Supporting Information

Terminal Gold-Oxo Complexes

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Figure S1. FT-IR spectra of **1** and **2**

Figure S2. Room temperature electronic absorption spectra of **1**, **2**, and $(\text{NH}_4)\text{AuCl}_4$ in water

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Figure S4. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thermograms of **1** and **2**

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) indicate that **1** and **2** are fairly stable as pure crystals. An Interesting difference between **1** and **2** with their isostructural all-tungsten complexes, P_2W_{19} and P_2W_{21} , respectively, in the thermogravimetric analysis (TGA) is worthy to note (Figure S4): both **1** and **2** lose additionally *ca.* 0.6% weights at high temperature, where the weights of P_2W_{19} and P_2W_{21} remain constant. These results suggest that both **1** and **2** may decompose by evolving dioxygen at high temperature (the contents of the terminal oxo oxygen on Au and its *trans* aqua ligand are 0.59% and 0.58% for **1** and **2**, respectively). The thermal evolution of O_2 is under investigation.

DSC of 1

DSC of 2

Magnetism. Variable-temperature measurements of the magnetic susceptibility at 0.1 and 1.0 Tesla between 2 and 290 K indicated temperature-independent diamagnetism, i.e. flat χ vs. T curves, for both **1** ($\chi_{\text{dia/TIP}}(\mathbf{1}) = -10.2 \times 10^{-4} \text{ emu mol}^{-1}$) and **2** ($\chi_{\text{dia/TIP}}(\mathbf{2}) = -9.8 \times 10^{-4} \text{ emu mol}^{-1}$). These numbers compare well to the corresponding non-functionalized isopolytungstate cluster compounds **P₂W₁₉** ($\chi_{\text{dia/TIP}}(\mathbf{P_2W_{19}}) = -10.0 \times 10^{-4} \text{ emu mol}^{-1}$) and **P₂W₂₁** ($\chi_{\text{dia/TIP}}(\mathbf{P_2W_{21}}) = -9.5 \times 10^{-4} \text{ emu mol}^{-1}$) if differences in the numbers of potassium cations and crystal water molecules are taken into account. Molar diamagnetic susceptibilities for **P₂W₁₉** and **P₂W₂₁** have been established for the same conditions. The substitution of a $\text{W}^{\text{VI}}(\text{O})(\text{OH}_2)$ group in **P₂W₁₉** and **P₂W₂₁** by a $\text{Au}(\text{O})(\text{OH}_2)$ group in **1** and **2** causes a slight increase in the absolute values, part of which is attributable to an increase in the number of counter cations. Note that temperature-independent paramagnetic (TIP) contributions are significant for all polyoxotungstates; corresponding diamagnetic values for compounds **1**, **2**, **P₂W₁₉** and **P₂W₂₁** calculated from tabulated Pascal constants would greatly overestimate the actual experimental susceptibilities.

Electrochemistry. Buffer solutions were prepared in Barnstead Nanopure[®] quality water by mixing desired amounts of chloroacetic acid (Aldrich, 99%) or sulfuric acid (Aldrich, ACS reagent) and sodium hydroxide (Aldrich, 99%). Cyclic voltammograms (CV) were obtained at room temperature with scan rates in the range 2-100 mV/s. All reduction potentials are given versus Ag/AgCl (3 M NaCl) reference electrode ($E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.250 \text{ V}$ at 25 °C). A coiled Pt-wire was used as an auxiliary electrode. A glassy carbon working electrode was always polished with alumina (Polishing Alumina Fluid, purchased from Bioanalytical Systems, Inc., USA) before use unless otherwise specified.

