Reversible Insertion of Methyl Isothiocyanate into Copper(I) Aryloxides

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MeNCS undergoes insertion into the copper(I)−aryloxide bond to form [*N*-methylimino(aryloxy)methanethiolato]-copper(I) complexes. This insertion occurs in the absence of ancillary ligands unlike the analogous insertion of PhNCS. The reaction with 4-methylphenoxide results in the formation of hexakis[[*N*-methylimino(4-methylphenoxy)methanethiolato]copper(I)] (**1**), which has been characterized by X-ray crystallography. Crystal data for **1**: hexagonal $R\bar{3}$, $a = 12.365(3)$ Å, $c = 36.734(16)$ Å, $\gamma = 120°$, $Z = 3$, $V = 4863(3)$ Å^3, $R = 0.0306$. Reactions of 2,6-dimethyl- and 4-chlorophenoxides also result in analogous copper(I) complexes **2** and **3**. Addition of stochiometric amounts of PPh_3 to the oligomeric complexes typically results in the extrusion of MeNCS. The ease of extrusion is dependent on the substituents on the aryloxide, and this deinsertion is accelerated by water. However, the extrusion reaction is slow enough in the case of the *N*-methylimino(2,6-dimethylphenoxy)-methanethiolate complex and the isolation of an intermediate monomeric product bis(triphenylphosphine)[*N*-methylimino(2,6-dimethylphenoxy)methanethiolato]copper(I) (**4**) is possible. Crystal data for **4**: triclinic $P\bar{1}$, $a = 10.088(2)$ Å, $b = 11.302(1)$ Å, $c = 17.990(2)$ Å, $\alpha = 94.06(1)°$, $\beta = 95.22(2)°$, $\gamma = 103.94(1)°$, $Z = 2$, $V = 1974.4(7)$ Å^3, $R = 0.0361$. In the presence of of PPh_3, the insertion reaction becomes reversible. This allows the exchange of the heterocumulene MeNCS or the aryloxy group in these molecules with another heterocumulene or a phenol, respectively, when catalytic amounts of PPh_3 are added. Oligomers with exchanged heterocumulmes and phenols could be characterized by independent synthesis.

Introduction

The reactivity of early[1−4] and middle[5−7] transition metal aryloxides and alkoxides has been extremely well studied. However late transition metal aryloxides and alkoxides[8−10] have received less attention.[11,12] The juxtaposition of a hard donor with a soft metal ion leads to interesting reactivity patterns.[13] Some of them are quite predictable on the basis of HSAB

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principles.[14−16] Studies on the insertion reactions of $Ir[(PR_3)_2(CO)(OR)]$ with CO show that the hard alkoxide ligand can be readily replaced by the softer carbon monoxide.[17] In this connection, the reactions of metal alkoxides with heterocumulenes are particularly illustrative of how reactions are based on HSAB preferences.[18−23] The iridium alkoxide hydride complex $Cp^*Ir(PPh_3)(OEt)(H)$ reacts with heterocumulenes (X═C═Y, X/Y = O, S, NR) to give products having Ir−S or Ir−N bonds like $Cp^*Ir[XC(Y)OEt](H)(PPh_3)$, (where X = S or NR)[13] rather than complexes with Ir−O bonds. Similarly the reactions of copper(I) aryloxide with CS_2 and PhNCS result in complexes with Cu(I)−S and Cu(I)−N bonds.[24] Both examples demonstrate the affinity that late transition metal ions have toward softer donor ligands. Not only do the metals maximize the soft−soft interactions, the ligands around the metal also maximize soft−soft and hard−hard interactions. A very good illustration of the selectivity of the ligands toward hard and soft centers is provided by the reaction of four-coordinate complexes of the type $[Mo(NR)_2(OR)_2]$ with PhNCO and PhNCS.[25] PhNCO undergoes insertion across the "hard" alkoxides to form two N,O chelating carbamate ligands whereas PhNCS inserts across one of the "softer" imido ligands to form a complex with a chelating *N*,*N*-thioureato ligand. Further, PhNCS can be displaced by PhNCO in the *N*,*N*-thioureato complex in order to increase hard−hard interactions. Thus most reactions known to date suggest the predictability of such insertion reactions on the basis of HSAB principles. It would be interesting to probe the limitations of this predictability.

A further reason for interest in these insertion reactions is the potential relevance of these heterocumulenes to serve as models for CO_2.[26−29] Heterocumulene insertion reactions have been studied extensively[30−38]in this context. However, when late transition metal alkoxides insert into PhNCS or CS_2, the metal−sulfur (soft−soft) interaction would be stronger than the corresponding metal−oxygen interaction formed from a CO_2 insertion. So, the validity of extending the reactions of these heterocumulenes to the reactions of CO_2 has been challenged.[39] The latter contention gains weightage from the fact that the insertion of soft heterocumulenes is irreversible while several insertion reactions of CO_2 are reversible.[40−43] One can then ask, would it be possible to make heterocumulene reactions reversible by electronic perturbations?

In this paper we report our recent findings on the insertion reactions of copper(I) aryloxides with MeNCS that has relevance to the two aspects mentioned above. MeNCS reacts with copper(I) aryloxides to give [*N*-methylimino(aryloxy)methanethiolato]copper(I) complexes, very similar to those isolated in the corresponding reactions with PhNCS.[24] The reactivity of Cu(I)−OAr with MeNCS is not altogether predictable from simple HSAB principles as in the reactions of copper(I) aryloxides with PhNCS or CS_2. There appears to be a tendency for copper(I) to balance the number of hard and soft donors in its coordination sphere rather than maximize the number of soft donors. Recent

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observations made by others[44] and us[45] suggest that this might be a general phenomenon. Second, just as the reactions of CO_2 with copper(I) alkoxides are reversible,[40] the reactions with MeNCS are also reversible in the presence of phosphines. A comparison of the reactions of PhNCS and MeNCS is made, throwing light on the electronic factors that govern the insertion reactions.

