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Synthesis and catalytic applications of 1,2,3-triazolylidene gold(1) complexes in silver-free oxazoline syntheses and C-H bond activation†

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A series of novel 1,2,3-triazolylidene gold(i) chloride complexes have been synthesised and fully characterised. Silver-free methodologies for chloride ion abstraction of these complexes were evaluated for their potential as Au-based catalyst precursors. Using simple potassium salts or MeOTf as chloride scavengers produced metal complexes that catalyse both the regioselective synthesis of oxazolines and the C-H activation of benzene or styrene for carbene transfer from ethyl diazoacetate. These results indicate that Ag-free activation of 1,2,3-triazolylidene gold(i) chloride complexes is feasible for the generation of catalytically active Au triazolylidene species. However, silver-mediated activation imparts substantially higher catalytic activity in oxazoline synthesis.

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Introduction

Homogeneous catalysts comprised of gold as the active centre have enjoyed increased attention in recent years as more and more unique reactivity patterns have been revealed. In particular, ligation by N-heterocyclic carbenes (NHCs) as for example in AuCl(IPr) (IPr = N,N'-bis(2,6-diisopropylphenyl)imidazolylidene) imparted exceptionally high catalytic activity, 1k , which spurred widespread efforts in this burgeoning area of catalysis. In comparison to classical, imidazole-derived NHCs, structurally related 1,2,3-triazolylidene (trz) ligands have been significantly less studied as ligands in gold chemistry. The triazole framework offers several benefits when compared with NHCs, including, for example, the ease of functional group incorporation, 3a,5 increased σ-donation compared to classical

We have recently demonstrated the non-innocent behaviour of silver(i) salts when activating 1,2,3-triazolylidene gold complexes. Specifically, silver mediated carbene transfer reactions have been demonstrated, likely *via* a reverse carbene transfer from gold(i) to silver(i). Considering the significant complications arising from such ligand transfer, we

NHCs, 3,6 and a mesoionic resonance form which is able to potentially stabilise different metal oxidation states.7 Catalytic activity in carbene gold complexes has typically been instigated by using a silver(1) salt as halide scavenger for catalyst activation.8 However, Ag+ can be a non-innocent activator in many Au-catalysed transformations, and often plays an active (and not always beneficial) role in the catalytic cycle. 1d,9 Current trends in Au catalysis are therefore focusing on using Ag-free protocols to avoid any undesired side-reactions. For example, pre-activation and subsequent silver salt removal from a stable cationic gold(1) complex as catalyst precursor has been described by Gagosz¹⁰ Echavarren, 11 and others. 12 Also, the use of a gold(1) hydroxide13 or acetate14 pre-catalyst in lieu of gold(1) chloride complexes has also been shown to be an effective method to avoid the necessity of silver salts for catalyst activation. Several approaches towards Ag-free activation have been probed, though almost none are based on simple and inexpensive (commercial) salts. Thus, the in situ generation of active gold(1) catalysts has been explored by using Lewis acids as activators such as metal triflates, 15 and alkali metal salts of borates, 4a,16 to name a few. 17 However, with the exception of Cu(OTf)₂ (OTf = CF₃SO₃), the activators are typically non-commercial and customised salts.

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endeavoured to establish alternative procedures for the activation of AuCl(trz) complexes for catalytic bond activation purposes, which do not rely on Ag⁺ for chloride abstraction. Herein we demonstrate that simple potassium salts can be used to form catalytically active triazolylidene gold complexes. These methodologies are of further use for exploring the specific impact of triazolylidene ligands in gold(1)-mediated catalytic activity.

Results and discussion

Synthesis of triazolylidene gold complexes

A set of novel triazolylidene gold complexes AuCl(trz) were synthesised as representative examples intending to probe ligand induced catalytic effects. The ligand precursor triazolium salts **1a-e** (Scheme 1) were readily available through copper(1)-catalysed [2 + 3] dipolar cycloaddition reactions and subsequent alkylation with either (Me₃O)BF₄, MeI, or MeOTf (OTf = SO₃CF₃⁻). Of note, triazolium **1b**, which contains a pendant acetate group was highly sensitive to hydrolysis and hence the alkylation of the triazole with MeOTf was performed at low temperature (below 0 °C). Subsequent storage of the triazolium salt 1b below -20 °C is paramount to avoid spontaneous degradation over time. Salt 1c was obtained in relatively low yields (about 30%) when compared to the other triazolium salts (≥79%), presumably because the electron withdrawing nature of the perfluorinated tail decreases the nucleophilicity of the triazole unit. The influence of the fluorocarbon unit is supported by the ¹H NMR chemical shifts for the NCH₂

X- R'-N\(\)	N-R" 2.	Ag ₂ O, NMe ₄ Cl AuCl(SMe ₂)	CI Au R'-N	R N N R"	
	R	R'	R"	х	yield of 2
a b c d e f	nBu CMe₂OAc nBu Ph Ph CMe₂OH	n Bu n Bu $(CH_2)_2C_6F_{13}$ adamantyl $2,6^{-}(I\!\!Pr)_2C_6H_3$ n Bu	Me Me (CH ₂) ₂ C ₆ F ₁₃ Me Me Me	BF ₄ OTf I OTf BF ₄	86% 78% 75% 77% 64% 88%

Scheme 1 Synthesis of triazolylidene gold(i) complexes 2.

signals, which are shifted downfield by 0.72 and 0.38 ppm, for N1 and N3 respectively, in comparison with the analogous protons of 1a. Moreover, the N-bound methylene group appears in the 13 C NMR spectrum as a triplet ($^{3}J_{CF} = 21$ Hz), indicating an interaction between the perfluorinated tail and the methylene group. In contrast, the ¹³C NMR chemical shifts do not show any significant variation due to the more electron withdrawing nature of the fluoro-chain.

The AuCl(trz) complexes were synthesised from the triazolium salts 1a-f using well established methodologies (Scheme 1).4g,18,19 Accordingly, treatment of the appropriate triazolium salt with Ag₂O vielded the corresponding carbene silver intermediate, which was not isolated and used in situ for transmetallation with AuCl(SMe2). To ensure that chlorido complexes were formed exclusively, all novel AuCl(trz) complexes were prepared from triazolium salts containing either a BF₄ or a OTf counterions, or alternatively by counterion exchange with AgBF4 directly before the reaction with Ag2O (for 1c). Only traces of triazolylidene silver intermediate were formed in the absence of a chloride source according to ¹H NMR spectroscopic monitoring of the reaction, while clean and essentially quantitative formation of the intermediate was observed in the presence of Me₄NCl. The subsequent transmetalation was straightforward and good yields ranging from 64-88% were obtained for all gold complexes 2a-f (see Experimental section).

