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Title: A nucleophilic gold complex

Year: 2019

Version: Accepted version (Final draft)

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Please cite the original version:

Hicks, J., Mansikkamäki, A., Vasko, P., Goicoechea, J. M., & Aldridge, S. (2019). A nucleophilic gold complex. *Nature Chemistry*, 11(3), 237-241. <https://doi.org/10.1038/s41557-018-0198-1>

A Nucleophilic Gold Complex

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Abstract

Solid-state auride salts featuring the negatively charged Au^- ion are known to be stable in the presence of alkali metal counter-ions. While such electron-rich species might be expected to be nucleophilic (cf. I^-), their instability in solution means that this has not been verified experimentally. Here we report the two-coordinate gold complex $(\text{NON})\text{AlAuP}^t\text{Bu}_3$ (**3**, NON = 4,5-bis(2,6-diisopropylanilido)-2,7-di-tert-butyl-9,9-dimethylxanthene) synthesised by the reaction of the potassium alumanyl complex $[\text{K}\{\text{Al}(\text{NON})\}]_2$ (**1**) with ${}^t\text{Bu}_3\text{PAuI}$, and which features a strongly polarized bond, $\text{Au}(\delta^-)\text{--Al}(\delta^+)$. **3** has been studied computationally, with QTAIM charge analysis implying a charge at gold (-0.82) which is in line with the relative electronegativities of the two metals (Au: 2.54; Al: 1.61 on the Pauling scale). Consistently, **3** is found to act as an unprecedented nucleophilic source of gold, reacting with

diisopropylcarbodiimide and CO_2 to give the Au–C bonded insertion products $(\text{NON})\text{Al}(\text{X}_2\text{C})\text{AuP}^t\text{Bu}_3$ ($\text{X} = \text{N}^i\text{Pr}$, **4**; $\text{X} = \text{O}$, **5**).

Transition elements are known to be able to access multiple oxidation states¹, a property which underpins widespread application in fields such as small molecule activation and catalysis^{2,3}. The vast majority of transition metal complexes however, feature cationic metals in positive oxidation states, ligated by neutral or anionic donors^{1,4}. Systems featuring formal negative oxidation states, such as the tetracarbonylferrate⁵ or bis(benzene)vanadium⁶ anions are much less common, and usually require strong π -acceptor ligands, most frequently CO⁷. In this regard, gold is unique, being the only transition metal to give rise to a stable “naked” monoanion (Au^- , auride) in the condensed phase⁸. In part, this is due to relativistic effects which contract the 6s orbital significantly, resulting in an electron affinity of 2.30 eV, the highest of any transition metal^{9,10}. This value is more comparable to those of the chalcogens (e.g. S: 2.08 eV; Se: 2.02 eV) than to the lighter group 11 congeners (Cu: 1.23 eV; Ag 1.30 eV)¹⁰. The 12-electron auride anion is typically generated by the reduction of metallic gold with alkali metals, to give salts such as CsAu and RbAu^{11,12}; the solution chemistry of these salts, however, is restricted to liquid ammonia^{13,14}. Reduction of *organometallic* gold compounds to give systems in low oxidation states (i.e. zero or below) has been attempted, but with limited success¹⁵⁻²⁰. Thermodynamics typically drive the aggregation of molecular Au(0) systems to clusters of colloidal gold¹⁵⁻¹⁸. Recently however, electron-rich gold complexes have been reported by Bertrand and co-workers, by making use of strongly π -accepting cyclic(alkyl)(amino)carbenes (CAAC) ligands (**I** and **II**, Figure 1)¹⁹. In addition, a four-coordinate molecular ‘boroauride’ was reported by Harman and co-workers last year in which the gold centre is stabilized by a diboraanthracene-based scaffold (**III**, Figure 1)²⁰. Notwithstanding these examples, and even though Au^- ions have previously been observed to react as nucleophiles in the gas phase²¹, examples of nucleophilic reactivity by molecular gold systems in solution have not been reported.

