

## Intercluster Compound between a Tetrakis{triphenylphosphinegold(I)} oxonium Cation and a Keggin Polyoxometalate (POM): Formation during the Course of Carboxylate Elimination of a Monomeric Triphenylphosphinegold(I) Carboxylate in the Presence of POMs

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The preparation and structural characterization of a novel intercluster compound,  $[\{Au(PPh_3)_4(\mu_4-O)\}_3[\alpha-PW_{12}O_{40}]_2 \cdot 4EtOH$  (**1**), constructed between a tetrakis{triphenylphosphinegold(I)} oxonium cation and a saturated  $\alpha$ -Keggin polyoxometalate (POM) are described. The tetragold(I) cluster oxonium cation was formed during the course of carboxylate elimination of a monomeric phosphinegold(I) carboxylate complex, i.e.,  $[Au((R,S)\text{-pyrrld})-(PPh_3)] [(R,S)\text{-Hpyrrld} = (R,S)\text{-2-pyrrolidone-5-carboxylic acid}]$ , in the presence of the free acid form of a Keggin POM,  $H_3[\alpha-PW_{12}O_{40}] \cdot 7H_2O$ . The liquid–liquid diffusion between the upper water/EtOH phase containing the Keggin POM and the lower  $CH_2Cl_2$  phase containing the monomeric gold(I) complex gave a pure crystalline sample of **1** in good yield (42.1%, 0.242 g scale). Complex **1** was formed by ionic interaction between the tetragold(I) cluster cation and the Keggin POM anion. As a matter of fact, the POM anion in **1** can be exchanged with the  $BF_4^-$  anion using an anion-exchange resin (Amberlyst A-27) in  $BF_4^-$  form. By using other Keggin POMs, such as  $H_4[\alpha-SiW_{12}O_{40}] \cdot 10H_2O$  and  $H_3[\alpha-PMo_{12}O_{40}] \cdot 14H_2O$ , the same tetragold(I) cluster cation was also formed, i.e., in the forms of  $[\{Au(PPh_3)_4(\mu_4-O)\}_2[\alpha-SiW_{12}O_{40}] \cdot 2H_2O$  (**2**) and  $[\{Au(PPh_3)_4(\mu_4-O)\}_3[\alpha-PMo_{12}O_{40}]_2 \cdot 3EtOH$  (**3**). Compounds **1–3**, as dimethyl sulfoxide-soluble, EtOH- and  $Et_2O$ -insoluble dark-yellowish white solids, were characterized by complete elemental analysis, thermogravimetric and differential thermal analyses, Fourier transform IR, X-ray crystallography, and solid-state (CPMAS  $^{31}P$  and  $^{29}Si$ ) and solution ( $^{31}P\{^1H\}$  and  $^1H$ ) NMR spectroscopy. The molecular structures of **1** and **2** were successfully determined. The tetragold(I) cluster cation was composed of four  $PPh_3Au^I$  units bridged by a central  $\mu_4$ -oxygen atom in the geometry of a trigonal pyramid or distorted tetrahedron.

### Introduction

Polyoxometalates (POMs) are discrete metal oxide clusters that are of current interest as soluble metal oxides and for their application in catalysis, medicine, and materials science.<sup>1</sup> The preparation of POM-based materials is therefore an active field of research. Some of the intriguing aspects are that a combination of POMs with cluster cations or macrocations has resulted in the formation of various interesting intercluster compounds, from the viewpoints of ionic crystals, crystal growth, crystal engineering, structure and sorption properties, and so on.<sup>2–5</sup> In many compounds, the POMs have been combined with separately prepared Ag/Au cluster cations.<sup>2–4</sup>

For example, depending upon the types of solvents and concentrations, two types of crystals of  $[Au_9(PPh_3)_8]^-$ - $[PW_{12}O_{40}]^{3-}$  have been obtained as orange needles of a first

compound and as greenish-black plates or prisms of a second compound. Both compounds contain  $[Au_9(PPh_3)_8]^{3+}$  and  $[\alpha-PW_{12}O_{40}]^{3-}$  in a 1:1 ratio but exhibit different  $Au_9$  skeletal isomers and packing types, i.e., NaCl and CsCl types.<sup>2a</sup> The crystal structure of the supramolecular intercluster compound  $[Au_9(PPh_3)_8]_2[V_{10}O_{28}H_3]_2$  is dominated by short-range bonding interactions, i.e., hydrogen bonds, and C–H/ $\pi$  interactions, avoiding simple AB packing.<sup>2b</sup> Intercluster compounds,<sup>2c</sup> such as  $[Au_9(dpph)_4][Mo_8O_{26}]$  [dpph = 1,6-bis(diphenylphosphino)hexane],  $[Au_9(dpph)_4][PW_{12}O_{40}]$ , and  $[Au_{11}(PPh_3)_8Cl_2]_2[W_6O_{19}]$ , have recently been reported. An Ag/1,2,4-triazole/POMs hybrid supramolecular family<sup>3</sup> has also been reported by Chinese workers and contains  $[Ag_4(dmtrz)_4][Mo_8O_{26}]$  (dmtrz = 3,5-dimethyl-1,2,4-triazole),  $[Ag_6(3atrz)_6][PMo_{12}O_{40}]_2 \cdot H_2O$  (3atrz = 3-amino-1,2,4-triazole),  $[Ag_2(3atrz)_2]_2[HPMo^{VI}_{10}Mo^V_2O_{40}]$ ,  $[Ag_2(dmtrz)_2]_2[HPMo^{VI}_{10}Mo^V_2O_{40}]$ ,  $[Ag_2(trz)_2]_2[Mo_8O_{26}]$  (trz = 1,2,4-triazole),  $[Ag_2(3atrz)_2][Ag_2(3atrz)_2(Mo_8O_{26})]$ ,  $[Ag_4(4atrz)_2Cl][Ag(Mo_8O_{26})]$

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(4atrz = 4-amino-1,2,4-triazole), and  $[\text{Ag}_5(\text{trz})_4]_2[\text{Ag}_2(\text{Mo}_8\text{O}_{26})] \cdot 4\text{H}_2\text{O}$ . On the other hand, Cronin et al. have reported a silver connection with POMs, i.e.,  $\{[\text{Ag}_3(\text{dmsO})_6][\text{Ag}_1(\text{dmsO})_3] \cdot [\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot \text{DMSO}\}_n$  (a 1D zigzag chain) and  $\{[\text{Ag}_3(\text{dmsO})_6] \cdot [\text{Ag}_1(\text{dmsO})_2][\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 2\text{DMSO}\}_n$  (a 2D network) (dmsO, DMSO = dimethyl sulfoxide).<sup>4a</sup> Using silver-based linkers, POM-based 0-, 1-, 2-, and 3D frameworks have been generated, in which silver ions are ligated mainly in an oxo-based ligand environment. The same research group has reported molecular growth processes utilizing POM-based building blocks with silver connecting units, such as  $[\text{Ag}_3(\text{bhepH})_8 \cdot (\text{W}_{11.5}\text{Na}_{0.5}\text{O}_{40}\text{P})_2] \cdot 8\text{H}_2\text{O}$  [bhep = *N,N'*-bis(2-hydroxyethyl)-piperazine] (representing a 0D dimer),  $[\text{Ag}_4(\text{DMSO})_8(\text{Mo}_8\text{O}_{26})]_n$  (forming 2D layered networks), and  $\{\text{Ag}_3[\text{MnMo}_6\text{O}_{18} \cdot \{(\text{OCH}_2)_3\text{CNH}_2\}_2(\text{DMSO})_5] \cdot 3\text{DMSO}\}_n$  and  $\{\text{Ag}_3[\text{MnMo}_6\text{O}_{18} \cdot \{(\text{OCH}_2)_3\text{CNH}_2\}_2(\text{DMSO})_6(\text{CH}_3\text{CN})_2] \cdot \text{DMSO}\}_n$  (forming 1D networks).<sup>4b</sup> Mizuno et al. have recently reported nanostructures and sorption properties based on a combination of macrocation  $[\text{Cr}_3\text{O}(\text{OOCH})_6(\text{H}_2\text{O})_3]^+$  and POMs such as  $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$  and  $[\alpha\text{-CoW}_{12}\text{O}_{40}]^{6-}$  to form  $\text{K}_3[\text{Cr}_3\text{O}(\text{OOCH})_6(\text{H}_2\text{O})_3][\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot 16\text{H}_2\text{O}$  and  $\text{Cs}_5[\text{Cr}_3\text{O}(\text{OOCH})_6(\text{H}_2\text{O})_3][\alpha\text{-CoW}_{12}\text{O}_{40}] \cdot 7.5\text{H}_2\text{O}$ .<sup>5</sup>

