

Role of bifunctional N/S bridging in the association of metals; syntheses and structures of heterobimetallic $[(\text{Ph}_3\text{P})_2\text{CuL}_2\text{Li}(\text{thf})_2]\cdot\text{thf}$ and tetrameric $[\{\text{CuL}(\text{PPh}_3)\}_4]$ ($\text{L} = 1,3\text{-benzoxazoline-2-thionate}$, $\text{thf} = \text{tetrahydrofuran}$)

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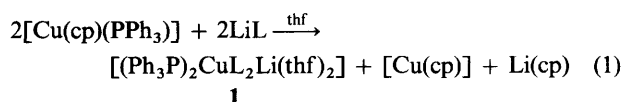
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Nucleophilic substitution of the $\text{cp}(\eta\text{-C}_5\text{H}_5)$ ligand of $[\text{Cu}(\text{cp})(\text{PPh}_3)]$ with LiL ($\text{L} = 1,3\text{-benzoxazoline-2-thionate}$) gave the heterobimetallic complex $[(\text{Ph}_3\text{P})_2\text{CuL}_2\text{Li}(\text{thf})_2]\cdot\text{thf}$ **1** ($\text{thf} = \text{tetrahydrofuran}$), the ligand-transfer reaction of which with CuCl_2 generated the tetrameric cage complex $[\{\text{CuL}(\text{PPh}_3)\}_4]$ **2**. The crystal structures of these complexes revealed that the association of the metal centres occurs by a variety of ligand co-ordination modes ($\mu\text{-S}$, N ; N , $\mu\text{-S}$; $\mu_3\text{-S}$). Electrochemical measurements have been used to probe the nature of the species present in solution.

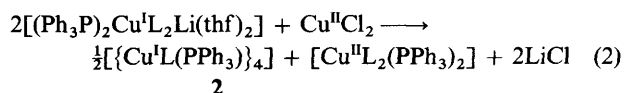
We have recently shown that p-block metal cyclopentadienides undergo nucleophilic addition and substitution reactions with organic nucleophiles, furnishing a halide-free route to a range of neutral and anionic organometallic species.¹ Our investigations of the nucleophilic substitution reactions of the cyclopentadienide derivatives of Group 11, $[\text{M}(\text{cp})(\text{PR}_3)]$ ($\text{M} = \text{Cu}$ or Ag , $\text{R} = \text{Ph}$ or Me , $\text{cp} = \eta\text{-C}_5\text{H}_5$) have illustrated that this simple approach can also be employed in the synthesis of the Group 11 organometallics.² Anionic species, such as the phosphine-stabilised Gilman reagent $[\text{Li}(\text{thf})_4]^+[\text{Cu}(\text{C}_{13}\text{H}_9)_2(\text{PPh}_3)]^-$ ($\text{C}_{13}\text{H}_9 = \text{fluorenyl}$, $\text{thf} = \text{tetrahydrofuran}$), and neutral complexes, such as the asymmetric dimer $[(\text{Ph}_3\text{P})_2\text{Cu}(\mu\text{-C}\equiv\text{CBu})_2\text{Cu}\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ are obtained from the substitution reactions of $[\text{Cu}(\text{cp})(\text{PPh}_3)]$.^{2a} The solid-state structures of tetrameric $[\{\text{Ag}(\mu\text{-C}\equiv\text{CPh})(\text{PPh}_3)\}_4]$ and polymeric $[\{\text{Ag}(\text{C}\equiv\text{CSiMe}_3)(\text{PMe}_3)\}_\infty]$, which are constructed from the association of $[\text{Ag}(\text{PR}_3)_2]^+$ cations and $[\text{Ag}(\text{C}\equiv\text{CR})_2]^-$ anions, illustrate a similar dependence on the steric bulk of the phosphine ligands and the organic groups present, as was found for the copper complexes.^{2b} We report here our first investigations of the nucleophilic substitution reactions of $[\text{Cu}(\text{cp})(\text{PPh}_3)]$ with metalloorganic anions and the syntheses and structures of the heterobimetallic complex $[(\text{Ph}_3\text{P})_2\text{CuL}_2\text{Li}(\text{thf})_2]\cdot\text{thf}$ **1** and of the asymmetric tetramer $[\{\text{CuL}(\text{PPh}_3)\}_4]$ **2** ($\text{L} = 1,3\text{-benzoxazoline-2-thionate}$, $[\text{C}_6\text{H}_4\text{O}-\text{C}(\text{S})\text{N}]^-$).

