Inorg. Chem. **2009**, *48*, 621−627

Inorganic Chemistry

Article

A Series of Mononuclear Quasi-Two-Coordinate Copper(I) Complexes Employing a Sterically Demanding Thiolate Ligand

Stanislav Groysman and R. H. Holm*

Department of Chemistry and Chemical Biology, Harvard University,
Cambridge, Massachusetts 02138

Received September 25, 2008

A series of two-coordinate thiolate complexes [Cu(SAr*)L] was synthesized as possible reactants in forming analogues of the active site of Mo/Cu-containing carbon monoxide dehydrogenase. Complexes with L = PPh_3 (**1**), 2,6-lutidine (**2**), and the *N*-heterocyclic carbene $Pr^i_2NHCMe_2$ (**3**) have been prepared by the reaction of $[CuCl(PPh_3)_3]$ (**1**) or $[CuBr(SMe_2)]$ (**2**, **3**) with ligand L and the exceptionally sterically encumbered ligand Ar*S = 2,6-bis(2,4,6-triisopropylphenyl)benzenethiolate(1-). The reaction of $[CuBr(SMe_2)]$ with the thiolate in the absence of added L afforded trinuclear $[Cu_3(SAr^*)_2Br]$ (**7**). The carbene complex (**3**) undergoes Cu−C bond insertion with sulfur to form the thiourea complex $[Cu(SAr^*)(Pr^i_2Me_2ImS)]$ (**4**). The complexes [Cu(Ar*)L] with L = tetrahydrothiophene (**5**) and 2,6-lutidine (**6**) were obtained by reaction of $Ar^*Li(OEt_2)$ with CuBr/L. These species did not undergo clean Cu−C bond insertion with sulfur transfer agents; the disulfide Ar^*SSCH_2Ph (**9**) was isolated from the reaction of **6** with $(PhCH_2S)_2S$. The structures of all complexes and **9** were determined. Whereas **5** and **6** are strictly two-coordinate with linear C−Cu−L angles, **1**−**4** are quasi-two-coordinate because of weak 3d-C(pπ) interactions with a phenyl group, leading to nonlinear structures (S−Cu−L = 135−164 °).

Introduction

We have recently synthesized structural analogues of catalytic sites in the xanthine oxidoreductase family of enzymes.[1,2] These molecules are exemplified by square-pyramidal $[W^{VI}O_2S(bdt)]^{2-}$ in which benzene-1,2-dithiolate occupies basal sites and simulates the stereochemical and electronic features of the native pyranopterindithiolate cofactor ligand.[3,4] A key feature of this molecule is the presence of one terminal sulfido ligand in a basal position; the two oxo ligands are apical and basal. As such, the molecule resembles the catalytic center of not only enzymes such as xanthine and aldehyde oxidoreductases but also molybdenum-containing carbon monoxide dehydrogenase, which catalyzes the interconversion of carbon monoxide and carbon dioxide. The structural relationship between $[WO_2S(bdt)]^{2-}$ and the oxidized site of CODH[5] from an aerobic bacterium[6,7] is evident from Figure 1. Inasmuch as isoligated Mo^{VI} and W^{VI} molecules are always isostructural, the tungsten complex is stereochemically acceptable as a precursor to a structural analogue of the CODH site. The analogous molybdenum

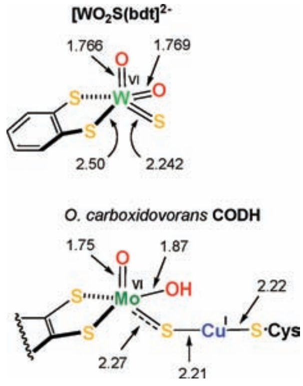


Figure 1. Depictions indicating the structural relationship between $[WO_2S(bdt)]^{2-}$ and the oxidized active site of a bacterial carbon monoxide dehydrogenase.

---

* Author to whom correspondence should be addressed. E-mail: holm@chemistry.harvard.edu.

(1) Hille, R. *Chem. Rev.* **1996**, *96*, 2757–2816.
(2) Hille, R. *Eur. J. Inorg. Chem.* **2006**, 1913–1926.
(3) Wang, J.-J.; Groysman, S.; Lee, S. C.; Holm, R. H. *J. Am. Chem. Soc.* **2007**, 7512–7513.
(4) Groysman, S.; Wang, J.-J.; Tagore, R.; Lee, S. C.; Holm, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 12794–12807.
(5) Abbreviations are given in Chart 1.
(6) Dobbek, H.; Gremer, L.; Kiefersauer, R.; Huber, R.; Meyer, O. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 15971–15976.
(7) Gnida, M.; Ferner, R.; Gremer, L.; Meyer, O.; Meyer-Klaucke, W. *Biochemistry* **2003**, *42*, 222–230.

10.1021/ic801836k CCC: $40.75

complex is unstable to autoreduction and has not been isolated.

Realization of the desired structure requires binding of a suitable Cu^I thiolate complex as a two-coordinate entity at the sulfido site. Copper(I) thiolates tend to be polymeric or, if molecular, polynuclear. Sterically bulky thiolates can form two-coordinate complexes of the type $[Cu(SR)_2]^{1-}$,[8−10] but these species do not contain a good leaving group. Potentially more effective as a reactant would be [Cu(SR)L], where L is labile neutral ligand and substituent R provides sufficient steric encumbrance to stabilize two-coordinate Cu^I. Several such species are known. These include $[Cu(SSiPh_3)(PBu^t{}_3)]$[11] with, however, the likelihood of oxo silylation, a known reaction type with $W^{VI}O$ groups.[4,12] The complexes [Cu(S-R)(carbene)] have been prepared, but with relatively small R groups and a hindered, N,N′-disubstituted heterocyclic carbene.[13] The lability of carbenes in such complexes has not been established. In this work, we have undertaken an investigation of the synthesis and structures of mononuclear complexes of the type $[Cu^I(SR)L]$ with a sterically demanding R group and variant ligands L. Among the potential applications of these compounds is their use in the synthesis of analogues of the CODH catalytic site by a building-block approach.

