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Synthesis and X-ray Crystal Structure of [Cu^{I}N(R$_2$PS)$_2$]$_3$

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We have been studying the coordination chemistry of dithioimidodiphosphinates LH since these ligands are related to the more well-known acac system. Generally, the LH molecules are readily deprotonated to give L$^-$ ligands, which coordinate with a range of metals to give homoleptic ML$_2$ complexes. We and others have reported on the interesting geometries at metal and on the nonplanar six-membered rings.[1−4] There have been some studies on reactions of LH to form copper complexes which have used Ph$_2$P(S)NHP(S)Ph$_2$ as the ligand. Siiman and co-workers reported the formation and X-ray characterization of a Cu$_4$L$_3$ cluster from the reaction of Cu^{II} salts with Ph$_2$P(S)NHP(S)Ph$_2$.[5−8] The Cu$_4$L$_3$ core has four copper atoms in a tetrahedral arrangement with three edges bridged by S donor atoms from the ligands; the counteranion is [Cu(I)Cl$_2$]$^-$. Further spectroscopic characterizations have been reported by Nakamoto.[9] The kinetics of the reaction have been studied;[10] Bereman suggested that the reaction proceeds via a CuCl$_2$ species which could be used as a model or metalloenzymes containing type I copper(II) centers. The copper(II) species was isolated by filtering and recrystallizing at −78 °C. The report also contains ESR spectra which suggest that the geometry at the copper(II) center is tetrahedral. There are some examples of the Cu$_3$S$_3$ core. Tiethof et al. reported [Cu{(CH$_3$)$_3$PS}Cl]$_3$ in 1973.[11] The Cu$_3$S$_3$ ring in this system was puckered into a chair conformation. The role of the solvent as the reducing agent was postulated in a recent paper by Herrmann,[12] who obtained [Cu^I{(C$_6$H$_5$O)$_2$P(S)NC(S)N(C$_2$H$_5$)$_2$}]$_3$ with a Cu$_3$S$_3$ core from a reaction in ethanol using a Cu(II) nitrate salt. Copper(I) species such as (Ph$_3$P)Cu(SPPh$_2$)$_2$N have also been studied.[13] The copper(I) in this case is three coordinate in a disorted trigonal geometry. Here we describe our studies on reactions involving R$_2$P(S)NHP(S)R$'_2$ (R, R$'$ = ^{i}Pr; R = ^{i}Pr, R$'$ = Ph; R = EtO, R$'$ = OPh) with Cu^{II} and Cu^I chlorides which give trimeric Cu$_3$L$_3$ rings. The X-ray structures of three examples are reported.

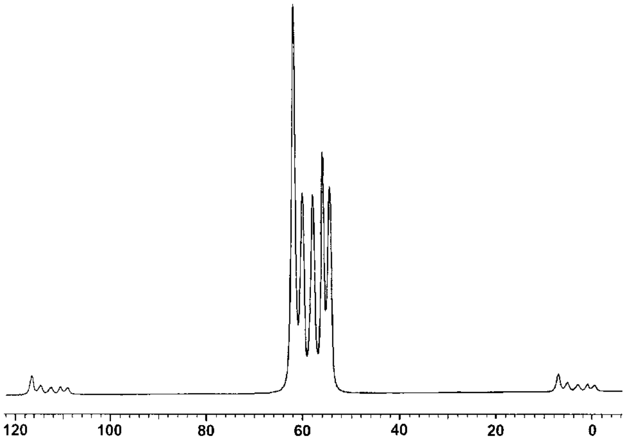

Figure 1. Solid state ^{31}P NMR spectrum of **1**.

Experimental Section

General reaction conditions are as described previously.[2] The various LH systems were prepared as described previously.[3,4,14]

[Cu^{I}N(^{i}Pr$_2$PS)$_2$]$_3$ (1). Method 1. CuCl$_2$ (0.10 g 0.45 mmol) was added to a solution of NH(^{i}Pr$_2$PS)$_2$ (0.280 g 0.90 mmol) and K^{t}BuO (0.1 g 0.089 mmol) in 5 mL of MeOH, and the mixture was stirred for 30 min. The solid purple product was collected by filtration and was dissolved in dichloromethane. The resulting purple solution was allowed to evaporate in air to yield a white solid. X-ray quality crystals were obtained by slow evaporation from dichloromethane. Yield: 0.168 g, 0.122 mmol, 60% (with respect to copper). Microanal. Calcd for C$_{36}$H$_{84}$N$_3$P$_6$S$_6$Cu$_3$: C, 38.3; H, 7.5; N, 3.7. Found: C 38.0; H 6.8; N, 4.0. ^{31}P{^{1}H} NMR (CDCl$_3$): 58.4 ppm. FTIR (KBr disk): ν (PNP) 1229(s); ν (PS) 650(s); δ (NPS) 424(w) cm^{-1}. FAB$^+$ positive MS: *m/z* 1127 corresponds to product + H$^+$.

