Deactivation of gold(i) catalysts in the presence of thiols and amines – characterisation and catalysis†

Paul C. Young, Samantha L. J. Green, Georgina M. Rosair and Ai-Lan Lee*

Thiols and amines, which are common heteroatom nucleophiles in gold-catalysed reactions, are known to dampen the reactivity of gold catalysts. In this article, the identity and activity of gold(i) catalysts in the presence of thiols and amines is investigated. In the presence of thiophenol, thiol and thiol, digold with bridging thiolate complexes \([\{\text{Au}(L)\}_2(\mu-\text{SR})\}[\text{SbF}_6]\) are formed and have been fully characterised by NMR and X-ray crystallography. In the presence of amines and anilines, complexes \([\{\text{Au-NH}_2R\}[\text{SbF}_6]\) are formed instead. All new isolated gold complexes were investigated for their catalytic activity in order to compare the level of deactivation in each species.

1 Introduction

In less than a decade, homogenous gold catalysis has undergone a transformation from rarity to an incredibly active and rapidly evolving field of research.1 Its popularity is partly result of the excellent selectivity and efficiency of gold catalysts as \(\pi\)-Lewis acids for activating \(C\ldots C\) \(\pi\) bonds, and also the ability to tune gold catalysts in order to vary the reactivity and selectivity of the reactions.2 One of the research efforts within our group is to explore the diverse chemistry of gold-catalysed reactions with cyclopropenes,3,4 alkenes4 and allylic alcohols.5 Within this context, we have used alcohols,2a,b,4,5 amines2f and thiols2f as nucleophiles in gold-catalysed reactions, and have observed that the presence of these nucleophiles can dramatically alter the reactivity as well as selectivity of the gold catalysts. For example, we have previously observed that although gold(i)-catalysed reactions can work very well with alcohol nucleophiles5 (Scheme 1, eqn (1)),2a,b,4a the equivalent reaction of anilines with cyclopropenes do not proceed to completion (Scheme 1, eqn (2)).2f,7 presumably due to deactivation of the catalyst by the \(N\)-nucleophile. On the other hand, despite the initial assumption that \(S\)-nucleophiles would fare worse than \(N\)-nucleophiles (as they are known strong coordinators to gold),2a reactions with thiols do proceed to completion.7 However, reactions are clearly slower with more nucleophilic \(S\)-nucleophiles (progressively slower from thioacid—thiophenol—alkyl thiols, Scheme 1, eqn (3)).2f Furthermore, functionalities such as furans2c and alcohols2a,b which usually react with cyclopropenes within minutes under gold(i)-catalysis, are no longer reactive in the presence of thiols.2f

In order to explain these observations, we were keen to elucidate the structure and activity of the actual gold(i) species involved in these reactions.8,9 So far, not much effort has been made to isolate, characterise10 and investigate the catalytic properties of these species. Nevertheless, heteroatom nucleophiles such as RSH and RNH₂ are commonly used in gold-catalysed reactions,1a,d so a better understanding of the nature and activity of gold(i) catalysts in the presence of these nucleophiles will be invaluable if we are to better understand the mechanisms of gold-catalysed reactions.11

In a recent publication describing the gold(i)-catalysed reactions of thiols with cyclopropenes, we briefly disclosed that \([\{\text{Au}(L)\}_2(\mu-\text{SR})\][\text{SbF}_6]\) species are likely to be the thiol-deactivated complexes formed in the reaction.2f,12 In this article, we present our full investigations into the nature of the gold-
species formed in the presence of thiols, and compare these with species formed in the presence of amines. Solution state NMR studies are presented, along with the isolation and characterisation of the thiol-deactivated species \([\text{[Au(L)}_2(\mu\text{-SR})][\text{SbF}_6]]\) \(6\text{a–c}\) and amine-deactivated species \([\text{LAu-NH}_2\text{R}][\text{SbF}_6]\) \(7\text{a–c}\) by NMR spectroscopy and X-ray crystallography (Scheme 2). Complexes of type \([\text{[Au(L)}_2(\mu\text{-SR})][\text{SbF}_6]]\) and \([\text{LAu-NH}_2\text{R}][\text{SbF}_6]\) have never been studied in the context of catalysis, so \(6\text{a–c}\) and \(7\text{a–c}\) were investigated for their catalytic activity in an effort to compare the level of deactivation in each of these species.

