

Controlling Cu...Cu distances using halides:

(8-phenylthionaphth-1-yl)diphenylphosphine copper halide dimers

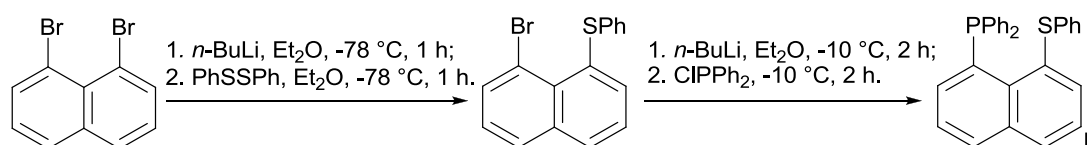
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Abstract: In the isomorphous binuclear $\text{Cu}_2\text{X}_2\text{L}_2$ systems ($\text{L} = (8\text{-phenylthionaphth-1-yl})\text{diphenylphosphine}$ the Cu...Cu separation is reduced as the halide size increases.

Copper(I) complexes are of special interest in biochemical coordination chemistry due to the involvement of Cu(I) in biological redox reactions in biomolecules such as *cytochrome c*.¹ The inclination for Cu(I) atoms to adopt a pseudo four-coordinate geometry as a result of dimer formation is of particular importance which is enhanced by the additional possibility of studying metal-metal interactions between the two d^{10} metal centres in these compounds.^{2,3}



Scheme 1 The reaction scheme for the preparation of the novel compound (8-phenylsulfanyl-1-yl)diphenylphosphine **L**.

We have been investigating sterically crowded 1,8 disubstituted naphthalenes⁴ with previous work focussing on dichalcogenide ligands⁴ or unusual phosphorus systems.⁵ We wished to develop our understanding of mixed P,S systems. We prepared ligand **L** as shown in scheme 1 using modifications of literature procedures^{6,7} The ^{31}P NMR spectrum of **L** consists of a single peak at $\delta = -5.3$ ppm which is in the appropriate region for a phosphine of this type⁸ The X-ray structure of **L** reveals that the PPh_2 and SPh groups are repelling each other and distorting the naphthalene backbone from ideal geometry.

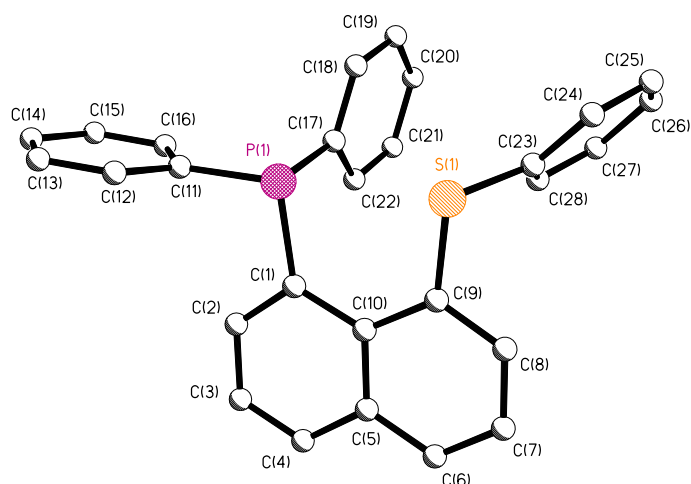
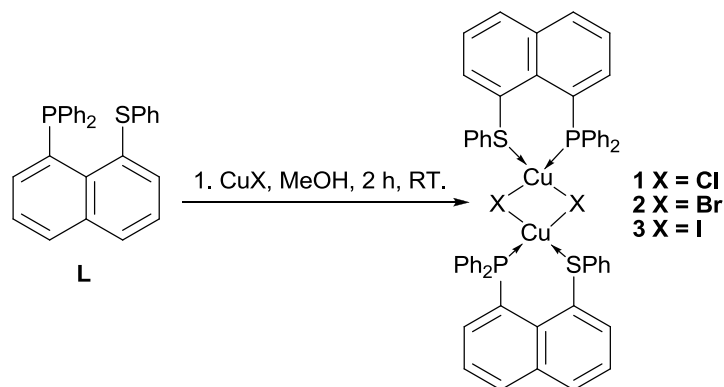


Fig. 1 The crystal structure of (8-phenylsulfanyl)naphth-1-yl)diphenylphosphine **L**.