Bulk electrolysis was performed under argon on a reticulated vitreous carbon working electrode with a coiled Pt-wire as an auxiliary electrode within a fritted glass isolated chamber. Vigorous agitation was provided by a magnetic stirrer and by the passing of argon as a purging gas. Air was rigorously excluded at all times. The total coulombs passed were monitored continuously. The potential for bulk electrolysis was usually set at values 50-300 mV more negative than the redox potential of Au-species

obtained on a freshly polished electrode. However, in most cases these potentials are much more positive than those required to reduce tungsten. The overall reduction proceeded to Au(0): gold metal deposition was easily seen after electrolysis as a yellow film on the working electrode. The following procedure was applied to minimize a contribution from the background current in bulk electrolysis. This contribution, while usually small, could reach up to 30%, and was dependent on the experimental conditions. After complete reduction of the Au-complex, the working electrode (with deposited metallic gold on its surface) was rinsed with distilled water and then used in bulk electrolysis. This electrolysis was conducted using the same buffer solution but in the absence of the Au complex. The number of coulombs measured, C_b , was subtracted from the charges passed during electrolysis in the presence of Au complex, C . The oxidation state of gold, n , in the Au-complex was obtained from the total number of electrons required for a complete reduction of Au(III) to Au(0): $n = (C - C_b)/FN$, where F is Faraday's constant (9.65×10^4 C/mole) and N is the number of moles of the initially present Au complex. The Au(0) deposited on the working electrode was dissolved by immersing the electrode into a solution of freshly prepared *aqua regia* for 10-15 min.

Figure S5. Cyclic voltammograms of 2.85 mM **1** and 2.0 mM **2** in sodium chloroacetate buffer (0.4 M, pH 3.0) solution. The initial potential was set at +800 mV. Room temperature, scan rate 100 mV/s

Figure S6. Corrected number of electrons, $n = (C - C_b)/FN$, passed during bulk electrolysis under controlled potentials as a function of time. (A) 3.37 mM $(\text{NH}_4)\text{AuCl}_4$, 50 mM sodium sulfate buffer, pH ~ 2 , 0.4 M NaCl, $E = 320$ mV; (B) 2.0 mM **1**, 50 mM sodium sulfate buffer, pH ~ 2 , 0.4 M NaCl, $E = 300$ mV; (C) 4.2 mM **2**, 0.2 M sodium chloroacetate buffer, pH ~ 3 , $E = 350$ mV.

Chemical titrations. Syntheses of $\alpha\text{-K}_4\text{SiW}_{12}\text{O}_{40}^1$ and $\alpha\text{-Na}_5\text{AlW}_{12}\text{O}_{40}^{2-4}$ were described in the literature. Solutions of their 1-electron reduced forms, $\text{SiW}_{12}\text{O}_{40}^{5-}$ and $\text{AlW}_{12}\text{O}_{40}^{6-}$, (henceforth POM_{red}) were obtained by electrochemical reduction of $\text{SiW}_{12}\text{O}_{40}^{4-}$ and $\text{AlW}_{12}\text{O}_{40}^{5-}$ at controlled potentials.⁵ The concentrations of the reduced forms of $\text{SiW}_{12}\text{O}_{40}^{5-}$ and $\text{AlW}_{12}\text{O}_{40}^{6-}$ were determined from the absorbance at 500 nm ($\epsilon = 8.9 \times 10^2$ and $9.7 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$, respectively). The solutions of the reduced complexes were stable under argon. The potentiometric titration was carried out under argon using a platinum VWR[®] sympHony combination redox electrode. The readings of this electrode are versus SCE. In a typical experimental procedure the redox potential of $\text{SiW}_{12}\text{O}_{40}^{4-}$ (or $\text{AlW}_{12}\text{O}_{40}^{5-}$) solution was measured as a function of the total amount of Au species added in small increments. All manipulations were carried out under argon in thoroughly deaerated solutions. The data were plotted as dependence of redox potential versus $(\text{Au})/(\text{POM}_{\text{red}})_0$, where (Au) is the total amount of Au-complex added in mmol, and $(\text{POM}_{\text{red}})_0$ is the initial amount of POM_{red} in mmol.