2 Results and discussion

2.1 Gold(i) catalyst with thiols, thiophenols and thioacids

Our investigations commenced with NMR studies of Echavarren catalyst \(8\) in the presence of sulfur nucleophiles RSH. Catalyst 8 is a commonly used, commercially available Au(i) catalyst and was chosen for our studies because it was previously found to have the best catalytic activity in the presence of thiols.\(^2\) The second reason for using 8 is one of practicality: the displacement of the MeCN in the complex by an S-nucleophile can be clearly monitored by \(^1\)H NMR spectroscopy, indicated by the appearance of unbound MeCN in the solution.

When catalyst 8 was subjected to 20 equiv. of an alky thiol, thiophenol or thiobenzoic acid (to replicate the ratio which would be present in a typical 5 mol% gold(I)-catalysed reaction), an almost instantaneous conversion to new complexes was observed by \(^{31}\)P NMR analysis (Fig. 1, top), backed up by the appearance of unbound MeCN in the \(^1\)H NMR spectra (Fig. 1, bottom).

The analyses were repeated with 1:1 equiv. of 8 with the same thiols (see ESI\(^1\)), and crystallisation by vapour diffusion method (CDCl\(_3\)-hexane) produced single crystals which were isolated and characterised by X-ray crystallography (Fig. 2). All three are revealed to be digold with bridging thiolate complexes\(^14\) \([\text{[Au(L)}_2(\mu\text{-SR})][\text{SbF}_6]]\) \(6\text{a–c}\), \(6\text{b}\) and \(6\text{c}\), which are now fully characterised by X-ray crystallography, \(^1\)H, \(^{31}\)P, \(^{13}\)C NMR, IR and HRMS (see section 4.2). Crystals of \(6\text{a–c}\) are all air-stable over a period of >3 months. There is no formal Au–Au bond,\(^15\) although the intramolecular Au–Au distance of 3.3987(3), 3.4066(4) and 3.4363(3) Å in \(6\text{a}, 6\text{b}\) and \(6\text{c}\) respectively may indicate weak aurophilic interactions (accepted range of aurophilic Au–Au distances ca. 2.85–3.50 Å).\(^16\) In addition, the aromatic ring from the ligand appears to be stabilising the Au centre through a weak Au(i)–arene interaction (Au–arene distances of 3.218/3.173, 3.212/3.183 and 3.218/3.204 Å for \(6\text{a}, 6\text{b}\) and \(6\text{c}\) respectively),\(^16\) an interaction which is also observed in the parent Echavarren catalyst 8.\(^\text{13}\) The \(^{31}\)P NMR shift moves more upfield the more nucleophilic the parent thiol RSH (63.61, 62.96, 62.68 for \(6\text{a}, 6\text{b}\) and \(6\text{c}\) respectively), consistent with a progressively more electron rich Au(i) centre.

A plausible mechanism for the formation of complexes \(6\text{a–c}\) is shown in Scheme 3. Acetonitrile is displaced by RSH to form 9, followed by loss of H\(^+\) to form 10. Complex 10 is nucleophilic and reacts with 8 to form the observed digold complex 6. Evidence for the reversibility of this process is discussed in section 2.3.

2.2 Gold(i) catalyst with amines and anilines

Having evaluated the identity of the gold complexes in the presence of thiols, we next carried out a similar study with N-nucleophiles. With nBuNH\(_2\), p-MeO-C\(_6\)H\(_4\)NH\(_2\) (p-anisidine) and aniline, a clear shift in the \(^{31}\)P NMR peak is observed (Fig. 3), once again, accompanied by the appearance of unbound MeCN in the \(^1\)H NMR spectra (see ESI\(^1\)). The \(^{31}\)P NMR shift appears to move more upfield the better the parent...
RNH₂ nucleophile, consistent with a progressively more electron rich Au(I) centre.