L reacts with CuX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in methanol/dichloromethane to afford CuX_2L_2 **1-3** (Scheme 2). The ^{31}P NMR spectra of **1-3** show single peaks with similar chemical shifts for the three compounds with values in the range for related sulfur/phosphorus copper dihalide complexes in the literature⁸ [**1 Cl** $\delta = 27.8$ ppm, **2 Br** $\delta = 27.7$ ppm, **3 I** $\delta = 28.7$ ppm].



Scheme 2 The reaction scheme for the preparation of the (8-phenylthionaphth-1-yl)diphenylphosphine copper halide dimers **1-3**.

In the molecular structures⁹ of **1-3** (Fig. 2, Table 1) the copper atom coordinates to two halide atom and to the bidentate ligand **L** via sulfur and phosphorus forming $[\text{Cu}_2(\mu\text{-X})_2\{\text{Nap}(\text{PPh}_2)(\text{SPh})\}_2]$. As a consequence of the symmetry the Cu_2X_2 rhombus core is strictly planar in the form of a parallelogram containing two unequal

Cu-X bond distances. With increasing size of the halide, as expected, the Cu-X bond lengths increase, in the range for similar bridged compounds in the literature¹⁰ (2.33-2.82 Å). The binuclear molecules contain a centre of symmetry and this results in the copper(I) atoms having identically distorted tetrahedral environments. Copper has a stereochemical preference for tetrahedral coordination with ‘ideal’ angles around the copper of 109.5°. **1-3** exhibit greater distorted tetrahedral geometry compared with other compounds containing the Cu₂X₂ rhombus core.¹⁰

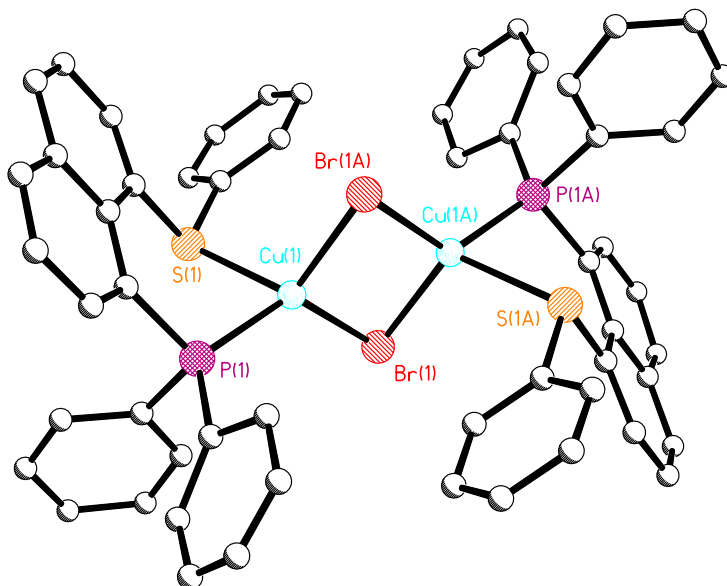


Fig. 2 The crystal structure of (8-phenylthionaphth-1-yl)diphenylphosphine copper bromide dimer **2**. Compounds **1** and **3** are very similar and are not illustrated

The P-Cu-S bond angles are comparable in **1-3** and are considerably more acute than similar compounds containing no rigid backbone^{10,11} (typical literature values 109.7-119.8 Å). The ligand geometry is hardly influenced by coordination to the copper centre suggesting the naphthalene backbone plays a significant role in the geometry around the copper atom and keeps the phosphorus and sulfur atoms from moving further apart and attaining a more ‘ideal’ tetrahedral geometry. The Cu-S bond lengths for **1-3** although comparable with one another are longer than for related compounds from the literature (2.27-2.34 Å).¹⁰ The increase in covalent radius from chloride to iodide causes the halide atoms to move further apart increasing the non-bonded intramolecular X...X distance across the series [**1** 3.710(2) Å, **2** 3.9193(14) Å, **3** 4.3287(8) Å] (Fig. 2). Dramatically and counter intuitively the two copper atoms are forced closer together as the halide gets larger with Cu...Cu distances approaching the sum of the van der Waals radii of two copper atoms (2.80 Å) [Cu...Cu **1** 2.990(1) Å,

