

## Electronic Supplementary Information (ESI)

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**Two types of tetranuclear phosphane-gold(I) cations as dimers of dinuclear units,**

**$[\{(\text{Au}\{\text{P}(p\text{-RPh})_3\})_2(\mu\text{-OH})\}_2]^{2+}$  (R = Me, F), synthesized by  
polyoxometalate-mediated clusterization**

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### Contents

Synthesis of  $[\text{Au}(RS\text{-pyrrld})\{\text{P}(p\text{-MePh})_3\}]$

Synthesis of  $[\text{Au}(RS\text{-pyrrld})\{\text{P}(p\text{-FPh})_3\}]$

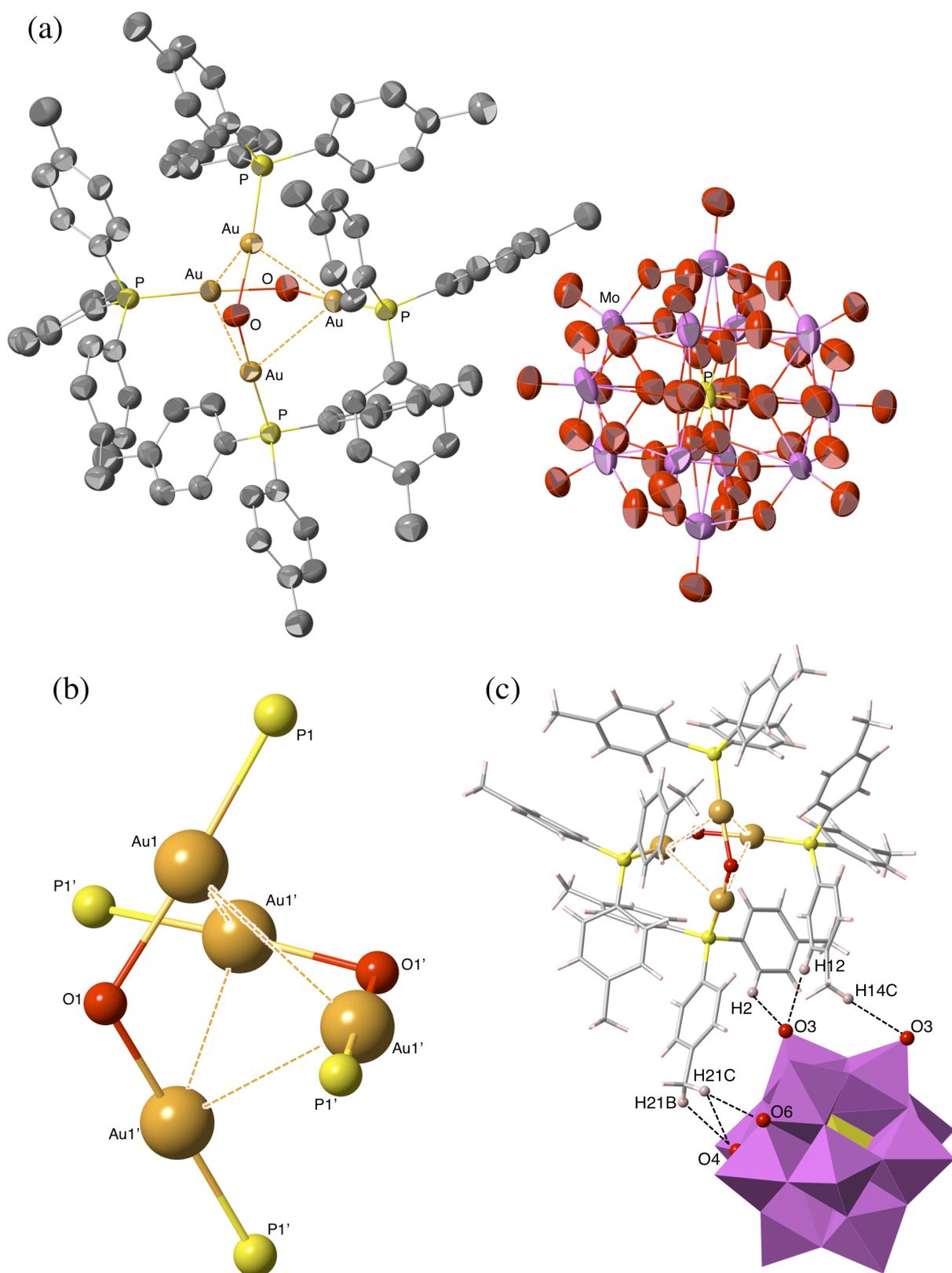
**Fig. S1** Molecular structure of 2.

**Table S1** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] of the tetragold(I) cluster cation of 2 and the distances [ $\text{\AA}$ ] of the short interactions between the tetragold(I) unit and the  $\alpha$ -Keggin POM unit.

