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Carbene Transfer from Triazolylidene Gold Complexes as a Potent Strategy for Inducing High Catalytic Activity

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Abstract. A series of gold(I) complexes [AuCl(trz)] were synthesized that contain 1,2,3-triazolylidene (trz) ligands with variable wingtip groups. In the presence of AgBF₄, these complexes undergo ligand redistribution to yield cationic complexes [Au(trz)₂]BF₄ in high yields as a result of efficient carbene transfer. Identical reactivity patterns were detected for carbene gold complexes comprised of Arduengo-type IMes ligands (IMes = *N,N'*-dimesityl-imidazol-2-ylidene). Reaction of cationic complexes [Au(trz)₂]⁺ with [AuCl(trz')] afforded the heteroleptic complex [Au(trz)(trz')]⁺ and [AuCl(trz)] (trz, trz' = triazolylidene ligands with different wingtip groups). Carbene transfer occurs spontaneously, yet is markedly rate-enhanced in the presence of Ag⁺. The facile carbene transfer was exploited as a catalyst activation process to form active gold species for the aldol condensation of isocyanides and aldehydes to form oxazolines. The catalytic activity is strongly dependent on the presence of Ag⁺ ions to initiate catalyst activation. High turnovers (10⁵) and turnover frequencies (10⁴ h⁻¹) were accomplished. Structural analysis at early stages of the reaction support the critical role of triazolylidene dissociation to activate the pre-catalyst and dynamic light scattering revealed the presence of nanoparticles (±100 nm diameter) as potential catalytically active species. Furthermore, the triazolylidene scaffold had no impact on the diastereoselectivity of the oxazoline formation, and chiral triazolylidenes did not induce any asymmetry in the product. The facile dissociation of carbenes from [AuCl(carbene)] in the presence of Ag⁺ ions suggests a less stable Au–C_{carbene} interaction than often assumed, with potential implications for gold-catalyzed reactions that employ a silver salt as (putative) halide scavenger.

Introduction

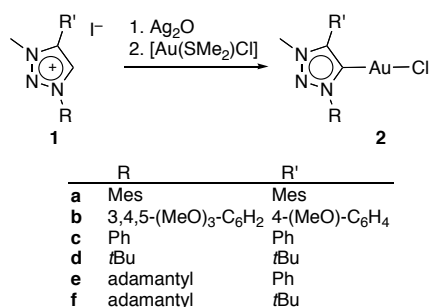
Catalysis using gold complexes has become one of the most vibrant areas of modern synthesis.^{1,2} In line with progress in the catalytic application of other (late) transition metals, the catalytic chemistry of gold has been strongly stimulated by the availability of *N*-heterocyclic carbenes (NHCs)³ as paramount and potent ligands in catalysis⁴ and beyond.^{5,6} These NHC ligands convey properties and constraints that are often complementary to the ubiquitous phosphine ligand classes.⁷ For example, NHCs stabilize highly unusual and hitherto elusive reactive species.⁸ Their success as spectator ligands has generally been associated with two key parameters: the strong donor ability and the high covalent contribution to the metal bond, which is markedly higher than in metal bonding of other dative ligands such as neutral N- and P-donors.^{8,9} Tight metal-ligand bonding has been assumed to impart high robustness of the catalytically active species and thus an essential factor for accomplishing large catalytic turnover numbers.¹⁰ This bonding situation is thus in sharp contrast to the dative bonding of phosphines, which are kinetically labile and undergo dissociation and re-coordination to a (catalytically active) metal center.¹¹

Early work has demonstrated the susceptibility of carbene ligands towards degradation, especially in redox processes and hydrogenations.¹² The presence of alkyl or hydride groups at the metal center has been demonstrated to induce reductive azolium elimination, and likewise, the reverse process has been used to synthesize metal carbene complexes.¹³ Typically, a given set of conditions favors the carbene formation or the carbene dissociation, and only rarely, carbene dissociation has been demonstrated to be a microscopically reversible process.¹⁴ In addition, recent transmetalation studies indicate that carbene transfer may occur from a range of different metals in addition to the most frequently used silver carbene intermediates,¹⁵ suggesting that the M–NHC bond may be less tight than often assumed. By using triazolylidenes¹⁶ as synthetically versatile analogues of Arduengo-type imidazolylidenes for the development of powerful catalytic systems,¹⁷ we have recently provided evidence that PdCl₂ and CuCl are leaving groups in the corresponding carbene complexes,^{18,19} thus providing access to catalytically active species where the triazolylidene ligand may not be bound to the active site. We have now expanded this concept and report here on gold triazolylidene complexes as catalyst precursors for the catalytic synthesis of oxazolines. Evidence is provided for triazolylidene dissociation from the gold coordination sphere as a pivotal step in catalyst activation. Similar carbene transfer is also

observed in Arduengo-type NHC gold systems, which has implications for a broad range of gold- (and indeed other metal-)catalyzed reactions starting from carbene metal catalyst precursors.

Results and discussion

Synthesis of triazolylidene gold complexes. The neutral gold(I) triazolylidene complexes **2a–f** were synthesized from the corresponding 1,2,3-triazolium halides and Ag₂O and subsequent transmetalation with AuCl(SMe₂) (Scheme 1), according to established procedures.^{17c} When starting from triazolium halides rather than tetrafluoroborate salts, additives are generally not required for the complex formation and yields of **2a–f** were generally good (60–80%). An exception was the metalation of triazolium salt **1d** with *tert*-butyl wingtips. Complex **2d** was only obtained in moderate yields upon addition of (NMeEt₃)I to the reaction mixture and after prolonged reaction times. Complexes **2a–f** are air and moisture stable in solution and in the solid state.



Scheme 1 Synthesis of neutral triazolylidene gold(I) complexes **2**.

Successful metalation of the triazolium salts is spectroscopically indicated by the disappearance of the low-field triazolium proton resonance in the ¹H NMR spectrum and a slight upfield shift of the N–CH₃ resonance. The gold-bound carbon appears in the δ_C 152–166 range, in agreement with previously related complexes^{17c} and significantly upfield shifted in comparison with imidazol-2-ylidene analogues (166–195 ppm)²⁰ or 1,2,4-triazolylidene gold(I) complexes (168–178 ppm).^{20a,21} Complexes **2a**, **2b**, **2d** and **2e** were analyzed by single-crystal X-ray diffraction (Fig. 1), which revealed the expected linear coordination geometry around the Au center. The Au–C_{trz} distances (1.980–1.993 Å) and the Au–Cl bond lengths (2.282–2.290 Å) are within expectation (Table 1).^{17c} When compared to sterically identical Arduengo-type imidazolylidene

complexes, a slight but consistent increase of the Au-Cl bond length is noted, which reflects the stronger *trans* influence of the triazolylidene ligand.²² For example, the Au-Cl bond length measures 2.2833(8) Å in **2a** compared to 2.2756(12) Å in AuCl(IMes),^{20c} and 2.2898(10) Å in **2d** vs. 2.2742(7) Å in AuCl(*It*Bu) (IMes = 1,3-dimesityl-2-imidazolylidene, *It*Bu = 1,3-di-*t*-butyl-2-imidazolylidene).^{20a}

