

Reactions of Copper(I) Aryloxides with PhNCS: Steric and Ligand Control in the Oligomerization of [*N*-Phenylimino(aryloxy)methanethiolato]copper(I) Complexes

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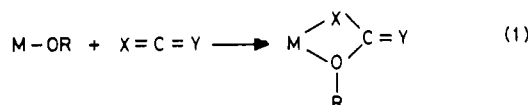
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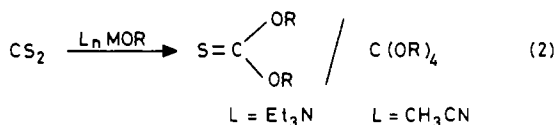
The preparation of five different copper(I) complexes $[\text{Cu}\{\text{SC}(\text{=NPh})(\text{OAr})\}\text{L}_n]_m$ (1-5) formed by the insertion of PhNCS into the Cu-OAr bond and the crystal structure analyses of three of them have been carried out. A monomeric species 1 (OAr = 2,6-dimethylphenoxide) is formed in the presence of excess PPh_3 ($n = 2, m = 1$) and crystallizes as triclinic crystals with $a = 12.419(4) \text{ \AA}$, $b = 13.298(7) \text{ \AA}$, $c = 15.936(3) \text{ \AA}$, $\alpha = 67.09(3)^\circ$, $\beta = 81.63(2)^\circ$, $\gamma = 66.54(3)^\circ$, $V = 2224(2) \text{ \AA}^3$, and $Z = 2$. The structure was refined by the least-squares method to final R and R_w values of 0.038 and 0.044, respectively, for 7186 unique reflections. Copper(I) 2,5-di-*tert*-butyl-4-methylphenoxide results in the formation of a dimeric species 2 in the presence of $\text{P}(\text{OMe})_3$ ($n = 1, m = 2$), where the coordination around Cu is trigonal. Crystals of 2 were found to be orthorhombic with $a = 15.691(2) \text{ \AA}$, $b = 18.216(3) \text{ \AA}$, $c = 39.198(5) \text{ \AA}$, $V = 11204(3) \text{ \AA}^3$, and $Z = 8$. Least-squares refinement gave final residuals of $R = 0.05$ and $R_w = 0.057$ with 6866 unique reflections. A tetrameric species 3 results when PPh_3 is replaced by $\text{P}(\text{OMe})_3$ in the coordination sphere of copper(I) 2,6-dimethylphenoxide. It crystallizes in the space group $P\bar{1}$ with $a = 11.681(1) \text{ \AA}$, $b = 13.373(2) \text{ \AA}$, $c = 20.127(1) \text{ \AA}$, $\alpha = 88.55(1)^\circ$, $\beta = 89.65(1)^\circ$, $\gamma = 69.28(1)^\circ$, $V = 2940(1) \text{ \AA}^3$, and $Z = 2$. Least-squares refinement of the structure gave final values of 0.043 and 0.05 for R and R_w respectively using 12214 unique reflections. In addition, a dimeric species 4 is formed when 1 equiv of PPh_3 is added to the copper(I) 4-methylphenoxide, while with an excess of PPh_3 a monomeric species 5 is isolated. Some interconversions among these complexes are also reported.

Introduction

In recent years the reactions of heterocumulenes with various coordination and organometallic compounds have been extensively explored as they serve as convenient models for the reactions of CO_2 .¹ In the case of the "M-O" bond, the most common reaction pathway is the insertion reaction² illustrated in eq 1.

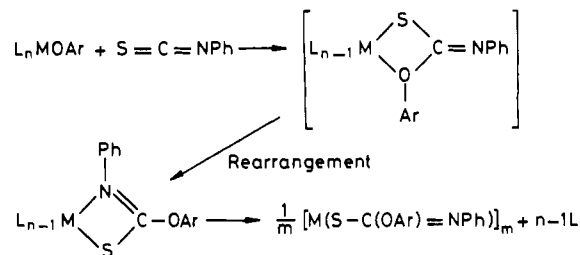


Indeed in the case of copper(I), such reactions have been known to occur with CO_2 , and with suitable ancillary ligands the reaction is reversible.³ Consistent with the thiophilicity of copper(I), the reaction of sulfur-containing heterocumulenes is extremely facile and in the case of CS_2 proceeds through multiple insertions to give organic products⁴ (eq 2).



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Scheme I



Here we report the reaction of PhNCS with Cu-OAr which leads to an insertion followed by a rearrangement (Scheme I). The resulting coordination sphere around the copper stabilizes the +1 oxidation state of copper. Furthermore in the absence of any other ligand it oligomerizes due to the excellent bridging tendency of sulfur.⁵ By using appropriate ligands and steric effects, one can effect the synthesis of a desired oligomer.

Experimental Section

Solvents and Reagents. CH_2Cl_2 was purified by conventional methods and distilled under N_2 prior to use. NaH obtained from Fluka was washed with petroleum ether and estimated by gasometric titration prior to use. CuCl was freshly prepared by following the reported procedure.⁶ $\text{P}(\text{OMe})_3$, obtained from Merck, and PhNCS, obtained from Fluka, were purified before use.

Preparation of Cu(I) Aryloxides. All the Cu(I) aryloxides were prepared by adding a solution of the phenol (3 mmol) in 25 mL of CH_2Cl_2 with stirring to a suspension of NaH (0.082 g, 3 mmol) in 25 mL of CH_2Cl_2 under an atmosphere of dry, oxygen-free N_2 . When the evolution of H_2 ceases, freshly prepared CuCl (0.30 g, 3 mmol) was added in one lot resulting in the formation of a yellow precipitate.

Preparation of $[\text{Cu}\{\mu\text{-SC}(\text{=NPh})(\text{OC}_6\text{H}_3(\text{Me})_2\text{-2,6})\}(\text{PPh}_3)_2]$ (1). To the copper(I) 2,6-dimethylphenoxide prepared as above was added solid

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PPh₃ (2.36 g, 9 mmol) and the mixture stirred for 1.5 h before adding PhNCS (0.41 g, 3 mmol). A reddish brown suspension resulted and was stirred for 8 h. This mixture was filtered and concentrated to about 10 mL. On addition of 30 mL of petroleum ether (bp 60–80 °C) pale yellow crystals of **1** separate on standing: yield 2.24 g (ca. 90%); mp 175–178 °C. Anal. Calcd for **1**: C, 72.54; H, 5.25; N, 1.66. Found: C, 72.54; H, 5.21; N, 1.94. ¹H NMR (CDCl₃, 298 K): δ 6.9–7.3 (m, 38H, PPh₃, C₆H₅NCS, –OC₆H₃–), δ 2.21 (s, 4.8H, CH₃), δ 1.87 (s, 1.2H, CH₃).

Preparation of [Cu{μ-SC(=NPh)(OC₆H₃(t-Bu)₂-2,6)(Me-4)}P(OMe)₃]₂ (2**).** To the Cu(I) aryloxoide of 2,6-di-*tert*-butyl-4-methylphenol prepared by the above mentioned procedure was added P(OMe)₃ (0.37 g, 3 mmol), and the reaction mixture was stirred for 1.5 h. PhNCS was added (0.41 g, 3 mmol) followed by stirring for about 8 h. The red-orange suspension that resulted was filtered and concentrated to about 10 mL, and 30 mL of petroleum ether (bp 60–80 °C) was added. The solution was again filtered, and the filtrate was concentrated to about 10 mL and kept at –10 °C for 72 h: yield 0.59 g (ca. 40%); mp 140 °C. Anal. Calcd for **2**: C, 55.39; H, 7.00; N, 2.58. Found: C, 54.03; H, 7.00; N, 2.73. ¹H NMR (CDCl₃, 298 K): δ 6.9–7.5 (m, 7H, C₆H₅NCS, –OC₆H₂–), δ 3.58 (s, 9H, P(OMe)₃), δ 1.02–1.38 (3s, 18H, –C(CH₃)₃).

