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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 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 SMe_2 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 $[\{(C^N\text{-}CH)Au(\mu\text{-}SAd)\}_2]^{2+}$ 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

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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**).[12] Reductive S-S elimination from Au(III) thiolates has also been observed.[13]

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.[14] Apart from a general interest in C^N^C-type pincer ligands to prevent reductive processes in gold(III) compounds[15] and as a means to supporting highly reactive gold(III) species,[16] the origin of this work on thiolates was the fact that gold carbene complexes supported by such pincer ligands show interesting anti-cancer activities.[17,18]. 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.[17] 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.[19] 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.

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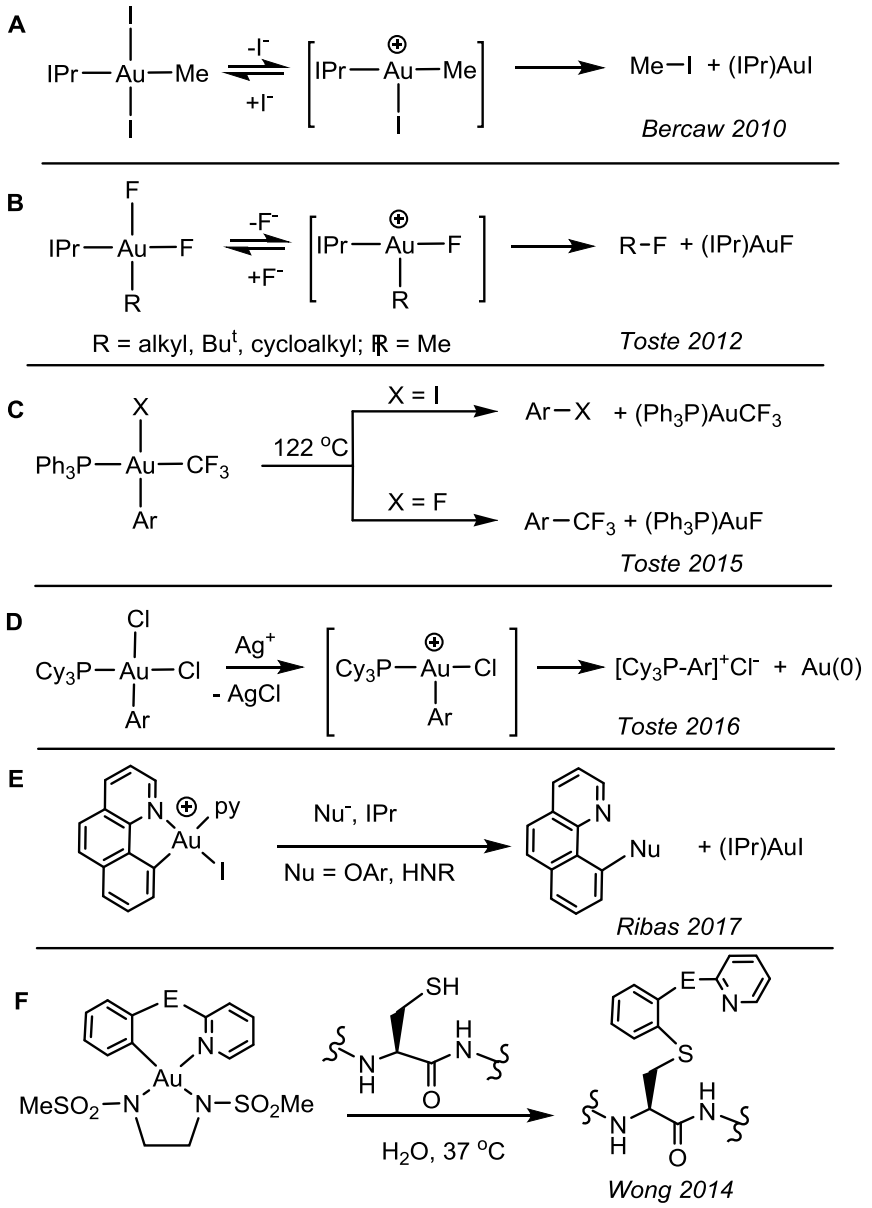

Scheme 1. Formation of C-heteroatom bonds by reductive elimination from gold(III) precursors.[3,4,6,7,12]

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).

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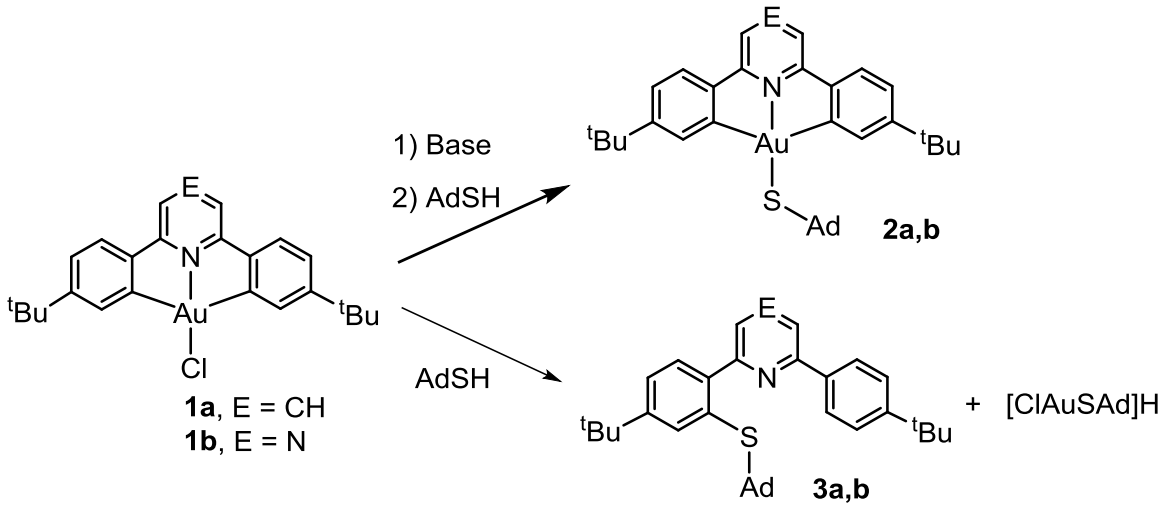

Scheme 2

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, $-d[\mathbf{1a}]/dt = k[\mathbf{1a}][AdSH]$, 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.