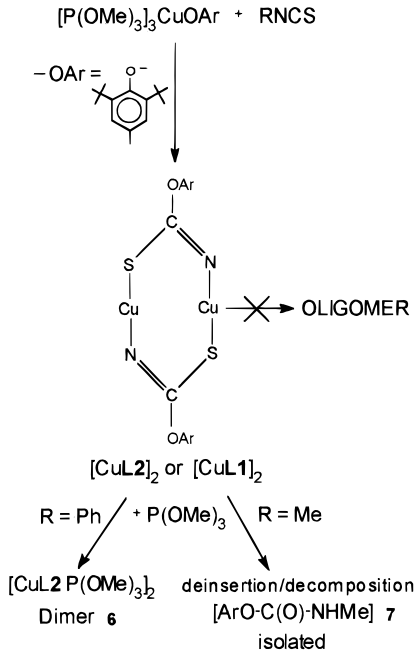
Results and Discussion

Insertion Reactions. MeNCS reacts with copper(I) aryloxides at room temperature to give [*N*-methylimino(aryloxy)methanethiolato]copper(I) complexes. From the IR and NMR spectroscopic data of these complexes, it is clear that MeNCS has been inserted across the Cu(I)−OAr bond. An [*N*-methylimino(aryloxy)methanethiolato]copper(I) complex is formed just as in the case of PhNCS, where an [*N*-phenylimino-(aryloxy)methanethiolato]copper(I) complex is formed. The insertion reaction occurs in the absence of ancillary ligands. This contrasts with the reactions of PhNCS which proceed only in the presence of ligands such as $P(OMe)_3$ and CH_3CN. These ligands facilitate the reaction by breaking down the polymeric structure of the copper(I) aryloxides.[24] A possible reason for this difference could be the smaller size of MeNCS which allows it to penetrate the polymeric structure of copper(I) aryloxide. A second reason could be the better coordinating ability of the MeNCS which would also make it possible for the MeNCS to break down the polymeric aryloxide. In the case of the more bulky and poorly coordinating PhNCS, an ancillary ligand is necessary.

However, MeNCS does not react with all copper(I) aryloxides. Thus the reaction of MeNCS with copper(I) 2,6-di-*tert*-butyl-4-methylphenoxide does not give characterizable copper-containing complexes with or without added ancillary ligands. The corresponding reaction with PhNCS,[24a] on the other hand, gives a dimeric complex bis{[μ-{*N*-phenylimino(2,6-di-*tert*-butyl-4-methylphenoxy)methanethiolato}](trimethyl phosphite)-copper(I)} (**6**) with the weak ancillary ligand $P(OMe)_3$ attached to the metal. It is likely that the steric bulk of the $[Cu\mathbf{L1}]_2$ complex (where **L1** is *N*-methylimino(2,6-di-*tert*-butyl-4-methylphenoxy)methanethiolate) prevents it from oligomerizing and forming a tetramer or a hexamer as in the case of $[Cu\mathbf{L2}]$ (where **L2** is *N*-phenylimino[2,6-di-*tert*-butyl-4-methyphenoxy]-methanethiolate) (see Scheme 1). The difference in reactivity is the result of the sensitivity of MeNCS clusters toward phosphine ligands. Unlike $[Cu\mathbf{L2}]_2$ which is stable in the presence of $P(OMe)_3$, the $[Cu\mathbf{L1}]_2$ dimer is unstable, due to a deinsertion reaction (*vide infra*). The isolation of the organic product MeNHC(O)O-(2,6-*t*-Bu_2-4-Me-C_6H_2) (**7**) from the reaction mixture suggests that the insertion of the phenoxide into the MeNCS is feasible. The available results do not allow us to distinguish between an insertion reaction occurring in the coordination sphere of the copper followed by a demetalation and an insertion reaction occurring outside the coordination sphere of copper(I). Either way, the difference in the heterocumulene part has made a significant impact on the outcome of the insertion reaction.

The reaction of 4-chlorophenol is an example of how insertion reactions of electron-deficient phenoxides are difficult. The reaction of copper(I) 4-chlorophenoxide and MeNCS gives no inserted product when CuCl is used as the source of Cu(I), whereas a 3% yield of the complex **3**, [*N*-methylimino(4-chlorophenoxy)methanethiolato]copper(I), is obtained when $[Cu(CH_3CN)_4]ClO_4$ is used as the source of Cu(I). The ancillary ligand CH_3CN promotes the insertion reaction. Such an increase in the nucleophilic reactions of copper(I) phenoxides has been observed before in reactions with CS_2.[46] Similarly, the insertion reaction of PhNCS with the 4-chlorophenoxide is more facile as shown by the marginally higher yield (7%) of the inserted product **5**, [*N*-phenylimino(4-chlorophenoxy)methanethiolato]-copper(I), obtained when $[Cu(CH_3CN)_4]ClO_4$ is used than when CuCl is used (3%). However, isolated yields need not necessarily reflect the stability of the products formed or the ease of insertion if crystallisation forces influence product formation.

Scheme 1



In the case of the [*N*-methylimino(4-methylphenoxy)methanethiolato]copper(I) complex **1** it was possible to obtain single crystals suitable for X-ray diffraction. Complex **1** is hexameric like the corresponding hexakis{[μ-*N*-phenylimino(4-methylphenoxy)methanethiolato]copper(I) complex **8**.[24b] The coordination geometry and the connectivity of the ligand remain the same. The six copper atoms are in an octahedral arrangement, and the six *N*-methylimino(4-methylphenoxy)methanethiolate ligands (**L3**) link the copper atoms through sulfur and nitrogen atoms. Each copper atom is coordinated to two sulfur atoms and one nitrogen atom, each belonging to three different ligands. In comparison with the hexamer **8**, there is considerably less distortion and a nearly perfect octahedral core of copper atoms is present due to the reduced steric constraints, resulting in the beautiful paddle wheel geometry shown in Figure 1.

