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Synthesis and reactivity of multinuclear gold complexes with (diphenylphosphanyl)ferrocene and oxygen ligands

Jiří Schulz,^[a] Ivana Čísařová,^[a] Róbert Gyepes^[a] and Petr Štěpnička*^[a]

Abstract: Au(I) complexes combining hard oxygen and soft (diphenylphosphanyl)ferrocene (L) ligands in their molecules were synthesised, viz. the gold hydroxides [Au(OH)(L-κP)] (**5**) and [Au(L-κP)₂(μ-OH)][BF₄] (**4**), and the trigold oxonium cluster [Au(L-κP)₃(μ₃-O)][BF₄] (**1**). *In-situ* auration of **1** produced [Au(L-κP)₄(μ₄-O)][BF₄]₂ (**2**), which, upon crystallisation, converted into a dimeric tetragold complex featuring bridging phosphanylferrocenyl groups geminally diaurated in position 2 of the ferrocene scaffold. The same complex and its isomer incorporating ferrocene-1,1'-diyl bridges resulted similarly from **4**. Upon crystallisation, compound **5** underwent a redox reaction, producing a structurally unique, crown-like, mixed-valent Au(0)/Au(I) cluster, [Au₇(L-κP)₆]OH. Complexes **1** and **5** were further used to prepare the analogous, N-bridged complexes, [Au(L-κP)₃(μ₃-NFC)][BF₄] (Fc = ferrocenyl) and [Au(L-κP)₄(μ₄-N)][BF₄]. All compounds were characterised using spectroscopic and X-ray diffraction methods and further studied by cyclic voltammetry and DFT calculations.

Among the noble metals, gold stands out for its aptitude to form polynuclear compounds and clusters.^[1] This property reflects the unique ability of gold(I) to generate attractive metal-metal contacts, aurophilic interactions,^[2] which control the stoichiometry and structure of gold complexes, influence their physicochemical properties (e.g., luminescence^[3]) and may account for unusual structural assemblies.^[4] Similar in strength to hydrogen bonding, aurophilicity is a weak non-covalent interaction originating from dispersion forces resulting from the correlated motion of electrons,^[5] which is amplified by relativistic effects, peaking just in gold. The typical Au...Au distances span the 2.5–3.2 Å range,^[6] with bond energies varying approximately between 20 and 45 kJ mol⁻¹.^[7]

Although the concept of aurophilicity was introduced by Schmidbaur in 1988,^[8] structural evidence of attractive interactions between gold(I) centres had already emerged in the 1970s, with oxonium salts [(μ₃-O){Au(PR₃)₃}₃]X representing one of the first compounds with a noticeable structural impact of the Au...Au contacts.^[9] Subsequently, these salts were used as aurating agents in the synthesis of clusters incorporating electronegative non-metal elements and metalloids. Surrounded by an array of interacting gold(I) ions, the central chalcogen,^[10] pnictogen^[11] and carbon atoms^[8a, 12] in these compounds typically exceeded their standard valences and adopted unusual geometries. Based on the above, we have decided to prepare a

trigold oxonium cluster supported by a redox-active metalloligand, (diphenylphosphanyl)ferrocene (L), [(μ₃-O){Au(L-κP)₃][BF₄] (**1**), and to study its reactivity. During these studies, we isolated several unique gold complexes, all of which are described herein.

Cluster **1** was obtained as an air-stable, crystalline solid by successively treating [AuCl(L-κP)] with Ag[BF₄] and KOH (1 equiv. each; Scheme 1). Its formulation was based on spectroscopic data and further corroborated by X-ray diffraction analysis (Figure S2). After preparing **1**, we explored its reactivity. Inspired by the work of Schmidbaur *et al.*,^[10c] we initially synthesised the tetragoldoxonium cluster **2** by treating **1** with *in-situ* formed [Au(L-κP)(MeCN)][BF₄] at -78 °C (Scheme 1). NMR spectroscopy confirmed the clean formation of a new gold complex (mainly through the shift in the ³¹P NMR signal to a lower field). This complex was identified as **2**, in conformity with ESI MS analysis, which showed the presence of abundant ions with *m/z* = 1142.5 due to the dication [(μ₄-O){Au(L-κP)₄]²⁺. However, subsequent experiments revealed that complex **2** is prone to water elimination during crystallisation, which is accompanied by auration of its ferrocene ligands at a position adjacent to the phosphanyl group, producing a new tetragold complex **3** (Scheme 1).