In this work, we unexpectedly found the formation of a novel intercluster compound,  $\{[\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})]_3[\alpha\text{-PW}_{12}\text{O}_{40}]_2 \cdot 4\text{EtOH} (\mathbf{1})$ , containing a phosphinegold(I) cluster cation,

which was obtained by the reaction of monomeric phosphinegold(I) carboxylate,  $[\text{Au}((R,S)\text{-pyrrld})(\text{PPh}_3)]$  [ $(R,S)\text{-Hpyrrld} = (R,S)\text{-2-pyrrolidone-5-carboxylic acid}$ ],<sup>6a</sup> with the free acid form of a saturated Keggin POM,  $\text{H}_3[\alpha\text{-PW}_{12}\text{O}_{40}] \cdot 7\text{H}_2\text{O}$ .<sup>7</sup> The synthesis, structure, and antimicrobial activities of the monomeric phosphinegold(I) carboxylate precursor have been unequivocally investigated.<sup>6a</sup> In relation to the present compound, the field of element-centered gold clusters  $[\text{E}(\text{AuL})_n]^{m+}$ , for example,  $[\text{E}(\text{AuPPh}_3)_4]^{2+}$  (E = S, Se),<sup>8a-c</sup> the angular flexibility of the Au–E–Au angles,<sup>8d</sup> and the new structural findings, i.e., the tetrahedral bonding of  $[\text{N}(\text{AuL})_4]^+$  and the pyramidal bondings of  $[\text{As}(\text{AuL})_4]^+$  and  $[\text{P}(\text{AuL})_4]^+$ ,<sup>8e,f</sup> has been extensively studied by the groups of Laguna<sup>8a-c</sup> and Schmidbaur.<sup>8d-f</sup>

There are several crucial issues concerning **1**: (1) the POM anion in **1** can be exchanged with  $\text{BF}_4^-$  (see the Experimental Section), suggesting that **1** is an ionic compound. (2) The  $\text{BF}_4^-$  salt of the {tetraphosphinegold(I)oxonium} cation  $[\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}^{2+}]$  has usually been synthesized by a quite different method, i.e., the reaction of tris{triarylphosphinegold(I)oxonium tetrafluoroborate}  $[\{\text{Au}(\text{PR}_3)_3(\mu_3\text{-O})\}\text{BF}_4]^{8g}$  with 1 equiv of a freshly prepared solution of the monomeric species  $[\text{Au}(\text{PR}_3)]\text{BF}_4$  (R = phenyl, *o*-tolyl) by Schmidbaur's group.<sup>8h</sup> (3) On the other hand, the present reaction significantly depends upon the POMs. As a matter of fact, the  $[\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}^{2+}]$  ion is also formed in the presence of other Keggin POMs, such as  $\text{H}_3[\alpha\text{-PMo}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O}$  and  $\text{H}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O}$ ,<sup>7</sup> the formulas of which have been determined as  $[\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}_2[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot 2\text{H}_2\text{O} (\mathbf{2})$  and  $[\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}_3[\alpha\text{-PMo}_{12}\text{O}_{40}]_2 \cdot 3\text{EtOH} (\mathbf{3})$ , respectively. (4) Formation of the intercluster compounds **1–3** suggests that the bulkiness and large anionic charge of the free-acid-type POMs contribute to the direct clusterization of  $[\text{Au}(\text{PR}_3)]^+$  species to the tetraphosphinegold cluster oxonium cation but not via the triphosphinegold oxonium cation, after removal of the  $(R,S)\text{-pyrrld}^-$  ligand. (5) Recently, several phosphinegold(I) complexes have become known as effective homogeneous catalysts for organic synthesis,<sup>9,10</sup> for example,  $[\{\text{Au}(\text{PPh}_3)_3(\mu_3\text{-O})\}\text{BF}_4]^{8g,11}$  has been used as an effective catalyst for a Claisen rearrangement of propargyl vinyl ethers,<sup>9,10</sup> and such a complex has also

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been utilized as a precursor for the synthesis of novel metal complexes.<sup>12</sup>

Herein, we report full details of the synthesis and characterization of intercluster compounds **1–3**. As related compounds using similar methods, we also report the synthesis and characterization of P(*o*-tolyl)<sub>3</sub> derivatives (Supporting Information), i.e., [ $\{\text{Au}(\text{P}(\textit{o}\text{-tolyl})_3)_4(\mu_4\text{-O})\}_3[\alpha\text{-PW}_{12}\text{O}_{40}]_2$  (**4**), [ $\{\text{Au}(\text{P}(\textit{o}\text{-tolyl})_3)_4(\mu_4\text{-O})\}_2[\alpha\text{-SiW}_{12}\text{O}_{40}]$  (**5**), and [ $\{\text{Au}(\text{P}(\textit{o}\text{-tolyl})_3)_4(\mu_4\text{-O})\}_3[\alpha\text{-PMo}_{12}\text{O}_{40}]_2$  (**6**).

## Experimental Section

**Materials.** The following reactants were used as received: H[AuCl<sub>4</sub>]·4H<sub>2</sub>O, EtOH, CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>2</sub>O, (*R,S*)-5-oxo-2-tetrahydrofuran-2-carboxylic acid [(*R,S*)-Hothf] (all from Wako); P(*o*-tolyl)<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN (all from Kanto); DMSO-*d*<sub>6</sub>, CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub> (all from Isotec); anion-exchange resin (Amberlyst A-27), PPh<sub>3</sub> (all from Aldrich); (*R,S*)-2-pyrrolidone-5-carboxylic acid [(*R,S*)-Hpyrrld] (TCI). As for the Keggin POM precursors, H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]·7H<sub>2</sub>O was derived from a separately prepared sodium salt using an H<sup>+</sup>-form cation-exchange column, and H<sub>3</sub>[α-PMo<sub>12</sub>O<sub>40</sub>]·14H<sub>2</sub>O and H<sub>4</sub>[α-SiW<sub>12</sub>O<sub>40</sub>]·10H<sub>2</sub>O were prepared according to the so-called ether-extraction method,<sup>7</sup> all of them being identified by Fourier transform (FT) IR, thermogravimetric and differential thermal analyses (TG/DTA), and solution (<sup>31</sup>P or <sup>29</sup>Si) NMR spectroscopy. The phosphinegold(I) carboxylate precursors, [Au((*R,S*)-pyrrld)(PPh<sub>3</sub>)] (R = Ph, *o*-tolyl) and [Au((*R,S*)-othf)(PPh<sub>3</sub>)], have been synthesized according to the literature<sup>6</sup> or its modification and identified by CHN elemental analysis, FTIR, TG/DTA, and solution (<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P) NMR spectroscopy.

**Instrumentation/Analytical Procedures.** CHN elemental analyses were carried out with a Perkin-Elmer 2400 CHNS Elemental Analyzer II (Kanagawa University). Complete elemental analyses were carried out with Mikroanalytisches Labor Pascher (Remagen, Germany). The samples were dried at room temperature under 10<sup>-3</sup>–10<sup>-4</sup> Torr overnight before analysis. IR spectra were recorded on a Jasco 4100 FTIR spectrometer in KBr disks at room temperature. TG/DTA were acquired using a Rigaku Thermo Plus 2 series TG/DTA TG 8120 instrument.

<sup>1</sup>H NMR (500.00 MHz) and <sup>31</sup>P{<sup>1</sup>H} NMR (202.00 MHz) spectra in a DMSO-*d*<sub>6</sub> solution were recorded in 5-mm-outer-diameter tubes on a JEOL JNM-ECP 500 FT-NMR spectrometer with a JEOL ECP-500 NMR data processing system. <sup>1</sup>H NMR (399.65 MHz) and <sup>31</sup>P NMR (161.70 MHz) spectra in a DMSO-*d*<sub>6</sub> solution were also recorded in 5-mm-outer-diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer with a JEOL EX-400 NMR data processing system. The <sup>1</sup>H NMR spectra were referenced to an internal standard of tetramethylsilane (SiMe<sub>4</sub>). The <sup>31</sup>P NMR spectra were referenced to an external standard of 25% H<sub>3</sub>PO<sub>4</sub> in H<sub>2</sub>O in a sealed capillary. The <sup>31</sup>P NMR data with the usual 85% H<sub>3</sub>PO<sub>4</sub> reference are shifted to +0.544 ppm from our data.