Chart 1. Designation of Compounds and Abbreviations[a]

$[Cu(SAr^*)(PPh_3)]$	**1**
$[Cu(SAr^*)(2,6\text{-lut})]$	**2**
$[Cu(SAr^*)(Pr^i{}_2NHCMe_2)]$	**3**
$[Cu(SAr^*)(Pr^i{}_2Me_2ImS)]$	**4**
$[Cu(Ar^*)(tht)]$	**5**
$[Cu(Ar^*)(2,6\text{-lut})$	**6**
$[Cu_3(SAr^*)_2Br]$	**7**
$[Cu_4(S\text{-}1\text{-}Ad)_4(PPh_3)_2]$	**8**
Ar^*SSCH_2Ph	**9**

[a] Ad = adamantyl, Ar* = 2,6-bis(2,4,6-triisopropyl)phenyl)phenyl, Ar*S = 2,6-bis(2,4,6-triisopropylphenyl)benzenethiolate(1-), CODH = carbon monoxide dehydrogenase, lut = lutidine, mes = mesityl, $Pr^i{}_2NHCMe_2$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-xylidene, $Pr^i{}_2Me_2ImS$ = 1,3-diisopropyl-4,5-dimethyl-2(3*H*)-thione, tht = tetrahydrothiophene, tu = thiourea (generalized).

Experimental Section

Preparation of Compounds. All operations were carried out under a pure dinitrogen atmosphere using standard Schlenk techniques or an inert atmosphere box. Solvents were passed through an MBraun or Innovative Technology solvent purification system prior to use. All volume reduction steps were performed in vacuo. Routine characterization of metal complexes included ^1H and ^{13}C ($^{13}C\{^1H\}$ and DEPT-135) NMR experiments, performed in benzene and referenced to the solvent peaks at 7.15 ppm (^1H) and 128.0 ppm (^{13}C). Compounds were identified by a combination of elemental analyses (representative compounds; H. Kolbe, Mulheim, Germany) and X-ray structure determinations. The compound 2,6-bis(2,4,6-triisopropylphenyl)benzenethiol was prepared by a reported procedure.[14] Its sodium salt was obtained from the thiol and NaOMe in THF. Compounds are designated according to Chart 1.

$[Cu(SAr^*)(PPh_3)]$ (1). A mixture of 5.0 mg (0.090 mmol) of NaOMe and 29 mg (0.055 mmol) of Ar*SH was stirred for 1 h, filtered, and added to 50 mg (0.056 mmol) of $[CuCl(PPh_3)_3]$[15] in 2 mL of THF. The reaction mixture was stirred for 2 h and filtered, and the filtrate was taken to dryness. The solid residue was extracted with 2 mL of hexane. The extract was filtered, and the filtrate was maintained at −30 °C overnight. The solid that separated was washed with a miminal amount of cold hexane and dried to afford the product as 30 mg (63%) of colorless crystals. ^1H NMR (C_6D_6): δ 7.33 (m, 6), 7.30 (s, 4), 6.73 (m, 12), 3.26 (sept, 4), 2.52 (sept, 2), 1.58 (d, 12), 1.25 (d, 12), 1.06 (d, 12). $^{13}C\{^1H\}$ NMR (100.59 MHz): δ 153.1 (*C*), 146.9 (*C*), 145.8 (*C*), 141.2 (*C*), 138.9 (*C*), 134.2 (*C*H, $^2J_{CP}$ = 17.5 Hz, o-P-Ph), 129.3 (br s, *C*H, p-P-Ph), 128.7 (*C*H, $^3J_{CP}$ = 7.6 Hz, m-P-Ph), 123.0 (*C*H), 120.6 (*C*H), 34.2 (Ar*C*H(CH$_3$)$_2$), 31.4 (Ar*C*H(CH$_3$)$_2$), 25.0 (ArCH(*C*H$_3$)$_2$), 24.9 (ArCH(*C*H$_3$)$_2$), 23.9 (ArCH(*C*H$_3$)$_2$). One *C*H resonance of the Ar*S ligand was not observed, being possibly obscured by the doublet at 128.7 ppm. The [*C*P] resonance of PPh$_3$ was not observed. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −15.8. Anal. Calcd for $C_{54}H_{64}CuPS$: C, 77.24; H, 7.68; S, 3.82. Found: C, 77.81; H, 7.43; S, 3.26.

$[Cu(SAr^*)(2,6\text{-lut})]$ (2). A solution of 37 mg (0.35 mmol) of 2,6-lutidine in 2 mL of THF was added to a stirred suspension of 18 mg (0.087 mmol) of $[CuBr(SMe_2)]$[16] in 2 mL of THF, resulting in a nearly clear solution. A solution of 46 mg (0.087 mmol) of NaSAr* in 1 mL of THF was added dropwise, producing a fine precipitate. The reaction mixture was stirred for 30 min and filtered, and the filtrate taken to dryness. The off-white oily residue was extracted with 4 mL of hexane, and solvent was removed from the extract. The residue was recrystallized from hexane at −30 °C. The crystalline solid was washed quickly with cold hexane and dried, giving the product as 20 mg (33%) of colorless crystals. ^1H NMR (C_6D_6): δ 7.23 (s, 4), 7.18 (d, 2), 7.04 (m, 1), 6.58 (br s, 1), 6.10 (br s, 2), 3.34 (sept, 4), 2.75 (sept, 2), 2.10 (s, 6), 1.64 (d, 12), 1.22 (d, 12), 1.14 (d, 12). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.59 MHz): δ 158.3 (*C*), 146.9 (*C*), 146.8 (*C*), 142.3 (*C*), 141.4 (*C*), 129.1 (*C*H), 123.1 (*C*H), 121.3 (*C*H), 120.6 (*C*H), 34.5 (Ar*C*H(CH$_3$)$_2$), 31.3 (Ar*C*H(CH$_3$)$_2$), 25.0 (ArCH(*C*H$_3$)$_2$), 24.6 (ArCH(*C*H$_3$)$_2$), 24.5 (lut-*C*H$_3$), 24.2 (ArCH(*C*H$_3$)$_2$).

$[Cu(SAr^*)(Pr^i{}_2NHCMe_2)]$ (3). A mixture of 4.0 mg (0.070 mmol) of NaOMe in 2 mL of THF and 29 mg (0.055 mmol) of Ar*SH was stirred for 2 h and filtered. The filtrate was added dropwise to a stirred mixture of 12 mg (0.057 mmol) of $[CuBr(SMe_2)]$ and 10 mg of $Pr^i{}_2NHCMe_2$ in 2 mL of THF. The nearly clear solution was stirred for 90 min and filtered, and the filtrate was reduced to dryness. The oily solid residue was extracted with 2 mL of hexanes, and the solvent was removed, giving the product as 28 mg (66%) of white solid. ^1H NMR (C_6D_6): δ 7.26 (s, 4), 7.20 (d, 2), 7.06 (t, 1), 4.54 (br s, 2), 3.66 (sept, 4), 2.81 (sept, 2), 1.67 (d, 12), 1.40 (s, 6), 1.34 (d, 12), 1.15 (d, 12), 1.07 (d, 12).