Repeated experiments confirmed that the conversion of **2** into geminally diaurated **3** is reproducible and complete and that only one product is formed, which was structurally characterised as a *meso* isomer (*vide infra*). The formation of **3** is manifested as a pair of doublets in the ³¹P{¹H} NMR spectrum corresponding to the non-equivalent phosphorus atoms at δ_P = 32.3 and 33.1 ppm (³J_{PP} = 3 Hz), while doubly-charged ions with *m/z* = 1133.4 are observed in the ESI MS, attributable to [Au₂(L-H)₂][Au(L)]₂²⁺. Intrigued by the unusually strong self-aurating ability of **2**, we extended our study towards gold(I) hydroxide complexes, [(μ-OH){Au(L-κP)₂][BF₄] (**4**) and [Au(OH)(L-κP)] (**5**) (Scheme 1). Nolan *et al.* have shown that gold(I) hydroxides supported by *N*-heterocyclic carbene ligands are useful reagents. In particular, [Au(OH)(IPr)] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) is a versatile synthetic precursor thanks to its pronounced Brønsted basicity,^[13] while hydroxide [(μ-OH){Au(IPr)₂][BF₄] is mainly used in catalysis.^[14] Thus, we successively treated [AuCl(L-κP)] with Ag[BF₄] (1 equiv.) and KOH (0.5 equiv.), thereby cleanly producing digold complex **4**, which was authenticated by NMR and ESI MS measurements. Complex **5** was also successfully prepared but required using a large excess of KOH (3 equiv.) to prevent the concomitant formation of the trigold oxonium cluster **1** (Scheme 1).

Although isolable, the gold hydroxide **5** was substantially more reactive than the analogous complexes supported by the carbene ligands, abstracting chloride from chlorinated solvents (CHCl₃, CH₂Cl₂) and regenerating the parent complex [AuCl(L-κP)].

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Importantly, both **4** and **5** underwent remarkable spontaneous structural transformations upon crystallisation (Scheme 1). Thus, the digold complex **4** eliminated a water molecule to produce a mixture of isomeric tetragold(I) complexes **3** and **6**, which could be separated by crystallisation. The formation of both **3** and **6** reflects the fact that two molecules of the parent complex are involved in the formation of the geminally diaurated compounds from **4**, in line with the tendency of $[(\mu\text{-OH})\{\text{Au}(\text{PPh}_3)_2\}(\text{CF}_3\text{SO}_3)_2]$ to dimerise *via* Au...Au interactions.^[15] In contrast, the transformation of the tetragold cluster **2** proceeds as a unimolecular process and thus gives rise exclusively to complex **3**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** displayed two doublets at $\delta_{\text{P}} = 31.8$ and 35.4 ppm ($^3J_{\text{PP}} = 3$ Hz), and the ESI MS spectra showed ions at $m/z = 1699.8$ attributable to $[\{\text{Au}_2(\text{L}-\text{H})_2\}\{\text{Au}(\text{L}-\kappa\text{P})\}]^+$, a fragment ion resulting from **6** by the loss of Au(L)⁺.

The molecular structures of **3** and **6** are depicted in Figure 1 (for additional diagrams and parameters, see Supporting Information). Structural data suggest that, while **3** can be described as a linear, tetranuclear cluster, **6** is a double geminally diaurated complex analogous to $[\text{Fc}\{\text{Au}(\text{PPh}_3)_2\}_2][\text{BF}_4]$ (Fc = ferrocenyl),^[16] whose equivalent parts are interlinked into a dimer through P,C-bridging phosphanylferrocenyl moieties.

