Electronic Supplementary Material (ESI) for ChemComm.

N-Heterocyclic Carbene Stabilized Ag-P Nanoclusters

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Supporting Information

Detailed Experimental

$[Ag_{12}(PSiMe_3)_6(^iPr_2\text{-bimy})_6]$ (1): $(^iPr_2\text{-bimy})_2AgOAc$ (0.35 g, 0.60 mmol) was dissolved in 25 ml of diethyl ether and cooled to -67 °C. $P(SiMe_3)_3$ (0.09 ml, 0.30 mmol) was added at -67 °C. The solution was stirred as the acetone-dry ice bath warmed gradually to -25 °C. The clear red solution was stirred for ~30 min at this temperature and then kept at -25 °C over night. This solution was layered with cold pentane for crystallization at -25 °C. Orange crystals of **1** formed after a few days beside some black powder. Yield: ~ 10 %.
$[Ag_{26}P_2(PSiMe_3)_{10}(^iPr_2\text{-bimy})_8]$ (2): $(^iPr_2\text{-bimy})_2AgOAc$ (0.37 g, 0.65 mmol) was dissolved in 25 ml of THF and cooled to -67 °C. $P(SiMe_3)_3$ (0.09 ml, 0.30 mmol) was added at -67 °C. The solution was stirred as the acetone-dry ice bath warmed gradually to -25 °C. The clear dark-red solution was stirred for ~30 min at this temperature and then kept at -25 °C over night. The solvent was removed cold *in vacuo* and 25 ml of diethyl ether was added to dissolve the solid. This solution was layered with cold pentane for crystallization at -25 °C. Dark-red crystals of **2** formed after two weeks beside some black powder. Yield: ~ 5 %.

EDX Analysis

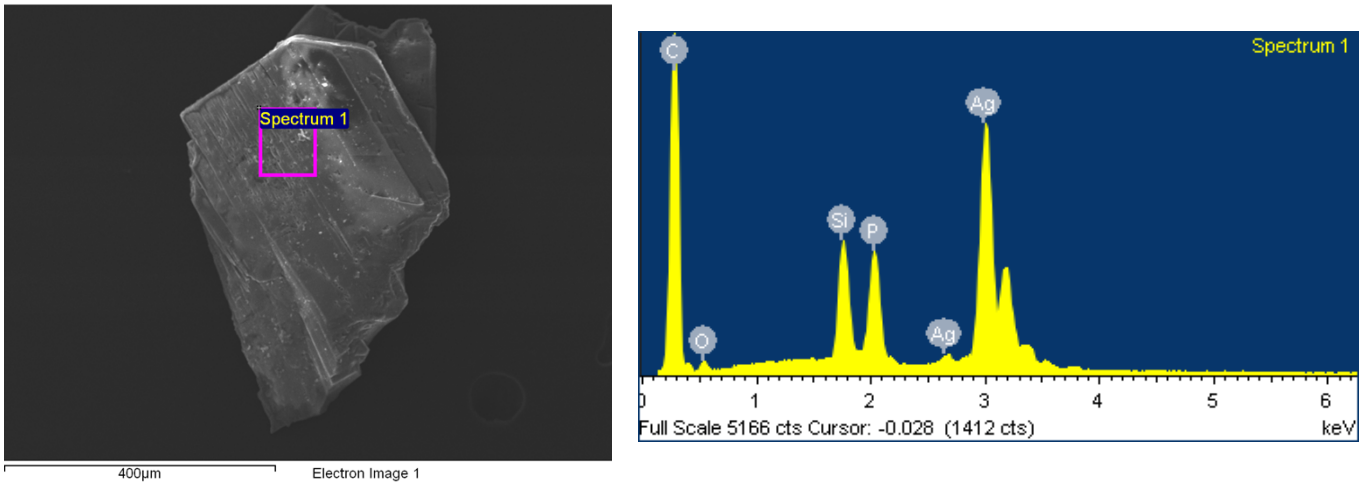

Figure S1. SEM image (left) and EDX spectrum (right) for the crystals of $[Ag_{12}(PSiMe_3)_6(^iPr_2\text{-bimy})_6]$ (**1**). Similar spectra were collected over three areas and the average Ag/P/Si ratios obtained are tabulated below.