Preparation of [Cu{μ-SC(=NPh)(OC₆H₃(Me)₂-2,6)}]₄ (3**).** The copper(I) aryloxoide of 2,6-dimethylphenol was stirred with P(OMe)₃ (0.37 g, 3 mmol) for 1 h. To this reaction mixture was added PhNCS (0.41 g, 3 mmol) resulting in an orange suspension. After stirring for 15 h, this suspension was filtered and concentrated to about 10 mL. To this was added 30 mL of petroleum ether (bp 60–80 °C). On standing overnight, an orange precipitate formed, which was filtered out, and the filtrate concentrated. Both the precipitate and the filtrate were found by TLC to contain a mixture of products and were subjected individually to column chromatography. The pure tetramer was isolated in the second colorless fraction of the filtrate by eluting the column with a 15:1 mixture of petroleum ether (bp 60–80 °C) and ethyl acetate and in the first colorless fraction of the precipitate by eluting the column with a 10:1 mixture of petroleum ether (bp 60–80 °C) and ethyl acetate. The fractions were combined, and slow evaporation of the solvent gave colorless crystals of **3**: yield 0.15 g (ca. 15%); mp 220 °C (decomposes). Anal. Calcd for **3**: C, 56.32; H, 4.41; N, 4.38. Found: C, 54.8; H, 4.3; N, 4.8. ¹H NMR (CDCl₃, 298 K): δ 6.9–7.3 (m, 8H, C₆H₅NCS, –OC₆H₃–), δ 2.07 (s, 3H, CH₃), δ 1.78 (s, 3H, CH₃).

Preparation of [Cu{SC(=NC₆H₅)(OC₆H₄Me-4)}(PPh₃)₂] (4**).** To the canary yellow suspension of copper(I) 4-methylphenoxide prepared as above was added a solution of PPh₃ (0.786 g, 3 mmol) in CH₂Cl₂ (40 mL) and stirred for 1.5 h. A light yellow solution resulted, to which a solution of PhNCS (0.41 g, 3 mmol) in CH₂Cl₂ (10 mL) was added over 10–15 min. The mixture was stirred for 4–5 h to give an orange solution, which was filtered under N₂ through a Celite bed. On removal of the solvent under vacuo, a crystalline yellow-orange fluffy solid precipitated out: yield 2.98 g (ca. 89%); mp 79 °C. Anal. Calcd for **4**: C, 69.61; H, 4.93; N, 2.54. Found: C, 67.78; H, 4.99; N, 2.57. ¹H NMR (CDCl₃, 298 K): δ 6.7–7.6 (m, 24H, PPh₃, C₆H₅NCS, –OC₆H₄–), δ 2.3 (s, 3H, CH₃).

Preparation of [Cu{SC(=NPh)(OC₆H₄Me-4)}(PPh₃)₂] (5**).** To the Cu(I) aryloxoide of 4-methylphenol prepared as above was added PPh₃ (2.36 g, 9 mmol), and the mixture was stirred for 1 h. To this reaction mixture was added PhNCS (0.41 g, 3 mmol). After 8 h of stirring, the resulting orange suspension was filtered and concentrated to about 20 mL. On slow evaporation of the solvent, crystals of **5** separate out: yield 0.747 g (ca. 30%); mp 138 °C. Anal. Calcd for **5**: C, 72.36; H, 5.10; N, 1.69. Found: C, 73.35; H, 5.23; N, 1.98. ¹H NMR (CDCl₃, 298 K): δ 6.8–7.3 (m, 39H, PPh₃, C₆H₅NCS, –OC₆H₄–), δ 2.3 (s, 3H, CH₃).

Interconversions. The conversion of the tetramer **3** to the monomer **1** was followed by recording the NMR spectrum of a solution of the tetramer (0.0102 g, 8 × 10^{–3} mmol) in 1.5 mL of CDCl₃. To this was added 3 equiv (0.0062 g) of PPh₃, and the spectrum was recorded. Finally, the spectrum was recorded again after the addition of a large excess of PPh₃ to the above solution. The complex **4** was found to convert to the hexamer **6**⁷ when dissolved in a mixture of CH₂Cl₂ and CH₃CN (3:2). The red orange compound which resulted melted at 198 °C and was identified to be the hexameric species from the NMR spectrum.

Experimental Details of Crystallography. Structure Determination of 1–3. As crystals of **2** and **3** were found to lose their crystallinity when removed from the mother liquor, suitable crystals along with the mother liquor were sealed in a Lindemann capillary, while a crystal of **1** was

Table I. Crystallographic Data for [Cu{μ-SC(=NPh)(OC₆H₃(Me)₂-2,6)}(PPh₃)₂]

chem formula	C ₅₁ H ₄₄ N ₁ O ₁ P ₂ Cu ₁	γ, deg	66.54(3)
fw	844.47	V, Å ³	2224(2)
cryst system	triclinic	Z	2
space group	P1̄	ρ _{calcd} , g cm ^{–3}	1.260
a, Å	12.419(4)	μ, cm ^{–1}	6.43
b, Å	13.298(7)	λ, Å (Mo Kα)	0.7107
c, Å	15.936(3)	T, °C	22
α, deg	67.09(3)	R ^a	0.038
β, deg	81.63(2)	R _w ^b	0.044

$$^a R = \sum(|F_o| - |F_c|) / \sum|F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; w = k / [\sigma^2(F_o) + gF_o^2].$$

mounted as such. Three intensity control reflections monitored every 1 h showed no significant change in intensity. Lorentz and polarization corrections were applied, but no absorption correction was done. The structure of **2** was solved by direct methods using the SHELXS-86 program,⁸ while those of **1** and **3** were solved by the Patterson heavy-atom method and subsequent difference Fourier syntheses. The hydrogen atoms were located from the difference Fourier map. Non-hydrogens were refined anisotropically, and the hydrogen atoms, isotropically by the full-matrix least-squares method using the program SHELX-76.⁹ In **2**, the carbon atoms C226, C227, and C228 of one P(OMe)₃ group showed high thermal vibrations and so were refined isotropically. Data collection parameters and details of the crystallographic analyses are summarized in Tables I–IX and in Table S (supplementary material).

Results

[N-Phenylimino(2,6-dimethylphenoxy)methanethiolato]-bis(triphenylphosphine)copper(I) (1**).** In the presence of an excess of PPh₃ (3 equiv), PhNCS reacts with copper(I) 2,6-dimethylphenoxide in dichloromethane to give **1** in 89% yield. ¹H NMR spectra of **1** in CDCl₃ contain resonances due to the phosphine and the methyl groups (δ 1.87, δ 2.21, 2s, 6H) on the aryloxy group. From the ratio of the NMR signals, the ratio *N*-phenylimino(2,6-dimethylphenoxy)methanethiolato (L2) ligand:PPh₃ was found to be 1:2. However the possibility of the structure being a dimeric species could not be ruled out, and hence a crystallographic study was carried out.