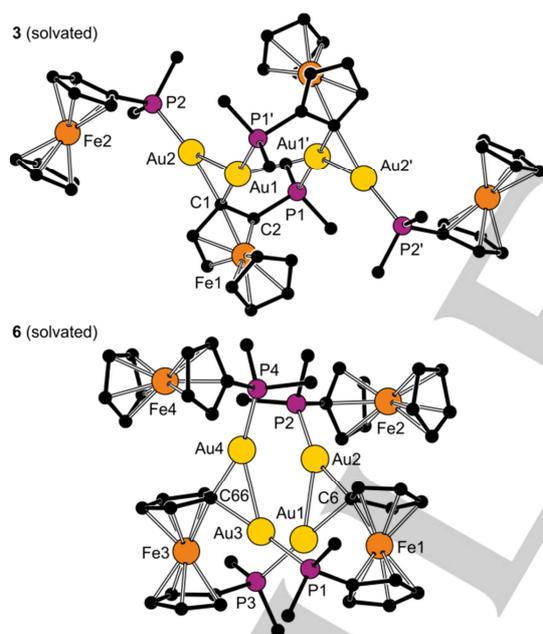


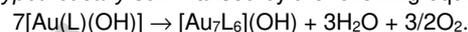
Figure 1. Simplified structural diagrams of complex cations in the structures of **3**·6CHCl₃ and **6**·2.6CH₂Cl₂. For clarity, all hydrogen and phenyl ring carbon atoms were omitted. Selected distances [Å] for **3**·6CHCl₃: Au1-Au2 2.7799(5), Au1-Au1' 3.0166(5), Au1-C1 2.132(3), Au2-C1 2.142(2), Au1-P1' 2.2798(8), Au2-P2 2.2669(7); for **6**·2.6CH₂Cl₂: Au1-Au2 2.7484(8), Au3-Au4 2.7827(8), C-Au 2.116(7)-2.137(7), Au-P 2.258(2)-2.284(2). The CCDC numbers can be found in the Supporting Information.

Such a description is consistent with the computed Mayer Bond Orders (MBO's). While the interactions between the adjacent Au atoms in **3** were of comparable magnitude (*cf.* MBO 0.280 for the Au1-Au1', and 0.218 for Au1-Au2/Au1'-Au2' pairs), for **6** a

slightly enhanced interaction was observed for the symmetrically equivalent Au1-Au2 and Au3-Au4 pairs (MBO 0.263), but a much weaker interaction with MBO 0.132 was noted for Au1-Au3. No significant interactions were detected between Au2 and Au4 in **6** and between the Au and Fe atoms in both compounds (for details, see Supporting Information).

When dissolved in anhydrous THF or stored for an extended period (even at -18°C under argon), hydroxide **5** gradually dehydrated into the elusive oxide complex, $[\{(\text{L}-\kappa\text{P})\text{Au}\}_2\text{O}]$,^[4c,17] which was also prepared independently (see Supporting Information). When crystallised from THF/Et₂O, complex **5** transformed into a unique, mixed-valent Au(0)/Au(I) heptagold cluster **7** (Scheme 1), wherein a central gold(I) cation is surrounded by a toroidal array of six Au⁰(L- κP) units. Notably, **7** is the first isolated representative of the $[\text{Au}_7(\text{PR}_3)_6]^+$ clusters^[18] that have been theoretically predicted but not yet prepared, and it diametrically differs from the known heptanuclear cluster $[\text{Au}_7(\text{PPh}_3)_7]^+$, which has a pentagonal bipyramidal arrangement.^[19,20]

Formally, compound **7** arises from a redox transformation, which can be *hypothetically* summarised by the following equation:



The reaction is clean and reproducible. Nonetheless, its real mechanism is certainly more complicated and involves stepwise condensation of **5** with an intermediacy of the oxide complex $[\{(\text{L}-\kappa\text{P})\text{Au}\}_2\text{O}]$ (*N.B.* this compound spontaneously converts into **7** in a THF solution) and additional redox steps.

