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Influence of a Very Bulky *N*-Heterocyclic Carbene in Gold-Mediated Catalysis

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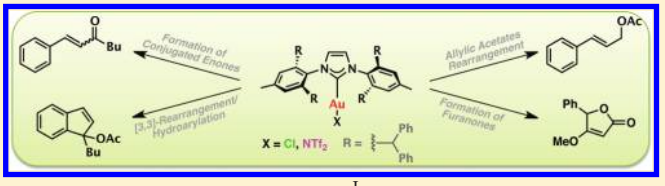
Supporting Information

ABSTRACT: The syntheses of the free carbene IPr* (IPr* = 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene) and related gold complexes [Au(IPr*)Cl] (**C1**) and [Au(IPr*)(NTf_2)] (**C2**) were achieved in high yields. The % V_{Bur} of IPr* for both gold complexes was measured, revealing IPr* as one of the bulkiest NHCs on gold complexes reported to date. In addition, the catalytic activity of **C1** and **C2** in several reactions, typically catalyzed by Au^I complexes, was investigated. Examples include the tandem alkoxylation/lactonization of γ-hydroxy-α,β-acetylenic esters, the [3,3]-rearrangement of propargylic acetates leading to the formation of conjugated enones and substituted indenes, and the rearrangement of allylic acetates. These studies revealed a strong solvent effect on the catalytic activity with 1,2-dichloroethane as the solvent of choice. The screening of **C1** and **C2** demonstrated only slightly diminished activities in comparison to [Au(NHC)(L)] complexes bearing bulky ligands such as IPr and SIPr.



INTRODUCTION

In the past decade, the popularity of gold complexes has grown exponentially due to their very broad catalytic activity,[1] e.g., in nitrile[2] and alkyne[3] hydration, hydroamination,[4] carboxylation[5] and decarboxylation[6] reactions, skeletal rearrangements,[7] and many others.[8] Initially, Au-catalyzed organic reactions were carried out using simple Au^I/Au^{III} salts such as AuCl, $AuCl_3$, or $NaAuCl_4$.[9] Recently, more elaborate organogold chloride complexes bearing monodentate ancillary ligands have been developed and used to this end. The catalytically active Au species are usually generated in the presence of a halogen abstractor, typically silver salts, generating a cationic Au^I complex.[10] Initially, gold catalysts bearing phosphine ligands such as [Au(PPh_3)Cl] were ubiquitous in literature reports.[11] During the past few years, the use of *N*-heterocyclic carbenes (NHCs) as ancillary ligands in gold complexes has, however, gained increased attention, as they provide unique properties such as unprecedented σ-donation and significant steric bulk.[8] Further advantages offered by NHC ligands, in practical terms, are their ease of synthesis and modification, providing straightforward access to a wide number of [Au(NHC)Cl] complexes.[12]

Recently, Markó *et al.* reported the synthesis of IPr* (**1**) (IPr* = 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene)[13] inspired by the NHCs with "flexible sterics" described by Glorius[14] and Bertrand.[15] This new NHC was found to be an extraordinarily sterically bulky ligand, with a $\%V_{Bur}$[16] of 53.6 calculated for [Ag(IPr*)Cl] (**2**), and also exhibits good electron-donating capability (Figure 1).[13]

To the best of our knowledge, the IPr* ligand has been employed only in the synthesis of [Ag(IPr*)Cl], [Rh(IPr*)($CO)_2$Cl], and [Rh(acac)(IPr*)(CO)] complexes.[13] Moreover, no catalytic studies have been performed to evaluate its role in metal-catalyzed organic reactions.