As shown in Figure 1, the complex has a simple monomeric structure in which the group (L2) functions as a chelating ligand. The Cu–N and Cu–S bond lengths observed in this case are significantly larger than those observed in complexes **6**, **2**, and **3** (see Table XI). However, the values are in accord with other tetrahedrally coordinated Cu(I) complexes.^{10,11a} Due to the rather strained four-membered ring formed by Cu–N–C–S, the angle N–Cu–S is smaller than the tetrahedral angle of 109° (see Table X). The IR spectrum of this complex is typical of these complexes with the characteristic C=N stretch occurring at 1515 cm^{–1} (see Table XII).

Bis[μ-{N-phenylimino(2,6-di-*tert*-butyl-4-methylphenoxy)methanethiolato}](trimethyl phosphite)copper(I) (2**).** The reaction of PhNCS with copper(I) 2,6-di-*tert*-butyl-4-methylphenoxide in the presence of P(OMe)₃ results in the formation

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Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters ($\times 10^4$) with Their Estimated Standard Deviations in Parentheses for [Cu $\{\mu$ -SC(=NPh)(OC₆H₃(Me)₂-2,6)\}(PPh₃)₂]

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} , Å ²
Cu	0.26861(2)	0.77691(2)	0.78689(2)	397(2)
P1	0.3001(1)	0.9036(1)	0.8310(0)	398(3)
P2	0.1446(1)	0.6818(1)	0.8518(0)	398(2)
S	0.4506(1)	0.6240(1)	0.7624(0)	477(2)
O	0.4428(2)	0.6903(2)	0.5800(1)	516(8)
N	0.2945(2)	0.8030(2)	0.6470(1)	401(8)
C	0.3904(2)	0.7116(2)	0.6567(2)	406(11)
C1	0.2379(2)	0.8793(2)	0.5617(2)	419(11)
C2	0.2111(3)	0.9995(2)	0.5358(2)	581(15)
C3	0.1507(3)	1.0770(3)	0.4553(2)	765(17)
C4	0.1154(3)	1.0380(3)	0.4004(2)	782(16)
C5	0.1409(3)	0.9197(3)	0.4252(2)	716(17)
C6	0.2024(2)	0.8404(2)	0.5055(2)	552(13)
C11	0.5459(3)	0.5901(3)	0.5913(2)	609(14)
C12	0.6493(3)	0.6018(4)	0.5774(3)	892(23)
C13	0.7531(3)	0.4952(5)	0.5845(3)	1148(32)
C14	0.7347(4)	0.3955(5)	0.6012(3)	1153(28)
C15	0.6283(4)	0.3823(4)	0.6161(3)	1071(24)
C16	0.5295(3)	0.4817(3)	0.6113(2)	802(18)
C17	0.6597(4)	0.7134(5)	0.5617(3)	1125(31)
C18	0.4102(4)	0.4764(3)	0.6240(3)	874(20)
C111	0.3673(2)	0.8417(2)	0.9440(2)	432(11)
C112	0.3380(3)	0.7540(3)	1.0121(2)	594(14)
C113	0.3884(3)	0.7024(3)	1.0980(2)	763(18)
C114	0.4685(4)	0.7368(4)	1.1163(2)	872(21)
C115	0.4985(4)	0.8228(4)	1.0498(3)	985(26)
C116	0.4498(3)	0.8758(3)	0.9637(2)	716(19)
C121	0.3950(2)	0.9775(2)	0.7575(2)	492(13)
C122	0.3828(4)	1.0894(3)	0.7466(3)	860(21)
C123	0.4623(4)	1.1375(4)	0.6918(3)	1125(29)
C124	0.5494(4)	1.0773(5)	0.6495(3)	1099(30)
C125	0.5639(4)	0.9653(5)	0.6628(4)	1171(31)
C126	0.4875(3)	0.9139(3)	0.7168(3)	801(22)
C131	0.1673(2)	1.0280(2)	0.8349(2)	459(11)
C132	0.1240(3)	1.0510(3)	0.9119(2)	630(15)
C133	0.0169(4)	1.1429(3)	0.9093(3)	886(21)
C134	-0.0444(3)	1.2122(3)	0.8302(3)	873(21)
C135	-0.0008(4)	1.1910(3)	0.7532(3)	967(22)
C136	0.1033(3)	1.0997(3)	0.7551(2)	792(17)
C211	0.1898(2)	0.5833(2)	0.9691(2)	427(11)
C212	0.3072(2)	0.5073(2)	0.9852(2)	538(13)
C213	0.3490(2)	0.4364(3)	1.0721(2)	607(13)
C214	0.2754(3)	0.4396(3)	1.1454(2)	628(16)
C215	0.1593(3)	0.5137(3)	1.1306(2)	594(14)
C216	0.1162(2)	0.5852(2)	1.0435(2)	500(11)
C221	-0.0102(2)	0.7715(2)	0.8588(2)	430(11)
C222	-0.0993(3)	0.7275(3)	0.8758(3)	713(17)
C223	-0.2142(3)	0.7991(3)	0.8816(3)	878(22)
C224	-0.2431(3)	0.9153(3)	0.8677(3)	781(18)
C225	-0.1561(3)	0.9596(3)	0.8509(2)	712(16)
C226	-0.0407(2)	0.8879(2)	0.8458(2)	547(13)
C231	0.1387(2)	0.5840(2)	0.7991(2)	475(12)
C232	0.1102(3)	0.6326(3)	0.7070(2)	681(17)
C233	0.1021(4)	0.5654(4)	0.6617(3)	890(25)
C234	0.1285(4)	0.4447(4)	0.7094(3)	900(26)
C235	0.1585(3)	0.3958(3)	0.7986(3)	815(21)
C236	0.1638(3)	0.4641(2)	0.8450(2)	616(14)

of **2** in 40% yield. Elemental analysis indicated the empirical formula C₂₅H₃₇NO₄PSCu corresponding to the structure Cu-(L3)P(OMe)₃, where L3 is the *N*-phenylimino(2,6-di-*tert*-butyl-4-methylphenoxy)methanethiolato group. The NMR spectrum was in accord with the elemental analysis of this product and indicated the presence of the L3 ligand. A variety of structural motifs are possible for a combination of the ligands indicated by NMR and elemental analysis. Hence a crystallographic study was taken up. An ORTEP plot of the structure is given in Figure 2. In this molecule the ligand is a bridge between two Cu(I) atoms such that each metal atom has a N, S, and P coordinating in a trigonal environment. There appears to be no strain in the bridge, and the Cu–ligand distances are in the range expected for the trigonal environment around Cu.¹¹

Table III. Selected Bond Distances (Å) and Angles (deg) with Their Estimated Standard Deviations in Parentheses for [Cu $\{\mu$ -SC(=NPh)(OC₆H₃(Me)₂-2,6)\}(PPh₃)₂]

(a) Bond Lengths			
Cu–P1	2.239(2)	S–C	1.703(3)
Cu–P2	2.261(2)	O–C	1.374(4)
Cu–S	2.469(2)	N–C	1.294(3)
Cu–N	2.115(2)		
(b) Bond Angles			
S–Cu–N	68.6(1)	Cu–N–C	96.8(2)
P2–Cu–N	112.5(1)	O–C–N	118.4(3)
P2–Cu–S	104.6(1)	S–C–N	119.8(2)
P1–Cu–N	115.6(1)	S–C–O	121.8(3)
P1–Cu–S	113.7(1)	Cu–S–C	74.8(1)
P1–Cu–P2	126.4(1)		

Table IV. Crystallographic Data for [Cu $\{\mu$ -SC(=NPh)(OC₅H₂((*t*-Bu)₂-2,6)(Me-4)\}(P(OMe)₃)₂]

chem formula	C ₅₀ H ₇₄ N ₂ O ₈ S ₂ P ₂ Cu ₂	Z	8
fw	1084.30	ρ_{calcd} , g cm ⁻³	1.286
cryst system	orthorhombic	μ , cm ⁻¹	9.36
space group	<i>Pbna</i>	λ , Å (Mo K α)	0.7107
<i>a</i> , Å	15.691(2)	<i>T</i> , °C	22
<i>b</i> , Å	18.216(3)	<i>R</i> ^a	0.050
<i>c</i> , Å	39.198(5)	<i>R</i> _w ^b	0.057
<i>V</i> , Å ³	11204(3)		

^a $R = \sum(|F_o| - |F_c|) / \sum|F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = k / [\sigma^2(F_o) + gF_o^2]$.