The ESI MS spectra confirmed that the cationic part of cluster **7** remains intact in solution, showing the ions $[\text{Au}(\text{AuL})_6]^+$ ($m/z = 3600.1$) and fragments resulting from ligand loss ($m/z = 3260.1$). Although the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum indicated high symmetry for **7** based on the sharp singlet at $\delta_{\text{P}} = 57.6$ ppm, the ultimate structural evidence was provided by X-ray diffraction analysis of 7·Me₂NCHO·THF (Figure 2). The distance from the hexacoordinate central atom (Au2) to the peripheral, phosphane-ligated gold atoms (Au1) is 2.6590(4) Å, while the distances between the neighbouring gold atoms Au1, which are arranged in crown-like fashion owing to the imposed symmetry (trigonal space group $R\bar{3}c$), are 2.7727(9) and 2.7837(8) Å (alternating). Considering the similar Au-Au separations, the geometry of the cluster can also be described as six equilateral Au₃ triangles fused into a hexagonal metallic framework. The equivalent Au2-Au1-P1 arms are slightly bent for steric reasons (168.27(7) Å), albeit with Au1-P1 distances within the usual range (2.295(1) Å).

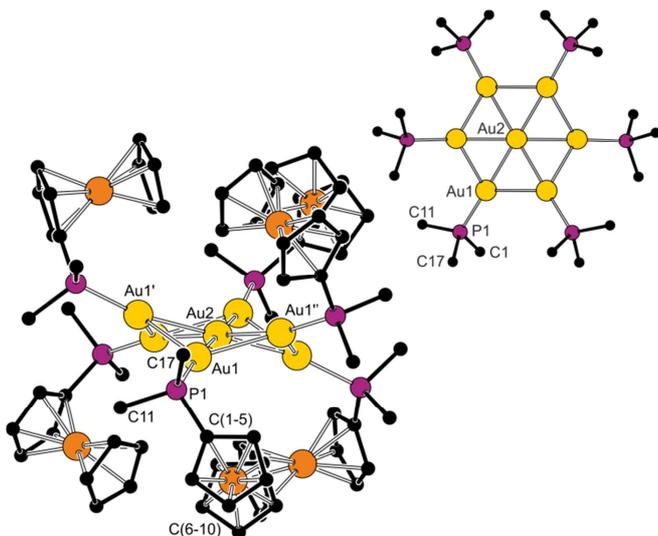


Figure 2. Simplified structural diagrams of the complex cation in 7-Me₂NCHO-THF (for additional drawings, data and the CCDC number, see Supporting Information).

DFT computations of the cation of cluster **7** suggested the presence of aurophilic bonds not only between all neighbouring Au pairs but also between more distal atom pairs on the ring perimeter. These long-range overlaps are mediated by the gold atom in the ring centre, which acts as a bridge between all atomic pairs within the Au₆ ring. The shape of the molecular orbitals that incorporate the interactions of the six ring Au atoms bear close resemblance to those of benzene. The fully bonding combination is depicted in Figure 3; further orbital combinations are provided in Supporting Information.

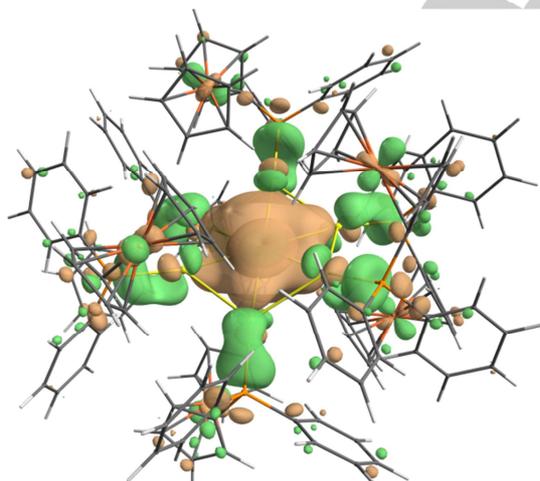


Figure 3. The HOMO-23 orbital of the heptagold cation in **7** depicting the fully bonding overlap of the six ring Au atoms and the central atom. Orbital contours are drawn with 2% probability.