---

(8) Koch, S. A.; Fikar, R.; Millar, M.; O'Sullivan, T. *Inorg. Chem.* **1984**, *23*, 122–124.
(9) Fujisawa, K.; Imai, S.; Kitajima, N.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 168–169.
(10) Zeevi, S.; Tshuva, E. Y. *Eur. J. Inorg. Chem.* **2007**, 5369–5376.
(11) Medina, I.; Jacobsen, H.; Mague, J. T.; Fink, M. J. *Inorg. Chem.* **2006**, *45*, 8844–8846.
(12) Wang, J.-J.; Holm, R. H. *Inorg. Chem.* **2007**, *46*, 11156–11164.
(13) Delp, S. A.; Munro-Leighton, C.; Goj, L. A.; Ramirez, M. A.; Gunnoe, T. B.; Petersen, J. L.; Boyle, P. D. *Inorg. Chem.* **2007**, *46*, 2365–2367.
(14) Niemeyer, M.; Power, P. P. *Inorg. Chem.* **1996**, *35*, 7264–7272.
(15) Reichle, W. *Inorg. Chim. Acta* **1971**, *5*, 325–332.

Table 1. Crystallographic Data[a] for Cu^I Complexes with Sterically Hindering Ligands

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**[d]
formula	$C_{54}H_{64}CuPS$	$C_{43}H_{58}CuNS$	$C_{47}H_{69}CuN_2S$	$C_{47}H_{69}CuN_2S_2$	$C_{40}H_{57}CuS$	$C_{43}H_{57}CuN$	$C_{72}H_{98}BrCu_3$	$C_{41}H_{52}Cu_2PS_2$	$C_{43}H_{56}S_2$
fw	839.62	684.50	756.64	789.70	633.46	651.44	1298.15	767.00	637.00
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$	$P2_1/n$	$P2_1/c$	$Pbca$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$
Z	4	8	4	4	8	2	4	4	8
a, Å	17.615(1)	32.258(2)	13.179(1)	13.676(3)	18.793(1)	12.249(5)	13.549(1)	11.389(1)	20.260(1)
b, Å	14.463(1)	18.700(1)	24.460(2)	19.847(4)	16.612 (1)	12.703(5)	17.287(1)	17.975(1)	16.548 (1)
c, Å	19.931(2)	16.959(1)	14.141(1)	17.741(3)	24.220 (1)	13.849(5)	28.753(2)	18.152(1)	25.200(1)
α, deg	90.00	90.00	90.00	90.00	90.00	112.348(5)	90.00	90.00	90.00
β, deg	108.956(1)	107.120(1)	100.244(4)	104.665(4)	90.00	102.337(5)	94.754(1)	94.287(1)	113.215(1)
γ, deg	90.00	90.00	90.00	90.00	90.00	90.850(5)	90.00	90.00	90.00
V, A^3	4802.4(6)	9776.8(9)	4485.8(5)	4659 (2)	7561.4(6)	1936(1)	6711.2(7)	3705.5(4)	7764.6(7)
d_{calcd}, g/cm^3	1.161	0.930	1.122	1.126	1.113	1.118	1.285	1.375	1.090
μ, mm^{-1}	0.565	0.512	0.565	0.590	0.657	0.592	1.639	1.332	0.164
2θ, deg	50.00	50.00	50.00	50.00	50.00	50.00	55.80	55.78	50.00
R_1[b] $[I > 2\sigma(I)]$	0.0569	0.0491	0.0732	0.0504	0.0525	0.0473	0.0406	0.0475	0.0808
wR_2[c] $[I > 2\sigma(I)]$	0.1231	0.1284	0.1713	0.1150	0.1476	0.1333	0.0998	0.1011	0.2255
GOF (F^2)	1.021	0.913	1.012	1.019	1.033	1.069	1.017	1.019	1.039

[a] Mo Kα radiation ($\lambda = 0.71073$ Å), 193(2) K. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2/(F_o^2)^2]\}^{1/2}$. [d] Organic disulfide.

Table 2. Selected Bond Distances (Å) and Angles (deg) in Mononuclear [Cu^I(SAr*)L] and [Cu^I (Ar*)L] Complexes

	L = PPh_3	2,6-lut[a]	$Pr^i_2NHCMe_2$	$Pr^i_2Me_2ImS$	tht	2,6-lut[b]
Cu−S(Ar*)	2.194(1)	2.122(1)	2.122(2)	2.157(1)		
Cu−C(Ar*)					1.915(3)	1.913(2)
Cu-L	2.210(1)	1.929(2)	1.902(6)	2.196(1)	2.181(1)	1.946(2)
(Ar*)S−Cu-L	134.84(4)	157.31(6)	164.0(2)	152.98(4)		
(Ar*)C−Cu-L					174.0(1)	178.5(1)
$C_6H_2Pr^i_3\cdots Cu$[c]	2.31	2.90	3.40	2.47	3.12, 3.21[d]	3.18, 3.20[d]

[a] Complex **2**. [b] Complex **6**. [c] Perpendicular distance of Cu atom to the nearest phenyl ring. [d] $Cu\cdots C_{ipso}$ distances; atom not positioned over phenyl rings.

$^{13}C\{^1H\}$ NMR (C_6D_6, 100.59 MHz): δ 176.9 (N*C*N), 150.1 (*C*), 146.63 (*C*), 146.59 (*C*), 142.4 (*C*), 141.5 (*C*), 128.8 (*C*H), 123.8 (N*C*), 121.3 (*C*H), 120.3 (*C*H), 53.1 (N*C*H(CH$_3$)$_2$), 34.9 (Ar*C*H(CH$_3$)$_2$), 31.3 (Ar*C*H(CH$_3$)$_2$), 25.2 (ArCH(*C*H$_3$)$_2$), 24.6 (ArCH(*C*H$_3$)$_2$), 24.3 (ArCH(*C*H$_3$)$_2$), 22.5 (NC(*C*H$_3$)), 9.5 (NCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{47}H_{69}CuN_2S$: C, 74.50; H, 9.18; N, 3.70. Found: C, 74.30, H, 9.20; N, 3.69.