2 2.9296(14) Å, **3** 2.8568(11) Å]. This is accompanied by an increase in the X(1)-Cu(1)-X(1) angle and a decrease in the Cu(1)-X(1)-Cu(1) angle (Table 1, Fig. 3). Searching the known crystals structures for similar central fragments we examined [Cu₂X₆]²⁻ dianions¹² X=Cl is the most common and has Cl...Cl and Cu...Cu separations of 3.1 with 3.3 Å whilst in the bromo case Br..Br is most commonly 3.31 Å and Cu...Cu 3.6 Å. The iodo cases have a much wider range of distances with no particular groupings of distances being identifiable. Lobana *et al* observed¹⁰ a very short Cu..Cu separation [2.504(1)Å] in an iodide bridged phosphine/thiosemicarbazone system with Cu₂SI₂ core but this triply bridged binuclear system is not directly related to the systems reported here. There are no/few structurally characterised homologous series of complexes like **1-3** and so it is not possible assess if the observations reported here are general though we would speculate that the unusual molecular scaffolding effect of the naphthalene based ligand is playing a significant role.

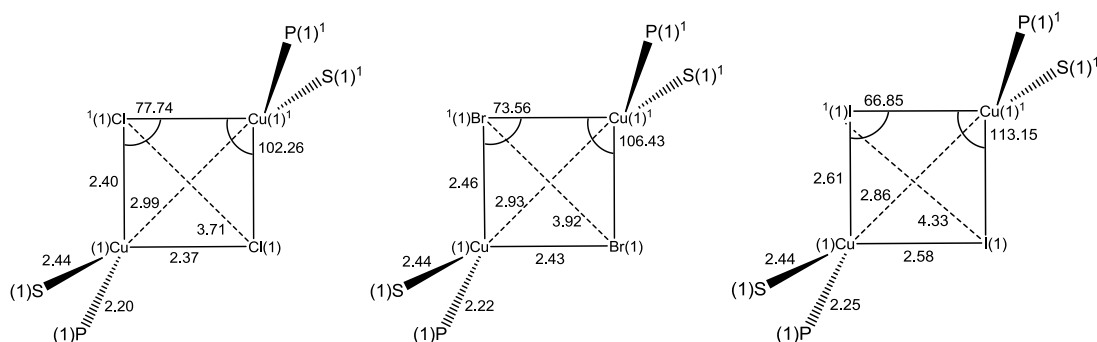


Fig. 3 A schematic illustration of the distances [Å] and angles [°] around the central diamond shaped core of the copper halide dimers.

We examined the three structures carefully to assess if other effects influence the Cu...Cu distance. In all three structures the CuSPC₃ six-membered ring is hinged about the P..S vector (Fig 4); P(1), S(1), C(1), C(10) and C(9) are approximately coplanar with the copper atom sitting in the *peri*-gap above this plane. The distance of the copper from the C(1)-C(10)-C(9)-P(1)-S(1) plane is comparable in all three compounds with the angle inclined by the Cu(1)-P(1)-S(1) plane being similar (**1** 59.9°, **2** 59.7°, **3** 59.6°)

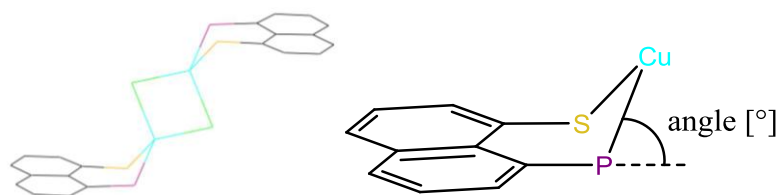


Fig. 4 An illustration showing the positioning of the copper atom in relation to the naphthalene plane.

The planar parallelograms comprising of the two copper atoms and the two halide bridges are close to perpendicular with respect to the Cu-S-P plane (Fig. 3) with angles between the plane and the core decreasing to the iodine complex (**1** 84.9°, **2** 84.41°, **3** 83.44°).