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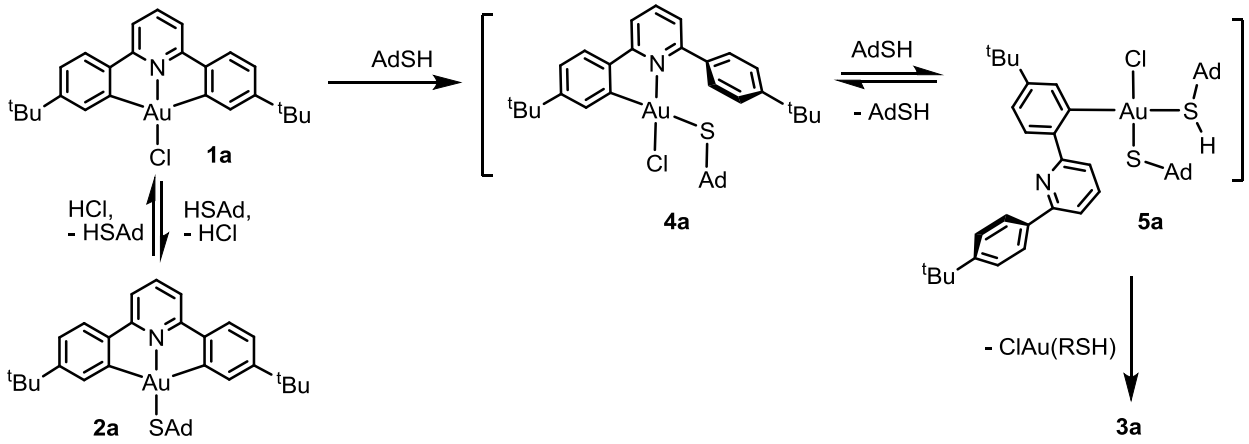
However, this reaction led to the instantaneous regeneration of the chloride **1a**, together with the release of AdSH. The mixture then evolved as described before, to give **3a** in 50% yield. It can be assumed therefore that a reversible chloride/thiolate exchange takes place, which explains why **2a** 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]

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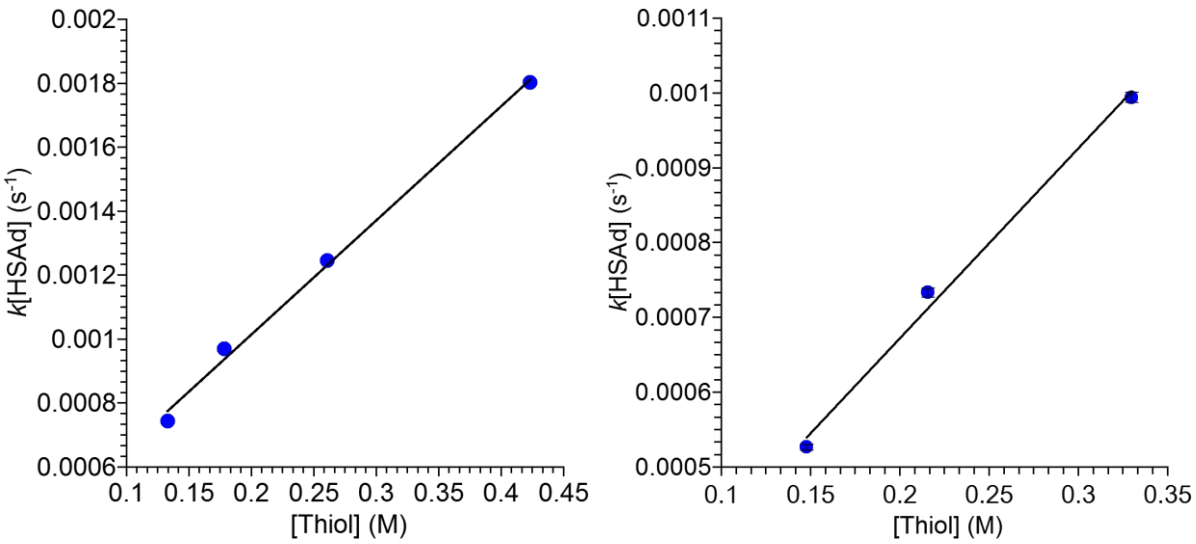

Fig. 1. Dependence of the rate of consumption of **1a** (left) and **1b** (right) on the thiol concentration (CD_2Cl_2, 25 °C).

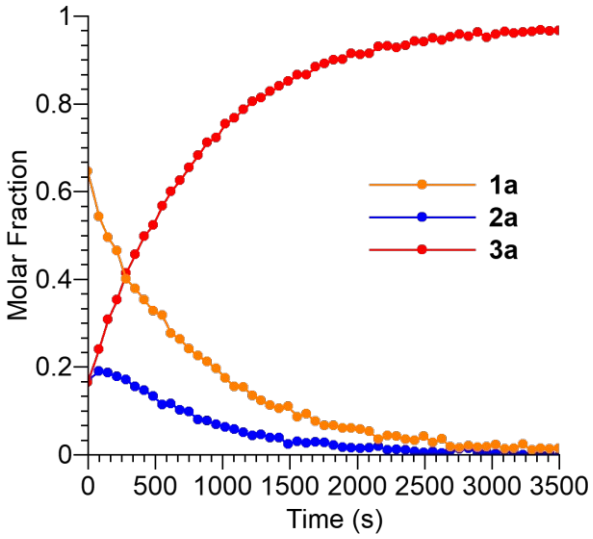

Fig. 2. Product distribution of the reaction of **1a** with AdSH as a function of time (CD_2Cl_2, 25 °C).

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 $[H(OEt_2)_2]^+$-$[H_2N\{B(C_6F_5)_3\}_2]$[21] ("HAB_2") to C^N^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

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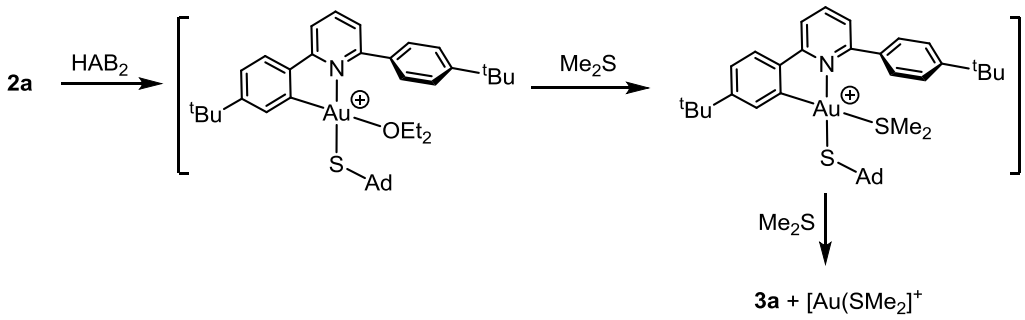
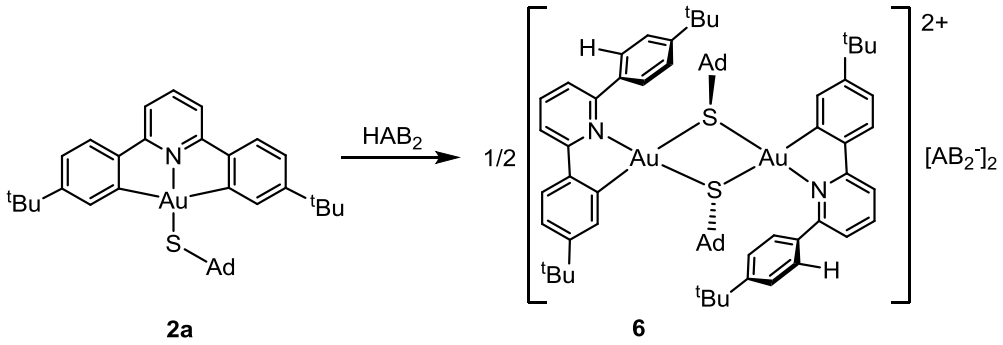
formation of **3a**, together with $[Au(SMe_2)_2]^+$.[23] The reaction rate increased with increasing SMe_2 concentration (Scheme 4).