In order to characterise these species, single crystals were grown by vapour diffusion (CDCl₃–hexane). In stark contrast to the digold species with thiols, single crystal X-ray crystallography reveals monogold [LAu-NH₂R][SbF₆] species 7a, 7b, and 7c (Fig. 4). These species are more than likely to be the cause of dampening of reactivity in some gold(I)-catalysed reactions with amines and anilines (e.g. eqn (2), Scheme 1). The intermolecular Au–Au distances are 7.5686(4), 8.1290(3) and 7.6009(4) Å respectively for 7a, 7b and 7c, showing that there are no significant aurophilic interactions. Weak Au–arene stabilisation of the Au centre by the ligand is once again evident in all of these structures (Au–arene distances of 3.154, 3.162 and 3.172 Å in 7a, 7b and 7c respectively). This interaction is thought to render extra stability to the gold complexes in this study, and allows them to be stable (e.g. 7c is air stable >6 months upon standing on the bench) and isolable for characterisation. In contrast, subsequent attempts to grow the corresponding NHC (IPr) versions of these complexes in the same manner led to decomposition.

While amines and anilines clearly react with the gold catalyst to form [LAu-NH₂R][SbF₆], the less nucleophilic amide (PhCONH₂) and protected amines BocNH₂ and TsNH₂ do not show the same reactivity. When a 1 : 1 mix of catalyst 8 and these N-nucleophiles are monitored by NMR, no displacement of MeCN is seen in the ¹H NMR spectra, and no appreciable shift in the ³¹P NMR is observed. While this observation does not rule out the formation of small amounts of [LAu-NH₂R]-
[SbF$_6$] in solution, the equilibrium firmly lies towards 8 (in Scheme 4). This observation is as expected as it reflects the catalytic activity of gold(I) in the presence of N-nucleophiles: protected amines such as Boc- and Ts- amines are more commonly used nucleophiles.

2.3 Catalytic studies with 6a-c and 7a-c

Having established, isolated and characterised the gold(i) species in the presence of RSH and RNH$_2$ (6a-c and 7a-c respectively), we set out to study the catalytic activity of these species. Complexes of type [(Au(L)$_2$)(μ-SR)][SbF$_6$] and [Au-NH$_2$R][SbF$_6$] have never been studied in the context of catalysis, so it will be useful to know whether these complexes are completely inactive or whether they can competently release active catalyst in situ. For example, in related work, formation of carbon bridged digold species have been shown to be inhibitory to catalysis as they are in competition with the product yielding protodeauration step. Related [(Au(L)$_2$)(μ-OH)][X] complexes have also been reported and utilised as active catalysts.

In addition, we were also keen to investigate the degree of deactivation in 6a-c and 7a-c relative to each other.

Firstly, [(Au(L)$_2$)(μ-SR)][SbF$_6$] was investigated in a reaction with RSH as a nucleophile, in order to ascertain whether it could be the actual catalytically active species in these reactions. When complex 6b was used as a catalyst in a reaction of a cyclopropene with thiophenol, the production of the gold(I) catalysed product 12 is nowhere near as good as with the parent catalyst 8 (Table 1, entry 3 vs. 1). Instead, the background (non gold(i)-catalysed) addition reaction to form cyclopropane 13 dominates. This initially suggests that 6b is most likely not the active catalyst in the reaction shown in entry 1, Table 1, and is instead a deactivation pathway in gold(I)-catalysed reactions with thiols.

