Supplementary Material (ESI) for Chemical Communications

Anion-templated syntheses of octanuclear silver clusters from a silver dithiophosphate chain

How-Wei Chang, Ching-Shiang Fang, Bijay Sarkar, Ju-Chun Wang, and C. W. Liu*

Department of Chemistry, National Dong Hwa University, Hualien, Taiwan 97401, R. O. C. Fax: +886-3-863 3570; Tel: +886-3-863 3608; E-mail: chenwei@mail.ndhu.edu.tw

Experimental Details

All the solvents *viz.* acetone, dichloromethane, THF were purchased from Mallinckrodt Chemicals and purified before use following standard procedures. Other reagent grade chemicals were purchased from Aldrich and used without further purification. All the reactions were carried out under inert atmosphere using Schlenk apparatus. Elemental analyses were done using a Heraeus VarioEL-III CNH analyzer. Multinuclear (^{1}H, ^{31}P) NMR spectra were recorded with a Bruker Advance DPX300 FT-NMR spectrometer. The NMR spectrometer was operating at 300.130 MHz for recording ^{1}H NMR spectra whereas it was operating at 121.495 MHz for ^{31}P NMR. The ^{31}P{^{1}H} NMR spectra were referenced externally against 85% H_3PO_4 ($\delta = 0$ ppm). $NH_4S_2P(O^iPr)_2$ was prepared by following the method reported by Wystrach (*J. Org. Chem.*, 1956, **21**, 705) whereas $NH_4S_2P(OEt)_2$ was obtained from Aldrich.

Synthesis

$[Ag_5\{S_2P(OEt)_2\}_4]_n(PF_6)_n$, 1. $[Ag(CH_3CN)_4](PF_6)$ (0.534 g, 1.28 mmol) and $NH_4[S_2P(OEt)_2]$ (0.196 g, 0.96 mmol) were charged in a 100 ml flask and 20 ml of THF was added to it. The solution was stirred at -20 °C for 1 h. Then it was then filtered to get rid of any solid and the filtrate was evaporated to dryness under a vacuum. The solid obtained, was washed with deionized water to remove any NH_4PF_6 formed during the reaction and dried under a vacuum to obtain $\{Ag_5[S_2P(OEt)_2]_4\}_n(PF_6)_n$ as a light-yellow powder. Yield: 0.28 g (80%). Mp. 72.8°C. Anal. calcd for $Ag_5H_{40}C_{16}O_8P_5F_6S_8{\cdot}3H_2O$: C, 12.99; H, 3.13. Found: C, 12.99; H, 2.94 %. ^1H NMR (acetone-d_6): 1.40 (t, $^3J_{HH}$ = 6.99 Hz, 24 H, CH_3), 4.33 (m, 16 H, CH); ^{31}P NMR (acetone-d_6): 103.9.

$[Ag_8(\mu_8\text{-}F)\{S_2P(OEt)_2\}_6](PF_6)$, 2. $[Ag(CH_3CN)_4](PF_6)$ (0.534 g, 1.28 mmol) and $NH_4[S_2P(OEt)_2]$ (0.196 g, 0.96 mmol) were charged in a 100 ml flask and 20 mL of THF was added to it. The solution was stirred at -20 °C for 1 h. Then, added tetrabutylammonium fluoride ($Bu_4NF.xH_2O$)) (0.04, 0.16 mmol) to the flask and stirring was continued for 12h. It was then filtered to get rid of any solid, and the filtrate was evaporated to dryness under a vacuum. The solid was washed with deionized water to remove any NH_4PF_6 formed during the reaction and dried under a vacuum to obtain $[Ag_8(F)\{S_2P(OEt)_2\}_6](PF_6)$ as a white powder. Yield: 0.09 g (25%). Mp. 137 °C. Anal. calcd for $C_{24}H_{60}Ag_8F_7O_{12}P_7S_{12}{\cdot}THF$: C, 15.21; H, 3.10. Found: C, 15.34; H, 3.28%. NMR (acetone-d_6): 1.4(t, $^3J_{HH}$ = 7.0Hz, 36H, CH_3), 4.3 (m, 24H, CH_2); ^{31}P NMR (acetone-d_6): 104.5, -143.0 (septet, PF_6). ^{19}F NMR (acetone-d_6): -72.35 (d, $^1J_{PF}$ = 707.7 Hz, PF_6), -150.46 (Ag-F).