[Cu(SAr*)($Pr^i_2Me_2ImS$)] (4). A solution containing 35 mg (0.046 mmol) of [Cu(SAr*)($Pr^i_2NHCMe_2$)] in 2 mL of THF at −30 °C was treated with a solution of 1.6 mg (0.05 mmol) of sulfur in 0.2 mL of THF. The reaction mixture was allowed to warm to room temperature and stirred for 20 min, resulting in a color change to bright orange. The solvent was removed. The yellow residue was extracted with 3 mL of hexane, and the extract was filtered. The filtrate was taken to dryness, and the solid residue was recrystallized from hexanes at −30 °C to yield the product as 23 mg (63%) of colorless crystals. ^1H NMR (C_6D_6): δ 7.36 (s, 4), 7.10 (d, 2), 6.98 (t, 1), 5.47 (br s, 2), 3.28 (sept, 4), 2.92 (sept, 2), 1.72 (d, 12), 1.33 and 1.32 (d, d, 24), 1.20 (br s, 6), 0.97 (br s, 12). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.59 MHz): δ 153.0 (*C*), 147.4 (*C*), 146.4 (*C*), 141.4 (*C*), 139.6 (*C*), 128.7 (*C*H), 123.1 (N*C*(CH$_3$)), 122.1 (*C*H), 120.3 (*C*H), 50.4 (N*C*H(CH$_3$)$_2$), 34.8 (Ar*C*H(CH$_3$)$_2$), 31.3 (Ar*C*H(CH$_3$)$_2$), 25.1 (ArCH(*C*H$_3$)$_2$), 24.9 (ArCH(*C*H$_3$)$_2$), 24.6 (ArCH(*C*H$_3$)$_2$), 20.4 (NCH(*C*H$_3$)$_2$), 9.5 (NC(*C*H$_3$)). The signal of the thione carbon atom was not observed. Anal. Calcd for $C_{47}H_{69}CuN_2S_2$: C, 71.48; H, 8.81; S, 8.12. Found: C, 71.55; H, 9.05; S, 7.89.

[Cu(Ar*)(tht)] (5). A solution of 411 mg (0.730 mmol) of [Ar*Li(OEt$_2$)][17] in 3 mL of ether was added to a suspension of CuBr (103 mg, 0.730 mmol) in 2 mL of ether at −30 °C in the dark. The mixture was stirred for 20 min, and 1.5 mL (17 mmol) of tetrahydrothiophene was added. The mixture was stirred for 30 min, and volatiles were removed. The solid residue was extracted with ether (4 mL), and the ether solution was concentrated to ca. 2 mL and was stored at −30 °C. The product was obtained as three successive crops of colorless crystals totaling 282 mg (61%). ^1H NMR (C_6D_6): δ 7.20−7.30 (m, 3), 7.13 (s, 4), 3.40 (sept, 4), 2.80 (sept, 2), 2.19 (br s, 4), 1.37 (d, 12), 1.25 (d, 12), 1.20 (d, 12), 1.16 (m, 4). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.59 MHz): δ 168.2 (Cu*C*), 149.6 (*C*), 146.9 (*C*), 146.5 (*C*), 145.9 (*C*), 124.9 (*C*H), 124.8 (*C*H), 120.4 (*C*H), 34.8 (Ar*C*H(CH$_3$)$_2$), 34.3 (S-*C*H$_2$), 30.56 (S-CH$_2$*C*H$_2$), 30.53 (Ar*C*H(CH$_3$)$_2$), 25.0 (ArCH(*C*H$_3$)$_2$), 24.59 (ArCH(*C*H$_3$)$_2$), 24.53 (ArCH(*C*H$_3$)$_2$). The product analyzed satisfactorily as a monoetherate solvate. Anal. Calcd for $C_{40}H_{57}CuS\cdot C_4H_{10}O$: C, 74.68; H, 9.54; S, 4.53. Found: C, 74.58; H, 9.12; S, 4.92.

[Cu(Ar*)(2,6-lut)] (6). A solution of 54 mg (0.096 mmol) of [Ar*Li(OEt$_2$)] in 2 mL of ether was added to a suspension of CuBr (14 mg, 0.097 mmol) in 2 mL of ether at −30 °C in the dark. The mixture was stirred for 30 min, and a solution of 32 mg (0.29 mmol) of 2,6-lutidine in 1 mL of ether was added. The mixture was stirred for 30 min, and volatiles were removed. The white residue was extracted with hexanes (4 mL), and the solvent was removed to give the product as 52 mg (83%) of a white solid. ^1H NMR (C_6D_6): δ 7.29 (m, 3), 7.15 (s, 4), 6.47 (t, 1), 6.05 (d, 2), 3.51 (sept, 4), 2.88 (sept, 2), 1.69 (s, 6), 1.35 (d, 12), 1.31 (d, 12), 1.28 (d, 12). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.59 MHz): δ 167.0 (Cu*C*), 159.4 (*C*), 150.2 (*C*), 147.2 (*C*), 146.49 (*C*), 146.46 (*C*), 137.8 (*C*H), 125.1 (*C*H), 124.3 (*C*H), 121.5 (*C*H), 120.4 (*C*H), 34.9 (Ar*C*H(CH$_3$)$_2$), 30.5 (Ar*C*H(CH$_3$)$_2$), 24.74 (ArCH(*C*H$_3$)$_2$), 24.71 (ArCH(*C*H$_3$)$_2$), 24.6 (ArCH(*C*H$_3$)$_2$), 23.7 (lut-*C*H$_3$).

[Cu_3(SAr*)$_2$Br] (7). A mixture of 4.0 mg (0.070 mmol) of NaOMe and 29 mg (0.055 mmol) of Ar*SH in 7 mL of THF was stirred for 4 h. The solution was filtered and added dropwise to a stirred suspension of 11 mg (0.053 mmol) of [CuBr(SMe$_2$)] in 2 mL of THF. The nearly clear reaction mixture was stirred overnight and filtered. The solvent was removed from the filtrate, and the oily solid residue was extracted with 2 mL of hexane. The solvent

---

(16) House, H. O.; Chu, C.-Y.; Wilkins, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460–1469.

