Inorganic Chemistry

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Reactions of $Ph_3Sb{=}S$ with Copper(I) Complexes Supported by N-Donor Ligands: Formation of Stable Adducts and S-Transfer Reactivity

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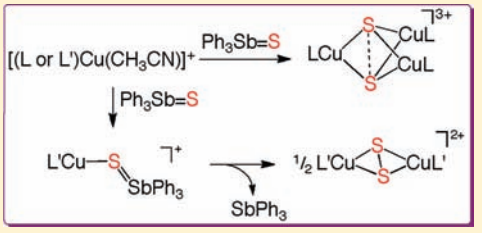
Supporting Information

ABSTRACT: In the exploration of sulfur-delivery reagents useful for synthesizing models of the tetracopper-sulfide cluster of nitrous oxide reductase, reactions of $Ph_3Sb{=}S$ with Cu(I) complexes of *N,N,N′,N′*-tetramethyl-2*R*,3*R*-cyclohexanediamine (TMCHD) and 1,4,7-trialkyltriazacyclononanes (R_3tacn; R = Me, Et, iPr) were studied. Treatment of $[(R_3tacn)Cu(NCCH_3)]SbF_6$ (R = Me, Et, or iPr) with 1 equiv of $S{=}SbPh_3$ in CH_2Cl_2 yielded adducts $[(R_3tacn)Cu(S{=}SbPh_3)]SbF_6$ (**1**−**3**), which were fully characterized, including by X-ray crystallography. The adducts slowly decayed to $[(R_3tacn)_2Cu_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)]^{2+}$ species (**4**−**6**) and $SbPh_3$, or more quickly in the presence of additional $[(R_3tacn)Cu(NCCH_3)]SbF_6$ to **4**−**6** and $[(R_3tacn)Cu(SbPh_3)]SbF_6$ (**7**−**9**). The results of mechanistic studies of the latter process were consistent with rapid intermolecular exchange of $S{=}SbPh_3$ between **1**−**3** and added $[(R_3tacn)Cu(NCCH_3)]SbF_6$, followed by conversion to product via a dicopper intermediate formed in a rapid pre-equilibrium step. Key evidence supporting this step came from the observation of saturation behavior in a plot of the initial rate of loss of **1** versus the initial concentration of $[(Me_3tacn)Cu(NCCH_3)]SbF_6$. Also, treatment of $[(TMCHD)Cu(CH_3CN)]PF_6$ with $S{=}SbPh_3$ led to the known tricopper cluster $[(TMCHD)_3Cu_3(\mu_3\text{-}S)_2](PF_6)_3$ in good yield (79%), a synthetic procedure superior to that previously reported (Brown, E. C.; York, J. T.; Antholine, W. E.; Ruiz, E.; Alvarez, S.; Tolman, W. B. *J. Am. Chem. Soc.* **2005**, *127*, 13752−13753).



INTRODUCTION

The environmentally important reduction of N_2O to N_2 is catalyzed enzymatically by nitrous oxide reductase,[1] which has been shown on the basis of X-ray crystallography[2] and other spectroscopic techniques[3] to contain a unique tetracopper-sulfide cluster supported by multiple histidine residues in its active site. The novel structure of this cluster and hypotheses for the mechanism of N_2O coordination and reduction at its copper centers[4] have stimulated extensive efforts to create copper−sulfur model complexes supported by N-donor ligands.[5,6] These efforts have focused on the use of relatively few types of sulfur-containing reagents (e.g., S_8 and Na_2S_2) in reactions with Cu(I) and Cu(II) species. Studies of the copper−sulfur compounds characterized so far have raised interesting bonding questions,[7,8] and, in one instance, have led to the discovery of reactivity with N_2O.[6] Nonetheless, only a limited array of N-donor ligated copper−sulfur motifs have been characterized, and an accurate model of the nitrous oxide active site has yet to be constructed.

In seeking to broaden the scope of available copper−sulfur complexes as a means to address mechanistic and electronic structural issues relevant to the enzyme active site, we are exploring reactions of copper precursors with an expanded array of sulfur-containing reagents. Several studies have shown that triphenyl antimony sulfide ($Ph_3Sb{=}S$) is useful for sulfur transfer reactions,[9] including for the preparation of transition metal sulfide complexes.[10,11] The utility of Ph_3SbS likely stems from the thermodynamic instability of the Sb−S bond, which is weaker than the related bonds in $R_3E{=}S$ (E = P or As) congeners.[12] Herein, we report the results of an investigation of the reactivity of $Ph_3Sb{=}S$ with selected Cu(I) complexes of *N,N,N′,N′*-tetramethyl-2*R*,3*R*-cyclohexanediamine (TMCHD) and 1,4,7-trialkyltriazacyclononanes (R_3tacn; R = Me, Et, iPr). Key findings include the isolation and structural characterization of novel $LCu(I)\text{-}S{=}SbPh_3$ (L = R_3tacn; R = Me, Et, iPr) adducts, which are the first examples of transition metal complexes bound to $Ph_3Sb{=}S$ to be structurally characterized by X-ray crystallography.[13] These complexes subsequently decay cleanly to $[Cu_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)]^{2+}$ species, particularly when treated with additional $[(R_3tacn)Cu(CH_3CN)]SbF_6$, and mechanistic insights for this process were obtained through kinetics studies. In addition, by using $Ph_3Sb{=}S$ an improved synthetic route to the $[Cu_3S_2]^{3+}$ core[8] was discovered.

