Stibine-Protected Au₁₃ Nanoclusters: Synthesis, Properties and Facile Conversion to GSH-Protected Au₂₅ Nanocluster

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Experimental

All solvents and reagents including HAuCl₄·3H₂O, Me₂S, SbPh₃, NaBH₄, FeCl₃, I₂, K₃[Fe(CN)₆], CuSO₄ and AgNO₃ were commercially available and used as received. KI₃ aqueous solution was prepared from I₂ and KI. Stibine ligands Sb(p-tolyl)₃ and Sb(Mes)₃,¹ complexes Me₂SAuCl² and (Mes)₃SbAuCl (1c)³ and ferrocenium picrate⁴ were prepared according to literature methods. UV-Vis absorption spectra were recorded on a Shimadzu UV-1800 Spectrophotometer and the peak integrations were directly obtained by the area integration function embedded in the UV Probe software. Fluorescence spectra were taken on a Varian Cary Eclipse fluorescence spectrophotometer in 1.00x 1.00 cm quartz glass cells. NMR spectra were recorded on a JEOL ECA400 SL NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm. The ¹H and ¹³C NMR chemical shifts were referenced to the residual proton resonance and the ¹³C resonance of the deuterated solvents used; the ³¹P, ¹¹B and ¹⁹F chemical shifts were referenced to external 85% aq. H₃PO₄, 15% (v/v) BF₃.OEt₂ in CDCl₃ and neat CFCl₃, respectively. Mass spectra were recorded on a UPLC-Q-TOF mass spectrometer using electrospray ionization mode (ESI). The elemental analysis was performed on a Perkin-Elmer 2400 Series II analyzer. TGA measurement was performed on a TGA-Q500 thermogravimetric analyzer at a heating rate of 10 °C/min under N₂ purge (60 ml/min).

Preparation of Au(L)Cl (L = Ph₃Sb, 1a; (*p***-tolyl)₃Sb, 1b): To the solution of Me₂SAuCl (120 mg, 0.41 mmol) in DCM (10 mL), a solution of SbPh₃ (140 mg, 0.40 mmol) in DCM (2 mL) was dropwise added. The resulting solution was stirred at room temperature in dark for 80 mins. Afterwards, the almost colorless reaction mixture was quickly filtered to remove small amount of decomposition products. The solvent of the filtrate was removed by rotary evaporator to give the product 1a** as a white solid, which was pure-enough for subsequent use. Analogue **1b** was prepared in the same way. **1a**: ¹H

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² M.-C. Brandys, M. C. Jennings, R. J. Puddephatt, J. Chem. Soc. Dalton 2000, 4601-4606

³ V. R. Bojan, E. J. Fernandez, A. Laguna, J. M. Lopez-de-Luzuriaga, M. Monge, M. E. Olmos, R. C. Puelles, C. Silvestru, *Inorg. Chem.* 2010, **49**, 5530-5541.

⁴ D. W. Johnson, G. W. Rayner-Canham, Ferricinium picrate. J. Chem. Educ. 1972, 49, 211.

NMR (CDCl₃, 400 MHz): δ 7.46-7.52 (m, 9H, Ph-*H*), 7.57 (d, 6H, ${}^{3}J_{H,H} = 8$ Hz, Ph-*H*). **1b**: 1 H NMR (CDCl₃, 400 MHz): δ 7.25 (d, 6H, ${}^{3}J_{H,H} = 8$ Hz, Ph-*H*), 7.41 (d, 6H, ${}^{3}J_{H,H} = 8$ Hz, Ph-*H*), 2.37 (s, 9H, C*H*₃). Complexes **1a** and **1b** are light and heat-sensitive in solution and hence should be used immediately after synthesis; decomposition is visible within 20 mins on exposure to natural light and especially UV irradiation. In comparison, **1c** is more stable.

Synthesis of [Au₁₃(SbPh₃)₈Cl₄]Cl (2a.Cl): A solution of SbPh₃ (140 mg, 0.40 mmol) in DCM (2 mL) was added dropwise into a solution of Me₂SAuCl (120 mg, 0.41 mmol) in DCM (10 mL), and then left to stir in dark at room temperature for 80 mins. The solvent was removed under vacuum to completely remove Me₂S, and then a solution of SbPh₃ (40 mg, 0.11 mmol) in DCM (12 mL) was added to the residue followed by dropwise addition of a solution of NaBH₄ (3.8 mg, 0.10 mmol) in ethanol (2 mL) within 4 min under ambient conditions. There was an immediate color change from colorless to darkred. The solution was further stirred for 6 h at room temperature. After filtration, the solvents were removed and the residue redissolved in 5.0 ml of DCM followed by addition of hexane (20 ml). The brown precipitate obtained was sequentially washed with DCM/hexane (5 x 10 mL, 1/4, v/v), DCM/hexane (2 x 8 mL, 1/3, v/v), and DCM/hexane $(2 \times 6 \text{ mL}, 1/2, \text{v/v})$. The brown precipitate obtained was dried under flow of nitrogen. Yield: 25 mg (15%). ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.43 (d, 12H, ³J_{H,H} = 8 Hz, Ph-*H*), 7.28 (d, 24H, ${}^{3}J_{H,H} = 8$ Hz, Ph-*H*), 7.21 (d, 12H, ${}^{3}J_{H,H} = 8$ Hz, Ph-*H*), 6.79-7.10 (m, 72H, Ph-H). ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz, not well resolved): δ (Ph) 135.83, 135.58, 132.65, 132.24, 131.83, 130.22, 130.18, 130.07, 129.80, 129.74. Anal. Calcd for C144H120Au13Cl4F6PSb8: C 30.49, H 2.13. Found: C 30.17, H 2.05. ESI-MS⁺ (m/z): 2746 [M-2Cl]²⁺, 2569 [M-2Cl-SbPh₃]²⁺, 2413 [M-2Cl-2SbPh₃+CH₃CN]²⁺.

Ionic exchange of 2a.Cl with NaPF₆: Cluster **2a**.Cl (18 mg, 3.2 µmol) was dissolved in EtOH (18 ml). To this was added dropwise a solution of NaPF₆ (8.5 mg, 50 µmnol) in EtOH (2 ml). The resulting suspension was further stirred at room temperature for 0.5 h, leading to brown precipitate and light yellow supernatant. The brown precipitate, **2a**.PF₆, was collected by centrifugation and dried under flow of nitrogen. Yield: 15 mg (82%). ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.43 (d, 12H, ³*J*_{H,H} = 8 Hz, Ph-*H*), 7.28 (d, 24H, ³*J*_{H,H} = 8

Hz, Ph-*H*), 7.21 (d, 12H, ${}^{3}J_{H,H} = 8$ Hz, Ph-*H*), 6.80-7.10 (m, 72H, Ph-*H*). ${}^{13}C{}^{1}H$ } NMR (CD₂Cl₂, 100 MHz, not well resolved): δ (Ph) 135.84, 135.58, 132.66, 132.25, 131.83, 130.23, 130.18, 130.09, 129.81, 129.74. ${}^{19}F{}^{1}H$ } NMR (CD₂Cl₂, 376 MHz): -73.6 (d, ${}^{1}J_{P,F} = 711$ Hz, PF₆). ${}^{31}P{}^{1}H$ } NMR (CD₂Cl₂, 160 MHz): -143.9 (sep, ${}^{1}J_{P,F} = 711$ Hz, PF₆).

Ionic exchange of 2a.Cl with NaBPh₄: Cluster **2a**.Cl (18 mg, 3.2 µmol) was dissolved in EtOH (18 ml). To this was added dropwise a solution of NaBPh₄ (14 mg, 42 µmol) in EtOH (1 ml). The resulting suspension was further stirred at room temperature for 1.5 h, leading to brown precipitate and light yellow supernatant. The brown precipitate, **2a**.BPh₄, was collected by centrifugation and dried under flow of nitrogen. Yield: 16 mg (85%). ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.43 (d, 12H, ³*J*_{H,H} = 8 Hz, Ph-*H*), 7.32 (m, 8H, Ph-*H*), 7.28 (d, 24H, ³*J*_{H,H} = 8 Hz, Ph-*H*), 7.21 (d, 12H, ³*J*_{H,H} = 8 Hz, Ph-*H*), 6.79-7.10 (m, 84H, Ph-*H*). ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz, not well resolved): δ (Ph) 135.92, 135.84, 135.63, 132.66, 132.25, 131.85, 130.18, 130.06, 129.79, 125.63, 125.61, 125.58, 121.70. ¹¹B{¹H} NMR (CD₂Cl₂, 128 MHz): -7.57 (s, *B*Ph₄).

