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# Synthesis, Characterisation and Luminescent Properties of Mixed-Ligand Copper(I) Complexes Incorporating N-Thiophosphorylated Thioureas and Phosphane Ligands

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 $(CH_2)_3PPh_2]_2L^{II}$  (8),  $[Cu_2\{Ph_2P(C_5H_4FeC_5H_4)PPh_2]_2L^{II}]$  (9) or  $[Cu_2(Ph_2PCH_2PPh_2)L^{II}]$  (10). The structures of these compounds were investigated by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR, UV/Vis spectroscopy and elemental analysis. The crystal structures of  $H_2L^{II}$ , 1, 3–6, 8 and 10 were determined by single-crystal X-ray diffraction. The luminescent properties of complexes 1–10 in the solid state are reported.

# Introduction

In preceding papers we described heteroligand complexes of Cu<sup>I</sup> with a number of *N*-thiophosphorylated thioureas and thioamide RC(S)NHP(S)(O*i*Pr)<sub>2</sub> [R = morpholin-4-yl, piperidin-1-yl,<sup>[1]</sup> (1-naphthyl)NH,<sup>[2]</sup> NH<sub>2</sub> (HL<sup>I</sup>),<sup>[1,3]</sup> (pyridin-2-yl)NH, (pyridin-3-yl)NH, H<sub>2</sub>N-6-Py-2-NH,<sup>[4]</sup> Ph, Et<sub>2</sub>N,<sup>[5-7]</sup> (EtO)<sub>2</sub>P(O)CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-4-NH,<sup>[8]</sup> MeNH, *i*PrNH, *t*BuNH, Me<sub>2</sub>N, PhNH, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NH<sup>[9-11]</sup>] and triphenylphosphane or Ph<sub>2</sub>P-(CH<sub>2</sub>)<sub>1-3</sub>PPh<sub>2</sub> and Ph<sub>2</sub>P(C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>4</sub>)PPh<sub>2</sub>. We also showed that the reactions of alkaline salts of the tetrakisthiourea containing a cyclam fragment with  $[Cu(PPh_3)_3I]$  lead to the tetranuclear  $Cu^I$  complex  $[\{Cu(PPh_3)_2\}_{4^-}$  (cyclam)] (Scheme 1).<sup>[12]</sup>

We have also described a number of *N*-(thio)phosphorylated bis(thio)ureas, which are potentially bridging ligands, and investigated their complexation properties towards various metal cations.<sup>[6,13–20]</sup> Only one dinuclear heteroligand complex of Cu<sup>I</sup> with *N*-thiophosphoryl bis(thiourea), containing 1,10-diaza-18-crown-6, and PPh<sub>3</sub> (Scheme 1) has been described.<sup>[6]</sup> To the best of our knowledge there are no crystal structures of such types of complexes. Furthermore, we have described two Cu<sup>I</sup> complexes



Scheme 1.

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 $[CuPPh_3{RC(S)NP(S)(OiPr)_2}]$  (R = H<sub>2</sub>N-6-Py-2-NH,<sup>[4]</sup> (EtO)<sub>2</sub>P(O)CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-4-NH<sup>[8]</sup>) containing one triphenylphosphane (PPh<sub>3</sub>) ligand. A number of heteroligand Cu<sup>I</sup> complexes containing both aryl-substituted pnictides and cyclic thioureas or pyridinethiolates have also been described.<sup>[21–23]</sup> A combination of these two types of ligands might lead to interesting and unusual photophysical and electrochemical properties.<sup>[24]</sup>

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In this contribution we describe new heteroligand complexes of Cu<sup>I</sup> with H<sub>2</sub>NC(S)NHP(S)(OiPr)<sub>2</sub> (HL<sup>I</sup>) and o-C<sub>6</sub>H<sub>4</sub>[NHC(S)NHP(S)(OiPr)<sub>2</sub>]<sub>2</sub> (H<sub>2</sub>L<sup>II</sup>; Scheme 2) and phosphanes [PPh<sub>3</sub>, Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>1-3</sub>PPh<sub>2</sub>, Ph<sub>2</sub>P(C<sub>5</sub>H<sub>4</sub>-FeC<sub>5</sub>H<sub>4</sub>)PPh<sub>2</sub>] along with their structural characterisation and luminescent properties. Mononuclear derivatives with non-bridging thiourea ligands and the phosphane ligands PPh<sub>3</sub>, Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>1-3</sub>PPh<sub>2</sub> or Ph<sub>2</sub>P(C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>4</sub>)PPh<sub>2</sub> have recently been described.<sup>[10,11]</sup>

# $\begin{array}{c|c} H \\ H_2N & H \\ S & S \\ HL^{\mathbf{I}} \\ HL^{\mathbf{I}} \end{array} \begin{array}{c} H \\ (iPrO)_2P \\ S \\ S \\ HL^{\mathbf{I}} \\ S \\ H \\ H_2L^{\mathbf{II}} \end{array} \begin{array}{c} H \\ H \\ S \\ H \\ H_2L^{\mathbf{II}} \\ H_2L^{\mathbf{II}} \end{array}$

Scheme 2.

## **Results and Discussion**

## Synthesis

*N*-Thiophosphorylated thiourea HL<sup>I</sup> was prepared as described previously.<sup>[1,3,25]</sup> *N*-Thiophosphorylated bis(thiourea) H<sub>2</sub>L<sup>II</sup> was prepared by addition of *o*-phenylenediamine to *O*, *O'*-diisopropylthiophosphoric isothiocyanate, (*i*PrO)<sub>2</sub>-P(S)NCS, similarly to the previously described method.<sup>[13]</sup> Reactions of the potassium salts of HL<sup>I</sup> and H<sub>2</sub>L<sup>II</sup> with [Cu(PPh<sub>3</sub>)<sub>3</sub>I] or a mixture of CuI and Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>1-3</sub>PPh<sub>2</sub> or Ph<sub>2</sub>P(C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>4</sub>)PPh<sub>2</sub> in aqueous EtOH/CH<sub>2</sub>Cl<sub>2</sub> led to the mononuclear complexes [Cu(PPh<sub>3</sub>)L<sup>I</sup>] (1), [Cu{Ph<sub>2</sub>P-(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>}L<sup>I</sup>] (2), [Cu{Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>}L<sup>I</sup>] (3) or [Cu{Ph<sub>2</sub>P(C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>4</sub>)PPh<sub>2</sub>}L<sup>I</sup>] (4), or the dinuclear complexes [Cu<sub>2</sub>(Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>}<sub>2</sub>L<sup>II</sup>] (7), [Cu<sub>2</sub>{Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>}<sub>2</sub>-L<sup>II</sup>] (8), [Cu<sub>2</sub>{Ph<sub>2</sub>P(C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>4</sub>)PPh<sub>2</sub>}<sub>2</sub>L<sup>II</sup>] (7), [Cu<sub>2</sub>{Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>}<sub>2</sub>-L<sup>II</sup>] (8), [Cu<sub>2</sub>{Ph<sub>2</sub>P(C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>4</sub>)PPh<sub>2</sub>}<sub>2</sub>L<sup>II</sup>] (9) or [Cu<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)L<sup>II</sup>] (10) (Scheme 3).



Scheme 3.

# **FULL PAPER**

The complexes obtained are colourless crystalline powders, soluble in acetone, benzene,  $CH_2Cl_2$ , DMSO and DMF and insoluble in *n*-hexane. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy indicated that the deprotonated thioureas L<sup>I,II</sup> are coordinated through the sulfur atoms of the thiocarbonyl and thiophosphoryl groups in all cases.