The stoichiometry of the reaction of **2** with 2,2'-azino-bis(3-ethyl benzothiazoline-6-sulfonic acid) (ABTS^{2-}) (ammonium salt, Aldrich, 98%) or $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ (potassium salt, Aldrich, 99%) were determined as follows: 0.05 mL of 1 mM **2** was added to 2.45 mL of 2 mM ABTS^{2-} in 50 mM sodium chloroacetate buffer. The yields of reaction products, $[\text{ABTS}^{\bullet-}]$, were quantified 2-3 min after mixing from the absorbances at 645 and 660 nm ($\epsilon_{645} = 1.35 \times 10^4$ and $\epsilon_{660} = 1.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$),^{6,7} an average value of the two numbers was used. A similar procedure was applied to determine the yield of $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$: compound **2** (final concentrations 0.2 mM) was added to 4.5 mM $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ in 50 mM sodium chloroacetate buffer (pH 3) or in 50 mM sodium phosphate buffer (pH 7.2). The $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$ product was quantified in 2-3 min after mixing from the absorbance at 420 nm ($\epsilon_{420} = 1.02 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$).

A similar technique was used in an attempt to determine the reaction stoichiometry of **2** reduction by $\text{SiW}_{12}\text{O}_{40}^{5-}$ using electronic absorption spectroscopy: **2** was mixed with a slight excess of $\text{SiW}_{12}\text{O}_{40}^{5-}$ and the amount of $\text{SiW}_{12}\text{O}_{40}^{5-}$ consumed was determined from the decrease in absorbance at 740 nm ($\epsilon_{740} = 1.53 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$). However, this technique resulted in irreproducible data due to a formation of unstable Au(0) particles with a relatively high absorbance at 740 nm (which also changed in time). All

manipulations described above were carried out under argon with meticulous exclusion of air.

Figure S7. Changes in the reduction potential of the $\text{SiW}_{12}\text{O}_{40}^{5-}/\text{SiW}_{12}\text{O}_{40}^{4-}$ solution (initial concentration 0.87 mM $\text{SiW}_{12}\text{O}_{40}^{5-}$) upon addition of **2** (1 mM in stock solution). Conditions: 25 mM sodium chloroacetate buffer (pH 3.0), room temperature, argon atmosphere.

Figure S8. Thermal ellipsoid plot and numbering scheme for **1** (173(2) K and 96(2) K), **2** and $[\text{P}_2\text{W}_{20}\text{O}_{70}(\text{OH}_2)_2]^{10-}$ (**3**, the stabilizing ligand of **2**)

1 (173(2) K)

1 (96(2) K)

Table S1. Crystal data and structural refinement for $\text{K}_{10}[\text{P}_2\text{W}_{20}\text{O}_{70}(\text{OH}_2)_2] \cdot 22\text{H}_2\text{O}$

complex	3
molecular formula	$\text{H}_{48}\text{K}_{10}\text{O}_{94}\text{P}_2\text{W}_{20}$
formula wt. (g mol^{-1})	5682.02
temperature (K)	173(2)
radiation (λ , Å)	0.71073
crystal system	orthorhombic
space group	$Pca2(1)$ (#29)
unit cell dimensions	
a (Å)	25.956(2)
b (Å)	19.0818(15)
c (Å)	33.801(3)
Volume (Å ³)	16741(2)
Z	4
ρ_{calcd} (g cm^{-3})	4.377
μ (mm^{-1})	27.972
$F(000)$	19276
crystal size (mm^3)	$0.39 \times 0.34 \times 0.29$
θ range for data collection	1.46 to 28.38°
index range	$-34 \leq h \leq 34$ $-25 \leq k \leq 25$ $-45 \leq l \leq 44$
reflections collected	229187
independent reflections	41719 [$R(\text{int}) = 0.0769$]
absorption correction	semi-empirical from equivalents
max. and min. transmission	0.0454 and 0.0324
refinement method	full-matrix least-squares on F^2
data/restraints/param.	41719/11/1026
goodness-of-fit on F^2	1.022
final R indices	$R1^a = 0.0483$
[$R > 2\sigma(I)$]	$wR2^b = 0.1172$
R indices (all data)	$R1^a = 0.0542$ $wR2^b = 0.1209$
largest diff. peak and hole (e Å^{-3})	7.969 and -9.547