	Ag/P	P/Si
Calculated	2.0	1.00
Observed	1.80	0.99

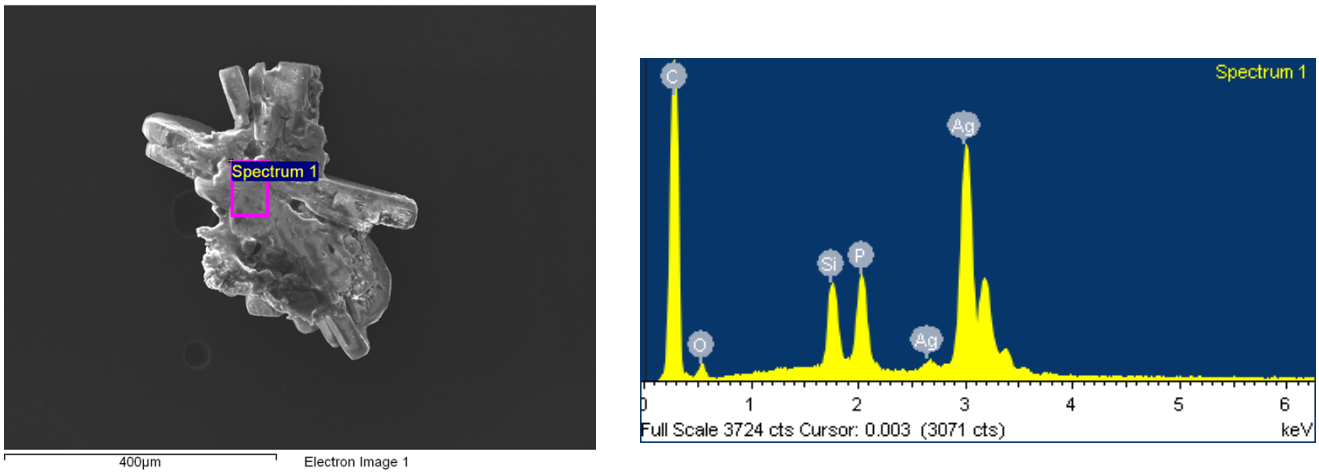

Figure S2. SEM image (left) and EDX spectrum (right) for the crystals of $[Ag_{26}P_2(PSiMe_3)_{10}(^iPr_2\text{-bimy})_8]$ (**2**). Similar spectra were collected over three areas and the average Ag/P/Si ratios obtained are tabulated below.

	Ag/P	P/Si
Calculated	2.16	1.20
Observed	2.04	1.18

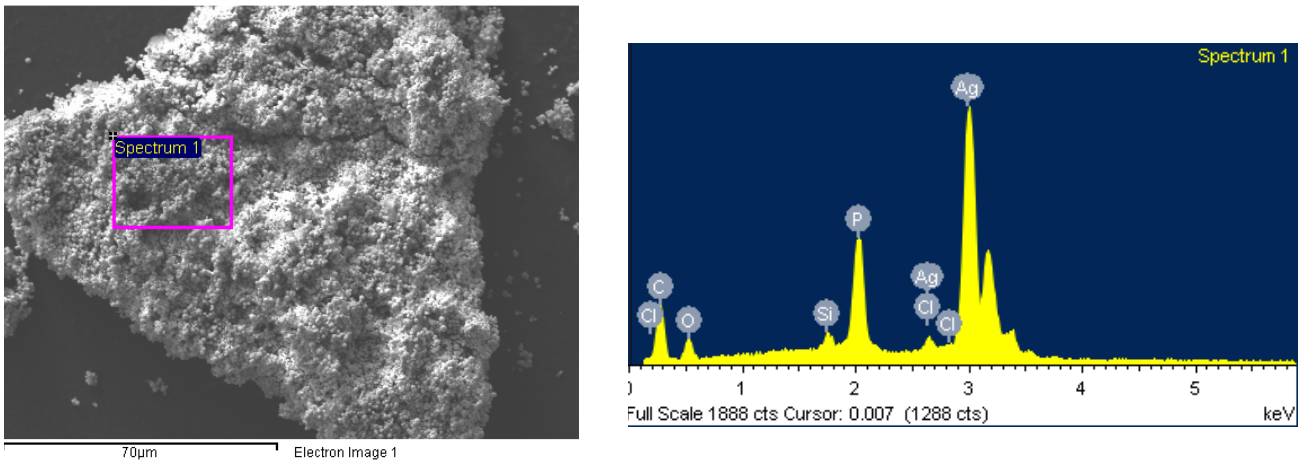

Figure S3. SEM image (left) and EDX spectrum (right) for the black powder. Similar spectra were collected over three areas and the average Ag/P ratios obtained are tabulated below.