Synthesis of {Au₁₃[Sb(*p***-tolyl)₃]₈Cl₄} (2b.Cl)**: A solution of Sb(*p*-tolyl)₃ (160 mg, 0.41 mmol) in DCM (2 mL) was added dropwise into a solution of Me₂SAuCl (120 mg, 0.41 mmol) in DCM (10 mL), and then left to stir in dark at room temperature for 80 mins. The solvent was removed under vacuum to completely remove Me₂S, and then a solution of Sb(*p*-tolyl)₃ (40 mg, 0.10 mmol) in DCM (12 mL) was added to the residue followed by dropwise addition of a solution of NaBH₄ (3.8 mg, 0.10 mmol) in ethanol (2 mL) within 4 min under ambient conditions. There was an immediate color change from colorless to dark-red. The solution was further stirred for 4 h at room temperature. After filtration, the solution was concentrated to *ca*. 3.0 ml followed by addition of hexane (150 ml), and the brown precipitate obtained was washed with hexane (3 x 10 mL). The brown precipitate obtained was dried under flow of nitrogen. Yield: 55 mg (30%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 7.33 (d, 12H, ³*J*_{H,H} = 8 Hz, Ph-*H*), 7.15 (d, 24H, ³*J*_{H,H} = 8 Hz, Ph-*H*), 7.10 (d, 12H, ³*J*_{H,H} = 8 Hz, Ph-*H*), 6.78 (d, 12H, ³*J*_{H,H} = 8 Hz, Ph-*H*), 6.66 (d, 12H, ³*J*_{H,H} = 8 Hz, Ph-*H*), 2.11 (s, 18H, CH₃), 2.08 (s, 36H, CH₃), 2.04 (s, 18H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz, not well resolved): δ (Ph)

140.43, 140.25, 136.10, 136.02, 135.81, 130.69, 130.59, 129.92, 129.62, 129.04; *δ* (*C*H₃) 21.40, 21.35, 21.31. Anal. Calcd for C₁₆₈H₁₆₈Au₁₃Cl₅Sb₈: C 34.21, H 2.87. Found: C 34.98, H 2.95. ESI-MS⁺ (*m/z*): 2913 [M-2Cl]²⁺, 2743 [M-2Cl-(*p*-tolyl)₃Sb+3H₂O]²⁺, 2547 [M-2Cl-2(*p*-tolyl)₃Sb+H₂O+CH₃CN]²⁺.

Conversion of 2b.Cl to [Au₁₁(PPh₃)₈Cl₂]Cl: Cluster 2b.Cl (15 mg, 2.5 µmol) was dissolved in DCM (10 ml). To the dark-red solution, a solution of PPh₃ (6.5 mg, 25 µmol) dissolved in 3 mL of ethanol was dropwise added. The solution was stirred rapidly at room temperature for 2 h. The solution was then concentrated to *ca*. 1.0 mL and poured into 10 mL of hexane and was left overnight. The brown-red precipitate obtained was washed with diethyl ether (3 x 5mL) and hexane (3 x 5mL) and dried in air. Yield: 6.4 mg (59%). ¹H{³¹P} NMR (CD₂Cl₂, 400 MHz) δ 7.32 (br, t, 48H, Ph-*H*), 6.94 (dd, 24H, ¹*J*_{H,H} = 8 Hz, Ph-*H*), 6.69 (dd, 48H, ¹*J*_{H,H} = 8 Hz, Ph-*H*). UV-Vis (DCM) λ_{max} (nm) = 312, 376, 416. Those values are in good agreement with those reported in literature.⁵

Conversion of 2b.Cl to $Au_{25}(GS)_{18}$, **4**: A solution of glutathione (12.5 mg, 41 µmol) in water (10 mL) was added into a solution of **2b**.Cl (12 mg, 2.0 µmol) in chloroform (10 mL). The reaction mixture, opened to air, was stirred rapidly at 45 °C for 6 h. The electronic spectra of the aqueous solution were recorded at an interval of 30 min. When the reaction was carried out under air, common solvents were used and the spectrum acquisitions also performed under ambient conditions. When the reaction was carried out under any to the solvents used were degassed before use. Typically, the aqueous solution (*ca.* 1.0 ml) was taken out from the reaction mixture with a syringe and tightly capped in a cuvette placed in a Schlenk tube under inert atmosphere. The cuvette containing the aqueous solution was then taken out and subject to the spectrum acquisition. After this, the cuvette containing the aqueous solution back to the reaction bottle, also under inert atmosphere, to make the volume of the aqueous solution constant. The amount of **4** was estimated by integration

⁵ McKenzie, L. C.; Zaikova, T. O.; Hutchison, J. E. J. Am. Chem. Soc. 2014, 136, 13426-13435.

of the characteristic peak, with background/baseline subtraction in the range from 610 nm to 710 nm.

Conversion of 2b.Cl to 4 in the presence of other oxidants: A solution of glutathione (12.5 mg, 41 μ mol) in water (10 mL) was added into a solution of **2b**.Cl (12 mg, 2.0 μ mol) in chloroform (10 mL). A solution of K₃[Fe(CN₆)] (0.33-4.60 mg, 1.0-14 μ mol) in water (1.0 mL) was added into the reaction mixture under inert atmosphere. The reaction mixture was stirred rapidly at 45 °C for 6 h. The monitoring was done according to the above procedure. After monitoring, the aqueous layer was washed with dichloromethane (3 x 25 mL) and then concentrated to *ca*. 3.0 ml. Upon standing at 4 °C in fridge overnight, small amount of blue species (Prussian blue) was formed on the bottom. Similar reactions with other oxidants (0.5-7.0 equiv) were conducted under the same condition with degassed solvents.

Electrochemical Analyses

Electrochemical measurements were carried out on a computer-controlled Eco ChemieAutolab PGSTAT302N potentiostat in a three-electrode cell with a 1 mm diameter planar glassy carbon disk (Cypress Systems) working electrode, a platinum wire (Metrohm) auxiliary electrode, and a silver wire (Cypress Systems) miniature reference electrode connected to the main solution via a salt bridge containing $^{n}Bu_{4}NPF_{6}$ in CH₃CN (0.50 M). A solution of $^{n}Bu_{4}NPF_{6}$ in DCM (0.10 M) was used as the electrolyte. Prior to each scan, the electrolyte was de-oxygenated by purging with high purity argon gas, and the working electrode was cleaned by polishing with an Al₂O₃ slurry (grain size 0.3 µm) on a Bueller Ultra-pad polishing cloth, rinsing with ultrapure water, acetone and then dried. Accurate potentials were obtained by using ferrocene as an internal reference, which was added to the electrolyte solution at the end of the measurements. All voltammetric experiments were performed at room temperature inside a Faraday cage.

X-ray Crystallographic Analyses

Diffraction-quality rod-like black crystal of 2a.BPh4 was obtained by slow evaporation of dry DCM/ethanol mixed solution (2/1, v/v) at -30 °C under inert atmosphere; colorless needle-like crystals of 1a and 1b were obtained by slow evaporation of dry DCM/diethyl ether mixed solutions (2/1, v/v) at -30 °C under inert atmosphere. Colorless plate-like crystals of **3a** and **3b** were obtained by direct crystallization of the corresponding crudes in DCM/Hexane (8/4, v/v) at 4 °C in fridge. The X-ray diffraction intensity data were collected on a Bruker APEX3 diffractometer equipped with a CCD detector, using Mo Ka radiation ($\lambda = 0.71073$ Å), with the SMART suite of programs;⁶ the data were processed and corrected for Lorentz and polarization effects with SAINT ⁷ and for absorption effects with SADABS.⁸ The crystal of **1b** was found to be twinned with four domains; the respective twin law and cell parameters were determined using the program Cell-NOW,⁹ and the reflection data were processed and corrections applied using program TWINS.¹⁰ All the structural solutions and refinements were performed with the SHELXTL suite of programs.¹¹ Two diethyl ether solvates with partial occupancy (fixed at 0.8) were found for the crystal of 1b. Dichloromethane solvate was found for crystal of **2a**.BPh₄ and refined over four positions with occupancies summed to unity; the C and Cl atoms were refined with common U[iso] while the C-Cl bonds and Cl-Cl contacts with common distance values, respectively; seven Au atoms and two Sb atoms were disordered and refined with two parts with occupancy for the minor part of ca. 6%. One of the DCM solvates in 3a was disordered and modelled with two alternative sites with occupancies summed to unity; appropriate distance and thermal parameters restraints were applied. The anion in **3a** was modelled as disordered between a $[Ph_2SbCl_2]^-$ and a chloride; with appropriate restraints, the final occupancies were ~93% and 7%, respectively. All non-hydrogen atoms were refined with anisotropic thermal parameters

⁶ APEX3 v2017.3-0, Bruker AXS Inc.: Madison, WI, USA, 2017.

