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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 thiols, digold with bridging thiolate complexes \([\text{[Au(L)]_2(\mu-SR)}][\text{SbF}_6]\) are formed and have been fully characterised by NMR and X-ray crystallography. In the presence of amines and anilines, complexes \([\text{[Lau-NH}_2\text{R}][\text{SbF}_6]\) 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. Its popularity is partly result of the excellent selectivity and efficiency of gold catalysts as Lewis acids for activating \(\pi\)-C–C \(\pi\) bonds, and also the ability to tune gold catalysts in order to vary the reactivity and selectivity of the reactions. One of the research efforts within our group is to explore the diverse chemistry of gold-catalysed reactions with cyclopropenes, allenes and allylic alcohols.

Within this context, we have used alcohols, amines, thiols and thiophenol, digold with bridging thiolate complexes \([\text{[Au(L)]_2(\mu-SR)}][\text{SbF}_6]\) are formed and have been fully characterised by NMR and X-ray crystallography. In the presence of amines and anilines, complexes \([\text{[Lau-NH}_2\text{R}][\text{SbF}_6]\) 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.

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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. So far, not much effort has been made to isolate, characterise and investigate the catalytic properties of these species. Nevertheless, heteroatom nucleophiles such as RSH and RNH\(_2\) are commonly used in gold-catalysed reactions, 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.

In a recent publication describing the gold(I)-catalysed reactions of thiols with cyclopropenes, we briefly disclosed that \([\text{[Au(L)]_2(\mu-SR)}][\text{SbF}_6]\) species are likely to be the thiol-deactivated complexes formed in the reaction. 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 $[\text{Au(L)}_2(\mu\text{-SR})][\text{SbF}_6]$ and amine-deactivated species $[\text{LAu-NH}_2\text{R}][\text{SbF}_6]$ 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 6a–c and 7a–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 alkyl 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†), 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$^{14}$ $[\text{Au(L)}_2(\mu\text{-SR})][\text{SbF}_6]$ 6a, 6b and 6c, 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 6a–6c 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 6a, 6b and 6c 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 6a, 6b and 6c respectively),$^{16}$ an interaction which is also observed in the parent Echavarren catalyst 8.13 The $^{31}$P NMR shift moves more upfield the more nucleophilic the parent thiol RSH (63.61, 62.96, 62.68 for 6a, 6b and 6c respectively), consistent with a progressively more electron rich Au(i) centre.

A plausible mechanism for the formation of complexes 6a–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$_2$, pMeO-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†). The $^{31}$P NMR shift appears to move more upfield the better the parent...
RNH$_2$ nucleophile, consistent with a progressively more electron rich Au(I) centre.

In order to characterise these species, single crystals were grown by vapour diffusion (CDCl$_3$–hexane). In stark contrast to the digold species with thiols, single crystal X-ray crystallography reveals monogold [LAu-NH$_2$R][SbF$_6$] 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-NH$_2$R][SbF$_6$], the less nucleophilic amide (PhCONH$_2$) and protected amines BocNH$_2$ and TsNH$_2$ 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 $^1$H NMR spectra, and no appreciable shift in the $^{31}$P NMR is observed. While this observation does not rule out the formation of small amounts of [LAu-NH$_2$R]-
[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 [LaU-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)
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 cyclopropene with p-anisidine, the conversion to 15 is 15% with 7b compared to 27% using catalyst 8 (entries 1–2, Table 2). As expected, addition of acid 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 cyclopropenes (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,b 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 basicity 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 [½[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 catalysis, 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 equilibrium increasingly towards the inactive complex [½[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 referenced 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 tetramethylsilane (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 chromatography was carried out using Matrix silica gel 60 from Fisher

Table 2 Comparison of the reaction of cyclopropene 14 with p-anisidine in the presence of 8 and 7b

| Entry | Catalyst | mol% | Conversion (%) |
|-------|----------|------|----------------|
| 1     | 8        | 5    | 27             |
| 2     | 7b       | 5    | 15             |
| 3     | 7b + HOTf | 5 + 5 | 13            |

* Determined by 1H NMR of crude reaction mixture.

