$ (**1**)

Figure S4. ^1H NMR Spectrum (CDCl_3) of $\text{CH}_2(\text{S-tim})_2$ (**2**)

Figure S5. NMR Spectrum of a sample of $\text{CH}_2(\text{S-tim})_2$ after heating at 150°C for 16 hours. The solvent resonance is marked by an asterisk. The resonances for $\text{CH}_2(\text{S-tim})_2$ are marked with triangles, those for $\text{CH}_2(\text{N-tim})_2$ are marked with circles, while those for a species assigned as $\text{CH}_2(\text{S-tim})(\text{N-tim})$ are marked with open squares. Inset: Magnification of the downfield portion of the spectrum.

Figure S6. ^1H NMR Spectrum (CDCl_3) of $\text{ClCH}_2(\text{S-tim})$ (**3**)

Figure S7. ^1H NMR Spectrum (300 MHz, CD_3OD) of $[\text{CH}_2(\mu\text{-C}_4\text{H}_5\text{N}_2\text{S})_2\text{CH}_2](\text{Cl})_2$ (**5**)

The solvent resonance is marked by an asterisk.

Figure S8. ^1H NMR Spectrum (300 MHz, CD_3CN) of $[\text{CH}_2(\mu\text{-C}_4\text{H}_5\text{N}_2\text{S})_2\text{CH}_2](\text{PF}_6)_2$ (**5**)

Figure S9. Cyclic and Square Wave Voltammogram for an equimolar mixture of ferrocene and $\text{CH}_2(\text{S-tim})_2$ (**2**).

Figure S10. Cyclic and Square Wave Voltammogram for $\text{ClCH}_2(\text{S-tim})$ (**3**).

Compound 3

Figure S11. Cyclic and Square Wave Voltammogram for $[\text{CH}_2(\mu\text{-C}_4\text{H}_5\text{N}_2\text{S})_2\text{CH}_2](\text{PF}_6)_2$ (**5**).