Solid-state cross-polarization magic-angle-spinning (CPMAS) <sup>31</sup>P (121.00 MHz) and <sup>29</sup>Si (59.71 MHz) NMR spectra were recorded in 6-mm-outer-diameter rotors on a JEOL JNM-ECP 300 FT-NMR spectrometer with a JEOL ECP-300 NMR data processing system. These spectra were referenced to external standards (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (δ 1.60) and poly(dimethylsilane) (δ -34.0), respectively.

**Preparations.** [ $\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}_3[\alpha\text{-PW}_{12}\text{O}_{40}]_2 \cdot 4\text{EtOH}$  (**1**). [Au((*R,S*)-pyrrld)(PPh<sub>3</sub>)] (0.352 g, 0.599 mmol) was dissolved in 50 mL of CH<sub>2</sub>Cl<sub>2</sub>. A clear solution of H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]·7H<sub>2</sub>O (0.301 g, 0.100 mmol) dissolved in 30 mL of an EtOH/H<sub>2</sub>O

(5:1, v/v) mixed solvent was slowly added along an interior wall of a round-bottomed flask containing a colorless clear solution of the gold(I) complex. The round-bottomed flask containing two layers, i.e., the gold(I) complex solution in the lower layer and the POM solution in the upper layer, was sealed and left in the dark at room temperature. After 5 days, pale-yellow, clear rod crystals formed around the interface of the two layers, which were collected on a membrane filter (JG 0.2 μm), washed with EtOH (5 mL × 1) and Et<sub>2</sub>O (10 mL × 2), and dried in vacuo for 2 h. Yield: 0.242 g (42.1%). The crystalline samples were soluble in DMSO but insoluble in water, acetonitrile, ethanol, and diethyl ether. Found (CHN analysis of an independent preparation): H, 1.67 (1.44); C, 23.18 (23.31); N, <0.1 (0.03); O, 11.9; P, 3.52; Au, 20.6; W, 38.1; total 98.97%. Calcd for C<sub>223</sub>H<sub>201</sub>O<sub>86.5</sub>P<sub>14</sub>Au<sub>12</sub>W<sub>24</sub> or [ $\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}_3[\alpha\text{-PW}_{12}\text{O}_{40}]_2 \cdot 3.5\text{EtOH}$ ]: H, 1.77; C, 23.34; O, 12.06; P, 3.78; Au, 20.60; W, 38.45. A weight loss of 0.21% was observed during the course of drying at room temperature at 10<sup>-3</sup>–10<sup>-4</sup> Torr overnight before analysis, suggesting the presence of 0.5 ethanol molecule. Thus, a total of 4 attached or solvated ethanol molecules was confirmed. TG/DTA under atmospheric conditions: a weight loss of 1.50% due to desorbed ethanol was observed below 215.5 °C; calcd 1.60% for 4 ethanol molecules. IR (KBr): 1479 m, 1437 s, 1180 vw, 1103 m, 1080 m, 982 m, 895 m, 816 vs, 746 vs, 712 s, 692 vs, 544 vs, 501 vs cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (24.5 °C, DMSO-*d*<sub>6</sub>): δ -14.79, 24.87. <sup>1</sup>H NMR (23.1 °C, DMSO-*d*<sub>6</sub>): δ 1.09 (t, *J* = 6.9 Hz, CH<sub>3</sub>CH<sub>2</sub>OH solvate), 3.38 (q, *J* = 7.3 Hz, CH<sub>3</sub>CH<sub>2</sub>OH solvate), 7.38–7.55 (m, PPh<sub>3</sub>). Solid-state CPMAS <sup>31</sup>P NMR: δ -14.6, 15.3, 25.8.

It should be noted that a less pure product was obtained in lower yield by the slow evaporation of the reaction mixture of the phosphinegold(I) carboxylate precursor, [Au((*R,S*)-pyrrld)(PPh<sub>3</sub>)], with the sodium salt of POM, i.e., Na<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]·8H<sub>2</sub>O. It should also be noted that the same product containing the tetragold(I) oxonium cluster cation was formed in good yield by a workup similar to the synthesis of **1** using H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]·7H<sub>2</sub>O and another phosphinegold(I) carboxylate precursor, i.e., [Au((*R,S*)-othf)(PPh<sub>3</sub>)].

[ $\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}_2[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot 2\text{H}_2\text{O}$  (**2**). In the synthesis of **1**, H<sub>4</sub>[α-SiW<sub>12</sub>O<sub>40</sub>]·10H<sub>2</sub>O (0.295 g, 0.097 mmol) was used in place of H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]·7H<sub>2</sub>O and [Au((*R,S*)-pyrrld)(PPh<sub>3</sub>)] (0.470 g, 0.800 mmol) was also used. The pale-yellow, clear granular crystals obtained in 50.6% yield (0.335 g scale) were soluble in DMSO but insoluble in water, ethanol, and diethyl ether. Found (CHN analysis of an independent preparation): H, 1.81 (1.44); C, 26.28 (26.12); N, <0.1 (0.01); O, 10.4; Si, 0.36; P, 3.53; Au, 23.9; W, 33.0; total 98.72%. Calcd for C<sub>144</sub>H<sub>120</sub>O<sub>42</sub>Si<sub>1</sub>P<sub>8</sub>Au<sub>8</sub>W<sub>12</sub> or [ $\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}_2[\alpha\text{-SiW}_{12}\text{O}_{40}]$ ]: H, 1.84; C, 26.28; O, 10.21; Si, 0.43; P, 3.77; Au, 23.95; W, 33.53. A weight loss of 0.43% was observed during the course of drying at room temperature at 10<sup>-3</sup>–10<sup>-4</sup> Torr overnight before analysis, suggesting the presence of 2 water molecules. Thus, a total of 2 water molecules, attached or solvated, was confirmed. TG/DTA under atmospheric conditions: a weight loss of 0.37% due to dehydration was observed below 131.5 °C; calcd 0.27% for 1 water molecule. In X-ray crystallography, 2 water molecules were identified. The title formula with 2 hydrated water molecules is based on complete elemental analysis and X-ray crystallography. IR (KBr): 1481 w, 1437 s, 1182 vw, 1101 m, 1011 w, 970 s, 920 vs, 800 vs, 746 s, 712 m, 692 s, 544 s, 511 m cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (24.4 °C, DMSO-*d*<sub>6</sub>): δ 24.76. <sup>1</sup>H NMR (23.0 °C, DMSO-*d*<sub>6</sub>): δ 7.38–7.57 (m, PPh<sub>3</sub>). Solid-state CPMAS <sup>31</sup>P NMR: δ 19.2, 25.1. Solid-state CPMAS <sup>29</sup>Si NMR: δ -83.11.

[ $\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}_3[\alpha\text{-PMo}_{12}\text{O}_{40}]_2 \cdot 3\text{EtOH}$  (**3**). In the synthesis of **1**, H<sub>3</sub>[α-PMo<sub>12</sub>O<sub>40</sub>]·14H<sub>2</sub>O (0.208 g, 0.100 mmol) was used in place of H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]·7H<sub>2</sub>O. The yellow, clear crystals obtained in 50.1% yield (0.234 g scale) were soluble in DMSO but insoluble in water, ethanol, and diethyl ether. Found (CHN analysis of an independent preparation): H, 2.07 (2.08);

(12) (a) Singh, A.; Anandhi, U.; Cinellu, M. A.; Sharp, P. R. *Dalton Trans.* **2008**, 2314–2327. (b) Singh, A.; Sharp, P. R. *Inorg. Chim. Acta* **2008**, 361, 3159–3164. (c) Blumenthal, A.; Beruda, H.; Schmidbaur, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1005–1006.