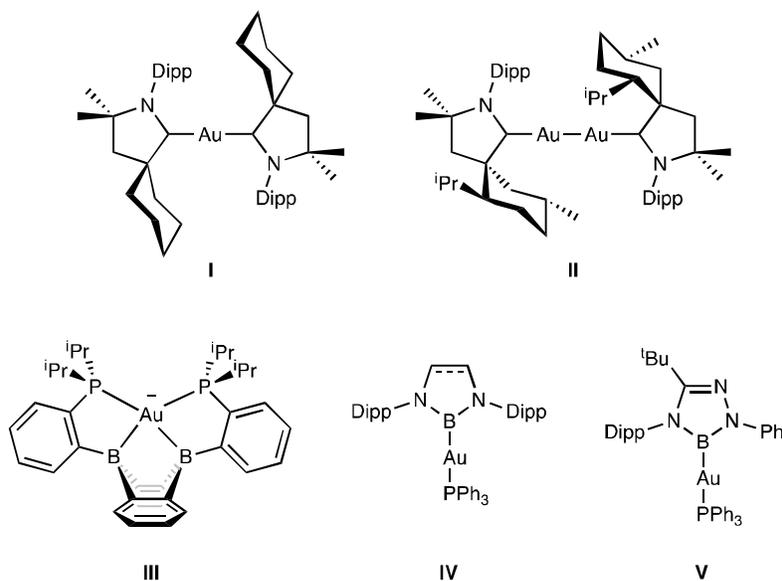


Figure 1. Selected examples of electron rich gold complexes. Gold complexes featuring cyclic amino alkyl carbene (cAAC) ligands (**I** and **II**); a four-coordinate complex described as a ‘boraauride’ (**III**) and two-coordinate gold boryl phosphine complexes (**IV** and **V**).

Over the last decade, boryl anions have been utilized as highly σ -donating ligands in conjunction with numerous metals from throughout the Periodic Table^{22,23}. Included in these studies are two-coordinate gold complexes of the type $\text{Ph}_3\text{PAu}(\text{boryl})$ (boryl = $\text{B}\{\text{N}(\text{Dipp})\text{CH}\}_2$ or $\text{B}\{\text{N}(\text{Dipp})\text{C}(\text{tBu})\text{NNPh}\}$; Dipp = 2,6-diisopropylphenyl) reported by Yamashita, Nozaki and co-workers (**IV**, Figure 1)²⁴ and by Kinjo et al. (**V**, Figure 1)²⁵. Even though boryl ligands are known to be highly electron donating, and the difference in electronegativity between gold and boron (2.54 and 2.04, respectively)²⁶ implies a $\text{Au}(\delta^-)\text{-B}(\delta^+)$ polarity to these bonds, no gold-centered nucleophilic reactivity has been reported for these systems. In the current study we make use of an extremely strongly donating aluminyl ligand to synthesise a two-coordinate molecular species featuring a highly polarized $\text{Au}(\delta^-)\text{-Al}(\delta^+)$ bond, that shows for the first time that gold can act as a nucleophile in the solution phase.

Results and Discussion

Syntheses

In recent work, we reported the preparation and characterization of the potassium aluminyll $[K\{Al(\mathbf{NON})\}]_2$ (**1**, where \mathbf{NON} = 4,5-bis(2,6-diisopropylanilido)-2,7-di-tert-butyl-9,9-dimethylxanthene) and demonstrated that this complex reacts as an aluminium-centred nucleophile²⁷. Reactions with $(\mathbf{NON})AlI$ and $(^{Mes}Nacnac)MgI(OEt_2)$ (where $^{Mes}Nacnac$ = $(NMe_3CMe)_2CH$, and Mes = 2,4,6- $Me_3C_6H_2$) lead to the formation of unsupported metal–metal bonds in $[Al(\mathbf{NON})]_2$ and $(\mathbf{NON})AlMg(^{Mes}Nacnac)$, respectively. We were interested in expanding this chemistry to the *d*-block metals, in particular gold, as systems of the type R_3PAuX are well known catalysts/precatalysts in numerous organic reactions involving alkynes in which gold acts exclusively as an electrophile²⁸. We hypothesized that by incorporating the extremely electron donating aluminyll fragment into such a system, the mode of reactivity could be reversed, i.e. making gold nucleophilic. Accordingly, **1** was found to react with two phosphine-ligated gold(I) iodide complexes, Ph_3PAuI and tBu_3PAuI , to give $(\mathbf{NON})Al(AuPPh_3)_2I$ (**2**) and $(\mathbf{NON})AlAuP^tBu_3$ (**3**), respectively (Figure 2). Compound **2** was synthesized by the addition of Ph_3PAuI to a solution of **1** in toluene at room temperature in a 2:1 ratio of Au:Al. It is proposed that the reaction proceeds via the two-coordinate gold intermediate $(\mathbf{NON})AlAuPPh_3$, which rapidly reacts with a further equivalent of Ph_3PAuI to give the isolated complex **2**. In an attempt to isolate this intermediate, one equivalent of Ph_3PAuI was added to a toluene solution of **1** at -78 °C, and the reaction mixture slowly warmed to room temperature. However this procedure simply led to a 1:1 mixture of **2** and unreacted aluminyll **1**. By contrast, the addition of one equivalent of the bulkier system tBu_3PAuI to a toluene solution of **1** resulted in a clean reaction to give the two-coordinate gold complex **3** in high crystalline yield (Figure 2). Presumably, the bulkier *tert*butylphosphine ligand prevents **3**