	Ag/P
Calculated	3.00
Observed	2.75

Table S1*. Summary of Crystal Data for *1

Formula	$C_{98}H_{167}Ag_{12}N_{12}O_{0.50}P_6Si_6$
Formula Weight (*g/mol*)	3170.23
Crystal Dimensions (*mm*)	0.154 × 0.117 × 0.040
Crystal Color and Habit	orange plate
Crystal System	monoclinic
Space Group	P 2_1
Temperature, K	110(2)
a, Å	15.889(8)
b, Å	18.207(12)
c, Å	23.994(15)
α,°	90
β,°	95.206(15)
γ,°	90
V, Å^3	6913(7)
Number of reflections to determine final unit cell	9878
Min and Max 2θ for cell determination, °	4.66, 39.56
Z	2
F(000)	3162
ρ (*g/cm*)	1.523
λ, Å, (MoKα)	0.71073
μ, (*cm^{-1}*)	1.821
Diffractometer Type	Bruker APEX-II CCD
Max 2θ for data collection, °	51.414
Measured fraction of data	0.932
Number of reflections measured	64639
Unique reflections measured	22050
R_{merge}	0.0616
Number of reflections included in refinement	22050
Cut off Threshold Expression	I > 2sigma(I)
Structure refined using	full matrix least-squares using F^2
Weighting Scheme	$w=1/[sigma^2(Fo^2)+(0.0624P)^2+10.4038P]$ where $P=(Fo^2+2Fc^2)/3$
Number of parameters in least-squares	1245
Flack parameter	0.29(5)
R_1	0.0572
wR_2	0.1149
GOF	1.024
Maximum shift/error	0.041
Min & Max peak heights on final ΔF Map (*e$^-$*/Å)	-0.996, 1.259

Table S2*. Summary of Crystal Data for *2

Formula	$C_{141}H_{250.80}Ag_{26}N_{16}P_{12}Si_{10}$
Formula Weight (*g/mol*)	5627.52
Crystal Dimensions (*mm*)	0.119 × 0.113 × 0.005
Crystal Color and Habit	red plate
Crystal System	triclinic
Space Group	P $\bar{1}$
Temperature, K	150(2)
a, Å	17.285(4)
b, Å	20.433(5)
c, Å	29.512(8)
α,°	95.465(12)
β,°	91.603(9)
γ,°	90.317(19)
V, Å^3	10371(4)
Number of reflections to determine final unit cell	9762
Min and Max 2θ for cell determination, °	5.08, 49.24
Z	2
F(000)	5502
ρ (*g/cm*)	1.802
λ, Å, (MoKα)	0.71073
μ, (*cm^{-1}*)	2.582
Diffractometer Type	Bruker APEX-II CCD
Max 2θ for data collection, °	49.556
Measured fraction of data	0.933
Number of reflections measured	128323
Unique reflections measured	35023
R_{merge}	0.0846
Number of reflections included in refinement	35023
Cut off Threshold Expression	I > 2sigma(I)
Structure refined using	full matrix least-squares using F^2
Weighting Scheme	$w=1/[sigma^2(Fo^2)+(0.0545P)^2+25.1214P]$ where $P=(Fo^2+2Fc^2)/3$
Number of parameters in least-squares	1940
R_1	0.0555
wR_2	0.1142
GOF	1.016
Maximum shift/error	0.001
Min & Max peak heights on final ΔF Map (*e$^-$*/Å)	-0.866, 2.185

Where:

$R_1 = \Sigma(|F_o| - |F_c|) / \Sigma F_o$

$wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w F_o^4)]^{½}$

$GOF = [\Sigma(w(F_o^2 - F_c^2)^2) / (\text{No. of reflns.} - \text{No. of params.})]^{½}$