Tetrakis[$\{\mu$ -*N*-phenylimino(2,6-dimethylphenoxy)methanethiolato}copper(I)] (3). When the reaction of copper(I) 2,6-dimethylphenoxy was carried out in the presence of P(OMe)₃ instead of PPh₃ a mixture of products was formed. At least three products were detected in a TLC of the reaction mixture. Column chromatography of the mixture allowed isolation of tetrakis[$\{\mu$ -*N*-phenylimino(2,6-dimethylphenoxy)methanethiolato}copper(I)] (3) in 15% yield. NMR spectrum of the complex in CDCl₃ showed that the complex had no phosphite and only the *N*-phenylimino(2,6-dimethylphenoxy)methanethiolato (L2) ligand was present. Elemental analysis confirmed the absence of phosphite and the 1:1 ratio of the ligand and Cu. A simple monomeric and dimeric structure could be ruled out on the grounds that there are insufficient donor atoms to satisfy the usual trigonal or tetrahedral environment around the Cu. A single-crystal structure determination resolved the question of nuclearity unambiguously. The ORTEP drawing of **3** shown in Figure 3 reveals the tetrameric nature of the complex. The copper atoms are found in trigonal environments with two sulfurs and a nitrogen coordinating each copper. The copper atoms lie more or less in the plane formed by the coordinating atoms at an average distance of 0.043 Å from it. Each ligand bridges three copper atoms, and each copper is bonded to three different ligands, as in the case of the hexamer.

Bis[$\{\mu$ -*N*-phenylimino(4-methylphenoxy)methanethiolato}(triphenylphosphine)copper(I)] (4). The reaction of PhNCS with copper(I) 4-methylphenoxy in the presence of PPh₃ led to the isolation of a yellowish orange compound in 89% yield. The NMR spectrum revealed the presence of the *N*-phenylimino(4-methylphenoxy)methanethiolato (L1) ligand and PPh₃ in 1:1 ratio. The IR spectrum showed that the C=N stretch occurred at 1524 cm⁻¹ (see Table XII). From the ratio of the ligands present in the complex obtained from the NMR spectra, the complex appeared to be a dimeric species. Attempts to obtain a single crystal of the complex led to the isolation of a complex with no PPh₃ in the coordination sphere of copper, which from its melting point and NMR was identified to be a hexameric species hexakis[$\{\mu$ -*N*-phenylimino(4-methylphenoxy)methanethiolato}copper(I)] (6) characterized earlier.⁷

[*N*-Phenylimino(4-methylphenoxy)methanethiolato]bis(tri-

Table V. List of Fractional Atomic Coordinates and Equivalent Thermal Parameters ($\times 10^4$) with Their Estimated Standard Deviations in Parentheses for

atom	x/a	y/b	z/c	$U_{eq}, \text{\AA}^2$
Cu1	0.2223(1)	0.6240(1)	0.3599(1)	471(3)
P1	0.1399(1)	0.7198(1)	0.3545(1)	518(7)
S1	0.1910(1)	0.5399(1)	0.4186(1)	470(6)
O1	0.1120(3)	0.4320(2)	0.3839(1)	435(14)
O11	0.1681(3)	0.7823(3)	0.3290(1)	707(21)
O12	0.1255(3)	0.7707(2)	0.3870(1)	610(18)
O13	0.0475(3)	0.7031(3)	0.3408(1)	707(20)
N1	0.1820(3)	0.5186(3)	0.3522(1)	431(19)
C1	0.1618(4)	0.4937(3)	0.3815(2)	421(26)
C11	0.1610(4)	0.4817(4)	0.3210(2)	492(29)
C12	0.1233(5)	0.5213(5)	0.2950(2)	648(29)
C13	0.1071(5)	0.4902(6)	0.2648(2)	802(40)
C14	0.1297(6)	0.4190(7)	0.2580(2)	900(45)
C15	0.1678(6)	0.3793(5)	0.2829(2)	746(35)
C16	0.1848(5)	0.4100(4)	0.3141(2)	674(32)
C111	0.0741(4)	0.4129(3)	0.4154(1)	399(21)
C112	-0.0081(4)	0.4410(3)	0.4221(2)	462(24)
C113	-0.0416(5)	0.4246(4)	0.4531(2)	614(29)
C114	0.0002(5)	0.3832(4)	0.4775(2)	610(29)
C115	0.0779(5)	0.3528(4)	0.4688(2)	588(29)
C116	0.1164(4)	0.3661(3)	0.4382(2)	420(20)
C117	0.2037(4)	0.3270(4)	0.4327(2)	556(29)
C118	0.2455(5)	0.3368(4)	0.3980(2)	707(32)
C119	0.2644(5)	0.3536(5)	0.4604(3)	902(40)
C120	0.1864(6)	0.2431(5)	0.4367(3)	854(35)
C121	-0.0614(4)	0.4857(4)	0.3966(2)	533(28)
C122	-0.0307(6)	0.5645(4)	0.3930(3)	901(40)
C123	-0.0617(5)	0.4502(5)	0.3605(2)	789(34)
C124	-0.1608(6)	0.4841(9)	0.4083(3)	1427(66)
C125	-0.0423(7)	0.3647(6)	0.5114(2)	1058(45)
C126	-0.0224(6)	0.7570(5)	0.3374(2)	850(37)
C127	0.0895(6)	0.7385(5)	0.4174(2)	817(37)
C128	0.2516(7)	0.8164(5)	0.3320(3)	1006(49)
Cu2	0.3297(1)	0.5698(1)	0.4121(1)	501(3)
P2	0.3915(2)	0.6225(1)	0.4550(1)	770(9)
S2	0.3632(1)	0.6500(1)	0.3553(1)	456(6)
O2	0.4714(2)	0.5520(2)	0.3275(1)	412(14)
O21	0.4905(4)	0.6156(4)	0.4550(2)	1173(32)
O22	0.3671(7)	0.6074(6)	0.4910(2)	2002(55)
O23	0.3819(6)	0.7105(4)	0.4579(2)	1506(41)
N2	0.3998(3)	0.5160(3)	0.3754(1)	406(20)
C2	0.4137(4)	0.5647(3)	0.3527(2)	362(20)
C21	0.4434(4)	0.4488(3)	0.3775(2)	454(24)
C22	0.4521(5)	0.4001(4)	0.3504(2)	599(28)
C23	0.4935(6)	0.3330(4)	0.3564(2)	766(34)
C24	0.5217(6)	0.3136(5)	0.3864(3)	848(40)
C25	0.5113(7)	0.3606(5)	0.4144(2)	905(38)
C26	0.4717(5)	0.4273(4)	0.4092(2)	690(32)
C211	0.5011(4)	0.6101(3)	0.3069(2)	433(22)
C212	0.4550(4)	0.6340(4)	0.2780(2)	496(26)
C213	0.4846(4)	0.6962(4)	0.2616(2)	546(26)
C214	0.5586(5)	0.7323(4)	0.2713(2)	587(30)
C215	0.6072(4)	0.7027(4)	0.2977(2)	561(27)
C216	0.5799(4)	0.6410(4)	0.3158(2)	477(24)
C217	0.3764(4)	0.5946(4)	0.2616(2)	515(24)
C218	0.3973(5)	0.5816(5)	0.2244(2)	691(29)
C219	0.3518(5)	0.5226(4)	0.2773(2)	651(29)
C220	0.2993(5)	0.6477(5)	0.2628(2)	756(32)
C221	0.6359(4)	0.6072(4)	0.3444(2)	601(30)
C222	0.7242(5)	0.6498(5)	0.3456(2)	767(32)
C223	0.6569(5)	0.5274(5)	0.3351(2)	755(37)
C224	0.5983(5)	0.6151(5)	0.3791(2)	729(31)
C225	0.5857(6)	0.8032(5)	0.2548(2)	959(39)
C226 ^a	0.5470(8)	0.6519(7)	0.4798(3)	1533(45)
C227 ^a	0.3346(9)	0.5403(8)	0.5043(4)	1667(50)
C228 ^a	0.3066(7)	0.7469(6)	0.4483(3)	1130(36)