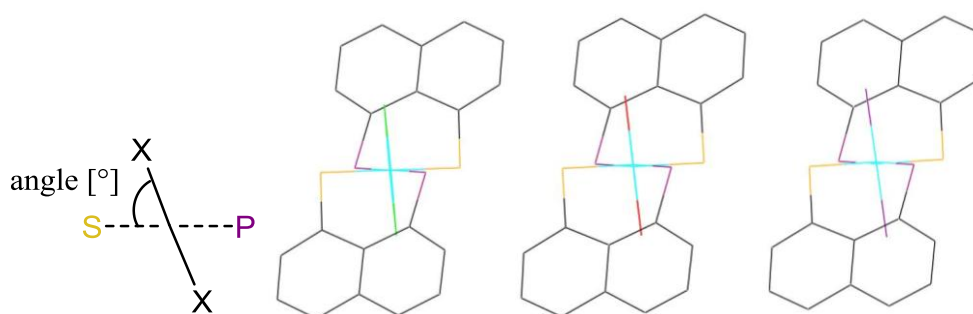


Fig. 5 The crystal structures of copper halide dimers showing the orientation of the copper-halide parallelogram with the sulfur-phosphorus plane.

The unequal Cu-P and Cu-S bond lengths results in the core parallelogram lying at an angle compared to the two parallel naphthalene planes (Fig. 5) [**1** 77.1°, **2** 79.0°, **3** 79.8°]. *Peri*-distances in the three dimers are comparable and very similar to the free ligand [**L** 3.0339(13) Å, **1** 3.061(2) Å, **2** 3.089(3) Å, **3** 3.067(2) Å] and in-plane distortion is equivalent with the *peri*-region angles of similar magnitudes.

We conclude that the shortening of the Cu..Cu separation is a consequence of the increasing size of the bridging halide ie that X...X repulsion plays a significant role here..

Table 1 Selected bond lengths [\AA] and angles [$^\circ$] in **L** and **1-3**

	Ligand	1	2	3
S(1)-P(1)	3.0330(7)	3.061(2)	3.089(3)	3.067(2)
P(1)-C(1)	1.8548(19)	1.833(8)	1.837(8)	1.847(8)
S(1)-C(9)	1.785(2)	1.806(8)	1.812(8)	1.805(8)
Cu(1)-Cu(1) ¹		2.990(1)	2.9296(14)	2.8568(11)
Cl(1)-Cl(1) ¹		3.710(2)	3.9193(14)	4.3287(8)
P(1)-Cu(1)		2.201(2)	2.217(2)	2.248(2)
S(1)-Cu(1)		2.475(2)	2.442(2)	2.444(2)
Cu(1)-Cl(1)		2.3706(18)	2.4301(14)	2.5809(11)
Cu(1)-Cl(1) ¹		2.395(2)	2.4630(16)	2.6055(12)
P(1)-C(1)-C(10)	124.07(13)	124.4(5)	124.1(6)	124.1(6)
C(1)-C(10)-C(9)	126.90(17)	127.7(5)	129.0(7)	129.1(7)
S(1)-C(9)-C(10)	123.11(13)	122.5(2)	121.4(5)	121.1(5)
	$\Sigma = 374.1$	$\Sigma = 374.6$	$\Sigma = 374.5$	$\Sigma = 374.3$
P(1)-Cu(1)-S(1)		81.55(6)	82.89(7)	81.52(7)
P(1)-Cu(1)-Cl(1) ¹		120.50(8)	116.52(9)	113.00(7)
Cl(1)-Cu(1)-Cl(1) ¹		102.26(6)	106.45(4)	113.15(3)
S(1)-Cu(1)-Cl(1)		108.23(7)	108.47(7)	106.70(6)
Distance from naphthalene mean plane				
P(1)	0.007	-0.229(8)	-0.196(9)	0.186(9)
S(1)	0.127	0.071(8)	0.111(9)	-0.09(1)
Torsion angle				
C(6)-C(5)-C(10)-C(1)	178.49(16)	179.4(11)	179.4(8)	179.0(7)
C(4)-C(5)-C(10)-C(9)	-179.51(16)	179.8(6)	179.7(7)	-179.0(7)

