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Gold(II) in Redox-Switchable Gold(I) Catalysis

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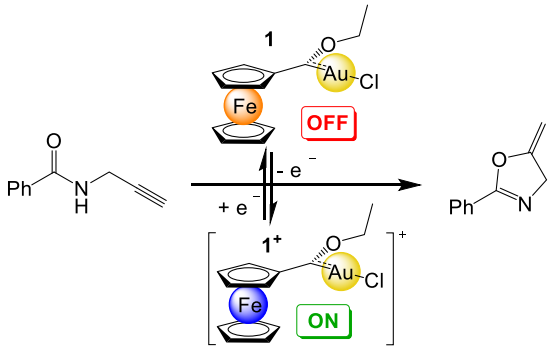
Gold(II) species catalyse the cyclisation of *N*(2-propyn-1-yl)benzamide to 2-phenyl-5-vinylidene-2-oxazoline without halide abstraction while the saturated gold(I) complex is inactive. Redox-switching between gold(II) and gold(I) turns catalytic turnover on and off.

Molecular gold complexes have attracted great attention as (pre-)catalysts in homogeneous catalysis, especially in the activation of alkynes.[1–3] (Pre-)catalysts and intermediates feature gold in its favoured oxidation states +I and +III.[4–7] In photocatalysis however, transient mononuclear gold(II) key intermediates have been postulated but remained elusive so far.[8–14] Apart from very few examples, the chemistry of mononuclear gold(II) complexes is underdeveloped due to the favoured disproportionation or dimerisation of gold(II).[15–19]
In gold(I) catalysed reactions, gold(I) halide complexes are usually employed as precatalysts. Typically, silver(I) salts, copper(II) triflate[20] or alkali metal salts[21] activate the precatalyst by halide abstraction. Chlorido gold(I) complexes with *N*-heterocyclic,[22] or acyclic diamino[23,24] carbene ligands are successfully employed in a plethora of catalytic applications in conjunction with halide scavengers.[1–7] The group of Peris recently reported a chlorido gold(I) complex bearing a redox-active ferrocenyl-imidazolylidene ligand. The presence of an oxidant increases the catalytic performance of the complex. Yet, this effect was ascribed to the formation of cationic protonated complexes under the reaction conditions.[25] On the other hand, the group of Sarkar demonstrated in seminal studies that ferrocenyl-substituted mesoionic carbene (Fc-MIC) ligands enable ON/OFF switching of the catalytic performance of gold(I) catalysts AuCl(Fc-MIC) by oxidation/reduction cycles (redox-switchable catalysis, RSC) without additional halide scavengers.[26–28] Indeed, RSC is a strongly expanding field in homogeneous catalysis.[26–40] The redox-switching event occurs either at a remote redox-active unit, e.g. a Fc unit located on the ligand[26–28,30,33,34,36–38] or directly at the catalytic metal centre, e.g. Ce^{III}/Ce^{IV}.[32] In gold(I) catalysis, activation by oxidation of the remote Fc unit increases the Lewis acidity of the Au^{I} ion.[26–28] Thus, carbene ligands with low donor ability should be beneficial for high catalytic activity in gold catalysis. The Tolman electronic parameter (TEP)[41] of the Fc-MICs increases from a very high donicity (TEP ≈ 2046 cm^{-1}) to a lower one (TEP ≈ 2054 cm^{-1}) upon oxidation of the Fc unit.[27,28] The neutral carbene ligand :C(Fc)OEt already possesses a similar donor strength (TEP = 2054 cm^{-1}) as the oxidised Fc-MICs.[27,28,42] Consequently, the oxidised carbene ligand $[:C(Fc)OEt]^+$ should have an even lower donor ability and could enable high catalytic activity with AuCl[C(Fc)OEt] **1** as precatalyst (Scheme 1).



Scheme 1 Switchable gold-catalysed cyclisation of *N*(2-propyn-1-yl)benzamide to 2-phenyl-5-vinylidene-2-oxazoline.

