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Synthesis and Structures of Cuprous Triptycylthiolate Complexes

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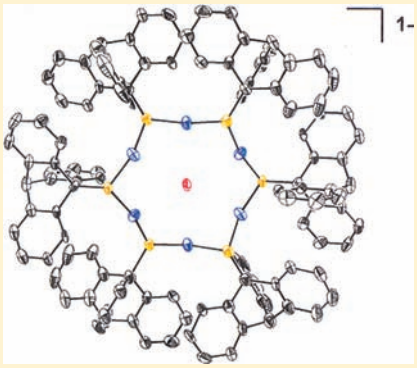
Supporting Information

ABSTRACT: A synthesis of 1-(thioacetyl)triptycene (**5**), a convenient protected form of 1-(thiolato)triptycene [STrip]$^-$, is described, a key transformation being the high yield conversion of *tert*-butyl 1-triptycenyl sulfide (**8**) to **5** by a protocol employing BBr_3/AcCl. Syntheses of the two-coordinate copper(I) compounds $[Bu_4N][Cu(STrip)_2]$, $[Bu_4N]$**10**, and [(Cu(IMes)(STrip)] (**13**) proceed readily by chloride displacement from CuCl and [Cu(IMes)Cl], respectively. Reaction of **10** with Ph_3SiSH or Me_3SiI produces the heteroleptic species $[Cu(STrip)(SSiPh_3)]^-$ (**11**) and $[Cu(STrip)I]^-$ (**12**), detected by mass spectrometry, in mixture with the homoleptic bis(thiolate) anions. Structural identification by X-ray crystallography of the ligand precursor molecules 9-(thioacetyl)anthracene (**4**, triclinic and orthorhombic polymorphs), *tert*-butyl 9-anthracenyl sulfide (**7**), **5**, and *tert*-butyl 1-triptycenyl sulfide (**8**) are presented. Crystallographic characterization of bis(9-anthracenyl)sulfide (**3**), which features a C−S−C angle of 104.0° and twist angle of 54.8° between anthracenyl planes, is also given. A crystal structure of $[Bu_4N]$[(STrip)], $[Bu_4N]$**9**, provides an experimental measure of 144.6° for the ligand cone angle. The crystal structures of $[Bu_4N]$**10** and **13** are reported, the former of which reveals an unexpectedly small C−S···S−C torsion angle of ∼41° (average of two values), which confers a near "cis" disposition of the triptycenyl groups with respect the S−Cu−S axis. This conformation is governed by interligand $\pi\cdots\pi$ and CH$\cdots\pi$ interactions. A crystal structure of an adventitious product, $[Bu_4N][(Cu\text{-}STrip)_6(\mu_6\text{-}Br)]\cdot[Bu_4N][PF_6]$, $[Bu_4N]$**14**$\cdot[Bu_4N][PF_6]$ is described, which reveals a cyclic hexameric structure previously unobserved in cuprous thiolate chemistry. The Cu_6S_6 ring displays a centrosymmetric cyclohexane chair type conformation with a Br^- ion residing at the inversion center and held in place by apparent soft−soft interactions with the Cu(I) ions.



INTRODUCTION

Sterically encumbered thiolate ligands find frequent application in the synthesis of metal sites designed to feature coordinative unsaturation and display atypical reactivity.[1−4] Among thiolate ligands with appreciable steric profile and ready access, either commercially or via a well-defined synthesis, are *tert*-butyl thiolate, 1-adamantyl thiolate, 2,4,6-trialkylthiophenolates,[5,6] and terphenyl thiolates.[7,8] A disadvantage to the first of these is a degree of vulnerability toward C−S bond scission and formation of inorganic sulfide.[2,3] A potential drawback to the latter two, as aryl-type thiolates, is their electronic difference from cysteinate, which is generally the supporting thiolate ligand in biological inorganic sites. Recourse to an alkyl-type thiolate ligand with enhanced steric hindrance, stability against decomposition, and availability in usable quantity by a clear synthetic pathway is therefore desirable for further advancements in thiolate coordination chemistry, especially work with a biological motivation.

Triptycenyl 1-thiolate is a ligand that meets the foregoing criteria and would usefully fill a place in the range of options available to the inorganic coordination chemist. Although a synthesis of 1-(thiolato)triptycene was reported by Kawada, Iwamura, and co-workers in 1987, its preparation was notably unattended by any procedural detail, indication of yield, or physical characterization.[9] Later work by Nakanishi identified the molecule spectroscopically and analytically.[10] In 2009, a first report appeared describing the synthesis of a transition metal complex with 1-(thiolato)triptycene, $[Pt(PPh_3)_2(H)(STrip)]$,[11] but this contribution also did not offer any elaboration upon the synthesis of the thiol.

We describe here a clear, three-step synthesis to 1-(thioacetyl)triptycene (**5**), a convenient protected form of 1-(thiolato)triptycene. Since the coordination chemistry of this ligand is essentially unexplored, we have also examined some of its chemistry with copper(I). Cuprous thiolate chemistry is of wide-ranging biological significance, examples being the active site of the Mo−S−Cu carbon monoxide dehydrogenase (CODH) in *Oligotropha carboxidovorans*,[12,13] the copper metallochaperones,[14−25] and copper regulatory proteins,[25−28] all of which feature or implicate copper(I) in a low-coordinate environment. The rich structural diversity found among homoleptic cuprous complexes with simple monothiolate ligands,[29−49] summarized pictorially in Figure 1, provides a context in which to gauge the capabilities of 1-(thiolato)-triptycene. It is noteworthy that common thiolates typically access multiple structure types, often in mixture with one another. Any capacity by 1-(thiolato)triptycene to add something new to this extensively developed area, for example, produce a new structure type, enable improved yields, confer

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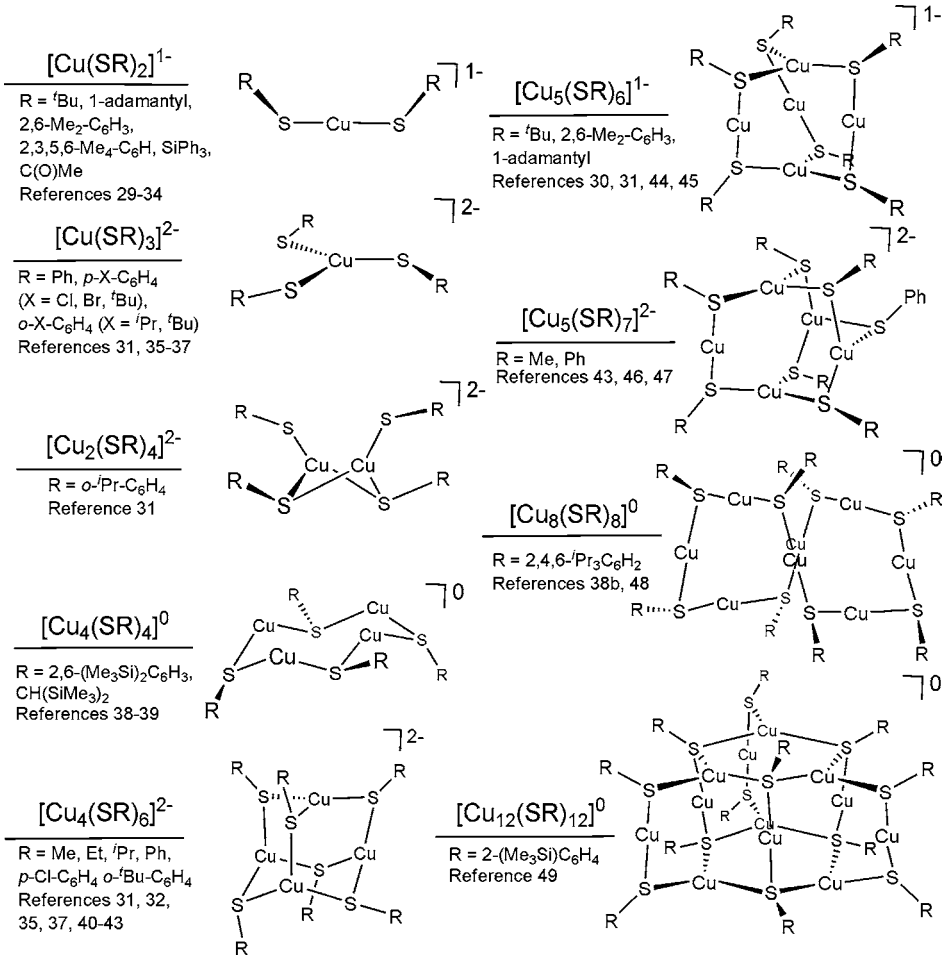

Figure 1. Crystallographically authenticated structure types among homoleptic monothiolate copper(I) complexes.

greater thermal stability, or selectively stabilize one structure type vs another of the same empirical formula, would speak persuasively of its broader possibilities to do new chemistry with other metals.