The nuclearity of clusters is known to be controlled by the steric requirements of the ligands.[47−49] In the case of [*N*-phenylimino(aryloxy)methanethiolato]copper(I) oligomers, it is primarily determined by the steric bulk of the substituents on the aryloxide.[24a] Thus the [*N*-phenylimino(2,6-dimethylphenoxy)methanethiolato]copper(I) forms a tetramer (**9**) rather than a hexamer because of steric interactions between the phenyl group of the *Ph*NCS and the methyl groups on *OAr*. Since the ligand *N*-methylimino(2,6-dimethylphenoxy)methanethiolate (**L4**) has reduced steric requirements, the possibilty of forming a hexamer or a higher nuclearity oligomer with [*N*-methylimino-

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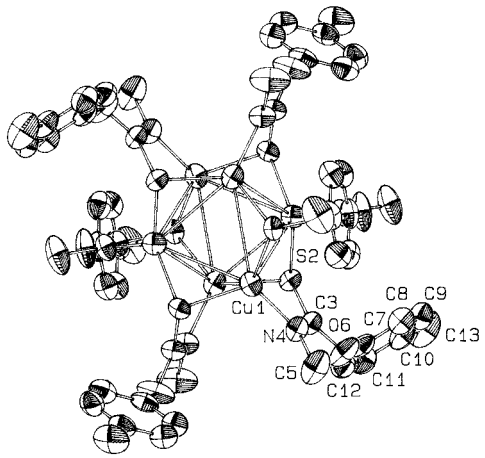

Figure 1. ORTEP view of $[CuSC(OC_6H_4\text{-}4\text{-}Me)=NMe]_6$ (**1**).

(2,6-dimethylphenoxy)methanethiolato]copper(I) must be considered. It was not possible to obtain single crystals of **2** suitable for X-ray diffraction studies. The ^{1}H NMR spectrum of this complex has two resonances for the methyls on the aryloxy group of the ligand, similar to the tetrameric complex **9** obtained in the reaction with PhNCS. Since it is not possible to form a mononuclear structure with this ligand and satisfy the coordination requirements of copper, this complex must be at least tetranuclear like the corresponding tetrakis{[μ-*N*-phenylimino-(2,6-dimethylphenoxy)methanethiolato]copper(I)} complex **9**.

Since all the hexameric structures isolated in this study have an orange color in the solid state, and the tetramers have a white color, one can infer that complex **2** is in fact a tetramer. However, in solution, the UV−visible spectral data available for the complexes are extremely similar indicating extensive dissociation and do not permit definitive conclusions. Modeling studies using the Insight program[50] show that a hypothetical hexamer formed with the ligand **L4** is not sterically congested. This result is quite different from that obtained in the case of the tetrameric complex **9**, where there is a phenyl instead of a methyl on the nitrogen.[24a] In the case of **9** a hexamer could not be constructed without steric congestion.

Reversible Insertion. The major difference between the clusters generated from PhNCS and MeNCS is the reactivity pattern that the clusters **1** and **2** exhibit on treatment with PPh_3. The [*N*-phenylimino(phenoxy)methanethiolato]copper(I) clusters **8** and **9** break down to give monomers $[Cu(SC(OAr)=NPh)(PPh_3)_2]$ (**10**, **11**) or dimers $[Cu\text{-}\mu\text{-}(SC(OAr)=NPh)(PPh_3)]_2$ (**12**, **13**) with 1 and 2 equiv of PPh_3, respectively. On the other hand, on the basis of the NMR spectra, it is clear that the MeNCS clusters undergo a series of reactions with PPh_3 which finally results in the extrusion of MeNCS from the cluster. Addition of 2 equiv of PPh_3 to the [*N*-methylimino(aryloxy)-methanethiolato]copper(I) complexes **1** and **2** resulted in the formation of a new peak in the NMR spectrum at 3.26 ppm, which corresponds to the peak position of free MeNCS. While the deinsertion of the MeNCS apppeared to be instantaneous in the case of the hexamer **1**, it was much slower in the case of **2**.

In order to understand the steps involved in the extrusion reaction, NMR experiments were carried out with **2** and added PPh_3. Immediate disappearance of the peaks corresponding to **2** and formation of three new peaks in the MeNCS region (3.02, 3.12, and 3.26 ppm) were observed. The intensity of the peak at 3.26 ppm (free MeNCS) increased with time. The intensities of the other two peaks were dependent on the amount of PPh_3 added. Adding 1 equiv of PPh_3 led to a 2.8:1 ratio of the peaks at 3.02 and 3.12 ppm, whereas addition of 2 and 3 equiv resulted in 1:3 and 1:2.8 ratios, respectively. Assuming that equilibria of phosphine-coordinated adducts exist (see Scheme 2), it is possible to explain the formation of the three peaks and their intensity variations with added PPh_3. The peak at 3.02 ppm corresponds to the dimer **II**, and the one at 3.12 ppm, to the monomer **III**. The ^{31}P NMR spectra of the monomeric and dimeric [*N*-phenylimino(aryloxy)methanethiolato]copper(I) complexes (**10**−**13**) are helpful in assigning the peaks and in understanding the equilibria in these systems as well. If the reaction mixture was allowed to stand for about 10 days, the formation of PPh_3S was detected (^{1}H NMR, ^{31}P NMR, and TLC) in the reaction mixture. The removal of PPh_3 as PPh_3S results in a shift of the equilibrium, and the formation of **2** could be inferred from the ^{1}H NMR spectrum. This indicates that the insertion and extrusion are in fact reversible.