EXPERIMENTAL SECTION

General Considerations. All solvents and reagents were obtained from commercial sources and used as received unless otherwise

Received: December 7, 2010
Published: February 21, 2011

noted. The solvents CH_2Cl_2, pentane, and Et_2O were dried over CaH_2 and distilled under vacuum or passed through solvent purification columns (Glass Contour, Laguna, CA). The complexes $[(R_3tacn)Cu(CH_3CN)]SbF_6$ (R = Me,[14] Et,[15] iPr[16]), $[(R_3tacn)Cu(CH_3CN)]BPh_4$ (R = Et[15] or iPr[17]), $[(Me_3tacn)_2Cu_2(S_2)](SbF_6)_2$,[14] and $[(TMCHD)Cu(CH_3CN)]PF_6$[18] were prepared according to published procedures. All metal complexes were prepared and stored in a glovebox under a dry N_2 atmosphere. Triphenylantimony sulfide ($Ph_3Sb{=}S$) and 2,3-dimethylbutadiene were purchased from Strem and Aldrich, respectively, and were used without purification. NMR spectra were recorded on either Varian VI-300 or VXR-300 spectrometers at ~20 °C. Chemical shifts (δ) were referenced to residual solvent signal and integrated intensities compared to 1,3,5-trimethyloxybenzene added as an internal standard. UV−vis spectra were recorded on an HP8453 (190−1100 nm) diode-array spectrophotometer. Elemental analyses were performed by Robertson Microlit Laboratory (Ledgewood, NJ). Electrospray ionization mass spectra (ESI-MS) were recorded on a Bruker BioTOF II instrument. IR spectra were obtained using a ThermoNicolet Avatar 370 FT-IR.

$[(R_3tacn)Cu(S{=}SbPh_3)]SbF_6$ (R = Me (1), Et (2), or iPr (3)). All three complexes were prepared according to this illustrative procedure: In an inert atmosphere, to a solution of the $S{=}SbPh_3$ (32 mg, 0.083 mmol) in CH_2Cl_2 (4 mL) was added $[(Me_3tacn)Cu(NCCH_3)]SbF_6$ (43 mg, 0.083 mmol) in CH_2Cl_2 (1 mL). After stirring for 1 h, the mixture was filtered and the volume of the filtrate was reduced to ~1 mL, and Et_2O (15 mL) was added, resulting in formation of a yellow precipitate. The supernatant was decanted, and the yellow powder was washed with Et_2O (3 × 6 mL). The product was isolated in crystalline form by layering Et_2O onto a concentrated tetrahydrofuran (THF) solution at −20 °C (65 mg, 92%). Analogous procedures were used to isolate **2** and **3** as yellow crystals in 41% and 32% yields, respectively. **1**: ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.77−7.61 (m, 15H), 2.59−2.53 Hz (m, 12H), 2.38 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR: (75 MHz, CD_2Cl_2): δ = 134.37, 133.44, 130.97, 55.03, 49.02 ppm. UV−vis [λ_{max}, nm (ε, M^{-1} cm^{-1}) in CH_2Cl_2]: 356 (2100). Anal. Calcd for $C_{27}H_{36}CuF_6N_3SSb_2$: C, 37.90; H, 4.24; N, 4.91. Found: C, 37.77; H, 4.24; N, 4.99. ESI-MS: $[Cu(Me_3tacn)(S{=}SbPh_3)]^+$ calc. m/z 620.0, found 620.3. FT-IR: 2859.2, 1480.5, 1460.1, 1437.5, 1363.4, 1300.0, 1152.8, 1130.2, 1089.4, 1065.5, 1017.0, 966.3, 984.1, 889.5, 773.5, 751.3, 735.4, 692.4, 656.4 cm^{-1}. **2**: ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.74−7.60 (m, 15H), 2.60−2.53 Hz (m, 18H), 1.10 (t, J = 6.0 Hz, 9H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 134.6, 133.4, 130.9, 55.3, 53.3, 13.0 ppm. UV−vis [λ_{max}, nm (ε, M^{-1} cm^{-1}) in CH_2Cl_2]: 356 (2300). Anal. Calcd for $C_{30}H_{42}CuF_6N_3SSb_2$: C, 40.13; H, 4.72; N, 4.68. Found: C, 39.76; H, 4.70; N, 4.65. ESI-MS: $[Cu(Et_3tacn)(S{=}SbPh_3)]^+$ calc. m/z 662.0, found 662.2. FT-IR: 2972.4, 1479.3, 1437.6, 1378.9, 1347.9, 1315.0, 1136.6, 1124.9, 1067.4, 1041.1, 1031.4, 995.7, 928.8, 897.9, 876.2, 860.3, 851.7, 827.1, 812.7, 796.8, 751.0, 739.1 cm^{-1}. **3**: ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.73−7.59 (m, 15H), 2.66−2.61 Hz (m, 9H), 2.47−2.44 Hz (m, 6H), 1.13 (d, J = 6.0 Hz, 18H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 138.75, 134.69, 133.38, 130.91, 58.29, 50.83, 19.70 ppm. UV−vis [λ_{max}, nm (ε, M^{-1} cm^{-1}) in CH_2Cl_2]: 356 (2300). Anal. Calcd for $C_{33}H_{48}CuF_6N_3SSb_2$: C, 42.17; H, 5.15; N, 4.47. Found: C, 42.11; H, 5.23; N, 4.46. ESI-MS: $[Cu(iPr_3tacn)(S{=}SbPh_3)]^+$ calc. m/z 704.1, found 704.3. FT-IR: 2965.7, 1491.5, 1478.4, 1437.0, 1386.8, 1368.5, 1351.5, 1299.1, 1265.1, 1167.0, 1129.4, 1067.2, 1020.3, 995.7, 968.1, 856.7, 841.0, 750.3, 737.9, 721.3, 692.6, 656.5 cm^{-1}.

