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Carbon-sulfur bond formation by reductive elimination of gold(III) thiolates†

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Abstract

Whereas the reaction of the gold(III) pincer complex \( (C^N^C)AuCl \) with 1-adamantyl thiol (AdSH) in the presence of base affords \( (C^N^C)AuSAd \), the same reaction in the absence of base leads to formation of aryl thioethers as the products of reductive elimination of the Au-C and Au-S ligands (\( C^N^C = \) dianion of 2-6-diphenylpyridine or 2-6-diphenylpyrazine). Although high chemical stability is usually taken as a characteristic of pincer complexes, results show that thiols are capable of cleaving one of the pincer Au-C bonds. This reaction is not simply a function of S-H acidity, since no cleavage takes place with other more acidic X-H compounds, such as carbazole, amides, phenols and malonates. The reductive C-S elimination follows a second-order rate law, \(-d[1a]/dt = k[1a][AdSH]\). Reductive elimination is enabled by displacement of the N-donor by thiol; this provides the conformational flexibility necessary for C-S bond formation to occur. Alternatively, reductive C-S bond formation can be induced by reaction of pre-formed thiolates \( (C^N^C)AuSR \) with a strong Brønsted acid, followed by addition of SMes as base. On the other hand, treatment of \( (C^N^C)AuR \) (\( R = Me, aryl, alkynyl \)) with thiols under similar conditions leads to selective C-C rather than C-S bond formation. The reaction of \( (C^N^C)AuSAd \) with \( H^+ \) in the absence of a donor ligand affords the thiolato-bridged complex \( \{((C^N-CH)Au(\mu-SAd))_2\}^{2+} \) which was crystallographically characterised.

Introduction

Reductive elimination is a common product-forming step in many homogeneously catalyzed reactions. In the chemistry of gold complexes this reaction has been extensively studied as a means of C-C bond formation.\(^1,2\) Reductive elimination leading to carbon-heteroatom bonds are comparatively rare but have also been observed, such as the formation of \( C(sp^3)-X \) and \( C(sp^2)-X \) carbon-halide bonds,\(^3,5\) as well as \( C(sp^2)-E \) bonds through reactions with \( P-,^6 \) \( O- \) and \( N- \) nucleophiles\(^7\) including phosphine ligands, via three-coordinate intermediates (Scheme 1 A - E). The formation of C-S bonds by reductive elimination of metal thiolates has been studied extensively for palladium\(^8,9\) and has also been observed for rhodium pincer complexes\(^10\) and applied to the rhodium-catalysed formation of diaryl thioethers.\(^11\) By
contrast, we are aware of only one example for C-S bond formation involving gold(III), the reaction of cyclometallated gold(III) C^N chelate complexes with –SH containing peptides, which allowed the transfer of the C^N moiety to the peptide via C-S linkages (Scheme 1 F). Reductive S-S elimination from Au(III) thiolates has also been observed. We have recently reported the synthesis, aggregation behaviour and photoluminescence of a series of gold(III) thiolates stabilized by cyclometallated C^N^C 2-6-diphenylpyridine and 2-6-diphenylpyrazine pincer ligands. Apart from a general interest in C^N^C-type pincer ligands to prevent reductive processes in gold(III) compounds and as a means to supporting highly reactive gold(III) species, the origin of this work on thiolates was the fact that gold carbene complexes supported by such pincer ligands show interesting anti-cancer activities. In cancer cells such compounds are frequently rendered harmless by reduction by the –SH containing tripeptide glutathione, which tends to be overexpressed and acts as a reducing defence mechanism. However, our [C^N^C)Au(NHC)]^+ compounds reacted with glutathione only very slowly, which may in part explain their high cytotoxicity. This behaviour contrasts with that of N^N^N pincer ligands, which were found to be reduced by thiols very easily, with loss of the pincer ligand. We therefore wished to explore which reaction pathways might be open to our C^N^C pincer-stabilised gold complexes on reaction with thiols. We show here that, unlike other mildly acidic protic reagents, alkyl thiols are capable of cleaving cyclometallated Au-C bonds, which leads to formation of aryl thioethers through reductive elimination of the thiolato and pincer ligands.
Scheme 1. Formation of C-heteroatom bonds by reductive elimination from gold(III) precursors.3,4,6,12

Results and Discussion

C-S bond formation. As previously reported,14a the reaction of (C^N^C)AuCl (1a,b) with 1-adamantyl thiol (AdSH) in the presence of base affords the corresponding thiolate 2a,b. We were therefore surprised to find that the addition of thiols in the absence of base leads to formation of aryl thioethers as the products of reductive elimination (Scheme 2).
For complete reductive elimination two molar equivalents of AdSH are required; with one equivalent the reaction remains incomplete and gives a mixture of starting material and 3. Complete conversion to 3a, b was achieved only after addition of further thiol. The reductive elimination product was identified by NMR spectroscopy and mass spectrometry. The gold(I) by-product, formulated as [AuCl(AdSH)]x, is formed as an aggregate according to diffusion NMR measurements (see ESI).