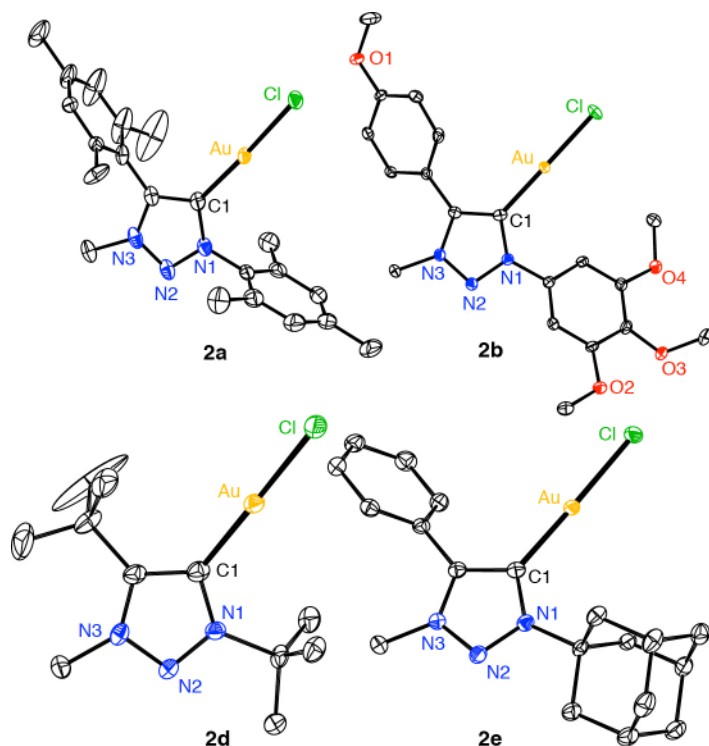


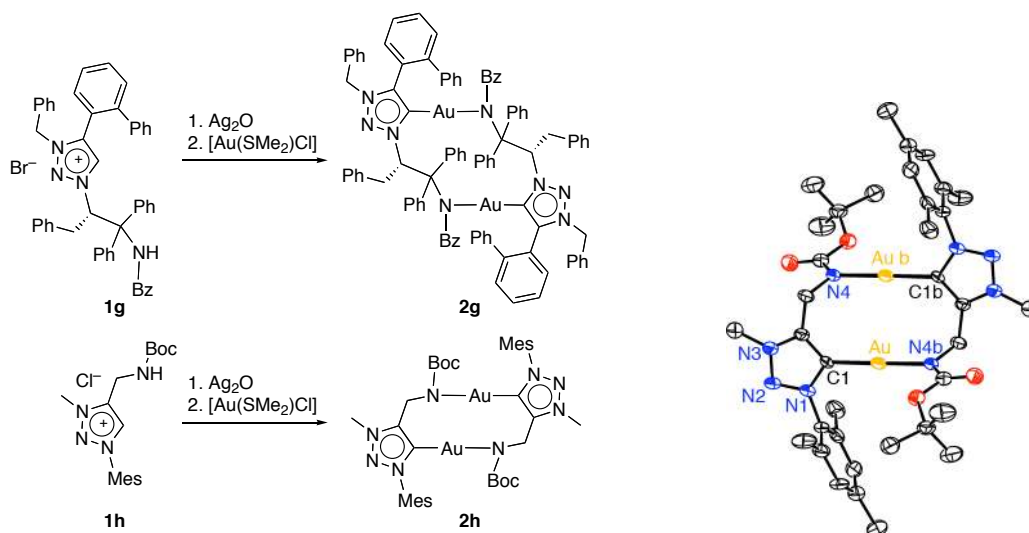
Figure 1 ORTEP diagrams of complex **2a,b,d,e** (50% probability level; co-crystallized solvent molecules and hydrogen atoms omitted for clarity; only one crystallographically independent molecule of **a** shown).

Table 1 Selected bond lengths [Å] and angles [°] in complexes **2a**, **2b**, **2d**, and **2e**.

complex	Au–C(1)	Au–Cl(1)	C(1)–Au–Cl(1)
2a	1.980(3)	2.2833(8)	176.95(10)
2b	1.987(3)	2.2821(7)	179.36(9)
2d	1.993(4)	2.2898(10)	174.25(12)
2e	1.990(2)	2.2881(6)	178.03(7)

Amide-functionalized triazolium salts gave different products upon metalation. In addition to the diagnostic features established for complexes **2a–f**, NMR spectra of complex **2g** derived from the enantiopure triazolium bromide **1g**²³ revealed the absence of the amide proton resonance.

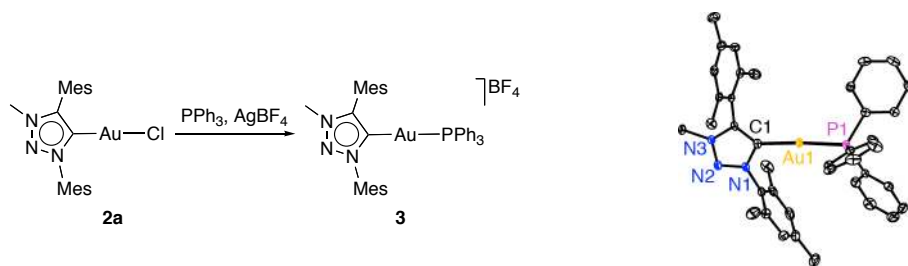
Moreover microanalysis indicated the halide-free molecular formula. Based on these data, a bimetallic complex was inferred with a bridged ligand coordination mode (Scheme 2). This bonding mode was also observed upon auration of the triazolium salt **1h** containing a Boc-protected amine wingtip group. Complex **2h** displayed similar spectroscopic features as **2g**, including the absence of the NH resonance. Furthermore, a single crystal X-ray analysis of complex **2h** confirmed the dimeric connectivity pattern (Fig. 2).²⁴



Scheme 2 Synthesis of the dimetallic complex **2g** and **2h**.

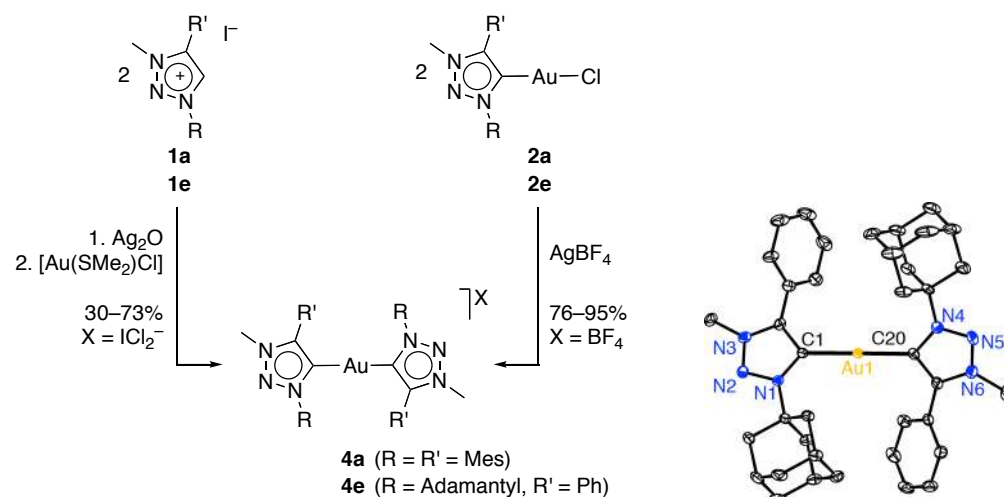
Figure 2 ORTEP presentation of complex **2h** (50% level), Au–C1 2.003(8) Å, Au–N4b 2.026(7) Å, C1–Au–N1 179.3(3)°.

The chloride ligand in complexes **2a–f** is readily substituted. For example, the cationic phosphine-ligated carbene gold(I) complex **3** was obtained from **2a** and PPh₃ in the presence of AgBF₄ as halide scavenger (Scheme 3).²⁵ This ligand exchange induced a small upfield shift of the N3-bound methyl proton resonances by 0.17 ppm and a substantial 15 ppm deshielding of the carbenic signal to δ_C 177.0 ppm ($^2J_{PC}$ = 122 Hz). The J_{PC} coupling constant is slightly smaller than that observed for the analogous complex containing an Arduengo-type carbene ligand,²⁵ in agreement with a stronger *trans* influence of the triazolylidene. The ³¹P NMR chemical shift in **3** is 40.9 ppm, similar to imidazolylidene analogues.²⁵ In the crystal structure of **3**, the Au–C_{trz} bond is about 0.05 Å longer than in the neutral analogue **2a** (2.028(3) Å vs 1.980(3) Å) due to the stronger *trans* influence of PPh₃ vs Cl[–].



Scheme 3 Synthesis and X-ray structure of complex **3** (50% probability, hydrogens and anion omitted for clarity); Au1–C1 2.028(3) Å, Au1–P1 2.2795(7) Å, C1–Au–P1 174.05(8)°.