Metallation of the hydroxyl-functionalised triazolium salt 1f gave a mixture of products, with ratios that were dependent on the reaction conditions. In the presence of an excess Ag₂O and in moist solvents, complex 2f was obtained in nearly 90% yield. Metallation of 1f under an atmosphere of dry nitrogen and substoichiometric amounts of Ag₂O afforded significant amounts (up to 46%) of complexes 2g and 2g' as the major products (Scheme 2). We have not been able to separate these two products preparatively, though fractional crystallisation afforded single crystals of pure 2g that were suitable for X-ray diffraction analysis (see below). Dissociation of the C-bound substituent in 2g and 2g' with formal loss of acetone was indicated by NMR spectroscopy. Two sets of resonances were observed, both featuring an additional resonance in the aromatic region and the disappearance of the two methyl groups of the wingtip unit of 1f. Integration of the ¹H NMR resonances of the NCH2 and NCH3 signals suggest a 5:4 ratio of 2g and 2g'. The spectroscopic assignment was based on long range ¹H-¹³C correlation spectroscopy (HMBC). Accordingly,

Scheme 2 Transmetallation of 1f and concurrent partial formal loss of acetone resulting in the formation of 2f, 2g, and 2g'.

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the NCH₃ group of the C4-metallated complex 2g resonantes at 4.20 ppm (cf. $\delta_{\rm H}$ = 4.17 ppm in the C5-metallated homologue 2g'), whereas the NCH2 group in 2g' appears at lower field than in 2g ($\delta_{\rm H}$ = 4.50 vs. 4.38 ppm) and provides the clearest spectroscopic distinction between the two isomers. The Ctrz-H resonance shift is essentially identical in both complexes and appears at 7.58 and 7.57 ppm, respectively. Similarly, the ¹³C NMR shifts of the two isomers are only marginally disparate. In agreement with the ¹H NMR data, the largest difference again pertains to the NCH₃ group ($\delta_{\rm C}$ = 42.1 and 38.8) and the NCH₂ group (δ_C = 52.5 and 55.4 for 2g and 2g', respectively). The resonances due to the CtrzH carbons were significantly upfield shifted ($\delta_{\rm C}$ = 134 ± 0.4) when compared to the normal 145-150 ppm range observed for C5-alkylated or -arylated triazolylidene gold complexes.

Formation of complexes 2g and 2g' may be rationalised by deprotonation of the hydroxyl group, which is followed by elimination of acetone from the ligand. The observation of isomers suggests that the ligand degraded before the triazolylidene silver intermediate is formed. Metallation of a C4,C5diprotonated triazolium salt is unselective and may thus account for the formation of a mixture of 2g and 2g'. The influence of Ag₂O was therefore investigated in more detail. Using various 1f/Ag₂O ratios (0.5, 1, 2) and monitoring of the triazolylidene silver complex formation indicated that higher equivalents of Ag₂O promoted the preservation of the wingtip group and hence promoted the formation of the silver intermediate that eventually leads to complex 2f, while sub-stoichiometric quantities of Ag₂O increased substituent degradation. The isomeric ratio of the unsubstituted triazolylidene silver complexes is independent of the quantity of silver salt (cf. Table S1†), remains unchanged over time, and is in good agreement with the final product distribution observed for formation of complexes 2g and 2g'. These data therefore suggest that wingtip degradation of the ligand occurs prior to transmetallation and that acetone elimination is a competitive process to triazolium Ctrz-H bond activation. Moreover, these results indicate that wingtip degradation only takes place from the triazolium salt, yet it is suppressed once the carbene silver precursor is formed. Otherwise, larger quantities of Ag₂O should

shift the isomeric ratio due to degradation of the silver precursor of 2f.

Characterisation of triazolylidene gold complexes

The 13C NMR spectra of all triazolylidene gold complexes feature a resonance in the 156-162 ppm range for the Aubound Ctrz nucleus, consistent with related triazolylidene gold complexes. 4,18-20 The carbenic carbon is most deshielded in complex 2e ($\delta_{\rm C}$ = 162.1 ppm), and resonates at higher field in the alkyl-substituted triazolylidene complexes ($\delta_{\rm C}$ = 157.5 ± 2.3 ppm) than in aryl-substituted triazolylidene complexes, suggesting that the electronic configuration of this carbon is affected by the triazolylidene substitution pattern. The polyfluorinated tail had no significant influence on the NMR frequency of the carbenic carbon. However, the NCH2 group in complex 2c is deshielded by 0.4 ppm (1H NMR) when compared to the butyl homolog 2a, and likewise shielded by about 8 ppm in the ¹³C NMR spectrum.

Single crystal X-ray diffraction analysis of complexes 2b, 2f, and 2g confirmed the bonding situation in these complexes and in particular demonstrated the wingtip dissociation in 2g (Fig. 1). Bond lengths and angles of these complexes (Table 1) do not significantly deviate from related carbene gold complexes characterised previously. 4,18-20 However, some packing trends are worth noting. Complex 2g displays a head-to-tail type packing, attributed to presumably weak aurophilic interactions (Au...Au separation of 3.46 Å) which may add to the electrostatic interaction between the chlorido ligand and the heterocyclic ring. 1f,21 This arrangement may be preferred due to the low steric demand of this ligand system, and hence allows for much closer packing than that of, for example, complex 2b.

Catalysis results and activation studies

Previous work has clearly shown that Ag(1) can be a non-innocent activator for Au-catalysed transformations. 1d,9c,d,18,22 In particular when using AuCl(trz) system, silver has multiple roles beyond solely abstracting the gold-bound chlorido ligand and likely induces a retro-transmetallation to (transiently) yield catalytically active triazolylidene silver complexes. 9c,18,23

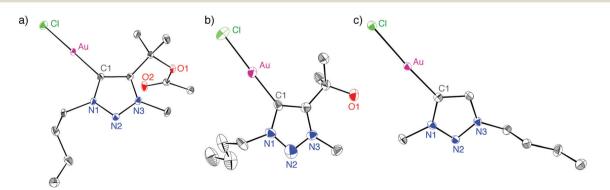


Fig. 1 ORTEP representations of complex 2b (a), 2f (b), and 2g (c; all 50% probability ellipsoids, H-atoms and second independent molecule of 2g in the unit cell omitted for clarity).

Table 1 Selected bond lengths [Å] and angles [°] in complexes 2b and 2g

Complex	Au-C1	Au-Cl	C1-Au-Cl
2b	1.995(2)	2.2896(6)	178.08(7)
2f	1.976(6)	2.2873(19)	178.1(2)
2g ^a	1.984(2)	2.2978(6)	175.90(7)

 a Only for one of the two non-symmetry related molecules in the unit cell of 2g.

