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NUCLEOPHILIC REACTIVITY - Changing the gold standard

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Gold — long presumed to be an inert metal — has been increasingly shaking this image over the past couple of decades, mostly through electrophilic behaviour. Now, a two-coordinate gold complex has been shown to exhibit nucleophilic reactivity, with the insertion of CO₂ into its polarized Au(δ^-)–Al(δ^+) bond.

First introduced in the 1970s by Dieter Seebach and Elias James Corey, the concept of umpolung is a cornerstone in organic chemistry. It describes the polarity inversion of an atom or a functional group, resulting in reactivity with an electronic flow inverse to that normally encountered. Now, using such an umpolung strategy, Jose Goicoechea, Simon Aldridge and co-workers have coaxed a gold complex into displaying nucleophilic reactivity in solution¹.

Gold complexes are typically known to be extremely powerful electrophiles, in particular towards C–C π -bonds, thereby promoting a number of useful catalytic transformations. Comparatively, transition-metal reactivity of gold (such as oxidative addition, migratory insertion, β -H elimination) has only started to be developed³, and nucleophilic behaviour was virtually unknown before this work. Ground-breaking studies by Martin Jansen and co-workers demonstrated in the 2000s the existence of anionic gold species (aurides) in liquid ammonia⁴, but no nucleophilic reactivity was reported. Conversely, gold was also found to behave as a Lewis basic metal in a few recently isolated complexes, *via* the formation of Au $\cdots$ H–X hydrogen bonds^{5,6} and Au $\rightarrow$ Lewis acid interactions⁷. In addition, Daniela Bezuidenhout and co-workers reported in 2016 a tricoordinate T-shaped gold complex featuring two 1,2,3-triazol-5-ylidenes flanking a carbazolid moiety. The gold center is unusually electron-rich, as illustrated by protonation and alkylation reactions⁸.

In 2018, Goicoechea, Aldridge and colleagues showed² that aluminium — a common Lewis acid used in many catalytic transformations — could be converted into a nucleophilic species through smart control of its coordination sphere with a tridentate (N,O,N) ligand (Fig. 1). Compound **1**, which exists as a dimer, was made to react with a variety of organic and organometallic electrophiles, enabling the formation of unsupported aluminium–carbon and aluminium–heteroelement bonds.

What this group now reports is a spectacular next step: the aluminyll anion **1** readily binds to gold to form the linear two-coordinate complex **2** (Fig. 1)¹. The presence of a bulky phosphine ligand at the gold centre (P^tBu₃) is required to prevent the formation of a dinuclear species. Complex **2**, isolated as colourless crystals, is stable for weeks at room temperature. The Au–Al bond length determined by X-ray diffraction analysis is, at 2.402(3) Å, the shortest yet to be reported. As expected from the very large difference in electronegativity between Au (2.54) and Al (1.61), the Au–Al bond is highly polarized Au(δ^-)–Al(δ^+). The description of metal–metal bonds involving gold is always a matter of debate, as the very high electronegativity tends to challenge the usual covalent and ionic bonding schemes, yet calculations leave no doubt that the formation of **2** results from a significant transfer of electron from Al to Au (by 1.56 electron according to quantum theory of atom in molecules (QTAIM) calculations) resulting in partial negative charge at Au (– 0.82) and positive charge at Al (+ 0.56). Thus, the conversion of **1** into **2** is accompanied by a transfer of umpolung. In other words, the electron-rich character of aluminium is transferred to gold.

Most remarkable and illustrative of the Au(δ^-)–Al(δ^+) bond polarity is the reaction of complex **2** with CO₂ leading to complex **3**. The gold atom binds to the central carbon atom, thus behaving as a nucleophile. In the meantime, the Lewis acidity of the aluminium centre is quenched by coordination of the oxygen atoms, resulting in a formal insertion of CO₂ into the Au–Al bond of **2**. The study also discloses similar reactivity of the Au–Al complex with a carbodiimide, ⁱPrNCNⁱPr, forming a similar Au–C insertion product to **2**, featuring a Au–C(NⁱPr)₂–Al moiety instead of the Au–C(O)₂–Al one. Here, DFT calculations would be very welcome to shed light into the mechanism of this unorthodox reaction. Is the addition of the Au–Al bond to CO₂ concerted? Which pole, the nucleophilic gold centre or the Lewis acidic aluminium centre, drives the reaction, if any?

The bonding situation in **2** is reminiscent of that of existing gold–boryl complexes, prepared from boryl anions⁸. In those, too, the gold centre is electron-rich and the gold–boron bond is polarized as Au(δ^-)–B(δ^+), although to a lesser extent. So far, no nucleophilic reactivity has been reported for those gold–boryl complexes, but given the behaviour of the related gold–aluminyl complex **2**, their reactions with CO₂, and heteroallenes in general, are definitely worth exploring.

In any case, the gold–aluminyl complex **2** that has been prepared through an umpolung transfer strategy, and features a polarized Au(δ^-)–Al(δ^+) bond, unambiguously displays nucleophilic reactivity at its gold centre. These findings emphasize the critical role of ancillary ligands in tuning the properties of both transition metals and main-group elements. Gold complexes have found tremendous interest as Lewis acids. Nucleophilic behaviour, as substantiated in this work, opens a new facet in gold chemistry. More generally, these findings underscore the importance of investigating new bonding situations and reactivity paths to advance our knowledge in molecular chemistry.

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Figure 1. Synthesis and reactivity of the gold complex **2**. i, Umpolung transfer from aluminium to gold. ii, Insertion of CO₂ into the polarized Au(δ^-)–Al(δ^+) bond. Dipp = 2,6-ⁱPr₂C₆H₃.