#### IR and NMR Spectroscopy and Photophysical Properties

The IR spectrum of H<sub>2</sub>L<sup>II</sup> contains a weak band centred at 652 cm<sup>-1</sup> assigned to the P=S groups. The S=C-N fragment in the spectrum of the bis(thiourea) is shown as a band at 1553 cm<sup>-1</sup>. There are two absorption bands at 3204 and 3422 cm<sup>-1</sup> corresponding to the NH groups in the spectrum of H<sub>2</sub>L<sup>II</sup>, whereas a unique band at 3348–3369 cm<sup>-1</sup> related to the (aryl)NH group is observed in the spectra of 6-10. The IR spectra of the complexes contain a band at 594–616 cm<sup>-1</sup> for the P=S group of the anionic forms L<sup>I,II</sup>. These bands are shifted to low frequencies relative to the parent ligands as a result of coordination to the Cu<sup>I</sup> ion. In the IR spectra of 1–10 there are bands at 1537-1562 cm<sup>-1</sup> corresponding to the conjugated SCN fragment. In the IR spectra of 1-5 there are also a number of bands at 1609-1629, 3120-3137, 3241-3261 and 3483-3501 cm<sup>-1</sup> corresponding to the NH<sub>2</sub> group. In addition, there is a broad intense band arising from the POC group at 988–1014 cm<sup>-1</sup> in the spectra of  $H_2L^{II}$  and the complexes.

In the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the complexes, the resonances in the range  $\delta = 54.4-58.7$  ppm correspond to the phosphorus atom of the thiophosphoryl group. These signals are shifted downfield relative to those in the spectra of HL<sup>I</sup> and H<sub>2</sub>L<sup>II</sup>. The signals of the phosphorus atoms of PPh<sub>3</sub> in the spectra of the complexes **1** and **6** are found at  $\delta = 0.4$  and -1.5 ppm, respectively, whereas the signals for the phosphane phosphorus atoms in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the complexes **2–5** and **7–10** exhibit chemical shifts from  $\delta = -22.4$  to -10.6 ppm.

The <sup>1</sup>H NMR spectra of H<sub>2</sub>L<sup>II</sup> and **1–10** contain only signals that correspond to the proposed structures. The spectra contain a set of signals for the *i*Pr protons: signals for the CH<sub>3</sub> protons at  $\delta = 0.85-1.47$  ppm and signals for the CH protons at  $\delta = 4.27-4.89$  ppm. The signals for the aromatic ring and (aryl)NH protons are observed at  $\delta =$ 6.70-8.29 ppm. Signals of the NH<sub>2</sub> group in the spectra of **1–5** are observed at  $\delta = 5.33-5.72$  ppm. In the <sup>1</sup>H NMR spectrum of H<sub>2</sub>L<sup>II</sup> the signal for the NHP proton is found at  $\delta = 9.12$  ppm. The signals for the NHP group proton are absent in the <sup>1</sup>H NMR spectra of 1–10. This confirms the anionic character of the ligands in the complexes. The <sup>1</sup>H NMR spectra of 2, 3, 5, 7, 8 and 10 contain signals for the CH<sub>2</sub> protons of the phosphanes Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>1–3</sub>PPh<sub>2</sub> at  $\delta$  = 1.56–2.97 ppm, whereas signals for the C<sub>5</sub>H<sub>4</sub> protons in the spectra of 4 and 9 are observed at  $\delta$  = 4.20–4.29 ppm.

The absorption spectra of the complexes 1-10 were studied in  $CH_2Cl_2$  solution (Figure S1 in the Supporting Information), whereas their luminescent properties were investigated in the solid state at room temperature (Figure 1). The data are reported in Table 1. Complexes 2-5 and 7-10 show emission in the solid state. The origin of the emission is believed to be based on intraligand transitions centred on the thiophosphoryl component of the ligands, which are influenced by the nature of the phosphane. PPh<sub>3</sub> complexes did not exhibit any luminescence properties. One interesting point in this respect is the unusually low energy and intensity of the emission of the complexes 5 and 10, which might be due to contributions from cluster-centred charge-transfer transition in these dinuclear aggregates, which show rather short Cu1···Cu2 distances.



Figure 1. Emission spectra of 2, 3, 4 and 5. The spectra of 7–10 are similar to the spectra of 2–5, respectively. The excitation wavelength was chosen from the  $\lambda_{max}$  of the absorption.

#### **Crystal Structures**

Crystals of  $H_2L^{II}$ , **1**, **3–6**, **8** and **10** were obtained by slow evaporation of the solvent from their solutions in acetone/*n*hexane (**1**) or CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane mixtures (1:5, v/v; see Exp. Sect.). The molecular structures of  $H_2L^{II}$ , **1**, **3**, **4**, **5**, **6**, **8** and

Table 1. UV/Vis absorption and emission maxima for complexes 1-10.<sup>[a]</sup>

Complex	$\lambda_{abs} \text{ [nm]} (\varepsilon \text{ [dm}^3 \text{mol}^{-1} \text{cm}^{-1} \text{]})$	$\lambda_{\rm em}$ [nm]	Complex	$\lambda_{abs} \text{ [nm]} (\varepsilon \text{ [dm}^3 \text{mol}^{-1} \text{cm}^{-1} \text{]})$	$\lambda_{\rm em}$ [nm]
1	310 (10221)	no emission	6	304 (17631)	no emission
2	254 (19853), 302 (9632)	478	7	247 (31269), 306 (17564)	473
3	250 (19122), 307 (9471)	472	8	253 (28113), 306 (18103)	470
4	247 (19390), 310 (9718)	483	9	259 (33728), 311 (20824)	486
5	252 (3529), 373 (13382)	508	10	255 (3602), 379 (13127)	513

[a] Emission data obtained with excitation at  $\lambda$  of the long-wavelength absorption. The absorption spectra of the corresponding potassium salts show weak absorption bands at 289 ( $\varepsilon = 172 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) (KL<sup>I</sup>) and 297 nm ( $\varepsilon = 238 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) (K<sub>2</sub>L<sup>II</sup>).

**10** are shown in Figures 2, 3, 4, 5, 6, 7, 8, and 9, respectively. Selected bond lengths and angles are given in Tables 2 and 3.



Figure 2. Thermal-ellipsoid representation of  $H_2L^{II}$  (hydrogen atoms have been omitted for clarity). Ellipsoids are drawn at the 30% probability level.



Figure 3. Thermal-ellipsoid representation of 1 (hydrogen atoms have been omitted for clarity). Ellipsoids are drawn at the 30% probability level.



Figure 4. Thermal-ellipsoid representation of 3 (hydrogen atoms have been omitted for clarity). Ellipsoids are drawn at the 30% probability level.

The bis(thiourea)  $H_2L^{II}$  crystallises in the monoclinic space group *C*2/*c*. The parameters of the C=S, C–N, P–N and P=S bonds observed for  $H_2L^{II}$  (Table 2) are in the range typical for *N*-thiophosphorylated thiourea derivatives.<sup>[14]</sup> The two NC(S)N moieties show significant planarity (Figure 2). The two chelate backbones C(S)NP(S) are in



Figure 5. Thermal-ellipsoid representation of the independent molecule A of 4 (hydrogen atoms have been omitted for clarity). Ellipsoids are drawn at the 30% probability level.



Figure 6. Thermal-ellipsoid representation of 5 (hydrogen atoms have been omitted for clarity). Ellipsoids are drawn at the 30% probability level.