Scheme 4. Reductive C-S elimination induced by a proton / SMe_2 combination.

Monitoring the reaction of HAB_2 with **2a** in the *absence* of SMe_2 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.



Scheme 5. Synthesis of **6**.

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 $[NH_2\{B(C_6F_5)_3\}_2]^-$ 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

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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 Au_2S_2 plane, with Au–S(1)–C(1) angles of 103.2(3) and 98.9(3) °.

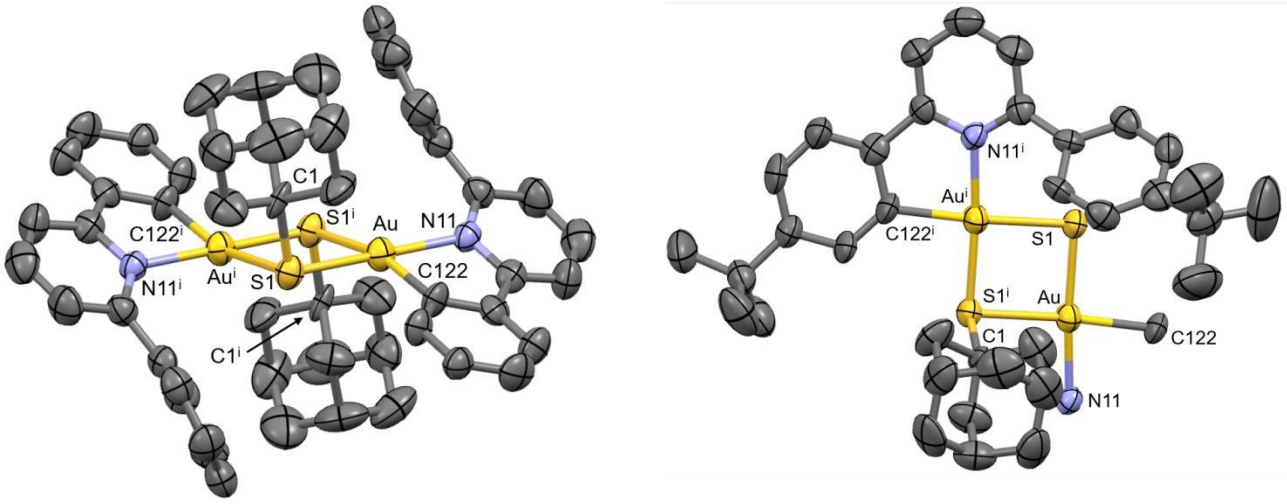

Fig. 3. Side and (partial) top view of the cation in **6**. Left: H atoms, *tert*.-butyl groups and anions are omitted for clarity. Ellipsoids are drawn at 50%. Selected bond distances [Å] and angles [°]:Au-C(122) 2.066(8), Au-N(11) 2.108(7), Au-S(1) 2.323(2), Au-S(1)#1 2.469(2), S(1)-C(1) 1.880(9);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

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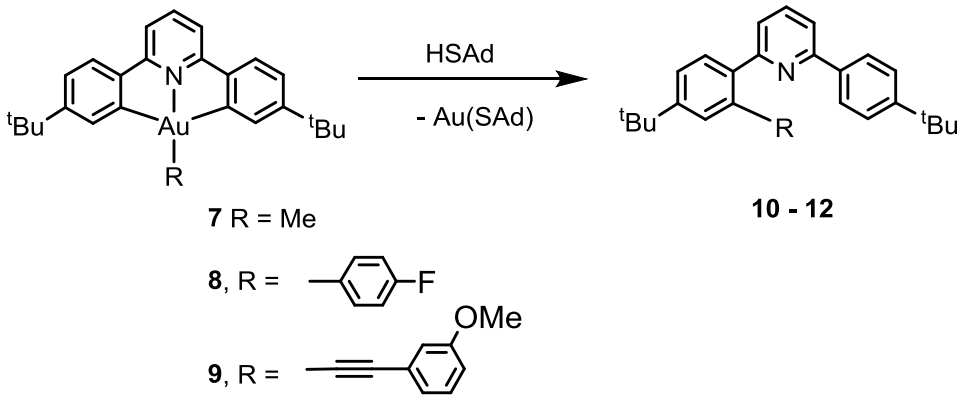
the alkynyl complex **9** is also observed, over a period of months, to give **12**. The trend in the rates of C-C bond formation under these conditions therefore follows the order aryl-aryl > aryl-methyl >> aryl-alkynyl.



Scheme 6. Thiol-triggered reductive elimination of $C(sp^2)$-$C(sp^3)$, $C(sp^2)$-$C(sp^2)$ and $C(sp^2)$-C(sp) bonds.

The HAB_2/SMe_2 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 HAB_2 to the phenolate **13**[24] gave the ether complex **14**, without Au-C cleavage. On the other hand, addition of HAB_2 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**/HAB_2 but slightly faster.[22] However, addition of SMe_2 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).

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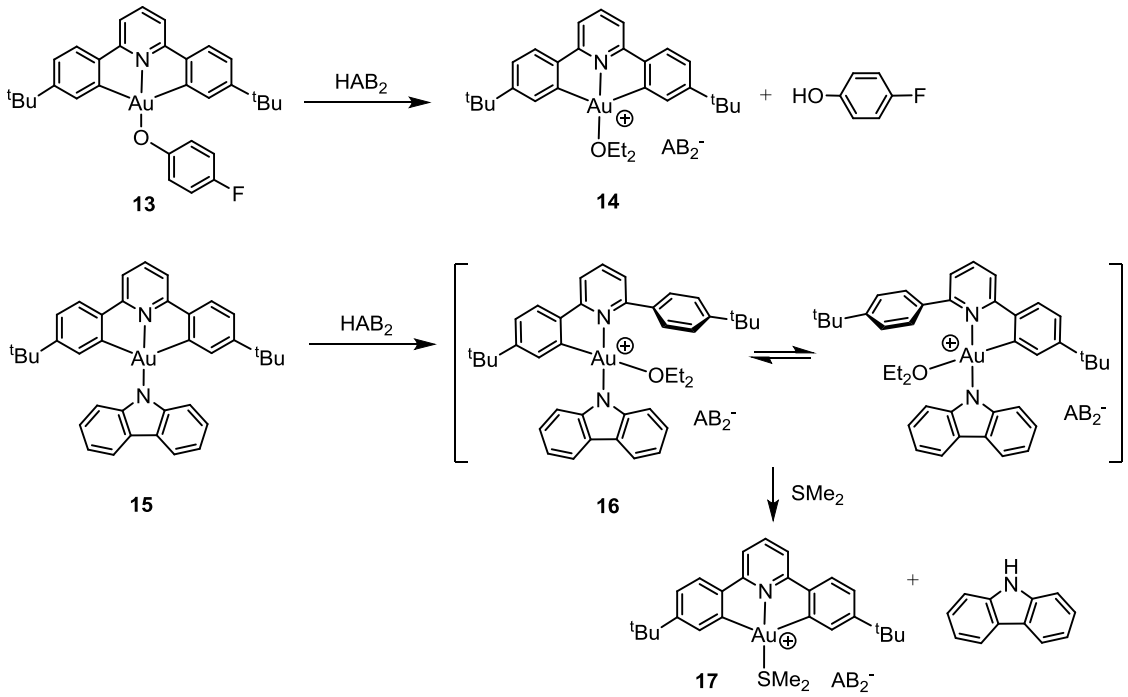

Scheme 7. Reactions of gold(III) phenolates and carbazolates with H^+/SMe_2.