Results and Discussion

Complexes **1** and **2** were prepared and handled under an argon atmosphere (see Experimental section). However, although they are hygroscopic neither compound is significantly air-sensitive and both can be handled for short periods in air. The 1:1 reaction of LiL with $[\text{Cu}(\text{cp})(\text{PPh}_3)]$ in thf produces the bis(thionato)copper(I) complex $[(\text{Ph}_3\text{P})_2\text{CuL}_2\text{Li}(\text{thf})_2]\cdot\text{thf}$ **1**. Both analytical and spectroscopic analyses are in accord with the later structural characterisation of the complex. This product results from the nucleophilic substitution of the cp ligand of $[\text{Cu}(\text{cp})(\text{PPh}_3)]$ followed by nucleophilic addition of a second L^- anion to Cu . The outcome of this reaction is similar to that observed with $\text{Li}(\text{C}_{13}\text{H}_9)$ and $[\text{Cu}(\text{cp})(\text{PPh}_3)]$ (1:1 or 1:2) which produces the phosphine-stabilised Gilman reagent $[\text{Li}(\text{thf})_4]^+[\text{Cu}(\text{C}_{13}\text{H}_9)_2(\text{PPh}_3)]^-$.^{2a} Unlike the latter, the formation of **1** is also accompanied by phosphine ligand transfer, presumably from the excess of $[\text{Cu}(\text{cp})(\text{PPh}_3)]$ present in the reaction [equation (1)].



In an attempt to prepare a mixed-oxidation state $\text{Cu}^{\text{I}}\text{-Cu}^{\text{II}}$ complex, **1** was treated with CuCl_2 (2:1) in thf . However, this reaction results in the unexpected formation of $[\{\text{CuL}(\text{PPh}_3)\}_4]$ **2**, produced by ligand transfer of one L^- anion from Cu^{I} to Cu^{II} [equation (2)]. This result is of particular interest since **2** cannot



be prepared by the 1:1 reaction of $[\text{Cu}(\text{cp})(\text{PPh}_3)]$ with LiL ; only **1** is formed in this case. Although elemental and spectroscopic analyses confirmed the empirical formula of **2**, these studies provided no indication of the asymmetrical structure of this complex. The low-temperature crystal structures (153 K) of complexes **1** and **2** were determined. Key bond lengths and angles are shown in Tables 1 and 2, respectively, details of the structural refinements in Table 3.

The X-ray study of complex **1** shows it to be a bis(thionato)copper(I) complex $[(\text{Ph}_3\text{P})_2\text{CuL}_2\text{Li}(\text{thf})_2]\cdot\text{thf}$ in which a phosphine-complexed copper(I) centre is linked *via* the S and N of two L ligands to a thf -solvated Li^+ cation. There are two independent chemically equivalent molecules of **1** [one of which is shown in Fig. 1(a)] and one lattice-bound thf ligand per formula unit in the crystal.

Overall, the structure of complex **1** illustrates clearly the structural consequences of the concept of hard and soft metal ions and ligands. Thus, the soft copper(I) centre is co-ordinated by terminal Ph_3P ligands (average P-Cu 2.276 Å) and by attachment to the S atoms of the L ligands (average S-Cu 2.359 Å, average S-Cu-S 113.4°), giving a pseudo-tetrahedral geometry for this ion (average angles about Cu 109.6°). The hard Li^+ cation is co-ordinated by terminal thf of solvation (average O-Li 1.978 Å) and by the nitrogen centres of the heterocyclic ring of the L ligand (average N-Li 2.033 Å, average N-Li-N 130.9°). A typical pseudo-tetrahedral geometry is realised at the lithium centre (average angles about Li 109.0°). The bridging of the metal ions of **1** by the heterocyclic ligands produces a central 'chair-shaped', eight-membered $\text{Cu}(\text{SCN})_2\text{Li}$ ring [Fig. 1(b)].

