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

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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 (¹H, ³¹P) NMR spectra were recorded with a Bruker Advance DPX300 FT-NMR spectrometer. The NMR spectrometer was operating at 300.130 MHz for recording ¹H NMR spectra whereas it was operating at 121.495 MHz for ³¹P NMR. The ³¹P{¹H} NMR spectra were referenced externally against 85% H₃PO₄ (δ = 0 ppm). NH₄S₂P(O'Pr)₂ was prepared by following the method reported by Wystrach (J. Org. Chem., 1956, 21, 705) whereas NH₄S₂P(OEt)₂ was obtained from Aldrich.

Synthesis
[Ag₅{S₂P(OEt)₂}₄]₄PF₆, 1. [Ag(CH₃CN)₄](PF₆) (0.534 g, 1.28 mmol) and NH₄[S₂P(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 NH₄PF₆ formed during the reaction and dried under a vacuum to obtain {Ag₅[S₂P(OEt)₂]₄}₄PF₆ as a light-yellow powder. Yield: 0.28 g (80%). Mp. 72.8 °C. Anal. calcd for Ag₅H₄O₁₆C₁₆O₈P₅F₆S₈·3H₂O: C, 12.99; H, 3.13. Found: C, 12.99; H, 2.94 %. ¹H NMR (acetone-d₆): 1.40 (t, ³J_HH = 6.99 Hz, 24 H, C₆H₃), 4.33 (m, 16 H, C₆H₂); ³¹P NMR (acetone-d₆): 103.9.

[Ag₈(μ₈-F){S₂P(OEt)₂}₆](PF₆), 2. [Ag(CH₃CN)₄](PF₆) (0.534 g, 1.28 mmol) and NH₄[S₂P(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 (Bu₄NF·xH₂O) (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 NH₄PF₆ formed during the reaction and dried under a vacuum to obtain [Ag₈(F){S₂P(OE)₂}₆](PF₆) as a white powder. Yield: 0.09 g (25%). Mp. 137 °C. Anal. calcd for C₂₄H₆₀Ag₈F₁₂P₁₂S₁₂·THF: C, 15.21; H, 3.10. Found: C, 15.34; H, 3.28%. NMR (acetone-d₆): 1.4(t, ³J_HH = 7.0Hz, 36H, CH₃), 4.3 (m, 24H, CH₂); ³¹P NMR (acetone-d₆): 104.5, -143.0 (septet, PF₆). ¹⁹F NMR (acetone-d₆): -72.35 (d, ¹J_PF = 707.7 Hz, PF₆), -150.46 (Ag-F).

[Ag₈(μ₈-Cl){S₂P(OEt)₂}₆](PF₆), 3. [Ag(CH₃CN)₄](PF₆) (0.536 g, 1.28 mmol) and NH₄[S₂P(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

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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$_4$PF$_6$ formed during the reaction and dried under a vacuum to obtain [Ag$_8$(Cl){S$_2$P(OEt)$_2$}]$_6$(PF$_6$) as a yellow powder. Yield: 0.26 g (74 %). Mp. 122 $^\circ$C. Anal. calcd for C$_{24}$H$_6$OAg$_8$ClF$_6$O$_{12}$P$_7$S$_{12}$·2THF: C, 16.72; H, 3.33. Found: C, 16.33; H, 3.36 %.

$^1$H NMR (acetone-d$_6$): 1.37 (t, $^3$J$_{HH}$ = 6.99 Hz, 36H, C$_3$H$_3$), 4.30 (m, 24H, OC$_2$H$_2$); $^{31}$P NMR (acetone-d$_6$): 106.8, -143.0 (septet, PF$_6$).

[Ag$_6$(μ$_4$-H){S$_2$P(OEt)$_2$}]$_6$(PF$_6$)$_4$. [Ag(CH$_3$CN)$_4$](PF$_6$) (0.547 g, 1.31 mmol) and NH$_4$[S$_2$P(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 $^\circ$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$_2$Cl$_2$ and dried under a vacuum to obtain {Ag$_8$(H){S$_2$P(OEt)$_2$}]$_6$(PF$_6$) as a light-brown powder. Yield: 0.20 g (57%). Mp. 149 $^\circ$C. Anal. calcd for C$_{24}$H$_6$OAg$_8$F$_6$O$_{12}$P$_7$S$_{12}$: C, 13.60; H, 2.90. Found: C, 13.84; H, 3.19 %.

$^1$H NMR (acetone-d$_6$): 1.34 (t, $^3$J$_{HH}$ = 15.93 Hz, 36H, C$_3$H$_3$), 4.20 (m, 24H, OC$_2$H$_2$), 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, $^1$J$_{AgH}$ = 29.4 Hz).

[Ag$_6$(D){S$_2$P(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 $^\circ$C. Anal. calcd for C$_{24}$H$_6$DAg$_8$F$_6$O$_{12}$P$_7$S$_{12}$: C, 13.59; H, 2.95. Found: C, 13.85; H, 3.15 %. $^1$H NMR (acetone-d$_6$): 1.3 (t, $^3$J$_{HH}$ = 6.33 Hz, 36H, C$_3$H$_3$), 4.2 (m, 24H, OCH$_2$)$_2$. $^2$H NMR (acetone-d$_6$): 5.53. $^{31}$P NMR (acetone-d$_6$): 110.1 (s, F), -143.0 (septet, PF$_6$).