$[(Et_3tacn)_2Cu_2(\mu\text{-}S_2)](BPh_4)_2$ (5). Elemental sulfur (1.8 mg, 0.007 mmol) was added to a solution of $[(Et_3tacn)Cu(NCCH_3)]BPh_4$ (36 mg, 0.056 mmol) in CH_2Cl_2 (4 mL). After stirring for 2 h, solvent was removed under reduced pressure to yield a brown solid. The brown solid was washed with Et_2O (2 × 6 mL), extracted with dimethylformamide (DMF, 2 mL), and then filtered. Slow diffusion of Et_2O into the dark brown filtrate at room temperature afforded the product as deep green crystals (16 mg, 46%). ^{1}H NMR (300 MHz, d_7-DMF): δ = 7.32 (s, 16H), 6.96 (t, 16H), 6.81 (t, 8H), 3.16−3.09 Hz (m, 36H), 1.36 (t, J = 6.0 Hz, 18H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, d_7-DMF): δ = 137.11, 135.71, 126.33, 122.62, 93.84, 56.04, 54.64, and 12.39 ppm. UV−vis [λ_{max}, nm (ε, M^{-1} cm^{-1}) in DMF]: 410 (7400), 378 (7600). Anal. Calcd for $C_{72}H_{94}B_2Cu_2N_6S_2$: C, 68.83; H, 7.54; N, 6.69. Found: C, 68.45; H, 7.42; N, 6.70. FT-IR: 3052.7, 2978.9, 1579.6, 1478.5, 1465.9, 1386.9, 1270.4, 1258.5, 1144.8, 1122.9, 1069.9, 1033.3, 1018.3, 999.5, 921.0, 862.4, 842.3, 821.8, 792.9, 771.5, 742.3, 732.0, 710.1, 700.6, 668.2 cm^{-1}.

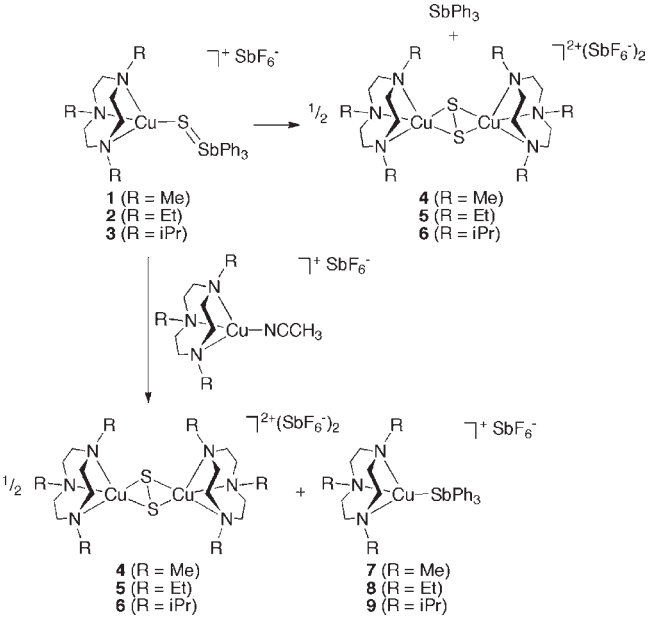
$[(iPr_3tacn)_2Cu_2(\mu\text{-}S_2)](BPh_4)_2$ (6). A similar procedure to that used for the preparation of **5** was followed, except THF was used as the reaction solvent and the product was isolated as dark red crystals from CH_2Cl_2 at −20 °C (37% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.33 (s, 15H), 7.04 (t, J = 6.0 Hz, 14H), 6.89 (t, J = 6.0 Hz, 11H), 3.15−3.06 Hz (m, 5H), 2.95−2.74 (m, 4H), 2.65−2.46 (m, 11H), 2.33−2.20 (m, 10H), 1.26−1.08 (d, J = 6.0 Hz, 36H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 136.44, 126.22, 122.42, 60.47, 51.75, 45.10, 19.79, and 18.46 ppm. UV−vis [λ_{max}, nm (ε, M^{-1} cm^{-1}) in CH_2Cl_2]: 476 (7200), 380 (11000). Anal. Calcd for $C_{78}H_{106}B_2Cu_2N_6S_2$: C, 69.88; H, 7.97; N, 6.27. Found: C, 69.91; H, 7.78; N, 6.24. FT-IR: 3053.5, 2978.0, 1579.8, 1480.7, 1467.0, 1451.0, 1426.7, 1390.1, 1369.2, 1347.1, 1291.9, 1268.7, 1166.3, 1141.9, 1129.4, 1067.3, 1046.6, 1033.5, 962.4, 943.1, 841.7, 761.0, 749.3, 734.1, 705.6, 680.6, 668.1 cm^{-1}.