⁷ SAINT v8.38a, Bruker AXS Inc.: Madison, WI, USA, 2017.

⁸ SADABS-2016/2; Bruker AXS Inc.: Madison, WI, USA, 2016.

⁹ Sheldrick, G. M., 2008, CELL_NOW, University of Göttingen.

¹⁰ Sheldrick, G. M., 2008, TWINABS, University of Göttingen.

¹¹ SHELXTL version 2014/7, Bruker AXS Inc.: Madison, WI, USA, 2014.

in the final models. Crystal data, data collection parameters, and refinement data are summarized in Table S1.

Computational Studies

DFT calculations were performed with the Gaussian 09W suite of programs.¹² For the optimization of the stibine complexes [Au(L)Cl] (L = SbPh₃, **1a**; Sb(*p*-tolyl)₃, **1b**; Sb(Mes)₃, **1c**), Becke's three-parameter hybrid function and Lee–Yang–Parr's gradient-corrected correlation function (B3LYP) was utilized; ¹³ the LanL2DZ (Los Alamos effective core potential double- ζ) basis set, together with d- or f-type polarization functions, was employed for the Au and Sb atoms while the 6-31G(d, p) basis set was used for the remaining atoms. ¹⁴ For the optimization of the cationic cluster [Au₁₃(SbPh₃)₈Cl₄]+, **2a**, the gradient-corrected MPW1PW91 exchange correlation functional, based on the generalized gradient approximation (GGA), ¹⁵ was used and LanL2DZ basis set was employed for the second and third row transition metal systems.¹⁶ Spin-restricted calculations were used for geometry optimization. Harmonic frequencies were then calculated to characterize the stationary points as equilibrium structures with all real frequencies, and to evaluate zero-point energy (ZPE) corrections. The TDDFT calculations were performed to get the most probable transitions and the orbitals

13 C. Lee, W. Yang, R. G. Parr, Phys. Rev. B, 1988, 37, 785-789.

¹² Gaussian 09, revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc.: Wallingford, CT, 2009.

^{14 (}a) *Gaussian Basis Sets for Molecular Calculations*, S. Huzinaga, J. Andzelm, Elsevier: Amsterdam; 1984, p. 23; (b) A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 111-114.

¹⁵ C. Adamo, V. Barone, J. Chem. Phys. 1998, 108, 664.

¹⁶ Q. S. Li, B. Xu, Y. M. Xie, R. B. King, H. F. Schaefer, Dalton Trans. 2007, 4312.

corresponding to the main peaks in the calculated electronic spectrum. One hundred singlet states (nstates = 100, singlet) are chosen in the calculations. The root is set as 1 in the TD-DFT calculations. Data for orbital composition analysis with Mulliken partition are from Gaussian 09 calculations and processed with Multiwfn software.¹⁷ The most probable transitions were determined based on the oscillator strength values and weights. The electronic plot of the intensity vs. energy (nm) spectrum was fit with a Gaussian with a half-width at half-height of 0.333 eV.

¹⁷ T. Lu, F. Chen, J. Comput. Chem. 2012, 33, 580.

Compound	1a	1b	2a.BPh ₄
Empirical formula	C ₁₈ H ₁₅ AuClSb	$C_{42}H_{42}Au_2Cl_2Sb_2$	$C_{168}H_{140}Au_{13}BCl_4Sb_8$
		0.9C4H9O	$\cdot CH_2Cl_2$
Formula weight	585.47	1321.79	5930.89
Temperature (K)	100(2)	103(2)	100(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	P212121	P21	$P2_1/c$
<i>a</i> (Å)	10.9035(3)	12.1481(10)	16.7528(8)
<i>b</i> (Å)	11.9862(4)	29.298(2)	46.762(2)
<i>c</i> (Å)	12.6785(5)	12.6050(10)	22.2312(11)
α (deg)	90	90	90
β (deg)	90	94.0574(15)	96.6202(16)
γ (deg)	90	90	90
V (Å ³)	1656.97(10)	4475.1(6)	17299.6(14)
Z value	4	4	4
$\rho_{calc}(g/cm^3)$	2.347	1.973	2.277
$\mu(Mo K_{\alpha}) (mm^{-1})$	10.625	7.882	12.337
Radiation $(\lambda, \text{\AA})$	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)
F(000)	1080	2503	10792
Crystal size, mm ³	$0.32 \times 0.06 \times 0.04$	$0.12 \times 0.08 \times 0.06$	$0.31 \times 0.11 \times 0.09$
θ_{\max} (°)	39.37	25.24	25.24
Reflections collected	25521	17915	209116
Independent reflections	9830	17915	32797
	[R(int) = 0.0638]		[R(int) = 0.0744]
Max and min.	0.68 and 0.30	0.65 and 0.29	0.41 and 0.12
transmission			
Data/parameters	10895/190	17915/958	32797/1481
Goodness of fit on F ²	0.899	1.080	1.066
Final R indices	R1 = 0.0419	R1 = 0.0786	R1 = 0.0734
[I>2sigma(I)]	wR2 = 0.0637	wR2 = 0.1930	wR2 = 0.1713
R indices (all data)	R1 = 0.0679	R1 = 0.0998	R1 = 0.0953
	wR2 = 0.0736	wR2 = 0.2134	wR2 = 0.1873
Largest diff. peak and hole $(e \cdot Å^{-3})$	1.471 and -1.942	4.383 and -3.124	3.572 and -2.443

Table S1. Crystallographic data for compounds 1a, 1b, 2a.BPh₄, 3a and 3b.

Compound	3a	3b
Empirical formula	C _{85.25} H _{73.25} AuCl ₆ Sb ₅	C77H77AuCl ₂ Sb ₄
Formula weight	2116.10	1757.25
Temperature (K)	100(2)	100(2)
Crystal system	Monoclinic	monoclinic
Space group	$P2_1/c$	P2/c
<i>a</i> (Å)	18.6854(3)	24.5859(4)
b (Å)	14.9411(3)	11.8194(2)
<i>c</i> (Å)	28.6570(5)	26.9019(4)
α (deg)	90	90
β (deg)	97.5030(10)	116.2770(10)
γ (deg)	90	90
V (Å ³)	7932.0(2)	7009.6(2)
Z value	4	4
$\rho_{calc}(g/cm^3)$	1.772	1.665
μ (Mo K _{α}) (mm ⁻¹)	3.767	3.725
Radiation $(\lambda, \text{\AA})$	Μο Κα (0.71073)	Μο Κα (0.71073)
F(000)	4083	3424
Crystal size, mm ³	0.10 x 0.08 x 0.02	0.04 x 0.22 x 0.24
θ_{\max} (°)	30.02	27.00
Reflections collected	90524	67565
Independent reflections	23126	15295
	[R(int) = 0.1411]	[R(int) = 0.0796]
Max and min. transmission	0.93 and 0.76	0.8650 and 0.4680
Data/parameters	23126/897	15295/768
Goodness of fit on F ²	1.026	1.047
Final R indices	R1 = 0.0628	R1 = 0.0440
[I>2sigma(I)]	wR2 = 0.0928	wR2 = 0.0806
R indices (all data)	R1 = 0.1416	R1 = 0.0765
	wR2 = 0.1186	wR2 = 0.0955
Largest diff. peak and hole (e·Å ⁻³)	1.443 and -1.618	3.151 and -1.809

Table S1 (continued). Crystallographic data for compounds 1a, 1b, 2a.BPh₄, 3a and 3b.

