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When Gold Cations Meet Polyoxometalates
Aurélien Blanc,*[a] and Pierre de Frémont*[b]

Dedication ((optional))
MINIREVIEW

Abstract: Merging gold(I) cations with polyoxometalate anions results in various interclusters and complexes. Herein, the syntheses of these newly emerging gold(I)/polyoxometalate materials are reviewed. The applications of these promising hybrids in organic catalysis are also summarized and evaluated in terms of the advantages and limitations of the catalysts including efficiency, synergistic effects and recyclability.

1. Introduction

In the periodic table of elements, gold (Au) is located in the sixth period (horizontal row) and belongs to group eleven (vertical column) with copper and silver (coignage metals). This specific position (Z = 79) is obviously due to its electronic configuration (\([\text{Xe}]4f^{10}5d^{10}6s^1\)) but provides to gold atom peculiar properties. Gold is indeed the most impacted metal by relativistic effects causing the contraction of the atomic 6s orbital and an expansion of the atomic 5d and 4f orbitals considering the increased shielding effect.\(^{[1]}\)

As a direct consequence, cationic gold(I/III) complexes possesses a strong carboxiphilic Lewis acid character and have thus excellent catalytic activities for different reactions.\(^{[2,3]}\) Moreover, gold catalysts are often tolerant toward air, moisture and to various organic functions. They exhibit a limited toxicity compared to other late-transition metals. Another property arising from the relativistic effects is the propensity of gold(I) to form Au–Au bonding.\(^{[3,4]}\) Theses (d\(^{10}\)-d\(^{10}\)) interactions with strength comparable to hydrogen bonds are attributed to dispersive forces and virtual charge transfers. This phenomenon called “aurophilicity” is at the origin of various supramolecular aggregates and gold(I) clusters with fascinating coordination numbers and geometries.\(^{[4,5]}\)

On the other hand, polyoxometalates (POMs) refer to polyanionic clusters formed by the assembly of early transition-metal oxide building blocks \([\text{MO}_x]\) (M = W, Mo, V…). Since their discovery two centuries ago, thousands of structurally different POMs with various properties have been reported, impacting all the areas of chemistry and notably catalysis.\(^{[5]}\) Among them, Keggin \([\text{XM}_4\text{O}_{12}]^n^−\) or Wells–Dawson \([\text{X}_2\text{M}_6\text{O}_{18}]^n^−\) heteropolyanions, where X is a p-block element of the periodic table (usually P or Si), are the most studied considering their well-known structures, their high stability and their simple preparation. POMs are versatile solids which can exhibit a strong acidity when their negative charges are compensated by protons or oxidative properties.\(^{[6]}\) Despite the limitations induced by their low surface area, POMs possess a strong potential for performing molecular design of hybrid materials associated with organic or inorganic molecules.\(^{[7]}\) In this area of research, POMs have notably been used to support and stabilize gold nanoparticles for various applications and have been recently reviewed in 2016.\(^{[8]}\) However, in the continuously growing field of POMs, new types of hybrid materials are emerging. This mini-review is thus focused on the synthesis of interclusters and complexes merging gold(I) cations and POM anions and their applications in gold catalysis.

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Pierre de Frémont received his M.S. degree in 2003 from Le Mans Université and his Ph.D. in 2007 from the University of New Orleans, in Prof. Steven P. Nolan’s group. In 2008, he was a postdoctoral fellow at the IBM Almaden centre with Dr. James Hedrick and in 2009, at the Université de Rennes 1 with Prof. Jean-François Carpentier. He was hired by the CNRS in 2009 and appointed to the University of Strasbourg. His research focuses mainly on the synthesis of metal NHC complexes for catalysis purpose, with a special interest on gold chemistry.

2. Cationic Gold Complexes with POM Anions (ionic pairs)

2.1. Phosphane Gold(I)-Polyoxometalate Compounds

2.1.1 Gold-POM Interclusters

The first gold-POM supramolecular intercluster compound (SICC) was synthesized and named this way by Jansen et al., in 2006.\(^{[9]}\) The term SICC describes a self-assembly material comprised of two different inorganic clusters with diameters of 1 nm or larger. In the solid-state, nanoparticles aggregate through superlattices generally built from non-directional interactions between more or less spherical particles and displaying limited translational order. By contrast, SICCs made with clusters of different shapes and ionic charges exhibit a lattice with directional interactions and higher translational order, providing
crystalline materials. Interestingly, their studies by single crystal X-ray diffraction (SC-XRD) give a direct observation of the different intermolecular interactions responsible for their self-assembly into supramolecular edifices.

All gold POM interclusters reported to date are made under air/moisture conditions. The reaction of 1 equiv. of the freshly prepared [Au$_8$(PPh$_3$)$_4$]$_3$[NO$_3$]$_3$ cluster (PPh$_3$ = triphenylphosphine) with 1 equiv. of [N(n-Bu)$_4$]$^+_2$[P(OMe)$_3$]$_3$ in acetonitrile yields the SICC [Au$_8$(PPh$_3$)$_4$]$_3$[PF$_6$] (1) as an orange microcrystalline powder. Dissolving both reagents in layers of solvents with different densities, respectively DMF/acetonitrile or DMF/acetone produces crystals being orange needles, or greenish black plates. SC-XRD studies reveal two crystal packings with P4/n or C2/c space group symmetries, and more importantly two isomers of the cationic [Au$_8$(PPh$_3$)$_4$]$^3+$ fragment (Figure 1). [9] The first isomer has a center crown shape featuring a D$_{3h}$ symmetry. The second isomer has a butterfly shape featuring a D$_{2h}$ symmetry. They represent the first successful structural characterization of the [Au$_8$(PPh$_3$)$_4$]$^3+$ cluster by SC-XRD. In this case, the presence of POM anions in the crystal lattice seems to freeze the geometry of the [Au$_8$(PPh$_3$)$_4$]$^3+$ isomers, suppressing the refinement issues related to heavy positional disorder. The second crystal structure less dense (C2/c) has voids filled with solvent molecules, and shatters easily by desolvation. Finally, using [Au$_8$(PPh$_3$)$_4$]$^3+$[NO$_3$]$_3$, also produces 1 via cluster rearrangement occurring during the crystallization step.

Following a similar synthetic protocol as for 1, the reactions of 1 equiv. of [Au$_8$(PPh$_3$)$_4$]$^3+$[NO$_3$]$_3$, or [Au$_8$(PPh$_3$)$_4$]$^3+$[NO$_3$]$_3$ solubilized in dichloromethane with a layer of 1 equiv. of [N(n-Bu)$_4$]$^+_2$[H]$^+$[V$_2$O$_8$]$_2^-$ solubilized in acetonitrile produce, after a few days, the SICC [Au$_8$(PPh$_3$)$_4$]$^3+$[H]$^+$[V$_2$O$_8$]$_2^-$ (2) as fragile dichroic crystals (red and green) which are prone to desolvation. SC-XRD studies reveal a packing with the P2/c space group symmetry. [10] Two POMs anions held together by H$^+$$^+$O bonds are associated with two crystallographically independent [Au$_8$(PPh$_3$)$_4$]$^3+$[NO$_3$]$_3$ clusters having a butterfly shape. Voids in the structures form a three dimensional network of canals filled with disordered molecules of solvent. In the solid state, 2 is best described as [Au$_8$(PPh$_3$)$_4$]$^3+$[H]$^+$[V$_2$O$_8$]$_2^-$.

Jansen et al. synthesized a series of SICCs to understand better the effects of the POM size and anionic charge on their crystal structures. The reactions of 1 equiv. of [Au$_8$(PPh$_3$)$_4$]$^3+$[NO$_3$]$_3$ or [Au$_8$(PPh$_3$)$_4$]$^3+$[NO$_3$]$_3$ solubilized in acetonitrile with a layer of 1 equiv. of [N(n-Bu)$_4$]$^+_2$[PMo$_{12}$O$_{40}$]$^3+$ or [N(n-Bu)$_4$]$^+_2$[SiMo$_{12}$O$_{40}$]$^3+$, or [N(n-Bu)$_4$]$^+_2$[CoW$_2$O$_8$]$^6-$ solubilized in DMF produce, after a week, the SICCs [Au$_8$(PPh$_3$)$_4$]$^3+$[PMo$_{12}$O$_{40}$]$^3+$ (3) or [Au$_8$(PPh$_3$)$_4$]$^3+$[H]$^+$[SiMo$_{12}$O$_{40}$]$^3+$ (4) (Figure 1) or [Au$_8$(PPh$_3$)$_4$]$^3+$[H]$^+$[CoW$_2$O$_8$]$^6-$ (5), as needle-like crystals. [11] SC-XRD studies reveal packings with the P4/n space group symmetry for 3-4 and the Pbcn space group symmetry for 5. The [P-PO$_5$]$_2^-$ and [PMo$_{12}$O$_{40}$]$^3+$ Keggin anions having similar sizes (ionic radii of Mo/W almost equal), compounds 1 and 3 are isostructural. For 2-3, the higher charge of the POM is balanced by protons to keep the ratio [Au$_8$]:[POM] equal to 1. The larger cation [N(n-Bu)$_4$]$^+$ is likely unable to squeeze into the crystal lattice. Contrary to 1-2, the crystal lattice of 3 is less dense, and four disordered molecules of co-crystallized anion are found by unit cell. In that sense, 3 is better described by [Au$_8$(PPh$_3$)$_4$]$^3+$[PMo$_{12}$O$_{40}$]$^3+$·4 MeCN. Interestingly, the SICC [Au$_8$(PPh$_3$)$_4$]$^3+$[SiMo$_{12}$O$_{40}$]$^3+$ (6) is exclusively obtained starting from [Au$_8$(PPh$_3$)$_4$]$^3+$[NO$_3$]$_3$ and crystallizing with a large excess of PPh$_3$. SC-XRD studies reveal a packing with the Pbcn space group symmetry forming a network of canal filled with a substantial amount of acetonitrile molecules, at least 25-30 per unit cell. Attempts on starting from the bulkier cationic gold cluster [Au$_8$(P(p-tol)$_3$)$_3$]$_2$[NO$_3$]$_3$ ($p$-tol$_3$ = tri(phenyl)phosphine) failed to provide crystalline SICCs, characterized by SC-XRD, with the exception of [Au$_8$(P(p-tol)$_3$)$_3$]$_2$[N(n-Bu)$_4$]$^+_2$[SiMo$_{12}$O$_{40}$]$^3+$ (7). [11] Its crystal symmetry is defined by the Cc space group symmetry. The SICC [Au$_8$(P(p-tol)$_3$)$_3$]$^3+$ fragment has a D$_{3h}$ symmetry. Contrary to 4-5, the crystal packing is less dense and the anionic charge of the POM is compensated by an ammonium cation. It also contains large voids (24% of cell volume) filled with 16 molecules of acetonitrile, 6 molecules of DCM, and likely 4 other solvent molecules undetected, per unit cell. So, 7 is best described by [Au$_8$(P(p-tol)$_3$)$_3$]$_2$[N(n-Bu)$_4$]$^+_2$[SiMo$_{12}$O$_{40}$]$^3+$·10×CH$_3$CN·3×CH$_3$CN with 0 ≤ s ≤ 2.