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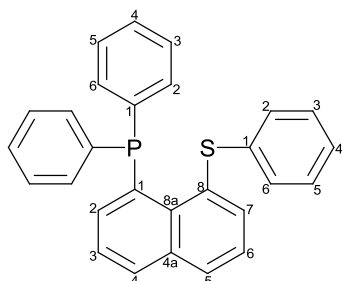
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- 9 Crystal data: For L Mercury CCD with Rigaku MM007 RA/confocal optics Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), 93K L C₂₈H₂₁PS, $M = 420.48$, monoclinic, space group $P2(1)/c$, $a = 11.1461(12)$, $b = 8.8914(10)$, $c = 21.587(2) \text{ \AA}$, $\beta = 90.837(4)^\circ$, $U = 2139.1(4) \text{ \AA}^3$, $Z = 4$, $D_c = 1.306 \text{ Mgm}^{-3}$, $\mu = 0.239 \text{ mm}^{-1}$, $F(000) = 880$. Of 13424 measured data, 3774 were unique ($R_{int} = 0.0325$) and 3348 observed ($I > 2\sigma(I)$) to give $R_1 = 0.0408$.

For **1-3** Saturn 724 robotic diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), 125K **1** $\text{C}_{56}\text{H}_{42}\text{P}_2\text{S}_2\text{Cu}_2\text{Cl}_2$, $M = 1039.01$, triclinic, space group $P-1$, $a = 10.1201(12)$, $b = 10.3276(13)$, $c = 11.6100(16) \text{ \AA}$, $\alpha = 77.472(9)$, $\beta = 81.445(10)$, $\gamma = 75.144(10)^\circ$, $U = 1139.4(3) \text{ \AA}^3$, $Z = 1$, $D_c = 1.514 \text{ Mgm}^{-3}$, $\mu = 1.252 \text{ mm}^{-1}$, $F(000) = 532$. Of 14126 measured data, 4557 were unique ($R_{int} = 0.068$) and 3967 observed ($I > 2\sigma(I)$) to give $R_1 = 0.0991$. **2** $\text{C}_{56}\text{H}_{42}\text{P}_2\text{S}_2\text{Cu}_2\text{Br}_2$, $M = 1127.29$, triclinic, space group $P-1$, $a = 10.218(2)$, $b = 10.400(3)$, $c = 11.690(3) \text{ \AA}$, $\alpha = 76.18(2)$, $\beta = 80.20(2)$, $\gamma = 74.909(18)^\circ$, $U = 1156.9(5) \text{ \AA}^3$, $Z = 1$, $D_c = 1.619 \text{ Mgm}^{-3}$, $\mu = 2.850 \text{ mm}^{-1}$, $F(000) = 568$. Of 12396 measured data, 3998 were unique ($R_{int} = 0.068$) and 3527 observed ($I > 2\sigma(I)$) to give $R_1 = 0.0858$. **3** $\text{C}_{56}\text{H}_{42}\text{P}_2\text{S}_2\text{Cu}_2\text{I}_2$, $M = 1221.92$, triclinic, space group $P-1$, $a = 10.3416(17)$, $b = 10.6256(13)$, $c = 11.988(2) \text{ \AA}$, $\alpha = 73.87(2)$, $\beta = 77.76(2)$, $\gamma = 73.326(18)^\circ$, $U = 1199.6(3) \text{ \AA}^3$, $Z = 1$, $D_c = 1.691 \text{ Mgm}^{-3}$, $\mu = 2.366 \text{ mm}^{-1}$, $F(000) = 604$. Of 13313 measured data, 4756 were unique ($R_{int} = 0.052$) and 4431 observed ($I > 2\sigma(I)$) to give $R_1 = 0.0684$. CCDC 737036 – 737039. For this data in .cif format, see http://www.rsc.org/suppdata/cc/*****/.