Method 2. CuCl (0.099 g 1.0 mmol) was added to a solution of NH(^{i}Pr$_2$PS)$_2$ (0.313 g 1.0 mmol) and K^{t}BuO (0.112 g 1.0 mmol) in 10 mL of MeOH, and the mixture was stirred for 30 min. The white solid product was collected by filtration. Yield: 0.245 g, 0.217 mmol, 65% (with respect to copper).

[Cu^I(EtO)$_2$P(S)NP(S)(OPh)$_2$]$_3$ (2). CuCl$_2$ (0.024 g 0.178 mmol) was added to a stirring solution of (EtO)$_2$P(S)NHP(S)(OPh)$_2$ (0.150 g 0.364 mmol) and K^{t}BuO (0.041 g 0.364 mmol) in 5 mL of MeOH, and the mixture was stirred for 30 min. The white product was collected by filtration. Yield: 0.079 g, 0.055 mmol, 89% (with respect to copper). Microanal. Calcd for C$_{48}$H$_{60}$N$_3$P$_6$O$_{12}$S$_6$Cu$_3$: C, 40.0; H, 4.2; N, 2.9. Found: C, 39.7; H, 4.0; N, 3.1. ^{31}P{^{1}H} NMR (CDCl$_3$): 49.6, 43.3 ppm, $^2J(^{31}\text{P}-^{31}\text{P})$ 39.6 Hz. FTIR (KBr disk): ν (PNP) 1201(s), 1198(s); ν (PS) 690(s), 635(s); δ (NPS) 478(w) cm^{-1}. FAB$^+$ positive MS: *m/z* 1440 corresponds to product.

[Cu^I(^{i}Pr$_2$P(S)NP(S)Ph$_2$)]$_3$ (3). CuCl$_2$ (0.027 g 0.19 mmol) was added to a solution of ^{i}Pr$_2$P(S)NHP(S)Ph$_2$ (0.150 g 0.390 mmol) and K^{t}BuO (0.044 g 0.390 mmol) in 5 mL of MeOH, and the mixture was stirred for 30 min. The white product was collected by filtration. Yield: 0.086 g, 0.065 mmol, 96.6% (with respect to copper). Microanal. Calcd for C$_{54}$H$_{72}$N$_3$P$_6$S$_6$Cu$_3$: C, 48.5; H, 5.4; N, 3.2. Found: C, 48.4; H, 5.1; N, 2.7. ^{31}P{^{1}H} NMR (CDCl$_3$): 60.8, 59.2 ppm, $^2J(^{31}\text{P}-^{31}\text{P})$ 22.1 Hz. FTIR (KBr disk): ν (PNP) 1262(s), 1238(s); ν (PS) 699(s), 655(s); δ (NPS) 475(w) cm^{-1}. FAB$^+$ positive MS: *m/z* 1331 corresponds to product + H$^+$.

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Table 1. Details of the Crystal Data and Refinements

	1	**3**	**4**
empirical formula	$C_{36}H_{84}N_3P_6S_6Cu_3$	$C_{54}H_{72}N_3P_6S_6Cu_3$	$C_{54}H_{72}N_3O_6P_6S_6Cu_3$
fw	1127.9	1331.9	1427.9
color/size (mm)	clear/0.1 × 0.15 × 0.2	clear/0.14 × 0.18 × 0.3	clear/0.17 × 0.26 × 0.3
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$(No. 2)	$P\bar{1}$(No. 2)
a	15.299(2)	12.642(1)	10.2234(1)
b	15.664(2)	18.136(1)	18.349(1)
c	14.665(3)	27.899(1)	18.943(1)
α	109.29(1)	97.80(1)	74.35(1)
β	118.16(1)	94.24(1)	87.92(1)
γ	94.90(1)	94.09(1)	75.35(1)
volume (Å^3)	2799	6288	3309
Z	2	4	2
density (calc) g/cm^3	1.34	1.39	1.43
μ/mm^{-1}	5.28^a	1.39	1.34
F(000)	1188	2760	1476
indep reflns/obs reflns	8331/6617	17870/17820	9353/9303
final R1/wR2^c	0.050/0.049^b	0.0393/0.083	0.0368/0.0882
GOF on F^2	3.59^b	0.980	1.015
largest diff peak/hole (e Å^{-3})	0.64, −1.05	0.62, −0.52	0.766, −0.502