from reacting with a further equivalent of ${}^t\text{Bu}_3\text{PAuI}$ at room temperature, even when excess ${}^t\text{Bu}_3\text{PAuI}$ is added.

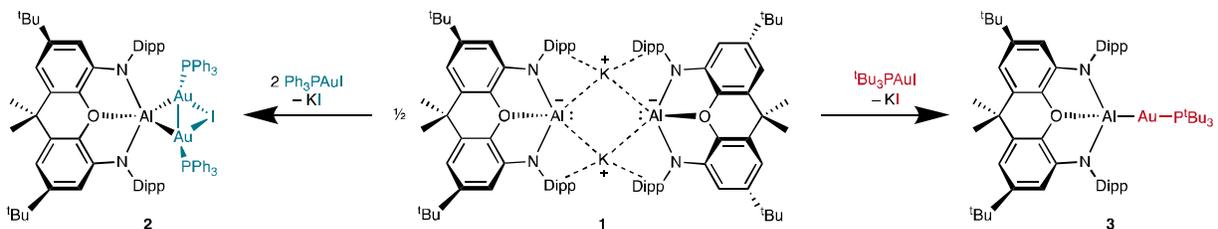


Figure 2. Synthesis of the tri- and bimetallic gold/aluminium complexes **2 and **3**.** Reaction of the potassium aluminyl species **1** with two equivalents of Ph_3PAuI yields the aluminium digold iodide species **2**, whereas the reaction of **1** with one equivalent of the bulkier system ${}^t\text{Bu}_3\text{PAuI}$ gives hetero-bimetallic species **3**.

Taking the relative electronegativities of gold and aluminium into account, both of the Al–Au bond forming reactions could be regarded as bringing about a *formal* two-electron oxidation of the aluminium centre from +1 to +3. In the reaction to give **2**, this would be accompanied by one-electron reduction of each of the two gold centres. The resulting Al(III)Au(0)_2 formalism is consistent with structural metrics – notably the Au–Au distance (*vide infra*). In the formation of **3** however, a similar redox *formalism* would necessitate two-electron reduction of the single gold centre from +1 to –1. With a view to providing a more rigorous interpretation of the Al–Au bonding in **3**, and the transfer of charge accompanying bond formation, NOCV calculations were carried out.^{29–31} Constructing **3** by bringing together $[\text{Al}(\text{NON})]^-$ and $[\text{AuP}^t\text{Bu}_3]^+$ fragments shows that the most important NOCV describes a polarized σ -bond corresponding to donation of the aluminium lone pair to the gold centre. This interaction contributes 70% of the total orbital interaction energy. Moreover, quantum theory of atoms in molecules (QTAIM) charge analysis indicates that Al–Au

bond formation in **3** induces a transfer of 1.56 electrons from the [(NON)Al]⁻ fragment to the [AuP^tBu₃]⁺ group. Notably, however, the lowest energy pathway for breakage of the Au-Al bond is homolytic, consistent with a description of **3** in valence terms as featuring a X-type aluminyl ligand and a Au(I)Al(III) valence formalism.

