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Hemilabile MIC^{AN} ligands allow oxidant-free Au(I)/Au(III) arylation-lactonization of γ -alkenoic acids†

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Oxidant-free Au-catalyzed reactions are emerging as a new synthetic tool for innovative organic transformations. Still, a deeper mechanistic understanding is needed for a rational design of these processes. Here we describe the synthesis of two Au(I) complexes bearing bidentated hemilabile MIC^{AN} ligands, [Au'(MIC^{AN})Cl], and their ability to stabilize square-planar Au(III) species (MIC = mesoionic carbene). The presence of the hemilabile N-ligand contributed to stabilize the ensuing Au(III) species acting as a five-membered ring chelate upon its coordination to the metal center. The Au(III) complexes can be obtained either by using external oxidants or, alternatively, by means of feasible oxidative addition with strained biphenylene C_{sp}²–C_{sp}² bonds as well as with aryl iodides. Based on the fundamental knowledge gained on the redox properties on these Au(I)/Au(III) systems, we successfully develop a novel Au(I)-catalytic procedure for the synthesis of γ -substituted γ -butyrolactones through the arylation-lactonization reaction of the corresponding γ -alkenoic acid. The oxidative addition of the aryl iodide, which in turn is allowed by the hemilabile nature of the MIC^{AN} ligand, is an essential step for this transformation.

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Introduction

Gold catalysis has been dominated by the Lewis acidity of gold towards activation of alkenes and alkynes for nucleophilic attacks.^{1–6} On the other hand, redox Au(I)/Au(III) catalysis has been less explored and mainly achieved in the presence of sacrificial external oxidants,^{7–17} especially due to the reluctance of Au(I) to undergo oxidative addition.^{18–21} In this regard, several strategies have been explored to overcome this limitation,^{22–46} among which the chelation-assisted strategy in pre-designed ligands^{30–34} or the oxidative addition using strained molecules such as biphenylene stand out.³⁵ Bourissou pioneered in 2014 the intramolecular oxidative addition of C_{sp}²–X bonds (X = Br, I) at Au(I) by utilizing rigid 8-halonaphthyl phosphine model substrates, which suitably place the C_{sp}²–X bond close to the Au(I) atom upon coordination

to the phosphine moiety. In this manner, facile stabilization of the (P,C)-cyclometalated Au(III) products is obtained *via* oxidative addition.³² In the same line, Hashmi and Hermange used a similar strategy taking advantage of pendant pyridine groups in monophosphine ligands to stabilize Au(III) systems upon reaction of Au(I) complexes with aryl diazonium salts.^{47,48} In these examples, the subtle change from linear to square-planar geometry is crucial for the facile reactivity of Au(I) species towards a key oxidative addition process. Noteworthy, P^{AN} MeDalpos ligand showed great performance at promoting the oxidative addition of aryl halides at Au(I), as well as at stabilizing Au(III) intermediates, which paved the way to Au(I)/Au(III) catalytic transformations using the (MeDalpos)AuCl catalyst (Scheme 1a).⁴¹ For instance, in 2019 Bourissou and coworkers reported the regioselective Au(I)/Au(III)-catalyzed C3 arylation of indoles, which is rarely attained by other transition metals (Scheme 1a),⁴⁹ additionally they described the Au(I)/Au(III) catalyzed C3 allylation of indoles using allyl alcohols or allyl acetates.⁵⁰ Significantly, two independent reports by the groups of Patil⁵¹ and Bourissou⁵² disclosed the C_{sp}²–N cross-coupling reactions of aryl iodides with amines mediated by the MeDalpos-enabled Au(I)/Au(III) catalysis (Scheme 1a). In 2020, Bourissou and Patil groups independently showed that the oxidative addition of aryl iodides and π -activation of olefins can be merged by the Au(I)/Au(III) platform using (MeDalpos)AuCl as catalyst, which involves the oxy- and aminoarylation reactions of alkenols and alkenamines (Scheme 1a).^{53,54} The 1,2-heteroarylation of alkenes was also achieved using external alcohols and amines.^{54–56} Interestingly, (MeDalpos)AuCl catalyst has proven to

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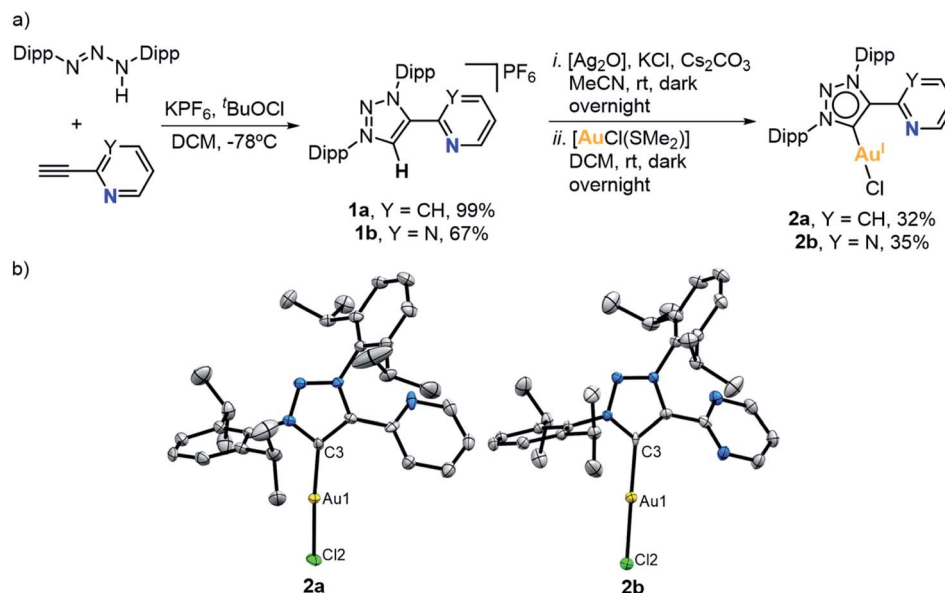