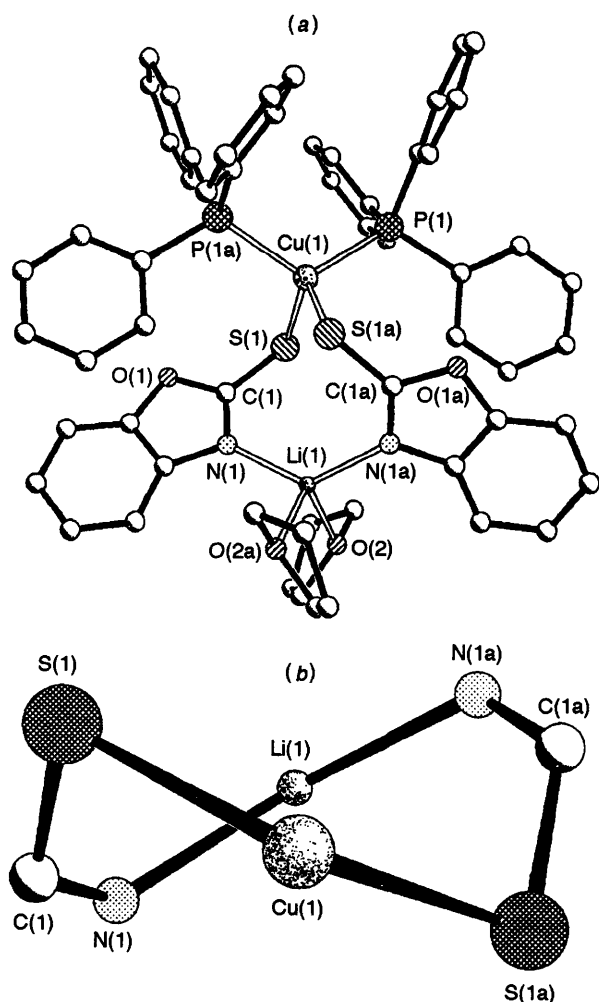


Fig. 1 (a) Structure of one molecule complex 1. Hydrogen atoms and lattice-bound thf of solvation have been omitted for clarity. (b) Core structure of 1, showing the eight-membered $\text{Cu}(\text{SCN})_2\text{Li}$ ring

Although of a simple structural design, we can find no other structurally characterised examples of ion-contacted bis(thiolato)copper(I) alkali-metal complexes related to **1**. However, the heterobimetallic anion $[\text{ClCaL}_4\text{Pt}]^{-3}$ and the neutral complex $[\{\text{CaCl}(\text{L})\cdot 2\text{P}(\text{NMe}_2)_3\text{O}\}_2\cdot \text{L}_2\text{Ca}(\text{HgCl}_2)_2]^{+4}$ contain similar N/S bridging of the L ligands between the Ca and the transition-metal centres Pt^{II} and Hg^{II} , as is observed in the structure of **1**. As with **1**, the N/S bridging of the metal centres in these species reflects the relative hardness and softness of the metal ions involved, the nitrogen centre of the L ligand being attached to Ca and the S to the Pt or Hg atoms.

The X-ray study of complex **2** shows it to have an unusual tetrameric structure, $[\{\text{CuL}(\text{PPh}_3)\}_4]$ in the solid state (Fig. 2). The complex is composed of a distorted tetrahedral Cu_4 core which is held together by bridging of the Cu_3 faces by two different L bonding modes. This ligand arrangement results in molecules with overall three-fold symmetry. The $\text{Cu}\cdots\text{Cu}$ distances within the core of **2** argue against there being any metal-metal interactions [range 3.670(4)–3.864(4) Å; cf. ca. 2.56 Å in metallic Cu⁵]. Three of the L ligands adopt a $\text{N},\mu\text{-S}$ bridging mode over three of the Cu_3 faces of the tetrahedron, in which the N of the heterocyclic ring is bonded to one Cu atom [$\text{Cu}(2,2a,2b)\text{-N}(1,1a,1b)$ 2.063(4) Å] and the S bridges the other two [$\text{Cu}(2,2a,2b)\text{-S}(1,1a,1b)$ 2.409(1), $\text{Cu}(1)\text{-S}(1,1a,1b)$ 2.345(1) Å]. The remaining Cu_3 face is capped symmetrically by the $\mu_3\text{-S}$ bridging of an L ligand [$\text{Cu}(2,2a,2b)\text{-S}(2)$ 2.368(1) Å], with the N not being involved in bonding to Cu. Thus, there are two different copper(I) environments in the tetrameric structure