$[(R_3tacn)Cu(SbPh_3)]SbF_6$ (7, R = Me; 8, R = Et; 9, R = iPr). These complexes were prepared similarly, according to the following representative procedure for **7**. In an inert atmosphere, to a solution of $SbPh_3$ (40.0 mg, 0.113 mmol) in CH_2Cl_2 (4 mL) was added $[(Me_3tacn)Cu(NCCH_3)]SbF_6$ (58.0 mg, 0.113 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred 3 h, filtered, and the volume of the filtrate was reduced to ~1 mL under reduced pressure. A portion of Et_2O (15 mL) was added to yield a white precipitate. The supernatant solution was decanted, and the white powder was washed three times with Et_2O (3 × 6 mL). The white product was recrystallized by diffusion of Et_2O into a concentrated CH_2Cl_2 solution at room temperature to generate the product as colorless crystals (71 mg, 76%). **7**: ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.48−7.43 (m, 15H), 2.90 Hz (s, 12H), 2.73 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 135.87, 130.89, 130.27, 55.98, 50.69 ppm. Anal. Calcd for $C_{27}H_{36}CuF_6N_3Sb_2$: C, 39.37; H, 4.41; N, 5.10. Found: C, 38.87; H, 4.61; N, 4.86. ESI-MS: $[Cu(Me_3tacn)(SbPh_3)]^+$ calc. m/z 588.0, found 588.1. FT-IR: 1463.1, 1434.1, 1363.8, 1299.2, 1153.8, 1127.8, 1085.8, 1069.8, 1057.1, 1015.0, 1000.3, 985.9, 768.3, 737.6, 697.7 cm^{-1}. **8** (68% yield): ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.48−7.41 (m, 15H), 2.90−2.85 Hz (m, 18H), 1.15 (t, J = 6.0 Hz, 9H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 135.85, 130.88, 130.26, 56.87, 54.68, 14.46 ppm. Anal. Calcd for $C_{30}H_{42}CuF_6N_3Sb_2$: C, 41.62; H, 4.89; N, 4.85. Found: C, 41.50; H, 5.20; N, 4.92. ESI-MS: $[Cu(Et_3tacn)(S{=}SbPh_3)]^+$ calc. m/z 662.0, found 662.2. FT-IR: 1434.2, 1375.8, 1338.5, 1121.2, 1067.2, 1037.6, 999.7, 931.38, 768.2, 737.3, 699.67 cm^{-1}. **9** (70% yield): ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.49−7.41 (m, 15H), 3.15−3.11 (m, 3H), 2.93−2.89 Hz (m, 6H), 2.80−2.75 Hz (m, 6H), 1.13 (d, J = 6.0 Hz, 18H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 135.9, 130.85, 130.25, 59.69, 51.77, 20.13 ppm. Anal. Calcd for $C_{33}H_{48}CuF_6N_3Sb_2$: C, 43.66; H, 5.33; N, 4.63. Found: C, 43.30; H, 5.72; N, 4.62. ESI-MS: $[Cu(iPr_3tacn)(SbPh_3)]^+$ calc. m/z 672.1, found 672.2. FT-IR: 1434.4, 1389.4, 1367.0, 1347.1, 1161.7, 1123.2, 1066.5, 997.3, 964.31, 756.2, 739.2, 720.6, 699.6 cm^{-1}.

$[(TMCHD)_3Cu_3(S)_2](PF_6)_3$ (12). In an inert atmosphere, to a solution of the $[(TMCHD)Cu(NCCH_3)]PF_6$ (31 mg, 0.073 mmol) in CH_2Cl_2 (3 mL) was added $S{=}SbPh_3$ (29 mg, 0.049 mmol) in CH_2Cl_2 (1 mL). After the mixture was stirred for 2 h, it was filtered, and the solvent was removed from the filtrate under vacuum to yield a deep

dx.doi.org/10.1021/ic102449m |Inorg. Chem. 2011, 50, 2606–2612

Scheme 1. Reactions of Cu(I)-S═$SbPh_3$ Adducts



green solid, which was washed with Et_2O (3 × 6 mL). The deep green powder obtained was crystallized from CH_2Cl_2 at −20 °C to form dark amber crystals of the product (28 mg, 79%). The product was identified by its X-ray crystal structure and by the similarity of its UV−vis spectrum to previously reported data.[8a]

General Procedures for NMR Kinetics. In a glovebox, appropriate volumes of starting materials in CD_2Cl_2 were mixed in a vial and the volumes were quickly adjusted to 1 mL so that the concentrations of adducts **1**−**3** and $[(R_3tacn)Cu(CH_3CN)]SbF_6$ were 4.7 mM and 47 mM, respectively. The solution was then quickly transferred to a J. Young NMR tube that was removed from glovebox and placed in the spectrometer probe. The progress of the reaction was monitored by ^1H NMR spectroscopy at room temperature with 1,3,5-trimethoxybenzene as an internal standard. The initial rates were determined in experiments in which the first 5−10% of the reaction was followed; the rate constants were obtained by linear fitting of the initial rate change. In the experiments with 2,3-dimethylbutadiene, identical procedures were used except 20 equiv of 2,3-dimethylbutadiene was added to the mixture. Data analysis and graphical representations were performed using the program Kaleidagraph.

RESULTS AND DISCUSSION

Synthesis and Characterization of LCu(I)-S═$SbPh_3$ Adducts and $[L_2Cu_2(S_2)]^{2+}$ Decay Products. Reaction of $[(R_3tacn)Cu(NCCH_3)]SbF_6$ (R = Me, Et, or iPr) with 1 equiv of S═$SbPh_3$ in CH_2Cl_2 yielded adducts **1**−**3**, respectively, as yellow crystalline solids (Scheme 1). The complexes are stable in the solid state when stored under nitrogen, but in solution they decompose slowly (see below). The formulations of **1**−**3** are based on NMR, UV−vis, and FT-IR spectroscopy, CHN analysis, ESI-MS, and X-ray crystallography. Notable identifying features include (a) ^1H NMR spectra with sharp peaks in the diamagnetic region and multiplets for the Ph_3Sb═S hydrogen atoms shifted ∼0.2−0.3 ppm downfield from uncomplexed Ph_3Sb═S (Supporting Information, Figure S1), (b) a shoulder in UV−vis spectra with λ_{max} at ∼350 nm (ε = ∼2100−2300 $M^{-1}cm^{-1}$), and (c) parent ions $[(R_3tacn)Cu(SSbPh_3)]^+$ with appropriate isotope patterns in ESI mass spectra (Supporting Information, Figure S2).