One expects the thiophilic nature of the copper(I) center to yield a stable η^1-S-bonded **L4**$Cu(PPh_3)_3$ complex, **IV** (where **L4** is NMe=C(OAr)*S*); however this species deinserts and gives $ArO-Cu(PPh_3)_3$ (**VI**). The formation of the latter complex can be explained by the tendency of copper(I) to balance the number of hard and soft donors in its coordination sphere, a fact that has been documented in the case of phosphine complexes of Cu(I).[44,45] The aryloxide complex is hydrolytically unstable and leads to the formation of the phenol (as seen from the NMR spectra). As a consequence, the deinsertion reaction is faster in the presence of trace amounts of water in NMR solvents.

The deinsertion reaction is a manifestation of the electronic requirements of the insertion reaction. The greater electrophilicity of the PhNCS drives the reaction to completion and makes the deinsertion reaction difficult. However, the MeNCS cluster readily deinserts since MeNCS is a weaker electrophile. The deinsertion reactions of the [*N*-methylimino(aryloxy)methanethiolato]copper(I) oligomers with PPh_3 help us understand why it is not possible to make the monomeric complex $(PPh_3)_2Cu[SC(OC_6H_4\text{-}4\text{-}Me)=NMe]$. Although the ^{1}H NMR spectra of the reaction mixtures indicate the initial formation of products with coordinated phosphine, these are unstable and cannot be isolated due to the ready extrusion of MeNCS.

The steric protection afforded by the *o*-methyl groups in **4**

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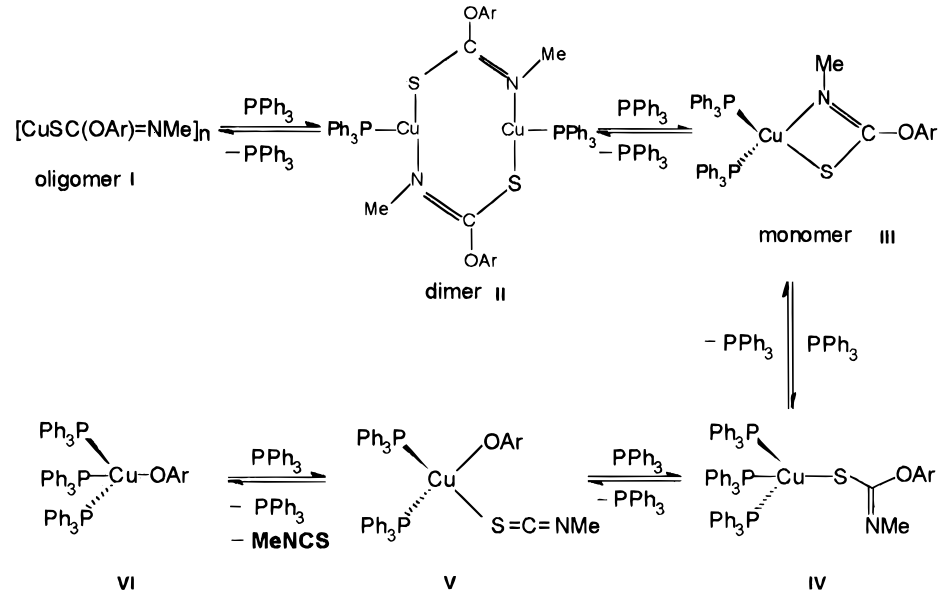
(50) Modeling results obtained using software programs from Biosym Technologies of San Diego, CA, and graphical displays using InsightII.

Scheme 2



slows down the deinsertion reaction. In the reaction of MeNCS with copper(I) 2,6-dimethylphenoxide in the presence of PPh_3, the reaction mixture, after removal of the solvent, can be extracted with petroleum ether to give the monomeric complex **4**, in 62% yield. The structure of **4** was obtained from a single-crystal X-ray crystallographic study. The tetracoordinate copper atom has two PPh_3 ligands and a chelating *N*-methylimino-(aryloxy)methanethiolate ligand as shown in Figure 2. The ^1H NMR spectrum of the monomer **4** has two peaks in the MeNCS region (3.02 and 3.12 ppm), and their nonintegral ratios show that the monomer is in equilibrium with the dimer. This equilibrium can be shifted by the addition of PPh_3. Solutions of the monomer undergo deinsertion with time although in the solid state **4** appears to be indefinitely stable.

Exchange Reactions. The reversible extrusion of MeNCS from the coordination sphere of the [*N*-methylimino(aryloxy)-methanethiolato]copper(I) complexes suggests that these clusters might exchange MeNCS for a more electrophilic heterocumulene. Addition of PhNCS to [*N*-methylimino(aryloxy)methanethiolato]copper(I) clusters **1** and **2** resulted in no reaction even after long reaction times. On the other hand, the addition of PhNCS to the monomeric complex **4** resulted in a rapid exchange reaction leading to the formation of the corresponding PhNCS-inserted monomer **10** (see Scheme 3). The addition of 1 equiv of phosphine to a mixture of **1** and PhNCS promotes an exchange reaction, resulting in the formation of the monomer **10** and the hexamer **8** as inferred from the ^1H NMR spectrum. The hexamer **1** and the tetramer **2** also exchange with PhNCS to give the corresponding PhNCS-inserted hexamer **8** and tetramer **9** with catalytic amounts of phosphine illustrating reversible insertion of heterocumulenes into Cu(I)−OAr bonds.

Treatment of the monomer **4** with CS_2 results in an exchange reaction giving the CS_2-inserted monomer **15** [Cu{SC(OC_6H_3-2,6-Me_2)=S}(PPh_3)$_2$]. The hexamer **1** can also undergo exchange with CS_2 in the presence of 2 equiv of PPh_3 to give a monomeric complex. The structure of the monomeric inserted product **14** [Cu{SC(OC_6H_4-4-Me)=S}(PPh_3)$_2$] has been determined by single-crystal X-ray crystallography[24c] and is similar to that of **4**.