Structural characterization of the Al–Au bonded complexes **2** and **3**

Both **2** and **3** could be isolated as analytically pure crystalline materials which are stable at room temperature in solution and in the solid state over the course of several weeks. The molecular structures of both complexes are monomeric in the solid state (Figure 3). That of **2** reveals an essentially planar AlAu₂I core, with one triphenylphosphine ligand coordinated to each of the two gold centres. The aluminium and iodine centres bridge the Au₂ unit in a slightly unsymmetrical fashion (Al–Au bond lengths: 2.6045(18) and 2.5093(19) Å; Au–I bond lengths: 3.1447(7) and 2.8431(7) Å). This asymmetry is likely due to steric buttressing between the bulky NON and triphenylphosphine ligands. The Al–O and Al–N bond lengths (Al–O = 1.992(4) Å, Al–N = 1.916(5) and 1.916(5) Å) are significantly shorter than those in the aluminyl starting material **1** (Al–O = 2.279(2) Å, Al–N = 1.956(2) and 1.963(2) Å)²⁷, and are more in line with [(NON)Al] complexes featuring trivalent aluminium (e.g. (NON)AlH; Al–O = 1.944(2) Å, Al–N = 1.873(1) and 1.872(1) Å)²⁷. The Au–Au distance (2.5897(6) Å) is towards the shorter end of the range of known complexes featuring Au–Au bonds, and is comparable to that of Bertrand's digold system [Au(CAAC)]₂ (**II**, Au–Au = 2.5520(6) Å)^{19,32}, consistent with a description of **2** featuring a formal Au–Au single covalent bond.

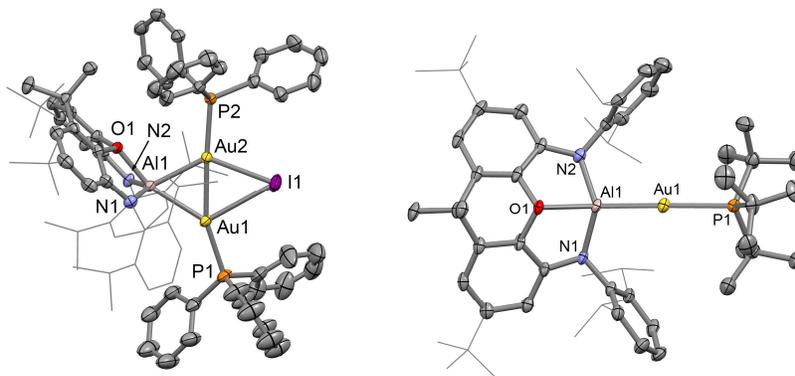


Figure 3. Molecular structures of 2 and 3 as determined by X-ray crystallography. Thermal ellipsoid plots of **2** (left) and **3** (right) at 50% probability level; hydrogen atoms are omitted and parts of the **NON** ligand are drawn in a wireframe format for clarity. Selected bond distances and angles: **2**, Au(1)–Au(2) 2.5897(6) Å, Al(1)–Au(1) 2.6045(18) Å, Al(1)–Au(2) 2.5897(6) Å, Au(1)–I(1) 3.1447(7) Å, Au(2)–I(1) 2.8431(7) Å, Au(1)–P(1) 2.3413(17) Å, Au(2)–P(2) 2.3328(16) Å, Al(1)–N(1) 1.916(5) Å, Al(1)–N(2) 1.916(5) Å, Al(1)–O(1) 1.992(4) Å, Al(1)–Au(1)–P(1) 140.50(6)°, Al(1)–Au(2)–P(2) 121.51(6)°; **3**, Al(1)–Au(1) 2.402(3) Å, Au(1)–P(1) 2.395(3) Å, Al(1)–N(1) 1.900(10)Å, Al(1)–N(2) 1.904(10) Å, Al(1)–O(1) 2.046(8) Å, Al(1)–Au(1)–P(1) 167.47(10)°.