However, this result was initially rather puzzling as the procedure in entry 1 involves pre-mixing catalyst 8 with PhSH in CH$_2$Cl$_2$ before addition to cyclopropene substrate 11: this forms 6b in situ almost instantaneously (see section 2.1). One difference between using isolated 6b (entry 3) and 6b made in situ from 8 (entry 1) is the presence of H$^+$, released upon formation of 6b from 8 (Scheme 3). If the formation of 6 from 8 is indeed reversible, then the presence of H$^+$ may allow for more active catalyst to be in solution for catalysis, whereas the absence of residual H$^+$ (entry 3) causes the equilibrium to be towards inactive 6. Indeed, when 6b is used with added H$^+$, the gold(i)-catalysed product 12 is once again the major product (entry 4). A control reaction using Brønsted acid alone (entry 5)

![Scheme 4](image)

**Fig. 4** X-ray structures of 7a, 7b and 7c. SbF$_6^-$ counterion is omitted for clarity. 7a: Au–N 2.1197(17) Å, N–Au–P 172.28(6)°; 7b: Au–N 2.116(4) Å, N–Au–P 175.76(11)°; 7c: Au–N 2.097(2) Å, N–Au–P 175.22(8)°.

**Table 1** Comparison of the reaction of cyclopropene 11 with thiophenol in the presence of 8 and 6b, and control reactions

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<th>mol%</th>
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<td>8</td>
<td>5</td>
<td>12 only</td>
</tr>
<tr>
<td>2</td>
<td>No catalyst</td>
<td>N/A</td>
<td>13 only</td>
</tr>
<tr>
<td>3</td>
<td>6b</td>
<td>2.5</td>
<td>1 : 20</td>
</tr>
<tr>
<td>4</td>
<td>6b + HOTf</td>
<td>2.5</td>
<td>2 : 1</td>
</tr>
<tr>
<td>5</td>
<td>HOTf</td>
<td>2.5</td>
<td>13 only</td>
</tr>
</tbody>
</table>

$^a$ Determined by $^1$H NMR analysis of crude reaction mixture. $^b$ 8 is pre-mixed with PhSH in CH$_2$Cl$_2$ before addition to 11.
shows that the reaction to form 12 in entry 4 is gold(i)
catalysed.

Next, [LAu-NH2R][SbF6] complex 7b was investigated in a
reaction where RNH2 is a nucleophile. When complex 7b was
used as a catalyst in a reaction of a cyclopropane with p-anisi
dine, the conversion to 15 is 15% with 7b compared to 27%
using catalyst 8 (entries 1–2, Table 2). As expected, addition of
catalyst does not improve the conversion to desired product (entry
3, Table 2 vs. entry 4, Table 1) as this time it does not affect the
equilibrium between 8 and 7 (Scheme 4). 31P NMR analysis of
a 1 : 1 : 1 ratio of 8 : 7b : p-anisidine in CD2Cl2 clearly shows
immediate formation of 7b in situ, which persists after 2 hours.

Finally, the gold(i)-catalysed reaction of alcohols with cyclo-
propenes (eqn (1), Scheme 1) was used to compare the catalytic
activities (or rather, the amount of dampening of catalytic
activity) of complexes 6a–c and 7a–c. We have previously
shown that this reaction goes to full conversion with a variety of
commercial gold(i) catalysts.2a In comparison, complexes
6a–c do not produce full conversions to product 16 (entries
1–3, Table 3). The conversions are moderate to low: 47%, 25%
and ≈5% respectively for 6a, 6b, and 6c. This observed trend
neatly reflects the Lewis basicity of the original RSH thiol
employed to form the complexes 6a–c. The increasing Lewis
basisity going from thioacid → thiophenol → alkyl thiol to form
6a, 6b, and 6c respectively is likely to push the equilibrium
towards 6 (Scheme 3), resulting in a lower concentration of
active catalyst in the reaction. Complexes 7a–c show a similar
trend (entries 4–6). The conversions, reflecting the catalytic
activity, also decrease going from 7a → 7b → 7c, reflecting the
increasing Lewis basicity of the parent aniline → anisidine → amine.