Although AdSH cleaves one of the Au-C bonds, the reductive elimination process is not related simply to the acidity of thiols. For example, no reaction was observed between 1a and other more acidic X-H compounds, such as carbazole, amides, phenols and malonates, even over extended periods of time. Monitoring mixtures of AdSH with 1a by NMR spectroscopy indicated that the reaction follows a second-order rate law, \(-d[1a]/dt = k[1a][AdSH]\), for [AdSH] = 0.04 – 0.4 M. The rate depends linearly on [AdSH], which implies that one equivalent of thiol and 1a are required in the rate determining step (Fig. 1). The reaction rate is unaffected by air and water. No intermediates were observed at low [AdSH] while, when a large molar excess of thiol was used, the formation of the gold(III) thiolate 2a was detected during the initial phase of the reaction, before it was consumed over a period of time (Fig. 2).

The observation of 2a at the beginning of the reaction implies that 1 equivalent of HCl is released upon ligand exchange. This could potentially induce protodeauration of 2a and open the path for C–S reductive elimination. As control experiment, isolated 2a was treated with 1 molar equivalent of HCl.
However, this reaction led to the instantaneous regeneration of the chloride 1a, together with the release of AdSH. The mixture then evolved as described before, to give 3a in 50% yield. It can be assumed therefore that a reversible chloride/thiolate exchange takes place, which explains why 2a is observed at high [AdSH] before reduction occurs. Furthermore, the possibility that AdSH is directly involved in Au-C bond cleavage cannot a priori be excluded. To check this hypothesis, we reacted the thiolato complex 2a with 30 equivalents of AdSH. Interestingly, we observed again reductive elimination to 3a, suggesting that AdSH induces Au–C bond breakage. However, thiol-induced reductive elimination starting from the pre-formed thiolate complex 2a proceeds very much more slowly (80% conversion after 2.5 weeks) than reductive elimination from the chloride 1a under otherwise identical conditions (complete reaction within 3 hours). It seems reasonable therefore to assume that protodeauration of 1a gives the bidentate intermediate 4a, which can undergo pyridine substitution by a further equivalent of AdSH generating 5a. Neither 4a nor 5a could be spectroscopically detected and must therefore be consumed rapidly. Since the aryl ligand in 5a is no longer a chelate but is conformationally flexible, fast reductive elimination is now enabled (Scheme 3).

Scheme 3. Reductive C-S elimination pathway induced by thiols.

The thiol-induced reductive elimination of the pyrazine complex 1b proceeds at comparable rates (Fig. 1), suggesting that displacement of the N-donor is not rate-limiting. Overall, the reaction sequence is reminiscent of the reductive aryl-aryl coupling process proposed by Vicente et al. for the reaction of bis-aryl gold(III) complexes (C^N)Au(aryl)Cl with phosphines.20
Fig. 1. Dependence of the rate of consumption of 1a (left) and 1b (right) on the thiol concentration (CD$_2$Cl$_2$, 25 °C).

Fig. 2. Product distribution of the reaction of 1a with AdSH as a function of time (CD$_2$Cl$_2$, 25 °C).

Given that the process shown in Scheme 3 requires both an acid and a sulfur-donor, it should be possible to achieve the same reductive elimination using an alternative acid with a non-coordinating anion, coupled with an alternative S-donor such as dimethylsulfide. This possibility was tested using 2a as starting material. We have shown before that the addition of the strong Brønsted acid [H(OEt)$_2$)$_2$]$^+$-[H$_2$N{B(C$_6$F$_5$)$_3$}]$_2$ ("HAB$_2"$) to C$^\wedge$N$^\wedge$C pincer complexes leads to protolytic cleavage of one of the Au-C bonds.$^{22}$ Treatment of 2a with HAB$_2$ followed by the addition of SMe$_2$ does indeed lead to the clean
formation of 3a, together with [Au(SMe₂)₂]⁺. The reaction rate increased with increasing SMe₂ concentration (Scheme 4).

Scheme 4. Reductive C-S elimination induced by a proton / SMe₂ combination.

Monitoring the reaction of HAB₂ with 2a in the absence of SMe₂ or base by ¹H NMR spectroscopy showed a series of intermediates and slow changes over a period of over 2 weeks, connected with Au-C bond cleavage and reversible diethyl ether coordination. Interestingly, under these conditions, i.e. in the absence of an S-donor, no reductive elimination takes place. The final spectrum showed only uncoordinated ether, together with the thiolato-bridged complex 6 (Scheme 5). This product gave no indication for proton shuttling.


Complex 6 was isolated as yellow crystals. The structure was confirmed by X-ray diffraction (Fig. 3). The crystal structure showed two metal centres linked by bridging thiolates. The unit cell contains a dimeric cation (lying about a centre of symmetry) and two [NH₂[B(C₆F₅)₃]₂⁻] anions. Each gold atom is supported by a cyclometallated 2-phenylpyridine ligand, with the protodeaurated dangling phenyl ring rotated ca 51.3(4)° about the C(16)–C(161) bond away from the Au atom, so that C(162) is far removed
from the coordinating site, now occupied by one of the bridging S atoms. The gold atom has an approximately square planar, fourfold coordination pattern, bonding to the pyridine N-atom, the ortho-carbon atom of one of its phenyl substituents, and the bridging sulfur atoms of the two S-adamantyl ligands. The two adamantyl substituents are mutually trans. The sterically congested ligand sphere leads to distortions of the gold coordination geometry, e.g. the trans C(122)-Au-S(1)#1 angle is reduced from the expected 180° to 163.4(3)°. The bridging Au–S bonds are quite different in length, with the one trans to the pyridine N-atom being 0.15 Å shorter than the bond trans to the phenyl C-atom. The adamantyl groups are positioned almost perpendicular to the central Au₂S₂ plane, with Au–S(1)–C(1) angles of 103.2(3) and 98.9(3)°.