Figure 7. Thermal-ellipsoid representation of 6 (hydrogen atoms have been omitted for clarity). Ellipsoids are drawn at the 30% probability level.

an *anti* disposition relative to the phenylene spacer. Intraand intermolecular hydrogen bonds of the type N–H···O–P and N–H···S=C, respectively, are present in the crystal of H<sub>2</sub>L<sup>II</sup> (Table 4). Intramolecular hydrogen bonds are formed between the oxygen atoms of the P–O groups and the hydrogen atoms of the (aryl)NH fragments, which in turn leads to an (*E*,*E*) conformation of the SCNP backbones. Intermolecular hydrogen bonds are formed between the hydrogen atom of one PNH group and the sulfur atom of the C=S group, and the same types of atoms of the two neighbouring molecules. As a result of the intermolecular hydrogen bonds (Table 4) a polymeric chain is formed in the crystal of H<sub>2</sub>L<sup>II</sup>.



Figure 8. Thermal-ellipsoid representation 8 (hydrogen atoms have been omitted for clarity). Ellipsoids are drawn at the 30% probability level.



Figure 9. Thermal-ellipsoid representation of 10 (hydrogen atoms have been omitted for clarity). Ellipsoids are drawn at the 30% probability level.

Note that in our recent publication we published the synthesis of the complex  $[Cu(PPh_3)_2L^I]$  (11), which contains two PPh<sub>3</sub> ligands.<sup>[1]</sup> Efforts to recrystallise 11 from a CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane mixture did not lead to crystals suitable for X-ray analysis, but according to the NMR spectroscopic data and elemental analysis, the material still contains two PPh<sub>3</sub> ligands. In the course of this work we tried to obtain crystals by the recrystallisation of 11 from an acetone/*n*-hexane mixture. Surprisingly, according to the NMR spectroscopic data and elemental analysis, the crystals obtained (suitable for X-ray diffraction) have the composition  $[Cu(PPh_3)L^I]$  (1).

In the structure of 1 the geometry around the Cu atom is trigonal, formed by two S atoms and one PPh<sub>3</sub> ligand (Figure 3). The Cu–P bond [2.2127(7) Å, Table 2] is of practically the same length as observed for the complexes [CuPPh<sub>3</sub>{RC(S)NP(S)(OiPr)<sub>2</sub>}] [R = H<sub>2</sub>N-6-Py-2-NH,<sup>[4]</sup> (EtO)<sub>2</sub>P(O)CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-4-NH<sup>[8]</sup>] with trigonally coordinated Cu<sup>I</sup>. The six-membered CuSPNCS metallocycle has the conformation of a distorted boat. The fragment NC(S)NP is almost planar with the sulfur atom of the thiophosphoryl group deviating significantly from the average plane of this fragment; the torsion angle S1–P1–N1–C1 is 49.1(3)°.

In the structures of **3** and **4** the Cu<sup>I</sup> cation is in a  $P_2S_2$  tetrahedral environment formed by the two sulfur atoms of the deprotonated thiourea L<sup>I</sup> ligand and the two phosphorus atoms of the Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub> or Ph<sub>2</sub>P(C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>4</sub>)-PPh<sub>2</sub> molecule, respectively (Figures 4 and 5). The asymmetric unit of **4** contains two independent molecules. The Cu–S(C), Cu–S(P) and Cu–P bonds in **3** and **4** are markedly longer than those in **1** (Table 2). The S–Cu–S angle in **3** and

Table 2. Selected bond lengths [Å] and angles [°] for  $H_2L^{II}$ , 1, 3, and 4.

	H <sub>2</sub> L <sup>II</sup>	1	3	4
C=S	1.6737(15), 1.6806(16)	1.752(3)	1.738(2)	1.730(9), 1.738(11) <sup>[a]</sup>
P=S	1.9133(6), 1.9162(6)	1.9594(9), 2.121(5)	1.9831(9)	1.987(3), 1.976(3) <sup>[a]</sup>
P–N	1.6775(14), 1.6838(14)	1.603(2)	1.602(2)	$1.610(7), 1.609(7)^{[a]}$
P–O	1.5733(12), 1.5797(13),	1.578(2), 1.582(2)	1.588(2), 1.589(2)	1.593(6), 1.594(6),
	1.5804(14), 1.5805(12)			1.578(6), <sup>[a]</sup> 1.583(6) <sup>[a]</sup>
C-N(P)	1.377(2)	1.314(3)	1.333(3)	$1.316(10), 1.312(11)^{[a]}$
C–N	1.340(2), 1.343(2)	1.338(3)	1.335(3)	$1.343(11), 1.356(12)^{[a]}$
Cu–S		2.2018(7)	2.3245(7)	$2.325(3), 2.329(3)^{[a]}$
Cu-S(P)		2.2463(8), 2.376(5)	2.3559(6)	$2.385(2), 2.358(2)^{[a]}$
Cu–P		2.2127(7)	2.2799(6), 2.2836(6)	2.280(2), 2.314(2),
				2.296(2), <sup>[a]</sup> 2.300(2) <sup>[a]</sup>
S-C-N	122.21(12), 122.93(12)	115.0(2)	117.5(2)	116.2(6), 115.8(6) <sup>[a]</sup>
S-C-N(P)	120.61(12), 121.32(12)	129.0(2)	127.1(2)	127.1(7), 127.5(8) <sup>[a]</sup>
N-C-N	116.44(14), 116.46(13)	116.0(2)	115.4(2)	116.6(8), 116.6(9) <sup>[a]</sup>
C-N-P	127.93(12), 128.32(12)	130.7(2)	124.9(2)	$125.3(6), 125.1(7)^{[a]}$
N–P–S	111.12(6), 111.86(6)	109.5(2), 121.94(9)	118.52(8)	119.1(3), 118.2(3) <sup>[a]</sup>
S-Cu-S		110.52(13), 115.86(3)	106.72(2)	106.21(9), 107.54(9) <sup>[a]</sup>
P–Cu–P			99.62(2)	110.68(9), 109.86(9) <sup>[a]</sup>
P-Cu-S		127.29(3)	107.96(2), 110.53(2)	104.22(9), 110.22(9),
				101.70(9), <sup>[a]</sup> 116.24(9) <sup>[a]</sup>
P–Cu–S(P)	116.76(3), 121.15(12)	113.35(2), 118.27(2)	105.55(8), 118.87(9),	121.81(3), 124.53(3) <sup>[b]</sup>
~ /			104.40(8), <sup>[a]</sup> 115.58(9) <sup>[a]</sup>	
Cu-S-C	107.21(8)	106.88(9)	$103.6(3), 108.5(3)^{[a]}$	104.30(9), 99.72(9) <sup>[b]</sup>
Cu-S-P	86.9(2), 94.65(3)	96.90(3)	97.10(11), 93.08(11) <sup>[a]</sup>	98.38(3), 97.74(4) <sup>[b]</sup>
Cu–S–Cu		× /		73.38(2), 69.95(2)

[a] Data for two independent molecules A and B. [b] Data for the Cu2-S4-C2(N4)-N3-P2(O3)(O4)-S3 backbone.

Table 3. Selected bond lengths [Å] and angles [°] for 5, 6, 8, and 10.