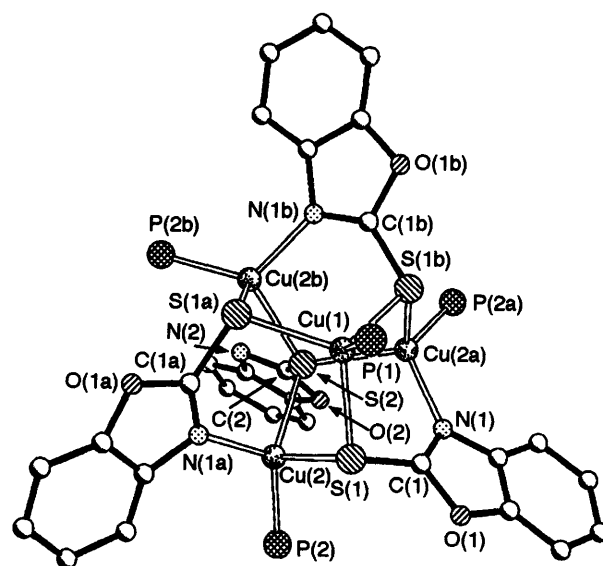


Fig. 2 Structure of complex 2. Hydrogen atoms and the phosphine Ph rings have been omitted for clarity

Table 1 Selected bond lengths (Å) and angles (°) for complex **1***

Molecule A		Molecule B	
Cu(1)–P(1)	2.275(1)	Cu(2)–P(2)	2.276(1)
Cu(1)–S(1)	2.360(1)	Cu(2)–S(2)	2.358(1)
Li(1)–O(2)	1.974(6)	Li(2)–O(4)	1.982(7)
Li(1)–N(1)	2.030(5)	Li(2)–N(2)	2.035(5)
C(1)–N(1)	1.308(5)	C(51)–N(2)	1.304(5)
C(1)–S(1)	1.704(4)	C(51)–S(2)	1.708(4)
P(1)–Cu(1)–P(1a)	119.20(6)	P(2)–Cu(1)–P(2b)	122.78(8)
S(1)–Cu(1)–S(1a)	112.30(6)	S(2)–Cu(1)–S(2b)	114.40(6)
P(1)–Cu(1)–S(1)	99.55(4)	P(2)–Cu(1)–S(2)	100.73(4)
P(1a)–Cu(1)–S(1)	113.45(4)	P(2)–Cu(2)–S(2b)	109.43(4)
Cu(1)–S(1)–C(1)	103.9(1)	Cu(2)–S(2)–C(51)	104.8(1)
Li(1)–N(1)–C(1)	124.4(3)	Li(2)–N(2)–C(51)	125.0(3)
N(1)–Li(1)–N(1a)	131.0(5)	N(2)–Li(2)–N(2b)	130.8(5)
N(1)–Li(1)–O(2)	105.7(1)	N(2)–Li(2)–O(4)	103.2(1)
N(1)–Li(1)–O(2a)	104.0(1)	N(2)–Li(2)–O(4b)	106.3(1)
O(2)–Li(1)–O(2a)	103.7(4)	O(4)–Li(2)–O(4b)	104.5(5)
Average angles about Cu	109.6		109.6
Average angles about Li	109.0		109.0

* Symmetry transformations used to generate equivalent atoms: a $-x, y, -z + \frac{1}{2}$; b $-x, y, -z + \frac{1}{2}$.

of **2**. Three of the copper centres [Cu(2), Cu(2a) and Cu(2b)] are bound to two S and one N atom, and the fourth [Cu(1)] is co-ordinated by three S centres. The terminal Cu–P distances in **2** reflect subtly the hardness and softness of the resulting copper environments, the bonds to Cu(2,2a,2b) being shorter [2.238(1) Å] than those to Cu(1) [2.271(1) Å].