Table 3 Comparison of catalytic activity of 6a–c and 7a–c

| Entry | Catalyst | Conversion (%) |
|-------|----------|----------------|
| 1     | 6a       | 47             |
| 2     | 6b       | 25             |
| 3     | 6c       | <5             |
| 4     | 7a       | 47             |
| 5     | 7b       | 43             |
| 6     | 7c       | 34             |

*5 mol% with respect to gold, i.e. 2.5 mol% for digold species 6a–c.

* Determined by 1H NMR analysis of crude reaction mixture.
Chemicals and TLC was performed using Merck silica gel 60 F254 precoated sheets and visualised by UV (254 nm) or stained by the use of aqueous acetic acid ammonium molybdate. Petrol ether 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 CDCl₃ (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 CDCl₃–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, 36H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ = 149.5 (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 (d, J (¹³C–¹³P) = 11.8 Hz, CH), 133.9 (CH), 133.3 (CH, 137.3 (d, J (¹³C–¹³P) = 7.7 Hz, CH), 131.4 (CH), 129.7 (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, CH), 38.2 (d, J (¹³C–¹³P) = 23.8 Hz, CH), 30.8 (d, J (¹³C–¹³P) = 6.7 Hz, CH). ³¹P NMR (121 MHz, CDCl₃) δ = 63.65. IR v max/cm⁻¹ 3056 w, 2955 m, 2853 m, 1673 m, 1615 w, 1602 w, 1472 m. HRMS (NESI): m/z calc for C₂₆H₃₄AuF₆N⁺: 622.8715 [M–SbF₆⁺]; found: 622.8716.

**Compound 7a.** Complex 7a was obtained as white crystals (21.0 mg, 0.025 mmol, 98%). M.p. 185 °C (decomposes).

¹H NMR (400 MHz, CDCl₃) δ = 7.85 (d, J = 7.9 Hz, 1H, Ar-H), 7.65–7.51 (m, 5H, Ar-H), 7.34–7.24 (m, 5H, Ar-H), 7.20–7.12 (m, 1H, Ar-H), 7.01 (d, J = 7.6 Hz, 2H, Ar-H), 4.67 (br. s, 2H, NH₂), 1.36 (d, J = 16.1 Hz, 18H, C(CH₃)ₙ). ¹³C NMR (100 MHz, CDCl₃) δ = 149.1 (d, J (¹³C–¹³P) = 12.1 Hz, C), 144.0 (d, J (¹³C–¹³P) = 6.3 Hz, C), 133.4 (CH), 133.3 (d, J (¹³C–¹³P) = 10.1 Hz, CH), 131.5 (d, J (¹³C–¹³P) = 2.1 Hz, CH), 130.5 (CH), 129.8 (CH), 129.2 (CH), 127.6 (d, J (¹³C–¹³P) = 7.3 Hz, CH), 127.2 (CH), 126.3 (broad, C), 125.1 (d, J (¹³C–¹³P) = 48.5 Hz, C), 121.7 (broad, CH), 38.0 (d, J (¹³C–¹³P) = 26.2 Hz, C), 30.9 (d, J (¹³C–¹³P) = 6.1 Hz, CH). ³¹P NMR (162 MHz, CDCl₃) δ = 58.86. IR v max/cm⁻¹ 3314 w, 3266 m, 3016 w, 2954 s, 1605 m, 1590 m, 1496 m, 1474 m, 1462 m. HRMS (NESI): m/z calc for C₄₆H₅₉Au₂OP₂S: 1079.3451 [M–SbF₆⁺]; found: 1079.3434.
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