C, 28.36 (28.49); N, <0.1 (0.21); O, 14.8; P, 4.51; Au, 25.1; Mo, 25.1; total 99.94%. Calcd for  $C_{221}H_{195}O_{85.5}P_{14}Au_{12}Mo_{24}$  or  $[\{Au(PPh_3)_4(\mu_4-O)\}_3[\alpha-PMo_{12}O_{40}]_2 \cdot 2.5EtOH$ : H, 2.11; C, 28.48; O, 14.68; P, 4.65; Au, 25.36; Mo, 24.71. A weight loss of 0.20% was observed during the course of drying at room temperature at  $10^{-3}$ – $10^{-4}$  Torr overnight before analysis, suggesting the presence of 0.5 ethanol molecule. Thus, a total of 3 ethanol molecules, attached or solvated, was confirmed. TG/DTA under atmospheric conditions: a weight loss of 1.59% due to desorbed ethanol was observed below 260.2 °C; calcd 1.48% for a total of 3 ethanol molecules. IR (KBr): 1479 w, 1435 m, 1181 vw, 1101 w, 1061 m, 957 s, 878 m, 803 vs, 744 vs, 712 s, 690 vs, 544 s, 500  $s\text{ cm}^{-1}$ .  $^{31}P\{^1H\}$  NMR (24.3 °C, DMSO- $d_6$ ):  $\delta$  -3.27, 25.21.  $^1H$  NMR (23.1 °C, DMSO- $d_6$ ):  $\delta$  1.09 (t,  $J$  = 6.9,  $CH_3CH_2OH$  solvate), 3.38 (q,  $J$  = 7.0 Hz,  $CH_3CH_2OH$  solvate), 7.40–7.57 (m,  $PPh_3$ ). Solid-state CPMAS  $^{31}P$  NMR:  $\delta$  -3.1, 25.5.

The crystals of **3** were not suitable for X-ray diffraction measurements. Although the existence of the tetragold(I) cluster was confirmed, the quality of the crystal data was poor.

**Anion Exchange of 1 with  $BF_4^-$  by the Batch Method.** An anion-exchange resin (Amberlyst A-27) in the  $BF_4^-$  form of 5 mL was mixed with **1** dispersed in 50 mL of  $CH_3CN$ , followed by stirring for 20 min. The supernatant solution was evaporated to dryness using an evaporator at ca. 30 °C. The resulting white powder was dried in vacuo for 2 h, and the  $^{31}P$  NMR spectrum was measured in  $CD_2Cl_2$ . The white powder obtained in 36.6% yield (0.02 g scale) was soluble in dichloromethane but insoluble in acetonitrile.  $^{31}P$  NMR (22.5 °C,  $CD_2Cl_2$ ):  $\delta$  25.10 (the  $[\alpha-PW_{12}O_{40}]^{3-}$ -free compound. Lit.<sup>8h</sup>  $\delta$  25.4 ( $CD_2Cl_2$ ) for  $[\{Au(PPh_3)_4(\mu_4-O)\}(BF_4)_2$ ).

**X-ray Crystallography.** A pale-yellow, clear rod crystal of **1** ( $0.20 \times 0.12 \times 0.06\text{ mm}^3$ ) and a pale-yellow, clear granular crystal of **2** ( $0.16 \times 0.13 \times 0.09\text{ mm}^3$ ) were surrounded by liquid paraffin to prevent their degradation. Data collection was done by a Bruker SMART APEX CCD diffractometer at 90 K in the range of  $0.77^\circ < \theta < 28.28^\circ$  for **1** and  $1.30^\circ < \theta < 28.33^\circ$  for **2**. The intensity data were automatically collected for Lorentz and polarization effects during integration. The structure was solved by direct methods (program *SHELXS-97*),<sup>13a</sup> followed by subsequent difference Fourier calculation and refined by a full-matrix, least-squares procedure on  $F^2$  (program *SHELXL-97*).<sup>13b</sup> Absorption correction was performed with *SADABS* (empirical absorption correction).<sup>13c</sup> The compositions and formulas of **1** and **2** containing several solvated molecules were determined by complete elemental analysis, TG/DTA, and  $^1H$  NMR. Because of the disorder of the solvated EtOH molecules in **1** and the central  $PO_4$  and  $SiO_4$  moieties of the saturated Keggin POMs in **1** and **2**, respectively, the residual electron densities in the final difference maps for **1** and **2** were rather large.

**Crystal data for 1:**  $C_{224}H_{204}Au_{12}O_{87}P_{14}W_{24}$ ;  $M$  = 11 497.45, rhombohedral, space group  $R\bar{3}$ ,  $a$  = 53.192(5) Å,  $b$  = 53.192(5) Å,  $c$  = 17.100(3) Å,  $V$  = 41902(10) Å<sup>3</sup>,  $Z$  = 6,  $D_c$  = 2.734  $Mg\text{ m}^{-3}$ ,  $\mu$ (Mo K $\alpha$ ) = 16.262  $mm^{-1}$ .  $R_1$  = 0.0843,  $wR_2$  = 0.1723 (for all data).  $R_{int}$  = 0.0882,  $R_1$  = 0.0559,  $wR_2$  = 0.1613, GOF = 0.978 [113 869 total reflections, 21 612 unique reflections where  $I > 2\sigma(I)$ ]. The maximum and minimum residual density (+11.013 and -2.169  $e\text{ Å}^{-3}$ ) holes were located at 3.12 Å from H71 and 0.84 Å from W2, respectively. For **1**, Keggin polyoxoanions consisting of 24 tungsten atoms, 2 phosphorus atoms, 80 oxygen atoms, and gold(I) cluster cations consisting of 12 gold atoms, 12 phosphorus atoms, 216 carbon atoms, 180 hydrogen atoms, and 3 bridged oxygen atoms, per formula unit, were identified, but the locations of 4 solvated ethanol molecules per formula unit were not determined as a result of disorder.

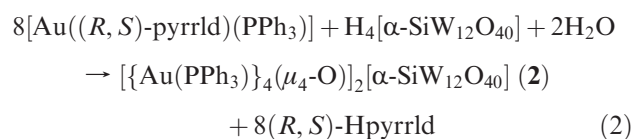
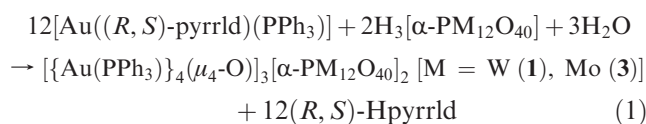
**Crystal data for 2:**  $C_{144}H_{124}Au_8O_{44}P_8SiW_{12}$ ;  $M$  = 6616.21, monoclinic, space group  $C2/c$ ,  $a$  = 28.6060(16) Å,  $b$  = 19.0414(16) Å,  $c$  = 32.434(2) Å,  $\beta$  = 107.659(2)°,  $V$  = 16834(2) Å<sup>3</sup>,  $Z$  = 4,  $D_c$  = 2.610  $Mg\text{ m}^{-3}$ ,  $\mu$ (Mo K $\alpha$ ) = 15.253  $mm^{-1}$ .  $R_1$  = 0.0671,  $wR_2$  = 0.1477 (for all data).  $R_{int}$  = 0.0437,  $R_1$  = 0.0549,  $wR_2$  = 0.1387, GOF = 1.159 [78 656 total reflections, 20 950 unique reflections where  $I > 2\sigma(I)$ ]. The maximum and minimum residual density (+12.767 and -3.048  $e\text{ Å}^{-3}$ ) holes were located at 2.94 Å from O15 and 0.03 Å from O16, respectively. In **2**, Keggin polyoxoanion consisting of 12 tungsten atoms, one silicon atom, 40 oxygen atoms, and gold(I) cluster cations consisting of 8 gold atoms, 8 phosphorus atoms, 144 carbon atoms, 120 hydrogen atoms, 2 bridged-oxygen atoms, and 2 hydrated water molecules, per formula unit, were identified.

CCDC reference numbers 766432 (code: ty04s) for **1** and 766433 (code: ty10s) for **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44-1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

## Results and Discussion

**Synthesis and Compositional Characterization.** The intercluster compounds were obtained as **1** in 42.1% (0.242 g scale) yield, as **2** in 50.6% (0.335 g scale) yield, and as **3** in 50.1% (0.234 g scale) yield. These compounds were prepared by reactions based on liquid–liquid diffusion at room temperature between  $[Au((R,S)\text{-pyrrld})(PPh_3)]$  (0.599 mmol for **1** and **3** and 0.800 mmol for **2**) in  $CH_2Cl_2$  and the free acid forms (0.100 mmol) of Keggin POMs in mixed EtOH/water solvents, i.e.,  $H_3[\alpha-PW_{12}O_{40}] \cdot 7H_2O$ ,  $H_4[\alpha-SiW_{12}O_{40}] \cdot 10H_2O$ , and  $H_3[\alpha-PMo_{12}O_{40}] \cdot 14H_2O$ , respectively. The molecular formulas of intercluster compounds **1–3** prepared here were consistent with all data of complete elemental analysis, TG/DTA, FTIR, solid-state CPMAS ( $^{31}P$  and  $^{29}Si$ ) NMR, and solution ( $^1H$  and  $^{31}P\{^1H\}$ ) NMR spectra and also with X-ray crystallography for **1** and **2**. Complex **3** was crystallized, but the crystal data were of low quality and the structure was poorly refined. The presence of solvated molecules, i.e., 4 ethanol molecules for **1**, 2 water molecules for **2**, and 3 ethanol molecules for **3**, was confirmed by elemental analysis of the dried samples under  $10^{-3}$ – $10^{-4}$  Torr overnight and the weight losses found before analysis, TG/DTA measurements under atmospheric conditions,  $^1H$  NMR for solvated ethanol molecules in **1** and **3**, and X-ray crystallography for 2 solvated water molecules in **2** (see the Experimental Section).