A number of copper(I) complexes containing N/S chelating organic ligands have been structurally characterised.⁶ In tetra[2-methylimidazoline-2(3H)-thionato]copper a flattened tetrahedral Cu_4 core results from the exclusive use of a $\text{N},\mu\text{-S}$ ligand bonding mode, giving chemically similar copper(I) (N, S, S bonded) co-ordination environments.⁷ The effects of partial phosphine complexation on such an arrangement can be gauged from the structure of $[(\text{CuL}')_4(\text{PPh}_3)_2]$ ($\text{L}' = \text{thiazoline-2-thionate}$) [$\text{Cu}\cdots\text{Cu}$ 2.617(2)–3.132(2) Å].⁸ The attachment of Ph_3P ligands to only two of the copper centres results in a butterfly-shaped Cu_4 core in which the pattern of N, $\mu\text{-S}$ bonding is very similar to that observed in the 2-

methylimidazoline-2-thionatocopper(I) complex. Presumably, the occurrence of two different ligand co-ordination modes in **2** stems from the steric congestion caused by the co-ordination of *all* the copper centres by phosphine ligands. However, here an elegant alternative to major reorganisation of the tetrahedral Cu₄ core or of the ligand periphery is realised. The adoption of a μ_3 -S co-ordination mode by one of the L ligands provides sufficient space for the Ph groups of the phosphine ligands attached to Cu(2), Cu(2a) and Cu(2b) to be accommodated. At the same time the (three-fold symmetric) propeller-arrangement adopted by the other three N, μ -S bridging L ligands (see Fig. 2) leaves Cu(1) exposed to phosphine complexation.

Comparison of the C \cdots S and C \cdots N distances in complexes **1** and **2** with those occurring in the L[−] anions of alkali- and alkaline-earth-metal derivatives⁹ indicates that there is a greater development of the negative charges on the S in the copper(I) complexes. Thus, the C \cdots S distances are longer (averages 1.706 in **1** and 1.716 Å in **2**) and the C \cdots N distances are shorter (averages 1.306 in **1** and 1.26 Å in **2**) than in the early main-group metal complexes {e.g. C \cdots S 1.692(4) and C \cdots N 1.314(5) Å in [LiL(tmen)(H₂O)] [tmen = (Me₂NCH₂)₂]}.^{9a} These observations can be attributed to the presence and strength of the sulfur–metal interactions in **1** and **2**, which are weak or non-existent in the alkali- and alkaline-earth-metal complexes.

In order to probe the nature of the species present in solutions

of complexes **1** and **2** their cyclic voltammograms were obtained in thf–0.5 mol dm^{−3} NBu⁺₄PF₆[−]. While it is impossible to draw unequivocal conclusions solely from these measurements (which are limited by the poor oxidation window afforded by the thf solvent) it is clear that solutions of [{CuL(PPh₃)}₄]**2** contain only one observable Cu-containing species. Thus, **2** exhibits a single irreversible Cu^I–Cu^{II} oxidation ($E_p = +0.20$ V) with a weak return wave [$E_p = -0.32$ V ($I_p: I_{p_c} = 0.15:1$)]. This daughter product is markedly unstable so that at a scan rate of 5 mV s^{−1} this cathodic peak is no longer present. Repeated scanning also causes substantial reductions in the intensities of the oxidation and daughter peaks. Interestingly, addition of Ph₃P to the sample does not affect the peak potential or reversibility of this oxidation, apart from causing a noticeable sharpening of the peaks. This behaviour is consistent with the suppression of phosphine dissociation or intermolecular phosphine exchange in solution, e.g. from the *intact* tetramers of **2**.