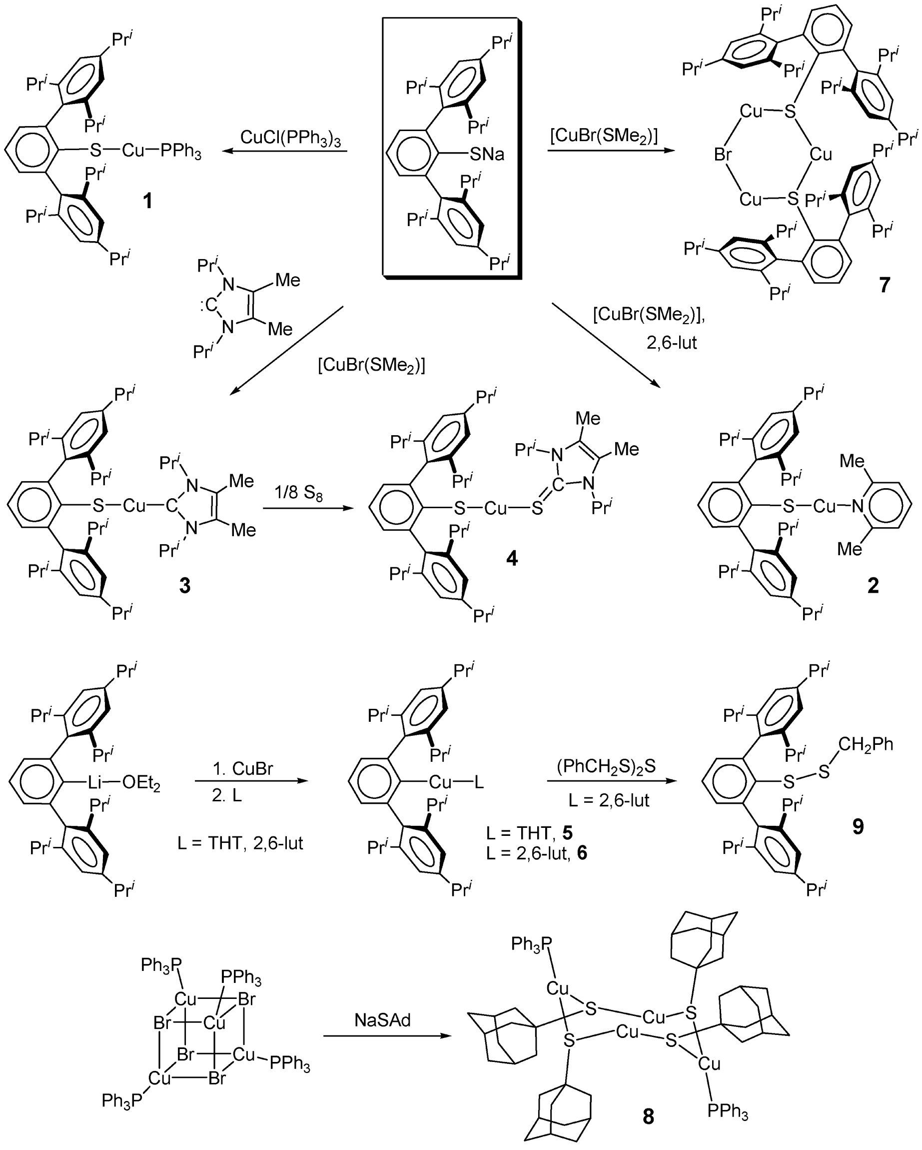


Figure 2. Synthesis of two-coordinate Cu^I complexes **1**−**6** and trinuclear **7** derived from Ar*S, complex **8** from S-1-Ad, and disulfide **9**.

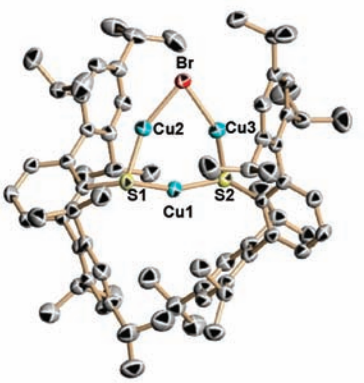
was removed from the extract, and the residue was recrystallized from hexane to afford the product as 20 mg (85% based on Cu) of colorless crystals. ^{1}H NMR (C_6D_6): δ 7.26 (s, 8), 6.82 (m, 6), 2.96 (sept, 4), 2.75 (sept, 8), 1.38 (d, 48), 1.07 (br d, 24). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.59 MHz): δ 149.4 (*C*), 145.5 (br s, *C*), 143.2 (*C*), 139.7 (*C*), 136.3 (*C*), 130.3 (*C*H), 124.7 (*C*H), 123.0 (*C*H), 34.8 (Ar*C*H(CH$_3$)$_2$), 31.5 (Ar*C*H(CH$_3$)$_2$), 24.9 (ArCH(*C*H$_3$)$_2$), 24.6 (ArCH(*C*H$_3$)$_2$), 24.5 (ArCH(*C*H$_3$)$_2$).

[Cu$_4$(S-1-Ad)$_4$(PPh$_3$)$_2$] (8). To a stirred solution of 44 mg (0.028 mmol) of [$Cu_4Br_4(PPh_3)_4$] in 4 mL of toluene was added a suspension of NaS-1-Ad (21 mg, 0.11 mmol) in 1 mL of toluene. The reaction mixture became yellow following the addition and was filtered. The filtrate was reduced to ca. 2 mL and was layered with 10 mL of hexanes. The mixture was maintained at −30 °C overnight, during which time the product separated as 29 mg (71%) of very pale yellow crystals. ^{1}H NMR (C_6D_6): δ 7.57 (t, 12), 7.06 (m, 18), 2.40 (s, 24), 1.92 (s, 12), 1.59 (d, 12), 1.50 (d, 12). ^{31}P NMR (C_6D_6): δ 3.72. The compound analyzed satisfactorily as a hexane monosolvate. Anal. Calcd for $C_{76}H_{90}Cu_4P_2S_4\cdot C_6H_{14}$: C, 64.20; H, 6.83. Found: C, 63.89; H, 6.31.

Ar*SSCH$_2$Ph (9). A solution of [Cu(Ar*)(2,6,-lut)] (28 mg, 0.043 mmol) in 0.5 mL of C_6D_6 was treated with 16 mg (0.057 mmol) of dibenzyltrisulfide in 0.5 mL of C_6D_6. As the solution was stirred, the reaction was monitored by ^{1}H NMR. After 2 days, no starting material was observed, and a brown precipitate was removed by filtration. Solvent was removed, and the residue was extracted with hexanes. The filtrate was concentrated to a colorless oily residue, which was heated at 90 °C/0.005 mm Hg for 2 h, resulting in the formation of 10 mg (37%) of colorless crystals. ^{1}H NMR (C_6D_6): δ 7.23 (s, 4), 7.13 (m, 2), 7.02 (m, 1), 6.86−6.95 (m, 5) 2.87 (sept, 4), 2.81 (sept, 2), 2.72 (s, 2), 1.38 (d, 12), 1.20 (d, 12), 1.12 (d, 12).). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.59 MHz): δ 148.9 (*C*), 146.7 (*C*), 145.7 (*C*), 138.3 (*C*), 137.9 (*C*), 136.9 (*C*), 131.0 (*C*H), 129.5 (*C*H), 128.3 (*C*H), 128.0 (*C*H), 127.2 (*C*H), 121.3 (*C*H), 44.0 (*C*H$_2$), 34.8 (Ar*C*H(CH$_3$)$_2$), 31.4 (Ar*C*H(CH$_3$)$_2$), 25.6 (ArCH(*C*H$_3$)$_2$), 24.4 (ArCH(*C*H$_3$)$_2$), 23.4 (ArCH(*C*H$_3$)$_2$).