Two homoleptic bis(carbene) gold(I) complexes were prepared from the corresponding triazolylidene silver intermediates by transmetalation with only half an equivalent of AuCl(SMe₂) (Scheme 4). Complex **4a** bearing mesityl wingtips was obtained in 73% yield, while complex **4e** was less efficient (30% yield) even when the reaction was stirred for extended periods because of competitive formation of the mono(triazolylidene) gold complex **2e**.²⁶ A one-pot synthesis without isolation of the silver carbene intermediate did not improve the yield and complex **2e** was the dominant product (80% conversion). A diagnostic signature of the bis(carbene) complex **4a** is the magnetic inequivalence of the *ortho*-methyl protons (δ_{H} 1.82 and 1.76 ppm) and the aromatic C_{Mes}–H protons (δ_{H} 6.92 and 6.86 ppm). No such desymmetrization was noted for the mono(triazolylidene) gold complex **2a**. Likewise, free rotation of the adamantyl wingtips is restricted in **4e** as indicated by the AB doublet centered at δ_{H} 1.62 and 1.44 ppm for the methylene groups. Furthermore, the ¹³C NMR data showed a lowfield Au–C_{trz} signal at 175.8 ppm and 166.5 ppm for **4a** and **4e**, respectively, which corresponds to a 13 ppm downfield shift compared to the corresponding mono(triazolylidene) analogues **2a** and **2e**. X-ray diffraction analysis of single crystals of **4e** confirmed the bonding of two triazolylidene ligands to the gold center. The Au–C_{trz} bond distance (2.029(4) Å) is similar to the bond length observed in the phosphine complex **3a** and thus slightly longer in the cationic complexes than in **2e**. Similar differences were observed in neutral mono(carbene) vs cationic bis(carbene) gold complexes of Arduengo-type NHCs.^{21b,25,27}

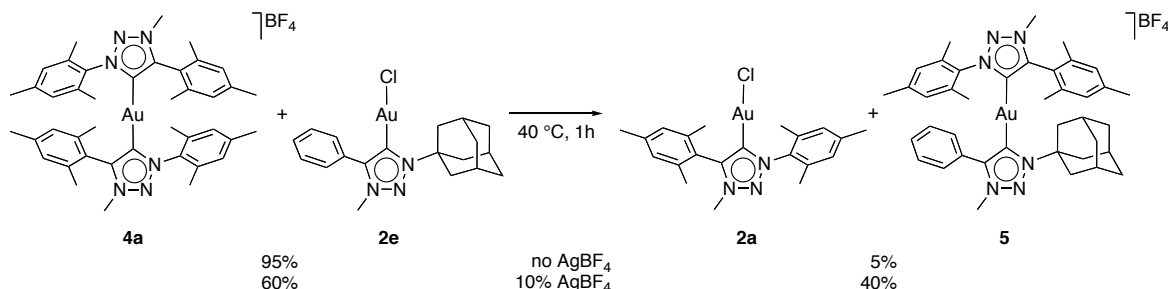


Scheme 4 Synthesis of bis(triazolylidene) gold(I) complexes **4a** and **4e** and ORTEP representation of one of the two crystallographically independent molecules of **4e** (50% probability level, Cl⁻/ICl₂⁻ anion, co-crystallized Et₂O and hydrogen atoms omitted for clarity); Au1–C1 2.029(4) Å, C1–Au1–C20 179.42(15)°.

Carbene transfer. Alternatively, the bis(carbene) gold complexes were formed by reacting the gold complexes **2a** or **2e** with AgBF₄ (Scheme 4). This procedure is straightforward and afforded the bis(carbene) complexes **4c** and **4e** in higher yields (95% and 76% respectively) and much better selectivity than via direct transmetalation (*cf* complex **4e**). No formation of by-products such as triazolium salts was observed. The spectroscopic data of the products are identical, irrespective of the nature of the non-coordinating anion (Cl⁻/ICl₂⁻ in the transmetalation, BF₄⁻ in the AgBF₄-mediated route). Silver-assisted formation of complexes **4** from **2** implies a carbene transfer from one Au center to another, indicating that the Au–C_{trz} bond is not very strong in the presence of Ag⁺ ions and that dissociation is facile.

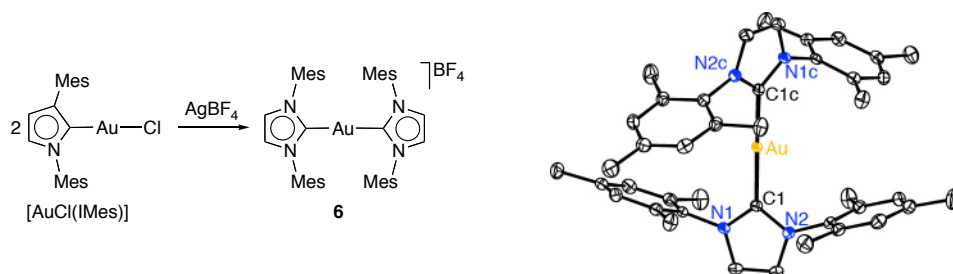
The kinetic lability of the carbene ligand in the triazolylidene gold complexes was further demonstrated by mixing **4a** and the gold complex **2e** (Scheme 5). ¹H NMR spectroscopy revealed unreacted **4a** by the diagnostic aromatic resonances at 6.93 and 6.87 ppm for the mesityl protons after 1 h. Furthermore, formation of the monocarbene gold complex **2a** was indicated in 5% by the appearance of the pertinent resonances (3.90 ppm for the N3-bound methyl group). In addition, a new heteroleptic gold complex **5** formed in small quantities (ca. 5%). Complex **5** is characterized by a lowfield signal (δ_H 4.11 ppm for the N3-methyl group), and an AB doublet for the adamantyl wingtip at 1.67 ppm and 1.48 ppm (²J_{HH} = 12.4 Hz) indicating a hindered rotation of this group as expected for bis(carbene) complexes (*cf* **4e**).

Subsequent addition of AgBF_4 (10 mol%) to this reaction mixture induced a marked increase of **2a** to about 40% and a concomitant decrease of **4a** within 1 h. These results highlight that carbene transfer occurs spontaneously, albeit slowly, and is strongly promoted by Ag^+ ions. Similar reactivity patterns have been established for triazolyidene palladium complexes in Suzuki cross-coupling catalysis,¹⁸ and in copper complexes for Huisgen cycloaddition reactions, where the catalytically active species presumably consists of a ligandless CuCl species generated by triazolyidene dissociation.¹⁹



Scheme 5 Carbene transfer from bis(carbene) gold complex **4a** to **2e**.

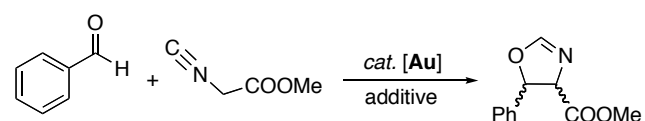
It is worth noting that this transfer process is not exclusive to triazolyidenes and also applies to Arduengo-type carbene gold complexes (Scheme 6).²⁸ Thus exposure of $\text{AuCl}(\text{IMes})^{20b}$ to AgBF_4 afforded the homoleptic complex **6** in high yield. The aromatic H_{Mes} and H_{imid} protons and also the para-positioned $\text{Ar}-\text{CH}_3$ group appear at essentially identical frequency as in the mono(carbene) gold precursor ($\Delta\delta < 0.12$ ppm), and only the ortho methyl protons shift upfield by a diagnostic 0.4 ppm ($\delta_{\text{H}} = 1.69$ ppm in **6**). The moderate shifts render ^1H NMR spectroscopy less suitable for probing the carbene transfer. More diagnostic is the characteristic 10 ppm downfield resonance in the ^{13}C NMR spectrum (δ_{C} 185.3 ppm in **6** vs 173.6 ppm in the monocarbene gold complex), similar to the shifts observed for mono- vs bis(triazolyidene) complexes (see above) and also related heteroleptic bis(imidazolyidene) gold complexes.²⁵



Scheme 6 Synthesis and molecular structure of bis(IMes) gold complex **6** (50% probability, hydrogens and anion omitted for clarity); $\text{Au}(1)-\text{C}(1)$ 2.007(2) Å, $\text{C}(1)\text{A}-\text{Au}(1)-\text{C}(1)\text{B}$ 176.32(10)°.