Conclusion.

The reaction of (C^N^C)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 (C^N^C)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 N_2 or in a MBraun Unilab glovebox with a high capacity recirculator (<1.0 ppm

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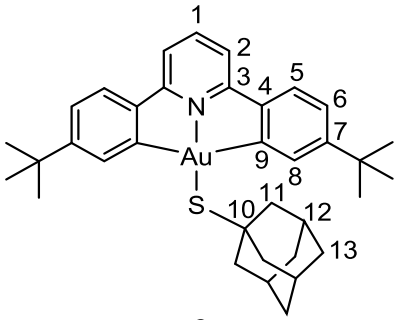
O_2 and H_2O). All solvents were dried by means of the appropriate drying agent and distilled. CD_2Cl_2 was stored in the glovebox over activated 4 Å molecular sieves. (C^N^{py}^C)AuCl (**1a**),[25] (C^N^{pz}^C)AuCl (**1b**),[14b] (C^N^C)AuMe (**7**),[26] (C^N^C)Au(*p*–C_6H_4F) (**8**),[26] (C^N^C)AuOC_6H_5 (**10**),[24] [AgC≡CC_6H_4-3-OMe]$_n$[27] and [H(OEt_2)$_2$][H_2N(B(C_6F_5)$_3$)$_2$] (HAB_2)[21] were synthesized according to literature procedures. ^{1}H, ^{1}H PGSE, ^{19}F, ^{13}C{^{1}H}, ^{1}H NOESY, ^{1}H,^{13}C HMQC and ^{1}H,^{13}C HMBC NMR experiments were recorded on a Bruker DPX–300 spectrometer equipped with a ^{1}H,BB smartprobe and Z-gradients. ^{1}H NMR spectra are referenced to the residual protons of the deuterated solvent. ^{13}C NMR spectra are referenced to the D-coupled ^{13}C signals of the solvent.

Synthesis and characterisation



2a

Under a N_2 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 %). ^{1}H NMR (CD_2Cl_2, 300.13 MHz, 298 K): δ 8.46 (d, $^4J_{H\text{-}H}$ = 2.0 Hz, 2 H, H^8), 7.83 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 1 H, H^1), 7.54 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 2 H, H^5), 7.47 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2 H, H^2), 7.27 (dd, $^3J_{H\text{-}H}$ = 8.1 Hz, $^4J_{H\text{-}H}$ = 2.0 Hz, 2 H, H^6), 2.14 (bd, $^3J_{H\text{-}H}$ = 2.4 Hz, 6 H, H^{11}), 1.92 (bs, 3 H, H^{12}), 1.61 (s, 6 H, H^{13}), 1.39 (s, 18 H, ^{t}Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.48 MHz, 298 K): δ 171.6 (s, *C*^{4}), 164.0 (s, *C*^{3}), 154.8 (s, *C*^{7}), 147.4 (s, *C*^{9}), 142.6 (s, *C*^{1}), 134.1 (s, *C*^{8}), 125.0 (s, *C*^{5}), 123.8 (s, *C*^{6}), 116.6 (s, *C*^{2}), 50.2 (s, *C*^{11}), 48.5 (s, *C*^{10}), 36.7 (s, *C*^{13}), 35.9 (s, *C*(CH_3)$_3$), 31.4 (s, C(*C*H_3)$_3$), 31.2 (s, *C*^{12}).

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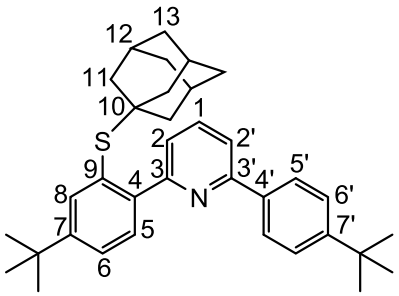
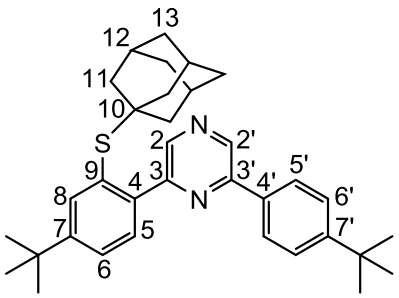


3a

In situ synthesis. Under a N_2 atmosphere, a J-Young NMR tube was charged with (C^N^{py}^C)AuCl **1a** (5 mg, 0.0087 mmol) and AdSH (4.4 mg, 0.026 mmol) in CD_2Cl_2 (0.6 mL). The tube was sealed and the reaction monitored by ^{1}H NMR spectroscopy. Over the period of 3 hours, the reaction went to completion and the fading of the yellow colour of (C^N^{py}^C)AuCl was observed to give a clear solution.

Bulk synthesis. Under a N_2 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.^{1}H NMR (CD_2Cl_2, 300.13 MHz, 298 K): δ 7.98 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 2 H, H$^{5'}$), 7.76 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 1 H, H^1), 7.68 (overlapped s, 1 H, H^8), 7.67 (overlapped d, 1 H, H$^{2'}$), 7.61 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 1 H, H^5), 7.5 (m, 4 H, H$^{6+6'+2}$), 1.86 (br s, 3H, H^{12}), 1.57 (br d, $^3J_{H\text{-}H}$ = 1.4 Hz, 6 H, H^{11}), 1.51 (m, 6 H, H^{13}), 1.39 (s, 9 H, ^{t}Bu), 1.36 (s, 9 H, ^{t}Bu'). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.48 MHz, 298 K): δ 156.0 (s, *C*$^{7'}$), 155.4 (s, *C*^{3}), 154.5 (s, *C*^{7}), 153.7 (s, *C*$^{3'}$), 142.9 (s, *C*^{1}), 137.5 (s, *C*^{8}), 136.1 (s, *C*^{4}), 131.5 (s, *C*^{5}), 130.7 (s, *C*^{9}), 130.0 (s, *C*$^{5'}$), 128.8 (s, *C*$^{4'}$), 127.6 (s, *C*^{2}), 126.4 (s, *C*$^{6+6'}$), 123.9 (s, *C*$^{2'}$), 50.5 (s, *C*^{10}), 44.0 (s, *C*^{11}), 36.2 (s, *C*^{13}), 35.4 (s, *C*Me$_3$'), 35.2 (s, *C*Me$_3$), 31.3 (s, C*Me*$_3$ + C*Me*$_3$'), 30.5 (s, *C*^{12}).