$$^a R_1 = \Sigma ||F_o| - |F_c|| / |F_o|$$

$$^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$$

Neutron diffraction studies

(a) Neutron data collection. Neutron diffraction data were obtained at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory using the time-of-flight Laue single-crystal diffractometer (SCD).^{8,9} At the IPNS, pulses of protons are accelerated into a depleted uranium target 30 times a second to produce pulses of neutrons by the spallation process. Exploiting the pulsed nature of the source, neutron wavelengths are determined by time-of-flight based on the de Broglie equation $\lambda = (h/m) \cdot (t/l)$, where h is Planck's constant, m is the neutron mass, and t is the time-of-flight for a flight path l , so that the entire thermal spectrum of neutrons can be used. With two position-sensitive area detectors and a range of neutron wavelengths, a solid volume of reciprocal space is sampled with each stationary orientation of the sample and the detectors. The SCD has two ^6Li -glass scintillation position-sensitive area detectors, each with active areas of $15 \times 15 \text{ cm}^2$ and a spatial resolution of $< 1.5 \text{ mm}$. One of the detectors is centered at a scattering angle of 75° and a crystal-to-detector distance of 23 cm, and the second detector is at 120° and 18 cm. Details of the data collection and analysis procedures have been published previously.¹⁰

A crystal of $\text{K}_{15}\text{H}_2[\text{Au}(\text{O})(\text{OH}_2)\text{P}_2\text{W}_{18}\text{O}_{68}] \cdot 25\text{H}_2\text{O}$ (**1**), with approximate dimensions of $4 \times 3 \times 3 \text{ mm}^3$ and a weight of 60 mg, was coated in fluorocarbon grease, wrapped in aluminum foil, and glued to an aluminum pin that was mounted on the cold stage of a closed-cycle helium refrigerator. The crystal was then cooled to $30 \pm 1 \text{ K}$. For each setting of the diffractometer angles, data were stored in three-dimensional histogram form with coordinates x, y, t corresponding to horizontal and vertical detector positions and the time-of-flight, respectively. An auto-indexing algorithm¹¹ was used to obtain an initial orientation matrix from the peaks in three preliminary histograms measured for 60 minutes each. This unit cell approximately matched the previously reported X-ray unit cell indicating that the neutron sample was the correct material. For intensity data collection, runs of 12 hours per histogram were initiated for the data set. Settings were arranged at χ and ϕ values suitable to cover at least one unique octant of reciprocal space (Laue symmetry mmm). With the above counting times, 18 histograms were completed in the 9 days available for the experiment. Bragg peaks in the recorded histograms were indexed and integrated using individual orientation matrices for each histogram, to allow

for any misalignment of the sample. Intensities were integrated about their predicted locations and were corrected for the Lorentz factor, the incident spectrum, and the detector efficiency. A wavelength-dependent spherical absorption correction was applied using cross sections from Sears¹² for the nonhydrogen atoms and from Howard *et al.*¹³ for the hydrogen atoms ($\mu \text{ (cm}^{-1}\text{)} = 0.540 + 0.405 \lambda$). Symmetry-related reflections were not averaged since different extinction factors are applicable to reflections measured at different wavelengths.

(b) Refinement. The GSAS software package was used for structural analysis.¹⁴ The atomic positions of the potassium cations and the $[\text{Au}(\text{O})(\text{OH}_2)\text{P}_2\text{W}_{18}\text{O}_{68}]$ core of the molecule from the X-ray diffraction structure were used as a initial model to phase the neutron data. Lattice water molecules were located from difference Fourier syntheses. Each of the oxygen atoms attributable to lattice water was associated with strong negative scattering-density peaks, which are indicative of hydrogen atoms. For these peaks that were assigned as hydrogen atoms, subsequent refinement showed significant fractional occupancy and supported their interpretation as “real” atoms. Atom positions from the original X-ray structure that did not appear to have any weight in the neutron structure were omitted from the model. The axial water ligand O1W, bound to Au *trans* to the O35 oxo ligand, appeared to be disordered. A large area of negative density was located close to this oxygen on the O35-Au-O1W axis; other areas of negative density were located off this axis and also close to O1W, indicative that O1W is indeed a water molecule bound to Au. The hydrogen atoms bound to O1W were not included in the refinement. No such area of negative scattering density was located about the O35 oxo ligand. The refinement was based on F^2 reflections with a minimum d -spacing of 1.0 Å. Weights were assigned as $w(F_o^2) = 1 / [(\sigma^2(F_o^2))]^2$ where $\sigma^2(F_o^2)$ is the variance based on counting statistics. In the final refinement all atoms, including hydrogen atoms, were refined with isotropic displacement parameters. After final refinement the maximum residual peak height in the difference Fourier map was 0.210 fm Å⁻³, which corresponds to approximately 10% of the peak height observed for atom O35 in the Fourier map. Data collection and refinement parameters are summarized in Table 2.