	5	6	8	10
C=S	1.769(3), 1.756(3) <sup>[a]</sup>	1.724(3), 1.733(3)	1.735(3), 1.741(3)	1.751(6), 1.774(5)
P=S	1.9934(10), 1.9917(10) <sup>[a]</sup>	1.9772(10), 1.9837(11)	1.9759(10), 1.9765(10)	1.987(2), 1.988(2)
P–N	$1.617(2), 1.613(2)^{[a]}$	1.606(2), 1.624(2)	1.615(2), 1.622(2)	1.598(5), 1.599(5)
P–O	1.577(2), 1.583(2),	1.570(2), 1.576(2),	1.571(2), 1.580(2),	1.571(4), 1.574(4),
	1.576(2), <sup>[a]</sup> $1.584(2)$ <sup>[a]</sup>	1.583(2)	1.5879(19), 1.590(2)	1.583(4), 1.584(4)
C-N(P)	$1.326(3), 1.311(4)^{[a]}$	1.315(4), 1.318(4)	1.318(4), 1.325(4)	1.296(7), 1.313(8)
C–N	$1.324(4), 1.346(4)^{[a]}$	1.355(4), 1.370(4)	1.358(3), 1.360(4)	1.347(8), 1.350(8)
Cu–S	2.3122(7), 2.5598(7),	2.3124(8), 2.3437(8)	2.3002(8), 2.3429(8)	2.3845(13), 2.4164(16),
	2.3799(7), <sup>[a]</sup> 2.4309(7) <sup>[a]</sup>			2.4204(14), 2.5020(17)
Cu–S(P)	2.3236(7), 2.3250(8) <sup>[a]</sup>	2.3618(8), 2.3812(8)	2.2967(8), 2.3429(8)	2.3327(16), 2.3371(17)
Cu–P	2.2364(7), 2.2422(7) <sup>[a]</sup>	2.2756(9), 2.2960(8),	2.2472(8), 2.2593(8),	2.2277(16), 2.2355(15)
		2.3121(8), 2.3155(9)	2.2702(8), 2.2808(9)	
S-C-N	116.2(2), 115.3(2) <sup>[a]</sup>	114.4(2), 114.5(2)	114.0(2), 115.2(2)	117.0(5), 117.2(4)
S-C-N(P)	125.9(2), 127.0(2) <sup>[a]</sup>	127.7(2)	127.1(2), 127.6(2)	125.3(5), 126.2(5)
N-C-N	117.8(2), 117.6(3) <sup>[a]</sup>	117.8(3), 117.9(3)	117.7(2), 118.4(3)	116.8(5), 117.5(5)
C-N-P	124.6(2), 125.8(2) <sup>[a]</sup>	125.4(2), 125.5(2)	123.3(2), 126.5(2)	127.4(4), 128.5(4)
N–P–S	118.55(9), 116.80(9) <sup>[a]</sup>	117.78(10), 119.41(10)	116.46(9), 119.65(10)	113.9(2), 115.19(19)
S–Cu–S	98.10(2), 106.57(3),	103.26(3), 104.27(3)	108.57(3), 110.49(3)	99.15(5), 100.57(5),
	108.96(2), 99.92(2), <sup>[a]</sup>			106.23(6), 115.15(6)
	107.24(3), <sup>[a]</sup> 107.34(3) <sup>[a]</sup>			
P–Cu–P		111.18(3), 121.11(3)	97.90(3), 99.81(3)	
P–Cu–S	122.16(3), 103.03(3) <sup>[a]</sup>	101.07(3), 105.63(3),	102.05(3), 103.03(3),	98.28(6), 104.58(5),
		106.95(3), 121.47(3)	107.53(3), 112.21(3)	114.95(6), 120.35(6)
P–Cu–S(P)	116.76(3), 121.15(12)	101.19(3), 105.98(3),	107.17(3), 115.21(3),	116.22(6), 120.18(6)
		113.02(3), 116.46(3)	123.04(3), 123.66(3)	
Cu–S–C	107.21(8)	102.64(10), 102.84(10)	102.28(9), 104.29(9)	93.50(17), 95.03(17),
				107.7(2), 107.92(19)
Cu–S–P	86.9(2), 94.65(3)	99.39(4), 102.05(4)	94.73(4), 95.81(4)	99.25(8), 99.85(7)
Cu–S–Cu				68.27(4), 70.27(4)

[a] Data for the Cu2-S4-C2(N4)-N3-P2(O3)(O4)-S3 backbone.

Table 4. Hydrogen-bond lengths [Å] and angles [°] for  $\rm H_2L^{II},\,1,\,3,\,4,\,5,\,6,\,8,$  and 10.

	D–H•••A	D–H	Н•••А	D···A	D–H•••A
H <sub>2</sub> L <sup>II[a]</sup>	N1-H1···S2 <sup>#1</sup>	0.79(2)	2.57(2)	3.3441(15)	170.0(18)
-	N2-H2-O2	0.83(2)	2.31(2)	2.9644(17)	135.9(19)
	N3-H3-S4#2	0.81(2)	2.56(2)	3.3286(16)	158(2)
	N4-H4···O3	0.87(2)	2.22(3)	2.8957(18)	134(2)
1 <sup>[b]</sup>	N2-H2A···N1 <sup>#1</sup>	0.89(3)	2.23(3)	3.115(3)	172(3)
	N2-H2A-O2#1	0.89(4)	2.47(3)	2.999(3)	118(3)
<b>3</b> <sup>[c]</sup>	N2-H2B···N1#1	0.86(3)	2.37(3)	3.222(3)	172(2)
	N2-H2B···O1#1	0.86(3)	2.53(3)	3.099(3)	124(3)
<b>4</b> <sup>[d]</sup>	N2-H2A···N1#1	0.88	2.10	2.978(10)	172.4
	N2A-H2AA···N1A <sup>#2</sup>	0.88	2.34	3.166(11)	156.4
<b>5</b> <sup>[e]</sup>	N2-H2A···S3	0.86(3)	2.72(3)	3.503(3)	153(3)
	N2-H2B···N1#1	0.94(4)	2.32(4)	3.244(3)	167(3)
	N4-H4B···S1	0.83(4)	2.85(4)	3.561(3)	145(4)
<b>6</b> <sup>[f]</sup>	N3-H3-N2	0.69(3)	2.26(3)	2.851(4)	144(4)
	N4-H4···Cl11 <sup>#1</sup>	0.77(4)	2.69(4)	3.437(4)	164(4)
8	N3-H3-S3	0.85(6)	2.72(6)	3.535(6)	161(5)
10 <sup>[g]</sup>	N3-H3-S2#1	0.84(2)	2.83(3)	3.628(2)	158(3)
	N4-H4…N1	0.86(2)	2.15(3)	2.842(3)	137(3)

[a] Symmetry codes: #1: -x + 1, y, -z + 3/2; #2: -x + 1, -y + 1, -z + 1. [b] Symmetry codes: #1: -x + 1, -y, -z. [c] Symmetry codes: #1: -x + 1, -y, -z + 1. [d] Symmetry codes: #1: -x + 1, -y + 1, -z. [e] Symmetry codes: #1: -x + 1, -y + 1, -z + 1; #2: -x + 1, -y + 1, -z + 2. [f] Symmetry codes: #1: -x + 1, -y + 1, -z + 1. [g] Symmetry codes: #1: -x + 1, -y + 2, -z + 1.

**4** is significantly smaller than that in **1**. The P–Cu–P angle in **4** is significantly larger than in **3** (Table 2), as expected for the replacement of the flexible  $-(CH_2)_3$ - group by the ferrocenediyl unit.