The molecular structure of **3** reveals a two-coordinate gold centre bound to one P^tBu₃ ligand and one (**NON**)Al unit, with the Al–Au–P unit defining a near linear geometry (167.47(10)°). The Al–Au bond length is 2.402(3) Å, which is by far the shortest Al–Au bond to be reported to date (previous shortest: 2.596(5) Å)³³ and well within the sum of the covalent radii of the two elements (2.57 Å)³⁴. Moreover, complex **3** represents the first example of a crystallographically characterized complex bearing an *unsupported* Al–Au bond.^{35,36} As with **2**, the Al–N and Al–O bond lengths (Al–N = 1.900(10) and 1.904(10) Å, Al–O = 2.046(8) Å) are significantly shorter

than those found in the aluminyl starting material **1**, being more in line with those found in trivalent systems such as (NON)AlH²⁷.

Charge analysis of **2** and **3**

In order to study the charge distribution in the two Al–Au bonded complexes, the effective atomic charges of all atoms in **2** and **3** were calculated using QTAIM (see Supplementary Information section 5 for further details)^{37,38}. In **2**, the total charge on the Al(NON) fragment is +0.50 whereas in **3** the corresponding charge is +0.56. In **2**, the balancing negative charge is mostly localized at iodine, and the (AuPPh₃)₂ fragment is approximately neutral, suggesting a covalent Au–Au bond. The effective charges on the aluminium centres in **2** and **3** are +2.27 and +2.21 respectively (Figure 4), i.e. considerably higher than that calculated for the [Al(NON)][–] fragment (+0.95). The effective charges on the gold atoms in **2** are –0.42 and –0.40, while that in **3** is –0.82 (Figure 4), consistent with a description of **3** as featuring a strongly polarized bond, Au(δ[–])–Al(δ⁺). The calculation of atomic charges is known to be method dependent, and with this in mind, the corresponding atomic charges in the boryl gold system {(HCDippN)₂B}AuPPh₃²⁴ (Figure 1, **IV**) were also calculated using the QTAIM approach in order to provide like-for-like comparison. This system was found to possess a significantly less polar B–Au bond (*cf.* the Al–Au bond in **3**), with a smaller positive charge located on the boron centre (+1.39) and a much smaller negative charge on the gold (–0.20).

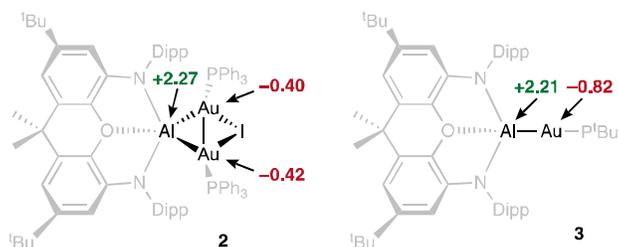


Figure 4. Calculated effective atomic charges for the Al and Au centres in 2 and 3. The effective atomic charges of all atoms in **2** and **3** were calculated using the QTAIM method. Both complexes were found to contain similar charges on the Al centres, +2.27 for **2** and +2.21 for **3**, but complex **3** was found to have a significantly higher negative charge located on the gold centre (−0.82) than in **2** (−0.40 and −0.42).

Reactivity of **3**

Given that the calculated charge on gold in compound **3** is close to -1 , its possible reactivity as a gold-centred nucleophile was investigated. Accordingly, **3** was reacted with a range of unsaturated carbon-centred electrophiles. Reactions with simple aldehydes and ketones were investigated, targeting complexes of the type $(\text{NON})\text{AlO}(\text{R})_2\text{CAuP}^t\text{Bu}_3$. However, these reactions lead to complex mixtures, presumably due to the fact that the initially-formed products contain a highly Lewis acidic aluminium centre, which reacts further with the carbonyl substrates. With this in mind, heteroallenes, such as carbodiimides and CO_2 were targeted, on the basis that the product might chelate the aluminium centre and quench its Lewis acidity. Accordingly, one equivalent of diisopropylcarbodiimide was added to a toluene solution of **3** at room temperature, leading to clean formation of the insertion product $(\text{NON})\text{Al}\{(\text{N}^i\text{Pr})_2\text{C}\}\text{AuP}^t\text{Bu}_3$ (**4**). In a similar fashion, exposure to one atmosphere of CO_2 at room temperature leads to the formation of $(\text{NON})\text{Al}(\text{O}_2\text{C})\text{AuP}^t\text{Bu}_3$ (**5**) (Figure 5). The identities of both **4** and **5** were verified crystallographically (Figure 5 and