3b

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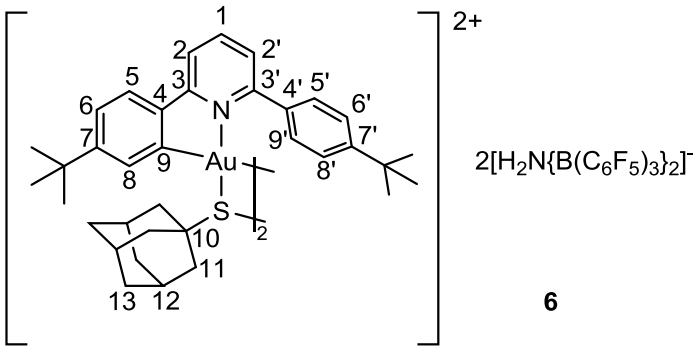
To a J. Young NMR tube charged with (C^N^{pz}^C)AuCl **1b** (5 mg, 0.0087 mmol) in CD_2Cl_2 (0.6 mL) was added AdSH (4.4 mg, 0.026 mmol). The tube was sealed and the reaction monitored by ^{1}H NMR over 3 h until the reaction was complete forming **3b** (100% by NMR) and $[ClAuSAd]_nH_n$. Over the course 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_2Cl_2, 300.13 MHz, 298 K): δ 8.91 (s, 1 H, H^2), 8.89 (s, 1 H, H$^{2'}$), 8.12 (d, $^3J_{H-H}$ = 8.6 Hz, 2 H, H$^{5'}$), 7.81 (d, $^3J_{H-H}$ = 8.1 Hz, 1 H, H^5), 7.77 (d, $^4J_{H-H}$ = 1.8 Hz, 1 H, H^8), 7.65 (partially overlapped dd, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 1.8 Hz, 1 H, H^6), 7.63 (d, $^3J_{H-H}$ = 8.6 Hz, 1 H, H$^{6'}$), 1.86 (bs, 3 H, H^{12}), 1.53 (d, $^3J_{H-H}$ = 1.8 Hz, 6 H, H^{11}), 1.47 (m, 6 H, H^{13}), 1.41 (s, 9 H, ^{t}Bu), 1.38 (s, 9 H, ^{t}Bu'). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.48 MHz, 298 K): δ 159.1 (s, *C*$^{3/3'}$), 156.2 (s, *C*$^{3/3'/7'}$), 156.1 (s, *C*$^{3/3'/7'}$), 154.7 (s, *C*^{7}), 138.9 (s, *C*^{4}), 137.7 (s, *C*^{8}), 134.4 (s, *C*^{2}), 131.5 (s, *C*$^{4'}$), 131.1 (s, *C*^{5}), 128.9 (s, *C*^{9}), 127.8 (s, *C*$^{2'}$), 127.4 (s, *C*$^{5'}$), 127.3 (s, *C*^{6}), 127.0 (s, *C*$^{6'}$), 51.2 (s, *C*^{10}), 43.9 (s, *C*^{11}), 36.2 (s, *C*^{13}), 35.4 (s, *C*Me$_3$'), 35.2 (s, *C*Me$_3$), 31.2 (s, C*Me*$_3$ + C*Me*$_3$'), 30.5 (s, *C*^{12}).



6

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_2Cl_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_2Cl_2 solution. ^{1}H NMR (CD_2Cl_2, 300.13 MHz, 298 K): δ 8.33 (t, $^3J_{H-H}$ = 7.7 Hz, 1 H, H^1), 8.05 (dd, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 0.7 Hz, 1 H, H^2), 7.80-7.50 (br m, 4 H, H$^{5'+6'+8'+9'}$), 7.79 (dd, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 0.9 Hz, 1 H, H$^{2'}$), 7.68 (d, $^3J_{H-H}$ = 8.3 Hz, 1 H, H^5), 7.57 (dd, $^3J_{H-H}$ = 8.2 Hz, $^4J_{H-H}$ = 1.3 Hz, 1 H, H^6), 7.00 (d, $^4J_{H-H}$ = 1.2 Hz, 1 H, H^8), 2.34 (d, $^2J_{H-H}$ = 11.2 Hz, 3 H, H^{11}), 2.16 (br s, 3 H, H^{12}), 2.08 (d, $^2J_{H-H}$ = 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, ^{t}Bu), 1.18 (s, 9 H, ^{t}Bu').

^{1}H NMR (CD_2Cl_2, 300.13 MHz, 263 K): δ 8.33 (t, $^3J_{H-H}$ = 8.0 Hz, 1 H, H^1), 8.04 (d, $^3J_{H-H}$ = 8.0 Hz, 1 H, H^2), 7.88 (d, $^3J_{H-H}$ = 7.8 Hz, 1 H, H$^{9'}$), 7.78 (d, $^3J_{H-H}$ = 7.7 Hz, 1 H, H$^{2'}$), 7.70 (d, $^3J_{H-H}$ = 8.2 Hz, 1 H, H$^{8'}$), 7.67 (d, $^3J_{H-H}$ = 8.5 Hz, 1 H, H^5), 7.55 (d, $^3J_{H-H}$ = 8.1 Hz, 1 H, H^6), 7.47 (br s, 2 H, H$^{5'+6'}$), 6.94 (s, 1 H,

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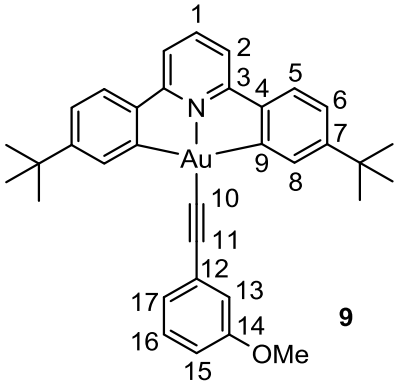
H^8), 2.31 (d, $^2J_{H\text{-}H}$ = 11.4 Hz, 3 H, H^{11}), 2.14 (br s, 3 H, H^{12}), 2.01 (d, $^2J_{H\text{-}H}$ = 10.9 Hz, 3 H, H^{11}), 1.74 (d, $^2J_{H\text{-}H}$ = 14.9 Hz, 3 H, H^{13}), 1.55 (d, $^2J_{H\text{-}H}$ = 14.9 Hz, 3 H, H^{13}), 1.36 (s, 9 H, ^{t}Bu), 1.14 (s, 9 H, ^{t}Bu' +Et_2O signal).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.48 MHz, 298 K): δ 162.8 (s, C^3), 161.3 (s, C^9), 160.5 (s, $C^{3'}$), 157.8 (s, $C^{7'}$), 157.3 (s, C^7), 148.2 (brd, $^1J_{C\text{-}F}$ = 243.8 Hz, *o*-*C*-F $H_2N[B(C_6F_5)_3]_2^-$), 144.8 (s, C^1), 139.5 (brd, $^1J_{C\text{-}F}$ = 246.1 Hz, *p*-*C*-F $H_2N[B(C_6F_5)_3]_2^-$), 139.3 (s, C^4), 137.0 (brd, $^1J_{C\text{-}F}$ = 248.3 Hz, *m*-*C*-F $H_2N[B(C_6F_5)_3]_2^-$), 135.3 (br s, C^{Anion}), 134.4 (s, $C^{4'}$), 129.2 (s, C^6), 128.7 (s, C^5), 128.3 (s, C^{Aryl}), 127.4 (s, C^{Aryl}), 127.0 (s, $C^{2'}$), 125.9 (s, C^8), 120.6 (s, C^2), 69.9 (s, C^2) 49.2 (s, C^{11}), 37.0 (s, CMe_3), 35.5 (s, CMe_3'), 35.4 (s, C^{13}), 31.7 (s, C^{12}), 31.3 (s, CMe_3), 30.1 (s, CMe_3').