| 6a | 6b | 6c |
|----|----|----|
| **Empirical formula** | C42H36OF3P2SbAu2 | C42H36AuF3P2Sb | C42H36AuF3P2SSb-0.5(CHCl3) |
| **Formula weight** | 1335.61 | 1001.15 | 1375.31 |
| **Temperature/K** | 100(2) | 120.01(10) | |
| **Crystal system** | Triclinic | Triclinic | Triclinic |
| **Space group** | P1 | Cc | P21/n |
| **a/Å** | 13.4006(7) | 24.6918(3) | 12.0540(8) |
| **b/Å** | 13.5192(7) | 13.0892(15) | 9.3903(8) |
| **c/Å** | 15.7860(8) | 29.3558(4) | 13.5903(8) |
| **α/°** | 80.115(2) | 90.7654(11) | 96.316(3) |
| **β/°** | 90.00 | 90.00 | 90.00 |
| **γ/°** | 90.00 | 90.00 | 90.00 |
| **Volume/Å³** | 2425.6(2) | 9486.84(19) | 6898.4(5) |
| **Z** | 4 | 4 | 4 |
| **ρcalc mg mm⁻³** | 1.867 | 1.870 | 1.865 |
| **m/mm⁻¹** | 6.752 | 17.388 | 6.765 |
| **f(000)** | 1316.0 | 5152.0 | 2660.0 |
| **Crystal size/mm³** | 0.40 × 0.40 × 0.30 | 2.78 to 52.74° | 2.7 to 66.64° |
| **Reflections collected** | 77 919 | 136 649 | 136 649 |
| **Independent reflections** | 19 283 [R(int) = 0.0447] | 18 698 [R(int) = 0.0549] | 18 698 [R(int) = 0.0549] |
| **Data/restraints/parameters** | 19 283/2/1069 | 18 698/13/600 | 18 698/13/600 |
| **Goodness-of-fit on F²** | 1.139 | 1.041 | 1.081 |
| **Final R indexes [I ≥ 2σ(I)]** | R₁ = 0.0313, wR₂ = 0.0819 | R₁ = 0.0315, wR₂ = 0.0820 | R₁ = 0.0328, wR₂ = 0.0713 |
| **Final R indexes [all data]** | R₁ = 0.0259, wR₂ = 0.0707 | R₁ = 0.0259, wR₂ = 0.0707 | R₁ = 0.0468, wR₂ = 0.0765 |
| **Largest diff. peak/hole/e Å⁻³** | 0.99/−1.48 | 1.53/−0.91 | 4.07/−4.72 |

| 7a | 7b | 7c |
|----|----|----|
| **Empirical formula** | C24H36NF5PSbAu | C24H36AuFeNP | C24H36AuFeNP |
| **Formula weight** | 824.23 | 854.25 | 854.25 |
| **Temperature/K** | 100.15 | 100(2) | 100(2) |
| **Crystal system** | Monoclinic | Monoclinic | Monoclinic |
| **Space group** | P2₁/c | P2₁/c | P2₁/c |
| **a/Å** | 7.5686(4) | 13.1268(4) | 7.6009(4) |
| **b/Å** | 17.4546(9) | 11.3732(4) | 17.7750(9) |
| **c/Å** | 20.8291(11) | 19.9682(7) | 20.5702(10) |
| **α/°** | 90.00 | 90.00 | 90.00 |
| **β/°** | 95.628(3) | 90.108(2) | 98.499(2) |
| **γ/°** | 90.00 | 90.00 | 90.00 |
| **Volume/Å³** | 2738.4(2) | 2953.75(17) | 2748.6(2) |
| **Z** | 4 | 4 | 4 |
| **ρcalc mg mm⁻³** | 1.999 | 1.920 | 1.943 |
| **m/mm⁻¹** | 6.453 | 5.985 | 6.426 |
| **f(000)** | 1584.0 | 1648.0 | 1552.0 |
| **Crystal size/mm³** | 0.43 × 0.38 × 0.26 | 0.22 × 0.12 × 0.08 | 0.4 × 0.38 × 0.04 |
| **2θ range for data collection** | 4.58 to 72.04° | 4.82 to 60.32° | 3.04 to 70.38° |
| **Index ranges** | −32 ≤ l ≤ 34 | 0 ≤ l ≤ 28 | −33 ≤ l ≤ 29 |
| **Reflections collected** | 69144 | 102285 | 82430 |
| **Independent reflections** | 12 891[R(int) = 0.0376] | 8722[R(int) = 0.0691] | 11 854[R(int) = 0.0375] |
| **Data/restraints/parameters** | 12 891/0/337 | 8722/2/359 | 11 854/6/349 |
| **Goodness-of-fit on F²** | 1.024 | 1.029 | 1.026 |
| **Final R indexes [I ≥ 2σ(I)]** | R₁ = 0.0235, wR₂ = 0.0458 | R₁ = 0.0294, wR₂ = 0.0508 | R₁ = 0.0285, wR₂ = 0.0639 |
| **Final R indexes [all data]** | R₁ = 0.0324, wR₂ = 0.0490 | R₁ = 0.0436, wR₂ = 0.0546 | R₁ = 0.0465, wR₂ = 0.0691 |
| **Largest diff. peak/hole/e Å⁻³** | 3.29/−2.04 | 0.72/−1.03 | 1.76/−1.80 |
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 cyclopropene 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 analysed by ¹H NMR in CDCl₃ to determine 12:13 ratio by comparison with literature known spectra.²