Supplementary Figure 7): they are essentially isostructural, with a single molecule of diisopropylcarbodiimide (**4**) or CO₂ (**5**) reductively inserted into the Al–Au bond. The resulting metalla-amidinate/-carboxylate fragment chelates the aluminium centre through the two heteroatoms (N in **4** and O in **5**), with the gold centre being bound to carbon in each case, consistent with nucleophilic attack by gold at the electrophilic central carbon atom. The N–C bond lengths in **4** (1.336(13) and 1.339(13) Å) and the O–C bond lengths in **5** (1.289(8) and 1.285(8) Å) associated with the Al(E₂C)Au unit fall between the typical ranges for N–C and C–O single and double bonds, supporting the idea of a formal two-electron reduction of the ⁱPrNCNⁱPr/CO₂ substrate. To the best of our knowledge, **5** represents the first crystallographically verified example of simple CO₂ insertion into any metal–metal bond^{39,40}. In addition, it represents the first example of gold(I) metalla-carboxylate complex⁴¹.

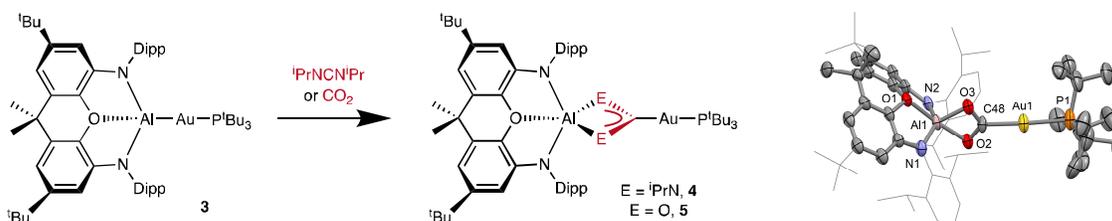


Figure 5. Reductive insertion of diisopropylcarbodiimide and CO₂ into the Al–Au bond of **3 and the molecular structure of **5** as determined by X-ray crystallography.** The reaction of **3** with one equivalent of diisopropylcarbodiimide or one atmosphere of CO₂ in toluene leads to the reductive insertion of the heteroallene to give **4** and **5** respectively. In both reactions, the gold centre is acting as a nucleophile, attacking the central carbon atom of both heteroallenes. Thermal ellipsoid plots of **5** at 50% probability level; hydrogen atoms are omitted and parts of the NON ligand are drawn in a wireframe format for clarity.

Spectroscopically, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **4** and **5** feature doublets corresponding to the gold-bound carbon atoms ($^2J_{\text{PC}} = 101$ and 134 Hz, respectively) at remarkably downfield chemical shifts (**4**: 219.9 ppm; **5**: 242.3 ppm), suggestive of carbene-like character in the $[(\text{NON})\text{AlE}_2\text{C}]$ moiety. These shifts are even more downfield than those reported for *triter*tbutylphosphine/*N*-heterocyclic carbene complexes of gold such as $[(\text{IPr})\text{AuP}^t\text{Bu}_3][\text{BF}_4]$ ($\delta_{\text{C}} = 191.9$ ppm; IPr = $\text{C}\{\text{N}(\text{Dipp})\text{CH}\}_2$)⁴², suggesting that significant contributing resonance forms for complexes **4** and **5** are as anionic carbene complexes of gold (Figure 6).

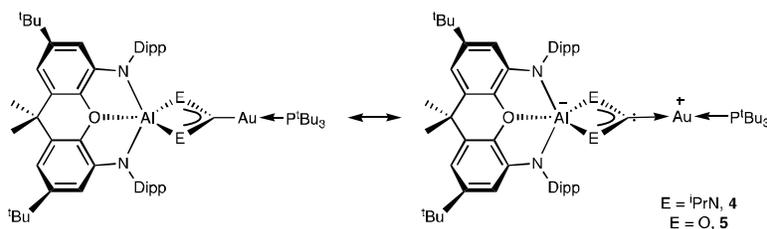


Figure 6. Resonance structures of 4 and 5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **4** and **5** show remarkably downfield chemical shifts for the AlE_2CAu carbon atoms (219.9 ppm for **4** and 242.3 ppm and **5**), suggestive of carbene-like character.