3 Conclusions
In conclusion, we found that thiols deactivate Au(i) catalysts by
forming digold with bridging thiolate complexes [([Au(L)]2-
(μ-SR))[SbF6]] (e.g. 6a–c, which have now been fully characterised).
These species are in equilibrium with the active gold
catalysts (Scheme 3) and the presence of residual H+ in situ is
required for enough active catalyst to be in solution for cataly-
sis, whereas the absence of residual H+ causes the equilibrium
to shift towards the inactive complex 6. In addition, the more
nucleophilic the parent thiol (RSH), the less active the resulting
gold(i) complex, presumably because this pushes the equi-
lbrium increasingly towards the inactive complex ([Au(L)]2-
(μ-SR))[SbF6]). In contrast, amines deactivate Au(i) catalysts by
forming the monogold species [LAu-NH2R][SbF6] (e.g. 7a–c).
The difference in behaviour between gold(i) complexes in
thiols and amines is possibly due to the difference in acidity of
the proton in 9 vs. 7. We hope that these results shed some light on the identity as well as activity of gold(i) catalysts when
thiols and amines are used as nucleophiles in gold(i)-catalysed
reactions.

4 Experimental
4.1 General experimental section
All reactions were carried out in air without the need for pre-
dried solvents, in order to replicate the reaction conditions in
gold(i) catalysed reactions, which are typically carried out in
air. 1H NMR spectra were recorded on Bruker AV 300 and AV
400 spectrometers at 300 and 400 MHz respectively and refer-
cenced to residual solvent. 13C NMR spectra were recorded
using the same spectrometers at 75 and 100 MHz respectively.
Chemical shifts (δ in ppm) were referenced to tetramethyl-
silane (TMS) or to residual solvent peaks (CDCl3 at δ = 7.26).
For 31P NMR, chemical shifts were referenced against H3PO4 at
δ 0 ppm. J values are given in Hz and s, d, dd, t, q and m
abbreviations correspond to singlet, doublet, doublet of
doublet, triplet, quartet and multiplet. Mass spectrometry data
was acquired at the EPSRC UK National Mass Spectrometry
Facility at Swansea University. Infrared spectra were obtained
on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling
Accessory, deposited neat or as a chloroform solution to a
diamond/ZnSe plate. Elemental analyses were determined by
the departmental service (HWU). Flash column chromatog-
raphy was carried out using Matrix silica gel 60 from Fisher

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<th>Entry</th>
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<th>Conversiona (%)</th>
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<td>2</td>
<td>7b</td>
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<tr>
<td>3</td>
<td>7b + HOTF</td>
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</tr>
<tr>
<td>6</td>
<td>7c</td>
<td>34</td>
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</tbody>
</table>

a 5 mol% with respect to gold, i.e. 2.5 mol% for digold species 6a–c.
b Determined by 1H NMR analysis of crude reaction mixture.
Chemicals and TLC was performed using Merek silica gel 60 F254 precoated sheets and visualised by UV (254 nm) or stained by the use of aqueous acidic ceric ammonium molybdate. Petroether refers to petroleum ether (40–60 °C). Dichloromethane (DCM) was purchased from Fisher and used without further purification. All nucleophiles were purchased from Sigma-Aldrich or Acros, and used without further purification.

4.2 General experimental procedure for crystals 6a-c and 7a-c

Catalyst 8 and the nucleophile RSH or RNH₂ (1 equiv.) were added to an NMR tube, and dissolved in DCD (0.75 mL). ¹H and ³¹P NMR were obtained from the resulting crude mixture. The solution was then decanted into a vial, and crystals were grown by vapour diffusion from DCD–hexane. The crystals were washed with hexane and dried under reduced pressure.