Addition of dimethyl sulfide (4 μL, 0.0034 mmol) to a solution of **6** in a J-Young NMR tube gave **3a**. Over the course of the 4 h the solution changed from yellow to colourless.



9

A flask was charged with **1a** (40.0 mg, 0.070 mmol), $[AgC{\equiv}CC_6H_4\text{-}3\text{-}OMe]_n$ (50.2 mg, 0.210 mmol) and dichloromethane (10 mL). The reaction was stirred in the dark for 21 d. The solution was filtered through Celite and evaporated to dryness giving a solid which washed with light petroleum. The pure product **9** was isolated as a light yellow powder (0.024 g, 51 %). ^1H NMR (CD_2Cl_2, 300.13 MHz, 298 K): δ 8.17 (d, $^3J_{H\text{-}H}$ = 2.0 Hz, 2 H, H^8), 7.85 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 1 H, H^1), 7.54 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 2 H, H^5), 7.44 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2 H, H^2), 7.32 (dd, $^3J_{H\text{-}H}$ = 8.2 Hz, $^4J_{H\text{-}H}$ = 2.0 Hz, 2 H, H^6), 7.26 (dd, $^3J_{H\text{-}H}$ = 8.0 Hz, 1 H, H^{16}), 7.19 (d psudu t, $^3J_{H\text{-}H}$ = 7.6 Hz, $^4J_{H\text{-}H}$ = 1.1 Hz, 1 H, H^{17}), 7.14 (brm, 1 H, H^{13}), 6.87 (ddd, $^3J_{H\text{-}H}$ = 8.0 Hz, $^4J_{H\text{-}H}$ = 2.4 Hz, $^4J_{H\text{-}H}$ = 1.1 Hz, 1 H, H^{15}), 3.84 (s, 3 H, O-*Me*), 1.39 (s, 18 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.48 MHz, 298 K): δ 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

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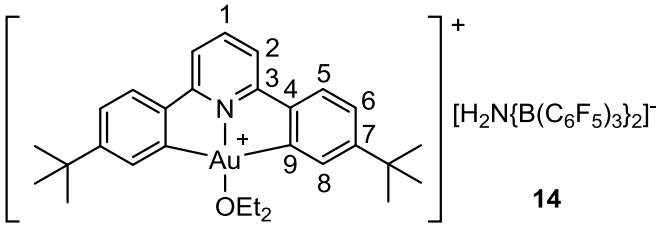
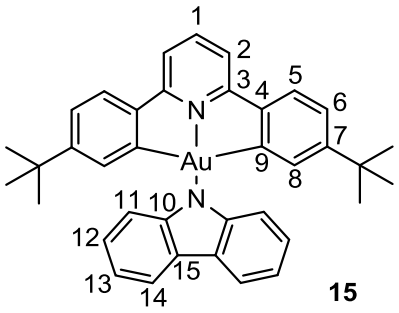
(s, C^{13}), 116.7 (s, C^{2}), 114.0 (s, C^{15}), 101.4 (s, C^{11}), 92.7 (s, C^{10}), 55.5 (s, O-CH_3) 35.7 (s, $C(CH_3)_3$), 31.3 (s, $C(CH_3)_3$).



14

[(C^N^C)AuEt$_2$O][AB$_2$] **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_2Cl_2, 300.13 MHz, 298 K): δ 7.96 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 1 H, H^1), 7.56 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 2 H, H^5), 7.47 (d, $^4J_{H\text{-}H}$ = 1.6 Hz, 1 H, H^8), 7.44 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2 H, H^2), 7.43 (dd, $^3J_{H\text{-}H}$ = 8.1 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz, 2 H, H^6), 7.93 (pst, $^3J_{H\text{-}F/H\text{-}H}$ = 8.0 Hz, 2 H, phenol H), 6.78 (m, 2 H, phenol H), 4.68 (q, $^3J_{H\text{-}H}$ = 7.0 Hz, 4 H, Et), 4.68 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 6 H, Et), 1.37 (s, 18 H, ^{t}Bu).



15

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_2Cl_2, 300.13 MHz, 298 K): δ 8.18 (d, $^3J_{H\text{-}H}$ = 7.4 Hz, 2 H, H^{14}), 7.94 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 1 H, H^1), 7.58 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 2 H, H^5), 7.53 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2 H, H^2), 7.49 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2 H, H^{11}), 7.25 (m, 4 H, H^{6+12}), 7.11 (pseudo triplet, $^3J_{H\text{-}H}$ = 7.4 Hz, 2 H, H^{13}), 6.93 (d, $^4J_{H\text{-}H}$ = 1.8 Hz, 2 H, H^8), 0.96 (s, 18 H, ^{t}Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.48 MHz, 298 K): δ 168.5 (s, C^4), 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, $C(CH_3)_3$).

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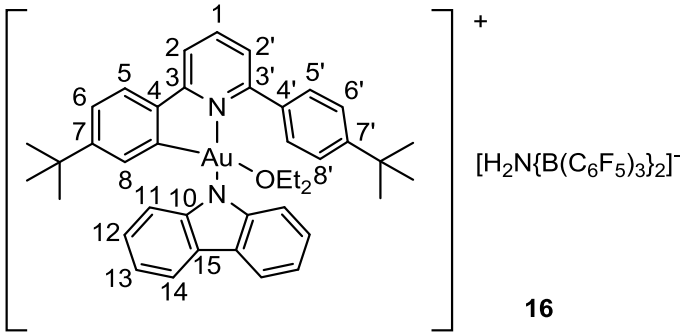
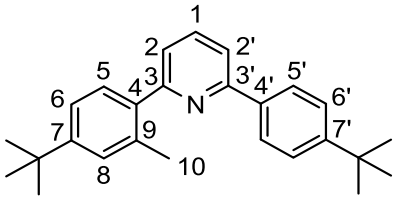


16 was synthesised from **15** using the general procedure for protodeauration, starting from 5 mg of **15**. The species decomposed over 3 h. ^{1}H NMR (CD_2Cl_2, 300.13 MHz, 298 K): δ 8.21 (d, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 2 H, H^{14}), 7.98 (t, $^{3}J_{H\text{-}H}$ = 8.0 Hz, 1 H, H^{1}), 7.90 (d, $^{3}J_{H\text{-}H}$ = 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, $^{3}J_{H\text{-}H}$ = 8.2 Hz, $^{4}J_{H\text{-}H}$ = 1.8 Hz, 1 H, $H^{6'}$), 5.62 (d, $^{4}J_{H\text{-}H}$ = 1.0 Hz, 1 H, $H^{8'}$), 3.49 (brs, 12 H, CH_2 (OEt_2)), 1.17 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 18 H, CH_3 (OEt_2)), 1.41 (s, 9 H, ^{t}Bu), 0.91 (s, 9 H, ^{t}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_2Cl_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_2Cl_2, 300.13 MHz, 298 K): δ 8.02 (d, $^{3}J_{H\text{-}H}$ = 8.5 Hz, 2 H, $H^{5'}$), 7.81 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 1 H, H^{1}), 7.70 (dd, $^{3}J_{H\text{-}H}$ = 7.9 Hz, $^{4}J_{H\text{-}H}$ = 0.9 Hz,1 H, $H^{2/2'}$), 7.50 (d, $^{3}J_{H\text{-}H}$ = 8.5 Hz, 2 H, $H^{6'}$), 7.40 (d, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 1 H, H^{5}),7.33 (m, 3 H, $H^{2/2'}$ + H^{6} + H^{8}), 2.46 (s, 3 H, H^{10}) , 1.37 (s, 9 H, ^{t}Bu/ ^{t}Bu'), 1.36 (s, 9 H, ^{t}Bu/^{t}Bu').