Fig. 1 (a) Synthesis of Au(I) complexes **2a** and **2b**. (b) Crystal structures of **2a** and **2b** (ellipsoids set at 50% probability and H atoms removed for clarity). Selected bond distances (Å): for **2a**, Au1–C3 1.982(6), Au1–Cl2 2.2854(17); for **2b**, Au1–C3 2.006(4), Au1–Cl2 2.2728(16).

coordination to gold had occurred. The ¹³C{¹H} NMR spectrum of **2a** showed the characteristic signal of the metalated carbon at 162.1 ppm, while in the case of the pyrimidine derivative **2b**, such signal was slightly shifted downfield, appearing at 165.3 ppm. Furthermore, the molecular structure of both Au(I) complexes **2a** and **2b** was unambiguously determined by X-ray diffraction analyses (Fig. 1b). Both complexes are isostructural, showing the mesoionic carbene ligand coordinated to an Au(I) atom, and a chlorine ligand completing the linear coordination sphere around the metal (C–Au–Cl angle is 174.31(18)° for **2a** and 179.30(9)° for **2b**). Noticeably, no coordination of the hemilabile pyridine or pyrimidine moieties at Au(I) was observed.

Then, Au(I) complexes **2a** and **2b** were reacted with silver hexafluoroantimonate (AgSbF₆) in CD₂Cl₂ at room temperature (Fig. 2a), seeking the engagement of the pendant pyrimidine or pyridine groups in the coordination to Au(I). The ¹H NMR spectra of the corresponding complexes showed some changes in the aromatic and aliphatic region. In particular, the signals of the pyridine or pyrimidine fragments were shifted due to gold coordination. The most significant change was observed in the ¹³C{¹H} NMR spectra. The signal of the carbenic carbon was shifted from 162.1 to 157.2 ppm in the case of the pyridine derivative (**3a**), and from 165.3 to 161.3 ppm in the case of the pyrimidine derivative (**3b**).

X-ray diffraction analysis of complex **3a** showed a head-to-tail dimeric Au(I) species where each ligand is bridging two metals (Fig. 2). The Au(I) centers adopted a linear dicoordinate arrangement, showing an auophilic interaction (Au...Au length of 2.8212(4) Å). Analogously to Bourissou's (MIC^N)Au(I) complex,⁶⁴ the formation of a dimeric Au(I) species was favored rather than a mononuclear Au(I) having both the MIC and py or pym pendant groups coordinated.

Reactivity of (MIC^N)Au(I) complexes with external oxidants and towards oxidative addition

In order to promote the coordination of the side arms of our MIC^N ligands, we attempted the 2 e[−] chemical oxidation of the Au(I) complexes to mononuclear Au(III). To that end, we studied the reactivity of complex **2a** against a 2 e[−] oxidant, namely PhIX₂ (X = Cl or OAc) (Fig. 2a). The reaction was performed at low temperature, from −80 °C to rt, in the presence of AgSbF₆ as halogen scavenger. Gratifyingly, the oxidation of Au(I) to Au(III) took place, with the concomitant coordination of the pendant N-moiety to gold. The ¹³C{¹H} NMR spectra of the resulting complexes **4a-Cl** and **4a-OAc** showed the characteristic signal of the carbenic carbon at higher field when compared to the Au(I) analogue **2a** (147.3 ppm for **4a-Cl** and 137.1 ppm for **4a-OAc** vs. 162.1 ppm for **2a**). The molecular structures of complexes **4a-Cl** and **4a-OAc** were elucidated by X-ray diffraction analyses (Fig. 2b). Both complexes showed a similar arrangement, i.e. the bidentate MIC^N ligand coordinated to Au(III), and two chlorides or acetates completing its tetracoordinated Au(III) center, which featured a slightly distorted square planar geometry. The C_{carbene}–Au(III) lengths were slightly longer than those found in the Au(I) analogue (2.017(8) Å for **4a-Cl** and 1.991(11) Å for **4a-OAc** vs. 1.982(6) Å for **2a**).