The cyclic voltammogram of [(Ph₃P)₂CuL₂Li(thf)₂]**1** is more complicated than that of **2**, with two equal-intensity oxidation processes occurring. The first of these ($E_p = -0.20$ V) gives rise to a daughter product at $E_p = -0.60$ V ($I_p: I_{p_c} = 0.6:1$) at 100 mV s^{−1}. At lower scan rates the potential of this return wave becomes markedly less negative ($E_p = -0.17$, $E_p = -0.38$ V and $I_p: I_{p_c} = 0.9:1$ at 5 mV s^{−1}) and both the forward and reverse waves are unchanged upon repeated scanning. This behaviour is characteristic of a chemically reversible process in which a slow chemical transformation (ligand co-ordination/deco-ordination or geometric rearrangement) follows electron transfer. The second oxidation ($E_p = 0.1$ mV s^{−1}) is irreversible at all scan rates and both oxidation waves decay significantly upon repeated scanning of this process. Upon addition of Ph₃P (*ca.* 5 molar equivalents), the lower-potential oxidation ($E_p = -0.20$ V) disappears while the other oxidation process ($E_p = +0.10$ V) increases in intensity but remains irreversible. No changes were observed upon addition of LiClO₄ to **1**, suggesting that dissociation of Li⁺ from the Cu(μ-L)₂Li unit is negligible. These data show that the two oxidations correspond to two different species in solution, which differ in their number of Ph₃P ligands and which are in dynamic equilibrium, e.g. *intact* [(Ph₃P)₂Cu(μ-L)₂Li(thf)₂]**1** in equilibrium with [(Ph₃P)Cu(μ-L)₂Li(thf)₂]**2** and Ph₃P. Comparison of the cyclic voltammograms of **1** and **2** shows that the species involved in the oxidation processes are clearly distinct.

Table 2 Selected bond lengths (Å) and angles (°) for complex **2***

Cu(1)–P(1)	2.271(2)	C(1)–N(1)	1.298(6)
Cu(1)–S(1)	2.345(1)	C(1)–S(1)	1.715(8)
Cu(2)–P(2)	2.238(1)	C(2)–S(2)	1.727(8)
Cu(2)–S(1)	2.409(1)	C(2)–N(2)	1.28(1)
Cu(2)–S(2)	2.368(1)		
P(1)–Cu(1)–S(1)	110.88(3)	Cu(2)–S(1)–C(1)	105.5(2)
S(1)–Cu(1)–S(1a)	108.02(4)	Cu(2)–S(2)–C(2)	109.64(4)
P(2)–Cu(2)–N(1a)	121.58(1)	S(1)–C(1)–N(1)	131.4(3)
P(2)–Cu(2)–S(1)	110.29(5)	Cu(2)–N(1a)–C(1a)	127.6(3)
Cu(2)–P(2)–S(2)	120.30(5)	S(2)–Cu(2)–N(1a)	106.3(1)
Cu(1)–S(1)–Cu(2)	101.06(5)	Cu(2)–S(2)–Cu(2a)	109.31(4)
S(1)–Cu(2)–S(2)	98.31(5)		

* Symmetry transformations used to generate equivalent atoms: a $-x + y, -x + 1, z$; b $-y + 1, x - y + 1, z$.

Table 3 Crystal data and structure solutions of complexes **1** and **2**^a

	1	2
<i>M</i>	C ₅₈ H ₅₄ CuLiN ₂ O ₄ P ₂ S ₂ ·C ₄ H ₈ O	C ₁₂₁ H ₁₀₀ Cu ₄ N ₄ O ₄ P ₄ S ₄
<i>M</i>	1111.68	2180.33
Crystal system	Monoclinic	Trigonal
Space group	<i>P</i> 2/ <i>c</i>	<i>P</i> 31 <i>c</i>
Crystal size/mm	0.5 × 0.3 × 0.2	0.4 × 0.4 × 0.2
<i>a</i> /Å	24.046(5)	18.687(6)
<i>b</i> /Å	13.574(3)	18.687(6)
<i>c</i> /Å	18.028(4)	17.497(7)
β/°	107.01(3)	—
<i>U</i> /Å ³	5627(2)	5264(3)
<i>Z</i>	4	2
<i>D_c</i> /Mg m ^{−3}	1.312	1.376
μ(Mo–Kα)/mm ^{−1}	0.570	0.994
θ Range/°	4.01–22.51	4.07–24.03
Reflections collected	7609	5684
Independent reflections	7281	5492
<i>R</i> 1 [<i>F</i> > 4σ(<i>F</i>)]	0.044	0.041
<i>wR</i> 2 (all data)	0.126	0.111
Final difference peak and hole/e Å ^{−3}	0.607, −0.554	0.645, −0.422
Absolute structure parameter	—	0.001(1)