| SICC | Gold Cluster | POM | Cation | Space group | Ref. |
|------|--------------|-----|--------|-------------|-----|
| 1    | [Au$_8$(PPh$_3$)$_4$]$^3+$ | [PF$_6$] | - | P4/n or C2/c | 9   |
| 2    | - | [V$_2$O$_8$]$_2^-$ | [H]$^+$ | P4/n | 10  |
| 3    | - | [PMo$_{12}$O$_{40}$]$^3+$ | - | P4/n | 11  |
| 4    | - | [SiMo$_{12}$O$_{40}$]$^3+$ | [H]$^+$ | P4/n | -   |
| 5    | - | [CoW$_2$O$_8$]$^6-$ | [H]$^+$ | Pbcn | -   |
| 6    | - | [Au$_8$(PPh$_3$)$_4$]$^3+$ | [SiMo$_{12}$O$_{40}$]$^3+$ | N(n-Bu)$_4$]$^+$ | Cc | -   |
| 7    | - | [Au$_8$(P(p-tol)$_3$)$_3$]$^3+$ | [SiMo$_{12}$O$_{40}$]$^3+$ | N(n-Bu)$_4$]$^+$ | Cc | -   |

Figure 1. Formula of the SICCs 1-7 and combined ball-and-stick/polyhedral representation of 4.

To obtain SICCs with cationic gold clusters of higher nuclearity, Jansen et al. suggested to use the chelating dpdp ligand (dpdp = 1,6-bis(diphenylphosphinyl)-hexane), taking into consideration the successful synthesis of [Au$_4$(dppp)$_3$]$_2$[SCN]$_3$ and [Au$_13$(dppm)$_4$]$^4+$[NO$_3$]$_4$ (dppm = 1,3-bis(diphenylphosphinyl)-propane, dppm = bis(diphenylphosphinyl)-methylene). [12, 13] The reaction of 1 equiv. of [Au$_8$(PPh$_3$)$_4$]$^3+$[NO$_3$]$_3$ and 4 equiv. of dppm, in DCM, followed by precipitation and washing with toluene yields a mixture of isolated but non-characterized gold clusters which is used as a source of [Au$_8$(dpph)$_4$]$^3+$[NO$_3$]$_3$. The latter solubilized in DCM and layered with an acetonitrile solution containing 1 equiv. of [N(n-Bu)$_4$]$^+_2$[Mo$_2$O$_7$]$_2$ produces, after a few weeks, the SICC [Au$_8$(dpph)$_4$]$^3+$[X]$^-$[β-Mo$_2$O$_7$]$_2$ (8) (X = H, or
N-(n-Bu)₂ as prism-like or needle-crystals, extremely sensitive to desolvation.

SC-XRD studies reveal two solvomorphs with a crystal symmetry described by the Pnna space group. Whereas all [Au₃(dphp)₂]³⁺ fragments have a crown shape, their packing (orientation / interaction with the POM) is very different for both isomers. The often-encountered isomerization of [MoO₂]⁺ anion occurs with 8 upon replacement of [N(n-Bu)₄]⁺ by [Au₃(dphp)₂]³⁺. Both crystal packings exhibit large voids (up to 40 % of cell volume) filled with solvent molecules. Due to heavy disorder, the cation [X⁺] needed to ensure the charge neutrality of 8 could not be modeled. Following a different synthetic approach, the reaction of 1 equiv. of [Au₃(dphp)₂]³⁺[NO₃]⁻ and 1 equiv. of [H][α-PW₁₂O₄₀]³⁻ in ethanol yields a red precipitate which is isolated but not characterized. The latter is dissolved in DMF and layered with toluene to afford, after a week, the SICC [Au₃(dphp)₂]³⁺[α-PW₁₂O₄₀]²⁻ (9) as crystals, with the P̅1̅ space group symmetry. Similarly to 8, the catiionic cluster features a crown shape. Voids account for 28% of the crystal cell volume, and are filled with solvent. As the dphp ligand failed to provide a phosphane gold cluster with higher nuclearity, [Au₃(PPh₃)Cl₃][PF₆]⁻ was made according to known procedure. The latter is dissolved in DCM and layered with an acetone solution containing 0.5 equiv. of [N(n-Bu)₄]Cl[P₃W₁₂O₄₀]²⁻ to afford the SICC [Au₃(PPh₃)Cl₃][P₃W₁₂O₄₀]²⁻ (10) as crystals, sensitive to desolvation, with the P̅1̅₁ space group symmetry. The [Au₃(PPh₃)Cl₃]²⁻ core displays a geometry similar to the known neutral clusters [Au₃(PPh₃)Cl₃]²⁻ (X = halide, pseudo-halide). Important voids filled with solvent molecules (24.1 % of the cell volume) are found.

Since 2010, Nomiya’s group well known in POM chemistry, has been steadily publishing on gold POM SICCs, and the next part of this review will cover their work. It is essential to acknowledge that all their syntheses are rationalized and associated to SICCs fully characterized by elemental analysis (EA), thermogravimetric and differential thermal analysis (DTA), infrared spectroscopy (FTIR), solid-state and liquid NMR spectroscopies and finally SC-XRD. Their first SICC was unexpectedly synthesized during the course of an acid-base reaction between a free acid form of POM and a gold(I) phosphane complex bearing a labile pyridilidinone-carboxylate ligand. Thus following this methodology, solutions of 12, 8, or 7 equiv. of triphenylphosphane gold(I) (S,R)-2-pyridilidinone-

| SICC | Gold Cluster | POM | Cation | Space group |
|------|--------------|-----|--------|-------------|
| 8    | [Au₃(dphp)₂]³⁺ | [MoO₂]⁺ | - | - |
| 9    | [PW₁₂O₄₀]³⁻ | - | - | - |
| 10   | [Au₃(PPh₃)Cl₃]²⁻ | [W₆O₁₉]²⁻ | - | - |
|      |            |            |      |            |

dpmm = 1,6-bis(diphenylphosphino)methane; dppp = 1,6-bis(diphenylphosphino)ethane; dppp = 1,6-bis(diphenylphosphino)propane.

Figure 2. Formula of the SICCs 8-10 and combined ball-and-stick/polyhedral representation of 10.

The one-pot reactions of 1 equiv. of [Au₃(PPh₃)₃][NO₃]³⁻ with 4 equiv. of dpmm and 1 equiv. of [N(n-Bu)₄]Cl[P₃W₁₂O₄₀]²⁻ or 1 equiv. of [N(n-Bu)₄]Cl[α-PW₁₂O₄₀]³⁻ yield, upon crystallization, the SICCs [Au₃(dpmm)₂]³⁺[P₃W₁₂O₄₀]²⁻ (11) or [Au₃(dpmm)Cl₂][N(n-Bu)₄][α-PW₁₂O₄₀]³⁻ (12). The dpmm ligand promotes the cleavage of the gold cluster instead of increasing its nuclearity. To capitalize on this unexpected reactivity, a series of [Au₃(dpmm)₂]²⁺[PF₆]⁻ clusters (dpmm = dpmp, dppm, dppe (bis(diphenylphosphanyl-ethane)) were made and isolated for further reactions with various POMs. Thus, 1 equiv. of [Au₃(dpmp)₂]²⁺[PF₆]⁻ dissolved in MeCN, 1 equiv. of [Au₃(dppe)₂]²⁺[PF₆]⁻ dissolved in DCM, 1 equiv. of [Au₃(dpmp)Cl₂][PF₆]⁻ dissolved in ethanol and 1 equiv. of [Au₃(dpmm)₂][PF₆]⁻ dissolved in ethanol are layered respectively with a solution of DCM containing ½ equiv. of [N(n-Bu)₄]Cl[SMO₂]⁴⁻, with a solution of acetone containing 1 equiv. of [N(n-Bu)₄]Cl[MoO₂]⁴⁻ with a solution of MeCN containing ½ equiv. of [N(n-Bu)₄]Cl[MoO₂]⁴⁻, or with a solution of MeCN containing ½ equiv. of [N(n-Bu)₄]Cl[PMO₁₂]⁴⁻ to afford the SICCs [Au₃(dpmp)₂]²⁺[SMO₂]⁴⁻ (11), [Au₃(dppe)₂][MoO₂]⁴⁻ (13), [Au₃(dpmm)Cl₂][MoO₂]⁴⁻ (14), or [Au₃(dpmm)₂][PMO₁₂]⁴⁻ (15) as crystals with the P̅1̅, P̅2̅₁/m, P̅2̅₁/n, or P̅2̅₁/n space group symmetries (Figure 3). As expected, different [Au₃]⁺[POM] ratios set fundamentally different self-assembly edifices in the solid-state.