Catalytic synthesis of oxazolines. The carbene transfer reactivity patterns have specific relevance in catalysis, especially in forming ligandless and hence highly reactive gold centers,²⁹ and we have exploited this concept in oxazoline synthesis. The new triazolylidene gold complexes are effective catalyst precursors for the aldol condensation of isocyanoacetate and aldehydes to afford oxazolines.^{30,31} An initial set of experiments was carried out using benzaldehyde and methyl isocyanoacetate as model substrates in order to determine the activity of the different gold complexes and the relevance of additives (Table 2). The results indicate that the phosphine triazolylidene gold(I) complex **3a** and the bis(triazolylidene) gold(I) complex **4a** are poor catalyst precursors (entries 2, 3) while the neutral monocarbene gold complex **2a** provides access to a moderately active species (entry 1). Addition of AgBF₄, in particular in combination with NEt₂Pr₂ as a Brønsted base^{31,32} accelerated catalytic transformations significantly (entries 4–6). Interestingly, this is a synergistic effect, as addition of only a base is detrimental to conversions (entry 5). The use of a base shifted the product distribution from an essentially 1:1 *cis/trans* ratio to 3:1 in favour of the *trans* isomer. In contrast, the reaction temperature had no impact on the stereoselectivity of the condensation (entries 6–9). However, the reaction temperature directly correlated with the conversion rate. While reactions at 0 °C required almost 24 h to reach completion, full conversions were accomplished within only 30 min at 40 °C under otherwise identical conditions.

Table 2 Evaluation of triazolylidene gold complexes as catalyst precursors^{a)}



entry	[Au]	additive	time (h)	Temp °C	conv. (%) ^{b)}	<i>cis/trans</i> ^{b)}
1	2a	---	24	20	72	48/52
2	3a	---	24	20	10	44/56
3	4a	---	24	20	0	---
4	2a	AgBF ₄	24	20	96	48/52
5	2a	NEt ₂ Pr ₂	24	20	9	23/77
6	2a	AgBF ₄ , NEt ₂ Pr ₂	6	20	96	27/73
7	2a	AgBF ₄	22	0	9	39/61

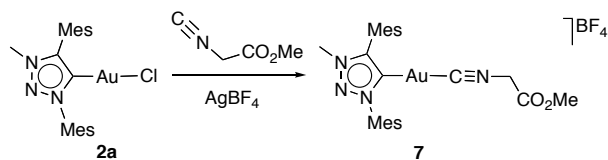
8	2a	AgBF ₄ , NEt ₂ Pr	22	0	98	26/74
9	2a	AgBF ₄ , NEt ₂ Pr	0.5	40	96	24/76

^{a)} General conditions: benzaldehyde (1.52 mmol), methyl isocyanoacetate (1.38 mmol), **2a** (14 μmol), CH₂Cl₂ (4 mL); as indicated: AgBF₄ (16 μmol), base (166 μmol).

^{b)} Conversions and *cis/trans* ratio determined by ¹H NMR spectroscopy.

Control experiments were performed in order to determine whether the condensation is gold-catalyzed. Catalytic runs using K[N(SiMe₃)₂] in the absence or presence of the triazolium salt **1a** gave no oxazoline product within 20 h, indicating that the condensation is unlikely to be base-catalyzed nor organo-catalyzed by an in-situ generated triazolylidene. The latter may be initiated by ligand dissociation from the gold complexes **2a**. Simple AuCl(SMe₂) gave only marginal conversions (13% in 20 h).

The beneficial effect of AgBF₄ was intriguing, especially when considering its role in mediating the formation of bis(triazolylidene) complexes such as **4**. We therefore performed a series of experiments to clarify the role of the silver additive with a particular focus on the early stages of the catalytic reaction. Thus complex **2a** did not yield any oxazoline in the absence of AgBF₄ within the first 10 min, but 75% conversion were reached with equimolar quantities of **2a** and AgBF₄ (Table 3, entries 1,2).³³ The role of Ag⁺ is usually to scavenge a halide in the catalyst activation step,³⁴ and we thus prepared the isonitrile complex **7** as a potential first intermediate in the catalytic cycle (Scheme 7).³⁵ Even though **7** should, not require AgBF₄ to turn over if the triazolylidene is a mere spectator ligand, this complex is completely inactive within 10 min under standard conditions and only accomplishes moderate conversions once AgBF₄ is added (28% conversion, entries 3,4). Hence Ag⁺ appears to have a role beyond abstracting the chloride from complex **2a** and is involved in removing the triazolylidene from the gold coordination sphere.³⁶ These observations together with the high yield of bis(triazolylidene) complexes **4** from **2a** in the presence of AgBF₄ suggests that triazolylidene dissociation from the gold complex is relevant for generating the catalytically active species.



Scheme 7 Synthesis of cationic triazolylidene complex **7**

Table 3 Catalytic synthesis of oxazolines with various triazolylidene gold complexes ^{a)}

entry	[Au]	AgBF ₄ (equiv)	conv'n (%) ^{b)}	cis/trans ^{b)}
1	2a	0	0	---
2	2a	1	73	25/75
3	7	0	0	---
4	7	1	28	36/64
5	4a	0	0	---
6	4a	1	59	36/64
7	4a	10	94	28/72
8	AuCl(SMe ₂)	0	0	---

^{a)} Benzaldehyde (1.5 mmol), methyl isocyanoacetate (1.4 mmol), [Au] (14 μmol), base (0.17 mmol), equiv AgBF₄ relative to [Au], CH₂Cl₂ (4 mL), 40 °C, 10 min ^{b)} Conversions and *cis/trans* ratio determined by ¹H NMR spectroscopy.

Based on this presumption, the catalytic inactivity of the bis(carbene) complex **4a** is not unexpected (entries 5–7). With added AgBF₄ (1 equiv per Au), activity is resumed, albeit relatively low (59% after 10 min). Performance is substantially increased, however, when 10 equiv AgBF₄ were added (94%). This reactivity pattern is commensurate with triazolylidene dissociation as catalyst activation step, yielding predominantly a weakly active mono(carbene) complex at low Ag/**4a** ratio, and inducing dissociation of both carbene ligands at higher Ag/**4a** ratios to give an active species identical to that obtained from **2a** and AgBF₄. Since the free carbene is catalytically silent (*vide supra*), these results taken together strongly suggest that the catalytically active species is a triazolylidene-free species, either a ligandless ‘hot’ Au⁺ ion or a gold aggregate (cluster or nanoparticle).³⁷ Small gold clusters have been recently reported to be extraordinary active in C–C bond forming reactions.³⁸ Further support for the formation of aggregates was obtained from analysis of the catalytic reaction mixture by dynamic light scattering, revealing the presence of particles in the 100 nm range once AgBF₄ was added to a solution containing complex **2a** and the substrate (Fig. S1). Repetitive experiments indicated consistently similarly sized particles, suggesting that additives (carbenes, triazolium salts, or amine) may be involved in stabilizing the particles and in preventing the formation of larger aggregates.³⁹ Such a model provides a rationale for the synergistic effect of Ag⁺ as carbene transfer agent and the base as particle stabilizer in catalytic reactions (*cf* Table 2). While the

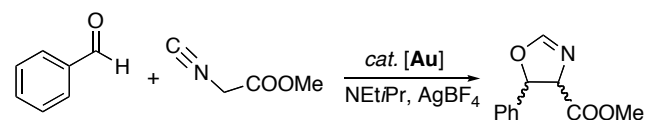
formation of smaller (and presumably more active) particles cannot be excluded due to the intrinsic principles of light scattering, these data reveal that aggregation of the ligandless gold ions is occurring under catalytic conditions. It is worth noting that these *in situ* generated nanoparticles induce substantially higher catalytic activity than AuCl(SMe₂), which probably suffers from aggregation in CH₂Cl₂ as the solvent for this catalytic reaction (entry 8).