X-Ray Structure Determinations. Structures of the nine compounds in Table 1 were determined. Diffraction-quality crystals were obtained as follows: recrystallization from concentrated hexane solutions at −30 °C (**1**−**4**, **7**, **9**), hexane diffusion into a concentrated toluene solution at −30 °C (**8**),

$[Cu_3(SAr^*)_2Br]$



$[Cu_4(S\text{-}1\text{-}Ad)_4(PPh_3)_2]$

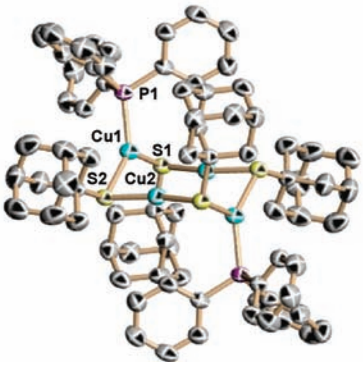


Figure 3. Structures of polynuclear Cu^I complexes showing 50% probability ellipsoids, partial atom numbering schemes, and selected bond distances (Å) and angles (deg). $[Cu_3(Ar^*S)_2Br]$ (upper): Cu1−S1 2.174(1), Cu1−S2 2.173(1), Cu2−S1 2.186(1), Cu3−S2 2.198(1), Cu2−Br 2.301(1), Cu3−Br 2.317(1), S1−Cu1−S2 161.27(3), Cu1−S1−Cu2 77.59(2), Cu1−S2−Cu3 73.36(2), S1−Cu2−Br 149.43(2), S2−Cu3−Br 148.24(2), Cu2−Br−Cu3 74.40(1). $[Cu_4(S\text{-}1\text{-}Ad)_4(PPh_3)_2]$ (lower, crystallographically imposed centrosymmetry): Cu1−P1 2.252(1), Cu1−S1 2.286(1), Cu1−S2 2.227(1), Cu2−S2 2.173(1), Cu2−S1 2.157(1), P1−Cu1−S1 105.75(3), P1−Cu1−S2 139.47(3), S1−Cu1−S2 113.34(3), S2−Cu2−S1′ 165.71(3).

and concentration of ether (**5**) and hexane (**6**) solutions. Crystal mounting and data collections were performed as described[18] on a Siemens (Bruker) SMART CCD instrument using Mo Kα radiation. Data out to a 2θ of 50° were used for **1**−**6** and **9** because of the somewhat lower quality of the high-angle data; for **7** and **8**, higher-angle data were employed.

Data reductions were performed with SAINT, which corrects for Lorentz polarization and decay. Space groups were assigned by analysis of symmetry and systematic absences determined by XPREP. Structures were solved by direct methods and SHELXL-97 and refined against all data in the 2θ ranges by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at idealized positions were included in final refinements. Compound **8** occupies a special position; therefore, only half a molecule constitutes an asymmetric unit. It contains one hexane solvate molecule per cluster. Compound **2** contained traces of unidentified solvate (one peak of ca. 2e$^-$, another of ca. 1.5e$^-$) which could not be modeled satisfactorily and was therefore removed using the SQUEEZE program of the PLATON package. In the structure of **5**, the disorder of the tht ligand was modeled by two conformations. In some of the structures (especially those of **3** and **9**), peripheral isopropyl groups display a wagging motion, affecting to some extent the quality of the structures. Two-site disorder modeling did not significantly improve resolution of the large thermal motion. Crystallographic data and final agreement factors are given in Table 1.[19]

Results and Discussion

The reactions leading to compounds **1**−**9** reported here are summarized in Figure 2. Selected structures of reaction products are provided in Figures 3−5, and selected metric features of Ar*S and Ar* complexes are summarized in Table 2.

Preparation of Two-Coordinate Cu^I Complexes. In view of the synthesis of linear $[Cu(S\text{-}1\text{-}Ad)_2]^{1-}$,[9] attempts to prepare mononuclear two-coordinate complexes of the type $[Cu^I(SR)L]$ first involved adamantane-1-thiolate. Reaction of $[CuCl(PPh_3)_3]$[14] with NaS-1-Ad did not yield a characterizable product. However, reaction with $[Cu_4Br_4(PPh_3)_4]$,[20] utilized because of a lesser Cu/PPh$_3$ ratio, afforded the tetranuclear complex **8**. The molecule is built of a $Cu_4(\mu_2\text{-}S)_4$ ring in which there are two trigonal-planar Cu^I sites with bound phosphine and two two-coordinate sites whose bond angles deviate 14° from linearity (Figure 3). The structure is similar to that of $[Cu_4(SBu^t)_4(PPh_3)_2]$.[21] Because of this result and a previous finding that adamantane-1-thiolate can form at least one polynuclear complex[9] in addition to mononuclear $[Cu(S\text{-}1\text{-}Ad)_2]^{1-}$, we directed our attention to a more hindered ligand system.

2,6-Bis(2,4,6-triisopropylphenyl)benzenethiolate(1-) (Ar*S) was introduced by Niemeyer and Power[14,22] as an especially capacious ligand, a property demonstrated by its ability to form homoleptic two-coordinate complexes with Mg^{II}, divalent ions of the first transition series,[23] and Eu^{II} and Yb^{II}.[24] Thiolate complexes were prepared by reactions 1 and 2. Complexes **1** (63%), **2** (33%), and **3** (66%) were obtained in the indicated yields by reaction 1. The only previously reported two-coordinate Cu^I phosphinethiolate species similar to **1** is nearly linear $[Cu(SSiPh_3)(PBu^t_3)]$.[11] No aminethiolate complexes related to **2** have been described; several complexes analogous to **3** have been prepared by thiolate ligand displacement of preisolated carbene complexes.[13] The reaction of $[CuBr(SMe_2)]$ with equimolar thiolate did not lead to