In the absence of *direct* structural evidence of the highly unstable **5**, we complemented our spectroscopic

characterisation with reactivity studies. Specifically, we treated hydroxide **5** with *p*-nitrophenylboronic acid and with ammonium chloride (Scheme 1), which produced the isolable arylgold complex **8** (Figure S10), and quantitatively regenerated [AuCl(L-κP)], respectively. Similar reactions with the digold complex **4** gave analogous results. Unfortunately, the geminally diaurated complex $[\{Au(L-κP)\}_2(C_6H_4NO_2)][BF_4]$ obtained in the reaction of **4** with *p*-nitrophenylboronic acid decomposed rapidly in solution, precluding its adequate characterisation. Lastly, we converted **5** into imido and nitrido complexes **9** and **10** *via* reactions with the respective ammonium salts (Scheme 1). Alternatively, complex **9** was prepared by treating **1** with aminoferrocene.^[21] Unlike their oxygen-bridged analogues, complexes **9** and **10** proved resistant to further transformations in solution, which allowed their full characterisation using spectroscopic methods and X-ray diffraction analysis (Figures S11 and S13).

Electrochemical measurements on **1**, **2** and **7-10** (the remaining compounds were insufficiently soluble or unstable; see Supporting Information) revealed that the ferrocene units in these complexes are oxidised during a single reversible step, which indicates an absence of significant electronic communication between the ferrocene units. In turn, such behaviour implies that (diphenylphosphanyl)ferrocene acts as a spectator ligand in these molecules, albeit with distinctive coordination properties and reactivity (especially tendency towards C-H activation).

In summary, our results illustrate the unique reactivity of gold complexes combining hard anionic oxygen donors (oxide and hydroxide) and the redox-active (diphenylphosphanyl)ferrocene (L) ligand in their structures, which led to the isolation of both conventional and unprecedented compounds. Among them, complexes comprising the ferrocene ligand as a standard auxiliary phosphine and supported by aurophilic interactions form a family of compounds related (not only formally!) by equilibria similar to protonation and hydration/dehydration reactions due to the isolobal relationship between Au(PR₃)⁺ and H⁺. The formation of these species is apparently facilitated by stabilisation of the {Au(L-κP)}⁺ fragment by the electron-rich ferrocene phosphane L.