Carbene dissociation from complex **2a** was further confirmed by NMR spectroscopy. Under catalytically relevant conditions (1 equiv AgBF₄, 40 °C) the mono(triazolylidene) complex furnishes 5–10% of **4a** within 10 min, as indicated by the appearance of the characteristic resonances at 6.92 and 6.86 ppm for the aromatic mesityl protons and the inequivalence of the three CH₃ groups of the mesityl wingtip group.⁴⁰ These results underline the kinetic lability of the Au-C_{trz} bond and support the formation of an active Au species via triazolylidene dissociation in the presence of Ag⁺.

Evaluation of complexes **2a–g** (Table 4, entries 1–6) revealed no direct correlation between catalytic activity (TON, TOF) and the steric or electronic properties of the triazolylidene wingtip groups. For example, sterically demanding adamantyl/phenyl substituents induce similar activity as two mesityl groups (entries 1,5). Furthermore, only very minor differences were observed in *cis/trans* selectivity of product formation, suggesting that the triazolylidene wingtip groups are not involved the condensation step. When using the chiral triazolylidene gold complex **2g**, no asymmetric induction was observed and the obtained product mixture was racemic according to chiral HPLC analysis. The absence of any enantio- or diastereoselective control even with **2g** suggests a common catalytic species from complexes **2a–g** that is not related to the triazolylidene ligand, in agreement with carbene dissociation as catalyst activation step.⁴¹ The rate of dissociation is likely dependent on the wingtip groups, hence providing a rationale for the different activities (yet identical selectivities) observed with complexes **2a–g**. Accordingly, the activities observed in the series of complexes reflect the lability of the carbene ligand rather than the ligand-induced differences at the gold center. Thus, methoxy-substituted aryl wingtip groups (**2b**) or *t*Bu wingtips (**2d**) imparted highest activity and gave complete conversion within 5 min (entries 2,4). Activity differences for these two complexes unveiled only when reducing the catalyst loading from 1 to 0.5 mol%. Under these conditions, catalysis initiated by complex **2b** was significantly faster and achieved full conversion within 30 min while complex **2d** required about twice as long (entries 7,8). Time-conversion profiles (Fig. S2) provided pertinent turnover

frequencies (TOFs). At 50% conversion, complex **2b** reached a $\text{TOF}_{50} = 2000 \text{ h}^{-1}$. To the best of our knowledge this is the highest activity reported for catalytic oxazoline synthesis to date.^{30,31} Further lowering the catalyst loading to 0.01 mol% is possible, though reaction time has to be considerably extended to accomplish the 10,000 turnovers for full conversion (**2d**, entry 9). Further lowering of catalyst loading was not productive (entry 10).

Table 4 Catalytic activity of different gold complexes ^{a)}



entry	[Au]	loading (mol%)	time (h)	conv'n (%) ^{b)}	<i>cis/trans</i> ^{b)}	TON	$\text{TOF}_{50} (\text{h}^{-1})$ ^{c)}
1	2a	1	0.5	98	24/76	98	660
2	2b	1	0.08	98	27/73	98	>1200
3	2c	1	1.5	98	30/70	98	160
4	2d	1	0.08	96	25/75	96	>1200
5	2e	1	0.5	98	24/76	98	800
6	2f	1	1	98	24/76	98	400
7	2b	0.5	0.5	95	26/74	190	2000
8	2d	0.5	1	97	24/76	194	350
9	2b	0.01	44	96	27/73	9600	1100
10	2d	0.001	240	< 2	---	---	---

^{a)} General conditions: benzaldehyde (1.52 mmol), methyl isocyanoacetate (1.38 mmol), AgBF_4 (16 μmol), [Au] (14 μmol), base (166 μmol), CH_2Cl_2 (4 mL).

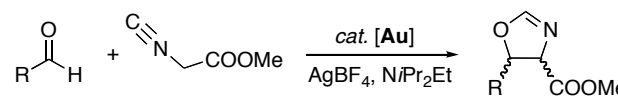
^{b)} Conversions and *cis/trans* ratio determined by ^1H NMR spectroscopy.

^{c)} TOF_{50} = turnover frequency at 50% conversion.

The substrate scope was investigated with the catalyst precursors **2b** and **2g** (Table 5). Benzaldehydes with electron donating and withdrawing substituents were converted well and no significant electronic differentiation was noted. Bulky *t*BuCHO was poorly converted, presumably due to steric limitations. However these restrictions increased substantially the selectivity towards the *trans* diastereoisomer, lending further support to a substrate-controlled regioselectivity of the condensation and a marginal role of the triazolylidene ligand in the

catalytic cycle, if any. In agreement with such a reactivity pattern, earlier work has demonstrated the critical role of (chiral) anions in determining the product selectivity in the protodeauration step of related condensation reactions.⁴²

Table 5 Substrate scope for the catalytic aldol condensation with complexes **2b** and **2g**.^{a)}



Entry	Complex	R	conv'n (%) ^{b)}	<i>cis/trans</i> (%) ^{b)}
1	2b	C ₆ H ₅	> 95	28/72
2	2g	C ₆ H ₅	> 95	25/75
3	2b	4-MeO-C ₆ H ₄	93	37/63
4	2g	4-MeO-C ₆ H ₄	84	20/80
5	2b	4-NO ₂ -C ₆ H ₄	> 95	35/65
6	2g	4-NO ₂ -C ₆ H ₄	91	16/84
7	2b	4-Cl-C ₆ H ₄	> 95	39/61
8	2g	4-Cl-C ₆ H ₄	78	30/70
9	2b	<i>t</i> Bu	20	5/95
10	2g	<i>t</i> Bu	46	0/100

^{a)} Aldehyde (1.5 mmol), methyl isocyanoacetate (1.4 mmol), AgBF₄ (16 μmol), [Au] (14 μmol), NiPr₂Et (0.17 mmol), CH₂Cl₂ (4 mL), RT, 18 h; ^{b)} Conversions and *cis/trans* ratio determined by ¹H NMR spectroscopy.

Conclusions

Triazolylidene gold complexes are precursors for highly active catalysts for the synthesis of oxazolines. Mechanistic investigations and stereoselective considerations provide strong evidence for triazolylidene dissociation as a critical step of catalyst activation. This dissociation is facilitated by the presence of AgBF₄ as carbene transfer mediator, a role of silver that is often underestimated in metal catalyzed reaction and that reaches significantly beyond classical halide scavenging. Once activated, appreciable turnover numbers (10⁵) and frequencies (10⁴ h⁻¹) are achieved. The carbene transfer is spontaneous, albeit slow, and considerably accelerated in the presence of Ag⁺ ions. Transfer is not restricted to triazolylidenes and is also demonstrated for the

more frequently used IMes as representative of Arduengo-type NHCs. These results call into question the often cited and generally assumed stability of the Au–C_{NHC} bond in catalytic applications, in particular when silver salts are used as additives.^{43,44} Carbene dissociation processes as demonstrated here provide ligandless metal centers that impart high catalytic activity. Noteworthy, in such a model the different observed catalytic activities do not reflect ligand-induced changes at the metal center, but different dissociation propensities of the ligands in the activation step. Such reactivity patterns may be relevant beyond gold-centered NHC chemistry and warrant a cautionary note when assuming a ‘strong’ or ‘kinetically inert’ bonding of NHCs to metal centers, especially to coinage metals. Metal-triggered ligand dissociation provides interesting perspectives, *e.g.* for supramolecular chemistry (self-assembly) and for generating latent catalysts that can be activated selectively, a process that is much harder to achieve with other neutral donor ligand systems such as imines or phosphines.

Experimental section

General. 1-(3,4,5,-trimethoxyphenyl)-4-(4-methoxyphenyl)-1,2,3-triazole⁴⁵ and the triazolium salts **1a**,⁴⁶ **1c**,⁴⁷ **1g**,²³ and AuCl(IMes)^{20c} were described previously. The synthesis of all new triazoles and triazolium salts is reported in the supporting information. All solvents used for the reactions were purified using an alumina/catalyst column system (Thermovac Co.). Ag₂O was freshly prepared according to literature procedures.⁴⁸ All other reagents are commercially available and were used as received. Unless specified otherwise, NMR spectra were recorded at 25 °C on Varian Innova spectrometers operating at 300, 400 or 500 MHz (¹H NMR) and 75, 100 or 125 MHz (¹³C{¹H} NMR), respectively. Chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to residual solvent resonances. Assignments are based on homo- and heteronuclear shift correlation spectroscopy. Elemental analyses were performed by the Microanalytical Laboratory at University College Dublin, Ireland, by using an Exeter Analytical CE-440 Elemental Analyzer.