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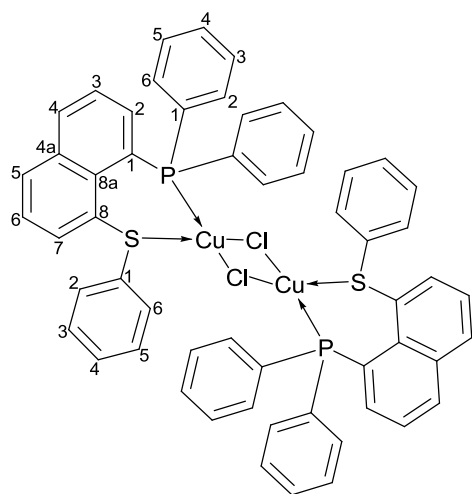
Supplementary Information: Details of the synthesis and spectroscopic data for **L** and **1-3**

(8-phenylsulfanyl)naphth-1-yl)diphenylphosphine L



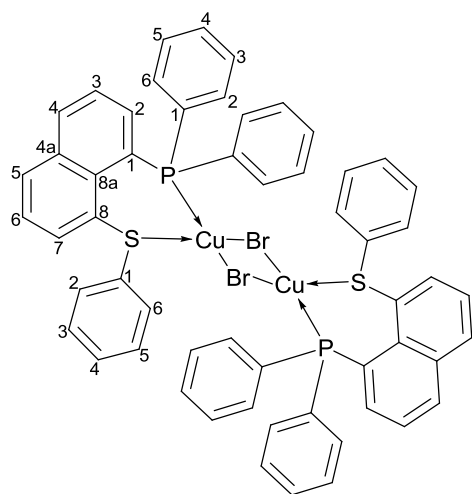
A solution of 2.5 M *n*-butyllithium in hexane (1.3 mL, 3.23 mmol) was transferred dropwise to a freshly prepared solution of 1-bromo-8-(phenylsulfanyl)naphthalene (1.019 g, 3.23 mmol) in diethyl ether (30 mL) at -10 – 0 °C (salted ice bath). The bright mixture was stirred for 2 h at this temperature, after which chlorodiphenylphosphine (0.713 g, 0.58 mL, 3.23 mmol) was added slowly. Stirring was continued for a further 2 h at -10 – 0 °C. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* and hexane (40 mL) was added to precipitate out unwanted salts. The solution was filtered under nitrogen and the solvent removed *in vacuo*. The crude yellow oil obtained was recrystallised from hexane. Yield 0.872 g (64 %); (Found: C, 79.67; H, 5.01; Calc. for C₂₈H₂₁PS: C, 79.98; H, 5.04 %); ν_{\max} (KBr tablet)/cm⁻¹: 3050s, 2963s, 1949w, 1884w, 1828w, 1579s, 1544s, 1472s, 1432vs, 1352w, 1308w, 1261vs, 1197s, 1092vs, 1021vs, 864w, 817vs, 801vs, 767vs, 740vs, 691vs, 592w, 539w, 499s, 474s, 424w, 387s; δ_{H} (270 MHz, CDCl₃) 7.93-7.81 (2 H, m, nap 4,5-H), 7.71 (1 H, d, *J* 1.5 Hz, nap 2-H), 7.45-7.36 (1 H, m, nap 3-H), 7.36-7.28 (1 H, m, nap 6-H), 7.26-7.13 (11 H, m, nap 2-H, 2 x *PPh*₂ 2-6-H), 7.09-6.97 (3 H, m, -*SPh* 3,4,5-H), 6.77-6.70 (2 H, m, -*SPh* 2,6-H); δ_{C} (67.9 MHz, CDCl₃) 140.0(q), 139.8(q), 137.6(s), 137.0(s), 135.6(q), 134.1(d, *J* 19.8 Hz), 132.2(q), 131.3(d, *J* 9.4 Hz), 130.9(s), 130.6(s), 128.6(s), 128.4(d, *J* 7.3 Hz), 128.1(d, *J* 3.1 Hz), 126.4(q), 125.9(s), 125.8(s), 125.4(s); δ_{P} (109.4 MHz, CDCl₃) -5.30; *m/z* (ES⁻) 459.20 ([M+K]⁺, 100 %).

(8-phenylsulfanyl)naphth-1-yl)diphenylphosphine copper chloride dimer 1.



