Supplementary Material for Chemical Communications

Supplementary Information

Reactions of P/S-containing proligands with coinage metal salts: a new route to polynuclear complexes with unusual structural types

Experimental

compound 1

A mixture of Lawesson's reagent 202 mg (0.50 mmol) and AgOAc 334 mg (2.00 mmol) was dissolved in 10 mL THF. The mixture was stirred for about 3 hours at room temperature, during which time the formation of a grey-yellow precipitate was observed. The mixture was filtered and the residue was dissolved by addition of a solution of dppm (0.26 M in thf, 7.2 mL). Solvent diffusion within a double-Schlenck tube of Et_2O (0 ºC) into the reaction mixture (RT) produced orange crystals of **1** after 7 days. 0.58 g, yield 51%. mp 149 ºC (decomposed, black solid); Found: C, 56.87; H, 4.63. $C_{114}H_{102}Ag_4O_4P_{10}S_4$ requires C, 56.92; H, 4.27 %; ν_{max}/cm^{-1} (KBr) 3051s, 2859s (CH_3O), 1592s, 1431s (P-C), 1241s, 1090s and 692s (P=S); δ_H (400 MHz; $CDCl_3$; 25 ºC) 1.25 (14H, t, *J* 7.2, 4.7 × $OCH_2\mathit{CH_3}$), 1.90 (14H, m, 3.5 × $OCH_2\mathit{CH_2}$), 3.52 (17H, t and br, s, *J* 7.2, 4.7 × $O\mathit{CH_2}CH_3$ and 4 × P-CH_2-P), 3.77-3.80 (14H, m, 3.5 × $O\mathit{CH_2}CH_2$), 6.90-7.05 (84H, m, ArH), 8.54 (4H, m, ArH); δ_P(162 MHz; $CDCl_3$; 25 ºC; 65% H_3PO_4) 66.7, -6.5 (br, s, dppm).

compound 2

A mixture of Lawesson's reagent 202 mg (0.50 mmol) and AgOAc 334 mg (2.00 mmol) was dissolved in 10 mL THF. The mixture was stirred for about 3 hours at room temperature, during which time the formation of a grey-yellow precipitate was observed. The mixture was filtered and the residue was dissolved by addition of a solution of PPh_3 (0.4 M in thf, 6 mL). Solvent diffusion within a double-Schlenck tube of Et_2O (0 ºC) into the reaction mixture (RT) produced orange crystals of **2** after 7 days. 0.33g, yield 52%. mp 140 ºC (decomposed, black solid); Found: C, 40.18; H, 2.95. $C_{300}H_{264}Ag_{28}O_{24}P_{24}S_{26}$ requires C, 40.71; H, 3.01 %; ν_{max}/cm^{-1} (KBr) 3043m, 2830w (CH_3O), 1592s, 1433s (P-C), 1245s, 1093s and 691s (P=S); δ_H (400 MHz; $CDCl_3$; 25 ºC) 1.25 (15H, t, *J* 7.2, 5 × $OCH_2\mathit{CH_3}$), 1.90 (20H, m, 5 × $OCH_2\mathit{CH_2}$), 3.52 (12H, t, *J* 7.2, 5 × $O\mathit{CH_2}CH_3$), 3.67-3.85 (56H, m, 5 × $O\mathit{CH_2}CH_2$ and 12 × $O\mathit{CH_3}$), 6.79-6.92 (24H, m, ArH), 7.26 (180H, br, P*Ph*$_3$) and 7.80-7.93 (24H, m, ArH); δ_P(162 MHz; $CDCl_3$; 25 ºC; 65% H_3PO_4) 72.1, 68.7, 2.4 (br, s, PPh_3).
Byproducts like Ac_2O or $[ArPOS]_3$ were found and characterised in similar reactions (see ref. 11 and 12 for details).

compound 3

A mixture of P_2S_5 111 mg (0.50 mmol), Cu^{t}OBu 137 mg (1.00 mmol) and PPh_3 524 mg (2.00 mmol) was dissolved in 10 mL Toluene. The resulting yellow solution was heated to 40~50ºC for about 3 hours. Storage of the yellow solution at 0ºC for 4 weeks produced colorless crystals of **3**. 0.05 g, yield 17%. mp 134 ºC (decomposed, brown solid); Found: C, 58.01; H, 4.65. $C_{80}H_{78}Cu_3O_4P_7S_6(+C_7H_8O)$ requires C, 57.68; H, 4.79 %; ν_{max}/cm^{-1} (KBr) 3047m, 2970w, 1584w, 1433s (P-C), 1093s, 868s (P-O-P) and 689s (P=S); δ_H (400 MHz; d_8-Toluene; 25 ºC) 1.60 (18H, s, 2 × $OC\mathit{(CH_3)_3}$), 6.96-7.46 (60H, m, ArH); δ_P(162 MHz; $CDCl_3$; 25 ºC; 65% H_3PO_4) 59.9, 42.6, -2.9 (br, s, PPh_3).