Figure 3. Formula of the SICCs 11-15 and ball-and-stick representations of gold clusters.
5-carboxylate [\(\text{Au(PPh}_3\text{)(R,S)-pyrrolid)}\) or tri(orthotolyloxy)phosphine gold(I) \((S,R):2\)-pyrrolidinone-5-carboxylate [\(\text{Au(P(o-tol)(S,R)-pyrrolid)}\)] dissolved in DCM and layered with mixtures of ethanol-water containing 2 equiv. of \([\text{H}]_2[\text{PMo}_{12}\text{O}_{40}]^3\) or 2 equiv. of \([\text{H}]_2[\text{AlW}_{12}\text{O}_{40}]^3\) or 1 equiv. of \([\text{H}]_2[\text{SiW}_{12}\text{O}_{40}]^3\) or 1 equiv. of \([\text{H}]_2[\text{AlW}_{12}\text{O}_{40}]^5\). Water supplies the oxygen atoms from the edge-shared WO octahedrons of the POMs are present in compounds 22 and 23. They might be considered as intermediates in the formation of \([\text{Au(PPh}_3\text{)(µ-O)}]\) clusters. The heptagold cluster is formed by the self-assembly of oxonium tetra- and tri-gold clusters having respectively distorted tetrahedral- and triangular-planar geometries. Co-crystallized ethanol is found in the crystal lattice, and this compound is best described by 24. EIOH. All \([\text{Au(PPh}_3\text{)}\) fragments, chemically equivalent in (solid/liquid) 31P NMR spectroscopy, along with the characteristic signals of the phosphorus-based POMs at higher field (around 0 ppm).

The clusterization also proceeds with POMs free of proton, in the presence of water. Thus, 7 equiv. of \([\text{Au(PPh}_3\text{)(R,S)-pyrrolid)}\) dissolved in DCM and layered with a solution of ethanol-water containing 1 equiv. of \([\text{Na}]_2[\text{PW}_{12}\text{O}_{40}]^3\) produces the SICCs \([\{\text{Au(PPh}_3\text{)(µ-O)}\}_4[\text{PMo}_{12}\text{O}_{40}]^3\text{P}]\) (24), with approximately 50 % yield, as crystals with the \(P2_1/n\) space group symmetry.22 The heptagold cluster is formed by the self-assembly of oxonium tetra- and tri-gold clusters having respectively distorted tetrahedral- and triangular-planar geometries. Co-crystallized ethanol is found in the crystal lattice, and this compound is best described by 24. EIOH. All \([\text{Au(PPh}_3\text{)}\) fragments, chemically equivalent in (solid/liquid) 31P NMR spectroscopy, along with the characteristic signals of the phosphorus-based POMs at higher field (around 0 ppm).

Contrary to the synthesis of \([\{\text{Au(PPh}_3\text{)(µ-O)}\}_4[\text{BF}_4]\}_2\) reported by Schmidbaur21 and occurring via addition of a cationic fragment \([\text{Au(PPh)}]^{3+}\), generated in situ, to the complex \([\{\text{Au(PPh}_3\text{)(µ-O)}\}_4[\text{BF}_4]\}, the formation of 16-23 follows a different mechanism in which the \([\text{Au(PPh)(R,S)-pyrrolid)}\) complex reacts with the acidic form of the POM to produce some \((S,R):2\)-pyrrolidinone-5-carboxylic acid, and the \([\text{Au(PPh)}]^{3+}\) fragment which further clusterizes in the presence of large and negatively charged POM anions. Water supplies the oxygen atom of the gold-oxonium cluster, and increases the reaction rate by solubilizing all species involved. The clusterization also proceeds starting from the complex triphenylphosphine gold(I) \((S,R):5\)-oxo-2-tetrahydrofurancarboxylate \([\text{Au(PPh)_3(R,S)-OThF)}\), and any carboxylate ligands seem appropriate to act as leaving group. The crystals of 16, 20, 22 and 23 analyzed by SC-XRD display \(R3\), \(C2/c\), \(R3m\) and \(R3m\) space group symmetries. Compared to \([\{\text{Au(PPh}_3\text{)(µ-O)}\}_4[\text{BF}_4]\}_2\) which has a gold oxonium cluster with a regular tetrahedral geometry \((T_4)\) symmetry, compounds 16, 20, 22 and 23 feature some gold clusters with distorted tetrahedral geometries \((C_3)\) symmetry. Such differences likely arise from the large size and high anionic charge of the POMs. Interestingly, three monomeric phosphine gold(I) moieties bound to oxygen atoms from the edge-shared WO octahedrons of the POMs are present in compounds 22 and 23. They might be considered as intermediates in the formation of \([\{\text{Au(PPh}_3\text{)(µ-O)}\}_4[\text{BF}_4]\}_2\).21,22 XRD and DTA confirm the presence of co-crystallized solvents. In the solid-state, the SICCs are best described by 16: 4 EIOH, 18: 3 EIOH, 20: 2 H2O, 22: 3 EIOH, and 23: 3 EIOH. For all SICCs, a signal assigned to the phosphine gold cluster is visible around 25 ppm, by 31P NMR spectroscopy, along with the characteristic signals of the phosphorus-based POMs at higher field (around 0 ppm).
tetragold clusters $[{{(Au(P(aryl))_2)(μ-OH)_{2}}}]^{2+}$ are made by dimerization of two $[{{Au(P(aryl))_2}(μ-OH)_{2}}]$ units in a cross-edge arrangement leading to distorted tetrahedral arrays of gold atoms ($C_3v$ symmetry). This geometry is encountered with the SICCs 16, 20, and the clusters $[{{(Au(PPh_3)_{2}(μ-OH)_{2}}}]^{2+}$[OTf]$_2$ and $[{{(Au(PPh_2Me_2C_6H_5))_2(μ-halide)_{2}}}]^{2+}$[SbF$_5$]$_2$. [24] For 25, 31, 32, 34, a parallel-edge arrangement leads to rectangular arrays of gold atoms capped by an oxygen atom ($D_{2h}$ symmetry). This geometry is only encountered with thiolate-bridged tetragold clusters $[{{(AuPR_3)_{2}(μ-SZ)_{2}}}]^{2+}$ ($R =$ alkyl, aryl; $Z =$ CMe$_3$, aniline, etc...). [24]

The structures of 33-34 comprised of two mononuclear phosphate gold cations bound to POM oxygen atoms, from edge- and corner-sharing MoO$_6$ octahedra, suggest that clustering is likely occurring at the POM surface. As expected, by $^3$P NMR, a singlet around 25 ppm characters all phosphate gold clusters, regardless of their nuclearities of geometric shapes (Figure 6). SC-XRD analyses and DTA reveal that 25-31, 26-32, 29-32, 31-32 and 32-33 provide better the SICCs in their crystalline forms. Similarly to the formation of 24, the reaction of 7 equiv. of $[{{Au(P(por))_3}(R,S)-pyrrld)]$ with 1 equiv. of $[{{Na}^{+}·[α-PMo_12O_{39}]}]$ produces the SICC $[{{Au(P(por))_3}(μ-O)]}^{2+}$[${{Au(P(por))_3}(μ-O)]}^{2+}$[${{α-PMo_12O_{39}]}]$ with 14.0 % yield, as crystals with the $P_3$ space group symmetry. The $[{{α-PMo_12O_{39}]}]$ anion of 31 and 32 was replaced by $[{{PF_6}^-}$ and [OTf] by using anion-exchange resin to evaluate the role of the POM on the geometry of the clusters-gold oxonium. The compounds $[{{(Au(P(ClPPh_3)_3)(μ-O)]}^{2+}$[${{PF_6}^-}$(36) + 3 EtOH, $[{{(Au(P(P-ClPh_3)_3)(μ-O)]}^{2+}$[${{PF_6}^-}$(37) and $[{{(Au(P(P-ClPh_3)_3)(μ-O)]}^{2+}$[${{PF_6}^-}$(38) + ½ EtO$_2$ are synthesized with 14.1 %, 66.1% and 56.0% yields, as crystals with the $P_3$, $P4/n$ and $P4_2/n$ space group symmetries. [25] For 36, the dimer of dinuclear gold clusters $[{{(Au(P(ClPPh_3)_3)(μ-O)]}^{2+}$ is converted to dimer of trinuclear gold clusters, by replacing the proton of the bridging hydroxyl group by a $[{{Au(P(ClPPh_3)_3)}]$ fragment (Figure 6). The rectangular geometry of the cluster cores is retained. During the formation of 38, the parallel-edge arrangement of the dimer of dinuclear gold clusters forming $[{{(Au(P(p-FPh)_3)(μ-O)]}^{2+}$ is converted to cross-edge arrangement. For 37, the $[{{(Au(P(ClPPh_3)_3)(μ-O)]}^{2+}$ cluster is formed by four basal gold cations capped by an oxygen atom. Compared to other tetragold oxonium clusters with $C_{2v}$ symmetry described previously, it has an unusual $C_{3v}$ symmetry which is characteristic of an electron deficient species with a ¾ bond order for each O–Au bond. [26]