^a Data in common: *T* = 153(2) K; Mo–Kα radiation, λ = 0.710 73 Å; *R*1 = Σ||*F*_o| − |*F*_c||/Σ|*F*_o|; *wR*2 = [Σ(*wF*_o² − *F*_c²)/Σ*wF*_o⁴]^{1/2}; *w* = 1/[σ²(*F*_o²) + (*xP*)² + *yP*], *P* = (*F*_o² + 2*F*_c²)/3; for **1**, *x* = 0.269, *y* = 15.31; for **2**, *x* = 0.0702, *y* = 6.25.

Experimental

General procedure

The products **1** and **2** are moisture-sensitive and the $[\text{Cu}(\text{cp})(\text{PPh}_3)]^{10}$ starting material is both air- and moisture-sensitive. All reactions were performed on a vacuum line using standard inert-atmosphere techniques¹¹ and under dry/ O_2 -free Ar. The thf and toluene solvents were dried using sodium-benzophenone and degassed prior to the reactions. All complexes were isolated and characterised with the aid of an Ar-filled glove-box (Faircrest) fitted with an O_2 - and H_2O -recirculation system (type B). Melting points were determined by using a conventional apparatus and sealing samples in capillaries under Ar. Infrared spectra were recorded as Nujol mulls using NaCl windows and were run on a Perkin-Elmer 2400 spectrophotometer. Elemental analyses were performed by first sealing samples under Ar in air-tight aluminium boats (1–2 mg). The C, H and N analyses were carried out using a Perkin-Elmer 240 Elemental Analyser, phosphorus analysis by spectrophotometric means. Proton and ^{31}P NMR spectra were recorded on a Bruker AC 250 MHz spectrometer in dry $[\text{}^2\text{H}_8]\text{thf}$; for ^1H the solvent resonances were used as the internal reference standard and for ^{31}P trimethylphosphine was employed as the external standard. The UV/VIS spectra were recorded on a Perkin-Elmer Lambda 12 spectrophotometer operating between 200 and 1100 nm, in a 1 cm quartz cell.

Preparations

Complex 1. 1,3-Benzoxazoline-2-thione (0.30 g, 2.0 mmol) was treated with LiBu^n (1.25 cm³, 1.6 mol dm⁻³ in hexanes, 2 mmol) in thf (10 cm³), producing a bright yellow solution. The complex $[\text{Cu}(\text{cp})(\text{PPh}_3)]$ (0.784 g, 2 mmol) was added and the solution changed to deep orange. Half the solvent was removed *in vacuo*, giving a white precipitate. The solid was heated until it dissolved and storage at 5 °C (24 h) produced long colourless crystalline needles. Yield 0.27 g (24% based on Ph_3P), m.p. 106–109 °C. IR (Nujol mull): $\tilde{\nu}_{\text{max}}/\text{cm}^{-1} = 3066, 3048$ (aryl C–H str.), 1584 (C=N str.), 1465 (aryl C=C str.), 1250 (C=S), 744, 696 (aryl monosubstituted), 741 (aryl, 1,2-disubstituted), 1116, 1074 and 917. NMR (25 °C, $[\text{}^2\text{H}_8]\text{thf}$): ^1H (250 MHz), δ 7.34 (m), 7.17 (m) and 6.88 (m) (38 H, overlapping Ph_3P and L aromatic resonances), 3.60 (12 H, m) and 1.75 (12 H, m) (CH_2 of thf); ^{31}P (101.27 MHz), δ –5.9 (s). UV/VIS (thf): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 325 (sh), 307 (34 000), 272 (sh) and 261 (39 000) (Found: C, 66.8; H, 5.7; N, 2.9; P, 5.6. Calc. for $\text{C}_{62}\text{H}_{62}\text{CuLiN}_2\text{O}_5\text{P}_2\text{S}_2$; C, 66.9; H, 5.6; N, 2.5; P, 5.6%). Analytical and ^1H NMR data confirm that the lattice-bound thf solvation is preserved upon isolation of **1**.