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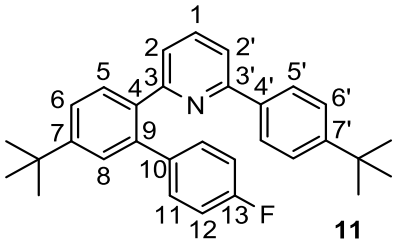
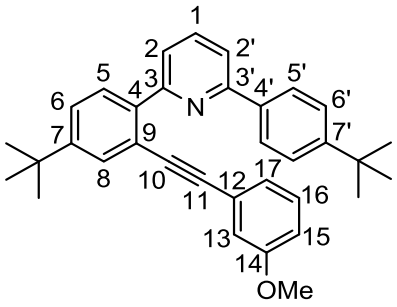


11

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_2Cl_2, 300.13 MHz, 298 K): δ 7.79 (d, $^{3}J_{H\text{-}H}$ = 8.4 Hz, 2 H, $H^{5'}$), 7.68 (d, $^{3}J_{H\text{-}H}$ = 8.1 Hz,1 H, H^{5}), 7.56 (m, 2 H, H^{1} + $H^{2'}$), 7.53 (dd, $^{3}J_{H\text{-}H}$ = 8.1 Hz, $^{4}J_{H\text{-}H}$ = 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, ^{t}Bu), 1.35 (s, 9 H, ^{t}Bu'). ^{19}F NMR (CD_2Cl_2, 282.36 MHz, 298K): δ -117.2 (br, *p*–F).



12

The alkynyl complex **9** reacts slowly, giving 50 % conversion to **12** after 6 months. ^{1}H NMR (CD_2Cl_2, 300.13 MHz, 298 K): δ 8.08 (d, $^{3}J_{H\text{-}H}$ = 8.5 Hz, 2 H, $H^{5'}$), 7.85 (m, 3 H, H^{1} + H^{2} + H^{5}), 7.75 (dd, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{4}J_{H\text{-}H}$ = 1.2 Hz, 1 H, $H^{2'}$), 7.72 (d, $^{4}J_{H\text{-}H}$ = 1.8 Hz, 1 H, H^{8}), 7.54 (dd, $^{3}J_{H\text{-}H}$ = 8.4 Hz, $^{4}J_{H\text{-}H}$ = 1.8 Hz, 1 H, H^{6}), 7.48 (d, $^{3}J_{H\text{-}H}$ = 8.5 Hz, 2 H, $H^{6'}$), 7.20 (pseudo t, $^{3}J_{H\text{-}H}$ = 7.9 Hz, 1 H, H^{16}), 6.98 (d pseudo t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, $^{4}J_{H\text{-}H}$ = 1.1 Hz, 1 H, H^{17}), 6.89 (brm, 1 H, H^{13}), 6.85 (ddd, $^{3}J_{H\text{-}H}$ = 8.5 Hz, $^{4}J_{H\text{-}H}$ = 2.5 Hz, $^{4}J_{H\text{-}H}$ = 0.9 Hz, 1 H, H^{15}), 3.71 (s, 3 H, O-*Me*), 1.40 (s, 9 H, ^{t}Bu), 1.36 (s, 9 H, ^{t}Bu'). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.48 MHz, 298 K): δ 159.8 (s, C^{14}), 157.6 (s, $C^{3/3'}$), 156.9 (s, $C^{3/3'}$), 152.5 (s, $C^{7'}$), 151.8 (s, C^{7}), 140.2 (s, C^{4}), 136.9 (s, $C^{4'}$), 136.8 (s, C^{1}), 130.6 (s, C^{8}), 130.0 (s, C^{5}), 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^{2}), 121.1 (s, C^{9}), 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, *C*Me$_3$' + *C*Me$_3$), 31.5 (s, C*Me*$_3$), 31.3 (s, C*Me*$_3$'). MS CI+: m/z $[M+H]^+$ 474.3 (calc. 474.3).

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Kinetic investigations

1a/b (0.005 g, 0.0087 mmol) was dissolved in dry CD_2Cl_2 (0.6 mL) in a J-Young NMR tube and an initial ^1H 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 ^1H 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:* $C_{70}H_{86}N_2S_2Au_2$, $2(C_{36}H_2B_2NF_{30})$, 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 $I > 2\sigma_I$. Data were processed using the CrysAlisPro-CCD and -RED (1) programs.[28] The structure was determined by the intrinsic phasing routines in the SHELXT program[27] and refined by full-matrix least-squares methods, on F^2's, in SHELXL.[29] 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 $w = [\sigma^2(F_o^2) + (0.0402P)^2]^{-1}$ 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[31] on a Dell Optiplex 780 PC at the University of East Anglia.

Acknowledgement

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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.

References

1 (a) M. N. Hopkinson, A. D. Gee, and V. Gouverneur, *Chem. Eur. J*. 2011, **17**, 8248; (b) H. A. Wegner and M. Auzias, *Angew. Chem. Int. Ed*. 2011, **50**, 8236.

2 M. Joost, A. Amgoune, and D. Bourissou, *Angew. Chem. Int. Ed*. 2015, **54**, 15022.

3 V. J. Scott, J. A. Labinger, and J. E. Bercaw, *Organometallics* 2010, **29**, 4090.

4 (a) N. P. Mankad and F. D. Toste, *Chem. Sci*., 2012, **3**, 72; (b) M. S. Winston, W. J. Wolf, and F. D. Toste, *J. Am. Chem. Soc*. 2015, **137**, 7921.

5 (a) A. Nijamudheen, S. Karmakar, and A. Datta, *Chem. Eur. J*. 2014, **20**, 14650; (b) R.Bhattacharjee, A. Nijamudheen, and A. Datta, *Chem. Eur. J*. 2017, **23**, 4169.

6 H. Kawai, W. J. Wolf, A. G. Di Pasquale, M. S. Winston, and F. D. Toste, *J. Am. Chem. Soc*. 2016, **138**, 587.

7 (a) S. Lavy, J. J. Miller, M. Pažický, A.-S. Rodrigues, F. Rominger, C. Jäkel, D. Serra, N. Vinokurov, and M. Limbach, *Adv. Synth. Catal*. 2010, **352**, 2993; (b) J. Serra, T. Parella and X. Ribas, *Chem. Sci*., 2017, **8**, 946.