General procedure for Table 2

Catalyst (5 mol%) was added to a stirred solution of cyclopropene 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.²

General procedure for Table 3

Catalyst (5 mol% with respect to gold) was added in one portion to a stirred solution of cyclopropene 11 (1 equiv.) and phenethyl alcohol (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).

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Notes and references

1 For selected reviews on gold catalysis, see: (a) A. Corma, A. Leyva-Peréz and M. J. Sabater, Chem. Rev., 2011, 111, 1657; (b) M. Bandini, Chem. Soc. Rev., 2011, 40, 1358; (c) T. C. Boorman and I. Larrosa, Chem. Soc. Rev., 2010, 40, 1910; (d) A. S. K. Hashmi and M. Bührle, Aldrichimica Acta, 2010, 43, 27; (e) N. D. Shaprio and F. D. Toste, Synlett, 2010, 675; (f) S. Sengupta and X. Shi, ChemCatChem, 2010, 2, 609; (g) N. Bongers and N. Krause, Angew. Chem., Int. Ed., 2008, 47, 2178; (h) D. J. Gorin, B. D. Sherry and F. D. Toste, Chem. Rev., 2008, 108, 3351; (i) E. Jiménez-Núñez and A. M. Echarvarren, Chem. Rev., 2008, 108, 3326; (j) Z. Li, C. Brouwer and C. He, Chem. Rev., 2008, 108, 3239; (k) A. Arcadi, Chem. Rev., 2008, 108, 3266; (l) J. Muzart, Tetrahedron, 2008, 64, 5815; (m) A. S. K. Hashmi and M. Rudolph, Chem. Soc. Rev., 2008, 37, 1766; (n) H. C. Shen, Tetrahedron, 2008, 64, 7847; (o) H. C. Shen, Tetrahedron, 2008, 64, 3885; (p) R. A. Widenhoefer, Chem.–Eur. J., 2008, 14, 5382; (q) D. J. Gorin and F. D. Toste, Nature, 2007, 446, 395; (r) A. Fürstner and P. W. Davies, Angew. Chem., Int. Ed., 2007, 46, 3410; (s) E. Jiménez-Núñez and A. M. Echarvarren, Chem. Commun., 2007, 333; (t) A. S. K. Hashmi, Chem. Rev., 2007, 107, 3180; (u) A. S. K. Hashmi and G. J. Hutchings, Angew. Chem., Int. Ed., 2006, 45, 7896; (v) M. Rudolph and A. S. K. Hashmi, Chem. Soc. Rev., 2012, 41, 2448.

2 (a) J. T. Bauer, M. S. Hadfield and A. L. Lee, Chem. Commun., 2008, 6405; (b) M. S. Hadfield, J. T. Bauer, P. E. Glen and A. L. Lee, Org. Biomol. Chem., 2010, 8, 4090; (c) M. S. Hadfield and A.-L. Lee, Chem. Commun., 2011, 47, 1333; (d) P. C. Young, M. S. Hadfield, L. Arrowsmith, K. M. Maceleod, R. J. Mudd, J. A. Jordan-Hore and A.-L. Lee, Org. Lett., 2012, 14, 898; (e) M. S. Hadfield, L. J. Häller, A.-L. Lee, S. A. Macgregor, J. A. T. O’Neill and A. M. Watson, Org. Biomol. Chem., 2012, 10, 4433; (f) R. J. Mudd, P. C. Young, J. A. Jordan-Hore, G. M. Rosair and A.-L. Lee, J. Org. Chem., 2012, 77, 7633.

3 For reviews on gold-catalysed reactions with cyclopropenes, see: (a) B.-L. Lu, L. Dai and M. Shi, Chem. Soc. Rev., 2012, 41, 3318; (b) F. Miege, C. Meyer and J. Cossey, Beilstein J. Org. Chem., 2011, 7, 717.