![Figure 5. Formula of the SICCs 25-32 and combined ball-and-stick/polyhedral representation of 31.](image)

![Figure 6. Formula of the SICCs 33-35, 37 and combined ball-and-stick/polyhedral representation of 33.](image)

Recently, Nomiya et al. extended the chemistry of gold POM SICCs with two electronic deficient species based on gold ammonium clusters. The reactions of 7.5 equiv. of $[{{Au(PPh_3)_{2}(R,S)-pyrrld)]}$ solubilized in a mixture of DCM-methanol, with 1.5 equiv. of aqueous ammonia, and 1 equiv. of $[{{H}^{+}·[α-PMo_12O_{39}]}]$ or $[{{H}^{+}·[α-PW_12O_{40}]}]$ contained in a layer of methanol afford the SICCs $[{{Au(PPh_3)_{2}(μ-N)]}^{2+}$[α-PMo$_{12}$O$_{39}$]$^2$ (39) or $[{{Au(PPh_3)_{2}(μ-N)]}^{2+}$[α-PW$_{12}$O$_{40}$]$^3$ (40) with 32.3 % or 30.2 % yields, as crystals with the $P3$ space group symmetry (Figure 7). [27] Both compounds are isomorph and best described by (39-40) + 2 DCM. Their unit cells contain two crystallographically independent $[{{Au(PPh_3)_{2}(μ-N)]}^{2+}$ clusters. One has a trigonal bipyramids shape with $D_{3h}$ symmetry, the other has a distorted square planar pyramid shape derived from $C_{4v}$ symmetry which is likely related to electron deficient species (bond order Au–N ≤ 1). Both geometries relate to the compound...
[(Au(PPh₃))ₓ{(µ-N)}ₙ]²⁺{BF₄}⁻ · x DCM (with x ≥ 0) reported by Schmidbaur et al. which has ammonium gold clusters with D₉₅ or C₄ᵥ symmetry, depending on the presence of co-crystallized molecules of DCM. The ³¹P NMR spectra of 39-40 are virtually identical to those of SICC with gold oxonium clusters. They exhibit a singlet around 25 ppm for the gold ammonium cluster and a singlet around 14 ppm for the POM. DFT calculations support the preferential formation of [(Au(PPh₃))ₓ{(µ-N)}ₙ]²⁺ compared to [(Au(PPh₃))ₓ{(µ-Cl)}ₙ]²⁺. [Au(PPh₃)]²⁺ or [(Au(PPh₃))ₓ{(µ-N)}ₙ]²⁺. They also demonstrate that clusters with D₉₅ symmetry are only 1.6 kcal/mol more stable than clusters with C₄ᵥ symmetry. In that sense, it is not surprising to find both geometries coexisting in the same crystal packing.

### 2.1.2 Gold(I)-POM Complexes

In 2014, Blanc et al. reported the first examples of phosphine gold POM hybrid complexes as silver free catalysts under heterogeneous conditions. The reactions of 1, 2, 3 or 4 equiv. of triphenylphosphine methylgold(I) [Au(PPh₃)](Me) with 1 equiv. of [H]⁺[α-SiW₁₂O₄₀]⁺ in acetonitrile afford the complexes [Au(PPh₃)(MeCN)]⁺[H]⁺[α-SiW₁₂O₄₀]⁺ (41), or [Au(PPh₃)(MeCN)]⁺[H]⁺[α-SiW₁₂O₄₀]⁺ (42), or [Au(PPh₃)(MeCN)]⁺[H]⁺[α-SiW₁₂O₄₀]⁺ (43), or [Au(PPh₃)(MeCN)]⁺[α-SiW₁₂O₄₀]⁺ (44) with yields above 95%, as powders with low solubility in organic solvents.[29] The only side-product of the reaction is methane. MAS-³¹P NMR studies reveal a singlet at 28.8 ppm assigned to the [Au(PPh₃)(MeCN)]⁺ moiety. A small amount (1%) of [Au(PPh₃)]²⁺ is detected via a signal at 44.4 ppm. The identity of 41, and importantly the homogeneous distribution of Au, W, P, O elements is further confirmed, in the solid-state, by powder XRD analysis and statistical energy dispersive X-ray (EDX) mapping. However, MS analyses reveal that once solubilized under sonication in hot acetonitrile, the complexes undergoes redistribution of [Au(PPh₃)(MeCN)]⁺ fragments and protons around the [α-SiW₁₂O₄₀]⁺ anion, yielding mixtures of 41-44 in equilibria. After various crystallization attempts, the complexes 44 and

### Figure 7. Formula of the SICCs 39-40 and combined ball-and-stick polyhedral representation of 39.

### Figure 8. Synthesis of the complexes 41-45 and combined ball-and-stick polyhedral representation of 44.

In 2015, the library of hybrid complexes was extended with other POMs and phosphine or phosphine ligands. Thus, the reactions of 1 equiv. of [Au(PPh₃)(Me)] or triphenylphosphine methylgold(I) [Au(PMe₃)(Me)] or tris(2,4-di-tert-butylyphenyl)phosphine methylgold(I) [Au(P(2,4-di-BuPhO))(Me)] with 1 equiv. of [H]⁺[α-PW₁₂O₄₀]⁺, or [H]⁺[α-PW₁₂O₄₀]⁺, or [H]⁺[α-P₂W₁₆O₄₈]⁺ produce the complexes [Au(PPh₃)(MeCN)]⁺[H]⁺[α-P₂W₁₆O₄₈]⁺ (46), [Au(PPh₃)(MeCN)]⁺[H]⁺[α-MO₁₂O₄₀]⁺ (47), or [Au(PPh₃)(Me)]⁺[H]⁺[α-MO₁₂O₄₀]⁺ (48), [Au(PMe₃)(Me)]⁺[H]⁺[α-MO₁₂O₄₀]⁺ (49), or [Au(P(2,4-di-BuPhO))(Me)]⁺[H]⁺[α-SiW₁₂O₄₀]⁺ (50), with yields above 98% (Figure 9).[30] Analyses by ³¹P NMR confirm the presence of the cationic phosphine gold acetonitrile fragments with singlets at 26.7 ppm (46-48), -12.9 ppm (49) and 85.6 ppm (50). Similarly to 41-44, MS analyses confirm the redistribution of protons and gold fragments around the POM anions. For 46-48, traces of [Au(PPh₃)]²⁺ are also detected by NMR and MS analyses. From hot solutions of acetonitrile, crystals of [Au(PPh₃)(MeCN)]⁺[α-P₂W₁₆O₄₈]⁺ (51), [Au(PPh₃)(MeCN)]⁺[α-P₂W₁₆O₄₈]⁺ (52), [Au(PPh₃)(MeCN)]⁺[H]⁺[α-P₂W₁₆O₄₈]⁺ · 4 MeCN · 2 H₂O (53), and [Au(PMe₃)(MeCN)]⁺[α-SiW₁₂O₄₀]⁺ · 2 MeCN (54) derived from 46-49 were collected in low yields.
etries. The crystallization of \(\text{50}^{+}\) was unsuccessful. The formation of \(\text{44-45}\) and \(\text{51-54}\), having POM anions surrounded by unexpectedly high contents of cationic gold fragments, illustrates perfectly the various equilibria in solution unveiled by MS analyses. In the solid-state, the less stearically demanding \([\text{Au}([\text{PMe}_3])\text{(MeCN)}]\) cation dimerizes via aurophilic interactions. Interestingly, in 2016, Nomiya et al. reported the synthesis of \(\text{52}^{\pm}\) with 45.1 % yield, as crystals, by reacting 7 equiv. of \([\text{Au}(\text{PPh}_3)](\text{R},\text{S}-\text{pyrrolid})\) dissolved in DCM and 1 equiv. of \([\text{H}]^{3+}[\alpha-\text{P}-\text{Mo}_2\text{O}_9\text{O}]^{3-}\) dissolved in a layer of acetonitrile-water: a protocol normally used to access the SICC \([\text{Au}(\text{IPr})(\text{MeCN})]\) \(\alpha\)-hydride \(\text{POM}\) anion. 