Excitation transition	Energy (ev)	Energy (nm)	Oscillator strength (a.u.)	Most probable transitions	Weight of transition	Nature of transition
13	2.845	435.80	0.3022	$HOMO-1 \rightarrow LUMO+3$	0.4318	M→M
14	2.876	431.07	0.1183	$HOMO-1 \rightarrow LUMO+4$	0.4350	
15	2.903	427.09	0.1612	$HOMO-2 \rightarrow LUMO+4$	0.5725	
37	3.563	348.02	0.1482	$HOMO-3 \rightarrow LUMO+4$	0.2923	L→M
				HOMO-7 \rightarrow LUMO+3	0.1816	
41	3.588	345.53	0.1159	$HOMO-9 \rightarrow LUMO+1$	0.4375	
				$HOMO-3 \rightarrow LUMO+4$	0.2044	
42	3.594	344.98	0.1068	$HOMO-2 \rightarrow LUMO+5$	0.4320	M→L
				$HOMO \rightarrow LUMO+7$	0.2486	
45	3.647	340.00	0.1682	HOMO-12 \rightarrow LUMO	0.3058	L→M
				HOMO-2 \rightarrow LUMO+6	0.3049	-
46	3.650	339.73	0.1142	$HOMO-5 \rightarrow LUMO+4$	0.4076	-
				HOMO-12 \rightarrow LUMO	0.3785	
47	3.661	338.67	0.1734	$HOMO-5 \rightarrow LUMO+4$	0.3246	
				HOMO-2 \rightarrow LUMO+6	0.2174	
48	3.666	338.19	0.2078	$HOMO-2 \rightarrow LUMO+6$	0.4326	
				HOMO-6 \rightarrow LUMO+2	0.2011	
50	3.693	335.69	0.1823	$HOMO-6 \rightarrow LUMO+2$	0.3492	
				HOMO-7 \rightarrow LUMO+2	0.3338	

Table S2. The excited states, energies, oscillator strengths, and the most probable transitions of **2a**, from TDDFT calculations.

Lower energy orbital		Higher energy orbital	
Orbital	Composition (%)	Orbital	Composition (%)
НОМО	Au – 61; L – 38	LUMO	Au – 69; L – 31
HOMO-1	Au – 63; L – 36	LUMO+1	Au – 67; L – 34
НОМО-2	Au – 63; L – 36	LUMO+2	Au – 67; L – 32
НОМО-3	Au – 55; L – 44	LUMO+3	Au – 64; L – 35
HOMO-5	Au – 54; L – 46	LUMO+4	Au – 68; L – 32
HOMO-6	Au – 36; L – 63	LUMO+5	Au – 51; L – 49
HOMO-7	Au – 39; L – 62	LUMO+6	Au – 68; L – 32
HOMO-9	Au – 38; L – 72	LUMO+7	Au – 46; L – 53
HOMO-12	Au – 34; L – 66		

Table S3. Summary of averaged Au-Au bond distances (Å) of 2a.	SPh4 and several other previously reported Au13 clusters with closed
icosahedral metal cores.	

Bond length ^{<i>a</i>}	2a .BPh ₄	$[Au_{13}(PPhMe_2)_{10}Cl_2][PF_6]_3^{18}$	$[Au_{13}(dppe)_5Cl_2][PF_6]_3^{19}$	$[Au_{13}(dppe)_5(CCPh)_2][PF_6]_3^{19}$
All Au-Au	2.810	2.841	2.865	2.861
Au (centre)-Au(per.)	2.731 [2.715-2.763]	2.769 [2.715-2.788]	2.737 [2.696-2.798]	2.757 [2.750-2.770]
Au (per.)-Au(per.)	2.889 [2.849-2.925]	2.912 [2.851-2.955]	2.906 [2.848-2.958]	2.899 [2.861-2.952]

^{*a.*} The minimum and maximum distances are given in square brackets.

¹⁸ C. E. Briant, B. R. C. Theobald, J. W. White, L. K. Bell, D. M. P. Mingos, A. J. Welch, J. Chem. Soc., Chem. Commun. 1981, 201-202.
19 (a) M. Sugiuchi, Y. Shichibu, T. Nakanishi, Y. Hasegawa, K. Konishi, Chem. Commun. 2015, 51, 13519-13522; (b) Y. Shichibu, K. Konishi, Small 2010, 6, 1216-1220.



Figure S1. Ortep diagram showing the molecular structure of **1a**. Thermal ellipsoids are drawn at the 50% probability level. Organic hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)-Sb(1) = 2.4818(4); Au(1)-Cl(1) = 2.2909(15); Sb(1)-Au(1)-Cl(1) = 177.68(4).



Figure S2. Unit-cell and stacking diagram of 1a.



Figure S3. Unit-cell and stacking diagram of 1b (Four diethyl ether solvent molecules are omitted for clarity).



Figure S4. ORTEP diagram showing the molecular structure of **3a**. Thermal ellipsoids are drawn at the 50% probability level. Two CH₂Cl₂ solvent molecules and organic hydrogen atoms in the phenyl rings are omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)-Sb(1) = 2.6399(6); Au(1)-Sb(2) = 2.6467(6); Au(1)-Sb(3) = 2.6468(5); Au(1)-Sb(4) = 2.6488(6); Sb(5)-Cl(1) = 2.588(2); Sb(5)-Cl(2) = 2.6466(2). The anion was modelled as disordered between a [Ph₂SbCl₂]⁻ and a chloride. With appropriate restraints, the final occupancies were ~93% and 7%, respectively.



Figure S5. ORTEP diagram showing the molecular structure of **3b**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Au(1)-Sb(1) = 2.6826(5); Au(1)-Sb(2) = 2.6366(5); Au(1)-Sb(3) = 2.6510(5); Au(1)-Sb(4) = 2.6206(5); Sb(1)-Cl(1) = 2.5652(17); Sb(1)-Cl(2) = 2.5935(17).



LUMO+3 (-0.134 eV)



(-0.137 eV)

(-0.136 eV)

LUMO+2



LUMO+1 (-0.141 eV)



LUMO (-0.145 eV)



HOMO (-0.258 eV)





Figure S6. Calculated frontier orbitals of **2a**. The HOMO and HOMO-1 show p character, corresponding to the "HOMO" orbital of the superatom complex, while the five orbitals with similar energies (LUMO to LUMO+3) show d character, corresponding to the "LUMO" orbital of the superatom complex. The orbitals are placed in different orientation for clearer visualization of the orbital character, and grouping of the orbitals are by their orbital energies.



Figure S7. TGA (top) and DTG (bottom) curves for 2a.PF6 and [Au11(PPh3)8Cl2]Cl.

Note: Weight loss at 300 °C for **2a**.PF₆ and $[Au_{11}(PPh_3)_8Cl_2]Cl$ is *ca*. 52.7% and 49.7%, respectively, corresponding to the loss of all ligands (eight SbPh₃ and four Cl ligands for **2a**.PF₆; eight PPh₃ and two Cl ligands for $[Au_{11}(PPh_3)_8Cl_2]Cl$), and is consistent with the theoretical value of 52.3% and 49.6%, respectively. While **2a**.PF₆ shows rapid weight loss at ~155 °C, this occurs at ~237 °C for $[Au_{11}(PPh_3)_8Cl_2]Cl$.



a. One of the transitions contributing to the calculated peak at 436 nm (M \rightarrow M transition)



HOMO-5 → LUMO+4





b. Several transitions contributing to the calculated peaks between 336 and 340 nm (peak maximum at 338 nm) (L \rightarrow M transitions)

Figure S8. Some of the calculated transition orbitals of 2a.



Figure S10. ¹H NMR spectrum of 1b in CDCl₃.



Figure S11. ¹H NMR spectrum of the supernatant in CDCl₃ from the reduction reaction of **1c** with NaBH₄. (Note: the DCM solvent in the supernatant was first removed and then the residue was re-dissolved in CDCl₃ for ¹H NMR measurement)





Figure S13. ¹H NMR spectrum of 2a.PF₆ in CD₂Cl₂.



Figure S14. ¹H NMR spectrum of 2a.BPh₄ in CD₂Cl₂.







Figure S18. ${}^{19}F{}^{1}H{}$ (top) and ${}^{31}P{}^{1}H{}$ (bottom) NMR spectra of 2a.PF₆ in CD₂Cl₂.



Figure S19. ¹¹B $\{^{1}H\}$ NMR spectrum of 2a.BPh₄ in CD₂Cl₂.



9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 Figure S20. ¹H NMR of 2b.Cl in CD₂Cl₂.



Figure S21. $^{13}C{^{1}H}$ NMR of 2b.Cl in CD₂Cl₂.