Because of these complications and the associated uncertainty whether the true catalytic species is (are) based on silver or gold, silver-free catalyst activation methodologies are of paramount importance.¹⁶ We considered two specific routes: (i) halide abstraction with a potassium salt, and (ii) the use of CH₃⁺ as an electrophile. Even though methyl cations are only rarely used to scavenge chloride, chloride to halide exchange reactions at the metal centre have been performed successfully with methyl iodide.24 Moreover, C-C bond formation by electrophilic activation of (NHC)Au(Aryl) complexes has been reported.²⁵ To probe this methodology, complex 2a was reacted with stoichiometric equivalents of MeOTf in MeCN. Initial attempts to isolate the putative cationic solvent complex [(trz)Au(solv)]OTf from the reaction mixture only afforded Au(0), indicated by the gold mirror that formed upon evaporation of all volatiles. Monitoring the reaction by 19F NMR spectroscopy (CD2Cl2) indicated a new resonance that is shifted 5 ppm upfield from MeOTf, attributed to the gradual formation of a new ion pair in solution (see ESI, Fig. S1†). The corresponding 1H NMR data showed only minor changes in the ligand, and a new resonance around 3 ppm which has been assigned to CH₃Cl. In order to overcome the apparent instability of the cationic species resulting from 2a, it was trapped by the addition of an exogenous ligand. Addition of isonitrile (methyl isocyanoacetate) gave the corresponding cationic complex (see ESI†).18 Likewise, addition of PPh3 before evaporation of the solvent afforded the cationic gold species 3a. This complex was unambiguously identified by NMR spectroscopy and X-ray diffraction (Fig. 2). However, it should be noted that the phosphine carbene gold complex cation is also formed upon treatment of 2a with PPh3 in the absence of any electrophilic chloride scavenger (albeit with a chloride counterion), which limits the relevance of phosphines as trapping reactions. In contrast, isonitrile binding does not occur with the [AuCl(trz)] complexes 2 spontaneously and was only observed in the presence of MeOTf, suggesting that isonitriles are more diagnostic trapping agents.

Analysis of complex 3a by ¹³C and ³¹P NMR spectroscopy reveals similar features when compared to related [(trz)Au- $(PPh_3)^{\dagger}$ and $[(NHC)Au(PPh_3)]^{\dagger}$ complexes (e.g. $\delta_P = 39.4$ for 3a). 18,26 The carbenic nucleus is deshielded by about 15 ppm compared to the chlorido analogue 2a and appears at $\delta_C = 172$, in agreement with a more electron-deficient metal fragment. X-ray diffraction analysis of single crystals of 3a indicates an elongation of the gold carbene distance compared to 2a (Au-C1 2.046(3) Å in 3a vs. 1.98 Å in complexes 2), a consequence of the higher trans influence of PPh₃ compared to the chlorido ligand. The coordination geometry slightly deviates from linearity, P-Au-C1 172.57(9)°, presumably due to packing constraints. Alternating layers of triflate ions and triazolium units with close contacts of 3.13 and 3.53 Å suggest electrostatic interactions in the solid state between the formally negatively charged triflate oxygen sites and the partially positively charged heterocycle.

Catalytic activity in oxazoline synthesis

Halide abstraction under catalytically relevant conditions was probed in the presence of isonitriles and bromobenzaldehyde to promote the catalytic formation of oxazolines. ^{12d-g},1^{8,27} Complex 2a was chosen as a representative AuCl(trz) complex because of the simple ligand design and the established benefit of the triazolylidene substitution pattern for monitoring catalytic reactions. ^{7d} Activation of this complex for initiating catalytic activity was investigated using MeOTf as well as different potassium salts (Table 2).

A systematic variation of the different reaction parameters revealed that the gold complex, amine, and a chloride scavenger are needed for generating an active species (entries 1–5).²⁸ Comparison of different chloride scavenging additives revealed that KPF₆ (entry 5) is superior to other potassium salts (entries 6 and 7). The addition of NⁱPr₂Et is essential for catalytic turnover, as no catalytic activity was observed in the absence of base (entry 4).¹⁸ Likewise the reaction is very slow when no scavenger was used (entry 3). Interestingly, KBF₄ has no activating effect (*cf.* entries 3 and 6). The utilisation of MeOTf enhanced

Fig. 2 Synthesis and ORTEP representation of complex **3a** (50% probability, hydrogens and OTf⁻ anion omitted for clarity); Au1–C1 2.046(3) Å, Au1–P1 2.2817(8), Cl1–Au–P1 172.57(9)°.

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Table 2 Catalytic oxazolines synthesis with various AuCl(trz) complexes and activators^a

Entry	[Au]	Additive	Base	Conversion (%)	cis/trans
1	_	_	_	6	_
2	_	KPF_6	N ⁱ Pr ₂ Et	25	_
3	2a	_	$N^i Pr_2 Et$	24	23/77
4	2a	KPF_6		<2	_
5	2a	KPF_6	$N^i Pr_2 Et$	93	26/74
6	2a	KBF_4	$N^i Pr_2 Et$	21	18/82
7	2a	KOTf	$N^i Pr_2 Et$	61	28/72
8	2a	MeOTf	$N^i Pr_2 Et$	62	27/73
9	2b	KPF_6	$N^i Pr_2 Et$	88	27/73
10	2c	KPF_6	$N^i Pr_2 Et$	75	29/71
11	2d	KPF_6	N ⁱ Pr ₂ Et	87	29/71

^a General conditions: 4-bromobenzylaldehyde (1.6 mmol), methyl isocyanoacetate (1.4 mmol), NⁱPr₂Et (0.14 mmol), AuCl(trz) (0.014 mmol), additive (0.028 mmol), trimethoxybenzene (0.36 mmol, internal standard), CH₂Cl₂ (4 mL), 40 °C, 8 h; yields and *cis/trans* ratio determined by ¹H NMR spectroscopy, averaged of at least 2 runs.

catalytic activity (entry 8), suggesting that chloride methylation is a viable strategy to generate the labile coordination site at the gold centre. It is remarkable that KOTf and MeOTf result in the same catalytic activity (entries 7 and 8) and give identical conversions, suggesting a distinct role for the OTf $^-$ anion in levelling catalyst activity. 1e Tentatively, weak triflate coordination may be surmised to slow down the turnover frequency when compared to the analogous species containing a $\mathrm{PF_6}^-$ counterion. The relevance of the counterion is also indicated by the variable catalytic activity in dependence of different anions in the potassium salts (entries 5–7).