Neutron diffraction structure -- calculations of the Au:W ratio for the central metal atom site: (refined Au occupancy)(Au neutron scattering length) = refined fractional occupancy value = x

$$(0.878)(7.63) = x = 6.701$$

$$y(\text{Au scattering length}) + (1-y)(\text{W scattering length}) = x$$

$$\left. \begin{array}{l} y(7.63) + (1-y)(4.86) = 6.701 \\ 7.63y + 4.86 - 4.86y = 6.701 \\ 2.77y = 1.841 \end{array} \right\} \longrightarrow \begin{array}{l} y (\text{Au } \%) = 0.665 \\ 1-y (\text{W } \%) = 0.335 \end{array}$$

Table S2. Electron binding energies for Au and W¹⁵

	Energy (eV)	
	Au	W
<i>L1</i>	14353	12100
<i>L2</i>	13734	11544
<i>L3</i>	11919	10207

Figure S9. pH dependent UV-vis spectra of **2**. The black line (pH 3.21, 1.80 mM) is the initial spectrum, the red line is the spectrum obtained after raising the pH to 7.53. The blue line is the spectrum after lowering the pH from 7.53 to 3.28. The spectra were not corrected for the increase in solution volume.

Figure S10. ^{17}O and ^{31}P NMR spectra of the stoichiometric oxo transfer reactions from **2** to Ph_3P

Computational methods. In these calculations we used SDD basis sets and ECP for Au¹⁶⁻¹⁸ and the aug-cc-pVTZ basis set for O atom.^{19,20} B3LYP calculations were done using the GAUSSIAN_2003 quantum chemical package.²¹ In the CASSCF calculations we used an active space that included all valence electrons and orbitals from the Au and O atoms: for AuO this is 17 el / 10 orbital active space, referred to as (17/10); for AuO⁺ this is a (16/10) active space; for AuO²⁺ this is a (15/10) active space, and for AuO³⁺ this is a (14/10) active space. All CASSCF and MRSD-CI calculations were performed by the MOLPRO quantum chemical package.²² Brief computational analysis of electronic structure and geometry of the AuO, AuO⁺, AuO²⁺ and AuO³⁺ systems performed at the DFT (B3LYP), CASSCF (Complete Active-State Self Consistent Field) and MRSD-CI (Multi-Reference Single-Double Correlation Interaction) levels of the theory clearly show that stability of Au-O bond reduces in the order AuO - AuO⁺ - AuO²⁺ - AuO³⁺. This trend is consistent with the molecular orbital diagram of AuO molecule presented in Figure S11. As seen from this figure, the ground electronic ²Π state of AuO with Au(II) has the ...[π(d_{yz}+p_y)]²[π(d_{xz}+p_x)]²[σ(sd_{zz})]²[δ(d_{xy})]²[δ(d_{xx-yy})]²[σ(sd_{zz}+p_z)]²[π*(d_{yz}-p_y)]²[π*(d_{xz}-p_x)]¹[σ*(sd_{zz}-p_z)]⁰ electronic configuration. The MRSD-CI calculated Au-O bond distance 1.930 Å is in a good agreement with its experimental value of 1.912 Å,²³ and previous computational data²⁴ of AuO. The Au-O bond dissociation energy calculated at the MRSD-CI level is 31.7 kcal/mol, which is also consistent with the previous theoretical studies.