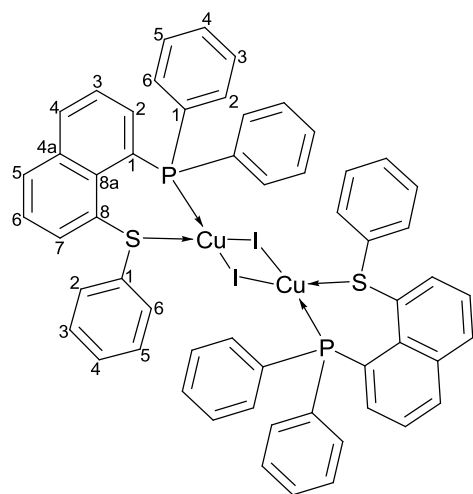
To a schlenk tube containing ligand (8-phenylthionaphth-1-yl)diphenylphosphine (0.678 g, 1.61 mmol) and CuCl (0.157 g, 1.61 mmol) was added dichloromethane (5 mL) and methanol (5 mL). The reaction was stirred for 2 h. Removal of the solvent and addition of hexane caused precipitation of excess CuCl. The excess salt was removed by filtration and the solvent was concentrated under reduced pressure. The oil was recrystallised from dichloromethane/pentane to give green crystalline needles. Yield 1.27 g (76 %); (Found: C, 50.70; H, 3.21; Calc. for $(C_{56}H_{42}P_2S_2Cu_2Cl_2)(CH_2Cl_2)_5$: C, 50.06; H, 3.58 %); ν_{max} (KBr tablet)/ cm^{-1} : 2957w, 2914w, 2859w, 2360vs, 2340vs, 2117w, 1771w, 1733w, 1715w, 1699w, 1651w, 1581w, 1476w, 1455w, 1435s, 1392w, 1360w, 1317w, 1261w, 1227w, 1185s, 1113s, 1066w, 1023w, 994w, 924w, 883w, 822s, 800w, 769w, 731s, 716s, 689s, 668s, 587w, 563s, 539s, 506w, 472w, 454w, 420w; δ_H (270 MHz, $CDCl_3$) 7.97 (1 H, d, J 8.2 Hz, nap 4-H), 7.90 (1 H, d, J 8.1 Hz, nap 5-H), 7.83 (1 H, dd, J 1.3 and 7.2 Hz, nap 7-H), 7.52-7.40 (6 H, m, nap 2,6-H, 2 x PPh_2 2,6-H), 7.32-7.23 (3 H, m, nap 3-H, 2 x PPh_2 4-H), 7.23-7.15 (4 H, m, 2 x PPh_2 3,5-H), 6.84-6.72 (3 H, m, SPh 3,4,5-H), 6.18-6.12 (2 H, m, SPh 2,6-H); δ_C (67.9 MHz, $CDCl_3$) 139.8(s) 138.4(d, J 12.4 Hz), 134.2(d, J 4.1 Hz), 131.2(d, J 9.3 Hz), 130.6(d, J 2.1 Hz), 128.2(s), 128.1(d, J 3.8 Hz), 127.1(s), 126.3(s), 124.6(s), 124.3(d, J 14.5 Hz); δ_P (109 MHz, $CDCl_3$) 27.78; m/z (ES^+) 903.10 ($[M-CuCl_2]^+$, 100 %).

(8-phenylsulfanyl)naphth-1-yl)diphenylphosphine copper bromide dimer 2.