**Compound 6a.** Complex 6a was obtained as yellow crystals (9.3 mg, 0.0068 mmol, 26%). M.p. 195 °C (decomposes). ¹H NMR (300 MHz, CDCl₃) δ 7.94–7.80 (m, 4H, Ar-H), 7.64–7.11 (m, 19H, Ar-H), 1.30 (d, J = 16.0 Hz, 36H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ = 189.5 (C), 149.2 (d, J (¹³C–¹³P) = 13.5 Hz, C), 143.1 (d, J (¹³C–¹³P) = 6.8 Hz, C), 138.3 (C), 134.5 (C), 130.5 (CH), 129.4 (CH), 129.1 (d, J (¹³C–¹³P) = 16.1 Hz, CH), 128.9 (CH), 128.7 (CH), 128.3 (CH), 128.0 (CH), 127.8 (d, J (¹³C–¹³P) = 7.0 Hz, CH), 125.4 (d, J (¹³C–¹³P) = 45.0 Hz, C), 38.2 (d, J (¹³C–¹³P) = 23.8 Hz, C), 130.8 (C), 128.0 (C), 127.5 (CH), 125.8 (d, J (¹³C–¹³P) = 44.3 Hz, C), 38.5 (d, J (¹³C–¹³P) = 23.7 Hz, C). ³¹P NMR (121 MHz, CDCl₃) δ = 63.65. IR νmax/cm⁻¹ 3056 w, 2955 m, 2853 m, 1673 m, 1615 w, 1602 w, 1472 m. HRMS (NESI): m/z calcd for C₂₇H₃₆AuNOP: 618.2195 [M⁺]; found: 618.2182. Anal. Calc. for C₂₇H₃₆AuNOP: C, 37.88; H, 4.26; N, 1.64. Found: C, 37.88; H, 4.13; N, 1.34.

**Compound 7b.** Complex 7b was obtained as white crystals (22.1 mg, 0.026 mmol, 99%). M.p. 173 °C (decomposes). ¹H NMR (300 MHz, CDCl₃) δ = 7.90–7.81 (m, 1H, Ar-H), 7.63–7.50 (m, 4H, Ar-H), 7.36–7.22 (m, 4H, Ar-H), 6.96 (d, J = 8.9 Hz, 2H, Ar-H), 6.80 (d, J = 8.9 Hz, 2H, Ar-H), 4.57 (br s, 2H, NH₂), 3.78 (s, 3H, OCH₃), 1.38 (d, J (¹³C–¹³P) = 16.1 Hz, 18H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ = 157.7 (broad, C), 149.2 (d, J (¹³C–¹³P) = 12.5 Hz, C), 144.0 (d, J (¹³C–¹³P) = 6.5 Hz, C), 133.4 (d, J (¹³C–¹³P) = 6.0 Hz, CH), 133.3 (d, J (¹³C–¹³P) = 10.3 Hz, CH), 131.4 (d, J (¹³C–¹³P) = 2.2 Hz, CH), 130.5 (CH), 129.2 (CH), 127.6 (d, J (¹³C–¹³P) = 7.4 Hz, CH), 127.2 (CH), 125.1 (d, J (¹³C–¹³P) = 48.4 Hz, C), 123.1 (broad, C), 114.9 (CH), 55.7 (CH₃), 38.0 (d, J (¹³C–¹³P) = 26.3 Hz, C), 30.9 (d, J (¹³C–¹³P) = 6.1 Hz, CH), 31.8 (d, J (¹³C–¹³P) = 6.2 Hz, C), 121.9 (MDC, CDCl₃) δ = 58.71. IR νmax/cm⁻¹ 3312 w, 2682 w, 2960 w, 1607 w, 1577 m, 1510 s, 1458 m, 1245 s. HRMS (NESI): m/z calcd for C₂₆H₃₄AuF₆NPSb: 987.3018 [M⁺]; found: 987.3014. Anal. Calc. for C₂₆H₃₄AuF₆NPSb: C, 37.88; H, 4.13; N, 1.70. Found: C, 37.88; H, 4.13; N, 1.34.
Crystal data

Single crystal X-ray diffraction data were collected on crystals 6a, 6c, 7a–7c which were coated in Paratone-N oil and mounted on an X8 Apex2 diffractometer with a MiTiGen Micromount. Diffraction data were collected at 100 K with graphite monochromated MoKα radiation from a sealed X-ray tube set at 50 kV and 35 mA. Diffraction data for 6b were collected on an Agilent SuperNova, Dual, Atlas diffractometer using Cu Kα radiation (1.5418 Å) with mirror optics. The crystal was kept at 120.01(10) K during data collection. Using Olex2,24 the structure was solved with the XS25 structure solution program using Direct Methods and refined with the XL25.