EXPERIMENTAL SECTION

All reactions and manipulations were performed under a pure dinitrogen or argon atmosphere using modified Schlenk techniques or an inert-atmosphere box. Literature procedures were employed for the syntheses of *tert*-butyl 9-anthracenyl sulfide,[50] $[Cu(CH_3CN)_4][PF_6]$,[51] and [(IMes)Cu(Cl)] (IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene).[52] Solvents either were dried with a system of drying columns from the Glass Contour Company (CH_2Cl_2, Et_2O, tetrahydrofuran (THF)) or freshly distilled according to standard procedures[53] (MeOH, CH_3CN). Other reagents and all solvents used in column chromatography purifications were used as received from commercial sources. Silica columns were run in the open air using 60–230 μm silica (Dynamic Adsorbents). The numbering system employed in compound identification is defined in Chart 1 and Schemes 1 and 2.

Chart 1. Numbering System for Compounds

9(10H)-anthracenone	**1**
bis-(9-anthracenyl)disulfide	**2**
bis-(9-anthracenyl)sulfide	**3**
9-(thioacetyl)anthracene	**4**
1-(thioacetyl)triptycene	**5**
9-(bromo)anthracene	**6**
tert-butyl 9-anthracenyl sulfide	**7**
tert-butyl 1-triptycenyl sulfide	**8**
1-(thiolato)triptycene(1-), $[STrip]^{1-}$	**9**
$[Cu^{I}(STrip)_2]^{1-}$	**10**
$[Cu^{I}(STrip)(SSiPh_3)]^{1-}$	**11**
$[Cu^{I}(STrip)I]^{1-}$	**12**
$[Cu^{I}(IMes)(STrip)]$	**13**
$[(Cu^{I}\text{-}STrip)_6(\mu^6\text{-}Br)]^{1-}$	**14**

SYNTHESES

***tert*-Butyl 1-triptycenyl Sulfide, 8.** A solution of 2-(trimethylsilyl) phenyl triflate (4.97 g, 0.017 mol) in 15 mL of dry MeCN was transferred via cannula to a yellow, stirring solution of **7** (4.44 g, 0.017 mol) in 40 mL of dry THF at 0 °C. Tetra-*n*-butylammonium fluoride (16.6 mL, 1 M in THF, 0.017 mol) was then added to the mixture dropwise at 0 °C, which induced a progressive fading of color to a light yellow. While being stirred for 12 h, the reaction mixture was slowly warmed to ambient temperature and then taken to dryness under reduced pressure to afford a yellow residue. This residue was dissolved in 100 mL of CH_2Cl_2. The resulting solution was washed with water (4 × 30 mL) and then dried over $MgSO_4$. This crude yellow product solution was evaporated onto silica (3.0 g), which then was dry-loaded onto a silica column packed as a slurry with *n*-pentane. The column was eluted with *n*-pentane to separate unreacted **7** (3.55 g, yellow band with

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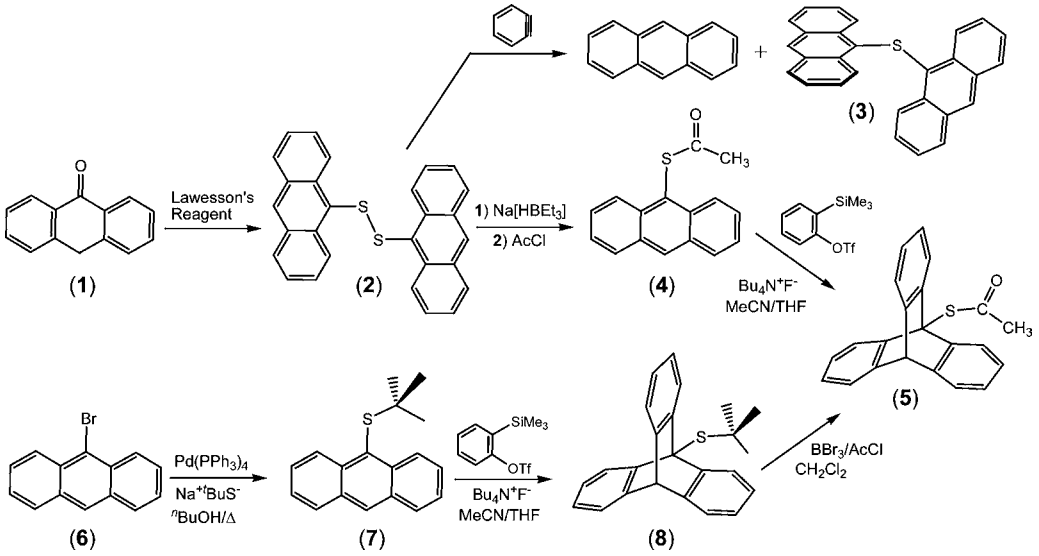
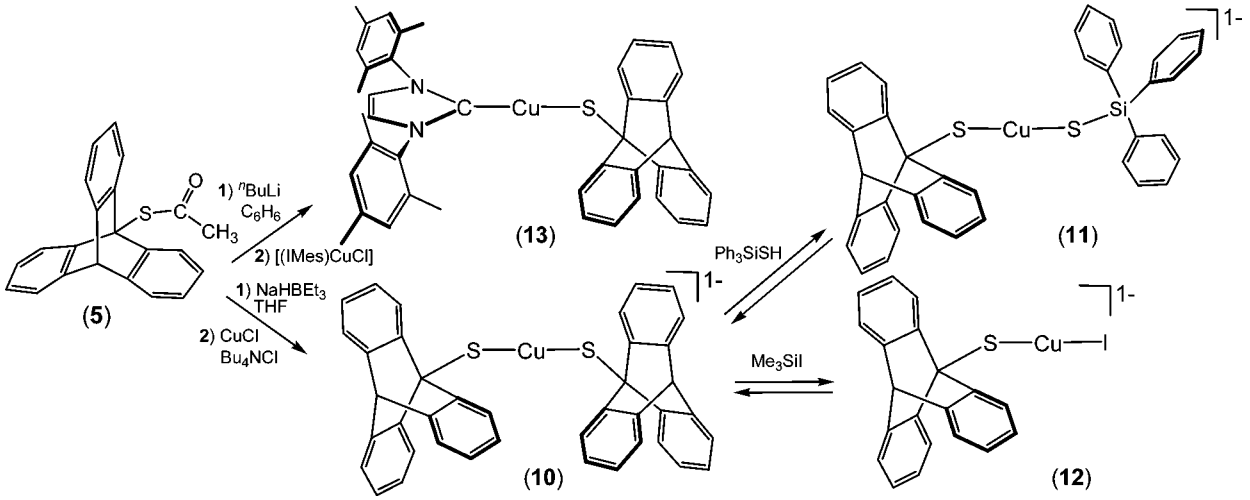
Scheme 1. Synthesis of 1-(Thioacetyl)triptycene



Scheme 2. Synthesis of Copper(I) Compounds with 1-(Thiolato)triptycene



streaking). Subsequent elution with *n*-pentane/CH_2Cl_2 (2:1) moved **8** as a pale yellow band. Concentration of the eluant to dryness gave **8** as a pale yellow solid (Yield: 0.78 g, 68% based on reacted *tert*-butyl 9-anthracenyl sulfide). Recrystallization from hot MeOH produced large colorless plates. R_f = 0.74 (1:2, CH_2Cl_2:*n*-pentane). ^{1}H NMR (δ, ppm in $CDCl_3$): 1.65 (s, 9H), 5.26 (s, 1H), 6.94 (m, 6H), 7.28 (d, 3H), 7.73 (d, 3H). ^{13}C NMR (δ, ppm in $CDCl_3$): 34.52, 47.43, 54.37, 65.86, 123.34, 124.14, 124.76, 125.61, 145.53, 146.43. Anal. Calcd for $C_{24}H_{22}S$: C, 84.16; H, 6.47; S, 9.36. Found: C, 84.18; H, 6.45; S, 9.25.

1-(Thioacetyl)triptycene, 5. To a stirring solution of **8** (1.02 g, 2.98 mmol) in 20 mL of dry CH_2Cl_2 and 5 mL of acetyl chloride (excess) was slowly added BBr_3 in CH_2Cl_2 (8 mL, 1 M in CH_2Cl_2, 8 mmol) at room temperature to generate a dark brown reaction mixture. This mixture was stirred at ambient temperature for 12 h, then poured into 100 mL of ice and extracted with 100 mL of CH_2Cl_2. The yellow organic phase was dried over $MgSO_4$, evaporated onto silica and dry-loaded onto a column that was packed as a slurry in hexanes. Elution of the column with CH_2Cl_2/hexanes (1:2) brought **5** forward as the first band (pale yellow). Slow evaporation of the corresponding column fraction yielded a white, crystalline product 0.69 g (Yield: 71%). R_f = 0.18 (1:2 CH_2Cl_2/hexanes). ^{1}H NMR (δ, ppm in $CDCl_3$): 2.75 (s, 3H), 5.41 (s, 1H), 6.99 (m, 6H), 7.31 (d, 3H), 7.39 (d, 3H). ^{13}C NMR (δ, ppm in $CDCl_3$): 31.94, 54.14, 63.76, 123.10, 123.84, 125.13, 126.10, 142.71, 144.91, 192.10. IR (KBr): 1699 cm^{-1} (C═O). ESI-MS$^+$: *m*/*z* 351 (M + Na$^+$), 679 (2 M + Na$^+$). Anal. Calcd for $C_{22}H_{16}OS$: C, 80.45; H, 4.91; S, 9.76. Found: C, 80.35; H, 4.96; S, 9.60.