Further studies on using MeOTf to activate the AuCl(trz) catalyst precursor included the variation of the equivalents of this activator, a modification which affected the conversion rates markedly. Using only 1.1 instead of 2 equiv. MeOTf with respect to 2a reduced the activity to about half (e.g. 21% vs. 38% conversion after 4 h, Fig. 3 and Table S2†). In the presence of 5 equiv. MeOTf, the catalytic activity is doubled and almost full conversion was accomplished after 8 h (45% already after 2 h), which matches the conversion rates achieved upon activation of the gold complex with KPF₆. The need for higher relative ratios of additive may be because MeOTf may interact with NⁱPr₂Et or undergo partial hydrolysis.

The enhancement of catalytic activity in the presence of KOTf, MeOTf and in particular KPF₆ suggests the successful formation of a [(trz)Au]⁺ species for substrate conversion. Therefore, KPF₆, was utilised as activator for a catalytic screening of the AuCl(trz) complexes 2a–d (entries 5, 9–11). In this series, the catalytic activity of 2a, 2b, and 2d is identical within the measurement errors (±5%). Complex 2c containing perfluorinated substituents on the triazolylidene induced slightly lower catalytic activity. This effect is particularly pronounced at

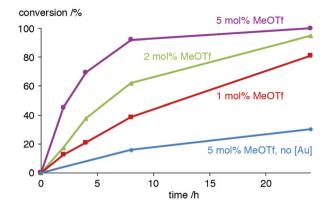


Fig. 3 Comparison of the conversion for catalytic oxazoline synthesis using 2a in combination with varying amounts of MeOTf (red, green, and purple traces), and using MeOTf in the absence of a gold complex (blue trace).

early conversion stages. Thus after 2 h and 4 h, runs with complex 2c achieved 25% and 43% conversion, respectively, while the other complexes are considerably more active (average 38% and 65% conversion after the same reaction time). The lower performance of complex 2c may be associated with the specific solubility and aggregation properties imparted by the perfluorinated substituents. Variation of the hydrocarbon substituents on the triazolylidene ligand from linear or branched alkyl groups to aryl substituents does not affect the catalytic performance (cf. 2a vs. 2b and 2d). These results therefore suggest that the catalytic rate-determining step is not significantly governed by steric or electronic effects induced by the triazolylidene ligand. This conclusion is further supported by the essentially unaltered cis/trans ratio, even when a sterically demanding adamantyl group was included in the ligand scaffold (2d, entry 11).

Importantly, activation of complex 2a with AgBF₄ affords a species that is two to three orders of magnitude more active than the species generated with KPF₆ or triflates, reaching quantitative oxazoline formation within 15 min at 0.5 mol% loading. Similarly high activities have been recorded when related triazolylidene silver complexes (trz)AgCl were used for catalysis in the absence of gold. Thus, the gold-based active species are considerably less competitive than their triazolylidene silver analogues in this catalytic heterocycle synthesis. These data further suggest that the catalytically active component in the AuCl(trz)/AgBF₄ system may be a [(trz)Ag]⁺ species resulting from a retro-transmetallation or the formation of Au nanoparticles. Starts, 29

C-H bond activation in metal-mediated carbene transfer from ethyl diazoacetate

The application of Ag-free $[(trz)Au]^+$ catalysis was further probed in carbene transfer chemistry by the metal-mediated decomposition of diazo compounds. This catalytic system is attractive for several reasons. Firstly, NaBAr F_4 (BAr F_4 = tetrakis (3,5-bis(trifluoromethyl)phenyl)borate) has been shown to be

an excellent activator for AuCl(NHC) catalysts in this area of catalysis and hence allows for Ag-free activation.³⁰ In particular the AuCl(IPr)/NaBArF4 system has given promising results with arenes as substrates. With previously described catalytic systems, 31 the reaction of benzene and ethyl diazoacetate (EDA) led to cycloheptatriene (4 in Table 3), as the result of consecutive double bond cyclopropanation and ring expansion in the so-called Buchner reaction. However, the gold-based system is selective towards C-H bond functionalisation of benzene and other arenes by formal carbene insertion affording an alkyl-arene (5 in Table 3). 30a-c Furthermore, it was shown that AuCl(trz)/AgSbF₆ systems are useful carbene transfer reagents from EDA to both reactive N- or O-containing substrates. 4g Since the activity of the AuCl(trz) systems for C-H insertion has not been studied, the catalytic C-H activation with EDA seems an attractive expansion to investigate Ag-free activation of AuCl(trz). Benzene was chosen as a representative substrate for preliminary screening, and the activity of complexes 2a-2e in catalytic carbene transfer was monitored using NaBAr^F₄ as additive (Table 3). While a mixture of the aforementioned cycloheptatriene 4 and benzyl acetate 5 is expected, these two products are easily distinguishable by their diagnostic NMR signals.

All AuCl(trz) complexes 2a-e favoured the formation of the cycloheptatriene product 4 over the product from C-H insertion in approximately a 3:1 ratio (Table 3, entries 1-5). The catalytic activity is essentially insensitive to the substitution pattern on the triazolylidene heterocycle with overall product ratios, i.e. 4 + 5, all in the 75-85% range. The influence of silver salts as halide scavengers was also considered to determine potential interactions of silver in the catalytic cycle (entries 6-8). While the use of AgBF₄ further promoted cyclopropanation and yielded a 8:1 selectivity towards 4 (entry 6),

Table 3 Triazolylidene gold-mediated carbene transfer from EDA to benzene^a

[Au]	Additive	Product ratio ^b		
		4	5	DEF/DEM
2a	NaBAr ^F ₄	68	17	15
2b	NaBAr ^F ₄	65	18	17
2c	$NaBAr_{4}^{F}$	61	19	21
2d	$NaBAr_{4}^{F}$	57	17	26
2e	$NaBAr_{4}^{F}$	67	16	17
2a	$AgBF_4$	77	9	14
2a	AgSbF ₆	64	18	18
2e	AgSbF ₆	62	22	16
	2a 2b 2c 2d 2e 2a 2a	2a NaBAr ^F ₄ 2b NaBAr ^F ₄ 2c NaBAr ^F ₄ 2d NaBAr ^F ₄ 2e NaBAr ^F ₄ 2e AgBF ₄ 2a AgSbF ₆		

^a General conditions: [Au] (0.012 mmol), benzene (3 mL), EDA (0.44 mmol), NaBArF₄ (0.015 mmol), ratios in % of product mixture. ^b Distribution of products according to ¹H NMR spectroscopy, ca. 15% of EDA were remaining after 24 h as quantified with benzaldehyde as internal standard. CDEF/DEM: diethyl fumarate/diethyl maleate, by products of the carbene coupling reaction from two molecules of EDA.