General procedure for the synthesis of the gold carbene complexes 2. Triazolium salt **1** (1.0 eq), Ag₂O (0.5 eq) and AuCl(SMe₂) (1.0 eq) in dry CH₂Cl₂ were stirred in CH₂Cl₂ in the dark at room temperature for 24 h and filtered through Celite. The solvent was removed in vacuo the

residue was washed with pentane (25 mL) and dried, then re-dissolved in CH₂Cl₂ (2 mL) and precipitated with pentane (50 mL). The precipitate was collected by filtration and passed through a short pad of SiO₂. Elution with dry CH₂Cl₂, and solvent evaporation yielded pure complex **2**.

Complex 2a. According to the general method, the title compound was obtained from **1a** (125 mg, 0.28 mmol), Ag₂O (33 mg, 0.14 mmol), and AuCl(SMe₂) (82 mg, 0.28 mmol) in dry CH₂Cl₂ (30 mL) as a white solid (92 mg, 60%). ¹H NMR (CDCl₃, 500 MHz): δ 7.03 (s, 4H, H_{Mes}), 3.90 (s, 3H, NCH₃), 2.38 (s, 6H, ArCH₃), 2.10 (s, 12H, ArCH₃). ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 162.0 (C_{trz}-Au), 146.1 (C_{trz}-Mes), 141.1, 140.9, 138.1, 135.7, 134.3, 129.6, 129.3, 122.3 (8 × C_{Mes}), 36.9 (NCH₃), 21.5, 21.4, 20.3, 17.6 (4 × Ar-CH₃). ¹H NMR (CD₂Cl₂, 500 MHz): δ 7.00 (s, 2H, H_{Mes}), 7.09 (s, 2H, H_{Mes}), 3.90 (s, 3H, NCH₃), 2.41 (s, 3H, ArCH₃), 2.39 (s, 3H, ArCH₃), 2.13 (s, 6H, ArCH₃), 2.10 (s, 6H, ArCH₃). ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz): δ 162.4 (C_{trz}-Au), 146.4 (C_{trz}-Mes), 141.7, 141.6, 138.6, 134.9, 129.9, 129.6, 129.3, 122.7 (8 × C_{Mes}), 37.4 (NCH₃), 21.7, 21.6, 20.4, 17.8 (4 × Ar-CH₃). Anal. Calcd for C₂₁H₂₅AuClN₃ (551.86): C, 45.70; H, 4.57; N, 7.61. Found: C, 45.77; H, 4.37; N, 7.55.

Complex 2b. According to the general method, reaction of **1b** (166 mg, 0.34 mmol), Ag₂O (41 mg, 0.17 mmol), and AuCl(SMe₂) (100 mg, 0.34 mmol) in dry CH₂Cl₂ (30 mL) gave **2b** as a yellow solid (160 mg, 80%). ¹H NMR (CDCl₃, 500 MHz): δ 7.61 (d, ³J_{HH} = 9.0 Hz, 2H_{Ar}), 7.60 (s, 2H_{Ar}), 7.02 (d, ³J_{HH} = 9.0 Hz, 2H_{Ar}), 4.18 (s, 3H, NCH₃), 3.95 (s, 6H, OCH₃), 3.92 (s, 3H, OCH₃), 3.89 (s, 3H, OCH₃). ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 161.5, 131.2, 114.9, 113.2 (4 × C_{Ar}), 153.7, 139.7, 134.5, 101.8 (4 × C_{Ar}), 156.7 (C_{trz}-Au), 147.8 (C_{trz}-Ar), 61.2 (OCH₃), 56.9 (OCH₃), 55.7 (OCH₃), 38.1 (NCH₃). Anal. Calcd for C₁₉H₂₁AuClN₃O₄ (587.80): C, 38.82; H, 3.60; N, 7.15. Found: C, 38.58; H, 3.30; N, 7.05.

Complex 2c. According to the general method, reaction of **1c** (120 mg, 0.33 mmol), Ag₂O (40 mg, 0.16 mmol), and AuCl(SMe₂) (98 mg, 0.33 mmol) in dry CH₂Cl₂ (30 mL) yielded **2c** as an off-white solid (107 mg, 70%). ¹H NMR (CDCl₃, 500 MHz): δ 8.05 (d, ³J_{HH} = 7.0 Hz, 2H, H_{Ar}), 7.68 (d, ³J_{HH} = 6.5 Hz, 2H, H_{Ar}), 7.56–7.50 (m, 6H, H_{Ar}), 4.18 (s, 3H, NCH₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 157.3 (C_{trz}-Au), 147.8 (C_{trz}-Ph), 139.2, 130.6, 130.4, 129.9, 129.7, 129.4,

126.4, 124.3 (8 × C_{Ar}), 38.3 (NCH₃). Anal. Calcd for C₁₅H₁₃AuClN₃ (467.70): C, 38.52; H, 2.80; N, 8.98. Found: C, 38.37; H, 2.50; N, 8.77.

Complex 2d. According to the general method, **1d** (150 mg, 0.46 mmol), Ag₂O (54 mg, 0.23 mmol), AuCl(SMe₂) (136 mg, 0.46 mmol) and [NEt₃Me]I (11 mg, 0.046 mmol) were reacted in dry CH₂Cl₂ (30 mL) for 72 h. Complex **2d** was obtained as a white solid (90 mg, 45%). ¹H NMR (CDCl₃, 500 MHz): δ 4.22 (s, 3H, NCH₃), 1.93, 1.67 (2 × (s, 9H C-CH₃)). ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 157.7 (C_{trz}-Au), 152.7 (C_{trz}-*t*Bu), 64.8 (N-CMe₃), 40.9 (NCH₃), 32.1 (C-CMe₃), 32.0, 30.9 (2 × C-CH₃). Anal. Calcd for C₁₁H₂₁AuClN₃ (427.72): C, 30.89; H, 4.95; N, 9.82. Found: C, 30.70; H, 4.59; N, 9.62. ¹H NMR (CD₂Cl₂, 500 MHz): δ 4.20 (s, 3H, NCH₃), 1.92, 1.66 (2 × (s, 9H C-CH₃)). ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz): δ 155.0 (C_{trz}-Au), 152.6 (C_{trz}-*t*Bu), 64.9 (N-CMe₃), 41.3 (NCH₃), 32.3 (C-CMe₃), 32.1, 31.0 (2 × C-CH₃).

Complex 2e. According to the general method, reaction of **1e** (73 mg, 0.17 mmol), Ag₂O (20 mg, 0.08 mmol), and AuCl(SMe₂) (52 mg, 0.17 mmol) in dry CH₂Cl₂ (30 mL) gave **2e** as a white solid (70 mg, 77%). ¹H NMR (CDCl₃, 500 MHz): δ 7.64 (bs, 2H_{Ar}), 7.50 (bs, 3H_{Ar}), 4.06 (s, 3H, NCH₃), 2.66 (m, 6H, CH₂_{ada}), 2.32 (bs, 3H, CH_{ada}), 1.81 (m, 6H, CH₂_{ada}). ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 152.8 (C_{trz}-Au), 147.7 (C_{trz}-Ph), 130.3, 129.8, 129.2, 127.4 (4 × C_{Ph}), 65.3 (C_{ada}-N), 43.3 (CH₂_{ada}), 37.8 (NCH₃), 35.9 (CH₂_{ada}), 30.0 (CH_{ada}). Anal. Calcd for C₁₉H₂₃AuClN₃ (525.82): C, 43.40; H, 4.41; N, 7.99. Found: C, 44.13; H, 4.22; N, 7.76.