[^{n}Bu$_4$N][Cu(STrip)$_2$], [^{n}Bu$_4$N]10. A suspension of cuprous chloride (0.031 g, 0.313 mmol) and anhydrous [^{n}Bu$_4$N]Cl (0.087 g, 0.313 mmol) in 15 mL of dry THF was stirred for 4 h at room temperature in the absence of light, during which time all components are brought into solution. A second flask containing a clear, colorless solution of **5** (0.205 g, 0.624 mmol) in 20 mL of dry THF was cooled to −78 °C, and $NaHBEt_3$ (0.65 mL, 1 M in THF, 0.65 mmol) was added dropwise to generate a yellow solution. This solution was stirred at −78 °C for 45 min and then was allowed to warm to ambient temperature with stirring for an additional 1.5 h. After the separate mixtures were stirred for their respective allotted reaction times, the copper solution was transferred dropwise via

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Table 1. Crystal and Refinement Data for Compounds

compound	4	4	7	3	5	8
solvent	none	none	none	none	none	none
formula	$C_{16}H_{12}OS$	$C_{16}H_{12}OS$	$C_{18}H_{18}S$	$C_{28}H_{18}S$	$C_{22}H_{16}OS$	$C_{24}H_{22}S$
fw	252.32	252.32	266.38	386.48	328.41	342.48
xtl system	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space grp	*Pbca*	$P\bar{1}$	*C*2/*c*	*C*2/*c*	$P2_1/c$	$P2_12_12_1$
color, habit	white block	yellow block	yellow column	yellow slat	colorless plate	colorless slab
a, Å	10.555(2)	8.2800(6)	25.546(1)	20.481(3)	27.442(9)	13.8394(7)
b, Å	14.071(3)	9.3040(7)	6.9794(3)	5.0204(8)	13.748(4)	15.6605(8)
c, Å	16.444(3)	16.872(1)	17.7731(8)	19.693(3)	8.789(3)	16.5178(9)
α, deg.	90	103.204(1)	90	90	90	90
β, deg.	90	96.846(1)	116.824(1)	114.562(2)	96.499(5)	90
γ, deg.	90	102.158(1)	90	90	90	90
V, Å^3	2442.2(9)	1217.7(2)	2827.9(2)	1841.6(5)	3295(2)	3579.9(3)
T, K	100	100	100	100	100	100
Z	8	4	8	4	8	8
R1,[a] wR2[b]	0.0577, 0.1374	0.0351, 0.0903	0.0362, 0.0947	0.0384, 0.0887	0.0412, 0.1047	0.0374, 0.0893
GoF	1.149	1.040	1.044	1.061	1.031	1.027

compound	$[Bu_4N]$**9**	$[Bu_4N]$**10**	$[Bu_4N]$**10**	$[Bu_4N]$**14**·$[Bu_4N][PF_6]$	**13**
solvent	none	Et_2O	$^1/_2C_6H_6$	none	none
formula	$C_{36}H_{49}NS$	$C_{60}H_{72}CuNOS_2$	$C_{59}H_{65}CuNS_2$	$C_{152}H_{150}BrCu_6F_6N_2PS_6$	$C_{41}H_{37}CuN_2S$
fw	527.82	950.85	915.78	2803.22	653.33
xtl system	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space grp	$P2_1/n$	$P\bar{1}$	$P2_1/n$	*C*2/*c*	$P\bar{1}$
color, habit	colorless prism	colorless prism	colorless prism	pale blue plate	colorless plate
a, Å	12.116(6)	11.5110(7)	12.841(1)	38.957(7)	8.355(2)
b, Å	16.180(8)	16.082(1)	20.226(2)	28.740(5)	9.899(2)
c, Å	16.321(8)	16.758(1)	18.384(1)	11.982(2)	20.568(4)
α, deg.	90	100.892(1)	90	90	78.984(2)
β, deg.	97.575(6)	105.633(1)	93.668(1)	91.710(2)	80.382(2)
γ, deg.	90	108.445(1)	90	90	80.950(2)
V, Å^3	3172(3)	2703.4(3)	4765.0(6)	13410(4)	1632.3(5)
T, K	100	100	100	100	100
Z	4	2	4	4	2
R1,[a] wR2[b]	0.0402, 0.1030	0.0614, 0.1828	0.0606, 0.1521	0.0810, 0.2026	0.0461, 0.1072
GoF	1.028	1.074	1.004	1.039	1.023

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

cannula to the solution of deprotected ligand, which was cooled to −78 °C. The color of the resulting mixture progressively faded to a lighter yellow as the copper solution was added. With stirring, the reaction mixture was then slowly warmed to room temperature overnight, during which time a pale yellow solution with a white precipitate formed. The white solid was removed by filtration under N_2, and the filtrate reduced to dryness under reduced pressure. The resulting solid residue was washed with Et_2O (5 mL) and dried under vacuum to afford 0.212 g of a pale yellow solid (Yield: 77%). Crystallization via diffusion of Et_2O or ^{t}BuOMe vapor into a concentrated THF solution afforded large, colorless, block-shaped crystals. ^{1}H NMR (*δ*, ppm in CD_3CN): 0.96 (t, -$NCH_2CH_2CH_2CH_3$, 12H), 1.34 (sextet, -$NCH_2CH_2CH_2CH_3$, 8H), 1.58 (pentet, -$NCH_2CH_2CH_2CH_3$, 8H), 3.06 (t, -$NCH_2CH_2CH_2CH_3$, 8H), 5.41 (s, 2H), 6.79 (t, 6H), 6.89 (t, 6H), 7.28 (d, 6H), 8.26 (d, 6H). MALDI-MS$^-$: *m*/*z* 633 (anion). Anal. Calcd for $C_{56}H_{62}NS_2Cu$: C, 76.71; H, 7.13; N, 1.60. Found: C, 78.16; H, 7.29; N, 1.91.

[1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] (triptycenylthiolato) Cuprate, [Cu(IMes)(STrip)], 13. To a clear, colorless solution of **5** (0.026 g, 0.079 mmol) in 5 mL of dry C_6H_6 was added ^{n}BuLi (32 *μ*L, 2.5 M in hexanes, 0.08 mmol) via gastight syringe at room temperature. This pale yellow solution was stirred for 2 h. A solution of [Cu(IMes)(Cl)] (0.032 g, 0.079 mmol) in 6 mL of 2:1 THF/C_6H_6 (v/v) was then slowly added via cannula to the solution of deprotected ligand. This reaction mixture was stirred for 12 h, during which time a white precipitate formed. The white solid was separated by filtration, and the solvent was removed from the filtrate under reduced pressure to yield an off-white residue. Extraction of this product residue with 5 mL of Et_2O was followed by anaerobic filtration through packed Celite and concentration of the filtrate to about 3 mL. Colorless plate crystals formed upon standing at room temperature after 2 d (Yield: 0.018 g, 35%). ^{1}H NMR (*δ*, ppm in $CDCl_3$): 2.03 (s, 12H, IMes *ortho*-CH_3), 2.27 (s, 6H, IMes *para*-CH_3), 5.23 (s, 1H, STrip bridgehead), 6.80 (t, 7H, IMes *meta*-H and STrip aryl, overlapping), 6.90 (t, 3H, STrip aryl), 7.01 (s, 2H, IMes NC*H*), 7.22 (d, 3H, STrip aryl), 7.90 (d, 3H, STrip aryl). ^{13}C NMR (*δ*, ppm in $CDCl_3$): 18.1 (IMes *ortho*-CH_3), 21.3 (IMes *para*-CH_3), 54.1 (STrip bridgehead), 61.8 (STrip *ipso*), 122.0 (IMes *ortho*-C), 123.7 (STrip aryl-C), 124.4 (STrip aryl-C), 125.1 (STrip aryl-C), 126.0 (STrip aryl-C), 129.5 (IMes *meta*-C), 134.6 (IMes NCH), 135.3 (IMes *para*-C), 139.3 (IMes NC-*ipso*), 144.4 (STrip aryl-C), 145.6 (STrip aryl-C), 150.1