At this point, we had demonstrated that these MIC^N ligands are indeed suitable platforms to stabilize Au(III) species. Thus, we were encouraged to explore the possibility of obtaining Au(III) complexes *via* oxidative addition. With this aim, we first attempted the oxidative addition of complex **2b** towards the strained C_{sp}²–C_{sp}² bond of biphenylene, by mixing equimolar amount of **2b** and biphenylene in dichloromethane, in the presence of a halide scavenger, from −80 °C to room temperature for 10 minutes (Fig. 3a). Unfortunately, we did not observe the desired Au(III) center with a biphenyl moiety but,



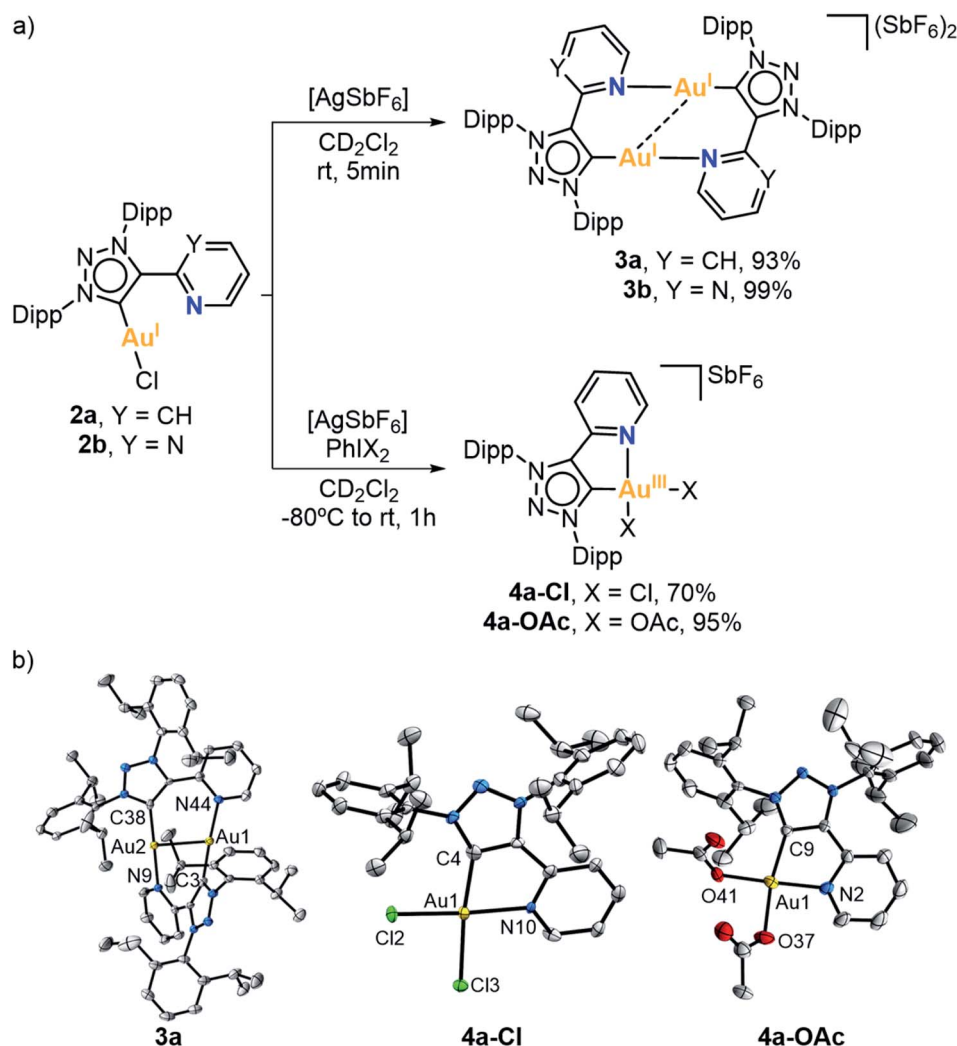


Fig. 2 (a) Reactivity of Au(I) complexes **2a** and **2b** towards halogen scavengers and strong oxidants. (b) Crystal structures of **3a**, **4a-Cl** and **4a-OAc** (ellipsoids set at 50% probability, H atoms and SbF₆[−] anions removed for clarity). Selected bond distances (Å): for **3a**, Au1–Au2 2.8212(4), Au1–N44 2.078(6), Au1–C3 1.988(8), Au2–N9 2.069(6), Au2–C38 1.990(8); for **4a-Cl**, Au1–C4 2.017(8), Au1–N10 2.089(6), Au1–Cl2 2.268(2), Au1–Cl3 2.302(2); for **4a-OAc**, Au1–C9 1.991(11), Au1–N2 2.052(11), Au1–O37 2.032(10), Au1–O41 1.998(9).

interestingly, crystallization of the reaction mixture revealed the co-crystallization of the dimeric complex **3b** with intact biphenylene (**3b**·biphenylene) (Fig. 3b). Even after 5 hours at 50 °C, the outcome of the reaction remained the same. To our delight, when the reaction was heated at 90 °C for 2 hours in 1,2-dichloroethane, the Au(I) center underwent oxidative addition of the strained biphenylene C_{sp}²–C_{sp}² bond, forming the expected Au(III) complex **5b** (Fig. 3a). Notably, the presence of a chloride source (such as KCl or tetrabutylammonium chloride) displaced the hemilabile pyrimidine, affording a neutral Au(III) species, **6b**. By adding AgSbF₆ as halide scavenger, we could reversibly form complex **5b**, also reinforcing the hemilabile character of the pyrimidine moiety. Indeed, the NMR spectra of **5b** showed a dynamic behaviour of the pyrimidine pendant arm, even at 248 K, as indicated by ¹H, ¹H-NOESY experiment (Fig. S49†). Both the cationic **5b** and the neutral **6b** Au(III) species were characterized by X-ray diffraction analyses (Fig. 3b), confirming the weak coordination of the

pyrimidine moiety with a long Au(III)–N_{pyrimidine} bond of 2.254 Å for **5b**. The carbene resonance signals were downfield shifted to 182.8 and 180.1 ppm for **5b** and **6b**, respectively.