In the dinuclear complex **5** the Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> ligand bridges two Cu<sup>I</sup> ions with two deprotonated thiourea groups coordinated to the Cu atoms through the thiophosphoryl and thiocarbonyl sulfur atoms of the ligand, the latter acting as a ( $\mu$ , $\eta^1$ , $\eta^1$ )-Cu–S–Cu bridge, thus forming a dinuclear entity (Figure 6). Both Cu<sup>I</sup> atoms in **5** are in a tetrahedral PS<sub>3</sub> environment. The same type of anionic thiourea ligand was observed in the structure of polynuclear Cu<sup>I</sup> complexes.<sup>[1,3,7,9–11]</sup> The Cu1···Cu2 distance of 2.8355(4) Å is slightly longer than the sum of two van der Waals radii of Cu<sup>I</sup> (2.80 Å).<sup>[26]</sup>

In the crystal, two molecules of the complexes 1 and 3– 5 form centrosymmetric dimers as a result of intermolecular hydrogen bonds (Table 4). These intermolecular hydrogen bonds are formed by the hydrogen atom of the NH group and the nitrogen or oxygen (1 and 3) or solely nitrogen (4 and 5) atoms of the N–P–O*i*Pr group of a further molecule. In the crystal of 5 there are also intramolecular hydrogen bonds formed by the NH hydrogen atom of one molecule of L<sup>1</sup> and the P=S sulfur atom of a second molecule of L<sup>1</sup> (Table 4).

In the structures of **6** and **8**, each Cu<sup>I</sup> cation is in a  $P_2S_2$  tetrahedral environment formed by two sulfur atoms of the deprotonated *N*-thiophosphoryl bis(thiourea) L<sup>II</sup> and two phosphorus atoms of two PPh<sub>3</sub> ligands (**6**) or one Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub> ligand (**8**; Figures 7 and 8). The Cu–S(C), Cu–S(P) and Cu–P bonds (Table 3) in **6** and **8** are similar to those found in the mononuclear analogues.<sup>[1–12]</sup> The S–Cu–S angles in **8** are significantly larger than those in **6**,

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whereas the P–Cu–P angles in **8** are smaller than those in **6** (Table 3). In the crystals of **6** and **8** an intramolecular hydrogen bond is formed by the NH hydrogen atom of one pendant arm of L<sup>II</sup> and the NPS nitrogen atom of the second pendant arm (Table 4). The second NH hydrogen atom of L<sup>II</sup> forms an intermolecular hydrogen bond with the chlorine atom of a CH<sub>2</sub>Cl<sub>2</sub> molecule in the crystal of **6** (Table 4). Two molecules of **8** form a centrosymmetric dimer in the crystal due to intermolecular hydrogen bonds between the second NH hydrogen atom of L<sup>II</sup> and the C=S sulfur atom (Table 4). This type of intermolecular hydrogen bonding is typical of mononuclear analogues.<sup>[1–12]</sup>

The structure of **10** is similar to that of **5**. In the complex **10**, the deprotonated thiourea  $L^{II}$  coordinates two  $Cu^{I}$  atoms, which are also interconnected by two C=S sulfur atoms, forming an S<sub>2</sub>Cu<sub>2</sub> four-membered ring (Figure 9). The Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> ligand also bridges the two Cu<sup>I</sup> atoms, thus completing a tetrahedral PS<sub>3</sub> environment. The Cu1...Cu2 distance [2.7629(10) Å] is slightly shorter than the sum of two van der Waals radii of Cu<sup>I</sup>.<sup>[26]</sup> In the crystal of **10** there is an intramolecular hydrogen bond formed by the NH hydrogen atom of the pendant arm and the P=S sulfur atom of the second pendant arm (Table 4).

It is reasonable to assume that the formation of **5** and **10** is mainly caused by the rather small bite angle of  $Ph_2PCH_2PPh_2$ , which often does not allow for perfect chelate binding of metal cations and consequently leads to a bridging coordination, thus forming dinuclear structures<sup>[27]</sup> and often even promoting M–M bond formation.<sup>[28]</sup>

## Conclusions

The potassium salts of L<sup>I</sup> or L<sup>II</sup> react with  $[Cu(PPh_3)_3I]$ or a mixture of CuI and  $Ph_2P(CH_2)_{1-3}PPh_2$  or  $Ph_2P$ - $(C_5H_4FeC_5H_4)PPh_2$  to form mononuclear (1–4) or dinuclear (5–10) complexes. Recrystallisation of 1 from an acetone/*n*-hexane mixture leads to a complex with one PPh<sub>3</sub> molecule, whereas recrystallisation of 1 from a  $CH_2Cl_2/n$ hexane mixture gave the product 11 with two PPh<sub>3</sub> ligands.<sup>[1]</sup> The formation of dinuclear complexes **5** and **10** is favoured by the small bite angle of  $Ph_2PCH_2PPh_2$ .

Complexes 2-5 and 7-10 exhibit emission in the solid state at ambient temperature, which can be assigned to <sup>3</sup>ILCT (or <sup>3</sup>MLCT) transitions. In contrast, 1 and 6 fail to emit under these conditions, probably due to fast relaxation.

## **Experimental Section**

**Physical Measurements:** Infrared spectra were recorded with a Bruker IFS66 $\nu$ S spectrometer in the range 400–3600 cm<sup>-1</sup>. NMR spectra were obtained with a Bruker Avance 300 MHz spectrometer at 25 °C. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra (CDCl<sub>3</sub>) were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to SiMe<sub>4</sub> (<sup>1</sup>H) and H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P{<sup>1</sup>H}). Absorption spectra of 10<sup>-4</sup> M (1–5) or 10<sup>-5</sup> M (6–10) solutions in

 $CH_2Cl_2$  were measured with a Lambda-35 spectrometer. Fluorescence was measured with a Spex FluoroMax-3 spectrofluorimeter on solid samples at room temperature. Elemental analyses were performed with a CHNS HEKAtech EuroEA 3000 analyser.

**Syntheses:** *N*-Thiophosphorylated thiourea HL<sup>1</sup> was prepared according to a previously described method.<sup>[25]</sup>

**H**<sub>2</sub>**L**<sup>II</sup>: A solution of *o*-phenylenediamine (0.540 g, 5 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was treated under vigorous stirring with a solution of (*i*PrO)<sub>2</sub>P(S)NCS (0.263 g, 1.1 mmol) in the same solvent. The mixture was stirred for 1 h. The solvent was removed in vacuo, and the product was purified by recrystallisation from a CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane mixture (1:5, v/v). Yield: 2.758 g (94%). <sup>1</sup>H NMR:  $\delta$  = 1.35–1.47 (m, 24 H, CH<sub>3</sub>, *i*Pr), 4.89 (dsept, <sup>3</sup>J<sub>H,H</sub> = 6.2, <sup>3</sup>J<sub>P,H</sub> = 10.5 Hz, 4 H, OCH), 7.07–7.32 (m, overlapping with the solvent signal, C<sub>6</sub>H<sub>4</sub> + NHP), 9.12 [br. s, 2 H, (aryl)NH] ppm. <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta$  = 53.0 (s) ppm. IR:  $\tilde{v}$  = 652 (P=S), 993, 1003 (POC), 1553 (S=C–N), 3204, 3422 (NH) cm<sup>-1</sup>. C<sub>20</sub>H<sub>36</sub>N<sub>4</sub>O<sub>4</sub>P<sub>2</sub>S<sub>4</sub> (586.72): calcd. C 40.94, H 6.18, N 9.55; found C 41.01, H 6.12, N 9.48.