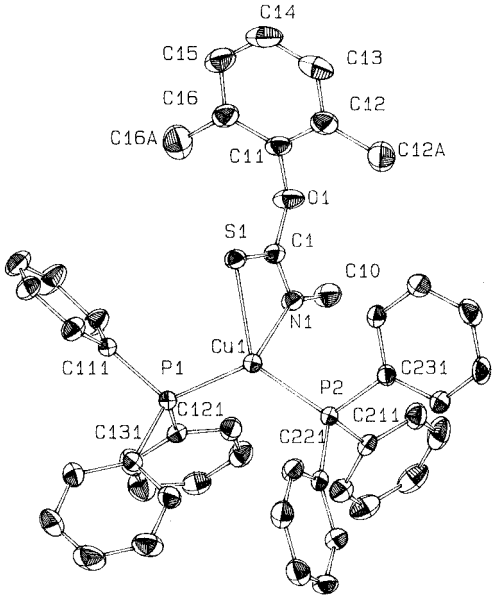
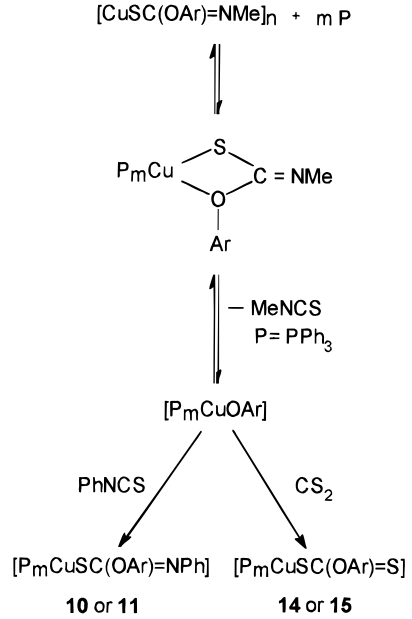


Figure 2. ORTEP view of [Cu{SC(OC_6H_3-2,6-Me_2)=NMe}(PPh_3)$_2$] (**4**).

Scheme 3



Although clusters having the *N*-phenylimino(aryloxy)-methanethiolate ligand (**8** and **9**) do not extrude PhNCS readily, exchange reactions with CS_2 could be carried out on these clusters also. In the presence of PPh_3 (2 equiv) PhNCS clusters formed the corresponding CS_2-inserted monomeric complexes (**14** and **15**). However these exchange reactions are not complete and a mixture of products is obtained. Such exchanges of the inserted heterocumulene have been observed before.[51,52]

Since metal alkoxides and aryloxides are known to undergo alcohol/phenol exchange reactions,[53−61] the intermediacy of a $Cu^{I}OAr(PPh_3)_3$ complex **VI** or a $Cu^{I}(OAr)(SCNR)(PPh_3)_2$ complex **V** as suggested in Scheme 3 would enable one to exchange the phenol. The exchange of the phenol can be represented by eqs 1 and 2.

$$[CuSC(OAr){=}NR]_n + mP \rightleftharpoons [P_mCuOAr] + RNCS \xrightarrow[R = Ph]{Ar'OH} [P_mCuSC(OAr'){=}NPh] \quad (1)$$

$$[CuSC(OAr){=}NR]_n + mP \rightleftharpoons [P_mCuOAr] + RNCS \xrightarrow[R = Me]{Ar'OH} \text{mixed clusters} \quad (2)$$

The addition of 4-methylphenol to the cluster **2** where 2,6-dimethylphenol is present resulted in the formation of mixed clusters having **L3** [$SC(OC_6H_4$-4-Me$){=}$NMe] and **L4** [$SC(OC_6H_3$-2,6-Me_2]. When an electron-deficient phenol is present in the cluster, it can be exchanged completely with an electron-rich phenol. Thus it was possible to replace the *p*-chlorophenol in the cluster **5**, $[CuSC(OC_6H_4$-4-Cl)NPh$]_n$, with 2,6-dimethylphenol to give the monomer **11** $[(PPh_3)_2CuSC(OC_6H_3$-2,6-$Me_2)$NPh] in the presence of 2 equiv of PPh_3. The *p*-chlorophenol in this cluster exchanged with 2,6-dimethylphenol in the presence of 1 equiv of PPh_3 to form the monomer **11** and the tetramer **9**. Even 4-methylphenol in the hexamer **1** can be replaced with 3,5-dimethylpyrazole which is more nucleophilic than 4-methylphenol. However the products formed with 3,5-dimethylpyrazole were unstable. These exchange reactions clearly bring out the electronic requirements for the insertion reaction besides the requirement for maximizing soft−soft interactions.

Conclusions

Insertion reactions of MeNCS with copper(I) aryloxides are similar yet different from the analogous reactions of PhNCS. The insertion of MeNCS, which is a weaker electrophile, is less facile. The addition of PPh_3 to the oligomeric complexes typically results in the extrusion of MeNCS contrary to the oligomers formed by the insertion of PhNCS which merely breakdown to complexes of lower nuclearity. The extrusion is dependent on the substituents present on the phenol and is accelerated and made irreversible by the presence of water. Thus, unlike the reactions with PhNCS, the insertion reaction is hampered by the presence of PPh_3 due to its reversible nature. In the case of copper(I) 2,6-dimethylphenoxide, however, a monomeric insertion product containing two PPh_3 ligands is obtained in high yield due to the steric protection afforded by the methyl groups. The reversible nature of this insertion permits exchange of the heterocumulene MeNCS or the aryloxy group of these molecules either by another heterocumulene or a phenol, respectively. Catalytic amounts of PPh_3 are sufficient to bring about the exchange reactions, which are driven to completion when the entering phenol is more nucleophilic and the incoming heterocumulene is more electrophilic. The reversible nature of the insertion reaction and the exchange reactions bring out the electronic requirements of the insertion reaction in addition to the need to maximize soft−soft interactions.