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Table 2. Summary of Structural Data for $[Cu(SR)_2]^-$ Compounds

compound	Cu−S, Å	S−Cu−S[a]	Cu−S−C[a]	C−S···S−C[a,b]
$[Cu(S\text{-}Trip)_2]^-$	2.1541(7),[c] 2.1605(7)[c] 2.1549(9),[d] 2.1624(9)[d]	177.80(3),[c] 174.88(4)[d]	103.23(9),[c] 106.12(9)[c] 103.95(9),[d] 106.16(9)[d]	44.1,[c] 37.9[d]
$[Cu(S\text{-}1\text{-}Ad)_2]^-$[30]	2.147(1)	180.0	106.7(4)	180.0
$[Cu(S\text{-}^t Bu)_2]^-$[e,32]	2.1380(7), 2.1410(6), 2.1422(6), 2.1434(6)	176.69(2), 179.54(3)	105.20(7), 107.02(8) 107.65(7), 107.90(7)	78.7
$[Cu(S\text{-}2,6\text{-}Me_2\text{-}C_6H_3)_2]^-$[31]	2.111(3), 2.127(1)	165.22(7)	103.7, 112.8	42.1
$[Cu(S\text{-}2,3,4,5\text{-}Me_4C_6H_1)_2]^-$[29]	2.137(2)	178.6(1)	108.2(2)	*f*
$[Cu(SSiPh_3)_2]^-$[33]	2.1508(6)[g]	180.0[g]	104.85(3)[g,h]	180.0[g]

[a]Value given in degrees. [b]Torsion angle between thiolate ligands. [c]Values from $[Bu_4N][Cu(S\text{-}Trip)_2]\cdot Et_2O$. [d]Values from $[Bu_4N][Cu(S\text{-}Trip)_2]\cdot{}^1/_2C_6H_6$. [e]Two independent anions occur in the asymmetric unit of the unit cell. [f]Atomic coordinates are unavailable for this structure. [g]These values are from a structure of $[Et_4N][Cu(SSiPh_3)_2]$ determined in our laboratory. The unit cell and space group found are the same as reported by Groysman and Holm. [h]Cu−S−Si angle.

(IMes NCCu). MALDI-MS$^+$: *m*/*z* 671 ($MH^+ + H_2O$). Anal. Calcd for $C_{41}H_{37}CuN_2S$: C, 75.37; H, 5.71; N, 4.29; Found: C, 75.06; H, 5.54; N, 4.40.

$[^nBu_4N][(Cu\text{-}STrip)_6(\mu_6\text{-}Br]$, $[^nBu_4N]$14. A clear, colorless solution of **5** (0.029 g, 0.088 mmol) in 5 mL of dry THF at −78 °C was treated dropwise with a solution of $NaHBEt_3$ (0.09 mL, 1 M in THF, 0.09 mmol) to produce a light yellow mixture. This solution was stirred at −78 °C for 45 min and then allowed to warm to room temperature with stirring for an additional 1.5 h. The solution was again cooled to −78 °C. A solution of $[Cu(CH_3CN)_4]PF_6$ (0.016 g, 0.043 mmol) in 5 mL of dry MeCN was then added dropwise, which progressively turned the reaction mixture to a lighter yellow color. This mixture was stirred at −78 °C for 1.5 h. A solution of $[^nBu_4N][Br]$ (0.014 g, 0.043 mmol) in 5 mL of dry MeCN was slowly added. With stirring, the reaction mixture was slowly warmed to room temperature overnight. The mixture was then reduced to dryness under reduced pressure, and the solid residue was washed with 5 mL of Et_2O. The remaining solid was redissolved in dry MeCN (6.0 mL) and filtered under an atmosphere of N_2 through packed Celite. Colorless block crystals of $[^nBu_4N]$**14**$\cdot[Bu_4N][PF_6]$, identified by X-ray crystallography, were obtained by diffusion of ^{t}BuOMe vapor into a concentrated MeCN solution of the crude product. Deliberate efforts to reproduce the synthesis of $[^nBu_4N]$**14** typically resulted in the formation of $[^nBu_4N]$**10** as the only identifiable species.

Physical Methods. IR spectra were taken as pressed KBr pellets with a Thermo Nicolet Nexus 670 FTIR instrument in absorption mode. All NMR spectra were recorded at 25 °C with a Varian Unity Inova spectrometer operating at 400 or 100.5 MHz for ^{1}H and ^{13}C, respectively, and were referenced to the solvent residual. Mass spectra were obtained by either MALDI-TOF (Bruker Autoflex III instrument) or by electrospray ionization methods (Bruker micrOTOF with Agilent Technologies 1200 Series LC). Elemental analyses were performed by Midwest Microlab, LLC of Indianapolis, IN. Details regarding growth of crystals, collection and processing of X-ray diffraction data, and the solution and refinement of all crystal structures are deferred to the Supporting Information. Unit cell and refinement data for all crystal structures are presented in Table 1.

RESULTS AND DISCUSSION

The first synthesis of triptycene-1-thiol was reported via lithiation of 1-(bromo)triptycene followed by reaction with elemental sulfur.[9] Efforts in our laboratory to follow this route produced mixtures of polysulfide species which were difficult to resolve by chromatographic or crystallization methods. This consideration motivated an examination of an alternative route to 1-(thiolato)triptycene via the corresponding alkyl 1-triptycenyl sulfides.

Initial efforts to prepare 1-(thiolato)triptycene proceeded by analogy to the synthesis of the corresponding alcohol as described by Wolczanski et al.[54] Thus, with Lawesson's reagent or P_2S_5, commercially available 9(10H)-anthracenone (Scheme 1, **1**) is converted to the corresponding thione, which then readily tautomerizes to anthracene-9-thiol. When conducted in the open air, this reaction conveniently affords disulfide (**2**).[55] Disulfide **2** itself does not permit direct ingress toward the triptycenyl group, as its reaction with benzyne results in facile sulfur atom abstraction to afford predominantly anthracene accompanied by minor quantities of bis(9-anthracenyl)sulfide (**3**, Scheme 1). This incompatibility of the disulfide group with the powerful electrophile benzyne requires its transformation to a protected form. Reduction of **2** by $NaHBEt_3$ followed immediately by introduction of acetyl chloride produces 9-(thioacetyl)anthracene (**4**, Scheme 1), a previous synthesis of which has been reported by a similar route.[56]

The condensation of 9-(acetyl)anthracene with benzyne generated by the classical anthranilic acid route produces 1-(acetyl)triptycene in 33% yield.[54] However, no identifiable quantity of **5** results when the same conditions are employed with **4**. Reasoning that more recently described benzyne-generating reagents, which typically operate under milder conditions, might lead to a better outcome, both 2-(trimethylsilyl) phenyl triflate[57] and (phenyl) [*o*-(trimethylsilyl)phenyl]iodonium triflate[58] were explored as alternative sources of benzyne. An advantage of these reagents is the facile generation of benzyne by introduction of F^- at reduced temperature rather than the reflux conditions required with anthranilic acid.[59] The importance of thermal control in this system is apparently affirmed by isolation of **5** (Scheme 1) in 5.3% yield when 2-(trimethylsilyl) phenyl triflate is employed as benzyne precursor at reduced temperature.

The rather modest yield found for the foregoing synthesis of **5** prompted some consideration of *tert*-butyl 1-triptycenyl sulfide (**8**), a successful synthesis of which has been described as proceeding by Diels−Alder condensation of benzyne with *tert*-butyl 9-anthracenyl sulfide, (**7**, Scheme 1).[60] Compound **7** in turn is readily prepared from commercially available 9-(bromo)anthracene (**6**) via a Pd-mediated coupling reaction with $Na^+{}^tBuS^-$ (**6** → **7**, Scheme 1).[50] With alkyl groups less sterically hindered than *tert*-butyl, alkyl 1-triptycenyl sulfides are prone to electrophilic attack by benzyne at sulfur and do not undergo the desired 4 + 2 cycloaddition. A yield of ∼13% is

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reproducibly found for **8** via **7** in our laboratory, although the reported yield is substantially higher at 36%.[60] Our observed invariance of yield for **8**, regardless of the particular method by which benzyne is generated, supports the suggestion that it is inherently restricted by a kinetic competiveness of other reaction pathways, such as condensation of benzyne to afford the 1,4 cycloadduct rather than the desired 9,10-adduct.[60]

Exchange of *tert*-butyl group for acetyl proceeds in straightforward fashion via a BBr_3/AcCl dealkylation protocol described by Bjørnholm and co-workers.[61] Although this protocol was first reported as a methodology for *tert*-butyl for acetyl exchange in aryl *tert*-butyl systems and has been widely applied[62] since then, we extend it successfully and in somewhat better yield to the triptycenyl system (**8** → **5**, Scheme 1). The thioacetyl protected form of 1-(thiolato)triptycene is a convenient, air-stable form of this ligand that is readily deprotected by introduction of a base such as H^-, RO^- or ^{n}BuLi. Thus, in three steps from commercially available **6**, 1-(thioacetyl)triptycene is attainable in an overall yield of 5%.

Treatment of **5** with $NaHBEt_3$ at reduced temperature under anaerobic atmosphere cleanly and conveniently unmasks the thiolate anion. Introduction of a CuCl/$[Bu_4N]Cl$ mixture to in situ generated thiolate anion in a 2:1 ratio readily affords $[Bu_4N][Cu(STrip)_2]$ in reproducible yields of ∼77% (**5** → **10**, Scheme 2). In addition to a yield for $[Bu_4N]$**10** that compares well to those for related compounds (Table 2), we qualitatively observe that **10** is quite robust in solution under N_2 and stable against the formation of yellowish colors typically associated with decomposition to various cage-species. This apparently enhanced stability is attributed to the 1-(thiolato)triptycene ligand's augmented steric bulk and a possible inability to support some of the structural motifs observed in the clusters of Figure 1, such as 3-coordinate Cu(I) or the μ_3-bridging mode for thiolate ligand.