We then explored the possibility of Au(I) complexes **2a** and **2b** to undergo oxidative addition of C_{sp}²–I bonds (Fig. 4a). For this purpose, we reacted the Au(I) complexes with *para*-substituted iodoaryls (R = OMe, Me, F) in the presence of AgSbF₆, in 1,2-dichloroethane and heating at 120 °C overnight. Unexpectedly, no Au-containing compounds were isolated, but on the contrary, the ¹H NMR and mass spectra were consistent with the full conversion to three triazolium salts (**8a-R**, **9a**, and **1a** when **2a** was used, and **8b-R**, **9b** and **1b** when **2b** was used; R = OMe, Me, F) (see yields in Fig. 4a). When using **2a** with 4-iodoanisole, the triazolium salts **8a-OMe** and **9a** were unambiguously characterized by X-ray diffraction. Both species co-crystallized, and the single crystal X-ray analysis revealed the presence of **8a-OMe** and **9a** in a 0.89 : 0.11 ratio (Fig. 4b). Likewise, when **2b** was reacted with 4-iodoanisole, the major product was **8b-OMe** with



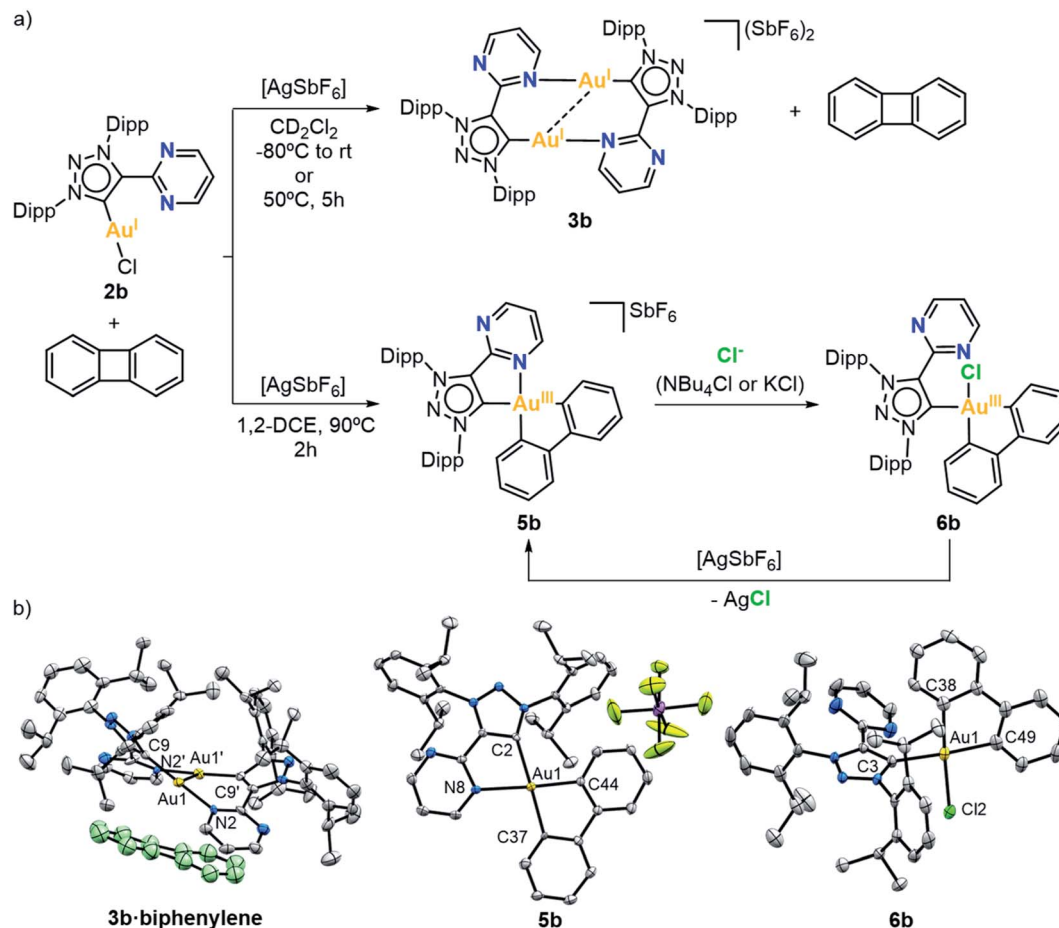


Fig. 3 (a) Study of the reaction conditions for the oxidative addition of a strained $\text{C}_{\text{sp}^2}\text{--C}_{\text{sp}^2}$ bond to complex **2b**. (b) Crystal structures of **3b**·biphenylene, **5b** and **6b** (ellipsoids set at 50% probability, H atoms removed for clarity; in the case of **3b**·biphenylene the SbF_6^- anions have been removed and the biphenylene molecule is painted in green for clarity). Selected bond distances (Å): for **3b**·biphenylene, Au1–Au1' 2.8768(10), Au1–N2 2.105(8), Au1–C9 2.027(10); for **5b**, Au1–C2 2.108(5), Au1–N8 2.254(5), Au1–C37 2.066(5), Au1–C44 2.019(5); for **6b**, Au1–C3 2.080(6), Au1–Cl2 2.376(3), Au1–C38 2.072(7), Au1–C49 2.057(7).

a 65% NMR yield, whereas **9b** and **1b** were both obtained in 16% NMR yield. In this case, **8b-OMe** could be isolated and characterized by ^1H NMR, HRMS and X-ray diffraction (Fig. 4b). The formation of such compounds suggested that gold(i) compounds underwent oxidative addition of the aryl iodide followed by a fast reductive elimination of the mesoionic carbene ligand either with