The one electron ionization of AuO corresponds to the removal of an electron from the σ(sd_{zz}+p_z) orbital with energy of -0.483 a.u., which is mainly the valence s-orbital of Au atom. This leads to the Au^{III}O⁺ cation with +1 charge located at the Au-center. Calculations show that Au^{III}O⁺ has ³Π ground electronic state with the ...[σ(sd_{zz}+p_z)]²[π(d_{yz}+p_y)]²[π(d_{xz}+p_x)]²[δ(d_{xy})]²[δ(d_{xx-yy})]²[π*(d_{yz}-p_y)]²[σ(sd_{zz}+p_z)]¹[π*(d_{xz}-p_x)]¹[σ*(sd_{zz}-p_z)]⁰ electronic configuration while its ³Σ state with the ...[σ(sd_{zz}+p_z)]²[π*(d_{yz}-p_y)]¹[π*(d_{xz}-p_x)]¹[σ*(sd_{zz}-p_z)]⁰ is energetically very close. The calculations clearly show that the AuO⁺, where Au is in Au(III) oxidation state can exist and is stable relative to the Au⁺ + O dissociation limit, while the increase in oxidation state of Au from +2 to +3 slightly reduces the stability of the AuO unit. Indeed, in Au^{III}O⁺, the Au-O bond distance, 1.981 Å, is slightly longer than that for AuO,

and the Au^+-O bond energy, 27.8 kcal/mol, is *ca.* 4 kcal/mol smaller than that in $\text{Au}^{\text{II}}\text{O}$.

One should note that the lowest singlet $^1\Sigma$ state of $\text{Au}^{\text{III}}\text{O}^+$ has multi-determinant character (the largest contributors to the total wavefunction are the $\dots[\pi^*(d_{yz}-p_y)]^2[\pi^*(d_{xz}-p_x)]^0$ and $\dots[\pi^*(d_{yz}-p_y)]^0[\pi^*(d_{xz}-p_x)]^2$ configurations with 44% weights each) which lie *ca.* 33 kcal/mol higher in energy.

The removal of an electron from the $\text{Au}^{\text{III}}\text{O}^+$ leads to AuO^{2+} , which is stable on potential energy surface at its ground $^4\Sigma$ electronic state corresponding to the $\dots[\sigma(sd_{zz}+p_z)]^2[\pi(d_{yz}+p_y)]^2[\pi(d_{xz}+p_x)]^2[\delta(d_{xy})]^2[\delta(d_{xx}-yy)]^2[\sigma^*(sd_{zz}-p_z)]^1[\pi^*(d_{yz}-p_y)]^1[\pi^*(d_{xz}-p_x)]^1$ electron configuration. The Au-O bond distance of AuO^{2+} is calculated to be 2.10 Å. Dissociation of AuO^{2+} to $\text{Au}^{2+} + \text{O}$ is found to be an endothermic by 58.3 kcal/mol, while the $\text{AuO}^{2+} \rightarrow \text{Au}^+ + \text{O}^+$ is found to be exothermic by 51.7 kcal/mol. Based on these electronic, geometric and energetic data one may conclude that the minimum corresponds to $\text{Au}^+(\text{O}^+)$. Indeed, all three singly occupied orbitals of the $^4\Sigma$ ground state of AuO^{2+} are mainly p-AO orbitals of O^+ , while all the double occupied σ -, π - and δ -MOs are mainly d-orbitals of Au^+ . The $\sigma(sd_{zz}+p_z)$ orbital is the only “real” Au-O bonding orbital. This also is consistent with the calculated (and experimental) ionization potentials of Au^+ and O, which are 19.7 (20.5) and 13.2 (13.614) eV, respectively.

Similarly, we could localize the minima on the potential energy surface of the reaction $\text{Au}^{2+} + \text{O}^+$ that corresponds to the $^3\Sigma$ of AuO^{3+} , with the $\dots[\pi(d_{yz}+p_y)]^2[\pi(d_{xz}+p_x)]^2[\delta(d_{xy})]^2[\delta(d_{xx}-yy)]^2[\sigma(sd_{zz}+p_z)]^2[\pi^*(d_{yz}-p_y)]^1[\pi^*(d_{xz}-p_x)]^1[\sigma^*(sd_{zz}-p_z)]^0$ electron configuration. Although the Au-O bond distance, 1.90 Å, is relatively short, the minimum corresponding to AuO^{3+} on the potential energy surface is extremely shallow, and AuO^{3+} dissociates to $\text{Au}^{2+} + \text{O}^+$ with 264.4 kcal/mol energy. This minimum is 150.4 kcal/mol stable relative to the $\text{Au}^{3+} + \text{O}$ dissociation limit. Again, these results are consistent with the calculated ionization potentials of Au^{2+} and O, which are 32.9 eV (758.67 kcal/mol) and 13.2 eV (the experimental value is 13.614 eV) (304.39 kcal/mol), respectively.