[a] Cu radiation. [b] Refinement on *F*. [c] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. $wR2 = \sum w(|F_o| - |F_c|)^2/\sum|wF_o^2|^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in the Structures of **1**, **3**, and **4**

	1	**3**^{a}	**4**
Cu(1)−S(1)	2.214(2)	2.2086(13)[2.138(1)3]	2.2188(11)
Cu(2)−S(3)	2.213(2)	2.2072(12)[2.203(13)]	2.2236(11)
Cu(3)−S(5)	2.210(2)	2.2432(13)[2.303(13)]	2.2226(13)
Cu(1)−S(2)	2.257(2)	2.2469(13)[2.2278(14)]	2.2388(11)
Cu(1)−S(6)	2.227(2)	2.2662(12)[2.2505(12)]	2.2815(10)
Cu(2)−S(2)	2.226(1)	2.2105(13)[2.2089(14)]	2.2217(10)
Cu(2)−S(4)	2.253(2)	2.2421(12)[2.2449(12)]	2.2576(10)
Cu(3)−S(4)	2.227(2)	2.2518(11)[2.2536(11)]	2.2425(10)
Cu(3)−S(6)	2.262(2)	2.2862(12)[2.2729(12)]	2.2472(10)
P(1)−S(1)	2.010(2)	2.019(2)[2.008(2)]	1.9820(14)
P(3)−S(3)	2.011(2)	2.014(2)[2.014(2)]	1.980(2)
P(5)−S(5)	2.022(2)	2.011(2)[2.014(2)]	1.964(2)
P(2)−S(2)	2.033(2)	2.027(2)[2.019(2)]	2.0399(13)
P(4)−S(4)	2.042(2)	2.060(1)[2.057(1)]	2.0493(13)
P(6)−S(6)	2.038(2)	2.046(2)[2.052(2)]	2.0516(13)
P(1)−N(1)	1.591(4)	1.588(3)[1.592(3)]	1.550(3)
P(3)−N(3)	1.576(4)	1.582(3)[1.584(3)]	1.553(3)
P(5)−N(5)	1.593(4)	1.600(3)[1.584(3)]	1.538(4)
P(2)−N(1)	1.585(4)	1.574(3)[1.572(3)]	1.586(3)
P(4)−N(3)	1.589(4)	1.581(3)[1.581(3)]	1.590(3)
P(6)−N(5)	1.569(4)	1.574(4)[1.573(3)]	1.586(4)
S(6)−Cu(1)−S(2)	110.88(6)	106.80(5)[111.11(5)]	108.35(4)
S(2)−Cu(2)−S(4)	109.94(6)	108.97(5)[108.09(5)]	108.74(4)
S(4)−Cu(3)−S(6)	108.67(6)	114.60(4)[112.82(4)]	113.32(4)
Cu(1)−S(2)−Cu(2)	124.30(7)	134.15(6)[131.42(6)]	128.00(5)
Cu(2)−S(4)−Cu(3)	126.58(7)	102.74(5)[105.05(5)]	108.04(4)
Cu(3)−S(6)−Cu(1)	129.67(7)	114.27(5)[110.46(5)]	113.54(4)
Cu(1)−S(1)−P(1)	100.98(7)	105.34(6)[100.36(6)]	101.69(5)
S(1)−P(1)−N(1)	120.7(2)	121.21(13)[120.46(14)]	123.45(12)
P(1)−N(1)−P(2)	137.9(3)	141.2(2)[138.1(2)]	144.2(2)
N(1)−P(2)−S(2)	114.6(2)	114.38(14)[114.68(14)]	114.13(12)
P(2)−S(2)−Cu(1)	114.95(8)	108.05(6)[108.12(7)]	106.94(5)
S(2)−Cu(1)−S(1)	120.57(6)	118.65(5)[118.17(5)]	123.82(4)
Cu(2)−S(3)−P(3)	102.06(8)	100.51(6)[101.42(6)]	97.16(5)
S(3)−P(3)−N(3)	119.4(2)	120.16(13)[120.52(13)]	120.91(14)
P(3)−N(3)−P(4)	140.3(3)	141.3(2)[142.1(2)]	136.1(2)
N(3)−P(4)−S(4)	114.6(2)	117.05(13)[115.61(13)]	115.60(12)
P(4)−S(4)−Cu(2)	102.91(7)	102.79(5)[103.82(5)]	103.10(5)
S(4)−Cu(2)−S(2)	109.94(6)	108.97(5)[108.09(5)]	108.74(4)
Cu(3)−S(5)−P(5)	102.31(7)	100.37(6)99.35(6)	100.67(6)
S(5)−P(5)−N(5)	119.2(2)	117.44(14)[118.18(13)]	120.8(2)
P(5)−N(5)−P(6)	139.6(3)	132.3(2)138.5(2)]	138.5(2)
N(5)−P(6)−S(6)	115.1(2)	114.43(14)[115.61(13)]	116.44(14)
P(6)−S(6)−Cu(3)	100.95(7)	97.76(5)[101.60(5)]	104.98(5)
S(6)−Cu(3)−S(4)	108.67(6)	114.60(4)[112.82(4)]	113.32(4)