Figure S22. ¹H NMR stability monitoring spectra of **2a**.Cl in CD₂Cl₂. (Procedure: *ca*. 5 mg of **2a**.Cl was dissolved in 0.5 ml of CD₂Cl₂ and tightly sealed in a Carius NMR tube under air atmosphere. The dark-red solution was left in fumehood under ambient conditions for monitoring the stability)



Figure S23. ¹H NMR stability monitoring spectra of **2a**.Cl in *d*-acetone. (Procedure: *ca*. 5 mg of **2a**.Cl was dissolved in 0.5 ml of *d*-acetone and tightly sealed in a Carius NMR tube under air atmosphere. The dark-red solution was left in fumehood under ambient conditions for monitoring the stability)



Figure S24. ¹H NMR stability monitoring spectra of **2a**.Cl in solid state. (**2a**.Cl solid powder was kept in fridge at 4 °C without exclusion of air and no obvious decomposition was observed after ten months)


Figure S25. ¹H NMR stability monitoring spectra of **2b**.Cl in CD₂Cl₂. (*ca.* 5 mg of purified **2b**.Cl was dissolved in 0.5 ml of CD₂Cl₂ in a NMR tube under ambient conditions and then the tube was tightly capped and the solution was left in fumehood under ambient conditions for monitoring the stability of **2b**.Cl.)





Figure S27. ${}^{13}C{}^{1}H$ NMR spectrum of 3a in CD₂Cl₂.



Figure S29. ${}^{1}H{}^{31}P$ NMR spectrum of [Au₁₁(PPh₃)₈Cl₂]Cl in CD₂Cl₂.



The peak at 903 correspond to the cation $[Au(SbPh_3)_2]^+$, probably from the major side product **3a**.



Most of the peaks between 1000 and 1500 were unidentified but some of them such as the peak at 1255 was identified as $[Au(SbPh_3)_3]^+$. The other set of peaks between 2500 and 3000 correspond to product **2a**.Cl.

Figure S30. ESI-MS(+) spectrum of the crude mixture of the reaction between **1a** and NaBH₄ (0.25 equiv).



m/z	Identity
2394	${Au_{13}(SbPh_3)_8Cl_3 - 2SbPh_3}^{2+}$
2413	${Au_{13}(SbPh_3)_8Cl_3 - 2SbPh_3 + CH_3CN}^{2+}$
2570	${Au_{13}(SbPh_3)_8Cl_3 - SbPh_3}^{2+}$
2591	$\{Au_{13}(SbPh_3)_8Cl_3 - SbPh_3 + CH_3CN\}^{2+}$
2746	${Au_{13}(SbPh_3)_8Cl_3}^{2+}$
2923	${Au_{13}(SbPh_3)_8Cl_3 + SbPh_3}^{2+}$

Figure S31. ESI-MS(+) spectrum of 2a.Cl (top) and assignments (bottom).



Figure S32. ESI-MS(+) spectrum of 2b.Cl (top) and assignments (bottom).



Figure S33. ESI-MS(+) spectrum of the decomposition products of **2a**.Cl (top: full spectrum; bottom: enlarged region)



Figure S34. ESI-MS spectra of 3a (top: positive mode; bottom: negative mode)



The three major peaks at 987, 1381 and 1777 correspond to cations $[Au(SbAr_3)_2]^+$, $[Au(SbAr_3)_3]^+$ and $[Au(SbAr_3)_4]^+$, respectively (Ar = *p*-tolyl).



The peaks at 1205 and 1187, probably ascribable to the decomposition-recombination species $[Au(SbAr_3)_2Ar_2Cl]^-$ and $[Au(SbAr_3)_2Ar_2(H_2O)]^-$ (Ar = *p*-tolyl).

Figure S35. ESI-MS spectra of 3b (top: positive mode; bottom: negative mode)



Solid line: 1st cycle; dashed line: 2nd cycle. Scan initiated towards the positive potential direction.



Solid line: 1st cycle; dashed line: 2nd cycle. Scan initiated towards the negative potential direction. **Figure S36**. CV spectra of **2a**.PF₆ in CH₂Cl₂ (1.0 mM) with 0.10 M ⁿBu₄NPF₆ as the supporting electrolyte. Working electrode: 1 mm diameter planar glassy carbon; auxiliary electrode: Pt wire; pseudo reference electrode: Ag wire (in 0.5 M ⁿBu₄NPF₆ in CH₃CN); scan rate: 0.1 V/S; ferrocene (Fc) was added as an internal reference at the end of the experiment.



Figure S37. UV-Visible spectra of the purified 2a.Cl and the crude for the reduction of 1a with 0.25 equivalent of NaBH₄.



Figure S38. UV-Visible spectra of the crudes for the reduction of 1a with 0.25 or 1 equivalent of NaBH₄.



Figure S39. UV-Vis spectrum of the crude mixture of the reaction between 1a (red) or 3a (black) and NaBH₄ (0.25 equiv).



Figure S40. UV-visible spectrum of [Au11(PPh3)8Cl2]Cl in CH2Cl2.



Figure S41. UV-visible spectra of 2b.Cl recorded in different solvents.



From literature for easy comparison²⁰: UV-visible spectra taken at different reaction times during exchange of $Au_{11}(PPh_3)_7Cl_3$ with 20 eq. GSH at 50 °C under inert atmosphere. The peak at 670 nm is characteristic of **4** and can be seen after 360 minutes.



Figure S42. UV-visible spectra of the reaction mixture (aqueous phase) taken at different reaction time under inert atmosphere. (The peak at 670 nm is characteristic of **4** and become apparent after 240 minutes)

^{20.} L. C. McKenzie, T. O. Zaikova, J. E. Hutchison, J. Am. Chem. Soc. 2014, 136, 13426-13435.



Figure S43. UV-visible spectra of the reaction mixture (aqueous phase) taken at different reaction time under air.



Figure S44. UV-visible spectra of reaction mixture (aqueous phase) under air and inert atmosphere after 240 mins.



Figure S45. Initial rate for formation of **4** in the reaction of **2b**.Cl with GSH. (The concentration of **4** was estimated by the peak integration at 670 nm, with range from 610 nm to 710 nm)



Figure S46. UV-visible spectra of the reaction mixture (aqueous phase) with $K_3[Fe(CN)_6]$ taken at different reaction time.







Figure S48. UV-visible spectra of the reaction mixture (aqueous phase) with FeCl₃ taken at different reaction time.



Figure S49. UV-visible spectra of the reaction mixture (aqueous phase) with KI₃ taken at different reaction time.



Figure S50. UV-visible spectra of the reaction mixture (aqueous phase) with CuSO₄ taken at different reaction time.



Figure S51. UV-visible spectra of the reaction mixture (aqueous phase) with AgNO₃ taken at different reaction time.



Figure S52. UV-visible spectra of the reaction mixture (aqueous phase) with $[Fe(Cp)_2]^+$ (Ferrocenium picrate) taken at different reaction time.



Figure S53. Plot of integration (UV-Vis absorption peak at 670 nm and after 240 mins) versus redox potential of a variety of oxidants. (No clear correlation between the conversion with redox potential)



Figure S54. Electronic spectra of the aqueous solution for the conversion of **2b**.Cl to **4** with varying amount of $K_3Fe(CN)_6$, at 60 mins reaction time (top), and plot of the characteristic peak integration vs amount of $K_3Fe(CN)_6$ (bottom)



Figure S55. Electronic spectra of the aqueous solution for the conversion of **2b**.Cl to **4** with varying amount of $K_3Fe(CN)_6$, at 120 mins reaction time (top), and plot of the characteristic peak integration vs amount of $K_3Fe(CN)_6$ (bottom)



Figure S56. Electronic spectra of the aqueous solution for the conversion of **2b**.Cl to **4** with varying amount of $K_3Fe(CN)_6$, at 180 mins reaction time (top), and plot of the characteristic peak integration vs amount of $K_3Fe(CN)_6$ (bottom)



Figure S57. Plot of integration (UV-Vis absorption peak at 670 nm and after 240 mins) versus reaction time with varying amount of K₃Fe(CN)₆.



Figure S58. IR (KBr) spectra of Prussian blue and related compounds in the dominant C=N stretching vibration region.

Note:

Pink: authenticated Prussian blue;

Green: the blue species formed in the reaction of 2b.Cl and GSH in the presence of $K_3Fe(CN)_6$;

Cyan: the crude mixture of the reaction between **2b**.Cl and K₃Fe(CN)₆ (3.5 equiv);

The above three peaks are all broad and has an absorbance maximum at ca. 2077 cm⁻¹.