The formation of **1–3** can be represented in eqs 1 and 2, respectively.



(13) (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473. (b) Sheldrick, G. M. *SHELXL-97 program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997. (c) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1996.

X-ray crystallography of **1** and **2** showed the formation of discrete intercluster compounds between tetrakis(triphenylphosphinegold(I))oxonium cluster cation

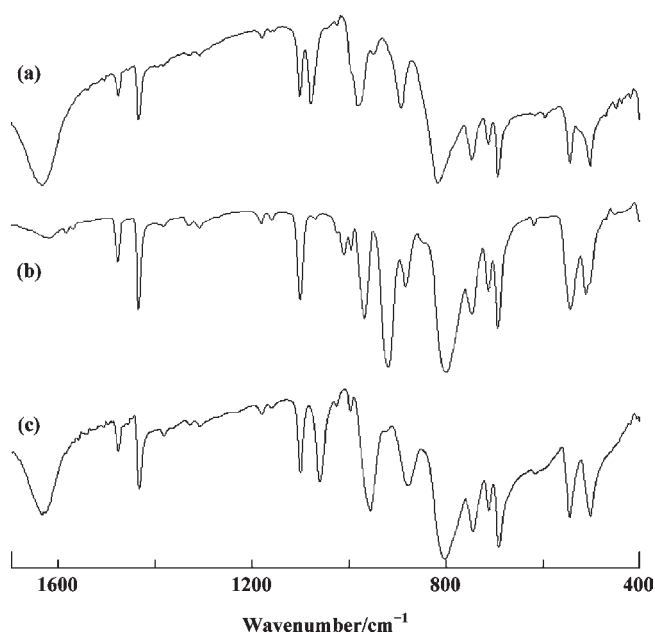
$[\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}^{2+}]$  and a saturated Keggin POM (see the Crystal and Molecular Structures of **1** and **2** section). Such an oxonium cluster cation (stable four-coordinate dicationic oxygen compound  $[\text{H}_4\text{O}]^{2+}$ ) was first prepared as  $[\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}(\text{BF}_4)_2]$  by Schmidbauer's group by the treatment of the separately prepared  $[\{\text{Au}(\text{PPh}_3)_3(\mu_3\text{-O})\}^+\text{BF}_4^-]$  with 1 equiv of a freshly prepared solution of  $[(\text{PPh}_3)\text{Au}]^+\text{BF}_4^-$ .<sup>8h</sup> On the other hand, in the present work,  $[\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}^{2+}]$  was directly formed during the course of carboxylate elimination of the monomeric  $\text{O}-\text{Au}^{\text{I}}-\text{P}$  bonding precursor,  $[\text{Au}((R,S)\text{-pyrrld})(\text{PPh}_3)]$ , in the presence of the free acid forms of saturated Keggin POMs. The reactions based on liquid–liquid diffusion around the interface gave crystalline samples suitable for X-ray diffraction measurements. Formation of the intercluster compounds **1–3** suggests that the bulkiness and large anionic charge of the free-acid-type POMs significantly contribute to the direct clusterization of  $[\text{Au}(\text{PR}_3)]^+$  species to the  $[\{\text{Au}(\text{PR}_3)_4\text{O}\}^{2+}]$  cation, but not via the  $[\{\text{Au}(\text{PPh}_3)_3(\mu_3\text{-O})\}^+]$  ion, after removal of the  $(R,S)$ -pyrrld<sup>−</sup> ligand. That is to say, the present reactions strongly depend upon the POMs. Such an effect of the POMs may be termed as the “reaction space/field” of the POM.

The central oxide ion encapsulated in  $[\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}^{2+}]$  comes from the water molecules contained in the reaction system and/or the solvated water molecules contained in the POMs. In fact, the present reaction cannot be carried out in the system without water because such a system is heterogeneous and the reaction does not proceed. Participation of water contained in the reaction system is crucial and also would be reasonable, as shown in other related reactions.<sup>8c,g</sup> There is no direct bonding between the  $[\{\text{Au}(\text{PPh}_3)_4(\mu_4\text{-O})\}^{2+}]$  cation and the Keggin POM anion. Thus, intercluster compounds are formed by ionic interaction between them. As a matter of fact, the POM anions in the compounds can be exchanged with  $\text{BF}_4^-$  using an anion-exchange resin in the  $\text{BF}_4^-$  form (see the Experimental Section).

The present reaction to obtain **1** was applicable to other carboxylate precursors such as  $[\text{Au}((R,S)\text{-othf})(\text{PPh}_3)]$  (see the Experimental Section). Thus, the carboxylate plays only the role of a leaving group.

In order to know the effect of the phosphine ligand, another ligand, such as  $\text{P}(o\text{-tolyl})_3$ , was examined. When the separately prepared precursor complex  $[\text{Au}((R,S)\text{-pyrrld})\{\text{P}(o\text{-tolyl})_3\}]$  was used in reactions with  $\text{H}_3[\alpha\text{-PM}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$  ( $n = 7$  for  $\text{M} = \text{W}$  and  $14$  for  $\text{M} = \text{Mo}$ ) and  $\text{H}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O}$ , the corresponding intercluster compounds  $[\{\text{Au}(\text{P}(o\text{-tolyl})_3)_4(\mu_4\text{-O})\}_3[\alpha\text{-PM}_{12}\text{O}_{40}]_2]$  [ $\text{M} = \text{W}$  (**4**),  $\text{Mo}$  (**6**)] and  $[\{\text{Au}(\text{P}(o\text{-tolyl})_3)_4(\mu_4\text{-O})\}_2[\alpha\text{-SiW}_{12}\text{O}_{40}]$  (**5**) were obtained in good yield (see the Supporting Information).

The solid-state FTIR spectra (Figure 1) of **1–3** showed the characteristic vibrational bands based on the coordinating  $\text{PPh}_3$  ligands. The FTIR spectra also showed prominent vibrational bands due to the saturated Keggin tungsto-POMs (1080, 982, 895, and  $816\text{ cm}^{-1}$ ) for **1**



**Figure 1.** FTIR spectra in the polyoxoanion region ( $1700\text{--}400\text{ cm}^{-1}$ ), measured as KBr disks, of (a) **1**, (b) **2**, and (c) **3**.