[a] The values in square brackets are for the second independent molecule, which is numbered sequentially.

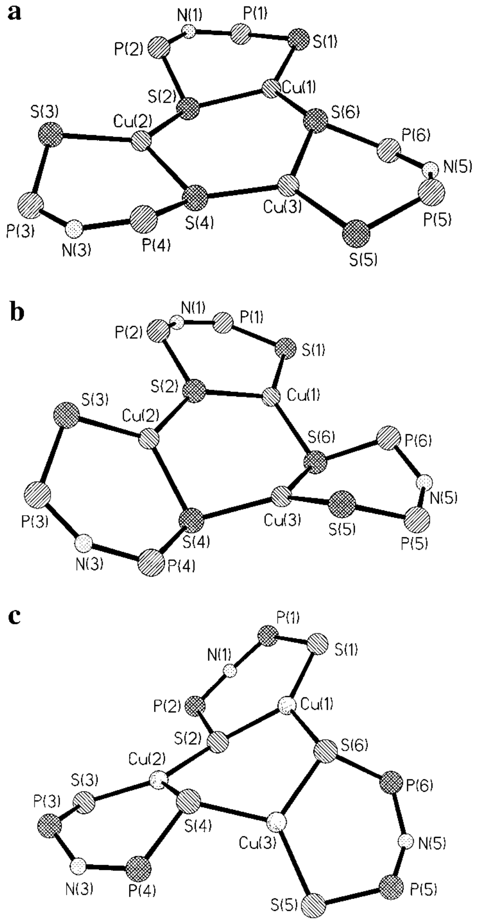


Figure 2. X-ray structure of the core geometries in (a) $[Cu^IN(^iPr_2PS)_2]_3$ (**1**), (b) $[Cu^I(^iPr_2P(S)NP(S)Ph_2)]_3$ (**3**), and (c) $[Cu^I(^iPr_2P(S)NP(S)(OPh)_2)]_3$ (**4**).

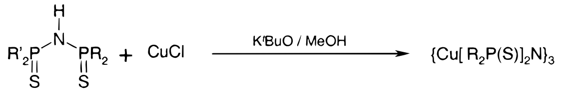
$[Cu^I(^iPr_2P(S)NP(S)(OPh)_2)]_3$ (4). $CuCl_2$ (0.025 g 0.187 mmol) was added to a solution of $^iPr_2P(S)NHP(S)(OPh)_2$ (0.150 g 0.364 mmol) and K^{t}BuO (0.041 g 0.364 mmol) in 5 mL of MeOH, and the mixture was stirred for 30 min. The white product was collected by filtration. Yield: 0.078 g, 0.062 mmol, 88% (with respect to copper). Microanal. Calcd for $C_{54}H_{66}N_3P_6S_6Cu_3$: C, 45.5; H, 4.6; N, 2.9. Found: C, 45.6; H, 4.5; N, 2.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 66.3, 38.8 ppm, $^2J(^{31}P-^{31}P)$ 21.5 Hz. FTIR (KBr disk): ν (PNP) 1202(s), 1196(s); ν (PS) 689(s), 658(s); δ (NPS) 473(w) cm^{-1}. FAB$^+$ positive MS: *m/z* 1427 corresponds to product + H$^+$.