### Table 4 Crystal data and structure refinements for 6a–c and 7a–c

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<th>6a</th>
<th>6b</th>
<th>6c</th>
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<td>Cc</td>
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<td>a = 90.0, b = 90.7654(11), c = 96.316(3)</td>
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<td><strong>2θ range for data collection</strong></td>
<td>2.78 to 52.74°</td>
<td>6.017 to 152.5034°</td>
<td>2.7 to 66.64°</td>
</tr>
<tr>
<td><strong>Final R indices: I ≥ 2σ(I)</strong></td>
<td>R₁ = 0.0235, wR₂ = 0.0545</td>
<td>R₁ = 0.0313, wR₂ = 0.0819</td>
<td>R₁ = 0.0328, wR₂ = 0.0713</td>
</tr>
<tr>
<td><strong>Largest diff. peak/hole/e Å⁻³</strong></td>
<td>0.99/–1.48</td>
<td>–0.91/4.07</td>
<td>1.53–0.91</td>
</tr>
</tbody>
</table>

### Table 5 Crystal data and structure refinements for 7a–c

<table>
<thead>
<tr>
<th></th>
<th>7a</th>
<th>7b</th>
<th>7c</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C24H38AuNP: 8722</td>
<td>C24H38AuNP: 8722</td>
<td>C24H38AuNP: 8722</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>568.2402</td>
<td>568.2402</td>
<td>568.2402</td>
</tr>
<tr>
<td><strong>Temperature/K</strong></td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2₁/c</td>
<td>P2₁/c</td>
<td>P2₁/c</td>
</tr>
<tr>
<td><strong>Cell parameters (Å)</strong></td>
<td>a = 7.5686(4), b = 18.4546(9), c = 20.8291(11)</td>
<td>a = 13.1268(4), b = 11.7372(4), c = 19.9682(7)</td>
<td>a = 90.0, b = 90.115(2), c = 96.316(3)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>Volume/Å³</strong></td>
<td>2738.4(2)</td>
<td>2738.4(2)</td>
<td>2738.4(2)</td>
</tr>
<tr>
<td><strong>ρ(calc, mg mm⁻³)</strong></td>
<td>1.999</td>
<td>1.902</td>
<td>1.943</td>
</tr>
<tr>
<td><strong>ρ(m, mm⁻³)</strong></td>
<td>6.453</td>
<td>5.985</td>
<td>6.426</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>1584.0</td>
<td>1648.0</td>
<td>1552.0</td>
</tr>
<tr>
<td><strong>Crystal size/mm³</strong></td>
<td>0.43 × 0.38 × 0.26</td>
<td>0.43 × 0.38 × 0.26</td>
<td>0.43 × 0.38 × 0.26</td>
</tr>
<tr>
<td><strong>2θ range for data collection</strong></td>
<td>4.58 to 72.04°</td>
<td>4.82 to 60.32°</td>
<td>3.04 to 70.38°</td>
</tr>
<tr>
<td><strong>Final R indices: I ≥ 2σ(I)</strong></td>
<td>R₁ = 0.0325, wR₂ = 0.0548</td>
<td>R₁ = 0.0325, wR₂ = 0.0548</td>
<td>R₁ = 0.0325, wR₂ = 0.0548</td>
</tr>
<tr>
<td><strong>Largest diff. peak/hole/e Å⁻³</strong></td>
<td>3.29/–2.04</td>
<td>3.29/–2.04</td>
<td>3.29/–2.04</td>
</tr>
</tbody>
</table>
refinement package using least squares minimisation. All non hydrogen atoms were refined anisotropically. All H atoms including water were constrained to idealised geometries apart from N bound H atoms in 7a–7c. CCDC 914704 (6a), 896069 (6b), 914705 (6c), 914706 (7a), 914707 (7b), and 914708 (7c), contain the supplementary crystallographic data for this paper (see Table 4 for crystal data and structure refinements).