Experimental Section

General Methods. Dichloromethane, petroleum ether (bp 60−80 °C) and acetonitrile were purified and dried by conventional methods. They were distilled under nitrogen and deoxygenated before use. CuCl and $[Cu(CH_3CN)_4]ClO_4$ (*Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts should be prepared, and they should be handled with great caution)* were freshly prepared before use. Phenols, MeNCS, PhNCS, and CS_2 were purified by distillation. A 60% suspension of NaH in mineral oil was washed with petroleum ether (bp 60−80 °C) and used. ^{1}H NMR spectra were recorded with a Bruker ACF 200 MHz spectrometer, and $^{31}P\{^1H\}$ NMR spectra, on a Bruker AMX 400 MHz spectrometer operating at 162 MHz and a Bruker ACF 200 MHz spectrometer operating at 81.1 MHz. IR spectra were recorded on a Bio-Rad FTS-7 spectrophotometer. Elemental analyses were done with a Carlo Erba Model 1106 elemental analyzer.

Preparation of Copper(I) Aryloxides. Copper(I) aryloxides were prepared by the reported procedure.[24] To a stirred suspension of NaH (0.12 g, 3 mmol) in about 40 mL of CH_2Cl_2 or CH_3CN was added the phenol (3 mmol) under an atmosphere of dry, oxygen-free N_2. When the evolution of H_2 ceased, CuCl (0.297 g, 3 mmol) was added. A yellow precipitate of copper(I) aryloxide was formed which was used immediately for further reactions.

Preparation of $[Cu\{\mu$-SC(=NMe)(OC_6H_4Me-4)$\}]_6$ (1). To copper(I) 4-methylphenoxide prepared as above in CH_2Cl_2 was added MeNCS (0.2 mL, 3 mmol) and the solution stirred for 8 h. The mixture was filtered and concentrated to about 10 mL. Layering with petroleum ether (bp 60-80 °C) yielded yellow-orange crystals. Yield: 37%. Anal. Calcd for **1**: C, 44.3; H, 4.11; N, 5.75. Found: C, 44.28; H, 4.18; N, 5.69. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.15 (d, J = 8.4 Hz, 2H, $-OC_6H_4-$), δ 6.89 (d, J = 8.37 Hz, 2H, $-OC_6H_4-$), δ 3.14 (S, 3H, MeNCS), δ 2.35 (S, 3H, Me). IR (neat) (in cm^{-1}): 2917 (m), 2864 (w), 161 (s), 1601 (m), 1503 (s) ($\nu_{C=N}$), 1260 (w), 1217 (s), 1157 (s), 1114 (s), 1017 (m), 895 (w), 818 (m), 467 (w).

Preparation of $[Cu\{\mu$-SC(=NMe)(OC_6H_3(Me)$_2$-2,6)$\}]_n$ (2). To the copper(I) aryloxide of 2,6-dimethylphenol prepared in CH_3CN was added MeNCS (0.2 mL, 3 mmol) and the solution stirred for 8 h. A dirty white precipitate was formed, which was filtered out and washed

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Table 1. Exchange Reactions Studied and the Products Formed

phenol part	heterocumulene part	starting compd	phosphine added/present	exchange with	products formed
p-cresol	MeNCS	hexamer	1 PPh_3	PhNCS	$[CuSC(OAr)=NPh(PPh_3)_2]$ + $[CuSC(OAr)=NPh]_6$ (monomer + hexamer)
2,6-dimethylphenol	MeNCS	monomer	2 PPh_3	PhNCS	$[CuSC(OAr)=NPh(PPh_3)_2]$ (monomer)
p-cresol	MeNCS	hexamer	2 PPh_3	CS_2	$[CuSC(OAr)=S(PPh_3)_2]$ (monomer)
2,6-dimethylphenol	MeNCS	monomer	2 PPh_3	CS_2	$[CuSC(OAr0=S(PPh_3)_2]$ (monomer)
p-cresol	MeNCS	hexamer	catal PPh_3	PhNCS	$CuSC(OAr)=NPh]_6$ (hexamer)
2,6-dimethylphenol	MeNCS	oligomer	catal PPh_3	PhNCS	$[CuSC(OAr)=NPh]_4$ (tetramer)
p-cresol	MeNCS	hexamer	1 PPh_3	3,5-dimethylpyrazole	$[CuSC(pyr)=NMe(PPh_3)_2]$ (monomer)
p-chlorophenol	PhNCS	oligomer	1 PPh_3	2,6-dimethylphenol	$[CuSC(OAr')=NPh(PPh_3)_2$ (monomer) + $[CuSC(OAr')=NPh]_4$ (tetramer)
2,6-dimethylphenol	PhNCS	tetramer	1 PPh_3	CS_2	$[CuSC(OAr)=S(PPh_3)_2$ (monomer) + unreacted starting material
p-cresol	PhNCS	hexamer	1 PPh_3	CS_2	$[CuSC(OAr)=S(PPh_3)_2]$ (monomer) + unreacted starting material
2,6-dimethylphenol	MeNCS	oligomer	catal PPh_3	*p*-cresol	mixed clusters containing both 2,6-dimethylphenol and *p*-cresol

with acetonitrile. The amorphous white solid that was thus obtained was only partially soluble in the usual organic solvents. The soluble part does not form crystals, and only amorphous powders are obtained. Redissolving this powder leaves an insoluble residue suggesting polymerization of the CuL unit. The solublity behavior of this complex is reminscent of other copper(I) complexes which have bridging ligands and polymerize slowly. Yield: 65%. Anal. Calcd for **2**: C, 46.60; H, 4.66; N, 5.44. Found: C, 44.47; H, 4.45; N, 4.91. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.07 (S, 3H, OC_6H_3-), δ 3.11 (s, 3H, MeNCS), δ 2.26 (S, 3H, Me), δ 2.16(S, 3H, Me). IR (neat) (in cm^{-1}) 1592 (m) ($\nu_{C=N}$), 1576 (s), 1474 (w), 1394 (w), 1267 (w), 1193 (m), 1149 (s), 1118 (s), 769 (w).