AgSbF₆ did not alter the product distribution when compared to the activation of AuCl(trz) with NaBAr^F₄ (entries 7 and 8). We also noted that the consumption of EDA was not complete (ca. 85%, see Table 3) even after 24 h. Furthermore, the species generated from AuCl(trz) and NaBArF4 in CH2Cl2 was unstable in the absence of coordinating substrates as displayed by the immediate formation of gold(0) and gold nanoparticles observed as purple particles in solution. This instability required addition of EDA before introducing the additive for generating the active catalyst. This sequence of addition resulted in the formation of fumarate and maleate as minor by-products. Such side-product formation is typically suppressed by slow addition of EDA,32 though this procedure is prohibited here because of the instability of the [Au(trz)]⁺/BAr^F₄ species.

Similar reactivity patterns were observed when using selected AuCl(trz) complexes for carbene transfer to styrene (Table 4). These runs were performed in CH2Cl2 solution, in contrast to the neat benzene catalysis. The results indicate that the active species is solvent tolerant and apparently does not react with CH2Cl2 but instead selectively activates the aromatic C-H bonds. As in the case of benzene, full conversion of EDA was not achieved within 24 h and about 10% EDA remained unconverted after that time, which resulted in a complex reaction mixture for NMR analysis. Nonetheless, the ratio of products confirmed the same trend noted for diazocarbene transfer to benzene. Thus, carbene addition to a C=C double bond and formation of the phenyl cyclopropane 6 is the major outcome of the reaction, while carbene insertion into a Caryl-H bond and formation of styryl acetate 7 is less favoured. The ratio between cyclopropanation and C-H bond activation is about 3:1 for complexes 2b,d,e and hence very similar to the ratios obtained when using benzene as substrate (entries 2-4).

Table 4 Triazolylidene gold-mediated carbene transfer from EDA to styrene

			Product ratio ^b		
Entry	[Au]	Additive	6	7	DEF/DEM ^c
1	2a	NaBAr ^F ₄	77	12	11
2	$2\mathbf{b}^b$	NaBAr ^F ₄	65	20	15
3	2d	NaBAr ^F ₄	59	17	24
4	2e	NaBAr ^F ₄	66	21	13
5	2a	AgSbF ₆	74	13	12
6	2d	NaBAr ^F ₄ , Hg drop	67	20	13

^a General conditions: [Au] (0.012 mmol), styrene (2.3 mmol), EDA (0.44 mmol), NaBAr $_4$ (0.015 mmol), CH₂Cl₂ (2 mL); average of 2 runs. Distribution of products according to ¹H NMR spectroscopy, ca. 10% of EDA were remaining after 24 h as quantified with benzaldehyde as internal standard. c DEF/DEM: diethyl fumarate/diethyl maleate, by products of the carbene coupling reaction from two molecules of EDA.

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Scheme 3 Resonance forms for the gold-carbene intermediate.

In contrast, complex 2a is considerably more selective and reaches a 6.5:1 product ratio (entry 1).

No significant change in activity or selectivity was observed upon substituting the chloride scavenger from NaBArF4 to a silver salt (entry 5). The similar performance suggests that unlike in the oxazoline syntheses (vide supra), the catalytically active species in the carbene transfer reaction remains the [(trz)Au]⁺ species. Finally, a Hg-drop test was performed using catalyst 2d. No significant deviation was noted when compared to the parent run (cf. entries 3 and 6), which is indicative of a homogeneous catalytic cycle rather than one involving nanoparticles as an active species.

It is worthwhile to compare complexes AuCl(trz) and AuCl (IPr) as catalyst precursors to give some insight into the ligand effects. Firstly, the activity of the [(trz)Au]+ species is substantially lower than that of [(IPr)Au]+, requiring more than 24 h rather than just 6 h to reach complete conversion under identical conditions.30c Secondly, and perhaps more importantly, the active species resulting from AuCl(trz) strongly favours cyclopropanation over C-H bond activation and carbene insertion, while the use of AuCl(IPr) favours C-H bond activation. However, the product ratio for the AuCl(trz) systems closely matches those found for functionalised AuCl(NHC) systems. 30d As the reactivity pattern was essentially identical for all the evaluated triazolylidene complexes, this facet likely reflects the different properties induced by triazolylidenes vs. classical NHC ligands. Previous work has suggested that decreasing electron density on the metal centre favours C-H insertion. In agreement with such a model, the increased σ-donor properties of mesoionic triazolylidenes indeed results in preferential cyclopropanation as compared to carbene insertion via C-H activation. 30a,33 Accordingly, an increased electron density at the metal centre favours a carbene type resonance structure for the diazo fragment (A, Scheme 3) while electron-poorer metal centres induce a carbocationic structure (B, Scheme 3).34 It is very likely that the relative weight of each limiting structure in the real structure influences the reaction outcome toward the addition (Buchner) or insertion (alkyl-carbene) products.

Conclusions

A range of Ag-free chloride scavenger reagents for application with triazolylidene gold(1) complexes has been tested and shown to be useful for the activation of these complexes prior to catalysis. The results indicate that the Au complexes are less active catalysts for oxazoline synthesis than the analogous silver complexes such as AgCl(trz).29 Also, due to the linear coordination sphere around the metal centre, variation of the ligand substituents only moderately modulated catalytic activity and did not alter the diastereoselectivity of the resulting product profile. The AuCl(trz)/NaBArF4 system also catalysed the carbene transfer from EDA via benzene and styrene C-H bond activation. This activity demonstrated further applications of Ag-free [(trz)Au]+ catalysis. In this case, cyclopropanation products were favoured over C-H insertions, in contrast to the AuCl(IPr) system, indicating that the strong σ-donor properties of triazolylidene can be used to modulate the selectivity of gold in catalytic processes. Considering these results in combination with previous studies, it can be concluded that the choice of chloride scavenger is important to effectively identify the activity of gold-based catalysts and to assess the impact of the metal, as well as that of the ligand framework.

Experimental

General

The precursor 4-butyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1H-1,2,3-triazole for the triazolium salts 1c, 35 the triazolium salts 1a,36 and 1e,3d and the triazolylidene gold complex 2d were synthesised using literature procedures. 18 The synthesis of all novel triazoles and triazolium salts is described in the ESI.† Ag₂O was used after regeneration by heating >160 °C under vacuum. Dry, degassed solvents were purified using an alumina/catalyst column (Thermovac Co.). All other reagents are commercially available and were used as received. All microwave experiments were carried out using a Biotage Initiator 2.5 instrument, operating at 0-400 W irradiation power. Unless specified otherwise NMR were recorded at 25 °C, on Varian and Bruker spectrometers operating at 300, 400, or 500 MHz (¹H NMR) and 75, 100, 125 MHz ($^{13}C\{^{1}H\}$ NMR) respectively. Chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to residual solvents. Assignments are based on homo- and heteronuclear shift correlation spectroscopy. Elemental analyses were performed by the Microanalytical Laboratory at University College Dublin, Ireland using an Exeter Analytical CE-440 Elemental Analyzer, with the exception of complex 2d which was performed in Unidad de Análisis Elemental of the Universidad de Huelva. Residual solvents were identified by NMR spectroscopy GC analysis were recorded on a Varian CP-3800 instrument. Highresolution mass spectrometry was carried out with a Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with an electrospray source.