**Complex 1:** Complex 1 was prepared according to a previously described method,<sup>[1]</sup> but the residue was recrystallised from an acetone/*n*-hexane mixture (1:5, v/v). **1:** Yield: 0.264 g (91%). M.p. 141–142 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.30$  (d,  ${}^{3}J_{\rm H,\rm H} = 6.0$  Hz, 6 H, CH<sub>3</sub>, *i*Pr), 1.31 (d,  ${}^{3}J_{\rm H,\rm H} = 6.1$  Hz, 6 H, CH<sub>3</sub>, *i*Pr), 4.75 (dsept,  ${}^{3}J_{\rm H,\rm H} = 6.0$ ,  ${}^{3}J_{\rm P,\rm H} = 10.8$  Hz, 2 H, OCH), 5.72 (br. s, 2 H, NH<sub>2</sub>), 7.28–7.51 (m, 15 H, Ph) ppm.  ${}^{31}{\rm P}{}^{1}{\rm H}$  NMR (CDCl<sub>3</sub>):  $\delta = 0.4$  (s, 1 P, PPh<sub>3</sub>), 54.4 (s, 1 P, NPS) ppm. IR:  $\tilde{v} = 601$  (P=S), 1008 (POC), 1546 (SCN), 1614, 3127, 3249, 3496 (NH<sub>2</sub>) cm<sup>-1</sup>. C<sub>25</sub>H<sub>31</sub>CuN<sub>2</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub> (581.15): calcd. C 51.67, H 5.38, N 4.82; found C 51.82, H 5.29, N 4.90.

Complexes 2-5: A suspension of HLI (0.128 g, 0.5 mmol) in aqueous ethanol (35 mL) was mixed with an ethanol solution of potassium hydroxide (0.031 g, 0.55 mmol). A mixture of CuI (0.095 g, 0.5 mmol) and Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub> (n = 1, 0.192 g; n = 2, 0.199 g; n= 3, 0.206 g; 0.5 mmol) or  $Ph_2P(C_5H_4FeC_5H_4)PPh_2$  (0.277 g, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was heated at reflux for 0.5 h and then added dropwise under vigorous stirring to the obtained potassium salt. The mixture was stirred for 1 h, and the resulting precipitate of KI was filtered off. The filtrate was concentrated until crystallisation started. Isolated crystals were obtained from a CH<sub>2</sub>Cl<sub>2</sub>/ *n*-hexane mixture (1:5, v/v). **2:** Yield: 0.265 g (74%). M.p. 107-108 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.13–1.34 (m, 12 H, CH<sub>3</sub>, *i*Pr), 2.25 (br. s, 2 H, CH<sub>2</sub>), 4.73 (dsept,  ${}^{3}J_{H,H} = 6.2$ ,  ${}^{3}J_{P,H} = 10.5$  Hz, 2 H, OCH), 5.70 (br. s, 2 H, NH<sub>2</sub>), 6.97-7.86 (m, overlapping with the solvent signal, Ph) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = -12.4$  (br. s, 2 P, PPh<sub>2</sub>), 56.8 (s, 1 P, NPS) ppm. IR:  $\tilde{v}$  = 607 (P=S), 1011 (POC), 1557 (SCN), 1611, 3120, 3241, 3491 (NH<sub>2</sub>) cm<sup>-1</sup>. C<sub>33</sub>H<sub>40</sub>CuN<sub>2</sub>-O<sub>2</sub>P<sub>3</sub>S<sub>2</sub> (717.28): calcd. C 55.26, H 5.62, N 3.91; found C 55.10, H 5.68, N 3.97. 3: Yield: 0.314 g (86%). M.p. 92-93 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.15$  (d,  ${}^{3}J_{H,H} = 6.2$  Hz, 6 H, CH<sub>3</sub>, *i*Pr), 1.18 (d,  ${}^{3}J_{H,H}$ = 6.1 Hz, 6 H, CH<sub>3</sub>, *i*Pr), 1.56–1.97 (m, 2 H, CH<sub>2</sub>), 2.36 (br. s, 4 H, CH<sub>2</sub>), 4.67 (dsept,  ${}^{3}J_{H,H} = 6.1$ ,  ${}^{3}J_{P,H} = 10.7$  Hz, 2 H, OCH), 5.51 (br. s, 2 H,  $NH_2$ ), 6.96–7.83 (m, overlapping with the solvent signal, Ph) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = -19.8$  (br. s, 2 P, PPh<sub>2</sub>), 58.0 (s, 1 P, NPS) ppm. IR:  $\tilde{v}$  = 610 (P=S), 1004 (POC), 1558 (SCN), 1621, 3132, 3258, 3501 (NH<sub>2</sub>) cm<sup>-1</sup>.  $C_{34}H_{42}CuN_2O_2P_3S_2$ (731.31): calcd. C 55.84, H 5.79, N 3.83; found C 55.68, H 5.84, N 3.78. 4: Yield: 0.345 g (79%). M.p. 174-175 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.19 (t, <sup>3</sup>*J*<sub>H,H</sub> = 6.0 Hz, 12 H, CH<sub>3</sub>, *i*Pr), 4.20 (br. s, 4 H, C<sub>5</sub>H<sub>4</sub>), 4.29 (br. s, 4 H, C<sub>5</sub>H<sub>4</sub>), 4.69 (dsept,  ${}^{3}J_{H,H} = 6.2$ ,  ${}^{3}J_{P,H} = 10.3$  Hz, 2 H, OCH), 5.33 (br. s, 2 H, NH<sub>2</sub>), 7.21-7.76 (m, overlapping with the solvent signal, Ph) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = -17.6$  (br.



s, 2 P, PPh<sub>2</sub>), 58.7 (s, 1 P, NPS) ppm. IR:  $\tilde{v} = 612$  (P=S), 996 (POC), 1553 (SCN), 1609, 3137, 3261, 3488 (NH<sub>2</sub>) cm<sup>-1</sup>. C<sub>41</sub>H<sub>44</sub>CuFeN<sub>2</sub>-O<sub>2</sub>P<sub>3</sub>S<sub>2</sub> (873.25): calcd. C 56.39, H 5.08, N 3.21; found C 56.54, H 4.99, N 3.26. **5:** Yield: 0.245 g (96%). M.p. 167–168 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.23$  (d, <sup>3</sup>J<sub>H,H</sub> = 6.2 Hz, 24 H, CH<sub>3</sub>, *i*Pr), 2.90 (br. s, 4 H, CH<sub>2</sub>), 4.64 (dsept, <sup>3</sup>J<sub>H,H</sub> = 6.1, <sup>3</sup>J<sub>P,H</sub> = 10.5 Hz, 4 H, OCH), 5.68 (br. s, 4 H, NH<sub>2</sub>), 6.76–7.74 (m, overlapping with the solvent signal, Ph) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = -10.6$  (br. s, 2 P, PPh<sub>2</sub>), 57.3 (s, 2 P, NPS) ppm. IR:  $\tilde{v} = 616$  (P=S), 994, 1013 (POC), 1538, 1562 (SCN), 1629, 3136, 3255, 3483 (NH<sub>2</sub>) cm<sup>-1</sup>. C<sub>39</sub>H<sub>54</sub>Cu<sub>2</sub>-N<sub>4</sub>O<sub>4</sub>P<sub>4</sub>S<sub>4</sub> (1022.11): calcd. C 45.83, H 5.33, N 5.48; found C 46.04, H 5.27, N 5.42.