The crystal lattices \([\text{Au}(\text{IPr})(\text{MeCN})]\) \(\alpha\)-hydride \(\text{POM}\) affords the complexes \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{SiW}_7\text{O}_{24}]^{4}\) (55), or \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{PMo}_{12}\text{O}_{40}]^{3}\) (56), or \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{P}-\text{W}_6\text{O}_{24}]^{5}\) (57), or \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{PMo}_5\text{O}_{24}]^{3}\) (58), or \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{PMo}_{12}\text{O}_{40}]^{3}\) (59), with yields above 75%, and water as by-product. In this case, changing the solvent system has a dramatic impact on the reaction outcome, reflecting magnificently the variability of the gold POM hybrid structures toward experimental conditions. Once formed, the complex \(\text{52}^{\pm}\) does not undergo clusterization in solutions of MeCN or DMSO.

| Hybrid | Gold Complex | POM | Space group |
|--------|--------------|-----|-------------|
| (46)   | \([\text{Au}(\text{PPh}_3])\text{(MeCN)}\]^+ | \([\text{H}]^{3+}[\text{PW}_{12}\text{O}_{40}]^{3-}\) | \(\text{Ih}\) |
| (47)   | \([\text{Au}(\text{PPh}_3])\text{(MeCN)}\]^+ | \([\text{H}]^{3+}[\text{MoO}^+\text{O}_3\text{O}]^{3-}\) | \(\text{Ih}\) |
| (48)   | \([\text{Au}(\text{PPh}_3])\text{(MeCN)}\]^+ | \([\text{H}]^{3+}[\text{P}_{2}\text{W}_{12}\text{O}_{40}]^{3-}\) | \(\text{Ih}\) |
| (49)   | \([\text{Au}(\text{PMe}_3])\text{(MeCN)}\]^+ | \([\text{H}]^{3+}[\text{SiW}_{12}\text{O}_{40}]^{6-}\) | \(\text{Ih}\) |
| (50)   | \([\text{Au}(\text{P}(2,4-\text{dip}-\text{BuPh})\text{H}))\text{(MeCN)}\]^+ | \([\text{H}]^{3+}[\text{SiW}_{12}\text{O}_{40}]^{6-}\) | \(\text{Ih}\) |
| (51)   | \([\text{Au}(\text{PPh}_3])\text{(MeCN)}\]^+ | \([\text{P}_{2}\text{W}_{12}\text{O}_{40}]^{3-}\) | \(\text{R}^3\) |
| (52)   | \([\text{Au}(\text{PPh}_3])\text{(MeCN)}\]^+ | \([\text{MoO}_5\text{O}_3\text{O}]^{3-}\) | \(\text{R}^3\) |
| (53)   | \([\text{Au}(\text{PPh}_3])\text{(MeCN)}\]^+ | \([\text{H}]^{3+}[\text{P}_{2}\text{W}_{12}\text{O}_{40}]^{6-}\) | \(\text{P}^6\) |
| (54)   | \([\text{Au}(\text{PMe}_3])\text{(MeCN)}\]^+ | \([\text{SiW}_{12}\text{O}_{40}]^{6-}\) | \(\text{P}^6\text{C}\) |

\([\text{H}]^{3+}[\text{POM}]^{x-}\) affords the complexes \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{SiW}_7\text{O}_{24}]^{4}\) (55), or \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{PMo}_{12}\text{O}_{40}]^{3}\) (56), or \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{P}-\text{W}_6\text{O}_{24}]^{5}\) (57), or \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{PMo}_5\text{O}_{24}]^{3}\) (58), or \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{PMo}_{12}\text{O}_{40}]^{3}\) (59), with yields above 75%, and water as by-product. In this case, changing the solvent system has a dramatic impact on the reaction outcome, reflecting magnificently the variability of the gold POM hybrid structures toward experimental conditions. Once formed, the complex 52 does not undergo clusterization in solutions of MeCN or DMSO.

![Figure 9. Formula of hybrids 46-54 and combined ball-and-stick/polyhedral representation of 53.](image)

**2.2. Carbenes Gold(I)-POM Complexes**

In 2018, de Frémont et al. reported the first examples of NHC gold POM hybrid complexes as silver-free catalysts. In acetonitrile, the reactions of 1 equiv. of \((1,3\text{-bis}(2,6\text{-disopropaphenyl})\text{imidazol}-2\text{-ylidene})\text{gold(I)}\) hydroxide) \([\text{Au}(\text{IPr})(\text{OH})]\) or \((1,3\text{-di(tert-butyl)}\text{imidazol}-2\text{-ylidene gold(I)}\) hydroxide) \([\text{Au}(\text{Bu})\text{(OH)}]\) with 1 or 3 equiv. of \([\text{H}]^{3+}[\alpha-\text{SiW}_7\text{O}_{24}]^{4}\), or \([\text{H}]^{3+}[\alpha-\text{PMo}_{12}\text{O}_{40}]^{3}\), or \([\text{H}]^{3+}[\alpha-\text{P}-\text{W}_6\text{O}_{24}]^{5}\), or \([\text{H}]^{3+}[\alpha-\text{PMo}_5\text{O}_{24}]^{3}\) afford the complexes \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{SiW}_7\text{O}_{24}]^{4}\) (55), or \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{PMo}_{12}\text{O}_{40}]^{3}\) (56), or \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{P}-\text{W}_6\text{O}_{24}]^{5}\) (57), or \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{PMo}_5\text{O}_{24}]^{3}\) (58), or \([\text{Au}(\text{IPr})(\text{MeCN})][\text{H}]^{3+}[\alpha-\text{PMo}_{12}\text{O}_{40}]^{3}\) (59), with yields above 75%, and water as by-product. In this case, changing the solvent system has a dramatic impact on the reaction outcome, reflecting magnificently the variability of the gold POM hybrid structures toward experimental conditions. Once formed, the complex 52 does not undergo clusterization in solutions of MeCN or DMSO.

**3. Gold complexes supported by POMs**

In 2012, a single publication from Lacôte et al. described the synthesis of hybrids with a covalent bond between neutral phosphane gold complexes and the functionalized surface of a POM anion.\(^{[25]}\) Thus, in acetonitrile, the reactions of 2 equiv. of \([\text{Au}(\text{dppp})\text{Cl}]\) or \([\text{Au}(\text{dppp})\text{Ba}2\text{Cl}]\), or \([\text{Au}(\text{dppp})\text{Ba}4\text{Cl}]\) (with \(\text{dppp} = \text{diphenylphosphinoethanamine})\) \(\text{dppp}2\text{Ba} = 2\)-diphenylphosphino(benzylamine) or \(\text{dppp}4\text{Ba} = 4\)-diphenylphosphino(benzylamine), 1.2 equiv. of triethylamine,

![Figure 10. Synthesis of complexes 55-60, formula of hybrids 55-62, and combined ball-and-stick/polyhedral representation of 61.](image)
and 1 equiv. of tetrabutylammonium activated α-organotin substituted polytungstate [TBA]4[P2W17O61(Sn(CH2)C=O)]8 afford the complexes [TBA]4[AuCl(dppea)]–P2W17O61(Sn(CH2)C=O)O2 (63), [TBA]4[AuCl(dpp2ba)]–P2W17O61(Sn(CH2)C=O)O2 (64), and [TBA]4[AuCl(dp4ba)]–P2W17O61(Sn(CH2)C=O)O2 (65), with yields above 90% (Figure 11). The triethylmonium formed during the coupling is removed by filtration through TBA-loaded cation exchange resin. The compounds are characterized by 31P NMR spectroscopy with two signals at -12.1 and -6.6 ppm (63-65) for the POM moiety, plus a signal at 28.3 ppm (63), 26.6 ppm (64), or 26.3 ppm (65) for the phosphane gold chloride moiety. Other analyses include FTIR spectroscopy and MS. No SC-XRD studies were made. Interestingly, the addition of 1 equiv. of silver(I) hexafluoroantimonate [Ag][SbF6] to 63 in acetonitrile or a mixture of water-acetonitrile, promotes the formation of cationic gold fragments which are likely coordinated to acetonitrile and/or the POM surface. Those species, active in homogeneous catalysis, are detected by 31P NMR spectroscopy with two singlets at 18.6 ppm and 27.1 ppm in acetonitrile or a singlet at 22.1 ppm in the mixture of water-acetonitrile.

![Figure 11. Synthesis of hybrids 63-65.](image)

The synthesis of gold complexes supported by POM anions remains a virtually unexplored field of research which might lead to robust catalysts easier to recycle. Indeed, having a POM covalently bond to the organogold fragment should preclude any undesired ion exchanges, altering the catalyst formulation and solubility. Moreover, it might also, via chelating effect, promote the stabilization on the cationic gold fragments by enhancing electrostatic interactions with the POM surface.[25]

4. Gold Cations inside Polyoxometalate Structures

In 2010, Kortz et al. reported the first example of POM made of gold, via a straightforward protocol in open-beaker. In water, the hydrolysis of hydrogen tetrachloroaurate(III) hydrate [H][AuCl4] · 3 H2O by caustic soda, at pH equal to 11.5, forms the tetrahydroxogold(III) complex [Na][AuOH4]. The released chloride anions are trapped by addition of silver(I) nitrate and removed by filtration as silver(I) chloride and silver(I) oxide precipitates. Then, reaction of 1 equiv. of [Na][AuOH4] with 1.01 equiv. of sodium arsenate dibasic hydrate [Na][HAsO4] · 7 H2O, at pH = 7.8 affords the POM [Au2O4(AsO3)3] isolated as hydrated sodium salt [Na][HAsO4(AsO3)3] · 39 H2O (66) with 22.0% yield, upon crystallization of the crude reaction mixture.[35] The pH has to be carefully controlled to minimize the formation of gold(III) hydroxide precipitate and colloidal gold(0). SC-XRD studies unveil the presence of two [Au2O4(AsO3)3] anions per unit cell. Their four gold(III) cations are in the same plane forming a slightly distorted square. The Au–O–Au bridges and Au–O–As bridges are pointing opposite directions from the (Au4) plane, giving the POM anions a bowl shape derived from idealized C4v symmetry. Both [Au2O4(AsO3)3] anions are held together by a belt containing five sodium cations forming a larger [Na12Au4As4] assembly. Overall, the POM 66 has a cuboid structure in the solid state (Figure 12). It is interesting to note that [Na12Au4As4] and [Pd2(AAsO4)]2+, found in polyoxopalladates, are structurally similar. In that sense, formation of the scaffold {Met1L4} (L = As, Se ligands) seems favored in the chemistry of noble metal based POMs. By adjusting the reaction conditions, the sodium salts [Na][ClNa5(H2AuAsO3O2)]10 · 39 H2O (67) and [Na][NO3Na5(H2AuAsO3O2)]10 · 25 H2O (68) are synthesized with 18% and 22% yields as crystals. In the solid-state, they are isostructural to 66. The identities of the salts 66-68 are also confirmed by FTIR spectroscopy and EA. Finally, cyclic voltammetry studies confirm the strong complexation of the gold(III) cations in 66 compared to [H][AuCl4] with a reduction wave shifted by -0.950 V. It leads directly to Au(0) without formation of Au(I) intermediates. Of note, the chemistry of polyoxoaurates was further applied with the selenide anion (SeO3)2−.[36]