Blue: K₃Fe(CN)₆ (2119 cm⁻¹);

Red: K₄Fe(CN)₆ (2046 cm⁻¹);

Black: the crude mixture of the reaction between $Sb(p-tolyl)_3$ and $K_3Fe(CN)_6$ (3.5 equiv), indicating the gradual formation of K₄Fe(CN)₆ from K₃Fe(CN)₆.

%V_Bur of SbPh₃



Coordinates of the optimized structure for $Ph_3SbAuCl$

Au	2.19454500	-0.00154300	0.00200200
Cl	4.54040600	-0.00403100	0.00194700
Sb	-0.36043300	-0.00042300	0.00050000
С	-1.27652900	1.90252400	-0.32829100
С	-2.52374400	2.22205600	0.22828800
С	-3.10221100	3.46865600	-0.02149300
Н	-4.06714600	3.71201300	0.41410800
С	-2.43881900	4.40135100	-0.82108200
С	-1.19292300	4.09108800	-1.36998900
Н	-0.67061500	4.81801000	-1.98505800
С	-0.61020700	2.84669300	-1.12337500
С	-1.28314500	-0.66608200	1.80987700
С	-0.62312400	-0.44647000	3.02800900
С	-1.21041400	-0.85539800	4.22664900
Н	-0.69294400	-0.68394400	5.16599600
С	-2.45465000	-1.48903400	4.21567900
С	-3.11188100	-1.71791600	3.00527700
Н	-4.07560400	-2.21909000	2.99420700
С	-2.52873200	-1.31076000	1.80312500
С	-1.27913300	-1.23391000	-1.48352900
С	-2.52414400	-0.90646000	-2.04015500
С	-3.10468900	-1.74323100	-2.99609700
Н	-4.06792000	-1.48349900	-3.42596100
С	-2.44551800	-2.90474700	-3.40332000
С	-1.20197700	-3.23050100	-2.85808800
Н	-0.68295500	-4.12877400	-3.17942900
С	-0.61719600	-2.39746400	-1.90255300
Н	-3.04176900	1.51084600	0.86598400
Н	-2.88894200	5.37154800	-1.01032000

Н	0.36580200	2.62044200	-1.54529700
Н	-3.04183300	-1.50921400	0.86607700
Н	0.35156900	0.03453800	3.04733900
Н	-2.90832500	-1.81048000	5.14871900
Н	-3.03868200	0.00325800	-1.74288200
Н	0.35689600	-2.65439700	-1.49398300
Н	-2.89717000	-3.55165500	-4.14980000

%V_Bur of (*p*-tolyl)₃Sb



Coordinates of the optimized structure for (p-tolyl)₃SbAuCl

Sb	-0.10401000	0.00156400	0.00088800
С	-1.02417900	-0.90304000	1.70140800
С	-2.26280100	-1.55191400	1.61062000
С	-2.84112800	-2.12382400	2.74525800
С	-2.20309600	-2.06741700	3.99100100
С	-0.95858900	-1.42543800	4.06907400
С	-0.37237600	-0.85117000	2.94259100
С	-2.84003200	-2.66795600	5.22115400
Н	-3.79982400	-2.62927200	2.65825700
Н	-0.43740400	-1.38150700	5.02220000
Н	0.59986700	-0.37343700	3.03476400
Н	-3.60088900	-3.40798800	4.95821900
Н	-3.32826600	-1.89514700	5.82771700
Н	-2.09605300	-3.15594500	5.85822900
С	-1.01877200	-1.01911600	-1.63558400
С	-1.01455100	1.93063200	-0.06746400
С	-2.26308900	-0.62646700	-2.14675600
С	-0.35757800	-2.11051800	-2.21867100
С	-2.26502600	2.17634300	0.51540700
С	-0.34518600	2.98240600	-0.71070400
С	-2.83770400	-1.32460300	-3.21045000

С	-0.94009000	-2.80031300	-3.28035600
Н	0.61922600	-2.42081000	-1.85597700
С	-2.83776600	3.44725500	0.43986000
С	-0.92573000	4.24755200	-0.77985800
Н	0.63625200	2.82325200	-1.15046500
С	-2.19031500	-2.42250800	-3.79144800
Н	-3.80109000	-1.00467400	-3.59989400
Н	-0.41153400	-3.64037300	-3.72413100
С	-2.18222200	4.50059300	-0.21043400
Н	-3.80609000	3.62422500	0.90154900
Н	-0.39091600	5.05292500	-1.27722300
С	-2.82286200	-3.18929600	-4.92791200
С	-2.81278300	5.86885400	-0.30967700
Н	-3.59877200	-2.60124500	-5.42565000
Н	-3.29100800	-4.11304100	-4.56595800
Н	-2.07964400	-3.47686200	-5.67793300
Н	-3.59926400	6.00330700	0.43799200
Н	-3.26696800	6.02129800	-1.29656400
Н	-2.07110300	6.66135800	-0.17016000
Н	-2.77605000	-1.62969400	0.65591100
Н	-2.78468600	0.23209400	-1.73221300
Н	-2.79263100	1.38691100	1.04406400
Au	2.45167300	-0.00479800	0.00416300
Cl	4.79967400	-0.01155400	0.00121900

%V_Bur of (Mes)₃Sb





Coordinates of the optimized structure for (p-tolyl)₃SbAuCl

Au	-0.21387900	-0.22541200	2.35399600
Cl	-0.42170800	-0.44636200	4.68991100
Sb	0.01548800	0.01516500	-0.20480000
С	0.61422300	2.04367100	-0.71842200

С	-0.00124100	2.81815900	-1.73069900
С	0.39442500	4.15247900	-1.89571800
Н	-0.07941100	4.73935600	-2.67956400
С	1.37824600	4.74619900	-1.10473500
С	1.99898300	3.95293400	-0.13844200
Н	2.79318200	4.38064000	0.46904300
С	1.64126600	2.61626000	0.07432800
С	-1.05097600	2.29213900	-2.68614500
Н	-1.18680900	2.99222400	-3.51493000
Н	-2.02461400	2.15843400	-2.20547800
Н	-0.77779000	1.32383000	-3.11482300
С	1.75588400	6.19648100	-1.28434100
Н	1.15154400	6.84102400	-0.63409200
Н	1.59343600	6.52912000	-2.31390400
Н	2.80529400	6.37178100	-1.02939300
С	2.40896000	1.85095500	1.13155000
Н	3.30068300	2.40739800	1.43124200
Н	2.74233500	0.86803500	0.78176000
Н	1.80813700	1.68393700	2.03311200
С	-1.89659400	-0.42065800	-1.14829300
С	-3.03988100	0.16958200	-0.55224600
С	-4.30905900	-0.16316800	-1.04015000
Н	-5.17919200	0.30136700	-0.58212000
С	-4.49105300	-1.06196700	-2.09194300
С	-3.35117000	-1.60629900	-2.68329800
Н	-3.46517900	-2.28335600	-3.52672100
С	-2.05561100	-1.30469600	-2.24119600
С	-2.97339600	1.17191000	0.58098000
Н	-3.92527700	1.70101600	0.67509100
Н	-2.19519800	1.92826800	0.43507800
Н	-2.77228100	0.68575000	1.54275300
С	-5.87369000	-1.43585200	-2.56821200
Н	-5.86745300	-1.74219200	-3.61820500
Н	-6.57394300	-0.60250100	-2.45907600
Н	-6.27428400	-2.27447000	-1.98551900
С	-0.90886900	-1.93940600	-2.99853400
Н	-0.42183600	-2.73505200	-2.42655100
Н	-0.12954800	-1.21817200	-3.26052000
Н	-1.27462400	-2.38099300	-3.92921900
С	1.52427200	-1.35785900	-0.96316300
С	2.53282000	-0.99301400	-1.88699600
С	3.53452000	-1.92386500	-2.19495800
Н	4.30376000	-1.63789200	-2.90899000
С	3.57131900	-3.20088200	-1.63366100
С	2.54193100	-3.55458800	-0.76033000
Н	2.52446200	-4.55673300	-0.33729800

С	1.51953600	-2.66389900	-0.41129200
С	2.59197800	0.33782200	-2.60636500
Н	2.91592100	1.15212800	-1.95230200
Н	1.62272900	0.63126700	-3.01947000
Н	3.29910700	0.28142000	-3.43807900
С	4.68602300	-4.16664700	-1.95704900
Н	4.33774300	-5.20417200	-1.93435000
Н	5.50087400	-4.08138600	-1.22657700
Н	5.11254200	-3.97025300	-2.94496800
С	0.44464900	-3.17483500	0.52524300
Н	0.47030200	-4.26709800	0.57234400
Н	-0.56479300	-2.88752900	0.21081000
Н	0.58079700	-2.79861700	1.54603800

Figure S59. Optimized coordinates and percent buried volumes of SbPh₃, Sb(*p*-tolyl)₃ and Sb(Mes)₃.