To a schlenk tube containing ligand (8-phenylthionaphth-1-yl)diphenylphosphine (0.568 g, 1.35 mmol) and CuBr (0.388 g, 1.35 mmol) was added dichloromethane (5 mL) and methanol (5 mL). The reaction was stirred for 2 h. Removal of the solvent and addition of hexane caused precipitation of excess CuBr. The excess salt was removed by filtration and the solvent was concentrated under reduced pressure. The oil was recrystallised from dichloromethane/pentane to give green crystalline needles. Yield 0.9272 g (61 %); (Found: C, 57.47; H, 4.35; Calc. for $(C_{56}H_{42}P_2S_2Cu_2Br_2)_2CH_2Cl_2$: C, 57.98; H, 3.70 %); ν_{max} (KBr tablet)/ cm^{-1} : 2963w, 2853w, 2361vs, 2340vs, 2215w, 1944w, 1699w, 1651w, 1580w, 1558w, 1541w, 1475w, 1435s, 1318w, 1261s, 1184w, 1098s, 1023w, 993w, 925w, 883w, 821s, 802s, 768w, 731s, 689s, 587w, 563s, 540s, 506w, 419w; δ_H (270 MHz, $CDCl_3$) 7.98 (1 H, d, J 8.1 Hz, nap 4-H), 7.91 (1 H, d, J 8.1 Hz, nap 5-H), 7.84 (1 H, dd, J 1.2 and 7.2 Hz, nap 7-H), 7.56-7.39 (6 H, m, nap 2,6-H, 2 x PPh_2 2,6-H), 7.34-7.26 (3 H, m, nap 3-H, 2 x PPh_2 4-H), 7.26-7.15 (4 H, m, 2 x PPh_2 3,5-H), 6.86-6.74 (3 H, m, SPh 3,4,5-H), 6.20-6.12 (2 H, m, SPh 2,6-H); δ_C (67.9 MHz, $CDCl_3$) 139.8(s), 138.4(d, J 12.1 Hz), 134.2 (d, J 4.0 Hz), 131.2(s), 131.2(d, J 8.7 Hz), 130.6(d, J 2.9 Hz), 128.2(d, J 8.1 Hz), 128.1(s), 127.1(s), 126.3(s), 124.6(s), 124.3(d, J 14.4 Hz); δ_P (109 MHz, $CDCl_3$) 27.73; m/z (ES^+) 903.23 ($[M-CuBr_2]^+$, 3%), 299.18 ($[C_{10}H_6SPhCu]^+$, 100 %).

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper iodide dimer 3.



To a schlenk tube containing ligand (8-phenylthionaphth-1-yl)diphenylphosphine (0.524 g, 1.25 mmol) and CuI (0.238 g, 1.25 mmol) was added dichloromethane (5 mL) and methanol (5 mL). The reaction was stirred for 2 h. Removal of the solvent and addition of hexane caused precipitation of excess CuI. The excess salt was removed by filtration and the solvent was concentrated under reduced pressure. The oil was recrystallised from dichloromethane/pentane to give green crystalline needles. Yield 0.471 g (31 %); (Found: C, 53.85; H, 3.50; Calc. for $(C_{56}H_{42}P_2S_2Cu_2I_2)_2CH_2Cl_2$: C, 53.67; H, 3.42 %); ν_{max} (KBr tablet)/ cm^{-1} : 3417w, 3050w, 2346w, 1956w, 1881w, 1806w, 1656w, 1548s, 1477s, 1433vs, 1358s, 1308s, 1196w, 1142w, 1095s, 1060w, 1023s, 998w, 980w, 912w, 816vs, 764s, 748vs, 689vs, 613w, 561w, 529s, 512vs, 490s, 440w; δ_H (270 MHz, $CDCl_3$) 7.98 (1 H, d, J 8.1 Hz, nap 4-H), 7.91 (1 H, d, J 8.1 Hz, nap 5-H), 7.84 (1 H, dd, J 1.3 and 7.2 Hz, 7-H), 7.55-7.42 (6 H, m, nap 2,6-H, 2 x PPh_2 2,6-H), 7.35-7.25 (3 H, m, nap 3-H, 2 x PPh_2 4-H), 7.25-7.16 (4 H, m, 2 x PPh_2 3,5-H), 6.86-6.74 (3 H, m, SPh 3,4,5-H), 6.20-6.13 (2 H, m, SPh 2,6-H); δ_C (67.9 MHz, $CDCl_3$) 139.9(s), 138.3(d, J 19.8 Hz), 134.6 (d, J 3.1 Hz), 131.4(s), 131.2(s), 130.6(d, J 3.1 Hz), 128.3(s), 128.12(d, J 4.1 Hz), 127.1(s), 126.4(s), 124.7(s), 124.4(d, J 17.7 Hz); δ_P (109 MHz, $CDCl_3$) 28.68; m/z (ES⁺) 903.20 ($[M-CuI_2]^+$, 1%), 299.19 ($[C_{10}H_6SphCu]^+$, 100 %).

INDEX ENTRY

In the binuclear copper complexes $\text{Cu}_2\text{X}_2\text{L}_2$ the Cu...Cu separation decreases on going from Cl to I.