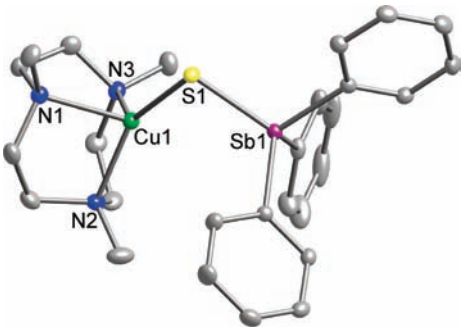


Figure 1. Representation of the X-ray crystal structure of **1**, showing the cationic portion with all non-hydrogen atoms as 50% thermal ellipsoids (H atoms omitted for clarity, only heteroatoms labeled).

Table 1. Selected Bond Distances (Å) and Angles (deg) for the X-ray Structures of 1−3[a]

	1	2	3
Cu1−N1	2.160(2)	2.006(6)	2.178(2)
Cu1−N2	2.107(2)	2.030(8)	2.161(2)
Cu1−N3	2.199(2)	2.157(4)	2.166(2)
Cu1−S1	2.1671(8)	2.1813(10)	2.2027(7)
S1−Sb1	2.2832(7)	2.2735(9)	2.2812(7)
Cu1···Sb1	3.411	3.490	3.547
N1−Cu1−N2	84.96(9)	91.3(3)	84.52(8)
N1−Cu1−N3	83.41(8)	71.1(2)	84.08(8)
N2−Cu1−N3	83.96(9)	82.2(3)	84.39(8)
N1−Cu1−S1	114.17(6)	115.8(2)	127.05(6)
N2−Cu1−S1	148.91(7)	150.2(2)	143.48(6)
N3−Cu1−S1	120.92(6)	117.09(10)	113.59(6)
Cu1−S1−Sb1	100.06(3)	103.14(4)	104.55(3)

[a] Estimated standard deviations indicated in parentheses.

The X-ray crystal structures of complexes **1**−**3** are shown in Figure 1 (**1**) and Supporting Information, Figure S3 (**2** and **3**), with selected bond distances and angles listed in Table 1. To our knowledge, they represent the first such structures with Ph_3Sb═S coordinated to a metal center.[19] They contain similar four-coordinate Cu(I) centers with highly distorted tetrahedral geometries characterized by τ_4 values: 0.640 (**1**), 0.657 (**2**), and 0.634 (**3**).[20] Essentially, the distortion involves perturbation of the Cu−S bonds from the idealized trigonal axis toward coplanarity with two of the N-donor atoms on the supporting ligand (N2 and N3 for **1**, Figure 1), presumably as a result of steric interactions between the N-donor ligand substituents and the phenyl rings of the coordinated Ph_3Sb═S moiety. These steric effects also appear to influence the Cu···Sb distance, which increases as the size of the R group of the ligand increases from 3.411 Å (**1**), 3.490 Å (**2**), to 3.547 Å (**3**). The Cu−S−Sb moiety adopts a "bent" conformation with Cu−S−Sb bond angles between 100.1 and 104.6°. The average Cu−N bond lengths range between 2.06 and 2.17 Å, comparable to those in other copper(I) complexes of R_3tacn ligands.[17,21] The Cu−S distances of complexes **1**−**3** (2.167−2.203 Å) are shorter than typical

dx.doi.org/10.1021/ic102449m |*Inorg. Chem.* 2011, 50, 2606–2612

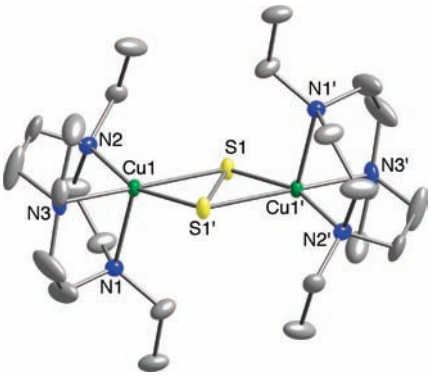


Figure 2. Representation of the X-ray structure of **5** (BPh_4^- salt), showing the dicationic portion with all non-hydrogen atoms as 50% thermal ellipsoids (H atoms omitted for clarity, only heteroatoms labeled). Selected bond distances (Å) and angles (deg) are as follows: Cu1−N1, 2.202(3); Cu1−N2, 2.017(2); Cu1−N3, 2.003(2); Cu1−S1, 2.2152(8); S1−S1′, 2.1501(14); Cu1···Cu1′, 3.876; N1−Cu1−N2, 86.17(10); N1−Cu1−N3, 86.13(10); N2−Cu1−N3, 88.50(10); N1−Cu1−S1, 108.49(7); N2−Cu1−S1, 160.58(7); N3−Cu1−S1, 104.76(8); S1−Cu1−S1′, 58.03(3).

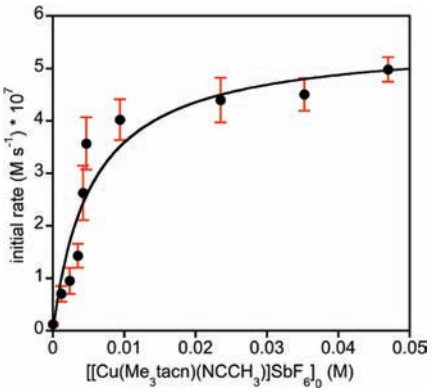


Figure 3. Plot of the initial rate of decay (^{1}H NMR) of **1** vs $[[(Me_3tacn)Cu(CH_3CN)]SbF_6]_0$ for the reaction of **1** with $[(Me_3tacn)Cu(CH_3CN)]SbF_6$ to yield **4** and **7** in CD_2Cl_2 at 20 °C. Each data point is an average of data for 3 replicate runs. Error bars span the range of values for the replicate runs. The line is a fit of the data to eq 1 (R = 0.95).