Compared to Fc-MICs with redox-active Fc substituents in a β position relative to the carbene donor, the Fc moiety in **1** located in the α position might have an even larger impact on the ligand's donor properties. Furthermore, the redox potentials for the Fc/Fc^+ oxidation of :C(Fc)OEt and Fc-MICs are very different,[28,42] opening the possibility of different valence isomers for cationic gold complexes $[AuCl(Fc\text{-}MIC)]^+$ and $\mathbf{1}^+$ and

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consequently a different reactivity. For comparison of [AuCl(Fc-MIC)]$^{0/+}$ and **1**$^{0/+}$, we studied the gold catalysed cyclisation of *N*(2-propyn-1-yl)benzamide to 2-phenyl-5-vinylidene-2-oxazoline (Scheme 1).[20,26–28]

Pre-catalyst AuCl[C(Fc)OEt] **1** is accessible by transmetalation[43] from $W(CO)_5$[C(Fc)OEt][44] to $AuCl(SMe_2)$ and fully characterised by ^{1}H and ^{13}C NMR, IR and UV/Vis spectroscopy, LIFDI mass spectrometry and cyclic voltammetry (ESI, Fig. S1 – S9). The cyclic voltammograms of **1** with [*n*Bu$_4$N][BAr$^F_4$] (Ar^F = C_6F_5) as supporting electrolyte show a reversible one-electron oxidation wave at $E_{½}$ = 0.58 V and 0.60 V in CH_2Cl_2 and THF, respectively (vs. FcH/FcH$^+$; ESI, Fig. S7, S9). These processes occur at significantly higher potential than the oxidation of Fc-MIC gold(I) complexes.[26–28] Changing the electrolyte from [*n*Bu$_4$N][BAr$^F_4$] to [*n*Bu$_4$N][PF_6] lowers the oxidation potential by approximately 100 mV similar to Fc-MIC gold(I) complexes.[27] Irreversible or quasireversible carbene reduction waves are additionally observed at negative potentials (ESI, Fig. S6 – S9). Interestingly, small oxidation waves appear at potentials 140 to 310 mV lower than the reversible oxidation wave. Potential and intensity depend on the solvent and the electrolyte but not on the batch of **1** employed. Hence, this is an intrinsic property of **1** in a given environment. We tentatively ascribe this wave to the oxidation of dimers **(1)$_2$** present to a minor extent in solution. In fact, dimers and oligomers of AuCl(carbene) complexes with small carbene ligands (but not for the Fc-MIC ligands[26–28]) held together by aurophilic interactions[45,46] form in the solid state.[43] The presence of Au···Au contacts in solution has been suggested using diffusion-ordered spectroscopy (DOSY).[47–49] ^{1}H DOSY experiments of **1** in dichloromethane with $W(CO)_5$[C(Fc)OEt] as internal monomeric reference confirm the mainly monomeric nature of **1** as suggested by the electrochemical experiments (ESI, Fig. S10). However, dimerisation via Au···Au contacts in the minor species **(1)$_2$** should hardly affect oxidation of the remote Fc substituents but rather the gold centres. Hence, we investigated the chemical oxidation of **1** by a suitable oxidant (Magic Blue, [N(*p*-$C_6H_4Br)_3$][$SbCl_6$] and ammonium cerium(IV) nitrate, CAN) using X-band EPR spectroscopy in more detail. Irrespective of the oxidant and solvent (THF, CH_2Cl_2/DMF) employed, a broad resonance around *g* = 2 is detected for the **1**/oxidant mixture both at 77 and 295 K (Fig. 1a, ESI, Fig. S11 – S16). Hence, the EPR resonance derives from **1**$^+$. The observation of a signal already at room temperature and the lacking axial symmetry in frozen solution rules out the assignment of this resonance to a Fc$^+$ ion.[39,50,51] On the other hand, gold(II) species have been reported to possess *g* tensors with small *g* anisotropy and hyperfine coupling to the gold nucleus (^{197}Au: *I* = $^3/_2$).[15–18] Due to the non-resolved coupling(s), only the g_{iso} value of 2.017 is given which fits to reported values for gold(II) complexes.[15-18] Furthermore, the resonance increases in intensity over time at room temperature converging to a limiting value after 5 h. Quantification of the EPR resonance after 5 h by double integration and calibration (ESI, Fig. S17, S18) confirms that the EPR resonance accounts for 75±5 % of the paramagnetic species (Fig. 1b). Hence, we suggest that Magic Blue first oxidises the Fc unit in **1** yielding the cationic Fe^{III}Au^I electromer of **1**$^+$. Ferrocenium is typically EPR-silent at room temperature and hence not observed at 295 K. The absence of an axial Fc$^+$ resonance also at 77 K may be ascribed to fast spin relaxation.[50] Then, the Fe^{III}Au^I isomer slowly converts to a Fe^{II}Au^{II} isomer almost quantitatively suggesting that significant reorganisation takes place after the initial Fc/Fc$^+$ oxidation. Some gold(II) might also form directly starting from minor amounts of a dimeric species **(1)$_2$**.

