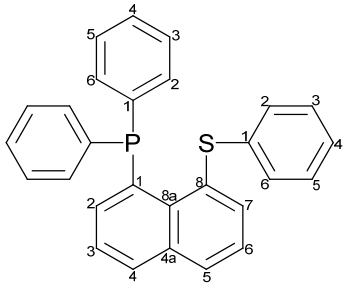
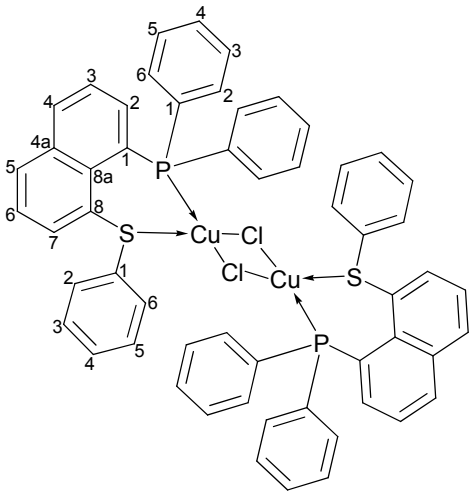
Supplementary Information: Details of the synthesis and spectroscopic data for **L** and **1-3**

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine **L**



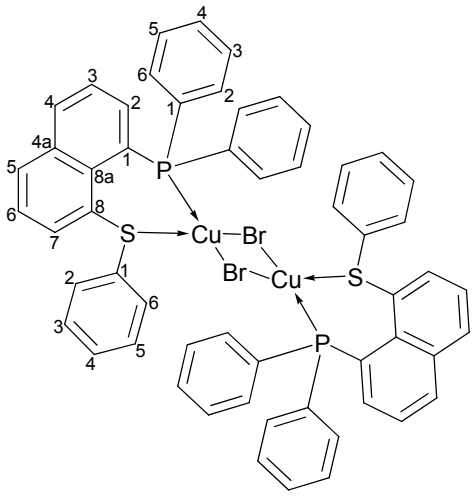
A solution of 2.5 M *n*-butyllithium in hexane (1.3 mL, 3.23 mmol) was transferred dropwise to a freshly prepared solution of 1-bromo-8-(phenylsulfanyl)naphthalene (1.019 g, 3.23 mmol) in diethyl ether (30 mL) at -10 – 0 ^{o}C (salted ice bath). The bright mixture was stirred for 2 h at this temperature, 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 ^{o}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 $C_{28}H_{21}PS$: C, 79.98; H, 5.04 %); $^{v}_{max}$ (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, $CDCl_3$) 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 P*Ph*$_2$ 2-6-H), 7.09-6.97 (3 H, m, -S*Ph* 3,4,5-H), 6.77-6.70 (2 H, m, -S*Ph* 2,6-H); δ_C (67.9 MHz, $CDCl_3$) 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, $CDCl_3$) -5.30; *m/z* (ES$^-$) 459.20 ([M+K]$^+$, 100 %).

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper chloride dimer 1.



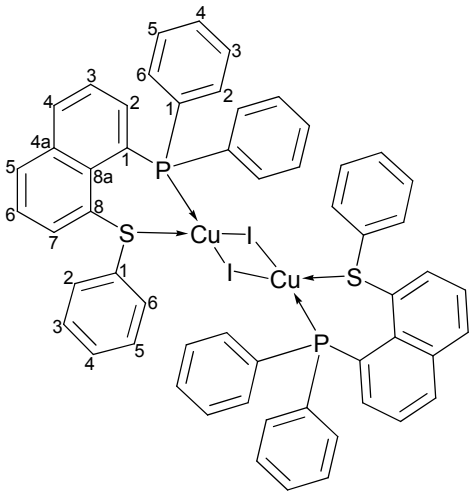
To a schlenk tube containing ligand (8-phenylthionaphth-1-yl)diphenylphosphine (0.678 g, 1.61 mmol) and CuCl (0.157 g, 1.61 mmol) was added dichloromethane (5 mL) and methanol (5 mL). The reaction was stirred for 2 h. Removal of the solvent and addition of hexane caused precipitation of excess CuCl. 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 P*Ph*$_2$ 2,6-H), 7.32-7.23 (3 H, m, nap 3-H, 2 x P*Ph*$_2$ 4-H), 7.23-7.15 (4 H, m, 2 x P*Ph*$_2$ 3,5-H), 6.84-6.72 (3 H, m, S*Ph* 3,4,5-H), 6.18-6.12 (2 H, m, S*Ph* 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 ($[M\text{-}CuCl_2]^+$, 100 %).

(8-phenylsulfanylnaphth-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 P*Ph*$_2$ 2,6-H), 7.34-7.26 (3 H, m, nap 3-H, 2 x P*Ph*$_2$ 4-H), 7.26-7.15 (4 H, m, 2 x P*Ph*$_2$ 3,5-H), 6.86-6.74 (3 H, m, S*Ph* 3,4,5-H), 6.20-6.12 (2 H, m, S*Ph* 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 ($[M\text{-}CuBr_2]^+$, 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 P*Ph*$_2$ 2,6-H), 7.35-7.25 (3 H, m, nap 3-H, 2 x P*Ph*$_2$ 4-H), 7.25-7.16 (4 H, m, 2 x P*Ph*$_2$ 3,5-H), 6.86-6.74 (3 H, m, S*Ph* 3,4,5-H), 6.20-6.13 (2 H, m, S*Ph* 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 ($[M\text{-}CuI_2]^-$, 1%), 299.19 ($[C_{10}H_6SphCu]^+$, 100 %).