Complex 2a. To a solution of 1a (290 mg, 1.0 mmol) in dry CH₂Cl₂/MeCN (20 mL, 1:1 v/v) were added Ag₂O (134 mg, 0.58 mmol), and NMe₄Cl (140 mg, 1.3 mmol), and the suspension was stirred for 16 h under the exclusion of light under a N₂ atmosphere. AuCl(SMe₂) (309 mg, 1.1 mmol) was added and stirring continued for 2 h. The reaction mixture was filtered through Celite and volatiles were removed under reduced pressure. The residue was redissolved in CH₂Cl₂ and filtered

through Celite a second time to remove residual salts. Volatiles were removed under reduced pressure yielding the product as a brown oil, which became crystalline after several days of drying *in vacuo* (0.376 g, 0.88 mmol, 86%). ¹H NMR (500 MHz, CDCl₃): δ 0.95 (m, 6H, 2 × CH₂CH₃), 1.32–1.44 (m, 4H, 2 × 2 CH₂CH₃), 1.68–1.74 (m, 2H, C_{trz}CH₂CH₂), 1.98–2.04 (m, 2H, NCH₂CH₂), 2.76 (t, ³ $J_{\rm HH}$ = 7.8 Hz, 2H, C_{trz}CH₂), 4.02 (s, 3H, NCH₃), 4.42 (t, $J_{\rm HH}$ = 7.3 Hz, 2H, NCH₂) 13 C{ 1 H} (126 MHz, CDCl₃): δ 13.4 (NCH₂CH₂CH₂CH₂CH₃), 13.9 (C_{trz}CH₂CH₂CH₂CH₂CH₃), 19.8 (NCH₂CH₂CH₂), 22.5 (C_{trz}CH₂CH₂CH₂CH₂), 24.9 (C_{trz}CH₂), 31.4 (C_{trz}CH₂CH₂), 32.3 (NCH₂CH₂), 36.4 (NCH₃), 55.1 (NCH₂), 147.5 ($C_{\rm trz}$ CH₂), 157.0 (C_{trz}-Au) HRMS (ESI+): m/z Found 450.0987 [M + Na]⁺ (calcd for C₁₁H₂₁N₃AuClNa, 450.1028) Anal. Calcd for C₁₁H₂₁N₃AuCl: C, 30.89; H, 4.97; N, 9.82%.

Found: C, 31.04; H, 4.72; N, 9.69%. Complex 2b. This complex was prepared according to the procedure described for 2a starting from triazolium salt 1b (200 mg, 0.51 mmol), Ag₂O (60 mg, 0.26 mmol), NMe₄Cl (60 mg, 0.55 mmol), and AuCl(SMe₂) (156 mg, 0.53 mmol). After filtration through Celite and concentration under reduced pressure, pentane was added. The formed black coloured solids were removed by filtration and the supernatant evaporated to dryness. The residue was repeatedly dissolved in CH₂Cl₂ and precipitated with Et₂O until a minor amount of white precipitate was observed. The supernatant was then decanted, evaporated to dryness, washed with pentane, and dried in vacuo. This procedure yielded complex 2b as a white solid (0.19 g, 0.40 mmol, 78%). Crystals were obtained by slow diffusion of Et₂O into a CH₂Cl₂ solution. ¹H NMR (500 MHz, CDCl₃): δ 0.96 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, CH₂CH₃), 1.33–1.40 (m, 2H, CH₂CH₃), 2.04-2.07 (m, 8H, NCH₂CH₂ and C(CH₃)₂), 2.10 (s, 3H, C=OCH₃), 4.14 (s, 3H, NCH₃), 4.49 (t, ${}^{3}J_{HH}$ = 7.1 Hz, 2H, NCH₂) 13 C{ 1 H} (126 MHz, CDCl₃): δ 13.6 (CH₂CH₃), 19.8 (CH_2CH_3) , 22.0 $(C=OCH_3)$, 29.1 $(C(CH_3)_2)$, 32.3 (NCH_2CH_2) , 39.6 (NCH₃), 56.1 (NCH₂), 76.7 (CC_{trz}), 149.4 (CC_{trz}), 156.6 $(C_{trz}-Au)$, 169.5 (C=O) HRMS (ESI+): m/z Found 494.0886 $[M + Na^{+}]$ (calcd for $C_{12}H_{21}N_{3}O_{2}ClAuNa$, 494.0886) Anal. Calc. for C₁₂H₂₁N₃AuClO₂: C, 30.55; H, 4.49; N, 8.91%. Found: C, 30.28; H, 4.31; N, 8.63%.

Complex 2c. AgBF₄ (41 mg, 0.21 mmol) was added to a solution of 1c (0.18 g, 0.19 mmol) in dry CH₂Cl₂/MeCN (30 mL, 1:1 v/v), an stirred with the exclusion of light under a N_2 atmosphere for 5 min. This mixture was treated with Ag₂O (27 mg, 0.12 mmol) and NMe₄Cl (26 mg, 0.24 mmol) and the reaction was stirred for 16 h in the dark. Then AuCl(SMe₂) (56 mg, 0.19 mmol) was added and the reaction stirred for a further 2 h. The reaction mixture was exposed to air and the product was purified as described for 2a by repeated filtering through Celite, affording complex 2c as a pale yellow solid (150 mg, 0.14 mmol, 75%). ¹H (500 MHz, CDCl₃): δ 0.97 (t, ³ J_{HH} = 7.3 Hz, 3H, CH₂CH₃), 1.39-1.47 (m, 2H, CH₂CH₃), 1.73-1.79 (m, 2H, CCH_2CH_2), 2.8-3.01 (m, CCH_2 , 6H, 2 × NCH_2CH_2), 4.62 (t, ${}^{3}J_{HH}$ = 7.1 Hz, 2H, N3C H_{2}), 4.82 (t, ${}^{3}J_{HH}$ = 6.8 Hz, 2H, N1CH₂) 13 C{ 1 H}(126 MHz, CDCl₃): δ 13.8 (CH₂CH₃), 22.4 (CH_2CH_3) , 24.9 $(C_{trz}CH_2)$, 30.9 $(t, {}^3J_{CF} = 22.2 \text{ Hz}, N3CH_2CH_2)$, 31.3 (t, ${}^{3}J_{CF} = 20.1 \text{ Hz}$, N1CH₂CH₂), 31.6 (C_{trz}CH₂CH₂), 42.2

(N3CH₂), 47.7 (N1CH₂), 146.7 (C_{trz}CH₂), 158.5 (C_{trz}-Au) 19 F{ 1 H}(470 MHz, CDCl₃): δ -126.27-(-126.12) (m, 4F), -123.4, -123.2 (2 × br, 2 × 2F), -122.9 (br, 4F), -121.97-(-121.79), -114.23-(-14.05) (2 × m, 2 × 4F), -80.88-(-80.80) (m, 6F) Anal. Calcd for C₂₂H₁₇AuClF₂₆N₃: C, 25.17; H, 1.63; N, 4.00%. Found: C, 25.18: H, 1.30; N, 3.80%.