$[Ag_8(\mu_8\text{-}Cl)\{S_2P(OEt)_2\}_6](PF_6)$, 3. $[Ag(CH_3CN)_4](PF_6)$ (0.536 g, 1.28 mmol) and $NH_4[S_2P(OEt)_2]$ (0.196 g, 0.96 mmol) were charged in a 100 ml flask and 20 mL of THF was added to it. The solution was stirred at -20 °C for 1 h. Then, added benzyltriethylammonium chloride (0.037 g, 0.16 mmol) to the flask and stirring was continued for 12h. It was then filtered to get rid of any solid, and the filtrate was evaporated to dryness under a vacuum. The solid was washed with deionized water to remove any NH_4PF_6 formed during the reaction and dried under a vacuum to obtain $[Ag_8(Cl)\{S_2P(OEt)_2\}_6](PF_6)$ as a yellow powder. Yield: 0.26 g (74 %). Mp. 122 °C. Anal. calcd for $C_{24}H_{60}Ag_8ClF_6O_{12}P_7S_{12}\cdot 2THF$: C, 16.72; H, 3.33. Found: C, 16.33; H, 3.36 %. ^1H NMR (acetone-d_6): 1.37 (t, $^3J_{HH}$ = 6.99 Hz, 36H, CH_3), 4.30 (m, 24H, CH_2); ^{31}P NMR (acetone-d_6): 106.8, -143.0 (septet, PF_6).

$[Ag_8(\mu_4\text{-}H)\{S_2P(OEt)_2\}_6](PF_6)$, 4. $[Ag(CH_3CN)_4](PF_6)$ (0.547 g, 1.31 mmol) and $NH_4[S_2P(OEt)_2]$ (0.200 g, 0.98 mmol) were charged in a 100 ml flask and 20 mL of THF was added to it. The solution was stirred at -20 °C for 1 h. $NaBH_4$ (0.006 g, 0.16 mmol) was added to this solution and stirred for 30 min more. It was then filtered to get rid of any solid, and the filtrate was evaporated to dryness under a vacuum. The solid was purified with CH_2Cl_2 and dried under a vacuum to obtain $\{Ag_8(H)[S_2P(OEt)_2]_6\}(PF_6)$ as a light-brown powder. Yield: 0.20g (57%). Mp. 149.°C. Anal. calcd for $C_{24}H_{61}Ag_8F_6O_{12}P_7S_{12}$: C, 13.60; H, 2.90. Found: C, 13.84; H, 3.19 %. ^1H NMR (acetone-d_6): 1.34 (t, $^3J_{HH}$ = 15.93 Hz, 36H, CH_3), 4.20 (m, 24H, OCH_2), 5.60 (bs, 1H, μ_4-H); ^{31}P NMR (acetone-d_6): 109.5, -143.0 (septet, PF_6). ^{109}Ag NMR (acetone-d_6):1108.3 (d, $^1J_{AgH}$ = 29.4 Hz).

$[Ag_8(D)\{S_2P(OEt)_2\}_6](PF_6)$, 4'. This was synthesized in a similar procedure described for **5a** using $NaBD_4$ instead of $NaBH_4$. Yield: 0.18 g (51.43%). Mp. 140.4 °C. Anal. calcd for $C_{24}H_{60}DAg_8F_6O_{12}P_7S_{12}$: C, 13.59; H, 2.95. Found: C, 13.85; H, 3.15 %. ^1H NMR (acetone-d_6): 1.3 (t, $^3J_{HH}$ = 6.33 Hz, 36H, CH_3), 4.2(m, 24H, OCH_2). ^2H NMR (acetone-d_6): 5.53. ^{31}P NMR (acetone-d_6): 110.1 (s, F), -143.0 (septet, PF_6).