Preparation of [Cu{μ-SC(=NMe)(-C_6H_4Cl-4)}]$_n$ (3). Copper(I) 4-chlorophenoxide was prepared by adding $Cu(CH_3CN)_4ClO_4$ (0.981 g, 3 mmol) to sodium 4-chlorophenoxide (3 mmol). To this deep yellow suspension was added MeNCS (0.2 mL, 3 mmol), and the mixture was stirred. Filtration yielded an orange solution. Orange crystals were obtained on layering with petroleum ether (bp 60-80 °C). Yield: 3%. A reaction carried out using CuCl instead of $Cu(CH_3CN)_4ClO_4$ does not yield the inserted product. Anal. Calcd for **3** (with 0.2 CH_2Cl_2): C, 35.01; H, 2.63; N, 4.98. Found: C, 34.98; H, 2.67; N, 4.63. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.32 (d, J = 8 Hz, 2H, $-OC_6H_4-$) δ 6.95 (d, J = 8 Hz, 2H, $-OC_6H_4-$), δ 5.3 (S, 0.4 H, CH_2Cl_2), δ 3.15 (S, 3H, MeNCS). IR (Nujol) (in cm^{-1}) 1595 (s) ($\nu_{C=N}$), 1570 (s), 1475 (s), 1375 (w) 1210 (s), 1155 (s), 1105 (s), 1075 (s), 1010 (m), 890 (w), 820 (m).

Synthesis of [Cu{SC(=NMe)(OC_6H_3(Me)$_2$-2,6)}(PPh_3)$_2$] (4). To copper(I) 2,6-dimethyl phenoxide was added 3 equiv of PPh_3 (2.36 g, 9 mmol), and the mixture was stirred for 0.5 h. MeNCS (0.2 mL, 3 mmol) was added and the stirring continued for 8 h. The resulting solution was filtered, and the filtrate was pumped dry. The residue was washed with petroleum ether (bp 60-80 °C) to obtain **4**. Yield: 62%. Anal. Calcd for **4**: C, 70.63; H, 537; N, 1.79. Found: C, 70.64; H, 5.47; N, 1.39. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.35−6.97 (m, 23H, PPh_3, $-OC_6H_3-$), δ 3.12 (s, 2.1 H, MeNCS), δ 3.02 (s, 0.9 H, MeNCS), δ 2.18 (s, 6H, Me). IR (Nujol) (in cm^{-1}): 1584 (w) ($\nu_{C=N}$), 1560 (s), 1476 (s) 1434 (s), 1393 (m), 1309 (w), 1265 (w), 1202 (m), 1148 (m), 1093 (s), 1028 (m), 997 (w), 767 (m), 745 (s), 696 (s), 527 (m), 513 (s), 488 (m), 443 (w), 416 (w).

Synthesis of [Cu{μ-SC(=NPh)(OC_6H_4Cl-4)}]$_n$ (5). PhNCS (0.36 mL, 3 mmol) was added to the suspension of copper(I) 4-chlorophenoxide (3 mmol). The resulting suspension was stirred for 8 h and then filtered. The filtrate was concentrated, and layering with petroleum ether (bp 60-80 °C) yielded yellow orange crystals. Yield: 3%. The yield was greater (7%) when $Cu(CH_3CN)_4ClO_4$ was used to prepare the copper(I) phenoxide. Anal. Calcd for **5**: C, 47.58; H, 2.76; N, 4.29. Found: C, 47.53; H, 3.02; N, 3.88. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.45−6.49 (m, PhNCS, $-OC_6H_4$). IR (neat) (in cm^{-1}): 1565 (s) ($\nu_{C=N}$), 1550 (m), 1479 (s), 1206 (s), 1120 (m), 1085 (m), 1066 (m), 1011 (w).

Synthesis of Complexes 6−15. Complexes **6**−**15** were prepared by the method described earlier.[24]

Table 2. Crystallographic Data for **1** and **4**

	1	**4**
chem formula	$C_{54}H_{60}N_6O_6S_6Cu_6$	$C_{46}H_{42}NOSP_2Cu$
fw	1462.74	782.397
space group	$R\bar{3}$	$P\bar{1}$
a, Å	12.365(3)	10.088(2)
b, Å		11.302(1)
c, Å	36.734(16)	17.990(2)
α, deg		94.06(1)
β, deg		95.22(2)
γ, deg	120	103.94(1)
V, Å^3	4863(3)	1974.4(7)
Z	3	2
ρ_{calcd}, g cm^{-3}	1.4981	1.316
μ, cm^{-1}	21.722	7.186
T, °C	20	20
λ, Å (Mo Kα)	0.7107	0.7107
final R^a	0.0306	0.0361
final $R_w{}^b$	0.0358	0.0361

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

Reaction of Copper(I) 4-Methylphenoxide with MeNCS in the Presence of PPh_3. To the copper(I) phenoxide (3 mmol) of 4-methylphenol was added 2 equiv (6 mmol; 1.572 g) or 3 equiv (2.358 g; 9 mmol) of PPh_3 followed by the addition of MeNCS (2 mL; 3 mmol). The mixture was stirred for 8 h. TLC revealed the formation of a mixture of products which could not be separated. IR and NMR spectra reveal the presence of free MeNCS in addition to several products containing MeNCS.

Exchange Reactions. (a) Exchange with PhNCS. In an NMR tube, 1 equiv of the starting compound was mixed with the required amount of PPh_3 (1 equiv, 2 equiv, or catalytic) and 1 equiv of PhNCS. $CDCl_3$ was added, and the spectrum was recorded immediately. The formation of the products with time was followed by recording the ^{1}H NMR spectra of the samples.