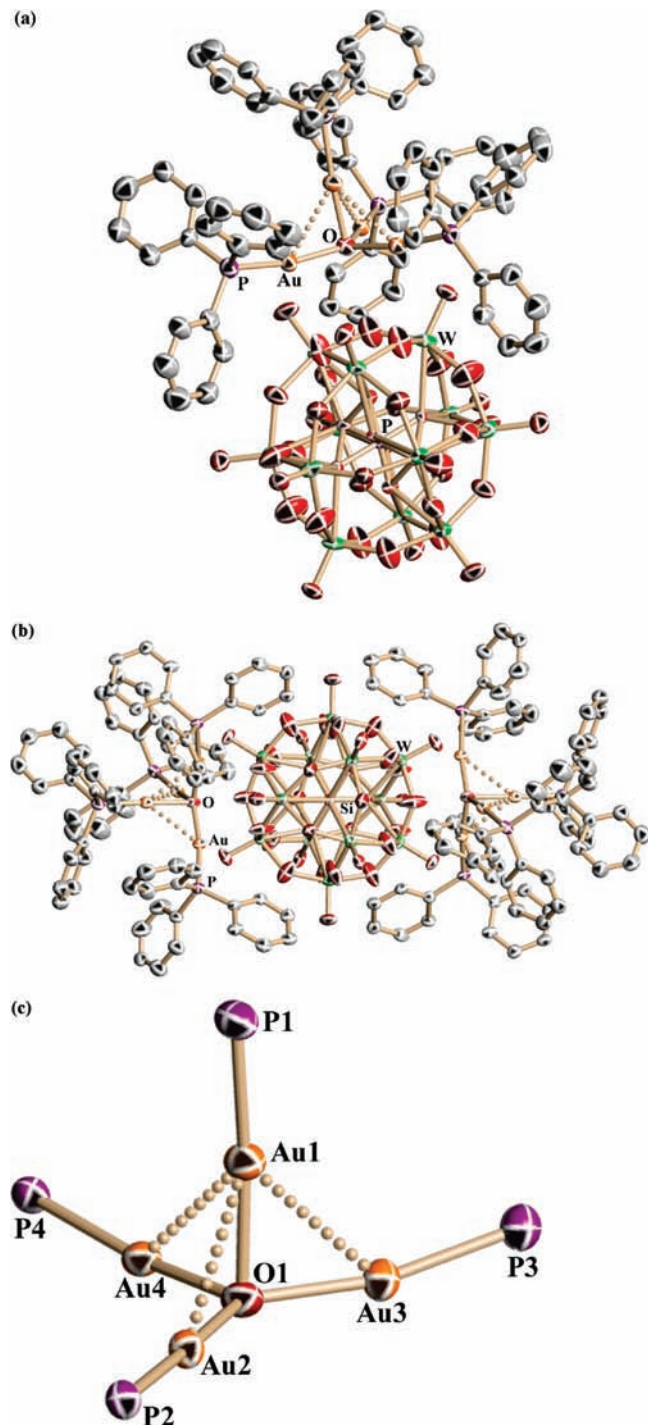
with heteroatom phosphorus and ( $1011$ ,  $970$ ,  $920$ , and  $800\text{ cm}^{-1}$ ) for **2** with heteroatom silicon and the Keggin molybdo-POM ( $1061$ ,  $957$ ,  $878$ , and  $803\text{ cm}^{-1}$ ) for **3** with heteroatom phosphorus.<sup>14</sup> Upon formation of **1–3**, the carbonyl vibrational bands of the anionic  $(R,S)$ -pyrrld ligand in  $[\text{Au}((R,S)\text{-pyrrld})(\text{PPh}_3)]$ , which were observed at  $1696$  and  $1632\text{ cm}^{-1}$ , disappeared, suggesting that the carboxylate ligand is eliminated. This fact was also confirmed by  $^1\text{H NMR}$  in  $\text{DMSO-}d_6$ .

**Crystal and Molecular Structures of 1 and 2.** The molecular structures of **1** and **2** are shown in parts a and b of Figure 2, respectively, and the framework of the tetrakis{phosphinegold(I)} cluster cation with an atom numbering scheme is shown in Figure 2c. Solid-state packing views of **1** and **2** are shown in Figures S1 and S2 (Supporting Information). Selected bond distances and angles are listed in Table 1.

The formulas and compositions of **1** and **2**, both being composed of tetragold(I) cluster cations, Keggin POM anions, and several solvated molecules, were determined by complete elemental analysis and TG/DTA. X-ray crystallography revealed that **1** and **2** were constructed by the tetragold(I) cluster cations encapsulating the bridged oxygen ( $\mu_4$ -oxygen) atom and the saturated  $\alpha$ -Keggin POMs as counterions. In **1**, 4 solvated ethanol molecules per formula unit were disordered, while in **2**, 2 solvated water molecules per formula unit were identified. The X-ray structure analysis of **1** and **2** also elucidated that the geometry of the tetra{phosphinegold(I)} cluster cation was a distorted tetrahedron, i.e., an approximate trigonal pyramid. To date, the molecular structure of such a tetragold(I) cluster is the second example reported. The first structural analysis, reported by Schmidbauer's group in 1995,<sup>8h</sup> was concerned with  $[\{\text{Au}(\text{P}(o\text{-tolyl})_3)_4(\mu_4\text{-O})\}(\text{BF}_4)_2]$ , which contained a regular tetrahedron of the tetragold(I) cluster cation.

Complex **1** crystallized in rhombohedral space group  $R\bar{3}$ . As shown in Figure 2c, the geometry of the  $\{(\text{PPh}_3)\text{-Au}\}_4$  cluster cation unit in **1** was a distorted tetrahedron

(14) (a) Rocchiccioli-Deltcheff, C.; Thouvenot, R.; Franck, R. *Spectrochim. Acta* **1976**, *32A*, 587–597. (b) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R. *Inorg. Chem.* **1983**, *22*, 207–216. (c) Thouvenot, R.; Fournier, M.; Franck, R.; Rocchiccioli-Deltcheff, C. *Inorg. Chem.* **1984**, *23*, 598–605.



**Figure 2.** Molecular structures of (a) **1**, (b) **2**, and (c) the partial structure around the gold(I) cluster in **1**.

composed of three shorter edges that originated from the Au1 atom [Au1–Au2 2.9728(11) Å, Au1–Au3 2.9302(9) Å, and Au1–Au4 2.9836(9) Å; average 2.962 Å], which formed on a triangular plane of the Au2, Au3, and Au4 atoms with longer edges [Au2–Au3 3.753 Å, Au2–Au4 3.428 Å, and Au3–Au4 3.556 Å; average 3.579 Å]. The three edges originating from the Au1 atom [average 2.962 Å] were longer than the Au–Au separation of metallic gold

**Table 1.** Selected Bond Lengths (Å), Angles (deg), and Distances (Å) around the Gold(I) Clusters in **1** and **2**

|            | <b>1</b>   | <b>2</b>  | ref 8h |
|------------|------------|-----------|--------|
| Lengths    |            |           |        |
| Au1–O1     | 2.142(11)  | 2.130(9)  |        |
| Au2–O1     | 2.043(10)  | 2.077(8)  |        |
| Au3–O1     | 2.095(10)  | 2.076(8)  |        |
| Au4–O1     | 2.074(11)  | 2.081(8)  |        |
| average    | 2.089      | 2.091     | 2.0571 |
| Au1–P1     | 2.237(4)   | 2.215(3)  |        |
| Au2–P2     | 2.219(4)   | 2.206(3)  |        |
| Au3–P3     | 2.218(4)   | 2.207(3)  |        |
| Au4–P4     | 2.217(4)   | 2.209(3)  |        |
| average    | 2.223      | 2.209     | 2.225  |
| Au1···Au2  | 2.9728(11) | 2.9607(7) |        |
| Au1···Au3  | 2.9302(9)  | 2.8931(7) |        |
| Au1···Au4  | 2.9836(9)  | 2.9186(6) |        |
| average    | 2.962      | 2.924     | 3.3593 |
| Distances  |            |           |        |
| Au2···Au3  | 3.753      | 3.802     |        |
| Au2···Au4  | 3.428      | 3.527     |        |
| Au3···Au4  | 3.556      | 3.428     |        |
| average    | 3.579      | 3.586     | 3.3593 |
| Angles     |            |           |        |
| Au2–O1–Au3 | 130.1(5)   | 132.5(4)  |        |
| Au2–O1–Au4 | 112.7(5)   | 116.0(4)  |        |
| Au3–O1–Au4 | 117.1(5)   | 111.1(4)  |        |
| average    | 120.0      | 119.9     | 109.5  |

(2.88 Å)<sup>15a</sup> but shorter than twice the van der Waals radius for gold (3.32 Å).<sup>15b</sup> Thus, there are three Au–Au interactions due to van der Waals contacts among Au1 and AuX (X = 2, 3, 4) atoms (dotted line in Figure 2c). One encapsulated  $\mu_4$ -oxygen atom was placed within the basal plane consisting of the Au2, Au3 and Au4 atoms because the sum of the three angles was almost 360° [Au2–O–Au3 130.1(5)°, Au2–O–Au4 112.7(5)°, and Au3–O–Au4 117.1(5)°; a total of 359.9°]. The angular flexibility has been considered on the basis of a very flat energy profile for the Au–O–Au angles owing to strong aurophilic bonding, which exceeds that of standard van der Waals interactions.<sup>8d</sup>

We can also see that the distorted tetrahedron is formed with one long Au1–O length [2.142(11) Å] and three shorter Au–O lengths that are almost the same [Au2–O, Au3–O, and Au4–O; average 2.071 Å]. The angle of Au2–O–Au3 [130.1(5)°] was larger than those of Au2–O–Au4 and Au3–O–Au4 [112.7(5)° and 117.1(5)°, respectively], resulting in a point group of a tetragold(I) cluster with an approximate  $C_s$  symmetry rather than a  $C_{3v}$  symmetry. All phosphorus atoms in the four PPh<sub>3</sub> groups were arranged along an approximate line through the oxygen, gold, and phosphorus atoms [O–Au–P angles: average 173.0°].