![Figure 12. Ball-and-stick representation of [Na12Au4As4] fragment of 66 in the solid state.](image)

The concept of polyoxo-noble-metalates was then extended to mixed gold-palladium POMs following a slightly modified experimental protocol used for 66. Indeed, the addition of 0.8 equiv. of palladium(II) nitrate to an aqueous solution containing 1.0 equiv. of POM 66, made in situ at pH comprised between 7 and 8, affords the POM [Na2Au2Pd2O4(AsO3)6]11 isolated as hydrated sodium salt [Na][HNa2Au2Pd2O4(AsO3)6] · 35 H2O · 6 [Na][CH3COO] (69), upon crystallization with 22% yield.[37] SC-XRD analyses reveal a POM with a cuboid shape already encountered with (MetPd2L4) polyoxometalates.[38] The packing crystal, represented by the Fm3m space group, is...
highly symmetric. It prevents from differencing the palladium and gold atoms in the structure, as they all come out as a single residual density peak in the asymmetric unit (which generates later the cuboid shape by symmetry operations). They all have a square planar molecular geometry as expected for d6 cations. However, SC-XRD clearly established a Pd:Au ratio equal to 2:1 which was further confirmed EA and MS. This ratio is surprising regarding the stoichiometry of Pd:Au (0.8:1) used to synthesize 

\[ \text{Au} \] (0.8:1) used to synthesize.

However, attempts on using a reaction stoichiometry Pd:Au close to 2:1 are not beneficial. They still produce 69 in low yields along with [Na]15[H3NaPd3O2(AsO3)15] byproducts. A total of 18 positional isomers exist for the \{AuPd4\} core. They represent all possible arrangements of the four gold cations and eight palladium cations over the different coordination sites in the cuboid structure. DFT calculations coupled with UV-vis spectroscopy suggest that only one isomer (with \( D_{4h} \) symmetry) is found in solution (Figure 13).

![Figure 13. Side views of the two lowest energy isomers with the most favorable arrangement of 4 Au and 8 Pd ions in the structure 69 (Figure from reference 36).](image)

The chemistry of gold-based POMs, which is in its infancy, offers the promises of exciting materials as precursors of noble metal nanoparticles or heterogeneous catalysts. Moreover, the encapsulation of the gold(III) cations in the POM structures might allow less conventional octahedral [6] or square pyramidal [5] geometry of coordination.

5. Encapsulation of gold and POM into MOF

In 2016, Espallagas et al. reported the synthesis of the metal-organic framework (MOF) \( \{\text{Gd(bipyNO)}\}_{3}\text{[TlO]}_{9} \) (with bipyNO = 4,4'-bipyridyl-2,2'-dioxide). In a two-step reaction, it was further loaded with [AlCl4] and [WO4]6 anions to afford the compound \( \{\text{Gd(bipyNO)}\}_{3}\text{[AlCl4]}_{x}\text{[WO4]}_{y} \) \((\text{x + 2 y} = 9)\). First the triolate anions were quantitatively exchanged by the \[ \text{AlCl4} \] anions. Then, the bulkier Lindqvist anions replace partially the \[ \text{AlCl4} \] anions, in the MOF area they can access. The MOF network was very sensitive to desolvation, and therefore kept in methanol solution, precluding EA or DTA. However, 70 was characterized by IR and SC-XRD. The crystal packing features the \( P \) space group symmetry, with very large cavities represented 70% of volume filled with highly disordered solvents’ molecules and POM or gold anions. It is important to note that 70 is not a “true gold POM hybrid”. Indeed, there is no ionic or covalent bonds between the POM and gold fragments present in the MOF.

6. Applications in Gold Catalysis

In the last 15 years, there has been a strong resurgence of interest in organogold chemistry and the associated homogeneous catalysis. The strong Lewis acidity and still softness of the gold(I) cation has rendered possible a broad array of catalytic transformations. Nowadays, gold(I) complexes are largely recognized as catalysts of choice to activate carbon–carbon multiple bonds toward intra- or intermolecular nucleophilic additions. In these catalytic processes, the first step is often the \textit{in-situ} formation of the reactive entity \( \{\text{Au} (\text{L})\} \) from a gold pre-catalyst. This is achieved by replacing a strongly coordinating ligand (halogen X or alkyl R) by a weakly bound anion in a way to liberate a coordination site for the unsaturated substrate. Two activation methods are generally employed: one by halogen abstraction of \( \{\text{Au(L)}\}^{+} [X] \) complexes using the driving force of the silane halide \( \text{[AgX]} \) formation and precipitation and the other by hydrolysis of organogold complexes (usually methylgold phosphates) with strong acids such as heteropolyacids (HPAs, acid form of POMs).

In line with the latter strategy, Hayashi and Tanaka have combined, for the first time, an organogold complex and an HPA in a catalytic system dedicated to the hydration of alkynes. Indeed, triphenylphosphane methylgold(I) complex (0.01 mol%), activated by an excess of phosphotungstic acid (0.05 mol%), catalyzed the hydration of oct-1-yne 71 leading to 80% of octan-2-one 72 (Scheme 1). Despite the good yield so-obtained with acidic POM, trifluoromethanesulfonic acid was a better activator and was thereafter used for the scope of the reaction. It is noteworthy to mention that control experiments using HPA alone do not catalyse the rearrangements/reactions reported in this section.

\[
\begin{align*}
\text{[Au(PPh3)(Me)]} (0.01 \text{ mol%}) & \quad \text{[H3PW12O40]} (0.05 \text{ mol%}) \\
\text{C}_8\text{H}_{13} & \quad \text{MeOH} + \text{H}_2\text{O} (10:1) \\
71 & \quad 70^\circ \text{C}, 1 \text{ h} \\
\end{align*}
\]

Scheme 1. Activation of triphenylphosphane methylgold(I) complex by phosphotungstic acid for the hydration of oct-1-yne.

However, in 2003, the same authors reported that HPAs were the best acidic promoters in the intermolecular hydroamination of alkenes with anilines. During the acid activators screening of \( \{\text{Au}(\text{PPh3})(\text{Me})\} \) for the addition of 4-bromoaniline 73 onto phenylacetylene 74, HPAs were particularly effective affording ketimines 75 in near quantitative yields (Scheme 2).

\[
\begin{align*}
\text{Ph} + \text{H}_2\text{N} & \quad \text{[Au(PPh3)(Me)]} (0.2 \text{ mol%}) \\
74, 1.0 \text{ equiv} & \quad \text{[H3PW12O40]} (1 \text{ mol%}) \\
\text{Solvent free} & \quad 70^\circ \text{C}, 2 \text{ h} \\
75 & \quad 97\% \text{ (GC yield)} \\
\end{align*}
\]

Scheme 2. Catalytic addition of 4-bromoaniline to phenylacetylene using HPA as a promoter.
MINIREVIEW

Scheme 2. Hydroammination of phenylacetylene with 4-bromoaniline catalyzed by gold(I) pre-catalyst/heteropolyacid mixture.

This methodology was applied to various aromatic and aliphatic alkynes 76 and substituted anilines 77 using low catalyst loadings: 0.1-0.2 mol% of gold pre-catalyst and 0.05-0.10 mol% of \( [\text{HPW}_{12}\text{O}_{40}]^{3-} \) (Table 1). Ketamines 78 were produced in high yields (70-98%) in a few hours at 70 °C under free-solvent conditions, with sometimes traces of the corresponding enamine tautomeric form.\(^{[43]}\)

Table 1. Intramolecular hydroamination of terminal alkyne derivatives with substituted anilines.

| Entry | Alkyne \( R^1 \) | Aniline \( R^2 \) | Au (mol%) | POM (mol%) | Time [h] | Yields\(^{\text{a}}\) [%] |
|-------|-----------------|-----------------|-----------|------------|---------|----------------|
| 1     | Ph              | Ph              | 0.2/1.0   | 2          | 98      |
| 2     | Ph              | F-FPh           | 0.1/0.5   | 2          | 94      |
| 3     | Ph              | 4-NCPh          | 0.1/0.5   | 1          | 89\(^{\text{b}}\) |
| 4     | Ph              | 4-NO\(_2\)-Ph   | 0.1/0.5   | 1          | 86\(^{\text{b}}\) |
| 5     | 4-FPh           | 4-BrPh          | 0.2/0.1   | 0.5        | 90      |
| 6     | 4-BrPh          | 4-BrPh          | 0.2/0.1   | 1          | 96      |
| 7     | 4-MeOPh         | 4-BrPh          | 0.2/0.1   | 2          | 70      |

[a] NMR Yields. [b] Along with the corresponding enamine (<10%).