---

(17) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958–964.
(18) Groysman, S.; Holm, R. H. *Inorg. Chem.* **2007**, *46*, 4090–4102.
(19) See the Supporting Information.
(20) Costa, G.; Reisenhofer, E.; Stefani, L. *J. Inorg. Nucl. Chem.* **1965**, *27*, 2581–2584.
(21) Dance, I. G.; Fitzpatrick, L. J.; Craig, D. C.; Scudder, M. L. *Inorg. Chem.* **1989**, *28*, 1853–1861.
(22) Niemeyer, M.; Power, P. P. *Inorg. Chim. Acta* **1997**, *263*, 201–207.
(23) Nguyen, T.; Panda, A.; Olmstead, M. M.; Richards, A. F.; Stender, M.; Brynda, M.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 8545–8552.
(24) Niemeyer, M. *Eur. J. Inorg. Chem.* **2001**, 1969–1981.
(25) Ferrari, M. B.; Fava, G. G.; Pelizzi, G.; Tarasconi, P. *Inorg. Chim. Acta* **1985**, *97*, 99–109.
(26) Skoulika, S.; Aubry, A.; Karagianidis, P.; Aslandis, P.; Papastefanou, S. *Inorg. Chim. Acta* **1991**, *183*, 207–211.
(27) Singh, R.; Dikshit, S. K. *Polyhedron* **1995**, *14*, 1799–1807.
(28) Aslandis, P.; Cox, P. J.; Karagianidis, P.; Hadjikakou, S. K.; Antoniadis, C. D. *Eur. J. Inorg. Chem.* **2002**, 2216–2222.
(29) Kaltzoglou, A.; Cox, P. J.; Aslandis, P. *Inorg. Chim. Acta* **2005**, *358*, 3048–3056.
(30) Niemeyer, M. *Organometallics* **1998**, *17*, 4649–4656.

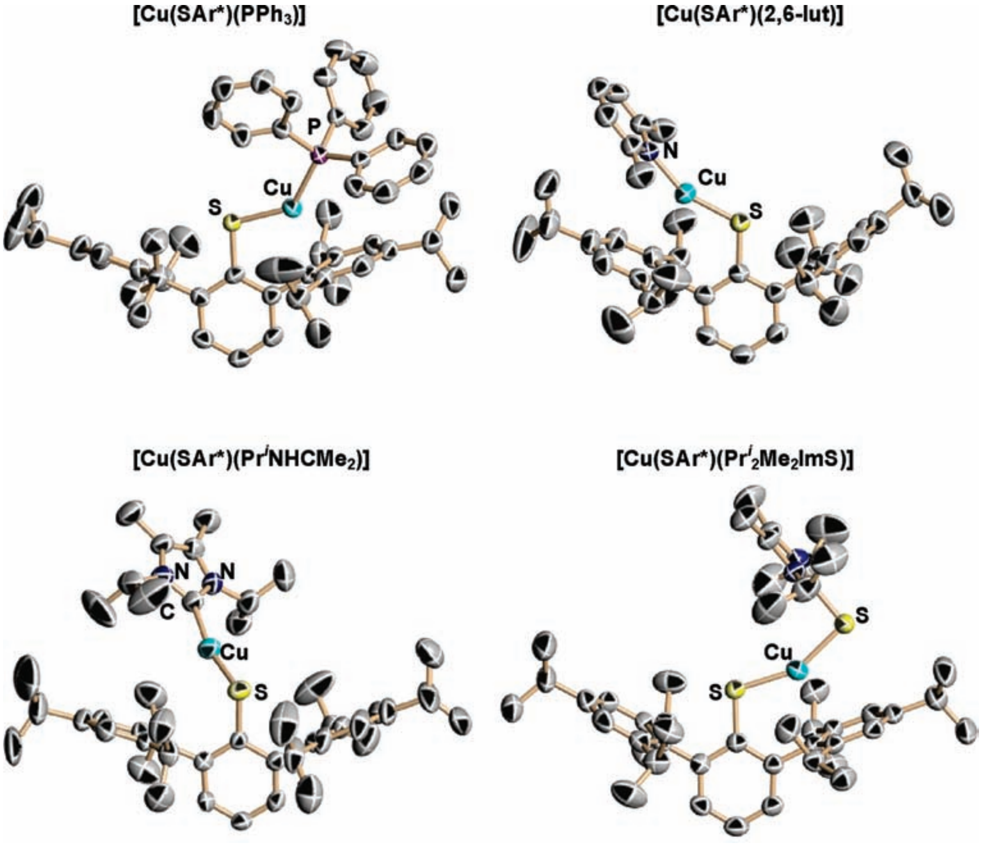


Figure 4. Structures of quasi-two-coordinate Cu^I complexes [Cu(SAr*)L]: L = PPh_3 and 2,6-lut (upper) and $Pr^i{}_2NHCMe_2$ and $Pr^i{}_2Me_2ImS$ (lower), showing 50% probability ellipsoids. Metric data are summarized in Table 2.

anticipated [Cu(SAr*)(Me_2S)] but instead to trinuclear **7** (85%, see below). Reaction 2 is exemplified by sulfur insertion into the Cu−C bond of **3** to afford complex **4** (63%). Three- and four-coordinate Cu^I−thiourea complexes with two, three, and four thiourea ligands are numerous. Those with one such ligand are nearly exclusively the tetrahedral species [$Cu(PR_3)_2X(tu)$].[25−29] Complex **4** is the first example of a [Cu(SR)(tu)] complex.

$$(ArS*)Na + [CuXL_n] \rightarrow [Cu(SAr*)L] + NaX + (n-1)L \qquad (1)$$

$$[Cu(Ar*S)L] + S \rightarrow [Cu(SAr*)(SL)] \qquad (2)$$

Because direct synthesis of the complex with L = Me_2S by reaction 1 was unsuccessful, its formation by sulfur insertion into a Cu^I−C bond was investigated. The two-coordinate complexes [Cu(Ar*)L] with L = tht (**5**, 61%) and 2,6-lut (**6**, 83%) were obtained by the reaction of [(Ar*)Li(OEt_2)] with CuBr and L in a manner similar to the preparation of [Cu(Ar*)(SMe_2)].[17] The reaction of **5** with the sulfur transfer reagents Ph_3SbS, $(PhCH_2S)_2S$, and elemental sulfur failed to give a well-defined product. Similarly, the reaction of **6** with Ph_3SbS and sulfur was unsuccessful. Treatment of **6** with $(PhCH_2S)_2S$ led unexpectedly to the mixed disulfide **9** (37%) together with an insoluble brown precipitate (presumably Cu_2S). The previously unknown disulfide was identified by an X-ray structure determination.[19]