copper(I)-thioether sulfur interactions (~2.30 Å),[22] and longer than copper(I)-thiolate interactions (2.13−2.18 Å),[23] but comparable to known Cu(I)-S=PPh_3 complexes (2.21−2.27 Å).[24] Complexation of Ph_3Sb=S to the copper center induces little if any change in the S−Sb bonding, as the S−Sb distances in **1**−**3** (2.281−2.283 Å) are only slightly longer than that in free S=$SbPh_3$ (2.244(1) Å).[25]

By monitoring solutions of **1** in CD_2Cl_2 by ^{1}H NMR spectroscopy with an internal standard (Supporting Information, Figure S4) at 20 °C the slow decay ($t_{1/2}$ ~12 h) of **1** to $SbPh_3$ and the disulfido-dicopper(II) species $[(Me_3tacn)_2Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}S_2)](SbF_6)_2$ (**4**) was observed in accordance with the stoichiometry shown in Scheme 1. A similar decay reaction of **2** occurred to yield the respective disulfido-dicopper(II) complex (**5**, with SbF_6^- counterion), but at a significantly slower rate ($t_{1/2}$ ~2 d). Complex **3** decayed at a similar rate as **2**, but the nature of the product(s) in this case was not clear. The disulfido-dicopper(II) complexes **4**−**6** formed much more rapidly and with higher yields/conversions upon addition of $[(R_3tacn)Cu(CH_3CN)]SbF_6$ to solutions of **1**−**3**, but in these reactions the adducts $[(R_3tacn)Cu(SbPh_3)]SbF_6$ (**7**, R = Me; **8**, R = Et; **9**, R = iPr) formed instead of free $SbPh_3$ (Scheme 1).

The disulfido-dicopper(II) complexes **4**−**6** were identified by comparison of ^{1}H NMR spectra with data reported previously (**4**)[14] or obtained from independently prepared samples of the variants **5** and **6**. These latter complexes were isolated as BPh_4^- salts by treating $[(R_3tacn)Cu(CH_3CN)]BPh_4$ with S_8 and were fully characterized by CHN analysis and NMR, FTIR, and UV−vis spectroscopy. Complexes **4**−**6** share similarly sharp ^{1}H NMR features in the diamagnetic region, consistent with singlet ground states arising from disulfide-mediated antiferromagnetic coupling between the Cu(II) ions. They also share diagnostic $S_2^{2-} \rightarrow$ Cu(II) LMCT transitions in UV−vis spectra at λ_{max} 380−400 nm (ε ~8000−14,000).[26,7b] In addition, the X-ray structure of **5** was solved (Figure 2). The X-ray structure of **5** is similar to that previously reported for **4**,[14] as illustrated by analogous S−S (**4**: 2.165(4) Å; **5**: 2.150(1) Å) and Cu−Cu (**4**: 3.84 Å; **5**: 3.88 Å) distances and square pyramidal coordination geometries (τ_5 = 0.03 for **4** and 0.01 for **5**).[27]

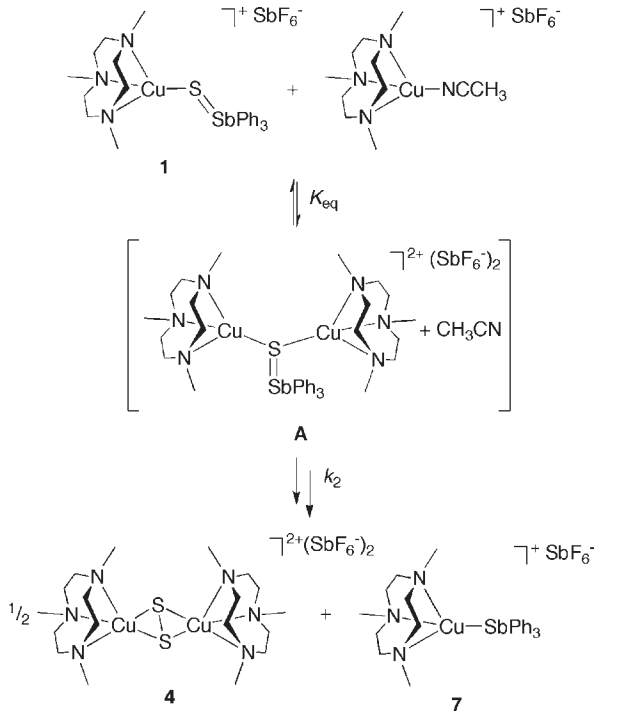
The adducts $[(R_3tacn)Cu(SbPh_3)]SbF_6$ (**7**, R = Me; **8**, R = Et; **9**, R = iPr) formed in the reactions of **1**−**3** with $[(R_3tacn)Cu(CH_3CN)]SbF_6$ also were identified by comparison of ^{1}H NMR spectra with data obtained from independently prepared samples. These samples were synthesized in good yield (~70%) from the reaction of $SbPh_3$ with $[(R_3tacn)Cu(CH_3CN)]SbF_6$. They were isolated as colorless crystalline solids and were fully characterized by CHN analysis, NMR and FTIR spectroscopy, and ESI-MS. Notably, the mass spectrum for each complex exhibits a parent ion with the appropriate isotope pattern for $[(R_3tacn)Cu(SbPh_3)]^+$ (illustrated for R = Me in Supporting Information, Figure S5).