^a The atoms C226, C227, and C228 showed high thermal vibrations and so were refined isotropically.

phenylphosphine)copper(I) (5). When the reaction of copper(I) 4-methylphenoxide with PhNCS was carried out in the presence of PPh₃ (3 equiv), a mononuclear species similar to the monomeric product **1** was isolated in 30% yield.

Table VI. Selected Bond Lengths (\AA) and Bond Angles (deg) with Their Estimated Standard Deviations in Parentheses for [Cu μ_2 -SC(=Ph)(OC₆H₂(t-Bu)_{2-2,6}(Me-4))₂](P(OMe)₃)₂

(a) Bond Lengths			
Cu1-Cu2	2.829(1)	O21-C226	1.473(14)
Cu1-P1	2.182(2)	O22-C227	1.423(18)
Cu1-N1	2.044(5)	O23-C228	1.406(14)
Cu1-S2	2.268(2)	Cu2-P2	2.166(4)
Cu2-N2	2.059(5)	S2-C2	1.747(6)
S1-C1	1.742(7)	O2-C2	1.360(8)
S1-Cu2	2.258(2)	N2-C2	1.275(8)
O1-C1	1.372(7)	N1-C1	1.275(9)
(b) Bond Angles			
N1-Cu1-S2	119.1(1)	S1-Cu2-N2	118.6(1)
P1-Cu1-S2	113.8(1)	S1-Cu2-P2	116.8(1)
P1-Cu1-N1	123.6(1)	P2-Cu2-N2	121.0(2)
C1-S1-Cu2	106.0(2)	Cu1-S2-C2	105.1(2)
Cu1-N1-C1	106.2(4)	Cu2-N2-C2	104.3(4)
O1-C1-N1	119.7(5)	S1-C1-N1	121.0(5)
O2-C2-N2	120.2(5)	S2-C2-O2	119.7(4)
S1-C1-O1	119.2(5)	S2-C2-N2	120.0(5)

Table VII. Crystallographic Data for [Cu μ_2 -SC(=NPh)(OC₆H₃(Me)_{2-2,6})₂]₄

chem formula	C ₆₀ H ₅₆ S ₄ O ₄ N ₄ Cu ₄	$V, \text{\AA}^3$	2940(1)
fw	1279.58	Z	2
space group	$P\bar{1}$	$\rho_{\text{calcd}}, \text{g cm}^{-3}$	1.446
$a, \text{\AA}$	11.681(1)	μ, cm^{-1}	16.31
$b, \text{\AA}$	13.373(2)	$\lambda, \text{\AA} (\text{Mo K}\alpha)$	0.7107
$c, \text{\AA}$	20.127(1)	$T, ^\circ\text{C}$	22
α, deg	88.55(1)	R^a	0.043
β, deg	89.65(1)	R_w^b	0.050
γ, deg	69.28(1)		

^a $R = \sum(|F_o| - |F_c|) / \sum|F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = k / [\sigma^2(F_o) + gF_o^2]$.

Discussion

Initial studies with copper(I) 4-methylphenoxide showed that it did not react with PhNCS. It is possible that the large size of PhNCS compared to CS₂ prevented it from penetrating the polymeric network of Cu-OAr. Structural characterization and reactivity studies have shown that polymeric alkoxides can be forced to adopt discrete structures in the presence of ancillary ligands. Alternatively steric congestion can be used to prevent extensive oligomerization.¹² Hence we studied the reactions in the presence of tertiary phosphorus donors of copper(I) aryloxides with PhNCS. As expected, the insertion reactions could be carried out in the presence of tertiary phosphorus donors.

As in the case of other metal alkoxides reacting with organic isocyanates,¹³ we feel that a likely route for the formation of these complexes might involve an insertion. However the intermediate corresponding to the O,S-bonded Cu(I) species could not be isolated, as it readily rearranges to give the N,S-coordinated species. Subsequent reactions of the N,S-coordinated species depend on steric factors or ancillary ligands present.

Steric Control. Following the successful reaction of copper(I) 4-methylphenoxide with PhNCS in the presence of trimethyl phosphite, we attempted a similar reaction of copper(I) 2,6-dimethylphenoxide with PhNCS. This resulted in the formation of a tetrameric species (CuL₂)₄ (**3**) in contrast with the reaction of copper(I) 4-methylphenoxide where we had isolated a hexameric species (CuL)₆ (**6**). These two results taken in con-

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- (13) (a) Cotton, F. A.; Shamshoum, E. S. *J. Am. Chem. Soc.* **1985**, *107*, 4662. (b) Chislom, M. H.; Cotton, F. A.; Folting, K.; Huffman, J. C.; Ratermann, A. L.; Shamshoum, E. S. *Inorg. Chem.* **1984**, *23*, 4423. (c) Bohra, R.; Rai, A. K.; Mehrotra, R. C. *Inorg. Chim. Acta* **1977**, *25*, L147. (d) Mahendra, K. N.; Bharara, P. C.; Mehrotra, R. C. *Ibid.* **1977**, *25*, L5. (e) Mehrotra, R. C.; Rai, A. K.; Bohra, R. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1887.