The use of a 3:1 ratio of $TripS^-$ in reaction with Cu(I) afforded no evidence of a $[Cu(S\text{-}Trip)_3]^{2-}$ species. Mononuclear cuprous tris(thiolate) complexes have thus far only been observed with aryl-type thiolates,[31,35−37] suggesting that the moderated basicity of this class of thiolate plays a role in enabling Cu(I) to tolerate this very reduced environment. However, the lack of clarity about the factor(s) governing the selection of $[Cu(SR)_2]^-$ vs $[Cu(SR)_3]^{2-}$ cautions against any conclusion that 1-(thiolato)triptycene is too large as to be able to form any $[M(STrip)_3]^n$ species. In one instance, when $[Cu(MeCN)_4][PF_6]$ and $[Bu_4N]Br$ were employed as starting materials, single crystals of $[Bu_4N][(CuSTrip)_6(\mu_6\text{-}Br)]\cdot[Bu_4N][PF_6]$, $[Bu_4N]$**14**$\cdot[Bu_4N][PF_6]$, were identified by X-ray crystallography (vide infra). Deliberate attempts to reproduce the synthesis of this interesting copper species, which appears not to have a precedent in copper thiolate chemistry, yielded only $[Bu_4N]$**10**.

The size and rigidity of the 1-(thiolato)triptycene ligand presents the possibility of supporting the existence of new, low coordinate copper(I) species that are of interest in their own right for further synthesis. For example, noting that silanethiols are more acidic than their alkanethiolate counterparts,[63,64] exchange of 1-(thiolato)triptycene for Ph_3SiS^- by protonolysis appeared to be a plausible route to the new heteroleptic species $[Cu^I(STrip)(SSiPh_3)]^-$, **11**. Assessed by mass spectrometry (Supporting Information, Figure S1), this ligand exchange by protonolysis does indeed proceed, but only to afford a product mixture. Although a modest enrichment of **11** can be effected by extraction of the crude solid mixture with benzene, the compound appears to be inherently vulnerable to ligand scrambling in solution. The high crystallinity of homoleptic **10** salts causes it to be the only retrievable species by typical crystallization methods. In a similar vein of thought, it seemed plausible that a Si−I bond of comparable, possibly lesser, strength than a typical Si−S bond,[65] might afford a route to two coordinate $[Cu^I(STrip)(I)]^-$, **12**. Again on the basis of a mass spectrometry assay, (Supporting Information, Figure S2), the 1:1 reaction of Me_3SiI with **10** affords **12** and unreacted **10** as a mixture. The greater crystallinity of the latter anion again militates against a selective crystallization of the heteroleptic anion. One heteroleptic species that can be isolated, although it has precedent,[66,67] is [Cu(STrip)(IMes)], prepared from the reaction of $TripS^-$ with [(IMes)CuCl].

STRUCTURES

In conjunction with spectroscopic methods, X-ray diffraction has been used to affirm the identity of all new compounds, as well as those already known but previously uncharacterized by crystallography. Compound **4** was identified in two polymorphs, a triclinic form ($P\bar{1}$) obtained by evaporation from CH_2Cl_2/hexanes and an orthorhombic form found by slow evaporation from EtOAc. The packing arrangement of **4** is more simple in the triclinic setting inasmuch as intermolecular $\pi-\pi$ interactions enforce columnar stacking in a direction approximately coincident with the *a* axis (Figure 2). Molecules

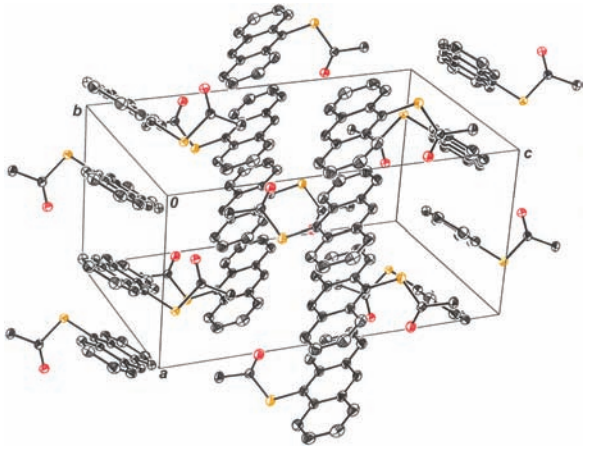

Figure 2. Cell packing diagram for triclinic polymorph of **4** illustrating the $\pi-\pi$ stacking of anthracenyl groups and alternating disposition of thioacetyl groups.

constituting a stack alternate by 180 degree rotations such that the thioester groups of adjacent molecules appear on opposites sides of the column in an orientation orthogonal to the anthracene plane (Figure 2). The orthorhombic polymorph completely lacks the columnar stacks. Instead, molecules are arranged as pairs with parallel anthacenyl groups and thioester groups on opposite side of the $\pi-\pi$ interface but directed toward the pairing partner. These pairs of molecules are then related to one another by the three sets of mutually orthogonal 2-fold screw axes in *Pbca*. In contrast, to the packing patterns for these two polymorphs of **4**, that for **7** reveals no intermolecular π-stacking, possibly because the *tert*-butyl group is near enough and large enough to disfavor an otherwise typical packing arrangement. Interatomic bond distances and angles in these two molecules are unexceptional.

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Bis(9-anthracenyl)sulfide, **3**, obtained as an unintended product, is moderately interesting as one of the more sterically crowded organic sulfides to be structurally characterized.[67−70] The sulfur atom of each molecule resides on a C_2 axis such that only half the molecule is crystallographically unique. The molecule features a C−S−C angle of 104.0(1)° and a S−C bond distance of 1.786(2) Å (Figure 3 (**a**)). This C−S−C angle

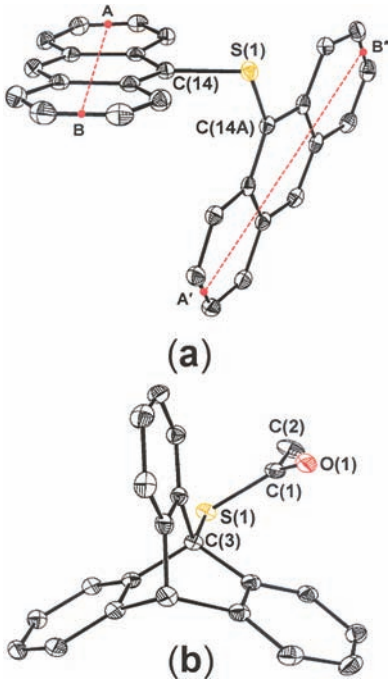

Figure 3. Thermal ellipsoid plots of bis(9-anthracenyl)sulfide (**a**) and 9-(thioacetyl)triptycene (**b**) at the 50% probability level. Hydrogen atoms are omitted for clarity.

is smaller than the corresponding values observed in the structures of other hindered organic sulfides (106.4−119.8°),[68−71] possibly because effective π-stacking between the anthracenyl groups in **3** offsets any energetic cost associated with contracting this bond angle. The twist between anthracenyl groups, defined here as the torsion angle between the AB and A′B′ line segments (Figure 3 (**a**)) when joined at their midpoints, is 54.8°. Molecules of **3** form highly ordered stacks along the *b* axis of the cell using both anthracenyl groups (Supporting Information, Figure S3).

The interatomic distances and angles for both **5** and **8**, reveal nothing atypical. A thermal ellipsoid image of **5** is shown in Figure 3 (**b**). Despite their similarity in size and shape, **5** and **8** pack rather differently in the crystalline state. Molecules of **5** pack in a "head to head", "tail to tail" fashion that juxtaposes the triptycenyl groups of neighboring molecules and arranges them approximately in the plane of the *b* and *c* axes (Supporting Information, Figure S4). Molecules of **8** arrange themselves approximately linearly along the *b* axis but with an alternating "up and down" disposition of triptycenyl groups (Supporting Information, Figure S5). The structure of $[Bu_4N][TripS^-]$, $[Bu_4N]$**9**, is interesting primarily as an unperturbed thiolate anion and reference point for defining a steric cone angle for the ligand. If the angle defined by one of the ortho hydrogen atoms with the thiolate sulfur and bridgehead carbon atoms is taken as subtending half of the steric cone angle, then this cone angle is quantified as 144.6° This value contrasts with the cone angle of 150° reported for the corresponding 1-(alkoxy)-triptycene,[54] the difference being attributable to the S−C single bond being longer than the C−O single bond.