Complex 2e. Triazolium salt 1e (87 mg, 0.9 mmol), Ag₂O (29.8 mg, 0.13 mmol), and NMe₄Cl (20.1 mg, 0.18 mmol) were stirred in dry CH₂Cl₂/MeCN (10 mL, 1:1 v/v) under a N₂ atmosphere, for 17 h with the exclusion of light. Volatiles were removed in vacuo, and the residue was suspended in dry CH₂Cl₂ (15 mL), and stirred with AuCl(SMe₂) (54.9 mg, 0.19 mmol) in the dark for 2 h. The reaction mixture was filtered through Celite, eluted with CH2Cl2 and all volatiles were removed. The product was obtained as a white solid (65 mg, 0.12 mmol, 64% yield). Crystals were obtained by slow diffusion of dry Et₂O into a CH₂Cl₂ solution at -20 °C. ¹H (500 MHz, CDCl₃): δ 1.14 (d, ³ J_{HH} = 6.9 Hz, 6H, CH(C H_3)₂), 1.34 (d, ${}^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH₃)₂), 2.31 (sept, ${}^{3}J_{HH}$ = 6.9 Hz, 2H, 2 × CH(CH₃)₂), 4.25 (s, 3H, NCH₃), 7.31 (d, ${}^{3}J_{HH}$ = 7.8 Hz, 2H, $C_{DiIPr}H$), 7.53–7.58 (m, 4H, $C_{Ar}H$), 7.80–7.82 (m, 2H, $C_{Ar}H$) ¹³C{¹H}(126 MHz, CDCl₃): δ 24.2, 24.5 (2 × CH*C*H₃), 28.9 (C_{DiIPr}H), 38.4 (NCH₃), 124.4 (C_{Ar}H), 126.0 (C_{Ph}), 129.4, 129.8, 130.7 (3 \times C_{Ph}H), 131.6 (C_{Ar}H), 135.2, 145.2 (2 \times C_{Ar}), 146.8 $(C_{\text{trz}}C)$, 162.1 $(C_{\text{trz}}-Au)$ Anal. Calcd for $C_{21}H_{25}AuClN_3^{-1}CH_2Cl_2$: C, 43.45; H, 4.41; N, 7.07%. Found: C, 43.28; H, 4.50; N, 6.79%.

Complex 2f. The triazolium tetrafluoroborate **1f** (77.5 mg, 0.27 mmol), NMe₄Cl (29 mg, 0.26 mmol), and Ag₂O (31.9 mg, 0.14 mmol) were stirred in CH₂Cl₂/MeCN (5 mL, 1:1 v/v) for 16 h protected from light. To this mixture was added AuCl (SMe₂) (79.5 mg, 0.27 mmol) and stirring was continued for 2 h. The suspension was filtered through Celite, eluted with CH₂Cl₂ and the volatiles were removed under reduced pressure yielding the crude product as an off-white solid (98 mg 23 mmol, 88%). Crystals were grown by slow evaporation of a CH₂Cl₂/Et₂O solution of **2f.** ¹H (400 MHz, CD₂Cl₂): δ 0.97 (t, ${}^{3}J_{\text{HH}} = 7.4 \text{ Hz}$, 3H, CH₂CH₃), 1.33–1.43 (m, 2H, CH₂CH₃), 1.89 (s, 6H, C(CH₃)₂), 1.99–2.06 (m, 2H, NCH₂CH₂), 4.29 (s, 3H, NCH₃), 4.47 (t, ${}^{3}J_{\text{HH}} = 7.3 \text{ Hz}$) ${}^{13}\text{C}\{{}^{1}\text{H}\}\{101 \text{ MHz}, \text{CD}_{2}\text{Cl}_{2}\}$: δ 13.8 (CH₂CH₃), 21.2 (CH₂CH₃), 32.6, 32.7 (NCH₂CH₂ and C(CH₃)₂), 41.0 (NCH₃), 56.2 (NCH₂), 151.7 (C_{trz} C), 155.2 (C_{trz} -Au).

Complex 2g and 2g'. A suspension of the triazolium tetrafluoroborate 1f (100 mg, 0.35 mmol), Ag₂O (80 mg, 0.35 mmol), NMe₄Cl (80 mg, 0.73 mmol), and activated molecular sieves in dry CH₂Cl₂ (25 mL) was stirred under the exclusion of light for 3 days, under a N₂ atmosphere. AuCl(SMe₂) (103 mg, 0.35 mmol) was added and the reaction stirred for 2 h. The reaction mixture was then filtered through Celite, and all volatiles were removed under reduced pressure, which yielded 2g as a pale yellow solid (37 mg, 0.10 mmol, 28% yield). Crystals were grown by slow evaporation of CH₂Cl₂. The same result was obtained when the reaction was started from the triazolium triflate analogue of 1f. 1 H (400 MHz, CDCl₃): δ 0.94–1.01 (m, 3H, CH₂CH₃), 1.32–1.44 (m, 2H, CH₂CH₃), 1.89–1.98 (m, 2H, NCH₂CH₂), 4.20 (s, 3H, NCH₃), 4.38 (t, ${}^{3}J_{\text{HH}} = 7.3 \text{ Hz}$, 2H, NCH₂), 7.57 (s, 1H, C_{trz}H) ${}^{13}\text{C}\{^{1}\text{H}\}\{(101 \text{ MHz}, \text{CDCl}_{3}): \delta 13.4 \text{ or } 13.6 \text{ (CH}_{2}\text{CH}_{3}), 19.7 \text{ (CH}_{2}\text{CH}_{2}), 31.6 \text{ (NCH}_{2}\text{CH}_{2}), 42.1 \text{ (NCH}_{3}), 52.5 \text{ (NCH}_{2}), 133.6 \text{ (C}_{\text{trz}}\text{H}), 158.4 \text{ (C}_{\text{trz}}\text{-Au}). 2g' \, {}^{1}\text{H} \text{ (400 MHz, CDCl}_{3}): \delta 0.94-1.01 \text{ (m, 3H, CH}_{2}\text{CH}_{3}), 1.32-1.44 \text{ (m, 2H, CH}_{2}\text{CH}_{3}), 1.99-2.06 \text{ (m, 2H, NCH}_{2}\text{CH}_{2}), 4.17 \text{ (s, 3H, NCH}_{3}), 4.50 \text{ (t, 2H, } {}^{3}J_{\text{HH}} = 7.3 \text{ Hz, NCH}_{2}\text{), } 7.58 \text{ (s, 1H, C}_{\text{trz}}\text{H}) \, {}^{13}\text{C}\{{}^{1}\text{H}\}\{101 \text{ MHz, CDCl}_{3}\}: \delta 13.4 \text{ or } 13.6 \text{ (CH}_{2}\text{CH}_{3}), 19.7 \text{ (CH}_{2}\text{CH}_{3}), 32.4 \text{ (NCH}_{2}\text{CH}_{2}), 38.8 \text{ (NCH}_{3}), 55.4 \text{ (NCH}_{2}), 134.7 \text{ (C}_{\text{trz}}\text{H}), 157.7 \text{ (C}_{\text{trz}}\text{-Au}) \text{ Anal. (%):Found: C, 23.66; H, 3.55; N, 11.08; Calcd for C₇H₁₃AuClN₃: C, 22.62; H,3.53; N,11.31.$