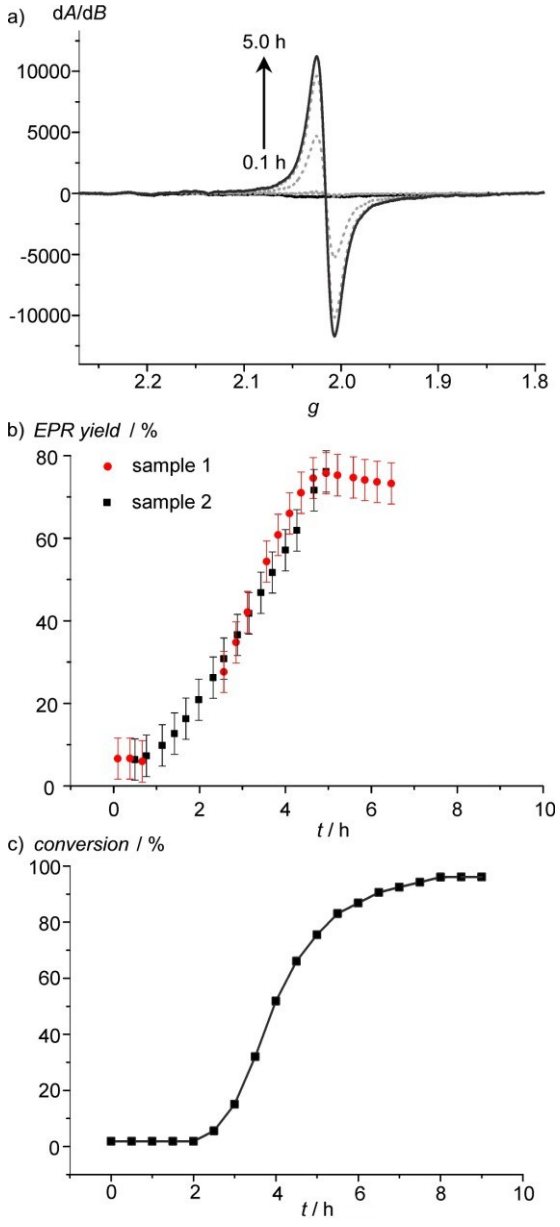

Fig. 1 a) EPR spectra of **1**/Magic Blue in THF over time at 295 K, b) doubly integrated intensity of the EPR resonance versus time plot and c) conversion versus time plot for the cyclisation catalysed by **1**/Magic Blue in dichloromethane (Scheme 1).

Gratifyingly, geometry optimisations using Density Functional Theory (DFT) calculations on **[1]**[$SbCl_6$] converged to two electromers, namely a gold(I)/iron(III) and a gold(II)/iron(II) isomer in a contact ion-pair with the counter ion coordinating the gold with an Au-Cl($SbCl_5$) distance of 2.47 Å (Fig. 2a). The spin density in the gold(II) isomer is mainly shared between the gold ion and the chlorido ligand (Fig. 2a). The original linear

coordination of the Au^{I} center with a 177° C-Au-Cl angle is expanded yielding a 3+1 coordination of the gold(II) ion with a 92° C-Au-Cl angle in the Au^{II} species. This bending might raise the activation barrier for the intramolecular electron transfer from Au^{I} to Fe^{III} giving the $Au^{II}Fe^{II}$ isomer (Fig. 2a).