Complex 6: A suspension of  $H_2L^{II}$  (0.293 g, 0.5 mmol) in aqueous ethanol (35 mL) was mixed with an ethanol solution of potassium hydroxide (0.062 g, 1.1 mmol). A solution of [Cu(PPh<sub>3</sub>)<sub>3</sub>I] (0.977 g, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was added dropwise to the obtained potassium salt under vigorous stirring. The mixture was stirred for 1 h, and the resulting precipitate of KI was filtered off. The filtrate was concentrated until crystallisation started. Isolated crystals were obtained from a CH<sub>2</sub>Cl<sub>2</sub>/n-hexane mixture (1:5, v/v). Yield: 0.880 g (86%). <sup>1</sup>H NMR:  $\delta$  = 1.19 (d, <sup>3</sup>J<sub>H,H</sub> = 6.1 Hz, 12 H, CH<sub>3</sub>, *i*Pr), 1.23 (d,  ${}^{3}J_{H,H} = 6.1$  Hz, 12 H, CH<sub>3</sub>, *i*Pr), 4.75 (dsept,  ${}^{3}J_{H,H} = 6.2$ ,  ${}^{3}J_{PH} = 10.7 \text{ Hz}, 4 \text{ H}, \text{ OCH}), 6.98-7.10 \text{ (m, 2 H, C}_{6}H_{4}), 7.28-7.47$ (m, 60 H, Ph), 7.58–7.70 (m, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.77 [d,  ${}^{4}J_{P,H}$  = 8.1 Hz, 2 H, (aryl)NH] ppm. <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta = -1.5$  (s, 4 P, PPh<sub>3</sub>), 54.4 (s, 2 P, NPS) ppm. IR:  $\tilde{v} = 597$  (P=S), 995 (POC), 1540 (SCN), 3348 (NH) cm<sup>-1</sup>. C<sub>92</sub>H<sub>94</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>4</sub>P<sub>6</sub>S<sub>4</sub> (1760.96): calcd. C 62.75, H 5.38, N 3.18; found C 62.58, H 5.27, N 3.25.

Complexes 7-10: A suspension of H<sub>2</sub>L<sup>II</sup> (0.293 g, 0.5 mmol) in aqueous ethanol (35 mL) was mixed with an ethanol solution of potassium hydroxide (0.062 g, 1.1 mmol). A mixture of CuI (0.19 g, 1.0 mmol) and  $Ph_2P(CH_2)_nPPh_2$  (n = 1, 0.384 g; n = 2, 0.398 g; n= 3, 0.412 g; 1.0 mmol) or  $Ph_2P(C_5H_4FeC_5H_4)PPh_2$  (0.554 g, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was heated at reflux for 0.5 h and then added dropwise to the obtained potassium salt under vigorous stirring. The mixture was stirred for 1 h, and the precipitate was filtered off. The filtrate was concentrated until crystallisation started. Isolated crystals were obtained from a CH2Cl2/n-hexane mixture (1:5, v/v). 7: Yield: 0.671 g (89%). <sup>1</sup>H NMR:  $\delta = 1.04$  (br. s, 12 H, CH<sub>3</sub>, *i*Pr), 1.14 (d,  ${}^{3}J_{H,H}$  = 6.2 Hz, 12 H, CH<sub>3</sub>, *i*Pr), 2.24 (br. s, 4 H, CH<sub>2</sub>), 4.59 (br. s, 4 H, OCH), 6.76-7.98 [m, overlapping with the solvent signal,  $C_6H_4 + Ph + (aryl)NH$  ppm. <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta = -13.2$  (br. s, 4 P, PPh<sub>2</sub>), 56.9 (s, 2 P, NPS) ppm. IR:  $\tilde{v}$ = 594 (P=S), 1006 (POC), 1551 (SCN), 3362 (NH) cm<sup>-1</sup>. C<sub>72</sub>H<sub>82</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>4</sub>P<sub>6</sub>S<sub>4</sub> (1508.64): calcd. C 57.32, H 5.48, N 3.71; found C 57.51, H 5.40, N 3.76. 8: Yield: 0.561 g (73%). <sup>1</sup>H NMR:  $\delta = 1.09$  (d,  ${}^{3}J_{H,H} = 6.0$  Hz, 12 H, CH<sub>3</sub>, *i*Pr), 1.18 (d,  ${}^{3}J_{H,H} =$ 6.0 Hz, 12 H, CH<sub>3</sub>, *i*Pr), 1.81 (br. s, 4 H, CH<sub>2</sub>), 2.33 (br. s, 8 H, CH<sub>2</sub>), 4.63 (dsept,  ${}^{3}J_{H,H} = 6.1$ ,  ${}^{3}J_{P,H} = 10.6$  Hz, 4 H, OCH), 6.81– 7.70 [m, overlapping with the solvent signal,  $C_6H_4 + Ph + (aryl)$ -NH] ppm. <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta = -20.2$  (br. s, 4 P, PPh<sub>2</sub>), 56.6 (s, 2 P, NPS) ppm. IR:  $\tilde{v} = 601$  (P=S), 991 (POC), 1548 (SCN), 3353 (NH) cm<sup>-1</sup>. C<sub>74</sub>H<sub>86</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>4</sub>P<sub>6</sub>S<sub>4</sub> (1536.70): calcd. C 57.84, H 5.64, N 3.65; found C 57.62, H 5.58, N 3.71. 9: Yield: 0.710 g (78%). <sup>1</sup>H NMR:  $\delta = 1.17$  (d,  ${}^{3}J_{H,H} = 6.1$  Hz, 24 H, CH<sub>3</sub>, *i*Pr), 4.25 (br. s, 16 H, C<sub>5</sub>H<sub>4</sub>), 4.65 (br. s, 4 H, OCH), 6.70-7.88 [m, overlapping with the solvent signal,  $C_6H_4$  + Ph + (aryl)NH] ppm. <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta$ = -18.1 (br. s, 4 P, PPh<sub>2</sub>), 58.1 (s, 2 P, NPS) ppm. IR:  $\tilde{v} = 604$ (P=S), 1014 (POC), 1552 (SCN), 3367 (NH) cm<sup>-1</sup>. C<sub>88</sub>H<sub>90</sub>Cu<sub>2</sub>-Fe<sub>2</sub>N<sub>4</sub>O<sub>4</sub>P<sub>6</sub>S<sub>4</sub> (1820.58): calcd. C 58.06, H 4.98, N 3.08; found C 58.19, H 4.90, N 3.02. **10:** Yield: 0.378 g (69%). <sup>1</sup>H NMR:  $\delta = 0.85$ (br. s, 12 H, CH<sub>3</sub>, *i*Pr), 1.11 (d,  ${}^{3}J_{H,H} = 6.2$  Hz, 12 H, CH<sub>3</sub>, *i*Pr), 2.97 (br. s, 2 H, CH<sub>2</sub>), 4.27 (br. s, 4 H, OCH), 7.06-7.38 (m, overlapping with the solvent signal,  $C_6H_4$  + Ph), 8.29 [d,  ${}^4J_{P,H}$  = 9.2 Hz, 2 H, (aryl)NH] ppm.  ${}^{31}P{}^{1}H$  NMR:  $\delta$  = -22.4 (s, 2 P, PPh<sub>2</sub>), 54.9 (s, 2 P, NPS) ppm. IR:  $\tilde{v}$  = 610 (P=S), 988 (POC), 1537, 1559 (SCN), 3369 (NH) cm<sup>-1</sup>.  $C_{45}H_{56}Cu_2N_4O_4P_4S_4$  (1096.19): calcd. C 49.31, H 5.15, N 5.11; found C 49.48, H 5.06, N 5.18.