On the other hand, the molecular structure of the saturated  $\alpha$ -Keggin POM, [ $\alpha$ -PW<sub>12</sub>O<sub>40</sub>]<sup>3–</sup>, as a counterion in **1**, was identical with that of previously reported POMs.<sup>16</sup> In **1**, the

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(16) (a) Brown, G. M.; Noe-Spirlet, M. R.; Busing, W. R.; Levy, H. A. *Acta Crystallogr., Sect. B* **1977**, *33*, 1038–1046. (b) Kearley, G. J.; Pressman, H. A.; Slade, R. C. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1801–1802. (c) Noe-Spirlet, M. R.; Busing, W. R. *Acta Crystallogr., Sect. B* **1978**, *34*, 907–910. (d) Noe-Spirlet, M. R.; Brown, G. M.; Busing, W. R.; Levy, H. A. *Acta Crystallogr., Sect. A* **1975**, *31*, S80.

W–O bond lengths of the saturated  $\alpha$ -Keggin units were in the normal range:<sup>1b,16</sup> bond lengths of W–Ot (terminal) [average 1.679 Å], W–Oc (corner-sharing) [average 1.891 Å], W–Oe (edge-sharing) [average 1.891 Å], and W–Oa (coordinating to the heteroatom) [average 2.457 Å] (Table S1 in the Supporting Information). In the Keggin unit, the central PO<sub>4</sub> moiety was disordered.

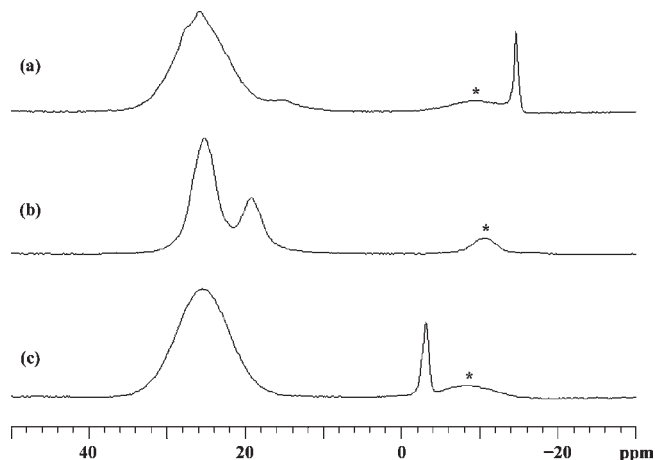
Because there was no bonding interaction between the tetragold(I) cluster cations and  $\alpha$ -Keggin POM anions, **1** comprises ionic crystals.

Complex **2** crystallized in the monoclinic space group *C2/c*. The general feature of the molecular structure of the tetra{phosphinegold(I)} cluster cation encapsulated with the  $\mu_4$ -oxygen atom in **2** was very similar to that of **1** (Figure 2b,c and Table 1). The molecular structure of the saturated  $\alpha$ -Keggin POM [ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup>, as a counterion in **2**, was also identical with that of previously reported POMs.<sup>1b,16</sup> In the Keggin unit, the central SiO<sub>4</sub> moiety was disordered. The W–O bond lengths can be compared with those of **1** (Table S1 in the Supporting Information).

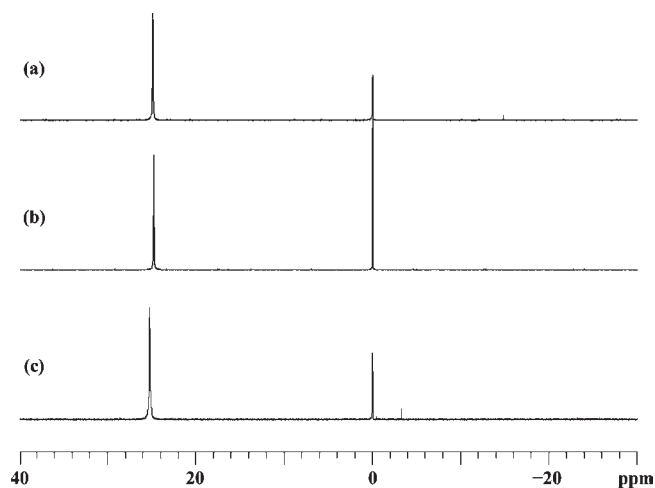
The molecular structure of the tetragold(I) cluster cation in [{Au(PR<sub>3</sub>)<sub>4</sub>O](BF<sub>4</sub>)<sub>2</sub> (R = *o*-tolyl) has been reported as a regular tetrahedral form [*T<sub>d</sub>* symmetry: Au–O–Au 109.5°, Au–O 2.0571(5) Å, distances of Au–Au edges 3.3593(8) Å] by Schmidbaur et al. (Table 1).<sup>8h</sup> As a related cluster, the tetra{phosphinegold(I)} cluster cation without the  $\mu_4$ -oxygen atom has also been reported by the same group.<sup>17</sup> The structural difference in the solid state between the two tetra{phosphinegold(I)} clusters, i.e., [{Au(PPh<sub>3</sub>)<sub>4</sub>O]<sub>3</sub>[ $\alpha$ -PW<sub>12</sub>O<sub>40</sub>]<sub>2</sub> in the present work and [{Au(P(*o*-tolyl)<sub>3</sub>)<sub>4</sub>O](BF<sub>4</sub>)<sub>2</sub> in Schmidbaur's group, may be attributed to the bulkiness and electrostatic interaction of the counterions constructing the ionic crystals [POMs ([ $\alpha$ -PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>, [ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup>), and BF<sub>4</sub><sup>-</sup>] and the crystallization conditions rather than the difference between R = Ph and *o*-tolyl in the PR<sub>3</sub> groups. The structural difference of the tetragold(I) cluster in **1** in the solid state and in solution is discussed based on solid-state and solution <sup>31</sup>P NMR.

Because of the disorder of the central PO<sub>4</sub> and SiO<sub>4</sub> moieties in **1** and **2**, respectively, the bond valence sums (BVS)<sup>18</sup> could not be estimated for the phosphorus and tungsten atoms in the Keggin POMs. The BVS values of the gold and phosphorus atoms and the encapsulated  $\mu_4$ -oxygen atom in the tetragold(I) cluster moieties in **1** and **2** were rather anomalous and did not correspond to the formal valences Au<sup>+</sup>, P<sup>5+</sup>, and O<sup>2-</sup> (Table S2 in the Supporting Information), the data of which were almost the same as the BVS data calculated herein using the bond lengths reported in [(P(*o*-tolyl)<sub>3</sub>)Au]<sub>4</sub>O(BF<sub>4</sub>)<sub>2</sub>.<sup>8h</sup> These anomalous BVS values may come from the unusual tetragold(I) structure itself.

**Solid-State (<sup>31</sup>P and <sup>29</sup>Si) and Solution (<sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H) NMR.** The solid-state CPMAS <sup>31</sup>P NMR spectrum of **1** (Figure 3) showed three resonances at –14.6, 15.3, and 25.8 ppm. The latter two signals were remarkably broadened. Because such resonances should correspond to the solid-state structure determined by X-ray crystallogra-



**Figure 3.** Solid-state CPMAS <sup>31</sup>P NMR spectra of (a) **1**, (b) **2**, and (c) **3**. Broad signals denoted by asterisks in the higher field are due to spinning sidebands.