The $[Cu(STrip)_2]^-$ anion, **10**, has been characterized as its $[Bu_4N]^+$ salt in two different crystal systems, triclinic and monoclinic, with the different unit cells being governed by the different solvent molecules available to fill the crystal interstices. In both cases, the anion resides on a general position in the asymmetric unit. Figure 4 (**a**) presents a thermal ellipsoid plot

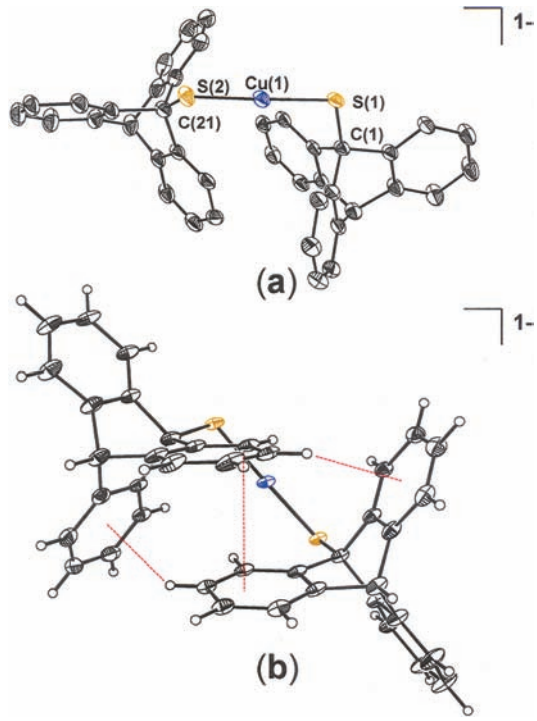

Figure 4. (**a**) Thermal ellipsoid plot (50%) of anion **10** with hydrogen atoms omitted for clarity. (**b**) Thermal ellsoid plot (50%) of **10** illustrating the interligand $\pi\cdots\pi$ and CH$\cdots\pi$ interactions that enforce the small C−S···S−C torsion angle.

of the anion from the determination with Et_2O in the lattice. The structural features in both determinations are highly similar and are presented in Table 2 along with corresponding data from known Cu(I) bis(thiolate) complexes of this type. One noteworthy difference between **10** and the other complexes of this type is that the Cu−S bond distances in the former are moderately longer by ∼0.01 Å. This difference is a significant one within the resolution limits of these data.

The unanticipated closeness of the two triptycyl groups in **10** is reflected by the modest C−S···S−C torsion angles of 37.9 and 44.1° for the two independent structures. This same torsion angle is given for related mononuclear copper bis(thiolate) complex anions whose structures have been reported (Table 2). It has been suggested that the torsion angle observed for $[Cu(S\text{-}^tBu)_2]^-$ may reflect a Cu−S $\pi-\pi$ interaction.[32] However, the wide variation seen in this torsion angle is indicative of the governance of this parameter by crystal packing effects. In **10**, interligand $\pi\cdots\pi$ (∼ 3.62 Å) and CH$\cdots\pi$ (2.84, 3.11 Å) interactions (Figure 4, (**b**)) clearly play a decisive role in enforcing this crystalline state arrangement. Typical $\pi\cdots\pi$ and CH$\cdots\pi$ interaction energies are each 2−3 kcal/mol,[72] which collectively would afford enough stabilization to supersede a more extended conformation with larger C−

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S···S−C torsion angle. The presence of only four aryl-type hydrogen atoms in a 1:1:1:1 ratio indicates that this configuration seen in the crystal structure of **10** does not persist in solution. It is probable that the juxtaposition and orientation of triptycyl groups in **10** that enable these $\pi\cdots\pi$ and CH$\cdots\pi$ interactions are produced at the expense of the elongated Cu−S bonds noted above.

In the course of initial efforts to prepare [Bu_4N]**10** from [$Cu(MeCN)_4$][PF_6]/[Bu_4N]Br, single crystals of [Bu_4N][$(Cu\text{-}STrip)_6(\mu_6\text{-}Br)$]·[$Bu_4N$][$PF_6$] were isolated and identified by X-ray crystallography (Figure 5 (**a**)). This copper thiolate

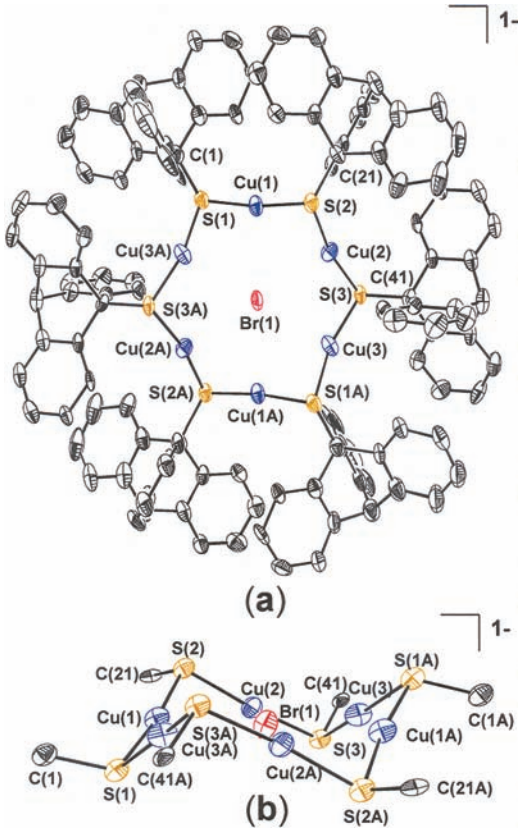

Figure 5. Thermal ellipsoid plots (50%) of (**a**) anion **14** with view orthogonal to Cu_6 plane and (**b**) anion **14** viewed side-on and with triptycyl groups truncated for clarity. All hydrogen atoms have been omitted for clarity.

species may be described as a charge neutral $Cu_6(STrip)_6$ cyclic hexamer with a cyclohexane-like conformation. Linear copper(I) ions reside at the midpoints of the cyclohexane line segments while the thiolate sulfur atoms, each of which bridges two copper ions, coincide with the vertices (or carbon atom positions) of the cyclohexane chair. The center of this cyclic hexamer, which resides on a crystallographic inversion center, is occupied by a bromide ion such that an overall uninegative charge is conferred upon the structure. The core of this $Cu_6(STrip)_6$ structure, neglecting the conformations of the triptycenyl groups, displays D_{3d} point group symmetry (Figure 5 (**b**)). The Br^- ion appears to be held in place by favorable soft−soft interactions with the copper(I) ions and may play a templating role in the formation of this structure. Copper-bromide distances and other select structural features are summarized in Table 3. Copper−sulfur distances in this compound are appreciably longer than found for [Bu_4N][$Cu(STrip)_2$], an observation that is typical when comparing bridging versus terminal thiolate ligands in homoleptic copper(I) thiolate compounds. Although not a deliberate result, the finding of this structure is useful in showing that **9**, while a relatively big and awkward thiolate, is nevertheless not rendered completely incapable of a bridging coordination mode. However, as the images in Figure 5 (**a**) and (**b**) suggest, the ligand's cone angle is probably too wide to support any of the cage structure types seen with other thiolate ligands (Figure 1).

Table 3. Selected Structural Parameters for 14[a]

Cu−S	2.166[1] Å[b]
Cu···Cu	3.011 Å[b]
Cu···Br	3.011 Å[b]
S−Cu−S	168.23[7]°[b]
Cu−S−Cu	88.07[6]°[b]
δ[c]	0.0179 Å
δ'[d]	0.00 Å

[a]All values except for δ' are averages. [b]Uncertainty propagation in averaged values is determined according to the general formula for uncertainty in a function of several variables as detailed in Taylor, J. R. *An Introduction to Error Analysis*; University Science Books: Sausalito, California, 1997, pp 73−77. [c]Average displacement of Cu atoms from Cu_6 mean plane. [d]Displacement of Br^- from Cu_6 mean plane.

The $Cu_6(SR)_6$ hexamer does not have a prior example among copper(I) thiolate complexes, but the structure type, without halide ion, is precedented in [Au_6(S-2,4,6-$^i Pr_3C_6H_2$)$_6$].[73] A topologically related set of homoleptic thiolate complexes are cyclic hexamers of the composition $M_6(SR)_{12}$ (M = Ni^{II}, R = Me,[74] Et,[75] ^{n}Pr;[76] M = Pd^{II}, R = Et,[77] ^{n}Pr;[78] M = Zn^{II}, R = Me;[79] M = Ru^{II}, R = Me[79]). Whereas one triptycenyl thiolate ligand bridges each pair of adjacent copper(I) ions in $Cu_6(STrip)_6$ with an alternating placement above and below the Cu_6 mean plane, two thiolate ligands bridge each pair of adjacent M(II) ions in the $M_6(SR)_{12}$ structures, six being on each side of the M_6 plane. Figure 6

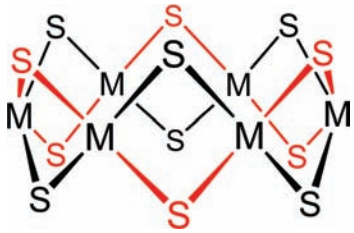

Figure 6. D_{3d} $M_6(SR)_6$ core structure inscribed within the D_{6h} homoleptic thiolate $M_6(SR)_{12}$ structure.

clarifies how the $M_6(SR)_6$ cyclohexane-type structure (black) derives from the $M_6(SR)_{12}$ by removal of alternating thiolate ligands (red, abbreviated as S) above and below the M_6 plane.