Crystallography (Table 1) was performed at room temperature (20 °C) using a Rigaku AFC7S diffractometer with Cu Kα radiation (λ =

1.541 78 Å) and ω scans for **1** and a Siemens SMART CCD diffractometer with Mo Kα radiation (λ = 0.710 73 Å) for **3** and **4** where a full hemisphere of data with 0.3° "slices" was collected. A semiempirical absorption correction based on ψ scans was used for **1** while sadabs[15] corrections were applied to **3** and **4**. All of the non-H atoms were refined anisotropically in all three structures. All SMART structure calculations employed the SHELXTL program system[15] while the refinement for **1** employed teXsan.[16] The complete listing of the crystal data is provided in the Supporting Information.

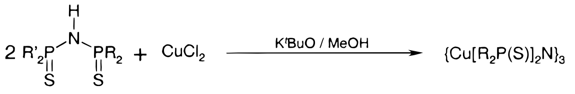
Results and Discussion

Reaction of $CuCl_2$ or CuCl with $R_2P(S)NHP(S)R'_2/KO^tBu$ in methanol gives trinuclear copper(I) complexes $[Cu^I(R_2P(S)NP(S)R'_2)]_3$ in good yield (60−97% with respect to copper depending on the nature of R). The reaction was carried out with excess LH: we found that the yield was reduced if we changed the ratio of reactants. The reaction was also tried with $[(PhO)_2P(S)]_2NH$ as the ligand. Several products were produced, none of which could be suceessfully isolated.



R, R' = ^{i}Pr **1**.

For the Cu^{II} reactions we assume that the reducing agent for the reaction is the solvent.



R, R' = ^{i}Pr **1**. R = EtO, R' = OPh **2**. R = Ph, R' = ^{i}Pr **3**. R = OPh, R' = ^{i}Pr **4**.

There is a related reaction[12] for the formation of $[Cu^I\{(C_6H_5O)_2P(S)NC(S)N(C_2H_5)_2\}]_3$ which also makes use of the alcohol solvent as a reductant, The trimeric complexes were characterized spectroscopically and by X-ray crystallography. All complexes gave satisfactory microanalyses and the appropriate parent ion by FAB MS. Their IR spectra showed the expected shifts associated with the changes in delocalization accompanying deprotonation/coordination.[2−4] The ^{31}P NMR data for the unsymmetrical imidophosphinates in **2**−**4** are simple AX systems with reasonable $^2J(^{31}P-^{31}P)$ coupling constants (**2**, 39.6 Hz; **3**, 22.1 Hz; **4**, 21.5 Hz]. The solid state ^{31}P NMR shows five peaks with relative intensities of 2:1:1:1:1 (Figure 1) and at least five independent phosphorus environments. The solution ^{31}P NMR for **1** is a singlet even at low temperature, suggesting that the molecule is fluxional in solution. The alternative explanation is that the trimeric system dissociates to monomers and dimers in solution, but cryoscopic measurements were inconclusive because of lack of solubility. We did test for this type of equilibrium by stirring mixtures of **1** with **4** to test for "scrambling" of the ligands. Over a period of 5 days no such mixing was observed. Similarly stirring **1** with a range of other dithioimidophosphinates did not result in ligand exchange. Some preliminary electrochemical studies were carried out on **1**; CV studies showed an irreversible oxidation reaction, but again solubility in the electrolyte solution hindered any detailed measurements.

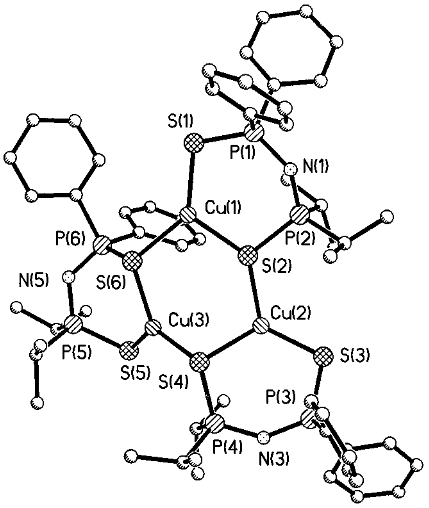


Figure 3. X-ray structure of $[Cu^I(^iPr_2P(S)NP(S)Ph_2)]_3$ (**3**).