Structures of Ar*S and Ar* Complexes. The structures of Ar*S complexes **1**−**4** (Figure 4) reveal varying departures from S−Cu−L linearity in structures described as quasi-two-coordinate, owing to interactions of Cu^I with a phenyl ring in the 2,6-position in each molecule (Table 2). Intramolecular Cu^I−olefin and −arene interactions are frequently encountered, including several recent instances.[30−32] Com-

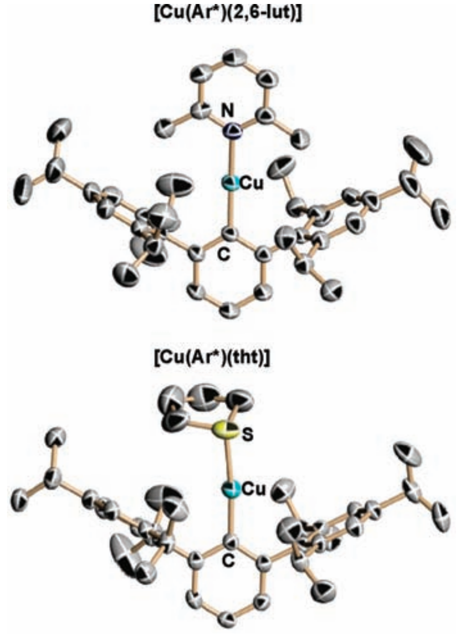


Figure 5. Structures of two-coordinate Cu^I complexes [Cu(Ar*)L]: L = tht and 2,6-lut, showing 50% probability ellipsoids. Metric data are summarized in Table 2.

putational results for Cu^I−arene interactions indicate that these are likely of 3d-C($p\pi^*$) origin.[32] In the set **1**−**4**, these interactions are described by the perpendicular distance between the metal and the interacting phenyl ring. This distance maximizes in the nonlinear phosphine complex **1** (2.31 Å) where the metal has pseudotrigonal coordination and the smallest Cu^I bond angle (135°). The weakest or nil interaction occurs in carbene complex **3** (3.40 Å), which displays the largest bond angle (164°). Complexes **4** (2.47 Å, 153°) and **2** (2.90 Å, 157°) are intermediate cases.

The structure of trinuclear **7** (Figure 3) is based on a Cu_3S_2Br ring, which is unique to this structure but reminiscent of the cyclic nonplanar $Cu_3(SR)_3$ motif relatively abundant in Cu^I−thiolates.[33−36] The ring contains two-coordinate Cu1 and quasi-two-coordinate Cu2 and Cu3, which show weak secondary interactions with nearly phenyl rings (2.44, 2.48 Å), similar to **1**, **2**, and **4**. It might be noted that these interactions in two-coordinate complexes were first observed in sterically crowded $[Fe(SC_6H_3\text{-}2,6\text{-}mes_2)_2]$ and $[Fe(SC_6H_3\text{-}2,6\text{-}mes_2)(N(SiMe_3)_2)]$ with Fe···C separations of ca. 2.5 Å.[37] In the molecules, the interactions likely involve C($p\pi$) electron donation to incompletely filled 3d iron orbitals as a means of redressing electron deficiency at the metal sites. In the present group of Cu^I thiolates, electron donation in the opposite sense is probable.

Structures of the two Ar* complexes **5** and **6** were also determined (Figure 5, Table 2); the structure of **5** resembles $[Cu(Ar^*)(SMe_2)]$.[17] These complexes manifest essentially negligible secondary interactions with phenyl rings and thus are strictly two-coordinate with nearly linear structures (Table 2). In **6**, the central phenyl and pyridyl rings are nearly coplanar, with a C−Cu−N bond angle of 178.5°, and a dihedral angle of 9°, and the rings in the 2,6- positions are nearly perpendicular to the central ring with dihedral angles of 81° and 87°. This stereochemistry sets a distance of ca. 3.4 Å between the 2,6-methyl groups of lutidine and the rings and leads to intramolecular $CH(\sigma^*)/\pi$ interactions of a type previously catalogued[38] and treated theoretically.[39] An apparent effect of this situation is enhanced shielding of the methyl protons in **6** (1.69 ppm) compared to **2** (2.10 ppm), which lacks the same ring orientation, and free 2,6-lutidine (2.38 ppm) in C_6D_6.

Summary

This work describes the synthesis of a set of complexes $[Cu^I(SAr^*)L]$ whose actual or quasi-dicoordinate formulation arises from the uncommon steric shielding of the metal center by the thiolate ligand Ar*S introduced by Niemeyer and Power.[14,22] Also demonstrated is the formation of a trinuclear structure from the reaction of $[CuBr(SMe_2)]$ and thiolate in the absence of ligand L, the conversion of a carbene complex to a thiourea complex by sulfur insertion into a Cu−C bond, and the occurrence of weak secondary bonding interactions between the metal and phenyl groups that contribute to nonlinear structures and quasi-two-coordination. Current research is concerned with the role of these complexes in constructing analogues of the CODH site.

Acknowledgment. This research was supported by NSF Grant CHE 00547734. We thank Dr. L. Deng for a sample of carbene.

Supporting Information Available: X-ray crystallographic files in CIF format for the nine compounds in Table 1 and a structural depiction of compound **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC801836K

(31) Sundararaman, A.; Lalancette, R. A.; Zakharov, L. N.; Rheingold, A. L.; Jäkle, F. *Organometallics* **2003**, *22*, 3526–3532.

(32) Osako, T.; Tachi, Y.; Doe, M.; Shiro, M.; Ohkubo, K.; Fukuzumi, S.; Itoh, S. *Chem.−Eur. J.* **2004**, *10*, 237–246.

(33) Dance, I. G.; Fitzpatrick, L. J.; Scudder, M. L. *J. Chem. Soc., Chem. Commun.* **1983**, 546–548.

(34) Pulla Rao, C.; Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1986**, *25*, 428–439.

(35) Knotter, D. M.; van Maanen, H. L.; Grove, D. M.; Spek, A. L.; Van Koten, G. *Inorg. Chem.* **1991**, *30*, 3309–3317.

(36) Togni, A.; Rihs, G.; Blumer, R. E. *Organometallics* **1992**, *11*, 613–621.

(37) Ellison, J. J.; Ruhlandt-Senge, K.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1178–1180.

(38) Umezawa, Y.; Tsuboyama, S.; Takahashi, H.; Uzawa, J.; Nishio, M. *Tetrahedron* **1999**, *55*, 10047–10056.

(39) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2000**, *122*, 3746–3753.