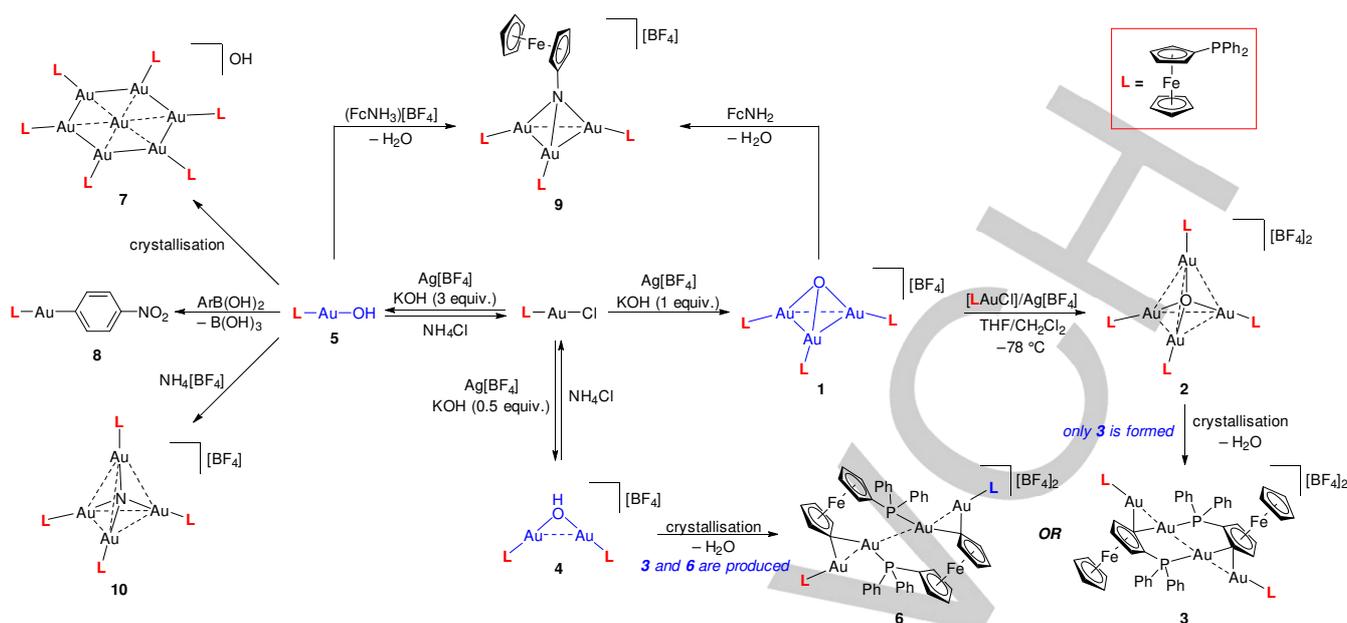
The mixed-valent Au(0)/Au(I) heptanuclear gold hydroxide **7** stands out in this family. Featuring the Au(0)(L-κP) moieties that assemble around the central Au(I) into a hexagonal array, **7** illustrates the inimitable ability of collectively operating aurophilic interactions which give rise to a structurally unprecedented, high-nuclearity cluster *unsupported* by any bridging ligands.^[22] Lastly, the formation and structures of the isomeric compounds **3** and **6**, resulting from electrophilic auration of the ferrocene CH groups, exemplify the unique control exerted by the rather weak Au...Au interactions over the structure of gold complexes and their transformations.

Acknowledgements

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Keywords: Gold • Cluster compounds • Auophilicity • Phosphane ligands • Metallocenes

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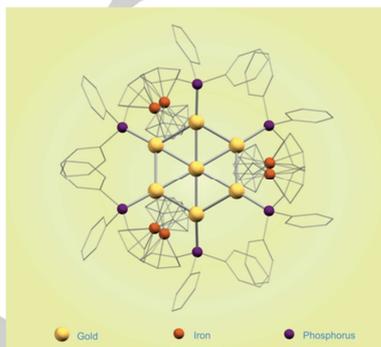


Scheme 1. Synthesis and reactions of gold(I) oxonium cluster **1** and hydroxides **4** and **5** stabilised by the (diphenylphosphanyl)ferrocene auxiliary ligands (Fc = ferrocenyl).

Entry for the Table of Contents

COMMUNICATION

Gold clusters. Compounds $[(\mu\text{-OH})\{\text{AuL}\}_2][\text{BF}_4]$ and $[(\mu_4\text{-O})\{\text{AuL}\}_4][\text{BF}_4]$ (L = (diphenylphosphanyl)ferrocene) undergo facile auration at their ferrocene units to produce isomeric tetragold(I) complexes. Conversely, the gold hydroxide $[\text{Au}(\text{OH})\text{L}]$ rearranges to a unique heptanuclear Au(0)/Au(I) cluster $[\text{Au}_7\text{L}_6]\text{OH}$. $[\text{Au}(\text{OH})\text{L}]$ also opens access to Au-aryl complexes and polynuclear Au complexes with N-bridging ligands.



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