**Fig. 3.** Side and (partial) top view of the cation in 6. Left: H atoms, tert.-butyl groups and anions are omitted for clarity. Ellipsoids are drawn at 50%. Selected bond distances [Å] and angles [°]:Au-C(122) 2.066(8), Au-N(11) 2.108(7), Au-S(1) 2.323(2), Au-S(1)#1 2.469(2), S(1)-C(1) 1.880(9); C(122)-Au-N(11) 81.2(3), C(122)-Au-S(1) 94.3(3), N(11)-Au-S(1) 174.4(2), C(122)-Au-S(1)#1 163.4(3), N(11)-Au-S(1)#1 101.2(2), S(1)-Au-S(1)#1 84.02(8).

**C-C and attempted C-E bond formation.** Under the same experimental conditions, and following similar mechanistic principles, the gold(III) methyl and aryl complexes 7 and 8, respectively, react with excess AdSH to give selective C–C bond formation, generating the corresponding coupling products 10 – 11 (Scheme 6). The reaction is selective for C-C rather than C-S reductive elimination. The process is however slow, and at 25 °C requires 6 days for quantitative aryl-aryl coupling, while aryl-methyl coupling is even slower (complete in 24 days). In the presence of a large excess of thiol C-C coupling of
the alkyne complex 9 is also observed, over a period of months, to give 12. The trend in the rates of C-C bond formation under these conditions therefore follows the order aryl-aryl > aryl-methyl >> aryl-alkynyl.

Scheme 6. Thiol-triggered reductive elimination of C(sp²)-C(sp³), C(sp²)-C(sp²) and C(sp²)-C(sp) bonds.

The HAB₂/SMe₂ protocol was extended to other heteroatom species in an effort to induce C-E bond formation for heteroatoms other than sulfur. However, rather different reactivity patterns were observed. For example, addition of HAB₂ to the phenolate 13 gave the ether complex 14, without Au-C cleavage. On the other hand, addition of HAB₂ to the carbazolato complex 15 gave the protodeaurated species 16, which demonstrates that given the low basicity of the carbazolate-N atom, the Au-C bond is the preferred site of proton attack. The NOE spectrum of 16 showed that the complex underwent ether-mediated proton shuttling between the two Au-C bonds at a rate of 1.23 s⁻¹, similar to the reversible protodeauration previously observed for 1/HAB₂ but slightly faster. However, addition of SMe₂ to solutions of 16 leads to protolytic cleavage of the carbazole ligand, without C-N bond formation, and the Au-C bond of the pincer ligand is regenerated to give 17 (Scheme 7).
The reaction of \((\text{C}^\text{N}^\text{C})\text{Au(III)}\) pincer complexes has rather unexpectedly shown that thiols are capable of cleaving one of the pincer Au-C bonds, followed by a reductive elimination process and formation of aryl thioethers. The reaction follows second-order kinetics. Displacement of the N-donor is required to access an intermediate with the conformational flexibility necessary to initiate the C···S bond forming step. Au-C cleavage with thiols proceeds independently of thiol acidity, since there is no reaction with other acidic reagents. The reaction sheds light on the likely fate of \((\text{C}^\text{N}^\text{C})\text{Au-based cytotoxic reagents under physiological conditions, such as in the presence of glutathione. With other gold starting materials (C^N^C)AuR (R = Me, aryl or alkynyl), the same thiol-treatment protocol leads to selective C-C rather than C-S bond formation, with rates decreasing in the order R = aryl > Me >> alkynyl.}

**Conclusion.**

The reaction of \((\text{C}^\text{N}^\text{C})\text{Au(III)}\) pincer complexes has rather unexpectedly shown that thiols are capable of cleaving one of the pincer Au-C bonds, followed by a reductive elimination process and formation of aryl thioethers. The reaction follows second-order kinetics. Displacement of the N-donor is required to access an intermediate with the conformational flexibility necessary to initiate the C···S bond forming step. Au-C cleavage with thiols proceeds independently of thiol acidity, since there is no reaction with other acidic reagents. The reaction sheds light on the likely fate of \((\text{C}^\text{N}^\text{C})\text{Au-based cytotoxic reagents under physiological conditions, such as in the presence of glutathione. With other gold starting materials (C^N^C)AuR (R = Me, aryl or alkynyl), the same thiol-treatment protocol leads to selective C-C rather than C-S bond formation, with rates decreasing in the order R = aryl > Me >> alkynyl.}

**Experimental**

**General Considerations.** When specified, manipulations were performed by using standard Schlenk line techniques under dry \(\text{N}_2\) or in a MBraun Unilab glovebox with a high capacity recirculator (<1.0 ppm
O₂ and H₂O). All solvents were dried by means of the appropriate drying agent and distilled. CD₂Cl₂ was stored in the glovebox over activated 4 Å molecular sieves. (C^N^py^C)AuCl (1a),²⁵ (C^N^py^C)AuCl (1b),¹⁴b (C^N^pz^C)AuCl (1c),²⁵ (C^N^C)AuCl (1d),¹⁴b (C^N^C)AuMe (2a),²⁶ (C^N^C)Au(p-C₆H₄F) (2b),²⁶ [AgC≡CC₆H₄–3-OMe]₂ and [H(OEt)₂][H₂N(B(C₆F₅)₃)₂] (HAB₂)²¹ were synthesized according to literature procedures.