Mechanistic Studies. A series of experiments were performed to gain insight into the reactions of the adducts **1**−**3** with $[(R_3tacn)Cu(CH_3CN)]SbF_6$ to yield the disulfido-dicopper(II) complexes **4**−**6** and the $SbPh_3$ adducts **7**−**9** (Supporting Information, Figure S6). First, the reactions of the complexes with identical supporting ligands under pseudo-first-order conditions (i.e., **1** + 10 equiv of $[(Me_3tacn)Cu(CH_3CN)]SbF_6$, **2** + 10 equiv of $[(Et_3tacn)Cu(CH_3CN)]SbF_6$, and **3** + 10 equiv of $[(iPr_3tacn)Cu(CH_3CN)]SbF_6$) in CD_2Cl_2 were monitored as a function of time by ^{1}H NMR spectroscopy. At initial concentrations $[\mathbf{1}-\mathbf{3}]_0$ = 4.7 mM at 20 °C, the consumption of **1**−**3** followed first-order kinetics (Supporting Information, Figures S6 and S7). The rates measured for the reactions of **2** and **3** are similar, with both being >~10 times slower than that of **1**, as reflected by the measured k_{obs} values (averages from 3 replicate runs) of $6.6(5) \times 10^{-4}$ s^{-1} (**1**), $8.4(1) \times 10^{-5}$ s^{-1} (**2**), and $6.0(4) \times 10^{-5}$ s^{-1} (**3**). The results are roughly consistent with the relative steric profiles of the reactant pairs (**1** < **2** ~ **3**) and support a mechanism wherein steric interactions among the reactant pairs influence the rate (e.g., involving interaction of the Cu(I)-S=$SbPh_3$ adduct with the added Cu(I) reactant).

To further test this hypothesis, reactions of $[(Me_3tacn)Cu(CH_3CN)]SbF_6$ with **1** were examined by measuring initial reaction rates of disappearance of **1** as a function of $[[(Me_3tacn)Cu(CH_3CN)]SbF_6]_0$ (Figure 3). The initial rate saturates as the initial concentration of the added Cu(I) reagent increases. This finding is consistent with a mechanism (Scheme 2) involving an initial rapid pre-equilibrium (K_{eq})

dx.doi.org/10.1021/ic102449m |*Inorg. Chem.* 2011, 50, 2606–2612

Scheme 2. Proposed Mechanism for the Formation of 4 from the Reaction of 1 with $[(Me_3tacn)Cu(CH_3CN)]SbF_6$

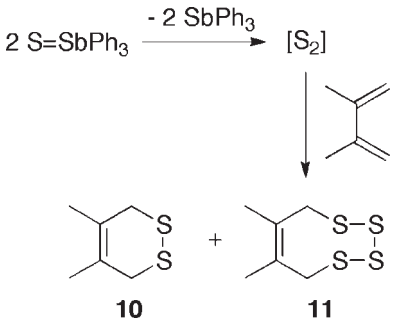


involving formation of a dicopper intermediate (**A**) followed by a rate-determining product formation step (k_2). The fit of the data to the corresponding eq 1 is shown in Figure 3 (solid line), yielding $K_{eq} = 200\ M^{-1}$ and $k_2 = 1.2 \times 10^{-4}\ s^{-1}$. The proposed structure for **A** is speculative, as it was not observed directly. While the product formation process from **A** (k_2) must involve multiple steps, including a step in which a second sulfur atom is added, the decay of **1** is first order in [**1**] (see above) which implies that a unimolecular reaction of **A** is rate-controlling (e.g., cleavage of the S−Sb bond).

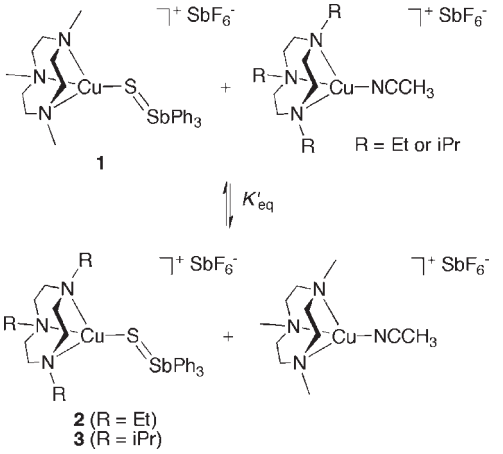
$$\text{rate} = \frac{k_2[\mathbf{1}][\text{Cu(I)}]}{K_{eq}^{-1} + [\text{Cu(I)}]} \qquad (1)$$

We also considered the possibility that the reactions of **1**−**3** to form the disulfido-dicopper(II) complexes **4**−**6** might involve decomposition of S═$SbPh_3$ to S_2.[9a] This decomposition was reported to occur in CS_2 via a second-order process with a rate constant of 0.014(2) $M^{-1}\ s^{-1}$ at 35 °C, with the release of S_2 suggested by the formation of cyclic sulfides **10** and **11** when 2,3-dimethylbutadiene was used as a trapping reagent (Scheme 3). We found that mixtures of S═$SbPh_3$ (4.7 mM) and 2,3-dimethylbutadiene (20 equiv) in CD_2Cl_2 at 20 °C were unchanged after ∼3 d, with no evidence for formation of **10** or **11**. In a second experiment, ^{1}H NMR spectroscopic monitoring of a mixture of **1** and 2,3-dimethylbutadiene (20 equiv) revealed slow generation of **10** and loss of **1** via a first-order process with a rate constant equal to $1.4(4) \times 10^{-5}\ s^{-1}$ ($t_{1/2}$ = ∼14 h). There was no evidence for the presence of the disulfido-dicopper(II) complex **4** during this process. Interestingly, under identical conditions **4** also decayed in the presence of 2,3-dimethylbutadiene to yield **10**. This reaction of **4** is characterized by a first-order rate constant of $1.7(3) \times 10^{-4}\ s^{-1}$, corresponding to a rate