### Reference

**[Au(*RS*-pyrrld){P(*p*-MePh)<sub>3</sub>}]**: To the solution of 0.537 g (1.00 mmol) of the gold(I) precursor [AuCl{P(*p*-MePh)<sub>3</sub>}] dissolved in 30 mL CHCl<sub>3</sub> was added 0.708 g (1.50 mmol) of the meso-form of silver(I) complex [Ag<sub>2</sub>(*R*-pyrrld)(*S*-pyrrld)]<sup>S1</sup>. After stirring for one day, white powder of AgCl produced was filtered off through a membrane filter (JV 0.1 μm). The colorless clear filtrate was evaporated to dryness with a rotary evaporator. The residue was dissolved in 10 mL acetone, followed by filtering through a folded filter paper (Whatman #5). The clear filtrate was added dropwise to 200 mL light petroleum. A white precipitate was collected on a membrane filter (JV 0.1 μm), washed with light petroleum (50 mL x 2) and dried in vacuo for 2 h. The white powder was obtained in 77.1% (0.97 g scale) yield Found: C, 48.98; H, 4.31; N, 2.21. Calc. for C<sub>26</sub>H<sub>27</sub>N<sub>1</sub>O<sub>3</sub>P<sub>1</sub>Au<sub>1</sub> or [Au(*RS*-pyrrld){P(*p*-MePh)<sub>3</sub>}] : C, 49.61; H, 4.32; N, 2.23 %. TG/DTA data: no weight loss was observed at below 183 °C. Decomposition began around 183 °C with exothermic peaks at 192.0, 241.9 °C. Prominent IR bands in the 1700–400 cm<sup>-1</sup> region (KBr disk): 1699 vs, 1637 s, 1598 s, 1498 m, 1447 w, 1397 m, 1378 m, 1309 w, 1258 m, 1188 m, 1147 vw, 1103 vs, 1038 vw, 1018 w, 845 vw, 807 m, 709 w, 648 m, 633 w, 621 w, 533 s, 513 m, 444 vw cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 26.8 °C): δ 2.17–2.51 (13H, m), 4.21–4.25 (1H, m), 6.00 (1H, s, *NH*), 7.25–7.42 (13H, m, Aryl) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 27.5 °C): δ 21.5, 25.6, 30.1, 58.1, 125.4 (d, *J*<sub>CP</sub> = 66.5 Hz), 129.9 (d, *J*<sub>CP</sub> = 12.4 Hz), 134.0 (d, *J*<sub>CP</sub> = 13.5 Hz), 142.6, 176.6, 177.8 ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 26.6 °C): δ 25.35 ppm

**[Au(*RS*-pyrrld){P(*p*-FPh)<sub>3</sub>}]**: To the solution of 0.549 g (1.00 mmol) of the gold(I) precursor [AuCl{P(*p*-FPh)<sub>3</sub>}] dissolved in 30 mL CHCl<sub>3</sub> was added 0.708 g (1.50 mmol) of the meso-form of silver(I) complex [Ag<sub>2</sub>(*R*-pyrrld)(*S*-pyrrld)]<sup>S1</sup>. After stirring for one day, white powder of AgCl produced was filtered off through a membrane filter (JV 0.1 μm). The colorless clear filtrate was evaporated to dryness with a rotary evaporator. The residue was dissolved in 10 mL acetone, followed by filtering through a folded filter paper (Whatman #5). The clear filtrate was added dropwise to 200 mL light petroleum. A white precipitate was collected on a membrane filter (JV 0.1 μm), washed with light petroleum (50 mL x 2) and dried in vacuo for 2 h. The white powder was obtained in 76.4 % (0.98 g scale) yield Found: C, 43.41; H, 2.73; N, 2.18. Calc. for C<sub>23</sub>H<sub>18</sub>N<sub>1</sub>O<sub>3</sub>F<sub>3</sub>P<sub>1</sub>Au<sub>1</sub> or [Au(*RS*-pyrrld){P(*p*-FPh)<sub>3</sub>}] : C, 43.07; H, 2.83; N, 2.18 %. TG/DTA data: a weight loss of 1.15 % was observed at below 156 °C. Decomposition began around 156 °C with an exothermic peak at 189.6 °C. Prominent IR bands in the 1700–400 cm<sup>-1</sup> region (KBr disk): 1697 vs, 1634 s, 1589 vs, 1496 vs, 1462 w, 1396 s, 1378 m, 1302 m, 1235 vs, 1161 vs, 1103 vs, 1040 vw, 1012 m, 970 vw, 946 vw, 829 vs, 777 w, 710 m, 641 m, 619 w, 535 vs, 497 w, 452 s, 443 s, 415vw cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 24.1 °C): δ 2.30–2.50 (4H, m), 4.25 (1H, dd, *J* = 8.5, 6.0 Hz), 5.86 (1H, s, *NH*), 7.19–7.23 (6H, m, Aryl), 7.50–7.55 (6H, m, Aryl) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 26.2 °C): δ 25.6, 30.0, 116.9–117.2, 123.6–124.1, 136.2–136.36, 164.22, 166.26 ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25.4 °C): δ 25.05 ppm



**Fig. S1** (a) Molecular structure of  $[\{(\text{Au}\{\text{P}(p\text{-MePh})_3\})_2(\mu\text{-OH})\}_2]_3[\alpha\text{-PMo}_{12}\text{O}_{40}]_2$  (**2**); (b) the partial structure around the tetragold(I) cluster core of **2** in a crossed-edge arrangement; (c) the short interactions between the tetragold(I) unit and the  $\alpha$ -Keggin POM unit.

**Table S1.** Selected bond lengths [Å] and angles [°] of the tetragold(I) cluster cation of **2** and the distances [Å] of the short interactions between the tetragold(I) unit and the  $\alpha$ -Keggin POM unit

Lengths			
Au1-Au1' (inter dimer)	2.991	O3-H14C	2.698
Au1-Au1' (intra dimer)	3.548	O4-H21B	2.753
O3-H2	2.427	O4-H21C	2.751
O3-H12	2.586	O6-H21C	2.681
Angles			
Au1-O1-Au1'	115.267		

## Reference

- S1. K. Nomiya, S. Takahashi and R. Noguchi, *J. Chem. Soc., Dalton Trans.* 2000, 4369.