4 (a) M. S. Hadfield and A. L. Lee, Org. Lett., 2010, 12, 484; (b) A. Heuer-Jungemann, R. G. McLaren, M. S. Hadfield and A.-L. Lee, Tetrahedron, 2011, 67, 1609; (c) K. J. Kilpin, U. S. D. Paul, A. L. Lee and J. D. Crowley, Chem. Commun., 2011, 47, 328.

5 P. C. Young, N. A. Schopf and A.-L. Lee, Chem. Commun., 2013, 49, 4262.

6 (a) A. Ulman, Chem. Rev., 1996, 96, 1533; (b) H. Gronbeck, A. Curioni and W. J. Andreoni, J. Am. Chem. Soc., 2000, 122, 3839; (c) K. Fujita, N. Nakamura, H. Ohno, B. S. Leigh, K. Niki, H. B. Gray and J. H. J. Richards, J. Am. Chem. Soc., 2004, 126, 13954.

7 Gold(0)-catalysed reactions with thiols are still relatively scarce, see for example: with allenes: (a) N. Morita and N. Krause, Angew. Chem., Int. Ed., 2006, 45, 1897; (b) M. N. Mengenbateer, G. Ferrara, N. Nishina, T. Jin and Y. Yamamoto, Tetrahedron Lett., 2010, 51, 4627. For mechanistic study, see: (c) K. Ando, J. Org. Chem., 2010, 75, 8516. With dienes: (d) C. Brouwer, R. Rahaman and C. He, Synlett, 2007, 1785. See also: (e) A. Arcadi, G. B. S. Di Giuseppe and F. Marinelli, Green Chem., 2003, 5, 64. Using heterogenised gold complexes: (f) A. Corma, C. González-Arellano, M. Iglesias and F. Sánchez, Appl. Catal., A, 2010, 375, 49. For examples of other low-valent sulfur employed
as nucleophiles in gold-catalyzed reactions, see: (g) I. Nakamura, T. Sato and Y. Yamamoto, Angew. Chem., Int. Ed., 2006, 45, 4473; (h) L. Peng, X. Zhang, S. Zhang and J. Wang, J. Org. Chem., 2007, 72, 1192; (i) P. W. Davies and S. J.-C. Albrecht, Chem. Commun., 2008, 238; (j) P. W. Davies and S. J.-C. Albrecht, Synlett, 2012, 70.

8 For a recent related NMR study of coordination chemistry of gold in solution, see: A. Zhdkano, M. Ströbele and M. E. Maier, Chem.–Eur. J., 2012, 18, 14732.

9 Isolation and characterisation of gold-alkyne, allene and alkene complexes are more prevalent. For examples of isolation and characterisation of gold complexes with: enol ether: (a) Y. Zhu, C. S. Day and A. C. Jones, Organometallics, 2012, 31, 7332; dienes: (b) R. A. Sanguramath, S. K. Patra, M. Green and C. A. Russell, Chem. Commun., 2012, 48, 1060; (c) R. A. Sanguramath, T. N. Hooper, C. P. Butts, M. Green, M. Green, J. E. McGrady and C. A. Russell, Angew. Chem., Int. Ed., 2011, 50, 7592; (d) R. E. M. Brooner and R. A. Widenhofer, Organometallics, 2011, 30, 3182; alkynyl: (e) T. N. Hooper, M. Green and C. A. Russell, Chem. Commun., 2010, 46, 2313; allene: (f) T. N. Hooper, M. Green, J. E. McGrady, J. R. Patel and C. A. Russell, Chem. Commun., 2009, 3877; (g) R. E. M. Brooner and R. A. Widenhofer, Organometallics, 2012, 31, 768; T. J. Brown, M. G. Dickens and R. A. Widenhofer, Chem. Commun., 2009, 6451; (h) T. J. Brown, M. G. Dickens and R. A. Widenhofer, J. Am. Chem. Soc., 2009, 131, 6350;
allene: (i) T. J. Brown, A. Sugie, M. G. D. Leed and R. A. Widenhofer, Chem.–Eur. J., 2012, 18, 6959–6971; (j) T. J. Brown, A. Sugie, M. G. Dickens and R. A. Widenhofer, Organometallics, 2010, 29, 4207.

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 predate 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. Ramirez de Arellano, Chem.–Eur. J., 2001, 7, 638; (b) K. Angerman 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.