Table VIII. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters ($\times 10^4$) with Their Estimated Standard Deviations in Parentheses for $[\text{Cu}\{\mu_2\text{-SC}(=\text{NPh})(\text{OC}_6\text{H}_3(\text{Me})_{2-2,6})\}_4]$

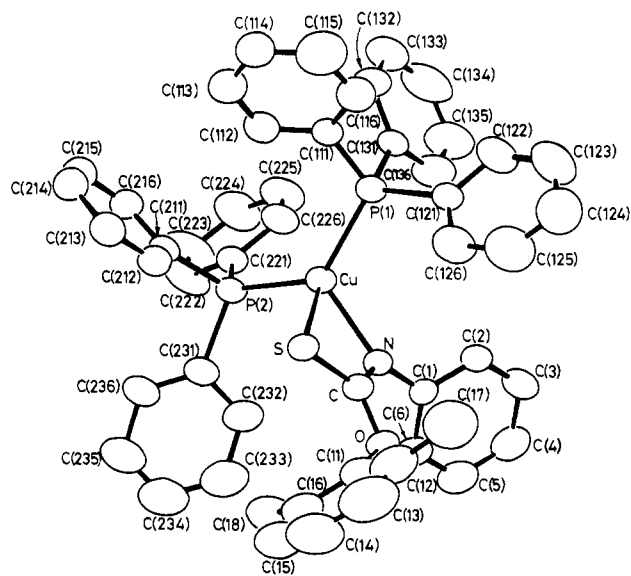
atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{\text{eq}}, \text{\AA}^2$	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{\text{eq}}, \text{\AA}^2$
Cu1	0.75512(2)	0.03492(2)	0.24903(2)	417(2)	Cu3	0.98952(2)	-0.00252(2)	0.20212(2)	373(2)
S1	1.0012(1)	0.0502(1)	0.3075(1)	432(4)	S3	0.7370(1)	0.0026(1)	0.1410(1)	434(4)
N1	0.7614(3)	0.1632(3)	0.2950(2)	464(14)	N3	0.9102(3)	0.0896(3)	0.1227(2)	391(14)
C11	0.6499(4)	0.2468(4)	0.3092(3)	532(18)	C31	0.9604(4)	0.1643(4)	0.0934(2)	433(15)
C12	0.6304(6)	0.3549(5)	0.2985(4)	955(33)	C32	0.9595(5)	0.1877(5)	0.0261(3)	613(25)
C13	0.5144(8)	0.4306(6)	0.3087(5)	1177(39)	C33	1.0152(5)	0.2561(6)	0.0032(3)	739(29)
C14	0.4204(8)	0.4021(7)	0.3276(5)	1166(42)	C34	1.0671(6)	0.3060(5)	0.0452(4)	760(28)
C15	0.4365(7)	0.2988(8)	0.3363(5)	1297(48)	C35	1.0731(6)	0.2797(5)	0.1114(3)	798(32)
C16	0.5501(6)	0.2198(5)	0.3260(4)	880(33)	C36	1.0192(5)	0.2099(4)	0.1349(3)	581(21)
C1	0.8640(4)	0.1592(4)	0.3190(2)	461(20)	C3	0.8047(4)	0.0885(3)	0.1046(2)	424(17)
O1	0.8705(3)	0.2408(3)	0.3547(2)	619(14)	O3	0.7418(3)	0.1584(3)	0.0568(2)	647(15)
C111	0.9659(5)	0.2217(4)	0.4013(3)	539(20)	C311	0.6228(4)	0.1631(5)	0.0405(3)	568(21)
C112	0.9580(6)	0.1720(4)	0.4604(3)	671(27)	C312	0.5277(5)	0.2289(5)	0.0778(3)	616(22)
C117	0.8575(8)	0.1297(7)	0.4752(4)	1166(46)	C317	0.5476(7)	0.2926(6)	0.1341(4)	968(36)
C113	1.0499(9)	0.1591(6)	0.5055(3)	922(41)	C313	0.4109(5)	0.2325(5)	0.0596(3)	759(27)
C114	1.1401(7)	0.1959(6)	0.4938(3)	872(32)	C314	0.3925(5)	0.1790(6)	0.0077(4)	778(30)
C115	1.1463(6)	0.2473(5)	0.4350(3)	793(29)	C315	0.4910(6)	0.1153(5)	-0.0311(3)	708(26)
C116	1.0545(5)	0.2650(4)	0.3860(3)	620(23)	C316	0.6093(5)	0.1076(4)	-0.0148(3)	582(21)
C118	1.0566(8)	0.3221(7)	0.3232(4)	1109(46)	C318	0.7179(6)	0.0421(5)	-0.0539(3)	798(28)
Cu2	0.88661(2)	-0.14421(2)	0.18521(2)	389(2)	Cu4	0.95112(2)	-0.10291(1)	0.31022(2)	392(2)
S2	0.7558(1)	-0.0930(1)	0.3285(1)	426(4)	S4	1.0877(1)	-0.1756(1)	0.1715(1)	394(4)
N2	0.8033(3)	-0.2346(3)	0.2314(2)	397(14)	N4	1.1005(3)	-0.2326(3)	0.3005(2)	415(13)
C21	0.7901(4)	-0.3250(3)	0.1982(2)	397(15)	C41	1.1551(5)	-0.3032(4)	0.3559(2)	555(21)
C22	0.7659(5)	-0.3150(4)	0.1317(2)	533(21)	C42	1.2649(7)	-0.3030(5)	0.3834(3)	811(28)
C23	0.7576(6)	-0.4011(5)	0.0973(3)	646(24)	C43	1.3139(10)	-0.3642(6)	0.4375(4)	1200(46)
C24	0.7835(6)	-0.4991(4)	0.1283(3)	657(26)	C44	1.2530(10)	-0.4234(9)	0.4659(4)	1532(67)
C25	0.8104(6)	-0.5076(4)	0.1937(4)	779(30)	C45	1.1453(10)	-0.4275(7)	0.4406(5)	1411(60)
C26	0.8129(6)	-0.4212(5)	0.2300(3)	676(27)	C46	1.0961(7)	-0.3655(5)	0.3839(4)	909(33)
C2	0.7363(4)	-0.1944(3)	0.2810(2)	394(16)	C4	1.1459(4)	-0.2548(3)	0.2423(2)	366(15)
O2	0.6416(3)	-0.2274(3)	0.2969(2)	548(14)	O4	1.2460(3)	-0.3458(2)	0.2350(1)	448(11)
C211	0.5568(6)	-0.1739(5)	0.3461(3)	736(30)	C411	1.2845(4)	-0.3770(3)	0.1697(2)	420(17)
C212	0.4592(6)	-0.0755(6)	0.3234(5)	1001(38)	C412	1.2274(5)	-0.4348(4)	0.1365(3)	557(20)
C217	0.6629(10)	-0.3208(8)	0.4212(4)	1262(60)	C413	1.2659(6)	-0.4627(4)	0.0719(3)	723(27)
C213	0.3792(9)	-0.0318(9)	0.3732(8)	1598(69)	C414	1.3564(6)	-0.4640(6)	0.0440(3)	812(29)
C214	0.3947(10)	-0.0763(10)	0.4354(8)	1852(104)	C415	1.4136(5)	-0.3800(5)	0.0787(3)	672(24)
C215	0.4842(10)	-0.1714(10)	0.4564(5)	1482(75)	C416	1.3790(4)	-0.3495(4)	0.1440(2)	499(19)
C216	0.5670(9)	-0.2183(7)	0.4056(4)	1069(48)	C417	1.1263(6)	-0.4653(5)	0.1682(4)	841(33)
C218	0.4530(8)	-0.0360(7)	0.2553(6)	1351(55)	C418	1.4384(6)	-0.2882(6)	0.1828(3)	820(32)

Table IX. Selected Bond Distances (\AA) and Angles (deg) with Their Estimated Standard Deviations in Parentheses for $[\text{Cu}\{\mu_2\text{-SC}(=\text{NPh})(\text{OC}_6\text{H}_3(\text{Me})_{2-2,6})\}_4]$