¹H, ¹H PGSE, ¹⁹F, ¹³C{¹H}, ¹H, ¹³C HMQC and ¹H, ¹³C HMBC NMR experiments were recorded on a Bruker DPX–300 spectrometer equipped with a ¹H,BB smartprobe and Z-gradients. ¹H NMR spectra are referenced to the residual protons of the deuterated solvent. ¹³C NMR spectra are referenced to the D-coupled ¹³C signals of the solvent.

Synthesis and characterisation

Under a N₂ atmosphere, (C^N^py^C)AuCl 1a (40.0 mg, 0.070 mmol) and potassium t-butoxide (9.4 mg, 0.084 mmol), were suspended in 5 mL of dry toluene in a Schlenk tube and stirred for 3 h. 1-Adamantanethiol (11.7 mg, 0.070 mmol) was added and reaction was stirred for a further 3 h. The solvent was removed under vacuum to give a solid with was dissolved in dichloromethane in air and passed through a Celite plug. The solution was evaporated to dryness and washed with light petroleum to give 2a as a bright yellow solid (45 mg, 0.059 mmol, 91%). ¹H NMR (CD₂Cl₂, 300.13 MHz, 298 K): δ 8.46 (d, 4J_H–H = 2.0 Hz, 2 H, H₈), 7.83 (t, 3J_H–H = 8.0 Hz, 1 H, H¹), 7.54 (d, 3J_H–H = 8.1 Hz, 2 H, H⁵), 7.47 (d, 3J_H–H = 8.0 Hz, 2 H, H²), 7.27 (dd, 3J_H–H = 8.1 Hz, 4J_H–H = 2.0 Hz, 2 H, H⁶), 2.14 (bd, 3J_H–H = 2.4 Hz, 6 H, H¹¹), 1.92 (bs, 3 H, H¹²), 1.61 (s, 6 H, H¹³), 1.39 (s, 18 H, tBu). ¹³C{¹H} NMR (CD₂Cl₂, 75.48 MHz, 298 K): δ 171.6 (s, C⁴), 164.0 (s, C³), 154.8 (s, C⁷), 147.4 (s, C⁹), 142.6 (s, C⁵), 134.1 (s, C⁸), 125.0 (s, C⁵), 123.8 (s, C⁸), 116.6 (s, C⁷), 50.2 (s, C¹¹), 48.5 (s, C¹⁰), 36.7 (s, C¹³), 35.9 (s, C(CH₃)₃), 31.4 (s, C(CH₃)₃), 31.2 (s, C¹²).
In situ synthesis. Under a N₂ atmosphere, a J-Young NMR tube was charged with (C^Npy^C)AuCl 1a (5 mg, 0.0087 mmol) and AdSH (4.4 mg, 0.026 mmol) in CD₂Cl₂ (0.6 mL). The tube was sealed and the reaction monitored by ¹H NMR spectroscopy. Over the period of 3 hours, the reaction went to completion and the fading of the yellow colour of (C^Npy^C)AuCl was observed to give a clear solution.