Complex 2f. The title compound was obtained according to the general method from **1f** (100 mg, 0.25 mmol), Ag₂O (29 mg, 0.13 mmol), and AuCl(SMe₂) (78 mg, 0.25 mmol) in dry CH₂Cl₂ (30 mL) as a white solid (86 mg, 65%). ¹H NMR (CDCl₃, 500 MHz): δ 4.21 (s, 3H, NCH₃), 2.64 (m, 6H, CH₂_{ada}), 2.28 (bs, 3H, CH_{ada}), 1.81 (m, 6H, CH₂_{ada}), 1.67 (s, 9H, C-CH₃). ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 154.5 (C_{trz}-Au), 151.5 (C_{trz}-*t*Bu), 65.2 (C_{ada}-N), 43.3 (CH₂_{ada}), 40.9 (NCH₃), 36.0 (CH₂_{ada}), 31.9 (C-CMe₃), 32.0 (C-CH₃), 30.0 (CH_{ada}). Anal. Calcd for C₁₇H₂₇AuClN₃ (505.83): C, 40.37; H, 5.38; N, 8.31. Found: C, 40.33; H, 5.22; N, 8.28.

Complex 2g

1g (94 mg, 0.12 mmol) was mixed with Ag₂O (14 mg, 0.06 mmol) and stirred for one hour in dry CH₂Cl₂ (30 mL) at room temperature. AuCl(SMe₂) (36 mg, 0.12 mmol) was added to the reaction mixture and stirred for additional 16 h. The workup and purification were carried out according to the general method to yield **2g** as a white solid (69 mg, 62%). ¹H NMR (CDCl₃, 600 MHz) δ 8.22 (br, 2H, H_{Ar}), 8.20–7.98 (m, 6H, H_{Ar}), 7.61 (m, 2H, H_{Ar}), 7.47–7.43 (m, 6H, H_{Ar}), 7.37–7.22 (m, 4H, H_{Ar}), 7.20–7.00 (m, 9H, H_{Ar}), 6.60–6.45 (m, 7H, H_{Ar}), 4.50, 4.21 (2 × AB doublet, ²J_{HH} = 14.3 Hz, 2H, NCH₂Ph), 3.34 (d, 1H, ³J_{HH} = 15.4 Hz, N1CHCH_{αβ}Ph), 3.03 (dd, 1H, ³J_{HH} = 15.4 Hz, N1CHCH_{αβ}Ph). ¹³C NMR (150 MHz, CDCl₃) δ 166.4 (NC=O), 165.9 (C_{trz}-Au), 139.6, 135.3, 132.5, 132.3, 132.2, 131.8, 131.3, 130.5, 129.8, 129.4, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.3, 127.0 (all C_{Ar}), 68.9 (N1CHCH_{αβ}Ph), 68.7 (NCPh₂), 54.3 (NCH₂Ph), 36.2 (NCHCH_{αβ}Ph). Anal. Calcd for (C₄₉H₃₉AuN₄O)₂ (1866.6): C, 65.62; H, 4.38; N, 6.25. Found: C, 65.52; H, 4.62; N, 6.03.

Complex 2h. Complex **2h** was obtained according to the general procedure from triazolium salt **1h** (110 mg, 0.30 mmol), freshly prepared Ag₂O (139 mg, 0.60 mmol), and AuCl(SMe₂) (90 mg, 0.30 mmol) in dry CH₂Cl₂ (25 mL). The mixture was stirred in the dark for 5 h and filtered through Celite. The solvent was concentrated to 1 mL and treated with pentane (150 mL). A white precipitate formed after storage at 4 °C for 16 h. This solid was collected by decantation and was dried in vacuo (60 mg, 36%). Recrystallized by slow diffusion of pentane into a CH₂Cl₂ solution of **2h** yielded single crystals suitable for X-ray diffraction analysis. ¹H NMR (CDCl₃, 400 MHz) δ 6.92 (s, 2H, H_{Ar}), 4.71 (s, 2H, CH₂N), 4.39 (NCH₃), 2.30 (s, 3H, Ar-CH₃), 2.00 (s, 6H, Ar-CH₃), 1.17 (s, 9H, CH₃ B_{oc}). ¹³C{¹H} NMR (CDCl₃, 100 MHz): 163.5 (N-C=O), 163.3 (C_{trz}-Au), 150.6 (C_{trz}-alkyl), 137.9, 136.3, 134.6, 129.3 (4 × C_{Mes}), 76.3 (CMe₃), 42.8 (CH₂N), 37.5 (NCH₃), 28.8 (CH₃ B_{oc}), 21.3, 18.0 (2 × Ar-CH₃). HR-MS (ES⁺) Calcd for C₃₆H₅₁Au₂N₈O₄ [M+H]⁺: 1053.3364. Found 1053.3409. Calcd for (C₁₈H₂₅AuN₄O₂)₂ (1052.8): C, 41.07; H, 4.79; N, 10.64. Found: C, 41.10; H, 4.81; N, 10.48.

Complex 3. Complex **2a** (50 mg, 0.09 mmol), PPh₃ (24 mg, 0.09 mmol), and AgBF₄ (35 mg, 0.18 mmol) in dry CH₂Cl₂ (30 mL) were stirred in the dark for 4 h, and then passed through by a small pad of Celite and eluted with CH₂Cl₂ (7 mL). After evaporation of all the volatiles the

residue was washed with pentane (20 mL), dissolved in CH₂Cl₂ (0.5 mL), and passed through a short pad of Celite. Elution with CH₂Cl₂ (7 mL) and evaporation of the solvent afforded pure **3** as a white powder (62 mg, 80%). ¹H NMR (CDCl₃, 500 MHz): δ 7.52 (t, ³J_{HH} = 7.2 Hz, 3H, H_{PPh3}), 7.40 (t, ³J_{HH} = 7.2 Hz, 6H, H_{PPh3}), 7.16 (dd, ³J_{HH} = 7.2 Hz, ³J_{HP} = 12.8 Hz, 6H, H_{Ph3P}), 7.07 (s, 4H, H_{Mes}), 4.07 (s, 3H, NCH₃), 2.41, 2.38 (2 × s, 3H, ArCH₃), 2.18, 2.13 (2 × s, 6H, ArCH₃). ³¹P{¹H} NMR (CDCl₃, 162 MHz): δ 40.9 (s, PPh₃). ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 177.0 (d, ²J_{CP} = 122.1 Hz, C_{trz}-Au), 147.4 (C_{trz}-Mes), 141.4, 141.3, 138.3, 135.8, 134.7 (5 × C_{Mes}), 134.1 (d, ³J_{CP} = 13.7 Hz, CH_{PPh3}), 132.3 (d, ⁴J_{CP} = 2.5 Hz, CH_{PPh3}), 129.7 (C_{Mes}), 129.5 (d, ²J_{CP} = 14.5 Hz, CH_{PPh3}), 128.5 (d, ¹J_{CP} = 57.4 Hz, C_{PPh3}), 121.6 (C_{Mes}), 37.7 (NCH₃), 21.5, 20.5, 20.4, 17.7 (3 × Ar-CH₃). Anal. Calcd for C₃₉H₄₀AuPN₃BF₄ (865.50): C, 54.12; H, 4.66; N, 4.86. Found: C, 53.73; H, 4.46; N, 4.55.

Complex 4a. Method A: Triazolium salt **1a** (200 mg, 0.45 mmol), and Ag₂O (55 mg, 0.23 mmol) in dry CH₂Cl₂ (10 mL) were stirred in the dark for 24 h. AuCl(SMe₂) (66 mg, 0.22 mmol) was added and the solution was stirred for 48 h and filtered through Celite. The solvent was removed in vacuo then the residue was washed with pentane (25 mL) and dried, then re-dissolved in CH₂Cl₂ (2 mL) and precipitated with pentane (50 mL). The solid was collected by filtration under air then dried over vacuum to yield **4a** as a yellow solid (150 mg, 73%). Microanalysis indicates a 1:7 mixture of chloride and dichloroiodate(I) anions; Anal. Calcd for 7/8 C₄₂H₅₀N₆AuCl₂ (1033.66) + 1/8 C₄₂H₅₀N₆AuCl₂ (1033.66): C, 49.78; H, 4.97; N, 8.29. Found: C, 49.79; H, 4.74; N, 8.17.