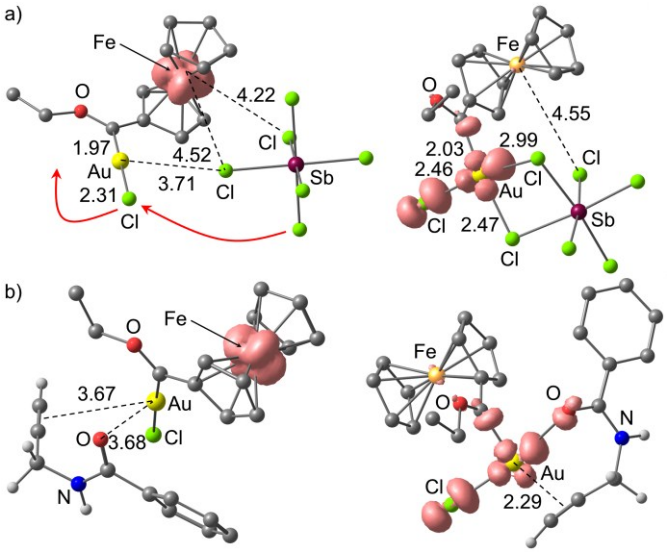

Fig. 2 DFT calculated optimised geometries and spin densities of $Fe^{III}Au^{I}$ and $Fe^{II}Au^{II}$ isomers of a) **[1]**[$SbCl_6$] and b) [**1**+substrate]$^+$. Distances given in Å, hydrogen atoms omitted (except for the propargyl amide unit), contour value at 0.01 a.u..

Coordination of $[SbCl_6]^-$ to Au (Fig. 2a, right) shifts the spin density to give gold(II). A similar impact of ion coordination is observed in gold(II) porphyrin/gold(III) porphyrin radical anion valence isomers.[17] Conceptually similar, heterobimetallic molybdenum(IV)/ferrocenium complexes $Mo^{IV}Fe^{III}$ undergo intramolecular electron transfer to yield $Mo^{V}Fe^{II}$ electromers.[39,40] Fully analogously, rhodium(I) complexes bearing a ferrocenyl phosphine-NHC ligand are first oxidised at the Fc unit, while the second oxidation is rhodium centered initiating a further intramolecular electron transfer from rhodium to Fc^+.[35] In these examples, the Fc/Fc^+ redox couple acts as intermediate parking position for a positive charge.