the aryl or the iodide moiety coordinated in *cis*, respectively (Fig. 4a). Interestingly, products **8a-R**/**8b-R** were obtained in higher yields than **9a/9b**, indicating that after the oxidative addition the major product is the one with the aryl ligand in *cis* (**cis-7a-I** or **cis-7b-I**), probably due to the *trans* effect of the NHC ligand. By an alternative route,⁴⁷ the analogous complex **cis-7a-Cl** was synthesized through the oxidative addition of an aryldiazonium salt promoted by blue LED irradiation ($\lambda = 447\text{ nm}$). This methodology has the advantage to occur at 25°C , allowing the isolation and fully characterization of the Au(III) species **cis-7a-Cl** (see XRD in Fig. 4b). When **cis-7a-Cl** was heated at 120°C overnight in 1,2-DCE, product **8a-OMe** was formed in 96% yield. This reaction supports that the formation of **8a-R/8b-R** and **9a/9b** from Au(i)

complexes **2a/2b** proceeds *via* an oxidative addition/reductive elimination pathway. We hypothesize that the hemilabile character of the nitrogen atom and the fast decomposition of Au(III) at high temperatures promote the reductive elimination process, which has only been observed, to our knowledge, for a 1,2,3-triazol-5-ylidene based palladium complex.^{66–68} Nevertheless, our observations sharply contrasted with the lack of reactivity described by Bourissou for a similar $(\text{MIC}^{\wedge}\text{N})\text{Au}(\text{i})$ system with aryl iodides.⁶⁴

Arylation-lactonization of γ -alkenoic acids

Based on the successful catalytic application of the $\text{P}^{\wedge}\text{N}$ hemilabile ligand strategy, we envisioned that our hemilabile $(\text{MIC}^{\wedge}\text{N})\text{Au}(\text{i})$ complexes may also mediate a cascade reaction involving the key oxidative addition step. Recently, Bourissou and coworkers described the coupling/cyclization reaction of aryl iodides with alkenol and alkenamine compounds catalyzed by a hemilabile $\text{P}^{\wedge}\text{N}$ MeDalPhos/Au(i) system.⁵³ Additionally, in 2017, Shi and coworkers reported a system that afforded coupling/cyclization products upon reacting aryldiazonium