Bulk synthesis. Under a N₂ atmosphere, a Schlenk tube was charged with 1a (0.030 g, 0.052 mmol) and AdSH (0.018 g, 0.105 mmol), which were then dissolved in 5 mL of dry dichloromethane (5 mL). The reaction was stirred at room temperature for 4 h until the solution turned from yellow to colourless. The solvent was removed under vacuum, light petroleum (5 mL) was added and the suspension filtered. The solvent was removed to give 3a as a white solid (0.025 g, 94 %). TOF MS ASAP+: m/z [3a+H]^+ 510.3194 (calc. 510.3195). The spectrum displays the expected isotopic pattern. ¹H NMR (CD₂Cl₂, 300.13 MHz, 298 K): δ 7.98 (d, ³J_H-H = 8.4 Hz, 2 H, H⁵'), 7.76 (t, ³J_H-H = 7.7 Hz, 1 H, H¹), 7.68 (overlapped s, 1 H, H⁸), 7.67 (overlapped d, 1 H, H²'), 7.61 (d, ³J_H-H = 8.0 Hz, 1 H, H⁵), 7.5 (m, 4 H, H⁶⁺⁶⁺²'), 1.86 (br s, 3H, H₁²), 1.57 (br d, ³J_H-H = 1.4 Hz, 6 H, H¹¹), 1.51 (m, 6 H, H¹³), 1.39 (s, 9 H, tBu), 1.36 (s, 9 H, tBu'). ¹³C{¹H} NMR (CD₂Cl₂, 75.48 MHz, 298 K): δ 156.0 (s, C⁷'), 155.4 (s, C³), 154.5 (s, C⁷), 153.7 (s, C³'), 142.9 (s, C¹), 137.5 (s, C⁵), 136.1 (s, C⁴), 131.5 (s, C⁵), 130.7 (s, C⁶), 130.0 (s, C⁵'), 128.8 (s, C⁴'), 127.6 (s, C⁵'), 126.4 (s, C⁶⁺²'), 123.9 (s, C⁵'), 50.5 (s, C¹⁰), 44.0 (s, C¹¹), 36.2 (s, C¹³), 35.4 (s, CMe³'), 35.2 (s, CMe³), 31.3 (s, CMe³ + CMe³'), 30.5 (s, C¹²).
To a J. Young NMR tube charged with (C^N^2^+^C)AuCl 1b (5 mg, 0.0087 mmol) in CD$_2$Cl$_2$ (0.6 mL) was added AdSH (4.4 mg, 0.026 mmol). The tube was sealed and the reaction monitored by $^1$H NMR over 3 h until the reaction was complete forming 3b (100% by NMR) and [ClAuSAd]$_n$H$_m$. Over the course of the reaction the solution turned from bright yellow to a clear colourless solution. TOF MS ASAP+: m/z [3b+H]$^+$ 511.141 (calc. 511.3129). Spectrum displays the expected isotopic pattern. $^1$H NMR (CD$_2$Cl$_2$, 300.13 MHz, 298 K): δ 8.91 (s, 1 H, H$^3$), 8.89 (s, 1 H, H$^2$), 8.12 (d, $^3$J$_{H-H}$ = 8.6 Hz, 2 H, H$^5$), 7.81 (d, $^3$J$_{H-H}$ = 8.1 Hz, 1 H, H$^8$), 7.77 (d, $^4$J$_{H-H}$ = 1.8 Hz, 1 H, H$^6$), 7.65 (partially overlapped dd, $^3$J$_{H-H}$ = 8.1 Hz, $^4$J$_{H-H}$ = 1.8 Hz, 1 H, H$^7$), 7.63 (d, $^3$J$_{H-H}$ = 8.6 Hz, 1 H, H$^6$), 1.86 (bs, 3 H, H$^{13}$), 1.53 (d, $^3$J$_{H-H}$ = 1.8 Hz, 6 H, H$^{11}$), 1.47 (m, 6 H, H$^{13}$), 1.41 (s, 9 H, $^1$Bu), 1.38 (s, 9 H, $^1$Bu$'$). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 75.48 MHz, 298 K): δ 159.1 (s, C$^1$), 156.2 (s, C$^3$), 156.1 (s, C$^{3'}$), 154.7 (s, C$^7$), 138.9 (s, C$^6$), 137.7 (s, C$^8$), 134.4 (s, C$^5$), 131.5 (s, C$^{4'}$), 131.1 (s, C$^5$), 128.9 (s, C$^6$), 127.8 (s, C$^{13}$), 127.4 (s, C$^5$), 127.3 (s, C$^6$), 127.0 (s, C$^{10}$), 51.2 (s, C$^{11}$), 43.9 (s, C$^{13}$), 36.2 (s, CMe$^3$'), 35.2 (s, CMe$^3$), 31.2 (s, CMe$^5$ + CMe$^5$').

A J-Young’s NMR tube was charged with 2a (5 mg, 0.0071 mmol), HAB$_2$ (8.4 mg, 0.0071 mmol) and CD$_2$Cl$_2$ (0.6 mL). The reaction monitored by $^1$H NMR spectroscopy for 11 d until no further changes were observed. Crystals of 6 suitable for X-ray crystallography were obtained from a CD$_2$Cl$_2$ solution. $^1$H NMR (CD$_2$Cl$_2$, 300.13 MHz, 263 K): δ 8.33 (t, $^3$J$_{H-H}$ = 7.7 Hz, 1 H, H$^1$), 8.05 (dd, $^3$J$_{H-H}$ = 8.0 Hz, $^4$J$_{H-H}$ = 0.7 Hz, 1 H, H$^2$), 7.80-7.50 (br m, 4 H, H$^5$+6$^+$+8$^+$+9$^+$), 7.79 (dd, $^3$J$_{H-H}$ = 7.7 Hz, $^4$J$_{H-H}$ = 0.9 Hz, 1 H, H$^3$), 7.68 (d, $^3$J$_{H-H}$ = 8.3 Hz, 1 H, H$^2$), 7.57 (dd, $^3$J$_{H-H}$ = 8.2 Hz, $^4$J$_{H-H}$ = 1.3 Hz, 1 H, H$^6$), 7.00 (d, $^4$J$_{H-H}$ = 1.2 Hz, 1 H, H$^8$), 2.34 (d, $^2$J$_{H-H}$ = 11.2 Hz, 3 H, H$^{11}$), 2.16 (br s, 3 H, H$^{12}$), 2.08 (d, $^2$J$_{H-H}$ = 11.4 Hz, 3 H, H$^{11}$), 1.78 (m, 3 H, H$^{13}$), 1.58 (m, 3 H, H$^{13}$), 1.40 (s, 9 H, $^1$Bu), 1.18 (s, 9 H, $^1$Bu$'$).