In 2009, Shi et al. reported the same transformation but mostly applied to internal alkynes 79 using 1 mol% of a triphenylphosphine bidentate gold(I) complex \([\text{Au(PPh)}_3](\text{Btz})\) activated by 2 mol% of acidic POM (Table 2).\(^{[44]}\)

This activation mode, the protonation of the bidentate gold(I) part, by HPA, generates an active and thermally stable gold catalyst associated to POM anions. Such reaction conditions proved to be applicable to various anilines 77 and internal alkynes 78. It produces, in excellent yields (83-91%), various reduced amines after treating the sensitive imine intermediates with BH\(_3\), in THF. Starting from dissymmetric alkynes, the hydroamination furnished a mixture of amines 80-81 in ratios of 6:1 to 2:1 always in favour of the Markovnikov adduct.

Table 2. Phosphotungstic acid co-catalyzed hydroamination of internal alkyne derivatives with anilines.

| Entry | Alkyne \( R^1 \) | Aniline \( R^2 \) | Yields\(^{\text{a}}\) [%] | Ratio 80:81 |
|-------|-----------------|-----------------|----------------|------------|
| 1     | Ph              | Ph              | 0.1/0.5 | 2          | 98          |
| 2     | Ph              | 4-FPh           | 0.1/0.5 | 2          | 94          |
| 3     | Ph              | 4-NCPh          | 0.1/0.5 | 1          | 89\(^{\text{b}}\) |
| 4     | Ph              | 4-NO\(_2\)-Ph   | 0.1/0.5 | 1          | 86\(^{\text{b}}\) |
| 5     | 4-FPh           | 4-BrPh          | 0.2/0.1 | 0.5        | 90          |
| 6     | 4-BrPh          | 4-BrPh          | 0.2/0.1 | 1          | 96          |
| 7     | 4-MeOPh         | 4-BrPh          | 0.2/0.1 | 2          | 70          |

[a] NMR Yields. [b] Along with the corresponding enamine (<10%).

By extension, from diyne 82 and aniline 83, substituted pyrrole 84 was prepared in excellent yield of 80% via an intramolecular cyclization of the imine intermediate formed in the hydroamination reaction conditions (Scheme 3).

Scheme 3. Synthesis of substituted pyrrole 84 by hydroamination reaction.

In 2008, Hayashi et al. tried to perform the hydrative cyclization of 1,6-diyne 85 to form the corresponding trimethylhex-2-enone 86 using \([\text{Au(PPh)}_3](\text{Me})\) (2 mol%) and HPA additives (4 mol%) in the presence of water (Scheme 4).\(^{[45]}\) Unfortunately, a maximum yield of 29% was obtained with silicotungstic acid while the desired product was obtained in almost quantitative yield using trifluoromethanesulfonic acid (50 mol%) as activator.

Scheme 4. Attempts to promote gold-catalyzed the hydrative cyclization of 1,6-diynes with silicotungstic acid as activator.

POM and organogold complex mixtures have also been employed by Echavarren et al.\(^{[46]}\) to promote the skeleton rearrangement of 1,6-enynes. Various substituted enynes 87 were engaged in alkoxycyclization in the presence of methanol affording 5-exo-dig products 88, in good to excellent yields, using only 1 mol% of \([\text{Au(PPh)}_3]\)Me pre-catalyst (67-96%, Table 3). For less reactive substrates, the reactions were carried out at reflux, in the unexplained presence of 3 mol% of the bulky and electron rich tricyclohexylphosphine (Entries 4 and 5).
Under these reaction conditions, the authors postulated that the active species generated was \([\text{Au}(\text{PPh}_3)(\text{ROH})]^{-}\)[POM] but without experimental evidences.

**Table 3.** Alkoxy cyclization of 1,6-enynes catalyzed by treatment with organogold(I) pre-catalyst and phosphonic acid.

| Entry | 1,6-Enyne | Time [h] | Yields [%] |
|-------|-----------|----------|------------|
| 1     | C(CO2Me)2 | H Me Me  | 4         | 96         |
| 2     | C(CO2Me)2 | H Me     | 7         | 67         |
| 4     | NTs       | H Me Me  | 174       | 85[b]      |
| 5     | C(SO3Ph)2 | Ph Me Me | 17        | 96[b]      |

[a] Isolated yields. [b] Reaction run at reflux. [c] PCy$_3$(3 mol%) was also added. Pr’ = Prenyl. Ts = Tosyl.

In the previously reported examples, the nature of the catalysts obtained by mixing gold pre-catalysts and POMs (structure, stability, heterogeneity, recyclability...) as well as the impact of the inorganic polyaniomic POM on the catalytic activity have not been established. However, in gold(I) catalysis, the role of the counterion is far from innocent affecting, the rate of reaction, the selectivity as well as the reactivity.[27]

In 2014, Bianc et al.[28] have started to investigate the synthesis, the characterization (see Section 2.1.2) and, obviously, the catalytic activity of \([\text{Au}(\text{L})]^{-}\)[H][POM]$^{-}\] complexes depending of the gold(I) cation stoichiometry (x \([\text{Au}(\text{L})]^{-}\) units by POM) and have later expanded their investigations to the variations of POMs and ligands (L) nature.[30,32]

These highly stable and pre-activated Au/POM hybrids have been classically tested in a transformation catalyzed by gold(I), i.e. the rearrangement of enyl acetate 89,[48] under heterogeneous conditions (Table 4). They all showed efficient catalytic activity affording selectively the cyclopentene 90 in wet dichloromethane (65-94%) or in mixture with the non-hydrolyzed product 91 in dry toluene. Regardless of the ratio gold cation:POM anion, the formation of 90 was obtained in comparable yields even if the acid free catalyst 44 exhibited a longer reaction time (Entries 1 vs 2-4). The reaction was obviously influenced by the electronic nature of gold ligand (for example phosphate vs phosphite, entry 4 vs 8). However, the nature of the POM also impacted the efficiency of the reaction (Entry 6 vs 7 and 10 vs 11).

**Table 4.** Catalytic activity of Au(I):POM complexes for the rearrangement of enyl acetate 89.

| Entry | Catalyst (mol%) | Time [h] | Yields [%] |
|-------|----------------|----------|------------|
| 1     |                | 24       | 80         |
| 2     |                | 84       | 65         |
| 3     |                | 24       | 75         |
| 4     |                | 24       | 75         |
| 5     |                | 24       | 75         |
| 6     |                | 24       | 75         |
| 7     |                | 24       | 75         |
| 8     |                | 24       | 75         |
| 9     |                | 24       | 75         |
| 10    |                | 24       | 75         |

*a* The catalytic loading of Au/POM complexes was used proportional to the amount of Au(I) present in each hybrid. [b] Yields were calculated by $^1$H NMR analysis relative to an internal standard (dimethyl terephthalate) taken from the crude mixture. [c] Reaction run in wet dichloromethane. [d] Reaction run in dry toluene. P(Car)$_3$ = tris(2,4,4-tri-tert-butylphenyl)phosphate.

Appealing and specific reactivity has thus been discovered using \([\text{Au}(\text{L})]^{-}\)[H][POM]$^{-}\] complexes. Indeed, complex \([\text{Au}(\text{PPh}_3)(\text{MeCN})]^{-}\)[H][POM]$^{-}\] 41 was able to furnished (E)-3-oxocarbonyl enone derivatives 93 through the stereoselective rearrangement of propargyl gem-diesters 92 (Table 5).[28] This unique and synergistic catalyst complex promoted the rearrangement more efficiently than a large range of homogeneous gold catalysts. Moreover, this transformation was successfully applied to various propargyl gem-diesters 92 with a good to excellent yields (34-95%).

**Table 5.** Selective rearrangement of propargyl gem-diesters 92 into E-enone 93 catalyzed by Au(I)/POM complex 41.

| Entry | R$^1$ | R$^2$ | Time [h] | Yields [%] |
|-------|-------|-------|----------|------------|
| 1     | Ph    | Bu    | 45       | 80         |
| 2     | Ph    | Me    | 45       | 65         |
| 3     | Ph    | Ph    | 45       | 65         |
| 4     | 2-MeOPh | Bu    | 45       | 75         |
| 5     | 4-MeOPh | Bu    | 45       | 75         |
| 6     | 2-FPh | Bu    | 45       | 75         |
| 7     | C$_6$H$_5$ | Bu    | 45       | 75         |
| 8     | Cyclohexyl | Bu    | 45       | 75         |
| 9     | Bu    | Bu    | 45       | 75         |
| 10    | Bu(O)CH$_3$ | Bu    | 45       | 75         |
Taking benefit of residual Bronsted acidities remaining on hybrids, Blanc and coworkers have also demonstrated the capacity of Au(I)/POM compounds to act as dual catalysts (Table 6,[23] in a two steps sequence, the cyclic enol ether 95 was generated from N,O-acetal 94 via anaza-Prins cyclization using 10 mol% of the strongly electron withdrawing tri(pentafluorophenyl)phosphine gold(I) complex, and was subsequently hydrolyzed to furnish the ketone 96 (Table 6, entry 1).[20] With Au(H)/H⁺/POM, the product 96 was obtained in a one-step procedure with only 2.5 mol% of catalyst loading in the same reaction conditions (67-89%, Table 6, entries 2-7). Interestingly, similar and even better yields were achieved with the Au(I)/POM compared to the homogeneous version.