General procedure for Table 1
A solution of thiophenol (1 equiv.) and catalyst (2.5 mol%) in CH2Cl2 (0.2 mL) was added to a solution of cyclopropane 11 (1 equiv.) in CH2Cl2 (0.52 mL) at 25 °C and stirred for 30 min. The solution was then filtered through a plug of silica with diethyl ether, and concentrated under reduced pressure. The reaction mixture was then analysed by 1H NMR in CDCl3 to determine reaction conversion by comparison with literature known spectra.2

General procedure for Table 2
Catalyst (5 mol%) was added to a stirred solution of cyclopropane 14 (1.2 equiv.) and p-anisidine (1 equiv.) in CH2Cl2 (0.1 M). The resulting solution was stirred for 18 h at 25 °C, filtered through a silica plug with ether and concentrated under reduced pressure. The reaction mixture was then analysed by 1H NMR in CDCl3 to determine reaction conversion by comparison with literature known spectra.3

General procedure for Table 3
Catalyst (5 mol% with respect to gold) was added in one portion to a stirred solution of cyclopropane 11 (1 equiv.) and phenyl ethanol (1 equiv.) in CH2Cl2 (0.48 M). The resulting solution was stirred for 19 h at 20 °C, the mixture was then filtered through a silica plug with ether and concentrated under reduced pressure. The reaction mixture was then analysed by 1H NMR in CDCl3 to determine reaction conversion by comparison with spectra of isolated 16 (see ESI).

Acknowledgements
We thank EPSRC (PCY) for funding, EPSRC UK National Mass Spectrometry Facility at Swansea University for analytical services and Dr Scott J. Dalgarno and Dr Gary Nichol for additional single crystal X-ray crystallography.

Notes and references


10 The formation of [Lau-NH2R][X] species is perhaps the best studied of the two in terms of X-ray crystallographic structures, but as far as the authors are aware, there are no catalytic studies with these species, as these studies pre-date the explosion of interest in homogenous gold(i)-catalysis of the last decade. See: (a) J. Vicente, M. T. Chicote, R. Guerrero, I. M. Saura-Llamas, P. G. Jones and M. C. Ramírez de Arellano, Chem.–Eur. J., 2001, 7, 638; (b) K. Angermaier and H. Schmidbaur, J. Chem. Soc., Dalton Trans., 1995, 559; (c) J. Vicente, M. T. Chicote, R. Guerrero and P. G. Jones, J. Chem. Soc., Dalton Trans., 1995, 1251.


12 The structure of complex 6b has been disclosed while investigating gold-catalysed reactions with thiois (see ref. 2f). All other crystal structures and complexes isolated: 6a, 6c, 7a, 7b and 7c are novel structures.


17 For related mechanistic studies of azaphilic versus carbophilic activation, see: J. J. Hirner, K. E. Roth, Y. Shi and S. A. Blum, Organometallics, 2012, 31, 6843.

18 For comparison, Maier and co-workers have shown that the equilibrium lies substantially towards 10 in the presence of alcohols (see ref. 8). In the presence of water, Tang and Yu have reported a related study on (phosphine)gold(i) hydrates and their equilibria: Y. Tang and B. Yu, RSC Adv., 2012, 2, 12686.


23 In related work, the formation of digold-phenylacetylene adducts from reacting 8 with phenylacetylene also liberates H2: A. Grirrane, H. Garcia, A. Corma and E. Alvarez, ACS Catal., 2011, 1, 1647.