Thus, the AuO^{2+} and AuO^{3+} minima on the potential energy surface, with formal Au oxidation states of +4 and +5, are highly unstable with respect to release of reactive O^+ . However, one can stabilize them under predictable conditions. One of the ways to

enhance their stability is by ligation of Au with negatively charged ligands (σ -donating ligands, which will reduce the Coulomb repulsion between the positively charged Au and O centers). The second way is by ligation of Au with strong π -electron withdrawing ligands (which will delocalize the π^* electrons in AuO units). Another way is by preventing O^+ dissociation by $(O^+)\dots X$ (non-covalent) interactions in AuO units embedded in the surfaces.

Indeed, calculations of the complexes $(NC)AuO^{q+}$ ($q = 0, 1$ and 2) support the aforementioned two hypotheses. The $(NC)AuO$ complex where Au is in the $+3$ oxidation state also has a triplet ground state with Au-O bond distance of $1.956 \text{ \AA}$. However, the triplet-singlet energy gap in $(NC)AuO$, 21.1 kcal/mol , is smaller than 33 kcal/mol in AuO^+ . In the other words, adding CN^- ligand to AuO^+ reduces both the Au-O bond distance and triplet-singlet energy gap. The calculated trend in the Au-O bond distance correlates with the calculated Au-O bond energy, which increases from 27.8 kcal/mol in AuO^+ to 31.0 kcal/mol in $(NC)AuO$.

Similarly, complexes $(NC)Au^{IV}O^+$ and $(NC)Au^V O^{2+}$ become more stable to both O-atom and O-cation dissociation limits relative to the corresponding AuO^{2+} and AuO^{3+} units. Clearly, having σ -electron donating and π -electron withdrawing ligands tends to stabilize the high oxidation states of Au in AuO fragments.

Figure S11. Schematic presentation of the MO-correlation diagram for the $^2\Pi$ electronic state of the AuO molecule

We also performed B3LYP/SDD calculations on $O=Au(OH_2)(OH)_4^{n-}$, $O=Au(OH_2)(W_2O_9H_4)_2^{n-}$, and $O=Au(OH_2)(W_2O_9H_4)_2^{n-}$, where $n = 1$ and 3 (with Au(V) and Au(III) centers respectively) to model the ligand environment of Au in **1** and **2**. However, these calculations were inconclusive because of instability in the ligand environment of the Au centers which indicates that these models are not yet sufficiently close to the actual polytungstate ligands in **1** and **2**. From these studies one concluded that the use of the full systems, $K_{15}H_2[Au(O)(OH_2)P_2W_{18}O_{68}]$ and $K_7H_2[Au(O)(OH_2)P_2W_{20}O_{70}(OH_2)_2]$, to computationally determine the oxidation state of the Au centers is necessary. Unfortunately, density functional calculations of such large systems are currently technically infeasible.

^{197}Au Mössbauer spectroscopy. The ^{197}Au Mössbauer spectrum of **1** was measured at 12 K on a sample containing 200 mg of gold, which corresponds to about 5 g of sample, as described previously. The $^{197}\text{Pt}/\text{Pt}$ source (360 MBq) was prepared by neutron irradiation of a 100 mg disc of enriched metallic ^{196}Pt in the HR-2 hole of the JRR-3M research reactor of the Japan Atomic Energy Agency. The spectra were measured for a week using a Mössbauer spectrometer from Wissel (MDU-1200, DFG-1200 and MVC-1200). Unfortunately, strong nonresonance absorption by the many tungsten atoms present rendered the Au signal unobservable for both complexes.

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