8 (a) G. Mann, D. Baranano, J. F. Hartwig, A. L. Rheingold, and I. A. Guzei, *J. Am. Chem. Soc*. 1998, **120**, 9205; (b) E. Alvaro, J. F. Hartwig, *J. Am. Chem. Soc*. 2009, **131**, 7858; (c) M. Platon, N. Wijaya, V. Rampazzi, L.-C. Cui, Y. Rousselin, M. Saeys, and J. C. Hierso, *Chem. Eur. J*. 2014, **20**, 12584; (d) M. Cong, Y. T. Fan, J. M. Raimundo, Y. Xia, Y. Liu, G. Quelever, F. Q. Qu, and L. Peng,

View Article Online
DOI: 10.1039/C8DT00906F

Chem. Eur. J. 2013, **19**, 17267; (e) M. Iwasaki, M. Iyanaga, Y. Tsuchiya, Y. Nishimura, W. J. Li, Z. P. Li, and Y. Nishihara, *Chem. Eur. J.* 2014, **20**, 2459; (f) X.-S. Zhang, G. X. Li, X.-G. Zhang and X.-H. Zhang, *Tetrahedron* 2015, **71**, 5458; (g) D. D. Xu, X. T. Qi, M. Duan, Z. Y. Yu, L. Zhu, C. H. Shan, X. Y. Yue, R. P. Bai and Y. Lan, *Org. Chem. Front*. 2017, **4**, 943.

9 Reviews: (a) C. C. Eichman and J. P. Stambuli, *Molecules* 2011, **16**, 590; (b) Z. J. Qiao and X. F. Jiang, *Org. Biomol. Chem*. 2017, **15**, 1942.

10 S. D. Timpa, C. J. Pell and O. V. Ozerov, *J. Am. Chem. Soc*. 2014, **136**, 14772.

11 Y. Yang, W. Hou, L.-H. Qin, J.-J. Du, H.-J. Feng, B. Zhou, and Y.-C. Li, *Chem. Eur. J.* 2014, **20**, 416.

12 K. K.-Y. Kung, H.-M. Ko, J.-F. Cui, H.-C. Chong, Y.-C. Leung and M.-K. Wong, *Chem. Commun.*, 2014, **50**, 11899.

13 R. E. Bachman, S. A. Bodolosky-Bettis, C. J. Pyle, and M. A. Gray, *J. Am. Chem. Soc*. 2008, **130**, 14303.

14 (a) L. Currie, J. Fernandez-Cestau, L. Rocchigiani, B. Bertrand, S. J. Lancaster, D. L. Hughes, H. Duckworth, S. T. E. Jones, D. Credgington, T. J. Penfold and M. Bochmann, *Chem Eur. J.* 2017, **23**, 105; (b) J. Fernandez-Cestau, B. Bertrand, M. Blaya, G. A. Jones, T. J. Penfold and M. Bochmann, *Chem. Commun*. 2015, **51**, 16629.

15 Reviews: (a) D.-A. Roşca, J. A. Wright and M. Bochmann, *Dalton Transactions* 2015, **44**, 20785; (b) R. Kumar and C. Nevado, *Angew. Chem. Int. Ed*. 2017, **56**, 1994.

16 (a) D.-A. Roşca, D. A. Smith, D. L. Hughes and M. Bochmann, *Angew. Chem. Int. Ed*. 2012, **51**, 10643. (b) N. Savjani, D.-A. Roşca, M. Schormann and M. Bochmann, *Angew. Chem. Int. Ed.* 2013, **52**, 874. (c) D.-A. Roşca, J. Fernandez-Cestau, J. Morris, J. A. Wright and M. Bochmann, *Science Adv*. 2015, **1**, e1500761. (d) A. Pintus, L. Rocchigiani, J. Fernandez-Cestau, P. H. M. Budzelaar, and M. Bochmann, *Angew. Chem. Int. Ed.* 2016, **55**, 12321. (e) L. Rocchigiani, J. Fernandez-Cestau, G. Agonigi, I. Chambrier P. H. M. Budzelaar, M. Bochmann, *Angew. Chem. Int. Ed*. 2017, **56**, 13861.

17 (a) B. Bertrand, J. Fernandez-Cestau, J. Angulo, M. M. D. Cominetti, Z. A. E. Waller, M. Searcey, M. A. O'Connell and M. Bochmann, *Inorg. Chem*. 2017, **56**, 5728. (b) B. Bertrand, M. A. O'Connell, Z. A. E. Waller and M. Bochmann, *Chem Eur. J.* 2018, **24**, 3613.

View Article Online
DOI: 10.1039/C8DT00906F

18 M. Williams, A. I. Green, J. Fernandez-Cestau, D. L. Hughes, M. A. O'Connell, M. Searcey, B. Bertrand and M. Bochmann, *Dalton Trans.*, 2017,**46**, 13397.

19 T. Zou, C. T. Lum, S. S.-Y. Chui, and C.-M. Che, *Angew. Chem. Int. Ed*. 2013, **52**, 2930.

20 (a) J. Vicente, M. Dolores Bermúdez, J. Escribano, M. P. Carrillo, and P. G. Jones, *J. Chem. Soc., Dalton Trans.* 1990, 3083; (b) J. Vicente, M. Dolores Bermúdez, and J. Escribano, *Organometallics* 1991, **10**, 3380.

21 S. J. Lancaster, A. Rodriguez, A. Lara-Sanchez, M. D. Hannant, D. A. Walker, D. L. Hughes and M. Bochmann, *Organometallics* 2002, **21**, 451.

22 L. Rocchigiani, J. Fernandez-Cestau, P.H.M. Budzelaar, and M. Bochmann, *Chem. Commun*., 2017, **53**, 4358.

23 N. Savjani, S. Bew, D. L. Hughes, S. J. Lancaster, and M. Bochmann, *Organometallics* 2012, **31**, 2534.

24 I. Chambrier, D.-A. Roşca, J. Fernandez-Cestau, D. L. Hughes, P. H. M. Budzelaar, and M. Bochmann, *Organometallics* 2017, **36**, 1358.

25 K.-H. Wong, K.-K. Cheung, M. C.-W. Chan, and C.–M. Che, *Organometallics* 1998, **17**, 3505.

26 D. A. Smith, D.-A. Roşca, M. Bochmann, *Organometallics* 2012, **31**, 5988.

27 J. Fernández-Cestau, N. Giménez, E. Lalinde, P. Montaño, M. T. Moreno, S. Sánchez, M. D. Weber and R. D. Costa, *Dalton Trans*. 2016, **45**, 3251.

28 Programs CrysAlisPro, Oxford Diffraction Ltd., Abingdon, UK (2014).

29 G. M. Sheldrick, SHELX-97 – Programs for crystal structure determination (SHELXT) and refinement (SHELXL), *Acta Cryst.* 2008, **A64**, 112; 2015, **A71**, 3, and 2015, **C71**, 3.

30 *'International Tables for X-ray Crystallography'*, Kluwer Academic Publishers, Dordrecht 1992, vol. C, pp. 500, 219 and 193.

31 L. J. Farrugia, *J. Appl. Cryst.* 2012, **45**, 849.

View Article Online
DOI: 10.1039/C8DT00906F

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.