Compound **13**, a compound type reported to be effective for the catalytic hydrothiolation of electron deficient olefins,[66] is also two-coordinate and linear at copper (Figure 7). The bond angle and bond lengths about copper(I) in **13** are compared to those observed in related structures (Table 4). Again it is noteworthy that the Cu−S bond length again defines the upper end of the range and is significantly longer within the experimental resolution than the corresponding values for other compounds. A shorter Cu−C bond length appears to

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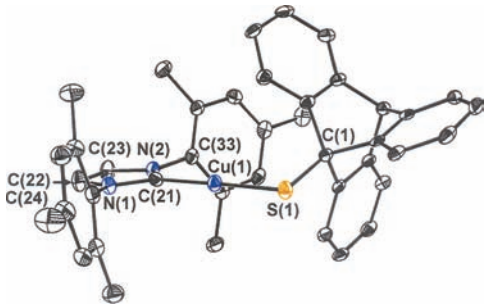

Figure 7. Thermal ellipsoid plot (50%) of **13** with hydrogen atoms omitted for clarity.

correlate to the longer Cu−S bond length according to the data in Table 4.

CONCLUDING REMARKS

In summary, we detail in this article a synthesis of 1-(thioacetyl)triptycene that affords usable quantities of this convenient protected form of (1-thiolato)triptycene. A key aspect of this synthesis is a dealkylation of *tert*-butyl 1-triptycenyl sulfide via a BBr_3/AcCl protocol that heretofore has seen its application limited to the unmasking of aryl thiolates that are protected as *tert* butyl sulfides. Triptycenyl-1-thiolate readily supports two-coordinate copper(I), evident by the preparation of $[Cu(STrip)_2]^-$ in good yield and by its stability. A structural characterization of $[Cu(STrip)_2]^-$ as its $[Bu_4N]^+$ salt reveals longer Cu−S bond distances than in any related $[Cu(SR)_2]^-$ structure and a surprising C−S···S−C torsion angle of 41° (average of two structures), both of which arise from multiple interligand $\pi\cdots\pi$ and CH$\cdots\pi$ interactions. The mononuclear heteroleptic species $[Cu(STrip)(SSiPh_3)]^-$ and $[Cu(STrip)I]^-$ could be generated in solution but only in mixture with the homoleptic bis(thiolate) anions, from which they were not separable. The cyclic hexameric species $[Bu_4N][(Cu\text{-}STrip)_6(\mu_6\text{-}Br)]$ was identified as an adventitious minor byproduct in the synthesis of $[Cu(STrip)_2]^-$ when $[Cu(MeCN)_4][PF_6]$/$[Bu_4N]Br$ were employed as starting materials, and its structure is important in establishing some of the coordination capabilities of 1-(thiolato)triptycene. The ligand can bridge metal ions, but it is unlikely to be able to accommodate $M_x(SR)_y$ cage structures or motifs involving μ_3-thiolate. A limitation of this ligand is the very modest solubility it will confer on symmetric, charge-neutral complexes. Nevertheless, the improved access to this ligand provided by this account should enable new, coordinatively unsaturated metal complexes to be prepared and investigated for their properties and reactivity.

ASSOCIATED CONTENT

Supporting Information

Full description of crystal growing procedures, data collection and processing, and structure solution and processing. Complete crystallographic data CIF format and enhanced ORTEP drawings with complete atom labeling for all structures. Figures as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Dilworth, J. R.; Arnold, P.; Morales, D.; Wong, Y.-L.; Zheng, Y. The Chemistry and Applications of Complexes with Sulfur Ligands. In *Modern Coordination Chemistry*; Leigh, G. J., Winterton, N., Eds.; Royal Society of Chemistry: Cambridge, U.K., 2002; pp 217−230.
(2) Dilworth, J. R.; Hu, J. *Adv. Inorg. Chem.* **1993**, *40*, 411−459.
(3) Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121−185.
(4) Dance, I. G. *Polyhedron* **1986**, *5*, 1037−1104.
(5) Field, L.; Grunwald, F. A. *J. Org. Chem.* **1951**, *16*, 946−953.
(6) Blower, P. J.; Dilworth, J. R.; Hutchinson, J.; Nicholson, T.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1985**, 2639−2645.
(7) Bishop, P. T.; Dilworth, J. R.; Nicholson, T.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **1991**, 385−392.
(8) Niemeyer, M.; Power, P. P. *Inorg. Chem.* **1996**, *35*, 7264−7272.
(9) Kawada, Y.; Ishikawa, J.; Yamazaki, H.; Koga, G.; Murata, S.; Iwamura, H. *Tetrahedron Lett.* **1987**, *28*, 445−448.
(10) Hayashi, S.; Nakamoto, T.; Minoura, M.; Nakanishi, W. *J. Org. Chem.* **2009**, *74*, 4763−4771.
(11) Nakata, N.; Yamamoto, S.; Hashima, W.; Ishii, A. *Chem. Lett.* **2009**, *38*, 400−401.
(12) Dobbek, H.; Gremer, L.; Kiefersauer, R.; Huber, R.; Meyer, O. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 15971−15976.
(13) Gnida, M.; Ferner, R.; Gremer, L.; Meyer, O.; Meyer-Klaucke, W. *Biochemistry* **2003**, *42*, 222−230.
(14) Pufahl, R. A.; Singer, C. P.; Peariso, K. L.; Lin, S.-J.; Schmidt, P. J.; Fahrni, C. J.; Cizewski Culotta, V.; Penner-Hahn, J. E.; O'Halloran, T. V. *Science* **1997**, *278*, 853−856.

Table 4. Summary of Structural Data for [Cu(carbene)(SR)] Compounds

compound	Cu−C, Å	Cu−S, Å	S−Cu−C, deg.	Cu−S−C, deg.
[Cu(IMes)(STrip)]	1.892(3)	2.1491(8)	178.83(8)	103.76(8)
[Cu(^{i}Pr$_2$NHCMe$_2$)(SAr*)][a,67]	1.902(6)	2.122(2)	164.0(2)	114.44(18)
[Cu(IPr)(SPh)][b,66]	1.895(2)	2.139(1)	178.3(1)	100.5(1)
[Cu(IPr)(SBz)][b,66]	1.898(2)	2.127(1)	171.5(1)	112.1(1)
[Cu(SIPr)(SPh)][c,66]	1.896(3)	2.145(1)	177.5(1)	105.8(1)
[Cu(SIPr)(SBz)][c,66]	1.897(3)	2.121(1)	169.5(1)	110.9(3)

[a]SAr* = 2,6-bis(2,4,6-triisopropylphenyl)benzenethiolate(1-); ^{i}Pr$_2$NHCMe$_2$ = 4,5-dimethyl-1,3-diisopropylimidazol-2-xylidene. [b]IPr = 1,3-bis(2,6-diispropylphenyl)imidazol-2-ylidene. [c]SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene.