Compound 3a. Neat MeOTf (12.5 µL, 0.11 mmol) was added to a solution of 2a (40 mg, 0.094 mmol) in dry MeCN (2 mL), and the reaction mixture stirred protected from light for 5 min. PPh₃ (31 mg, 0.12 mmol) was added, and the reaction stirred for a further 15 min. The solvent was removed in vacuo, and the residue was purified by dissolving the product in CH2Cl2 and precipitation with pentane, followed by drying in vacuo. Complex 3a was obtained as a white solid in quantitative yield (76 mg, 0.095 mmol). Crystals were grown by slow diffusion of Et₂O into a CH₂Cl₂ solution of 3a. ¹H (400 MHz, CDCl₃): δ 0.88 (t, ${}^{3}J_{HH}$ = 7.3 Hz, 3H, C(CH₂)₃CH₃), 0.92 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, N(CH₂)₃CH₃), 1.32–1.49 (m, 4H, CH₂CH₃), 1.79-1.87 (m, 2H, C_{Trz}CH₂CH₂), 2.00-2.08 (m, 2H, NCH₂CH₂), 2.90 (t, ${}^{3}J_{HH}$ = 7.8 Hz, 2H, $C_{Trz}CH_{2}$), 4.18 (s, 3H, NCH₃), 4.46 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H, NCH₂), 7.44–7.54 (m, 12H, C_{Ar}H), 7.54–7.59 (m, 3H, $C_{Ar}H$) $^{13}C\{^{1}H\}(101 \text{ MHz, CDCl}_{3}): \delta 13.6 (N(CH₂)₃CH₃),$ 13.9 (C_{Trz}(CH₂)₃CH₃), 19.9 (N(CH₂)₂CH₂), 22.5 (C_{Trz}(CH₂)₂CH₂), 24.7 (C_{Trz}CH₂), 31.7 (CCH₂CH₂), 32.9 (NCH₂CH₂), 37.2 (NCH₃), 55.5 (NCH₂), 129.7 (d, J_{PC} = 11.0 Hz, $C_{Ar}H$), 132.1 (d, J_{PC} = 2.2 Hz, $C_{Ar}H$), 134.1 (d, $J_{PC} = 14.2$ Hz, $C_{Ar}H$), 149.9 ($C_{trz}C$), 172.0 (C_{trz} -Au) ³¹P{¹H}(162 MHz,CDCl₃): δ 39.4 (br) ¹⁹F{¹H} (282 MHz, CDCl₃): δ -78.12 (s) HRMS (ESI+): m/z Found $654.2339 [M - OTf]^+$ (calcd for $C_{29}H_{36}N_3PAu$, 654.2312).

Catalytic procedures

Dalton Transactions

General procedure for the catalytic synthesis of oxazolines. To a solution of 4-bromobenzaldehyde (290 mg, 1.57 mmol) and trimethoxybenzene (60. mg, 0.36 mmol, internal standard) in CH₂Cl₂ (4 mL) in thick walled 5 mL vail was added methyl isocyanoacetate (130 μ L, 1.43 mmol), followed by N^IPr₂Et (25 μ L, 0.14 mmol), complex 2 (14 μ mol), and the additive according to Table 2 (28 μ mol). The vial was sealed, protected from light, and heated to 40 °C in an oil bath. Conversions and *cis/trans* ratios were monitored by 1 H NMR spectroscopy in CDCl₃ and compared to previously reported literature values. 37

For reactions involving 1.1 mol% and 2 mol% MeOTf, a solution of MeOTf (0.265 M in dry, degassed CH_2Cl_2) was used and added before N^iPr_2Et . The volume of CH_2Cl_2 was adjusted to a total reaction volume of 4 mL.

General procedure for catalytic carbene transfer of EDA to benzene. Under a N_2 atmosphere and protected from light, anhydrous benzene (3 mL) was added to a Schlenk flask containing 2 (12 μ mmol). Then EDA (53 μ L, 0.44 mmol) was added and either NaBAr^F₄ (13.7 mg, 15 μ mol) or the appropriate silver salt (13 μ mol, see Table 3). The reaction was

monitored by GC at 3–5 h and 20–24 h. After 24 h, the reaction was filtered, concentrated, and analysed by 1 H NMR spectroscopy (CDCl₃ solution). 30c,38 For runs with 2c, the quantities were lower: 2a (6.1 mg, 5.8 μ mol), benzene (2 mL), EDA (25 μ L, 0.21 mmol) and NaBAr $^{F}_{4}$ (7.6 mg, 8.6 μ mol).

For experiments probing the carbene transfer to styrene, the experimental procedure was identical to that described above, 30c,39 except benzene was replaced by a mixture of CH₂Cl₂ (2 mL) and styrene (267 μ L, 2.3 mmol).

Crystal structure determinations. Crystal data for 2b,f,g, and 3a were collected using a Rigaku (former Agilent Technologies) Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector and using monochromated Mo-K_α radiation (0.71073 Å). A complete dataset was collected, assuming that the Friedel pairs are not equivalent. The intensities were corrected for Lorentz and polarisation effects, and a numerical absorption correction based on Gaussian integration over a multifaceted crystal model was applied. The structures were solved by direct methods using SHELXS-97 and refined by fullmatrix least squares fitting on F^2 for all data using SHELXL-97.40 Hydrogen atoms were added at calculated positions and refined by using a riding model. Anisotropic thermal displacement parameters were used for all nonhydrogen atoms. Further crystallographic details are compiled in Tables S5-S8.† Crystallographic data for all four complexes have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1481152 (2b), 1481154 (2f), 1481151 (2g), and 1481153 (3a).

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