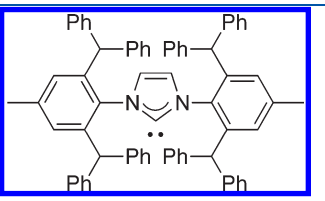


Figure 1. IPr* ligand reported by Markó *et al.*

Intrigued by the steric and electronic properties of IPr*, we decided to study its effect on the catalytic activity of Au^I complexes. Herein, we report the synthesis of [Au(IPr*)Cl] (**C1**) and [Au(IPr*)(NTf_2)] (**C2**) complexes and a study of their catalytic activity in several reactions known to be mediated by bulky NHC-gold complexes.

RESULTS AND DISCUSSION

Synthesis and Characterization. [Au(NHC)Cl] complexes are generally synthesized using three different routes: (a) transfer of the NHC ligand from a silver complex,[12a] (b) the recently disclosed method involving transmetalation with copper-NHC complexes,[17] or (c) direct reaction of a free carbene with a gold(I) precursor (Scheme 1).[12a] Since Markó reported the failure of the silver complex **2** as a transmetalation agent but did not specify on

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what metal the reaction was tested,[13] the transmetalation between [Ag(IPr*)Cl] and [Au(DMS)Cl] (DMS = dimethylsulfide) was carried out in order to synthesize **C1**. Unfortunately, no product was generated (route A, Scheme 1). As the transmetalation with silver was also invalid for gold, [Cu(IPr*)Cl] (**3**) was tested as a NHC transfer agent. Copper complex **3** was easily obtained as a white crystalline material, following (with slight modifications) the literature protocol for the synthesis of [Cu(NHC)Cl] complexes,[18] in 98% yield. Crystals suitable for single-crystal diffraction studies were obtained. An ORTEP representation of complex **3** is presented in Figure 2. Unfortunately, the transmetalation using **3** also proved ineffective (route B, Scheme 1). This was, as in the case of silver, presumably because of the steric bulk of IPr*.

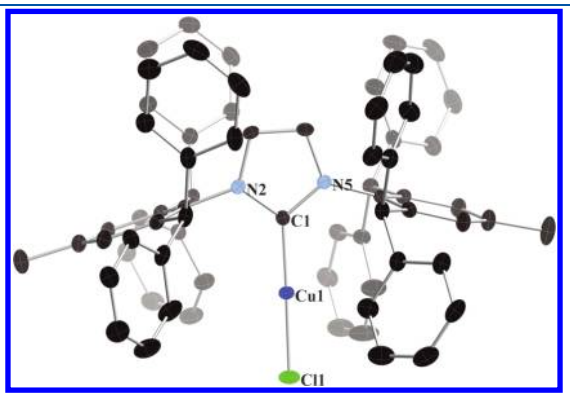


Figure 2. ORTEP representation for [Cu(IPr*)Cl] showing 50% thermal ellipsoid probability. H atoms were omitted for clarity purposes. Selected bond distances (Å) and angles (deg): Cu1−C1 1.867(3), Cu1−Cl1 2.0944(9), C1−N2 1.351(4), C1−N5 1.364(4), C1−Cu1−Cl1 176.21(9), N2−C1−N5 103.8(2).

The synthesis of [Au(IPr*)Cl] (**C1**) was next attempted using the reaction between the free carbene **1** and [Au(DMS)Cl] (route C, Scheme 1). Noteworthy, our optimized standard procedure for the synthesis of the free NHC involves the use of the corresponding BF_4 salt; therefore IPr*·HCl (**4**)[13] was first reacted with aqueous HBF_4, affording IPr*·HBF_4 (**5**) in 87% yield (route D, Scheme 1). A significant upfield shift of the imidazolium proton can be observed by ^{1}H NMR spectroscopy, shifting from 12.95 to 10.13 ppm. Crystals suitable for single-crystal diffraction studies were obtained by slow diffusion, at −20 °C, of pentane in a saturated dichloromethane solution of **5** (Figure 3).