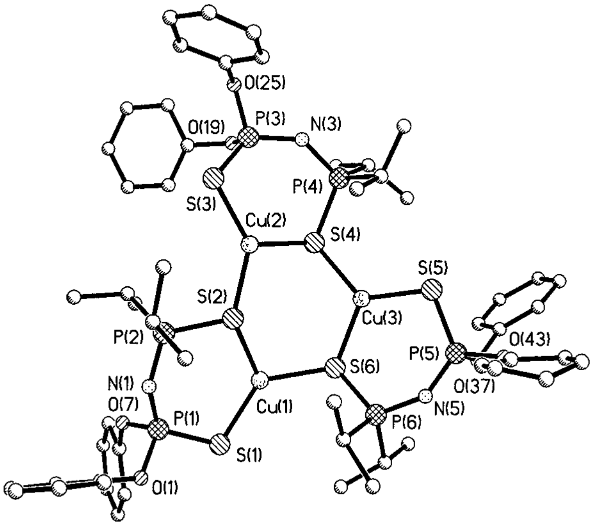


Figure 4. X-ray structure of $[Cu^I(^iPr_2P(S)NP(S)(OPh)_2)]_3$ (**4**).

The X-ray structures of **1**, **3**, and **4** (Table 2, Figures 2 and 3) reveal that the molecules contain a six-membered Cu_3S_3 ring in their core with each copper atom being tricoordinate in approximately trigonal geometry as a result of two bridging and one terminal sulfur donor atoms. Generally it appears that the two-coordinate sulfur atoms have slightly shorter Cu−S and P−S bond lengths than the three-coordinate sulfur atoms though the statistical significance of some individual distances is slight. The most noticeable difference is that the P−S bond lengths associated with the OPh-substituted phosphorus atoms in **4** are substantially shorter than those at Ph- or Pr-substituted phosphorus atoms in any of the structures. This effect is also statistically significant for the P−N bond lengths, which are slightly shorter for the $P(OPh)_2$ centers than elsewhere. The Cu_3S_3 rings are similar in all three structures but do display differences in conformation; in **1** this core is close to planar [mean deviation 0.16 Å, maximum deviation 0.31 Å for Cu(2)] and the core in **3** is puckered in a "half-chair" conformation while the core in **4** has a pseudo boat conformation. The intraring S−Cu−S and Cu−S−Cu angles lie in the ranges 108.67(6)−114.60(4)° and 102.74(5)−134.15(6)°, respectively. The six-membered CuS_2P_2N rings are not perfectly symmetric and display a range of geometries such as planar, boat, and chair as has been observed previously.[1] The Cu−S−P and S−P−N angles are in the ranges 97.15(5)−114.95(8)° and 114.43(4)−123.45(12)°, respectively, while the N−P−N angles lie between 137.9(3)° and 144.2(2)°. In the structures of **3** and **4** it is possible to envisage a number of possible isomers though there was no

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(15) *SHELXTL*; Bruker AXS: Madison, NY, 1998.

(16) *teXsan*; Molecular Structure Corporation: The Woodlands, TX, 1996.

evidence for this from NMR studies. In **4** we observe the "symmetric" isomer which has pseudo-3-fold symmetry about an axis running through the center of the Cu_3S_3 ring while in **3** one of the ligands is reversed, resulting in loss of symmetry. We speculate that the weaker donor ability of a $(PhO)_2P{=}S$ group relative to a $(Ph)_2P{=}S$ group limits the ability of the phenoxy system to use its sulfur atom for bridging within the Cu_3S_3 ring while this is not a significant constraint for the phenyl system; there do not appear to be any steric constraints to any isomer formation. X-ray examination of several crystals and the bulk material revealed no evidence of any other isomers in **3**.

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Supporting Information Available: Three tables giving experimental crystallographic details, bond lengths, bond angles, and anisotropic displacement parameters for non-hydrogen atoms for **1**, **3** (two independent molecules), and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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