Crystal Structure Determination and Refinement for H<sub>2</sub>L<sup>II</sup>, 1, 3-6, 8, 10: The X-ray diffraction data for crystals of H<sub>2</sub>L<sup>II</sup>, 1, 3-6, 8 and 10 were collected with a STOE IPDS-II diffractometer. The images were indexed, integrated and scaled by using the X-Area package.<sup>[29]</sup> Data were corrected for absorption by using the PLA-TON<sup>[30]</sup> program. The structures were solved by direct methods using the SHELXS<sup>[31]</sup> program and refined first isotropically and then anisotropically using SHELXL97.[31] Hydrogen atoms were revealed from  $\Delta \rho$  maps and those bonded to C were refined by using a riding model. Hydrogen atoms bonded to N were freely refined in  $H_2L^{II}$ , 6 and 8. In 10, U(H) values were set to  $1.2U_{eq}(N)$ , and N-H distances were restrained to 0.90(3) Å. All figures were generated by using the Mercury program.[32] CCDC-746321  $(H_2L^{II})$ , -742126 (1), -742127 (3), -742128 (4), -742129 (5), -746318 (6), -746320 (8) and -746319 (10) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. H<sub>2</sub>L<sup>II</sup>: C<sub>20</sub>H<sub>36</sub>N<sub>4</sub>O<sub>4</sub>P<sub>2</sub>S<sub>4</sub>, M<sub>r</sub> = 586.71, monoclinic, space group C2/c, a = 20.9638(11), b =11.7659(5), c = 25.9717(15) Å,  $\beta = 110.682(4)^{\circ}$ , V = 5993.3(5) Å<sup>3</sup>,  $Z = 8, \rho = 1.300 \text{ g cm}^{-3}, \mu(\text{Mo-}K_{\alpha}) = 0.455 \text{ mm}^{-1}, \text{ reflections: } 18620$ collected, 5240 unique,  $R_{int} = 0.0527$ ,  $R_1(all) = 0.0368$ ,  $wR_2(all) =$ 0.0847. 1:  $C_{25}H_{31}CuN_2O_2P_2S_2$ ,  $M_r = 581.12$ , monoclinic, space group  $P2_1/n$ , a = 18.5869(14), b = 8.3540(8), c = 19.9721(15) Å,  $\beta$ = 115.697(5)°,  $V = 2794.5(4) \text{ Å}^3$ , Z = 4,  $\rho = 1.381 \text{ g cm}^{-3}$ ,  $\mu$ (Mo- $K_{\alpha}$  = 1.070 mm<sup>-1</sup>, reflections: 36121 collected, 5191 unique,  $R_{\text{int}}$  = 0.0710,  $R_1(all) = 0.0534$ ,  $wR_2(all) = 0.0709$ . **3:**  $C_{34}H_{42}CuN_2O_2P_3S_2$ ,  $M_{\rm r} = 731.27$ , monoclinic, space group  $P2_1/n$ , a = 16.4108(6), b =12.2076(4), c = 20.0240(6) Å,  $\beta = 100.177(3)^\circ$ , V = 3948.4(2) Å<sup>3</sup>, Z = 4,  $\rho$  = 1.230 gcm<sup>-3</sup>,  $\mu$ (Mo- $K_{\alpha}$ ) = 0.810 mm<sup>-1</sup>, reflections: 20673 collected, 7208 unique,  $R_{int} = 0.0526$ ,  $R_1(all) = 0.0483$ ,  $wR_2(all) =$ 0.0873. 4:  $C_{41}H_{44}CuFeN_2O_2P_3S_2$ ,  $M_r = 873.20$ , triclinic, space group  $P\overline{1}$ , a = 11.5630(8), b = 19.9018(14), c = 22.1295(13) Å, a =116.568(5),  $\beta = 99.682(5)$ ,  $\gamma = 90.364(5)^\circ$ , V = 4470.7(5) Å<sup>3</sup>, Z = 4,  $\rho = 1.297 \text{ g cm}^{-3}, \mu(\text{Mo-}K_{\alpha}) = 1.035 \text{ mm}^{-1}, \text{ reflections: } 36215 \text{ col-}$ lected, 15725 unique,  $R_{int} = 0.1939$ ,  $R_1(all) = 0.1530$ ,  $wR_2(all) =$ 0.1990. 5:  $C_{39}H_{54}Cu_2N_4O_4P_4S_4$ ,  $M_r = 1022.06$ , monoclinic, space group  $P2_1/c$ , a = 13.1707(5), b = 32.2392(13), c = 11.1962(4) Å,  $\beta = 98.891(3)^{\circ}$ ,  $V = 4696.9(3) \text{ Å}^3$ , Z = 4,  $\rho = 1.445 \text{ g cm}^{-3}$ ,  $\mu$ (Mo- $K_{\alpha}$ ) = 1.262 mm<sup>-1</sup>, reflections: 22460 collected, 8202 unique,  $R_{\text{int}} = 0.0490, R_1(\text{all}) = 0.0459, wR_2(\text{all}) = 0.0686.$  6:  $C_{92}H_{94}Cu_2N_4O_4P_6S_4$ ·2CH<sub>2</sub>Cl<sub>2</sub>,  $M_r = 1930.70$ , triclinic, space group  $P\bar{1}, a = 13.4500(5), b = 17.3046(7), c = 22.2429(8)$  Å, a = 74.416(3), c = 22.2429(8) $\beta = 85.214(3), \ \gamma = 70.672(3)^{\circ}, \ V = 4705.5(3) \text{ Å}^3, \ Z = 2, \ \rho =$ 1.363 g cm<sup>-3</sup>,  $\mu$ (Mo- $K_{\alpha}$ ) = 0.808 mm<sup>-1</sup>, reflections: 50169 collected, 17546 unique,  $R_{\text{int}} = 0.0446$ ,  $R_1(\text{all}) = 0.0639$ ,  $wR_2(\text{all}) = 0.1201$ . 8:  $C_{74}H_{86}Cu_2N_4O_4P_6S_4$ ·CH<sub>2</sub>Cl<sub>2</sub>,  $M_r = 1621.53$ , triclinic, space group  $P\overline{1}$ , a = 13.1235(5), b = 18.1183(6), c = 19.0561(7) Å, a =69.187(3),  $\beta = 74.416(3)$ ,  $\gamma = 69.245(3)^{\circ}$ ,  $V = 3907.4(2) \text{ Å}^3$ , Z = 2,  $\rho = 1.378 \text{ g cm}^{-3}, \mu(\text{Mo-}K_{\alpha}) = 0.892 \text{ mm}^{-1}, \text{ reflections: } 68964 \text{ col-}$ lected, 14595 unique,  $R_{int} = 0.0605$ ,  $R_1(all) = 0.0584$ ,  $wR_2(all) =$ 0.1125. 10:  $C_{45}H_{56}Cu_2N_4O_4P_4S_4$ ,  $M_r = 1096.14$ , monoclinic, space group  $P2_1/c$ , a = 13.8418(13), b = 33.901(3), c = 11.1897(10) Å,  $\beta$ = 98.988(7)°,  $V = 5186.3(8) \text{ Å}^3$ , Z = 4,  $\rho = 1.404 \text{ g cm}^{-3}$ ,  $\mu$ (Mo- $K_{\alpha}$  = 1.148 mm<sup>-1</sup>, reflections: 67245 collected, 9156 unique,  $R_{\text{int}}$  =  $0.1228, R_1(all) = 0.1561, wR_2(all) = 0.1106.$ 

Supporting Information (see footnote on the first page of this article): Absorption spectra of 1-10 in  $CH_2Cl_2$ .

# **FULL PAPER**

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