11 For a recent review on intermediates in gold catalysis, see: A. S. K. Hashmi, Angew. Chem., Int. Ed., 2010, 49, 5323.

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

13 C. Nieto-Oberhuber, S. López, M. P. Muñoz, D. J. Cáceres, E. Buñuel, C. Nevado and A. M. Echavarren, Angew. Chem., Int. Ed., 2003, 44, 6146.

14 For related crystal structures, see: (a) P. G. Jones and A. Weikaua, Z. Kristallogr., 1994, 209, 87; (b) W. J. Hunks, M. C. Jennings and R. J. Puddephatt, Inorg. Chem., 2000, 39, 2699; (c) A. Sladek, K. Angerman and H. Schmidbaur, Chem. Commun., 1996, 1959.

15 For a review on aurophilic interactions, see: H. Schmidbaur and A. Schier, Chem. Soc. Rev., 2012, 41, 370.

16 (a) P. Pérez-Galán, N. Delpont, E. Herrero-Gómez, F. Maseras and A. M. Echavarren, Chem.–Eur. J., 2010, 16, 5324; (b) Q.-S. Li, C.-Q. Wan, R.-Y. Zou, F.-B. Xu, H.-B. Song, X.-J. Wan and Z.-Z. Zhang, Inorg. Chem., 2006, 45, 1888.

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.

19 Review: (a) A. Gómez-Suárez and S. P. Nolan, Angew. Chem., Int. Ed., 2012, 51, 8156. Selected papers: (b) D. Weber, T. D. Jones, L. L. Adduci and M. R. Gagné, Angew. Chem., Int. Ed., 2012, 51, 2452; (c) D. Weber, M. A. Tarselli and M. R. Gagné, Angew. Chem., Int. Ed., 2009, 48, 5733; (d) T. Brown, D. Weber, M. R. Gagné and R. A. Widenhofer, J. Am. Chem. Soc., 2012, 134, 9134; (e) A. S. K. Hashmi, I. Braun, P. Nösel, J. Schädlich, M. Wietreck, M. Rudolph and F. Rominger, Angew. Chem., Int. Ed., 2012, 51, 4456; (f) J. E. Heckler, M. Zeller, A. D. Hunter and T. G. Gray, Angew. Chem., Int. Ed., 2012, 51, 5924.

20 For examples of related [{Au(L)2}2(μ-OH)][X] complexes, see: (a) R. S. Ramón, S. Gaillard, A. Poater, I. Cavallo, A. M. Z. Slawin and S. P. Nolan, Chem.–Eur. J., 2011, 17, 1238; (b) S. Gaillard, J. Bosson, R. S. Ramón, P. Nun, A. M. Z. Slawin and S. P. Nolan, Chem.–Eur. J., 2010, 16, 13729 and ref. 8.

21 For other gold(i)-catalysed reactions with cyclopropenes, see ref. 2 and 3 and: (a) Z. B. Zhu and M. Shi, Chem.–Eur. J., 2008, 14, 10219; (b) C. K. Li, Y. Zeng and J. B. Wang, Tetrahedron Lett., 2009, 50, 2956; (c) C. K. Li, Y. Zeng, H. Zhang, J. Feng, Y. Zhang and J. B. Wang, Angew. Chem., Int. Ed., 2010, 49, 6413; (d) F. Miege, C. Meyer and J. Cossy, Org. Lett., 2010, 12, 4144; (e) E. Seraya, E. Slack, A. Ariafard, B. F. Yates and C. J. T. Hyland, Org. Lett., 2010, 12, 4768; (f) G. Seidel, R. Mynott and A. Fürstner, Angew. Chem., Int. Ed., 2009, 48, 2510; (g) D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard III and F. D. Toste, Nat. Chem., 2009, 1, 482; (h) F. Miege, C. Meyer and J. Cossy, Chem.–Eur. J., 2012, 18, 7810.

22 Recent review on cyclopropene chemistry: Z.-B. Zhu, Y. Wei and Y. M. Shi, Chem. Soc. Rev., 2011, 40, 5534.

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. Álvarez, ACS Catal., 2011, 1, 1647.

24 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2011, 44, 143.

25 G. M. Sheldrick, Acta Crystallogr., Sect. A: Fundam. Crystallogr., 2008, 64, 112.