(b) Exchange with CS_2. A 1 equiv amount of the starting compound was mixed with the required amount of PPh_3 (1 or 2 equiv) and 0.2 mL of CS_2 in an NMR tube. The spectrum was recorded immediately after adding $CDCl_3$ to the sample. Product formation was followed by recording the ^{1}H NMR spectra of the samples periodically over a few days.

(c) Exchange with 2,6-Dimethylphenol. A 1 equiv amount of the starting compound was mixed with 1 equiv of PPh_3 and 1 equiv of 2,6-dimethylphenol. $CDCl_3$ was added to this, and an NMR spectrum was recorded. The formation of the products was confirmed by comparison of the NMR spectrum with that of authentic samples. The progress of the reaction was monitored by recording the ^{1}H NMR spectra periodically.

(d) Exchange with 3,5-Dimethylpyrazole. A 1 equiv amount of the hexamer **1** was mixed with 1 equiv of PPh_3 and 1 equiv of 3,5-dimethylpyrazole in an NMR tube. An NMR spectrum was recorded as soon as the solvent ($CDCl_3$) was added. The progress of the reaction

Table 3. Selected Bond Distances (Å) and Angles (deg) with Their Estimated Standard Deviations in Parentheses for $[Cu\{\mu\text{-}SC(=NMe)(OC_6H_4\text{-}4\text{-}Me)\}]_6$ (**1**)

Cu1−S2	2.239(1)	Cu1−S2−C3	103.2(1)
Cu1−S2′	2.2432(9)	Cu1−S2−Cu1′	89.6(1)
Cu1−N4′	2.005(3)	S2−Cu1−S2′	115.5(1)
Cu1−Cu1′	3.1583(8)	N4−Cu1−S2	119.8(2)
Cu1−Cu1″	2.8719(9)	N4−Cu1−S2′	117.9(2)
S2−C3	1.742(3)	S2−C3−O6	118.6(2)
C3−N4	1.272(4)	S2−C3−N4	123.6(3)
C3−O6	1.363(4)	N4−C3−O6	117.9(3)
N4−C5	1.467(6)	C3−N4−C5	119.2(3)
O6−C7	1.402(4)	C3−O6−C7	120.1(3)

was monitored by TLC and the appearance/disappearance of peaks characteristic of the reactants and products.

A summary of the various exchange reactions studied is given in Table 1.

Deinsertion Reactions. A 1 equiv amount of the oligomer was mixed with the required amount (1, 2, or 3 equiv) of PPh_3 in an NMR tube. $CDCl_3$ was added, and the spectrum was recorded immediately. The progress of the reaction was followed by recording the NMR spectra periodically. The formation of various products was identified by the appearance of characteristic peaks in the NMR spectrum.

Experimental Details of Crystallography. An orange crystal of **1** suitable for the diffraction study was obtained by crystallization of **1** from a mixture of dichloromethane and petroleum ether (bp 60−80 °C) (1:1). Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Data collection parameters are summarized in Table 2. Three intensity control reflections, measured once in every 3600 s of exposure time, showed no significant decay. Data was corrected for Lorentz, polarization, and absorption (DIFABS;[62] transmission coefficient, 0.933−1.046) also. The filtrate obtained in the reaction between copper(I) 2,6-dimethylphenoxide and MeNCS in the presence of 3 equiv of PPh_3 was pumped dry. Crystals of **4** were obtained from the petroleum ether (bp 60−80 °C) extract of this residue. A pale yellow crystal of **4** was sealed in a Lindemann capillary along with the mother liquor as it was unstable outside the mother liquor. Data collection procedures were similar to that of **1**.

The structures of **1** and **4** were solved by the heavy atom method and subsequent Fourier syntheses using the SHELX system[63] of programs. The hydrogen atoms were located from the difference Fourier map. Non-hydrogen atoms were refined anisotropically, and the hydrogen atoms, isotropically. The refinement converged at $R = 0.0306$ and 0.0361 for **1** and **4**, respectively. Details of the crystallographic analyses are summarized in Tables 2−4 and in the Supporting Information.

Table 4. Selected Bond Distances (Å) and Angles (deg) with Their Estimated Standard Deviations in Parentheses for $[Cu\{SC(=NMe)(OC_6H_3\text{-}2,6\text{-}(Me)_2\}(PPh_3)_2]$ (**4**)

Cu1−N1	2.14(2)	P1−C111	1.828(4)
Cu1−S1	2.460(1)	P1−C121	1.817(3)
Cu1−P1	2.265(1)	P1−C131	1.836(3)
Cu1−P2	2.268(1)	P2−C211	1.824(4)
Cu1−C1	2.602(3)	P2−C221	1.842(4)
N1−C1	1.280(7)	P2−C231	1.828(3)
N1−C10	1.46(2)	C1−O1	1.383(4)
S1−C1	1.716(4)	O1−C11	1.388(5)
P1−Cu1−P2	126.91(6)	Cu1−P1−C131	116.1(1)
S1−Cu1−P2	120.54(6)	Cu1−P1−C121	113.1(1)
S1−Cu1−P1	108.78(5)	Cu1−P1−C111	116.6(1)
N1−Cu1−P2	104.4(1)	N1−C1−S1	120.60(5)
N1−Cu1−P1	111.0(1)	Cu1−C1−S1	65.8(1)
N1−Cu1−S1	68.8(1)	Cu1−C1−N1	54.9(4)
Cu1−N1−C10	144.3(4)	S1−C1−O1	122.3(3)
Cu1−N1−C1	95.9(5)	N1−C1−O1	117.1(5)
C1−N1−C10	119.8(5)	Cu1−C1−O1	171.6(3)
Cu1−S1−C1	74.7(2)	C1−O1−C11	120.6(3)

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Supporting Information Available: For complexes **1** and **4**, tables listing positional and *U* parameters for all atoms, anisotropic thermal parameters, and complete bond lengths and bond angles (12 pages). Ordering information is given on any current masthead page.

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