Complex 2. Complex **1** (2.78 g, 2.5 mmol) was treated with CuCl_2 (0.17 g, 1.25 mmol) in thf (10 cm³) at 25 °C. The solvent was removed *in vacuo*, replaced with toluene (30 cm³) and then filtered to give a light yellow solution. Reduction of the solvent volume (to 25 cm³) gave a precipitate which was heated until it dissolved. Storage (12 h, 25 °C) gave cubic light yellow crystals of complex **2**; 0.92 g (56% based on Cu^I), m.p. 182–186 °C. IR (Nujol mull): $\tilde{\nu}_{\text{max}}/\text{cm}^{-1} = 3070$ (aryl C–H str.), 1460 (aryl C=C str.), 1246 (C=S str.), 729, 692 (aryl monosubstituted), 1120, 1075 and 930. NMR (25 °C, $[\text{}^2\text{H}_8]\text{thf}$): ^1H (250 MHz), δ 7.51 (m), 7.15 (m) and 6.89 (m) (19 H, overlapping Ph_3P and L aromatic resonances); ^{31}P (101.27 MHz), δ –146.3 (s). $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 318 (sh), 303 (sh), 277 (sh) and 260 (60 000) (Found: C, 66.7; H, 4.7; N, 2.1; P, 5.7. Calc. for $\text{C}_{121}\text{H}_{100}\text{Cu}_4\text{N}_4\text{O}_4\text{P}_4\text{S}_4$; C, 66.6; H, 4.6; N, 2.6; P, 5.7%).

X-Ray crystallography

Crystals of complexes **1** and **2** were mounted directly from

solution at room temperature under Ar using a perfluorocarbon oil which protects them from atmospheric moisture and oxygen (Riedel-de Haën). The oil ‘freezes’ at reduced temperatures and holds the crystal static in the X-ray beam.¹² Data were collected on a Stoe AED diffractometer, and a semiempirical absorption correction based on ψ -scans was employed. The structures were solved by direct methods (SHELXTL PLUS)¹³ and refined by full-matrix least squares on F^2 (SHELXL 93).¹⁴ All H atoms were fixed geometrically in **1** and **2**. In **2** the $\mu_3\text{-S}$ ligand is disordered over three sites on the three-fold axis of the molecule. Details of the structure solutions and refinements are listed in Table 3.

Atomic coordinates, thermal parameters, and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/189.

Electrochemistry

All electrochemical measurements were carried out using an Autolab PGSTAT20 voltammetric analyser, in dry thf containing 0.5 mol dm⁻³ $\text{NBu}^n_4\text{PF}_6$ (prepared from aqueous NBu^n_4OH and HPF_6) as the supporting electrolyte and under an argon atmosphere. Voltammetric measurements involved the use of a double platinum working/counter electrode and a silver-wire reference electrode. All potentials quoted are referenced to an internal ferrocene–ferrocenium standard and were obtained at a scan rate of 100 mV s⁻¹ unless otherwise stated. In addition to the oxidation processes observed for complexes **1** and **2**, both exhibit irreversible reductions ($E_{\text{pc}} = -1.81$ for **1** and -2.09 V for **2**) which are assignable to an L ligand reduction (*cf.* -2.04 V for free HL under the same conditions). An additional irreversible reduction occurs for **1** ($E_{\text{pc}} = -2.11$ V, with an associated desorption spike at $E_{\text{pa}} = +0.22$ V). This corresponds to a $\text{Cu}^{\text{I}}\text{--Cu}^0$ reduction.

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