Scheme 3. Decay of S═$SbPh_3$ to S_2 as Determined by Trapping with 2,3-Dimethylbutadiene



Scheme 4. Equilibration of Cu(I)-S═$SbPh_3$ and Cu(I)-$NCCH_3$ Complexes



approximately 10 times faster than that of the reaction of **1** to yield **10**. The rate of decay of **1** to yield **10** in the presence of 2,3-dimethylbutadiene is similar to that observed for the decay of **1** to **4** in its absence, suggesting that S_2 formation cannot be ruled out in the pathways of both reactions. However, these reactions are significantly slower than that for the reaction of **1** with $[(Me_3tacn)Cu(CH_3CN)]SbF_6$ to give **4** and **7**. On this basis and in view of the kinetic data described above, it appears unlikely that S_2 formation is important in the reaction of **1** with $[(Me_3tacn)Cu(CH_3CN)]SbF_6$.

This latter reaction is further complicated by exchange of the S═$SbPh_3$ unit between the Cu(I) centers. This exchange was identified by ^{1}H NMR spectroscopy and ESI-MS analysis of the reaction of **1** with $[(R_3tacn)Cu(CH_3CN)]SbF_6$ (R = Et or iPr). Shortly after mixing, the ^{1}H NMR spectrum showed peaks due to all four species in the equilibrium shown in Scheme 4. From the relative integrations after equilibrium was reached (∼10 min), K'_{eq} values of 0.41 (R = Et) or 0.054 (R = iPr) were measured. These results were corroborated by ESI-MS (Supporting Information, Figure S8), where parent ion peak envelopes for the cationic portions of **1** and **2** (R = Et, ∼1:1 ratio) or **1** and **3** (R = iPr, ∼6:1 ratio) were observed immediately after mixing of the respective reagents. The trend in K'_{eq} values correlates inversely with the degree of steric interactions between the ligand substituents and the bound S═$SbPh_3$ moiety (K'_{eq} decreases as the

dx.doi.org/10.1021/ic102449m |*Inorg. Chem.* 2011, 50, 2606–2612

steric interactions increase, R = Et < iPr). Importantly, equilibration is rapid relative to the decay to the disulfido-dicopper(II) complexes, and thus occurs prior to the suggested pathway for the decay reaction shown in Scheme 2.

Reaction of S═SbPh$_3$ with [(TMCHD)Cu(NCCH$_3$)]PF$_6$. In contrast to the reactions with the Cu(I) complexes of R$_3$tacn ligands that led to isolable Cu(I)-S═SbPh$_3$ adducts, no such adducts were identified when the Cu(I) complex of the bidentate diamine TMCHD was treated with S═SbPh$_3$. Instead, the known tricopper cluster [(TMCHD)$_3$Cu$_3$(S)$_2$](PF$_6$)$_3$ (**12**) was isolated cleanly in good yield (79%). This procedure for the synthesis of **12** is superior to that previously reported involving use of S$_8$,[8a] facilitating advanced spectroscopic studies of the cluster aimed at addressing contentious bonding and oxidation state issues.[8] Presumably, an initial Cu(I)-S═SbPh$_3$ adduct forms in the reaction, but because of its lower coordination number is more prone to oligomerization than the analogues supported by the tridentate R$_3$tacn ligands.

SUMMARY AND CONCLUSIONS

In explorations ultimately aimed at preparing copper−sulfur complexes to model the active site of nitrous oxide reductase, we have found that Ph$_3$Sb═S forms stable adducts [(R$_3$tacn)-Cu(S═SbPh$_3$)]SbF$_6$ (**1**−**3**), the first examples of which have been structurally characterized by X-ray crystallography. These adducts undergo slow decay in solution to form [(R$_3$tacn)$_2$Cu$_2$(μ-η^2:η^2-S$_2$)]$^{2+}$ species (**4**−**6**) and SbPh$_3$. Conversion to **4**−**6** is accelerated by addition of [(R$_3$tacn)Cu(NCCH$_3$)]SbF$_6$ to **1**−**3**, and yield [(R$_3$tacn)-Cu(SbPh$_3$)]SbF$_6$ (**7**−**9**) as coproduct instead of free SbPh$_3$. Mechanistic studies of this reaction revealed rapid exchange of Ph$_3$Sb═S between the Cu(I) sites and pre-equilibrium formation of a dicopper intermediate. We speculate that the dicopper intermediate contains a bridging Ph$_3$Sb═S moiety and that the rate-controlling step in the reaction involves loss of Ph$_3$Sb from that intermediate. Subsequent more rapid events that ultimately result in [Cu$_2$(μ-η^2:η^2-S$_2$)]$^{2+}$ core formation remain unclear. Reaction of [(TMCHD)Cu(CH$_3$CN)]PF$_6$ with S═SbPh$_3$ did not lead to an observable adduct, and instead led to the known tricopper cluster [(TMCHD)$_3$Cu$_3$(μ_3-S)$_2$](PF$_6$)$_3$ in good yield. Overall, the results demonstrate the utility of Ph$_3$Sb═S for delivering sulfur to Cu(I) centers supported by N-donor ligands, cleanly yielding thermodynamically stable [Cu$_2$(μ-η^2:η^2-S$_2$)]$^{2+}$ and [Cu$_3$S$_2$]$^{3+}$ cores.

ASSOCIATED CONTENT

Supporting Information. Illustrative experimental procedures, spectra, and kinetics results, and representions of the X-ray crystal structures of complexes **2** and **3** (PDF); X-ray structural data (CIFs). This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

We thank the NIH (R37 GM47365 to W.B.T.) for financial support of this research and Victor G. Young, Jr., for assistance with the X-ray crystallography.

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