$^1$H NMR (CD$_2$Cl$_2$, 300.13 MHz, 263 K): δ 8.33 (t, $^3$J$_{H-H}$ = 8.0 Hz, 1 H, H$^1$), 8.04 (d, $^3$J$_{H-H}$ = 8.0 Hz, 1 H, H$^2$), 7.88 (d, $^3$J$_{H-H}$ = 7.8 Hz, 1 H, H$^3$), 7.78 (d, $^3$J$_{H-H}$ = 7.7 Hz, 1 H, H$^2$), 7.70 (d, $^3$J$_{H-H}$ = 8.2 Hz, 1 H, H$^8$), 7.67 (d, $^3$J$_{H-H}$ = 8.5 Hz, 1 H, H$^6$), 7.55 (d, $^3$J$_{H-H}$ = 8.1 Hz, 1 H, H$^6$), 7.47 (br s, 2 H, H$^{5+6'}$), 6.94 (s, 1 H, H$^1$).
$^1$H NMR (CD$_2$Cl$_2$, 300.13 MHz, 298 K): $\delta$ 8.17 (d, $^3J_{H-H} = 2.0$ Hz, 2 H, H$^8$), 7.85 (t, $^3J_{H-H} = 8.0$ Hz, 1 H, H$^1$), 7.54 (d, $^3J_{H-H} = 8.2$ Hz, 2 H, H$^5$), 7.44 (d, $^3J_{H-H} = 8.0$ Hz, 2 H, H$^2$), 7.32 (d, $^3J_{H-H} = 8.2$ Hz, $^4J_{H-H} = 2.0$ Hz, 2 H, H$^6$), 7.26 (dd, $^3J_{H-H} = 8.0$ Hz, 1 H, H$^{16}$), 7.19 (d psiud t, $^3J_{H-H} = 7.6$ Hz, $^4J_{H-H} = 1.1$ Hz, 1 H, H$^{17}$), 7.14 (brm, 1 H, H$^{15}$), 6.87 (dd, $^3J_{H-H} = 8.0$ Hz, $^4J_{H-H} = 2.4$ Hz, $^4J_{H-H} = 1.1$ Hz, 1 H, H$^{15}$), 3.84 (s, 3 H, O-Me), 1.39 (s, 18 H, t-Bu). $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$, 75.48 MHz, 298 K): $\delta$ 167.3 (s, C$^9$), 165.2 (s, C$^3$), 159.8 (s, C$^{14}$), 155.6 (s, C$^7$), 147.0 (s, C$^4$), 142.7 (s, C$^1$), 133.7 (s, C$^8$), 129.6 (s, C$^{16}$), 128.1 (s, C$^{12}$), 125.4 (s, C$^5$), 124.7 (s, C$^{17}$), 124.3 (s, C$^6$), 116.8
(s, C\(^{13}\)), 116.7 (s, C\(^2\)), 114.0 (s, C\(^{15}\)), 101.4 (s, C\(^{11}\)), 92.7 (s, O-CH\(_3\)) 35.7 (s, C(CH\(_3\))\(_3\)), 31.3 (s, C(CH\(_3\))\(_3\)).

\[\text{[(C\(^\text{N}\text{N}\text{C})\text{AuEt}_2\text{O})[\text{AB}_2\text{]}]}\] 14 was obtained as a transient species upon protodeauration of 5 mg of 13 with 9.1 mg of HAB\(_2\). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 300.13 MHz, 298 K): \(\delta\) 7.96 (t, \(^3J_{H-H} = 8.0\) Hz, 1 H, H\(^1\)), 7.56 (d, \(^3J_{H-H} = 8.2\) Hz, 2 H, H\(^3\)), 7.47 (d, \(^3J_{H-H} = 1.6\) Hz, 1 H, H\(^6\)), 7.44 (d, \(^3J_{H-H} = 8.0\) Hz, 2 H, H\(^5\)), 7.43 (dd, \(^3J_{H-H} = 8.1\) Hz, \(^4J_{H-H} = 1.6\) Hz, 2 H, H\(^8\)), 7.93 (ps, \(^3J_{H-F/H-H} = 8.0\) Hz, 2 H, phenol H), 6.78 (m, 2 H, phenol H), 4.68 (q, \(^3J_{H-H} = 7.0\) Hz, 4 H, Et), 4.68 (t, \(^3J_{H-H} = 7.0\) Hz, 6 H, Et), 1.37 (s, 18 H, tBu).

Under an N\(_2\) atmosphere a flask was charged with 1a (0.050 g, 0.087 mmol), carbazole (0.015 g, 0.087 mmol) and KOBu\(_t\) (0.029 g, 0.26 mmol). Dry toluene (5 mL) was added and reaction was stirred at 60 °C for 16 h. The solution was filtered through Celite and evaporated to dryness, then washed with light petroleum. The pure product 15 was isolated as a orange powder (0.036 g, 59.1 %). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 300.13 MHz, 298 K): \(\delta\) 8.18 (d, \(^3J_{H-H} = 7.4\) Hz, 2 H, H\(^{14}\)), 7.94 (t, \(^3J_{H-H} = 8.0\) Hz, 1 H, H\(^1\)), 7.58 (d, \(^3J_{H-H} = 8.2\) Hz, 2 H, H\(^3\)), 7.53 (d, \(^3J_{H-H} = 8.0\) Hz, 2 H, H\(^5\)), 7.49 (d, \(^3J_{H-H} = 8.3\) Hz, 2 H, H\(^{11}\)), 7.25 (m, 4 H, H\(^{6+12}\)), 7.11 (pseudo triplet, \(^3J_{H-H} = 7.4\) Hz, 2 H, H\(^{15}\)), 6.93 (d, \(^3J_{H-H} = 1.8\) Hz, 2 H, H\(^9\)), 0.96 (s, 18 H, tBu).