Method B: Complex **2a** (50 mg, 0.09 mmol), and AgBF₄ (18 mg, 0.09 mmol) in dry CH₂Cl₂ (10 mL) were stirred in the dark for 12 h at RT. The solution was passed through a short pad of Celite and eluted with CH₂Cl₂ (5 mL) and concentrated to approximately 1 mL. Addition of pentane (50 mL) afforded **4a** as a white powder. The solid was collected by filtration and dried under vacuum (40 mg, 95%). Anal. Calcd for C₄₂H₅₀N₆AuBF₄ (922.66) × 0.5H₂O: C, 54.14; H, 5.52; N, 9.02. Found: C, 54.10; H, 5.28; N, 8.66.

Spectroscopic analyses were identical for both products: ¹H NMR (CDCl₃, 400 MHz): δ 6.92 (s, 4H, H_{Mes}), 6.86 (s, 4H, H_{Mes}), 3.88 (s, 6H, NCH₃), 2.42 (s, 12H, ArCH₃), 1.82 (s, 12H, ArCH₃), 1.76 (s, 12H, ArCH₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 175.8 (C_{trz}-Au), 146.7 (C_{trz}-Mes),

140.6, 140.4, 138.0, 135.6, 134.2, 129.2, 128.9, 122.1 ($8 \times C_{Mes}$), 37.1 (NCH₃), 21.6, 21.5, 20.1, 17.3 ($4 \times Ar-CH_3$).

Complex 4e. *Method A:* Triazolium salt **1e** (200 mg, 0.47 mmol), and Ag₂O (55 mg, 0.23 mmol) in dry CH₂Cl₂ (10 mL) were stirred in the dark for 24 h. AuCl(SMe₂) (70 mg, 0.24 mmol) was added and the solution was stirred for 48 h and filtered through Celite. The solvent was removed in vacuo the residue was washed with pentane (25 mL) and dried, then re-dissolved in CH₂Cl₂ (2 mL) and precipitated with pentane (50 mL). The solid was collected by filtration under air then dried in vacuum to yield a yellow solid comprised of a mixture of **2e** and **4e** (152 mg, ca. 1:1). Pure **4e** was obtained from recrystallization by slow diffusion of Et₂O into a saturated solution of complex **4e** in acetone (64 mg, 30%). Microanalysis indicates a 3:2 mixture of chloride and dichloroiodate(I) anions; Anal. Calcd for 0.6 C₃₈H₄₆AuN₆[Cl₂I] (981.59) + 0.4 C₃₈H₄₆AuN₆[Cl] (819.23): C, 51.62; H, 5.24; N, 9.50. Found: C, 51.65; H, 5.50; N, 8.95.

Method B: Complex **2e** (40 mg, 0.08 mmol), and AgBF₄ (15 mg, 0.08 mmol) in dry CH₂Cl₂ (10 mL) were stirred in the dark for 12 h at 40 °C. The solution was passed through a short pad of Celite and eluted with CH₂Cl₂ (5 mL) and concentrated to approximately 1 mL. Addition of pentane (50 mL) afforded **4e** as a white powder. The solid was collected by filtration and dried under vacuum. (25 mg, 76%). Anal. Calcd for C₃₈H₄₆AuBF₄N₆ (870.57) × 0.5H₂O: C, 51.89; H, 5.39; N, 9.55. Found: C, 51.80; H, 5.22; N, 9.16.

Spectroscopic analyses were identical for both products: ¹H NMR (CDCl₃, 400 MHz): δ 7.63 (d, ³J_{HH} = 7.2 Hz, 4H, H_{Ph}), 7.51–7.45 (m, 6H, H_{Ph}), 4.11 (s, 6H, NCH₃), 2.37 (br s, 12H, CH₂_{ada}), 2.06 (br s, 6H, CH_{ada}), 1.63, 1.48 (2 × AB doublet, ²J_{HH} = 12.4 Hz, 12H, CH₂_{ada}). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 166.5 (C_{trz}-Au), 149.0 (C_{trz}-Ph), 130.4, 130.1, 129.6, 127.6 (4 × C_{Ph}), 64.8 (C_{ada}-N), 43.4 (CH₂_{ada}), 38.0 (NCH₃), 35.7 (CH₂_{ada}), 29.7 (CH_{ada}).

Complex 6. AuCl(IMes) (100 mg, 0.18 mmol), and AgBF₄ (35 mg, 0.18 mmol) in dry CH₂Cl₂ (10 mL) were stirred in the dark for 12 h at 40 °C. The solution was passed through a short pad of Celite, eluted with CH₂Cl₂ (5 mL) and concentrated to 1 mL. Addition of pentane (50 mL) afforded **6** as a white powder, which was collected by filtration and dried under vacuum (75 mg, 83%). ¹H NMR (CDCl₃, 400 MHz): δ 7.10 (s, 4H, H_{imi}), 6.88 (s, 8H, H_{Mes}), 2.43 (s, 12H, ArCH₃), 1.69 (s, 24H, ArCH₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 185.3 (C_{imi}-Au), 139.5,

134.7, 134.3, 129.3 (4 × C_{Mes}), 123.3 (H_{imi}), 21.4, 17.3 (2 × Ar-CH₃). Anal. Calcd for C₄₂H₄₈N₄AuBF₄ (892.63): C, 56.51; H, 5.42; N, 6.28. Found: C, 56.45; H, 5.26; N, 6.15.

Complex 7. Complex **2a** (50 mg, 0.09 mmol), methyl isocyanoacetate (11 mg, 0.11 mmol), and AgBF₄ (35 mg, 0.18 mmol) in CD₂Cl₂ (2.0 mL) were stirred in the dark for 16 h, and then passed through a small pad of Celite and eluted with CD₂Cl₂ (0.5 mL). ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.11 (s, 4H, H_{Mes}), 4.55 (s, 2H, CNCH₂), 3.95 (s, 3H, NCH₃), 3.80 (s, 3H, COOCH₃), 2.41, 2.39 (2 × s, 3H, ArCH₃), 2.11, 2.08 (2 × s, 6H, ArCH₃). ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz): δ 167.9 (COO), 163.0 (C_{trz}-Au), 148.5 (C_{trz}-Mes), 142.3, 142.2, 138.5, 135.5, 134.7, 130.2, 129.8, 121.4 (8 × C_{Mes}), 54.5 (CH₃), 46.1 (broad, CNCH₂), 37.7 (NCH₃), 21.7, 21.6, 20.5, 17.7 (4 × Ar-CH₃), Au-CN not resolved.

General procedure for the catalytic synthesis of oxazolines. In a typical procedure, benzaldehyde (0.15 mL, 1.5 mmol), methyl isocyanoacetate (0.130 mL, 1.4 mmol), complex **2** (14 μmol, 1 mol%), and NEt^{*i*}Pr₂ (24 μL, 0.17 mmol) were dissolved in CH₂Cl₂ (3.2 mL). A solution of AgBF₄ (0.8 mL, 20 mM in CH₂Cl₂/MeOH 4:1, 16 μmol) was added and the reaction was stirred at 40 °C protected from light. Samples were taken at indicated times by removing 0.1 mL of the reaction mixture by syringe and dilution with CDCl₃ (0.7 mL) for analysis by ¹H NMR spectroscopy.

Crystallographic details. Crystal data for complexes **2a**, **2b**, **2d**, **2e**, **2h**, **3**, **4e** and **6** were collected by using an Agilent Technologies SuperNova A diffractometer fitted with an Atlas detector. **2a**, **2b**, **2e**, **3**, **4e** and **6** were measured with Mo-K_α radiation (0.71073 Å), **2d** and **2h** with Cu-K_α (1.54178 Å). A complete dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical numeric absorption correction was performed.⁴⁹ The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares fitting on F² for all data using SHELXL-97.⁵⁰ Hydrogen atoms were added at calculated positions and refined by using a riding model. Anisotropic thermal displacement parameters were used for all nonhydrogen atoms. Crystallographic details are compiled in the supporting information (Tables S1-S8). CCDC numbers 945559–945566 contain 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.

Associated Content

Supporting Information: Experimental procedures for the triazolium salts, DLS data, representative time-conversion profiles and crystallographic details for all reported structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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