**Figure 4.** <sup>31</sup>P{<sup>1</sup>H} NMR spectra in DMSO-*d*<sub>6</sub> of (a) **1**, (b) **2**, and (c) **3**.

phy, the three signals are assignable to the heteroatom phosphorus in the  $\alpha$ -Keggin POM anion and the two inequivalent phosphorus atoms due to the PPh<sub>3</sub> groups in the distorted tetrahedron of the tetragold(I) cluster cation. [Note: The inequivalent phosphorus atoms should be due to the 1:3 ratio (*C<sub>3v</sub>* symmetry) or 1:1:2 ratio (*C<sub>s</sub>* symmetry) of the apical and basal PPh<sub>3</sub> groups in the distorted tetrahedron.] On the other hand, the solution <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1** in DMSO-*d*<sub>6</sub> (Figure 4) showed two sharp signals at –14.79 and 24.87 ppm due to the  $\alpha$ -Keggin POM and PPh<sub>3</sub> groups of the tetragold(I) cluster, respectively. The peak at 24.87 ppm is an averaged signal due to motion in the solution of the tetragold(I) cluster, which can be compared with the signal at 25.10 ppm in CD<sub>2</sub>Cl<sub>2</sub> of the sample obtained by experiments of the anion exchange of **1** with BF<sub>4</sub><sup>-</sup> (see the Experimental Section) and that at 25.4 ppm in CD<sub>2</sub>Cl<sub>2</sub> of [{Au(PPh<sub>3</sub>)<sub>4</sub>O]( $\mu_4$ -O)(BF<sub>4</sub>)<sub>2</sub> reported by Schmidbaur et al.<sup>8h</sup>

The solid-state CPMAS <sup>31</sup>P NMR spectrum of **2** (Figure 3) showed two broad signals at 19.2 and 25.1 ppm based on the two inequivalent phosphorus atoms in the tetragold(I) cluster, which corresponded to the solid-state, distorted tetrahedral structure determined by X-ray crystallography. In solution <sup>31</sup>P{<sup>1</sup>H} NMR, such signals were also observed as

(17) Zeller, E.; Beruda, H.; Schmidbaur, H. *Inorg. Chem.* **1993**, *32*, 3203–3204.

(18) (a) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244–247. (b) Brown, I. D.; Shannon, R. D. *Acta Crystallogr., Sect. A* **1973**, *29*, 266–282. (c) Brown, I. D. *Acta Crystallogr., Sect. B* **1992**, *48*, 553–572. (d) Brown, I. D. *J. Appl. Crystallogr.* **1996**, *29*, 479–480.

a single peak at 24.76 ppm, which is an averaged peak due to motion in the solution. Such a peak was coincident with the peak at 24.87 ppm of **1** in solution, suggesting that the tetragold(I) cluster cation in solution is less influenced by electrostatic interaction with Keggin POM anions having different charges (3<sup>-</sup> vs 4<sup>-</sup>). The solid-state CPMAS <sup>29</sup>Si NMR signal of **2** at -83.11 ppm is due to the heteroatom silicon of the Keggin POM anion.

The solid-state CPMAS <sup>31</sup>P NMR spectrum of **3** (Figure 3) showed two broad signals at -3.1 and 25.5 ppm, which are assignable to the heteroatom phosphorus in the  $\alpha$ -Keggin molybdo-POM anion and the phosphorus atoms due to the PPh<sub>3</sub> groups in the tetragold(I) cluster, respectively. On the other hand, the solution <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **3** in DMSO-*d*<sub>6</sub> (Figure 4) showed two sharp signals at -3.27 and 25.21 ppm due to the Keggin molybdo-POM and the tetragold(I) cluster, respectively. The latter chemical shift was almost the same as that of the solid-state <sup>31</sup>P NMR spectrum of **3** and close to the chemical shift at 25.10 ppm in CD<sub>2</sub>Cl<sub>2</sub> of the sample obtained by anion exchange of **1** with BF<sub>4</sub><sup>-</sup> and, also, that at 25.4 ppm in CD<sub>2</sub>Cl<sub>2</sub> of [{Au(PPh<sub>3</sub>)<sub>3</sub>]<sub>4</sub>( $\mu$ <sub>4</sub>-O)](BF<sub>4</sub>)<sub>2</sub>.<sup>8h</sup>

The solution <sup>31</sup>P NMR spectra in DMSO-*d*<sub>6</sub> of **4** and **6** showed signals at -14.90 and -3.42 ppm due to the heteroatom phosphorus in [ $\alpha$ -PM<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> [M = W (**4**), Mo (**6**)], which can be compared with those (-14.79 and -3.27 ppm) of **1** and **3**, respectively. The solution <sup>31</sup>P NMR spectra in DMSO-*d*<sub>6</sub> of **4**-**6** (see the Supporting Information) also showed signals at -0.27 (**4**), -0.42 (**5**), and -0.21 (**6**) ppm due to the P(*o*-tolyl)<sub>3</sub> groups in the tetragold(I) clusters, which were much more shifted to higher fields in comparison with the signals at 24.87 (**1**), 24.76 (**2**), and 25.21 (**3**) ppm due to the PPh<sub>3</sub> groups. The <sup>1</sup>H NMR spectra in DMSO-*d*<sub>6</sub> of **4**-**6** showed signals at 2.38-2.40 ppm due to the methyl groups in the P(*o*-tolyl)<sub>3</sub> groups. The solution <sup>31</sup>P and <sup>1</sup>H NMR data of **4** in DMSO-*d*<sub>6</sub> can be compared with the data at 2.7 and 2.25 ppm in CD<sub>2</sub>Cl<sub>2</sub>, respectively, of [{Au(P(*o*-tolyl)<sub>3</sub>)<sub>3</sub>]<sub>4</sub>( $\mu$ <sub>4</sub>-O)](BF<sub>4</sub>)<sub>2</sub>.<sup>8h</sup>

## Conclusion

In the presence of the free acid forms of saturated Keggin POMs, such as H<sub>*n*</sub>[ $\alpha$ -XM<sub>12</sub>O<sub>40</sub>] $\cdot$ *m*H<sub>2</sub>O (*n* = 3, 4; *m* = 7, 10, 14; X = P, Si; M = W, Mo), a novel reaction of the monomeric phosphinegold(I) complexes, [Au((*R,S*)-pyrrld)(PR<sub>3</sub>)] [(*R,S*)-Hpyrrld = (*R,S*)-2-pyrrolidone-5-carboxylic acid; R = Ph,

*o*-tolyl], to form the tetra{phosphinegold(I)} cluster cations, [{Au(PR<sub>3</sub>)<sub>3</sub>]<sub>4</sub>( $\mu$ <sub>4</sub>-O)]<sup>2+</sup>, as countercations of the POM anions in **1**-**3** for R = Ph and **4**-**6** for R = *o*-tolyl, was exploited. These complexes, **1**-**6**, have been unequivocally characterized in the solid state and in solution. Formation of the intercluster compounds **1**-**6** significantly depends upon the POMs: the bulkiness and large anionic charge of the free-acid-type POMs contribute to the direct clusterization of [Au(PR<sub>3</sub>)<sub>3</sub>]<sup>+</sup> species to the [{Au(PR<sub>3</sub>)<sub>3</sub>]<sub>4</sub>( $\mu$ <sub>4</sub>-O)]<sup>2+</sup> cation after removal of the (*R,S*)-pyrrld<sup>-</sup> ligand. The bridged oxide ion ( $\mu$ <sub>4</sub>-O<sup>2-</sup>) encapsulated in the cluster came from water molecules contained in the reaction system and/or the solvated water molecules in the POMs. Complexes **1**-**3** were obtained as ionic crystals. In fact, the POM anion in **1** can be exchanged with the BF<sub>4</sub><sup>-</sup> anion using an anion-exchange resin. The distorted tetrahedral structures of the tetragold(I) clusters in **1** and **2** were contrasted with the molecular, regular tetrahedral structure of the previously reported [{Au(PR<sub>3</sub>)<sub>3</sub>]<sub>4</sub>( $\mu$ <sub>4</sub>-O)](BF<sub>4</sub>)<sub>2</sub> by Schmidbaur et al.<sup>8h</sup> The present work would provide the synthetic routes of novel phosphinegold(I)/phosphinesilver(I) cluster cations by a combination of the (Au or Ag)/carboxylate/phosphine complexes<sup>19</sup> and the different POMs such as lacunary species of Keggin- and Dawson-type POMs, saturated Dawson- and Anderson-type POMs, and so on. Also, we are expecting the combined catalysis of both the phosphinegold(I) cluster cations and the saturated Keggin POMs and not just catalysis of the tetra{phosphinegold(I)} cluster. Studies in such a direction are in progress, and the data will be reported in due course.

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**Supporting Information Available:** X-ray crystallographic data in CIF format, synthesis and characterization of **4**-**6**, solid-state packing views of **1** and **2** (Figures S1 and S2), average bond lengths (Å) around the Keggin polyoxoanions in **1** and **2** (Table S1), and BVS calculations of the gold, oxygen, and phosphorus atoms of the tetragold(I) cluster moieties in **1** and **2** and BVS data calculated herein using bond lengths reported for the regular tetrahedron in [{(P(*o*-tolyl)<sub>3</sub>)Au]<sub>4</sub>O}(BF<sub>4</sub>)<sub>2</sub>.<sup>8h</sup> (Table S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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