In summary, the potassium aluminyl complex **1** reacts with two phosphine-ligated gold iodide complexes, Ph_3PAuI and $^t\text{Bu}_3\text{PAuI}$, to give the tri- and bimetallic systems $(\text{NON})\text{Al}(\text{AuPPh}_3)_2\text{I}$ (**2**) and $(\text{NON})\text{AlAuP}^t\text{Bu}_3$ (**3**), respectively. Crystallographic and computational analyses of complex **3** is in line with a description as a heterobimetallic complex featuring a strongly polarized covalent bond, $\text{Au}(\delta^-)\text{--Al}(\delta^+)$, and is supported by a QTAIM calculated charge of -0.82 at Au. Consistently, **3** reacts as a gold centred nucleophile; its reactions with diisopropylcarbodiimide and CO_2 give the reductive insertion products **4** and **5** featuring Au–C bonds. To our knowledge this is the first time that nucleophilic reactivity by a molecular gold compound has been observed

in solution.

Methods

Manipulations were carried out under a dry, oxygen-free argon or dinitrogen atmosphere, with reagents dissolved or suspended in aprotic solvents, and combined or isolated using cannula and glove box techniques. **(NON)Al(AuPPh₃)₂I (2)** and **(NON)AlAuP^tBu₃ (3)** were synthesized by the addition of the appropriate gold phosphine iodide (Ph₃PAuI for **2** and ^tBu₃PAuI for **3**) to a toluene solution of [K{Al(NON)}]₂ (**1**). It was found that **2** could also be synthesised by the addition of Ph₃PAuI to a toluene solution of **3**. The reactions of **3** with the heteroallenes diisopropylcarbodiimide and CO₂ lead to reductive insertion of the substrates into the Al–Au bond, to give **(NON)Al{(NⁱPr)₂C}AuP^tBu₃ (4)** and **(NON)Al(O₂C)AuP^tBu₃ (5)** respectively. All new compounds **2** – **5** were characterized by elemental analysis, multinuclear NMR spectroscopy and single-crystal X-ray diffraction. Density Functional Theory (DFT), as implemented in the Amsterdam Density Functional code, was employed to calculate molecular geometries, bonding energies, natural orbitals of the chemical valence (NOCV) and quantum theory of atoms in molecules (QTAIM) charges for complexes **2** and **3**. Scalar relativistic effects were treated using the zeroth order regular approximation (ZORA) in all DFT calculations. A comprehensive computational methods section is included in the Supporting Information, section 5.

Data availability statement

Data are available via the Oxford University Research Archive (<https://ora.ox.ac.uk>). X-ray crystallographic data for compounds **2**, **3**, **4** and **5** are available from the Cambridge Crystallographic Data Centre (CCDC 1854971-1854974).

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

Acknowledgments This work was supported by the SCG-Oxford Centre of Excellence. P.V. thanks the Magnus Ehrnrooth, Finnish Cultural and Emil Aaltonen Foundations for postdoctoral funding. Computational resources were provided by CSC – IT Center for Science, Finland, the Finnish Grid and Cloud Infrastructure (persistent identifier [urn:nbn:fi:research-infras-2016072533](https://nbn-resolving.org/urn:nbn:fi:research-infras-2016072533)), and the University of Jyväskylä.

Author Contributions J.H. carried out the synthetic and reaction studies, A.M. and P.V. carried out the computational analyses, J.H. conducted the crystallographic studies, J.H, J.M.G. and S.A. wrote the manuscript and J.M.G. and S.A managed the project.

Author Information X-ray crystallographic data for compounds **2**, **3**, **4** and **5** are freely available from the Cambridge Crystallographic Data Centre (CCDC 1854971-1854974). Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to S.A. (simon.aldridge@chem.ox.ac.uk) or J.M.G. (jose.goicoechea@chem.ox.ac.uk).

Competing financial interests The authors declare no competing financial interests.

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Supplementary Information

General considerations and starting material preparations; synthetic, spectroscopic and analytical data; ^1H NMR spectra; X-ray crystallographic studies; computational studies and CIFs for all crystal structures.