0.34850700	-2.37531600	-1.67019200
-2.21613000	-1.75561400	-0.25676900
-1.52999000	-0.17478500	2.18331700
0.22292600	-2.35717200	1.29539500
-1.38124500	-0.17141600	-2.59268000
0.00813500	-0.00984800	-0.16791100
4.88086900	-2.52127400	0.00123000
0.76913000	-4.41831900	-3.24795400
-4.19632400	-3.45901200	-0.55080200
-4.88299100	2.46526600	-0.24461100
4.15998100	3.51456400	-0.50837400
-2.83010900	-0.38402000	4.45150600
2.59646400	-1.20834000	-0.08216700
-2.57421300	1.20007600	-0.20150300
-0.27731500	2.34644300	-1.70782500
2.21713600	1.77885100	-0.19333900
1.45423700	0.20085400	2.22536200
1.54217300	0.14295600	-2.50565100
-0.28097700	2.36705500	1.25014200
-0.62189100	4.39984800	-3.27561500
2.65072500	0.46088100	4.54003000
0.27720800	-4.37477000	2.73306100
-2.74353900	-0.07013500	-4.63508900
3.16384700	0.27687300	-4.34696300
-0.38350500	4.43751400	2.60263900
6.27648900	-2.10154800	1.55912000
6.23968500	-2.83594400	2.76030200
7.18189300	-2.58617500	3.76888000
8.16944200	-1.60763200	3.58495900
	0.34850700 -2.21613000 -1.52999000 0.22292600 -1.38124500 0.00813500 4.88086900 0.76913000 -4.19632400 -4.88299100 4.15998100 -2.83010900 2.59646400 -2.57421300 -0.27731500 2.21713600 1.45423700 1.54217300 -0.28097700 -0.62189100 2.65072500 0.27720800 -2.74353900 3.16384700 -0.38350500 6.23968500 7.18189300 8.16944200	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

С	8.20419900	-0.86719400	2.39381500
С	7.25638100	-1.10308300	1.38745900
С	6.17914800	-2.42231900	-1.68186400
С	7.53175500	-2.80816600	-1.57602600
С	8.36842800	-2.75536300	-2.69925900
С	7.86521200	-2.30904800	-3.93230500
С	6.52392300	-1.91543400	-4.03798700
С	5.67997200	-1.97376100	-2.91847100
С	4.60370300	-4.60754400	0.33205600
С	3.35241500	-5.07116200	0.77804700
С	3.15175900	-6.43777900	1.02969800
С	4.19907300	-7.34813100	0.83345600
С	5.45134900	-6.89056700	0.38967300
С	5.65504400	-5.52658900	0.13992400
С	2.74405400	-4.86762000	-3.91095700
C	3.60616300	-5.64638200	-3.11452200
Ċ	4.88643500	-5.97655100	-3.58168500
C	5.31657300	-5.52779400	-4.83855000
C	4.46527900	-4.74156100	-5.62857000
Ċ	3.18384300	-4.40857100	-5.16798100
Ċ	0 19999800	-6 31564500	-2 47684600
Č	-0.59181700	-6.38088800	-1.31537900
Ċ	-0 98786700	-7 62287600	-0 79825300
Č	-0 59096100	-8 80700100	-1 43554000
Ċ	0 21206600	-8 74952500	-2 58540600
Č	0 61049500	-7 50987400	-3 10370500
Č	-0 17885200	-4 22830800	-5 14161400
Č	-0 46232400	-5 35282800	-5 94095700
Č	-0 99855900	-5 18340300	-7 22446000
C	-1 25890900	-3 89361600	-7 71614400
Č	-0 99302200	-2 77307000	-6 91715900
Č	-0 45301400	-2 93832300	-5 63249400
C	-4 19838700	-4 38944400	-2.46388400
C	-3 91021200	-3 60427200	-3 59778800
C	-3 98092500	-4 17033100	-4 87897300
C	-4 32570500	-5 51997300	-5 03456600
C	-4 59257700	-6 30978700	-3 90605800
C	-4 53058400	-5 74889500	-2 62278400
C C	-6 22716800	-2 80227000	-0 46447300
C C	-6.85115000	-2.00227000	-1 62134400
C C	-8 19493100	-1 89634500	-1 58111400
Č	-8 92833500	-2 00925900	-0 39014800
č	-8 30724700	-2 50329200	0 76643700
č	-6 95874100	-2 88897200	0 73566400
Č	-4 25065200	-5 09427400	0.80699900
č	-3 13409800	-5 34255000	1 62748100
-	2.12.00000	2.2 2 2 0 0 0 0	

С	-3.13314700	-6.43619200	2.50719100
С	-4.24665200	-7.28592600	2.57455300
С	-5.36674400	-7.03813700	1.76409100
С	-5.37178400	-5.94670100	0.88433400
С	-6.17003700	2.09044200	-1.89547400
С	-5.65935300	1.42287400	-3.02352100
С	-6.49035500	1.16099300	-4.12338300
С	-7.83218100	1.56699500	-4.10503700
С	-8.34748600	2.23032600	-2.97922700
С	-7.52288200	2.48821400	-1.87568000
С	-4.65899000	4.57842300	-0.12079500
С	-3.48711700	5.09631500	0.46261600
С	-3.34547600	6.47940500	0.65349800
С	-4.37065100	7.35080700	0.26052400
С	-5.53624000	6.83892900	-0.33163900
С	-5.68178300	5.45842400	-0.52415400
С	-6.28603000	2.19548500	1.34376900
С	-7.23833300	1.15961700	1.27723100
С	-8.21317700	1.03405500	2.27739200
С	-8.23430300	1.92558300	3.36024400
С	-7.27026100	2.94142200	3.44522300
С	-6.30109500	3.07930700	2.44064800
С	0.17421500	6.20424100	-2.47937600
С	0.38816700	6.27970500	-1.08936100
С	0.87064000	7.46375400	-0.51206200
С	1.14146600	8.57830100	-1.31900700
С	0.93647200	8.50564900	-2.70589400
С	0.45730400	7.32283900	-3.28664800
С	-2.60184700	4.98808500	-3.78636400
С	-3.40037500	4.10117000	-4.53698500
С	-4.67578100	4.49864700	-4.96123900
С	-5.16126600	5.77560800	-4.64082300
С	-4.37345300	6.65313600	-3.88291700
С	-3.09729000	6.26136800	-3.45133600
С	0.14536800	4.17222600	-5.24390500
С	1.00891700	3.10259200	-5.53858600
С	1.47427600	2.91392900	-6.84820000
С	1.08691300	3.79561900	-7.86645300
С	0.22123300	4.86316800	-7.57762100
С	-0.25616400	5.04806100	-6.27330200
С	4.34531800	5.05592100	0.94101400
С	3.35795400	5.17657800	1.93743200
С	3.43073300	6.21252500	2.88093700
С	4.48965900	7.13001500	2.83988400
С	5.47635700	7.01642000	1.84740000
С	5.40482600	5.98709400	0.89899900