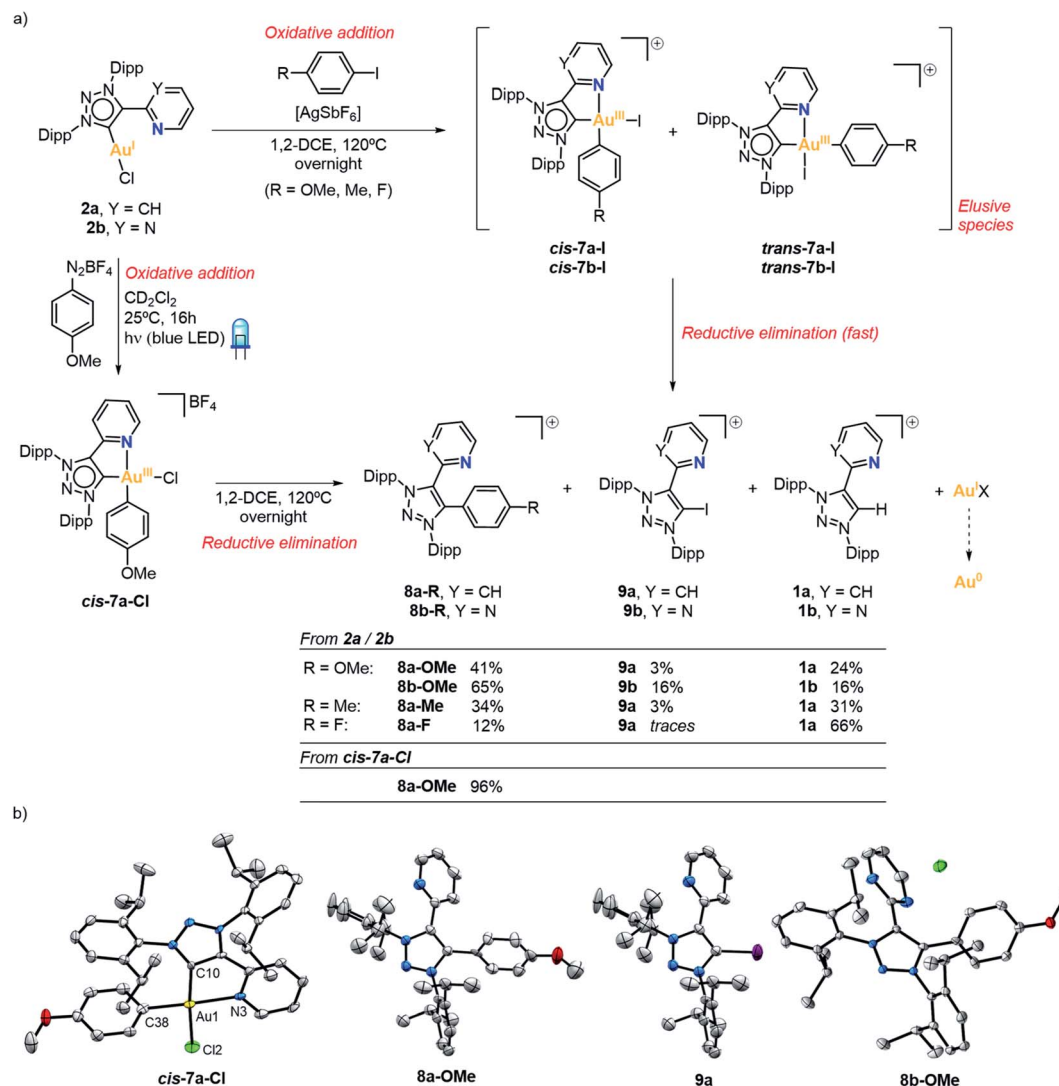


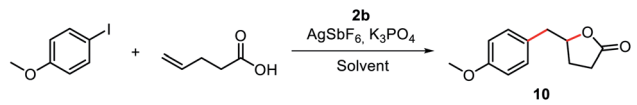
Fig. 4 (a) Reactivity towards aryl iodides and decomposition route of Au(I) species 2a and 2b, and synthesis of cis-7a-Cl by oxidative addition of an aryldiazonium salt. NMR yield of the reactions calculated using 1,3,5-trimethoxybenzene as internal standard. (b) Crystal structures of cis-7a-Cl, 8a-OMe, 9a and 8b-OMe (ellipsoids set at 50% probability, H atoms removed for clarity; for cis-7a-Cl, BF₄[−] anion is removed for clarity; for 8a-OMe and 9a, SbF₆[−] anion is not shown for clarity). Selected bond distances for cis-7a-Cl (Å): Au1–C10 2.009(7), Au1–N3 2.154(7), Au1–C38 2.006(8), Au1–Cl2 2.303(2).

salts with either alkenamines, alkenols or alkenoic acids, using [(Ph₃P)AuCl] under photo-free conditions.⁶⁹ Thus, we envisioned that our MIC[^]N/Au(I) system should afford γ -benzyl- γ -butyrolactone products when reacting aryl iodides with γ -alkenoic acids, *via* coupling/lactonization, provided the oxidative addition step takes place (see reaction scheme embedded in Table 1). Our first attempts consisted in a stoichiometric reaction between 4-iodoanisole, 4-pentenoic acid, complex 2b, K₃PO₄, and AgSbF₆ at 80 °C. When the reactions were carried out in the presence of an excess of base or AgSbF₆, we did not observe any conversion, probably due to the rapid decomposition of the Au(I) complex. We also found that by using chlorinated solvents such as 1,2-dichloroethane, the conversion reached up to 49% (Table S3†). We determined by ¹H NMR analysis that the catalyst decomposes under the reaction conditions, forming the triazolium salt 1b. Interestingly, the

conversion was significantly higher using 2,2,2-trifluoroethanol (TFE) (up to 92%) instead of 1,2-dichloroethane (Table 1 and S3†). When the reaction was carried out at 100 °C, the conversion was quantitative, but the yield was very similar to that found at 80 °C (67% yield at 100 °C vs. 63% yield at 80 °C, entries 1–2 in Table 1), and we also observed the formation of the triazolium salt 8b-OMe. This was a strong indication that complex 2b underwent an oxidative addition of the C_{sp}²–I bond, but rapid reductive elimination to form the coupling product 8b-OMe occurred.