dx.doi.org/10.1021/ic300124n | *Inorg. Chem.* 2012, 51, 6567−6576

(15) Poulos, T. L. *Nat. Struct. Biol.* **1999**, *6*, 709−711.
(16) Rosenzweig, A. C.; Huffman, D. L.; Hou, M. Y.; Wernimont, A. K.; Pufahl, R. A.; O'Halloran, T. V. *Structure* **1999**, *7*, 605−617.
(17) Lamb, A. L.; Wernimont, A. K.; Pufahl, R. A.; Culotta, V. C.; O'Halloran, T. V.; Rosenzweig, A. C. *Nat. Struct. Biol.* **1999**, *6*, 724−729.
(18) Wernimont, A. K.; Huffman, D. L.; Lamb, A. L.; O'Halloran, T. V.; Rosenzweig, A. C. *Nat. Struct. Biol.* **2000**, *7*, 766−771.
(19) O'Halloran, T. V.; Cizewski Culotta, V. *J. Biol. Chem.* **2000**, *275*, 25057−25060.
(20) Rosenzweig, A. C. *Acc. Chem. Res.* **2001**, *34*, 119−128.
(21) Arnesano, F.; Banci, L.; Bertini, I.; Huffman, D. L.; O'Halloran, T. V. *Biochemistry* **2001**, *40*, 1528−1539.
(22) Lamb, A. L.; Torres, A. S.; O'Halloran, T. V.; Rosenzweig, A. C. *Nat. Struct. Biol.* **2001**, *8*, 751−755.
(23) Ralle, M.; Lutsenko, S.; Blackburn, N. J. *J. Biol. Chem.* **2003**, *278*, 23163−23170.
(24) Arnesano, F.; Banci, L.; Bertini, I.; Ciofi-Baffoni, S. *Eur. J. Inorg. Chem.* **2004**, 1583−1593.
(25) Finney, L. A.; O'Halloran, T. V. *Science* **2003**, *300*, 931−936.
(26) Chen, K.; Yuldasheva, S.; Penner-Hahn, J. E.; O'Halloran, T. V. *J. Am. Chem. Soc.* **2003**, *125*, 12088−12089.
(27) Changela, A.; Chen, K.; Xue, Y.; Holschen, J.; Outten, C. E.; O'Halloran, T. V.; Mondragón, A. *Science* **2003**, *301*, 1383−1387.
(28) Chen, P. R.; He, C. *Curr. Opin. Chem. Biol.* **2008**, *12*, 214−221.
(29) Koch, S. A.; Fikar, R.; Millar, M.; O'Sullivan, T. *Inorg. Chem.* **1984**, *23*, 121−122.
(30) Fujisawa, K.; Imai, S.; Kitajima, N.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 168−169.
(31) Zeevi, S.; Tshuva, E. Y. *Eur. J. Inorg. Chem.* **2007**, 5369−5376.
(32) Kohner-Kerten, A.; Tshuva, E. Y. *J. Organomet. Chem.* **2008**, *693*, 2065−2068.
(33) Groysman, S.; Majumdar, A.; Zheng, S.-L.; Holm, R. H. *Inorg. Chem.* **2010**, *49*, 1082−1089.
(34) Sampanthar, J. T.; Vittal, J. J.; Dean, P. A. W. *J. Chem. Soc., Dalton Trans.* **1999**, 3153−3156.
(35) Coucouvanis, D.; Murphy, C. N.; Kanodia, S. K. *Inorg. Chem.* **1980**, *19*, 2993−2998.
(36) Garner, C. D.; Nicholson, J. R.; Clegg, W. *Inorg. Chem.* **1984**, *23*, 2148−2150.
(37) Fujisawa, K.; Imai, S.; Suzuki, S.; Moro-oka, Y.; Miyashita, Y.; Yamada, Y.; Okamoto, K. *J. Inorg. Biochem.* **2000**, *82*, 229−238.
(38) (a) Block, E.; Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chim. Acta* **1990**, *167*, 147−148. (b) Schröter-Schmid, I.; Strähle, J. *Z. Naturforsch., B: Chem. Sci.* **1990**, *45*, 1537−1542.
(39) Hu, S.-Z. *Jiegou Huaxue* **1999**, *18*, 476.
(40) Dance, I. G.; Calabrese, J. C. *Inorg. Chim. Acta* **1976**, *19*, L41−L42.
(41) Dance, I. G.; Bowmaker, G. A.; Clark, G. R.; Seadon, J. K. *Polyhedron* **1983**, *2*, 1031−1043.
(42) Baumgartner, M.; Schmalle, H.; Dubler, E. *Polyhedron* **1990**, *9*, 1155−1164.
(43) Baumgartner, M.; Schmalle, H.; Baerlocher, C. *J. Solid State Chem.* **1993**, *107*, 63−75.
(44) Dance, I. G. *J. Chem. Soc., Chem. Commun.* **1976**, 68−69.
(45) Bowmaker, G. A.; Clark, G. R.; Seadon, J. K.; Dance, I. G. *Polyhedron* **1984**, *3*, 535−544.
(46) Dance, I. G. *J. Chem. Soc., Chem. Commun.* **1976**, 103−104.
(47) Dance, I. G. *Aust. J. Chem.* **1978**, *31*, 2195−2206.
(48) Yang, Q.; Tang, K.; Liao, H.; Han, H.; Chen, Z.; Tang, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1076−1077.
(49) Block, E.; Gernon, M.; Kang, H.; Ofori-Okai, G.; Zubieta., J. *Inorg. Chem.* **1989**, *28*, 1263−1271.
(50) Jennings, W. B.; Kochanewycz, M. J.; Lunazzi, L. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2271−2274.
(51) Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90.
(52) Goj, L. A.; Blue, E. D.; Delp, S. A.; Gunnoe, T. B.; Cundari, T. R.; Pierpont, A. W.; Petersen, J. L .; Boyle, P. D. *Inorg. Chem.* **2006**, *45*, 9032−9045.
(53) Armarego, W. L.; Perrin, D. D. *Purification of Laboratory Chemicals*; Butterworth-Heinemann, Linacre House, Jordan Hill: Oxford, Great Britain, 2000.
(54) LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1985**, *4*, 1810−1818.
(55) (a) Majumdar, K. C.; Chattopadhyay, S. K.; Sen, B. K. *Indian J. Chem.* **1986**, *25B*, 1261−1262. (b) Kansikas, J.; Sipilä, K. *Acta Crystallogr., Sect C.* **2000**, *56*, 72−73.
(56) Beckwith, A. L. J.; Low, B. S. *J. Chem. Soc.* **1961**, 1304−1311.
(57) Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211−1214.
(58) Kitamura, T.; Yamane, M.; Inoue, K.; Todaka, M.; Fukatsu, N.; Meng, Z.; Fujiwara, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11674−11679.
(59) Fieser, L. F.; Williamson, K. L. *Organic Experiments*, 5th ed.; D. C. Heath: Lexington, MA, 1983; pp 246−249.
(60) Nakamura, N. *Chem. Lett.* **1983**, 1795−1798.
(61) Stuhr-Hansen, N.; Christensen, J. B.; Harrit, N.; Bjørnholm, T. *J. Org. Chem.* **2003**, *68*, 1275−1282.
(62) See, for example: (a) Greger, J. G.; Yoon-Miller, S. J. P.; Bechtold, N. R. *J. Org. Chem.* **2011**, *76*, 8203−8214. (b) Wen, H.-M.; Zhang, D.-B.; Zhang, L.-Y. *Eur. J. Inorg. Chem.* **2011**, 1784−1791. (c) Petersen, A. B.; Thyrhaug, E.; Jain, T.; Kilsaa, K.; Bols, M.; Moth-Poulsen, K.; Harrit, N.; Bjørnholm, T. *J. Phys. Chem. B* **2010**, *114*, 11771−11777. (d) Zeng, X.; Wang, C.; Batsanov, A. S. *J. Org. Chem.* **2010**, *75*, 130−136. (e) Babudri, F.; Farinola, G. M.; Naso, F. *Synlett* **2009**, 2740−2748. (f) Moth-Poulsen, K.; Bjørnholm, T. *Nat. Nanotechnol.* **2009**, *4*, 551−556.
(63) Salinger, R. M.; West, R. *J. Organomet. Chem.* **1968**, *11*, 631−633.
(64) Herman, A.; Wojnowski, W. *Struct. Chem.* **1992**, *3*, 239−244.
(65) Tacke, R.; Wannagat, U. *Top. Curr. Chem.* **1979**, *84*, 1−75.
(66) Delp, S. A.; Munro-Leighton, C.; Goj, L. A.; Ramírez, M. A.; Gunnoe, T. B.; Petersen, J. L.; Boyle, P. D. *Inorg. Chem.* **2007**, *46*, 2365−2367.
(67) Groysman, S.; Holm, R. H. *Inorg. Chem.* **2009**, *48*, 621−627.
(68) Jeffrey, G. A.; Robbins, A. *Acta Crystallogr., Sect. B* **1980**, *36*, 1820−1826.
(69) Bard, A. J.; Cowley, A. H.; Leland, J. K.; Thomas, G. J. N.; Norman, N. C.; Jutzi, P.; Morley, C. P.; Schlüter, E. *J. Chem. Soc., Dalton Trans.* **1985**, 1303−1307.
(70) Grilli, S.; Lunazzi, L.; Mazzanti, A. *J. Org. Chem.* **2001**, *66*, 4444−4446.
(71) Arnold, P. L.; Natrajan, L. S.; Hall, J. J.; Bird, S. J.; Wilson, C. *J. Organomet. Chem.* **2002**, *647*, 205−215.
(72) Hayashi, N.; Higuchi, H.; Ninomiya, K. In *X/π Interactions in Aromatic Heterocycles: Basic Principles and Recent Advances*; Matsumoto, K., Hayashi, N., Eds.; Topics in Heterocyclic Chemistry: Heterocyclic Supramolecules II 18; Springer: Heidelberg, Germany, 2009; pp 1−35.
(73) (a) Schröter, I.; Strähle, J. *Chem. Ber.* **1991**, *124*, 2161−2164. (b) LeBlanc, D. J.; Lock, C. J. L. *Acta Crystallogr., Sect. C* **1997**, *53*, 1765−1768.
(74) Wark, T. A.; Stephan, D. W. *Organometallics* **1989**, *8*, 2836−2843.
(75) Miyamae, H.; Yamamura, T. *Acta Crystallogr., Sect. C* **1988**, *44*, 606−609.
(76) Xiao, H. L.; Jian, F. F.; Zhang, K. J. *Bull. Korean Chem. Soc.* **2009**, *30*, 846−848.
(77) Thomas, P. J.; Lavanya, A.; Sabareesh, V.; Kulkarni, G. U. *Proc.—Indian Acad. Sci., Chem. Sci.* **2001**, *113*, 611−619.
(78) Kunchur, N. R. *Acta Crystallogr., Sect. B* **1968**, *24*, 1623−1633.
(79) Xie, M.-H.; Wang, M.; Wu, C.-D. *Inorg. Chem.* **2009**, *48*, 10477−10479.