DFT calculations suggest that coordination of oxygen nucleophiles such as amides (e.g. *N*(2-propyn-1-yl)benzamide) to the gold centre of $\mathbf{1}^+$ instead of counter ions also stabilises the $Au^{II}Fe^{II}$ valence isomer over the $Au^{I}Fe^{III}$ isomer (Fig. 2b). In the gold(II) isomer the C-Au-Cl angle is compressed to 93° and the triple bond of the substrate coordinates to gold(II) (Fig. 2b). Hence, we employed the gold(I) complex **1** and **1**/Magic Blue in the cyclisation reaction of *N*(2-propyn-1-yl)benzamide to the oxazoline in dichloromethane (Scheme 1). Neither **1** nor oxidant alone yield the heterocyclic product, while the mixture **1**/Magic Blue (1 mol-%) quantitatively converts the substrate to the product within a few hours (Fig. 1c, TOF = $(8.3\pm1.1)\times10^{-3}$ s^{-1}; ESI, Fig. S19, S20). This is significantly faster than observed with the oxidised Fc-MIC gold complexes.[26–28] Interestingly, an induction period of ca. 2.5 h is observed (Fig. 1c). This time scale matches the development of the gold(II) EPR resonance (Fig. 1). Complementary, the paramagnetically broadened and shifted ^{1}H NMR resonances of the initial mixture of **1** and Magic Blue re-appear at typical diamagnetic values during a similar time span suggesting the re-reduction of an initially formed Fc$^+$ species (ESI, Fig. S21). With these spectroscopic correlations, we propose that a gold(II) centre slowly forms from the initially present ferrocenium ion. The gold(II) centre presumably features a C-Au-Cl angle close to 90° (Fig. 2b), which enables substrate coordination in contrast to the initially present linearly coordinated gold(I) centre. The exact nature of the active gold(II) catalyst remains speculative, yet three[52] and four coordinate[17,18] gold(II) species are conceivable with coordination of counter ions, coordination of the substrate (via the amide oxygen atom) or aggregation via chlorido ligands and aurophilic interactions (Fig. 2). Attempts to get more insight into the structure of the active species using Mößbauer (iron) and X-ray absorption near edge structure spectroscopy at the gold L_3-edge were inconclusive as removing the solvent leads to the formation of elemental gold and several iron(II) and iron(III) species (ESI, Fig. S22 – S25). In the absence of coordinating solvents (DMF, THF) or substrates, a dark precipitate forms (ESI, Fig. S26). Obviously, stabilising ligands (solvent, substrate) are required to keep the gold(II) catalyst active. The majority of the catalyst remains active for some time as a second batch of substrate is converted to the product with similar TOF but without induction period after a full initial conversion (ESI, Fig. S27). The presence of [nBu$_4$N]Cl (42 eq) inhibits the catalysis (ESI, Fig. S28) suggesting that free coordination sites or only weakly coordinating donor ligands are required to enable catalysis. Activation of **1** using $AgSbF_6$ as halide scavenger initiates a conventional gold(I) catalysis with a smaller TOF = 3.2×10^{-3} s^{-1} but without induction period (ESI, Fig. S29).

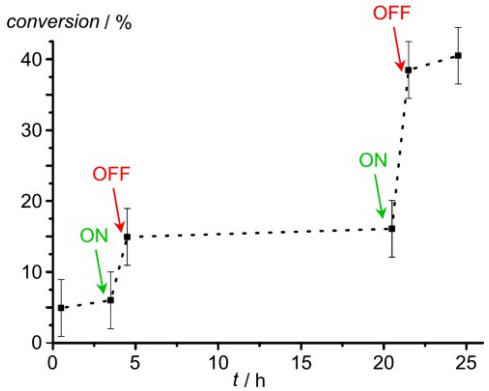

Fig. 3 Conversion versus time plot of the cyclisation (Scheme 1) during ON/OFF redox switching using Magic Blue (1.00/1.05 eq; ON) and $FeCp^*_2$ (1.05/1.10 eq; OFF).

Addition of decamethylferrocene $FeCp^*_2$ as reductant stops catalytic turnover, while re-oxidation using Magic Blue re-starts the catalysis (Fig. 3). This second oxidation initiates catalysis almost instantaneously without induction period and with a similar TOF as during the first cycle. Hence, the catalytic mixture **1**/oxidant forms catalytically active gold(II) species which can be reversibly switched off and on by reduction and oxidation, respectively. The catalytically active species, however, still relates structurally to the precatalyst, as 84±5 % of **1** are recovered after ca. 63 % conversion and quenching with $FeCp^*_2$ according to ^{1}H NMR spectroscopy (ESI, Fig. S30).

In summary, we report a redox-switchable gold-catalysed cyclisation with the gold centre of the precatalyst **1** reversibly switching between highly active, presumably coordinatively unsaturated gold(II)[17,18,52] and inactive, coordinatively saturated gold(I) centres. Our studies complement previous work on gold(I) pre-catalysts activated by redox-active ligands.[26-28,53] The very high activity may be due to the electrophilic nature of the gold(II) ion with free coordination sites. To prevent aggregation or disproportionation, the gold(II) centre must be stabilised by further donor ligands (counter ions, substrates) which should not coordinate too strongly. The Fc/Fc^+ couple temporarily stabilises $\mathbf{1}^+$ via valence isomerisation preventing aggregation or disproportionation of the unsaturated gold(II) centre in the absence of donor ligands. Detailed studies on Au^I complexes with carbene ligands using the $Au^{I/II}$ switch are ongoing.

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Conflicts of interest

There are no conflicts to declare.

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