With these results in hand, we explored the possibility to perform the catalytic version of the arylation-lactonization of γ -alkenoic acids. Thus, we carried out the reaction decreasing the loading of 2b, first using substoichiometric 70 mol% of the gold complex. Product 10 was obtained in 65% yield (entry 3), so effectively a quantitative transformation was achieved with



Table 1 Synthesis of γ -benzyl- γ -butyrolactone **10** promoted by complex **2b**^a


Entry	[Ag] (eq.)	[Au] mol%	K ₃ PO ₄ (eq.)	Solvent	Conversion% (yield%)
1 ^b	2.8	100	1.0	TFE	92(63)
2 ^{b,c}	2.6	100	1.2	TFE	>99(67)
3 ^d	2.2	70	1.2	TFE	81(65)
4 ^d	2.0	40	1.1	TFE	79(44)
5 ^b	1.5	10	1.0	TFE	51(28)
6	1.5	10	0.5	TFE	51(24)
7 ^d	1.5	10	1.1	TFE	54(15)
8 ^d	1.1	1	0.5	TFE	38(1.6)
9	1.5	10	1.0	HFIP	56(29)

^a Reaction conditions: [Ar-I] = 0.08 M, [4-pentenoic acid] = 0.08 M, 80 °C, 16 h. V = 0.55 – 1.40 mL (¹H NMR yield obtained with 1,3,5-trimethoxybenzene as internal standard). ^b [Ar-I] = 0.02 M, [4-pentenoic acid] = 0.1 M, V = 1 mL. ^c T = 100 °C. ^d Reaction time = 24 h.

respect to Au loading. By using 40 mol% of Au(I) complex the yield was 44%, reaching about 1 TON (entry 4). Interestingly, using a lower amount of **2b** (10 mol%) the yield was around 28% (~3 TON, entry 5). Similarly, by using hexafluoro-2-propanol (HFIP) the yield was 29% (~3 TON, entry 9); therefore, the best optimized results were obtained with fluorinated alcohols.

To exclude the possibility of oxidizing Au(I) to Au(III) in the presence of Ag(I), complex **2a** (1 eq.) was reacted with AgSbF₆ (15 eq.) in HFIP at 80 °C for 16 hours. Quantitative formation of the Au(I) dimer **3a** was observed by NMR, confirming the role of silver as halide scavenger (see Scheme S12†).

The scope of the reaction was examined with different aryl halides and γ -alkenoic acids (Fig. 5). The arylation-lactonization using iodobenzene and complex **2b** reached 50% yield (~5 TON) in product **11**. As expected, by increasing the catalyst loading to 20 mol%, the yield of **11** increased up to 87%, thus maintaining the turnover number (~4–5 TON). Gratifyingly, the best yields were reached using 4-iodotoluene, obtaining product **12** in 60% yield using **2a** (~6 TON) and 81% yield using **2b** (~8 TON). However, the presence of the strong electron-withdrawing group CF₃ in the *para*-position of the iodoaryl produced product **13** in a lower yield (~13%). Following this trend,^{36,38} 1-iodo-4-nitrobenzene produced a more dramatic drop of the yield of the corresponding product **14** (1%).

Interestingly, the γ -alkenoic acid with α -methyl groups reacted smoothly, yielding 37% of **15** using **2a** and 41% of **15** using **2b**. Also, complexes **2a** and **2b** performed very similar, except in the case of using iodobenzene and 4-pentenoic acid, yet complex **2b** is almost two-fold more active than **2a** (31% vs. 50% yield of compound **11**, for **2a** and **2b**, respectively). The molecular structure of compound **16** was determined by X-ray diffraction analysis and revealed the formation of the (*R*)-enantiomer by spontaneous resolution.

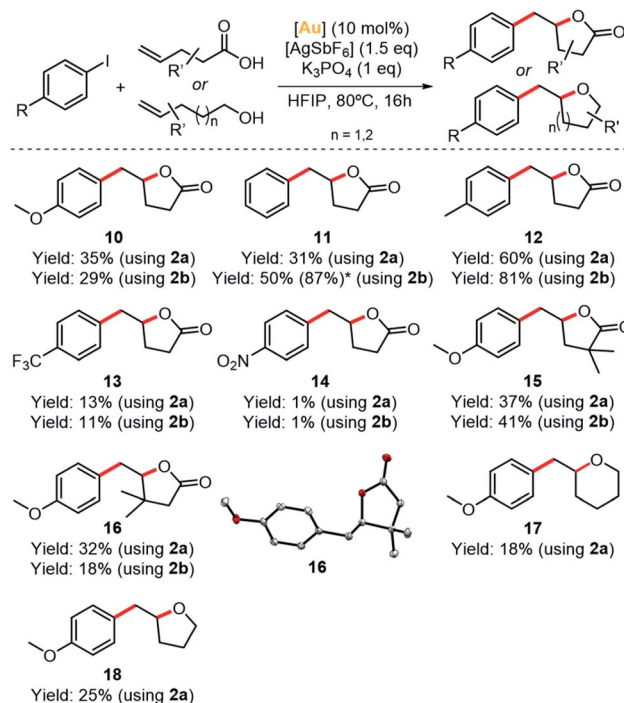


Fig. 5 Scope of the arylation-lactonization of alkenoic acids (**10–16**) and oxyarylation of alkenes (**17–18**). *NMR yield using 20% of [Au] is shown in parenthesis. Crystal structure of **16** is shown (ellipsoids set at 50% probability, H atoms removed for clarity).