Table 6. bifunctional catalytic activity of Au(I)/H⁺/POM complexes in tandem gold-catalyzed Aza-Prins cyclization/enol ether.

| Entry | Catalyst (2.5 mol%) | Time [h] | Yields [%] |
|-------|---------------------|----------|-----------|
| 1     | [Au(P[C(=O)H]3)][BF4]⁻ (10 mol%) then pTsOH·H2O | 2 then 24 | 80[^b] |
| 2     | [Au(PPh₃)(MeCN)][H][PMO₁₂O₄₀]²⁻ | 1 | 70 |
| 3     | [Au(PPh₃)(MeCN)][H][PW₁₂O₄₀]²⁻ | 0.5 | 75 |
| 4     | [Au(PPh₃)(MeCN)][H][PMo₁₂O₄₀]²⁻ | 0.5 | 86 |
| 5     | [Au(PPh₃)(MeCN)][H][PW₁₂O₄₀]²⁻ | 48 | 67 |
| 6     | [AuCl][MeCN][H][SiW₁₂O₄₀]²⁻ | 0.5 | 89 |
| 7     | [AuCl][MeCN][H][SiW₁₂O₄₀]²⁻ | 3 | 68 |

[a] Isolated yields. [b] Two-steps yield using homogeneous conditions.

The complex [Au(PPh₃)(MeCN)][H][PMo₁₂O₄₀]²⁻ 47 was also applied to various other gold-catalyzed transformations confirming its polyvalence, multifunctionality as well as its competitive activity compared to other homogenous catalysts.[23] Additionally, the Au/POM hybrids have been evaluated in the oldest gold-catalyzed reaction: the hydration of alkynes. Diphenylacetylene 97 was efficiently converted into 1,2-diphenylethan-1-one 98 in an ether/water mixture (88-98%, Table 7) using phosphate or NHC gold(I) cations associated with acid-free POMs.[31,32]

Table 7. Hydration of diphenylacetylene catalyzed by POM/Au(I) complexes.

| Entry | Catalyst (Au (mol%)) | Time [h] | Yields [%] |
|-------|----------------------|----------|-----------|
| 1     | [Au(PPh₃)(MeCN)][PMo₁₂O₄₀]²⁻ | 52 (0.67) | 24 | 92 |
| 2     | [Au(PPh₃)][μ-O][PW₁₂O₄₀]²⁻ | 16 (0.67) | 24 | 90 |
| 3     | [Au(PPh₃)][μ-O][Au(PPh₃)][μ-O][PW₁₂O₄₀]²⁻ | 24 (0.67) | 24 | 88 |

[a] Additive: [TBA][AuCl(dpppea)·[Sn-POM]]⁻ 65 | 3 | 95 |
| 4     | 4-FPh | 2 | 88 |
| 5     | 3,5-Me₂Ph | 2 | 97 |
| 6     | 4-MeOOPh | 2 | 96 |
| 7     | 4-MeOOPh | 10 | 55[^f] |
| 8     | 4-MeOOPh | [Au(PPh₃)][Ag(SbF₆)]²⁻ | 2 mol%) | 10 | 76[^f] |

[a] HPLC Yields. [b] Yield was calculated by ¹H NMR analysis relative to an internal standard (dimethyl terephthalate) from the crude mixture.

Gold(I) complexes tethered to a Dawson σ,σ-organotin-substituted polyoxotungstate 63-65 (see Section 3) prepared by Lâcote et coworkers[33] have been developed in order to cyclize very sensitive allenol derivatives and facilitate recycling of the gold catalysts.

In homogeneous gold catalysis, β,β-diaryl β-hydroxy allenenes 99, are known to rapidly generate vinylallene derivatives by dehydration, presumably due to adventitious traces of acid brought by the catalyst.[34] Pre-catalyst diarylphosphine gold(I) chloride complex 63, covalently bound to POM and activated in dichloromethane with silver(I) hexafluoroantimonate was engaged in the catalytic cyclization of such derivatives. The oxacyclization products 100 were formed at room temperature after 2 days in excellent yields (88-97%, Table 8, entries 1-4), whatever the substitution of β,β-diaryl part. Triarylphosphine gold(I) POM derivatives 64 and 65 showed the same reactivity despite longer reaction times (5 days, entries 5 and 6). Control experiments using activated triphenylphosphine gold(I) chloride in the presence of buffer additives such as [TBA][P₂W₁₀O₄₀]²⁻ or pyridine also afforded the cyclic ethers but with significant amount of elimination products after prolonged reaction time demonstrating the advantage of POM-Au tethering strategy (Entries 7 and 8). The high selectivity observed in such cyclocosimerization of sensitive allenols was attributed to the ability of the tetrabutylammonium POM-gold hybrids to act efficiently as an intramolecular buffer able to capture protons on the metal-oxide surface.

Table 8. POM-Au Hybrids-catalyzed the cyclization of acid-sensitive β,β-diaryl β-hydroxy allenenes 99.

| Entry | Ar | Pre-catalyst (5 mol%) | Time [days] | Yields [%] |
|-------|----|----------------------|------------|-----------|
| 1     | Ph | [TBA][AuCl(dpppea)·[Sn-POM]]⁻ | 63 | 3 | 95 |
| 2     | 4-FPh | 2 | 88 |
| 3     | 3,5-Me₂Ph | 2 | 97 |
| 4     | 4-MeOOPh | 2 | 96 |
| 5     | 4-MeOOPh | 64 | 5 | 96 |
| 6     | 4-MeOOPh | 65 | 5 | 80 |
| 7     | 4-MeOOPh | 10 | 55[^f] |
| 8     | 4-MeOOPh | [Au(PPh₃)][Ag(SbF₆)]²⁻ | 2 mol%) | 10 | 76[^f] |

[a] Additive: [TBA][P₂W₁₀O₄₀]²⁻ (5 mol%). [b] Isolated along with 37% (entry 7) and 6% (entry 8) of elimination product, i.e. 4,4′-[(5-methylhexa-1,3,4-triene-1,1-diy)bis(methoxybenzene). [c] Additive: Pyridine (2 mol%). Sn-POM = [P₂W₁₀O₄₀][Sn(H₂O)₂Cl₂].

Taking advantage of a gold/POM interactions on activated hybrid 63, which might stabilize the gold cation, recycling process in the cyclocosimerization of allenols 99 was performed (Scheme 5, Eq. 1). The catalyst could be recovered
by precipitation and centrifugation up to 3 times without any loss of yield, but the reaction rate dropped significantly in the third cycle.

\[ \text{Scheme 5. Recycling of pre-activated POM-Au hybrid catalysts 41, 48, 56 and 63 in various organic transformations.} \]

Other attempts on recycling have been investigated on various reactions with \([\text{Au(L)}]^{+},[\text{H}]^{+} \cdot \text{POM}^{y-}\) complexes allowing to recover the catalysts up to 5 times (Scheme 5, Eq. 2–4).\(^{[28,30,32]}\) In all cases, the best results were obtained using hybrids with a 1 to 1 gold:POM ratio \((x = 1)\) which maximized the heterogeneity of the catalyst. However, the composition and the size of the POM clusters as well as the nature of the ligand are important factors to stabilize the gold(I) cation and these parameters should be tuned in function of the targeted transformation. Despite the relatively low number of recovered cycles, the results were promising, and improvements are doubtlessly expected in a near future.

7. Conclusion

The chemistry of gold/POM hybrids is at an early stage, but its development has accelerated during the recent years with the idea to merge the remarkable properties of both entities in the same material.

In one hand, gold/POM supramolecular intercluster compounds (SICCs) have emerged but are so far restricted to phosphane gold oxonium or phosphane gold ammonium clusters. Their chemistry is facing two challenges: 1/ find the suitable conditions (solubilization/crystallization) to have reproducible experiments which can be scaled up; 2/ understand better the formation of the gold clusters to predict in accordance their future geometries in the solid-state. From the SICCs previously described, it seems likely that: 1/ the clusterization of the gold complexes is occurring at the POM surface; 2/ the counter-ions associated with the POMs influence the nucleation of the gold clusters formed (e.g. tetra- versus hepta-gold clusters); 3/ the bulkiness and charge of the POMs influence the formation of gold dimers (e.g. \([\text{Au(PR)}]_{2}(\mu-\text{O})^{2-}\) versus \([\text{Au(PR)}]_{2}(\mu-\text{OH})^{2-}\)) and the substituents on the phosphanes influence the aggregations of dimers (e.g. cross-edge arrangement versus parallel-edge arrangement). Very soon, there is no doubt that the chemistry of gold SICCs will be extended to ligands other than phosphanes and to clusters containing elements other than oxygen or nitrogen, thus providing exciting self-assembly structures.

On the other hand, phosphane or NHC gold/POM complexes are even more emerging compounds than gold POM SICCs. In solution, their chemistry is dominated by various equilibria involving gold fragments and protons redistribution around the POM anions. Thus, crystallization trends to favor the formation of species with high contents of gold, likely associated with better solubility in organic solvents. These highly stable complexes denote excellent abilities as pre-activated, efficient and recyclable catalysts in various gold-catalyzed reactions. Moreover, the boundary between formation of mononuclear complexes of SICCs appears quite thin. Hopefully, as these hybrids complexes will become more popular, their chemistry will be better understood, giving rise to valuable catalytic and multifunctional systems under both homogeneous and heterogeneous conditions.

Appendix

After completion of the manuscript, an updated survey of the bibliography was made. A publication has appeared relevant to the section 2.2 of this review.\(^{[51]}\)

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Keywords: gold • polyoxometalates • cluster compounds • phosphane ligands • catalysis

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The self-assembly of “aurophilic” gold(I) cations and polyoxometalate clusters offer promising opportunities in the design of new materials for catalysis, thanks to strong relativistic effects impacting the gold atom.

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When Gold Cations Meet Polyoxometalates Anions