\(^{13}\)C\(^{1}\)H NMR (CD\(_2\)Cl\(_2\), 75.48 MHz, 298 K): \(\delta\) 168.5 (s, C\(^i\)), 165.6 (s, C\(^3\)), 155.4 (s, C\(^7\)), 146.2 (s, C\(^{10}\)), 146.2 (s, C\(^9\)), 143.4 (s, C\(^1\)), 133.1 (s, C\(^8\)), 125.3 (s, C\(^{15}\)), 125.2 (s, C\(^5\)), 124.4 (s, C\(^{6+12}\)), 124.3 (s, C\(^{6+12}\)), 120.0 (s, C\(^{14}\)), 117.2 (s, C\(^{13}\)), 116.8 (s, C\(^2\)), 35.2 (s, C(CH\(_3\))\(_3\)), 30.8 (s, C(CH\(_3\))\(_3\)).
16 was synthesised from 15 using the general procedure for protodeauration, starting from 5 mg of 15. The species decomposed over 3 h. $^1$H NMR (CD$_2$Cl$_2$, 300.13 MHz, 298 K): $\delta$ 8.21 (d, $^3$J$_{H-H}$ = 7.5 Hz, 2 H, H$^{14}$), 7.98 (t, $^3$J$_{H-H}$ = 8.0 Hz, 1 H, H$^1$), 7.90 (d, $^3$J$_{H-H}$ = 7.9 Hz, 2 H, H$^{11}$), 7.76 (m, 3 H, H$^{5+13}$), 7.60 (m, 5 H, H$^{8+6+12+2}$), 7.41 (m, 3 H, H$^{2+5'}$), 7.12 (dd, $^3$J$_{H-H}$ = 8.2 Hz, $^4$J$_{H-H}$ = 1.8 Hz, 1 H, H$^6$), 5.62 (d, $^4$J$_{H-H}$ = 1.0 Hz, 1 H, H$^8$), 3.49 (brs, 12 H, CH$_2$(OEt$_2$)), 1.17 (t, $^3$J$_{H-H}$ = 7.1 Hz, 18 H, CH$_3$(OEt$_2$)), 1.41 (s, 9 H, 'Bu), 0.91 (s, 9 H, 'Bu').

General procedure for reductive elimination investigations

Under a nitrogen atmosphere a J-Young NMR tube was charged with 5 mg of the desired gold complex and 0.6 ml of CD$_2$Cl$_2$. An initial $^1$H NMR spectrum was acquired. 4.0 molar equivalents of AdSH were added and the reaction was monitored by $^1$H NMR spectroscopy until formation of the coupling product was complete.

Starting from 7, complete reductive elimination to 10 was observed after 24 days (yield 100% by NMR). No side products were observed. $^1$H NMR (CD$_2$Cl$_2$, 300.13 MHz, 298 K): $\delta$ 8.02 (d, $^3$J$_{H-H}$ = 8.5 Hz, 2 H, H$^5$), 7.81 (t, $^3$J$_{H-H}$ = 7.8 Hz, 1 H, H$^1$), 7.70 (dd, $^3$J$_{H-H}$ = 7.9 Hz, $^4$J$_{H-H}$ = 0.9 Hz, 1 H, H$^{2+2'}$), 7.50 (d, $^3$J$_{H-H}$ = 8.5 Hz, 2 H, H$^6$), 7.40 (d, $^3$J$_{H-H}$ = 7.8 Hz, 1 H, H$^7$), 7.33 (m, 3 H, H$^{2+2'}$ + H$^6$ + H$^8$), 2.46 (s, 3 H, H$^{10}$), 1.37 (s, 9 H, 'Bu/’Bu'), 1.36 (s, 9 H, 'Bu/’Bu').
Starting from 8, complete reductive elimination to 11 was observed after 6 days. Only the C-C coupling product was observed (yield 100% by NMR). No side products were observed. $^1$H NMR (CD$_2$Cl$_2$, 300.13 MHz, 298 K): $\delta$ 7.79 (d, $^3J_{H-H} = 8.4$ Hz, 2 H, H$^5$), 7.68 (d, $^3J_{H-H} = 8.1$ Hz, 1 H, H$^3$), 7.56 (m, 2 H, H$^1$ + H$^2$), 7.53 (dd, $^3J_{H-H} = 8.1$ Hz, $^4J_{H-H} = 1.9$ Hz, 1 H, H$^6$), 7.45 (m, 3 H, H$^6$ + H$^8$), 7.45 (m, 2 H, H$^{11}$), 6.96 (m, 3 H, H$^2$ + H$^{12}$), 1.40 (s, 9 H, tBu), 1.35 (s, 9 H, tBu$'$).

$^19$F NMR (CD$_2$Cl$_2$, 282.36 MHz, 298K): $\delta$ -117.2 (br, p–F).