С	6.11977700	2.66723100	-0.62227200
С	6.37232200	1.70499000	-1.62176300
С	7.66482500	1.18936400	-1.79534400
С	8.71340200	1.62205800	-0.96912200
С	8.46087000	2.55725500	0.04535900
С	7.16869000	3.07633000	0.22259100
С	4.14230700	4.62011000	-2.33419500
С	4.17408400	6.02758400	-2.33372800
С	4.24142400	6.72903800	-3.54616400
С	4.27346600	6.03403400	-4.76312000
С	4.21702400	4.63306900	-4.76698600
С	4.14525300	3.92444400	-3.55949800
С	1.50035800	1.33523000	6.10037000
С	0.69535900	2.45378600	5.80534900
С	0.00946500	3.11321800	6.83604400
С	0.11703800	2.65962700	8.15882900
С	0.90346100	1.53547800	8.45106900
С	1.59304100	0.87150600	7.42626600
С	4.38000800	1.70371900	4.64850900
С	4.41331600	2.81793200	5.50900600
С	5.56535200	3.61428500	5.58768800
С	6.68998100	3.30481500	4.80996100
С	6.65914600	2.19800500	3.94899500
С	5.50911600	1.40155700	3.86270400
С	3.39771900	-1.34160800	5.38586800
С	4.37464000	-1.31292200	6.40125600
С	4.84463800	-2.51064000	6.95832400
С	4.35270200	-3.74290800	6.49773600
С	3.39130800	-3.77547900	5.47696700
С	2.91234400	-2.57879100	4.92250100
С	-3.56469500	1.44331900	5.25006100
С	-3.05892300	2.65486800	4.74234300
С	-3.50432700	3.87924400	5.26245200
С	-4.45453500	3.90120900	6.29341700
С	-4.96453700	2.69560600	6.80197200
С	-4.52518700	1.47007200	6.28206600
С	-1.75010100	-1.27534200	6.05539600
С	-0.88348000	-2.35098500	5.78010100
С	-0.24848900	-3.02588000	6.83375400
С	-0.46797000	-2.62952300	8.16032300
С	-1.31608800	-1.54608700	8.43457000
С	-1.95504400	-0.86807200	7.38726900
С	-4.57783300	-1.60991900	4.52809800
С	-4.44784400	-2.98854200	4.78956300
С	-5.58634500	-3.80177800	4.87754600
С	-6.86408500	-3.24486600	4.71594900

С	-6.99715600	-1.87538500	4.44483200
С	-5.86017900	-1.06020700	4.33947100
Н	4.26444600	7.81366800	-3.53511700
Н	4.32935300	6.57784500	-5.70029100
Н	4.13725300	6.58454800	-1.40399300
Н	4.07982000	2.84066800	-3.59845900
Н	4.21764300	4.08813800	-5.70393200
Н	-0.09245800	5.53934200	-8.36618700
Н	-0.95928400	5.85230300	-6.07630200
Η	2.12784400	2.07431000	-7.05800300
Н	1.44436500	3.64707200	-8.88024800
Η	-2.50050500	6.95006000	-2.86193500
Η	-4.74668800	7.63866800	-3.62513000
Н	-6.14670000	6.08110300	-4.97694900
Н	-5.28538400	3.81167300	-5.53747300
Н	-3.04052200	3.11074100	-4.80312800
Η	0.18077000	5.42862900	-0.44624400
Η	1.03300500	7.50614900	0.55944300
Η	1.51181500	9.49545000	-0.87256100
Н	1.14920400	9.36493600	-3.33351900
Н	0.31896200	7.27995300	-4.36230600
Η	2.51932900	4.48825800	1.98357600
Η	2.65665800	6.29535100	3.63591300
Η	4.54521800	7.93028800	3.57065200
Η	6.29409600	7.72858100	1.80716900
Н	6.16845800	5.92602900	0.12942000
Η	5.57933200	1.34952600	-2.27407500
Η	7.84673900	0.45526400	-2.57234600
Η	9.71537400	1.23199800	-1.11484000
Η	9.26762000	2.89370400	0.68917600
Η	6.99120300	3.79441500	1.01599600
Η	-2.67980500	4.44364400	0.78327200
Η	-2.43936000	6.85956100	1.11175800
Η	-4.26356800	8.41993500	0.41230500
Η	-6.32962600	7.51116100	-0.64172200
Η	-6.58511800	5.08298400	-0.99357400
Η	-4.62446700	1.09667400	-3.06990300
Η	-6.07776100	0.64322900	-4.98260300
Η	-8.47346000	1.36732500	-4.95761000
Η	-9.38670300	2.54219500	-2.95826700
Η	-7.94511500	2.97752600	-1.00298400
Н	-5.57781400	3.88533500	2.51244700
Н	-7.27434600	3.63002900	4.28306300
Н	-8.99499400	1.83360000	4.12871100
Н	-8.95501300	0.24644200	2.20078900
Н	-7.24560200	0.46098100	0.44650000

Н	-4.94119500	0.54742700	6.67583500
Н	-5.70055300	2.70824100	7.59928900
Н	-4.79596200	4.84835300	6.69871900
Н	-3.10246500	4.80214500	4.85826000
Н	-2.31592800	2.66607000	3.95027800
Н	0.59269300	2.82568800	4.78867800
Н	-0.60651000	3.97322900	6.59950300
Н	-0.41257100	3.17414800	8.95387700
Н	0.98104800	1.17413500	9.47122900
Н	2.18668600	-0.00469000	7.66630400
Н	3.55307300	3.06898800	6.12087000
Н	5.58140900	4.47054500	6.25372000
Н	7.58120000	3.92044700	4.87436500
Н	7.52446800	1.94795700	3.34569900
Н	5.51242600	0.54750300	3.19200300
Н	-0.69412200	-2.68131000	4.76160700
Н	0.41376400	-3.85445800	6.61053800
Н	0.02105700	-3.15657700	8.97297800
Н	-1.48173700	-1.22903100	9.45904800
Н	-2.59592500	-0.02329600	7.61697700
Н	-5.47368000	-4.86156600	5.07869100
Н	-7.74496200	-3.87246600	4.80389100
Н	-7.98062900	-1.43483700	4.32032400
Н	-5.98947700	-0.00406500	4.12679200
Н	-3.47086400	-3.43606700	4.94295000
Н	4.71832200	-4.66872500	6.93030900
Н	5.59146500	-2.48156700	7.74512900
Н	4.78081800	-0.36788100	6.74985700
Н	2.16402100	-2.63282000	4.13709400
Н	3.00828100	-4.72042400	5.10652600
Н	5.49443900	-3.60972800	2.91433700
Н	7.14225900	-3.15651400	4.69014700
Н	8.90334500	-1.42300700	4.36234100
Н	8.96938600	-0.11331700	2.23984500
Н	7.30303000	-0.52027100	0.47285600
Н	4.65050200	-1.64867900	-3.03220300
Н	6.12347300	-1.55782700	-4.97993900
Н	8.51560800	-2.26476200	-4.79989300
Н	9.40750500	-3.05560000	-2.61044600
Н	7.94588000	-3.12749600	-0.62425200
Н	3.28963600	-6.01138000	-2.14213800
Н	5.54043800	-6.58098800	-2.96281400
Н	6.30794000	-5.78413900	-5.19707200
Н	4.79343400	-4.38903300	-6.60063900
Н	2.53504800	-3.80664900	-5.79622700
Н	-0.27919700	-6.35717200	-5.57337800

Н	-1.21027400	-6.05328000	-7.83773900
Н	-1.67064600	-3.76547000	-8.71191600
Н	-1.21060300	-1.77306100	-7.27437100
Н	-0.26722700	-2.05585600	-5.02824200
Н	-3.61922600	-2.56053200	-3.51020400
Н	-3.74986200	-3.55725600	-5.74211600
Н	-4.37338900	-5.95594400	-6.02681600
Н	-4.84527000	-7.35866200	-4.02194800
Н	-4.72834200	-6.37783500	-1.76095900
Н	-6.30976800	-2.22253900	-2.55940800
Н	-6.49797400	-3.26602500	1.64314000
Н	-8.86805300	-2.59781500	1.69056500
Н	-9.97325000	-1.71763500	-0.36682700
Н	-8.66485500	-1.50683700	-2.47749200
Н	-6.25084200	-5.76208100	0.27406800
Н	-6.23207600	-7.69082100	1.81577900
Н	-4.24528600	-8.13256500	3.25349400
Н	-2.26287200	-6.60866900	3.13109100
Н	-2.26010100	-4.69766400	1.60451500
Н	1.32265600	2.40077200	-4.77262400
Н	2.52448200	-4.38847100	0.94398400
Н	6.62787000	-5.19340700	-0.20721000
Н	6.26581000	-7.59249800	0.24219000
Н	2.18170700	-6.77182700	1.37961900
Н	4.04479900	-8.40469700	1.02589300
Н	1.25571500	-7.48319700	-3.97684000
Н	0.53139500	-9.66445000	-3.07347200
Н	-0.89733600	-9.76805700	-1.03561800
Н	-1.59693700	-7.65952200	0.09821700
Н	-0.88877100	-5.47214700	-0.79977100

Figure S60. Optimized coordinates of 2a.