(a) Bond Lengths			
Cu1-Cu2	2.6973(5)	Cu3-N3	2.010(4)
Cu1-Cu3	2.7679(5)	Cu3-S1	2.272(2)
Cu1-Cu4	2.6622(5)	Cu3-S4	2.289(1)
Cu2-Cu3	2.6078(3)	S3-C3	1.754(5)
Cu2-Cu4	2.7550(2)	N2-C3	1.292(6)
Cu3-Cu4	2.6468(2)	C3-O3	1.348(5)
Cu1-N1	1.994(4)	Cu4-N4	1.991(3)
Cu1-S2	2.310(2)	Cu4-S1	2.319(2)
Cu1-S3	2.253(2)	S4-C4	1.744(4)
S1-C1	1.762(1)	C4-O4	1.367(4)
Cu4-S2	2.266(2)	Cu2-S4	2.252(1)
N1-C1	1.278(6)	C2-O2	1.362(7)
C1-O1	1.346(9)	Cu2-S3	2.281(1)
N4-C4	1.281(6)	N2-C2	1.272(5)
Cu2-N2	2.009(4)	S2-C2	1.758(5)

(b) Bond Angles			
S2-Cu1-S3	119.19(0.06)	S1-C1-N1	122.9(4)
S3-Cu2-S4	123.13(0.06)	S2-C2-N2	123.0(4)
S1-Cu3-S4	121.64(0.06)	S3-C3-N3	123.1(3)
S1-Cu4-S2	120.76(0.06)	S4-C4-N4	123.9(3)
N1-Cu1-S3	132.2(1)	N3-Cu3-S1	127.8(1)
N1-Cu1-S2	108.5(1)	N3-Cu3-S4	110.4(1)
N2-Cu2-S4	129.6(1)	N4-Cu4-S1	110.6(1)
N2-Cu2-S3	107.3(1)	N4-Cu4-S2	128.5(1)
Cu3-S1-Cu4	70.39(0.06)	Cu1-S3-Cu2	73.01(0.06)
Cu1-S2-Cu4	71.13(0.05)	Cu2-S4-Cu3	70.10(0.05)

junction point to the steric effect of the two methyl groups in the ortho position of the aryloxy group. While the methyl groups appear at first sight to be fairly remote from the Cu₄ core, their steric effect is sufficient to prevent further oligomerization.

**Figure 1.** ORTEP view of $[\text{Cu}\{\text{SC}(=\text{NC}_6\text{H}_5)(\text{OC}_6\text{H}_3(\text{Me})_{2-2,6})\}(\text{PPh}_3)_2]$ (1).

This could be visualized using the molecular modeling program Insight II.¹⁴ The coordinates for the initial geometry for the modeling studies were those derived from the X-ray structure. Severe bumping between two ligand moieties on the cluster occurs when methyl groups were introduced on the 2 and 6 positions of the aryloxy moiety of the hexamer. Thus, methyl groups on the

(14) Modeling results obtained using software programs from Biosym Technologies of San Diego, CA, and graphical displays using Insight II.

Table X. Selected Bond Angles (Average) for 1–3 and 6

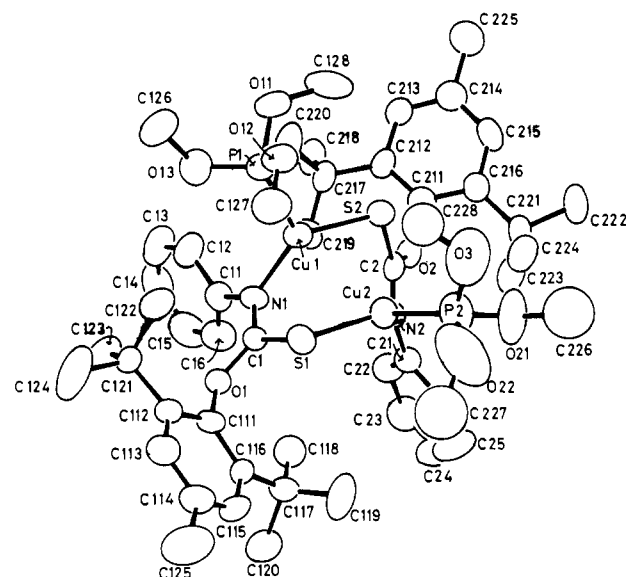
atoms	angles (deg)			
	monomer 1	dimer 2	tetramer 3	hexamer 6
P–Cu–P	126.4(1)			
P–Cu–S	109.1(1)	111.0(1)		
P–Cu–N	114.1(1)	122.3(1)		
S–Cu–N	68.6(1)	118.9(1)	119.4(1)	119.4(1)
S–Cu–S			121.2(1)	114.9(1)
Cu–S–C	74.8(1)	105.6(2)	104.8(2)	104.0(3)
Cu–N–C	139.8(2)	105.3(4)	117.5(3)	116.6(6)
Cu–S–Cu			71.2(1)	90.2(1)

Table XI. Selected Bond Distances (Average) for 1–3 and 6

atoms	distances (Å)			
	monomer 1	dimer 2	tetramer 3	hexamer 6
Cu–Cu		2.828(1)	2.690(1)	2.957(1)
Cu–P	2.250(2)	2.174(2)		
Cu–S	2.469(2)	2.263(2)	2.280(2)	2.245(2)
Cu–N	2.115(2)	2.052(5)	2.001(4)	2.021(6)
C=N	1.294(3)	1.275(9)	1.281(6)	1.295(10)
C–S	1.703(3)	1.744(7)	1.755(5)	1.752(8)

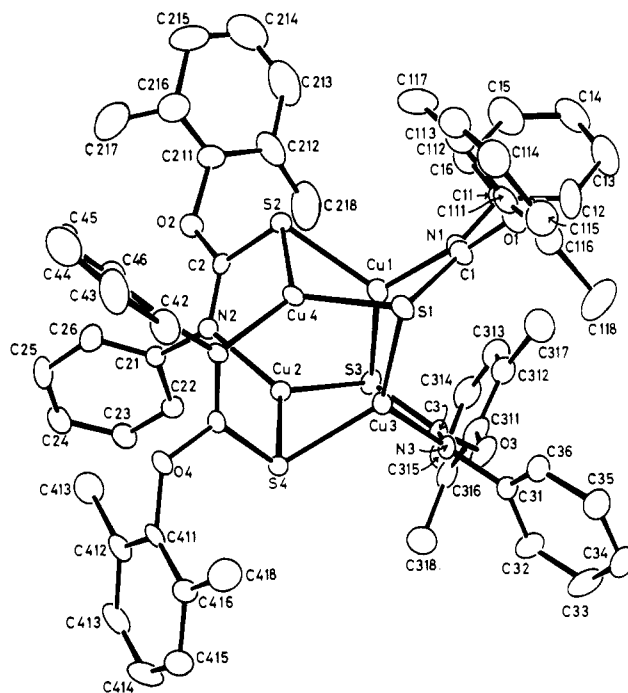
Table XII. IR Data for the Complexes 1–5

complex	$\nu(\text{C}=\text{N})$, cm^{-1}	$\nu(\text{C}-\text{O})$, cm^{-1}	$\nu(\text{P}-\text{C})$, cm^{-1}	$\nu(\text{Cu}-\text{S})$, cm^{-1}
1	1515	1182, 1110	1437	600–700
2	1539	1125, 1101		600–700
3	1565	1190, 1140		600–700
4	1524	1209, 1104	1380	600–700
5	1520	1200, 1100	1430	600–700

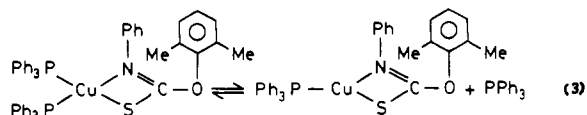
Figure 2. ORTEP view of $[\text{Cu}\{\mu\text{-SC}(\text{=NC}_6\text{H}_5)(\text{OC}_6\text{H}_2((t\text{-Bu})_2\text{-}2,6)\text{-}(\text{Me}\text{-}4))\}\text{P}(\text{OMe})_3\}_2$ (2).

ortho positions of the aryloxy group have significant impact on the oligomerizations of the CuL moiety, preventing the tetramer from becoming a hexamer.