The alkynyl complex 9 reacts slowly, giving 50 % conversion to 12 after 6 months. $^1$H NMR (CD$_2$Cl$_2$, 300.13 MHz, 298 K): $\delta$ 8.08 (d, $^3J_{H-H} = 8.5$ Hz, 2 H, H$^5$), 7.85 (m, 3 H, H$^1$ + H$^2$ + H$^5$), 7.75 (dd, $^3J_{H-H} = 7.5$ Hz, $^4J_{H-H} = 1.2$ Hz, 1 H, H$^2$), 7.72 (d, $^4J_{H-H} = 1.8$ Hz, 1 H, H$^6$), 7.54 (dd, $^3J_{H-H} = 8.4$ Hz, $^4J_{H-H} = 1.8$ Hz, 1 H, H$^8$), 7.48 (d, $^3J_{H-H} = 8.5$ Hz, 2 H, H$^6$), 7.20 (pseudo t, $^3J_{H-H} = 7.9$ Hz, 1 H, H$^{16}$), 6.98 (d pseudo t, $^3J_{H-H} = 7.5$ Hz, $^4J_{H-H} = 1.1$ Hz, 1 H, H$^1$), 6.89 (brm, 1 H, H$^{13}$), 6.85 (ddd, $^3J_{H-H} = 8.5$ Hz, $^4J_{H-H} = 2.5$ Hz, $^4J_{H-H} = 0.9$ Hz, 1 H, H$^{15}$), 3.71 (s, 3 H, O-Me), 1.40 (s, 9 H, tBu), 1.36 (s, 9 H, tBu$'$). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 75.48 MHz, 298 K): $\delta$ 159.8 (s, C$^{14}$), 157.6 (s, C$^{33}$), 156.9 (s, C$^{33}$), 152.5 (s, C$^7$), 151.8 (s, C$^7$), 140.2 (s, C$^4$), 136.9 (s, C$^3$), 136.8 (s, C$^3$), 130.6 (s, C$^8$), 130.0 (s, C$^8$), 129.7 (s, C$^{16}$), 126.9 (s, C$^5$), 126.5 (s, C$^6$), 126.0 (s, C$^6$), 124.8 (s, C$^{12}$), 124.2 (s, C$^{17}$), 122.5 (s, C$^5$), 121.1 (s, C$^6$), 118.7 (s, C$^2$), 116.4 (s, C$^{13}$), 115.2 (s, C$^{15}$), 92.0 (s, C$^{11}$), 90.0 (s, C$^{10}$), 55.5 (s, O-Me), 34.9 (s, CMe$_3$ + CMe$_3$), 31.5 (s, CMe$_3$), 31.3 (s, CMe$_3$). MS Cl+: m/z [M+H]$^+$ 474.3 (calc. 474.3).
Kinetic investigations

1a/b (0.005 g, 0.0087 mmol) was dissolved in dry CD$_2$Cl$_2$ (0.6 mL) in a J-Young NMR tube and an initial $^1$H NMR spectrum was recorded to lock and shim the sample. In the open air, 1-AdSH (at varying concentrations) was added to the NMR tube and the reaction was followed by $^1$H NMR spectroscopy. Concentrations were determined by relative integration to an external standard. The spectra were processed and the normalized concentration of 1a/b was monitored over the course of the reaction by comparing the intensity of $t$-butyl signal with the spectrum at t = 0.

X-ray crystallographic analysis of compound 6. Crystal data: C$_{70}$H$_{86}$N$_2$S$_2$Au$_2$, 2(C$_{36}$H$_2$B$_2$NF$_30$), 2‘O’. M = 3525.47. Triclinic, space group P-1 (no. 2), a = 15.0100(8), b = 15.8427(8), c = 16.5234(7) Å, α = 70.367(4), β = 84.345(4), γ = 70.653(5) °, V = 3491.5(3) Å$^3$. Z = 2, Dc = 1.677 g cm$^{-3}$, F(000) = 1736, T = 295(1) K, μ(Mo-Kα) = 22.6 cm$^{-1}$, λ(Mo-Kα) = 0.71073 Å.

Crystals are large colourless blocks. A fragment of one, ca 0.19 x 0.10 x 0.07 mm, was fixed in oil on a glass fibre and mounted on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-Kα radiation and graphite monochromator. Intensity data were measured by thin-slice ω- and φ-scans. Total no. of reflections recorded, to θ$_{max}$ = 22.5°, was 37382 of which 9083 were unique (R$_{int}$ = 0.122); 6857 were ‘observed’ with I > 2σ$_i$. Data were processed using the CrysAlisPro-CCD and RED (1) programs. The structure was determined by the intrinsic phasing routines in the SHELXT program and refined by full-matrix least-squares methods, on F$^2$’s, in SHELXL. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their U$_{iso}$ values were set to ride on the U$_{eq}$ values of the parent carbon and nitrogen atoms. Two persistent difference peaks in the ‘solvent void’ were assigned as half-occupancy oxygen atoms, but were not fully resolved. At the conclusion of the refinement, wR$_2$ = 0.132 and R$_1$ = 0.093 (2B) for all 9083 reflections weighted w = [σ$^2$(F$_o^2$) + (0.0402P$^2$)]$^{1/2}$ with P = (F$_o^2$ + 2F$_c^2$)/3; for the ‘observed’ data only, R$_1$ = 0.065. In the final difference map, the highest peak (ca 1.2 eÅ$^{-3}$) was near to C(12). Scattering factors for neutral atoms were taken from reference 30. Computer programs used in this analysis have been noted above, and were run through WinGX on a Dell Optiplex 780 PC at the University of East Anglia.

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Conflicts of interest

There are no conflicts to declare.

†Electronic supplementary information (ESI) available: Experimental details, Crystal structure diagrams, NMR spectra. See DOI: 10.1039/xxxxxx. CCDC code: 1818966 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Thiols were found to cleave Au-C bonds in (C^N^C)gold(III) pincer complexes and to induce C-S reductive elimination reactions, to give aryl thioethers.