Finally, in order to broaden the scope of these (MIC^N)Au(I) complexes, we tested complex **2a** in the oxyarylation of alkenols and 1,2-diarylation of alkenes under the same catalytic conditions (Scheme S11†). The oxyarylation products **17** and **18** were obtained in low but significant yields (18–25%, ~2 TON) (Fig. 5 and Table S6†). On the contrary, the 1,2-diarylation reaction was unsuccessful.

Based on the fundamental understanding of the redox behaviour of complexes **2a** and **2b**, and the previously reported gold-catalyzed processes combining aryl halide oxidative addition and π -activation of alkenes,⁵³ a mechanistic proposal is depicted in Fig. 6. First, the oxidative addition of the C_{sp}²-I bond into a cationic gold(I) species occurs, affording a cationic aryl-gold(III) species. Then, the silver salt abstracts the iodide from this Au(III) species to generate a vacant site that can be occupied by the π -coordination of the olefin. Subsequent intramolecular γ -lactonization is enabled by the presence of base and the π -activation of the alkene produced by the gold center, to yield an alkylaryl gold(III) intermediate. The latter is proposed to undergo a reductive elimination step that affords the γ -benzyl- γ -butyrolactone product and closes the catalytic cycle by regenerating the initial catalytically active hemilabile [Au^I(-MIC^N)]⁺ species.

To gain mechanistic insight, the stoichiometric reaction of **cis-7a-Cl** with AgSbF₆ (1.2 eq.), 4-pentenoic acid (1.3 eq.) and K₃PO₄ (1.0 eq.) was carried out in HFIP at 80 °C. After 16 hours, γ -benzyl- γ -butyrolactone **10** was obtained in 73% yield (Scheme S13†). Therefore, it is plausible to propose the formation of an



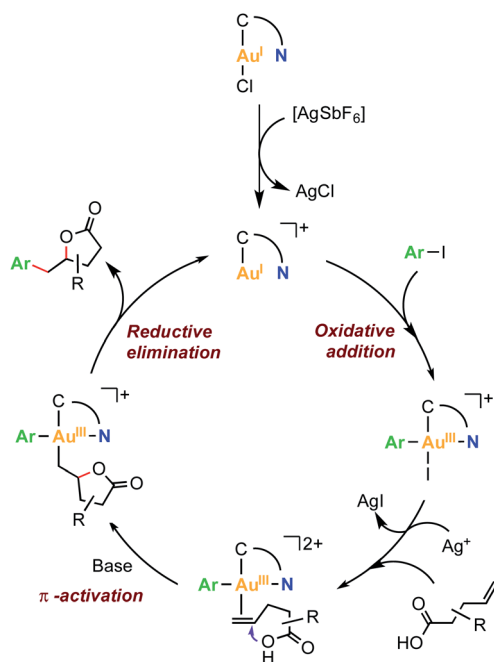


Fig. 6 Proposed reaction mechanism for the Au(I)/Au(III)-mediated arylation-lactonization of alkenoic acids.

arylgold(III) intermediate formed by an oxidative addition reaction of the C_{sp^2} -I bond to Au(I).

Conclusions

We synthesized two Au(I) complexes bearing bidentate hemilabile MIC[^]N ligands, [Au^I(MIC[^]N)Cl], **2a** and **2b**, and explored their redox reactivity. The formation of the Au(III) complexes **4a-Cl** and **4a-OAc** was achieved by using 2 e[−] oxidants of the type PhIX₂ (X = Cl, OAc), demonstrating a suitable design of the MIC[^]N ligand to stabilize Au(III) centers. Next, we showed that effective oxidative addition of a strained C_{sp^2} - C_{sp^2} bond was obtained when reacting **2b** with biphenylene in the presence of a halide scavenger and heating at 90 °C. In this case, complex **5b** was obtained as the desired ensuing Au(III) species.

On the other hand, the oxidative addition of aryl iodides to Au(I) required a temperature of 120 °C, and under these conditions the reductive elimination reaction of Au(III) species is also favored, yielding a series of triazolium salts (**8a-R/8b-R**, **9a/9b** and **1a/1b**). Although the expected Au(III) complexes were not directly detected, we independently synthesized the analogous Au(III) complex **cis-7a-Cl**, which after heating produced the same triazolium product (**8a-OMe**), thus supporting the oxidative addition/reductive elimination pathway for aryl iodides.

Finally, we combined all the redox knowledge gained with this system to develop a novel reaction for the synthesis of γ -benzyl- γ -butyrolactones upon arylation-lactonization of γ -alkenoic acids. The reaction was catalyzed by **2a** and **2b** (10 mol% catalyst loading), obtaining up to 8 TON. The catalytic activity shown by MIC[^]N/Au system is significant because it shows that readily available hemilabile C[^]N ligands are a real alternative to

hemilabile P[^]N ligands, where MeDalpos system stands out among catalytic examples of oxidant-free oxidative addition of aryl halides allowed by the presence of pendant N-groups. Current efforts are devoted to extending the application of these hemilabile [Au^I(MIC[^]N)Cl] complexes to novel catalytic transformations.

Data availability

Data for this work, including experimental procedures, NMR spectra and crystallographic data, are provide in the ESI.†

Author contributions

P. F., H. V. and G. G.-B. performed the experiments. All authors discussed the results and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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