Confirmation of the steric control in the oligomerization process comes from the reactions of copper(I) 2,6-di-*tert*-butyl-4-methylphenoxide in the presence of $\text{P}(\text{OMe})_3$. The complex isolated from this reaction is a dimeric species $[\text{CuL}_3\text{P}(\text{OMe})_3]_2$ in which phosphite is retained in the coordination sphere of the copper(I). Since the phosphite is generally lost readily from the coordination sphere (cf. formation of the hexamer and tetramer), isolation of this dimer is a direct result of the fact that oligomerization of the $(\text{CuL}_3)_2$ core is highly unfavorable due to steric congestion. Efforts to remove the trimethyl phosphite from the coordination sphere using $\text{Fe}_2(\text{CO})_9$ as a phosphite scavenger¹⁵ led to an inseparable mixture of products.

Figure 3. ORTEP view of $[\text{Cu}\{\mu\text{-SC}(\text{=NC}_6\text{H}_5)(\text{OC}_6\text{H}_3(\text{Me})_2\text{-}2,6)\}_4$ (3).

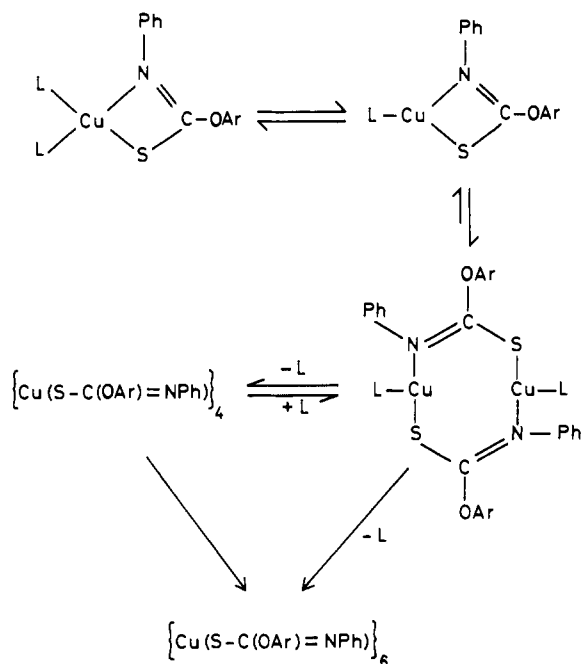
Ligand Control. The reaction is also controlled by the nature and amount of the phosphorus donor in the coordination sphere. In order to arrest the reaction at the early stages a large excess of triphenylphosphine was added to the suspension of copper(I) 2,6-dimethylphenoxide. Subsequent reaction with PhNCS led to the isolation of a crystalline product. X-ray crystal structure determination showed it to be a monomer. The ORTEP plot of the molecular structure (Figure 1) shows that the ligand chelates to the metal. Tetrahedral coordination around the metal is achieved through two phosphines and the N and S from the ligand. Surprisingly, the ^1H NMR of freshly dissolved crystals of the monomer invariably showed two different signals for the methyl groups on the aryloxy group at δ 2.21 (4.8H) and δ 1.78 (1.2H). The nonintegral ratios of these two peaks led us to suspect formation of a new species in solution, probably from loss of PPh_3 (eq 3).



In accord with this hypothesis, addition of PPh_3 to these solutions resulted in the suppression of the equilibrium. Complete disappearance of the smaller signal occurred on addition of excess PPh_3 . Similarly the use of a large excess PPh_3 in the reaction of $\text{Cu}(\text{I})$ 4-methylphenoxide led to the formation of a monomeric species 5. The *N*-phenylimino(aryloxy)methanethiolato ligand prefers to bridge copper atoms through S rather than act as a chelating ligand. So even in the presence of 1 equiv of PPh_3 , it would rather bridge two coppers than chelate (see Scheme II). Only in the absence of strong donors such as PPh_3 , one tends to form an oligomeric species where the coordination sphere of Cu is satisfied by only N and S.

Ligand-Controlled Interconversions. In principle, one should be able to convert these oligomers by addition or removal of the ligand. However loss of PPh_3 from the monomer 5 could lead to the formation of a dimer followed by the facile oligomerization of this dimer to the hexamer 6 through a tetramer. While the

Scheme II



dimeric species **4** could be obtained through a ligand-controlled reaction of copper(I) 4-methylphenoxide with PhNCS in the presence of 1 equiv of PPh_3 , the intermediate tetramer could not be isolated.

While it is possible to proceed from the monomer **5** to the hexamer **6** by the loss of PPh_3 , the reverse is not facile. Addition of PPh_3 to a solution of the hexamer results in no change after long periods of time. This contrasts with the reaction of the tetramer **3** with PPh_3 to form the monomer **1**. This conversion of **3** to **1** could be followed by monitoring the NMR signals of the methyl groups on the aryloxy group. Addition of 3 equiv of PPh_3 led to the appearance of the peaks corresponding to the methyl groups of the monomer and a decrease in the intensity of the peaks corresponding to the methyl groups of the tetramer. We attribute the lability of the tetrameric species **3** to the strained S bridges as reflected by the Cu–S–Cu angles (see Table XI). This seems to indicate why one is unable to observe the tetramer with sterically less demanding ligands such as L1. Conversion of the corresponding tetramer to the hexamer would be faster than the formation of the tetramer, in the absence of steric constraints.

The facile oligomerizations and interconversions in these complexes are in line with the tendency of copper(I) to oligomerize.¹⁶ The favorable change in entropy due to the loss of monodentate ligands is an obvious reason for oligomerization. In addition, extraordinarily short Cu(I)–Cu(I) distances have resulted in discussions about favorable Cu(I)–Cu(I) interactions.¹⁷ However in complexes **2**, **3**, and **6** the metal–metal distances are quite long and do not require one to invoke attractive copper–copper interactions. EHT calculations rule out significant attractive Cu–Cu interactions in these Cu_n clusters.¹⁸

Summary

The reactions of several copper(I) aryloxides with PhNCS have been presented. The role of the ligand and the steric control on the oligomerization and interconversion processes have been highlighted by the syntheses and characterization of various [*N*-phenylimino(aryloxy)methanethiolato]copper(I) complexes. The most significant factor leading to the formation of these oligomeric complexes appears to be the bridging characteristics of the *N*-phenylimino(aryloxy)methanethiolato ligand, which bridges a triangular array of Cu(I) atoms through the N=C–S–framework and the S–atom. The variety of coordination modes it exhibits allows for a stepwise formation of the oligomers and their interconversions. The formation of a tetramer and a hexamer through S–C=S and S–P=S frameworks have been observed before,¹⁹ but here, with steric and ligand control, a systematic study is made possible.

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Supplementary Material Available: For complexes 1–3, tables listing experimental details for structure determination, positional parameters, anisotropic thermal parameters, and complete bond lengths and angles (40 pages). Ordering information is given on any current masthead page.

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