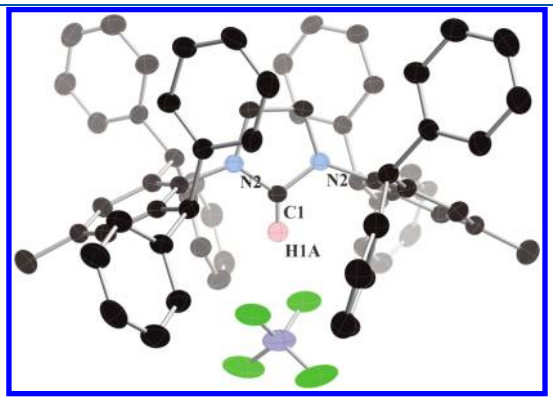
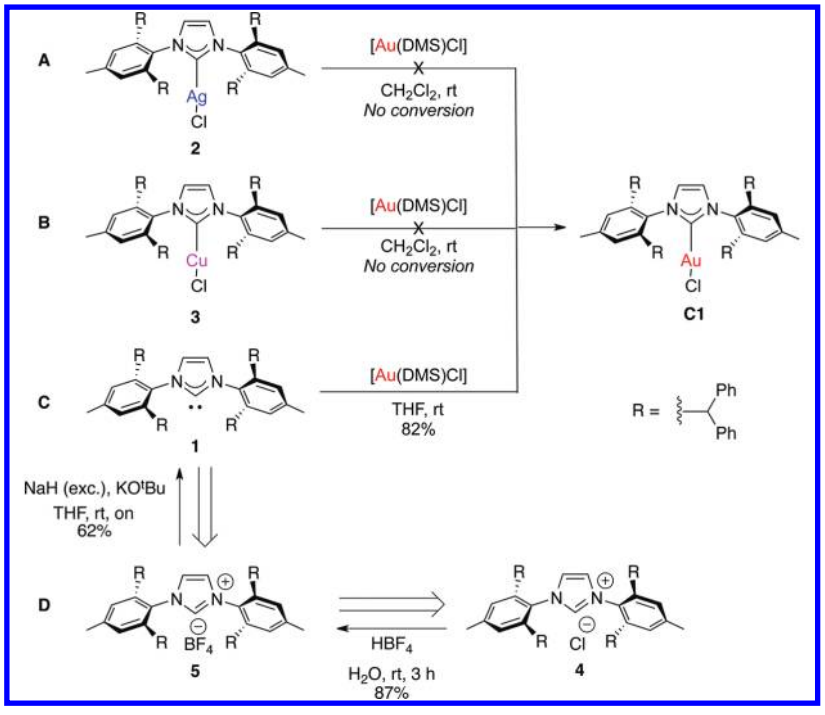


Figure 3. ORTEP representation for IPr*·HBF_4 showing 50% thermal ellipsoid probability. H atoms, except the imidazolium proton, were omitted for clarity purposes. Selected bond distances (Å) and angles (deg): C1−N2 1.337(4), C1−N2 1.337(4), N2−C1−N2 108.1(4).

IPr*·HBF_4 (**5**) was then deprotonated in the presence of a slight excess of NaH and a catalytic amount of KO^{t}Bu to afford carbene **1** as a white powder in 62% yield (route D, Scheme 1). After recrystallization of the free NHC, **1** was reacted with [Au(DMS)Cl] leading to the desired complex **C1** in 82% yield (route C, Scheme 1).

Scheme 1. Synthetic Approaches to [Au(IPr*)Cl]



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Crystals suitable for single-crystal diffraction studies were obtained by slow diffusion, at −20 °C, of pentane in a saturated dichloromethane solution of **C1** (Figure 4). As expected, **C1** is a linear complex with a C1−Au1−Cl1 angle of 178.3(2)° and a Au1−C1 bond length of 1.987(7) Å. The Au1−C1 bond length is longer than the corresponding bond in Au complexes bearing IPr (1.942(3) Å) or SIPr (1.979(3) Å) ligands, but within the normal range for [Au(NHC)Cl] complexes.[12a]

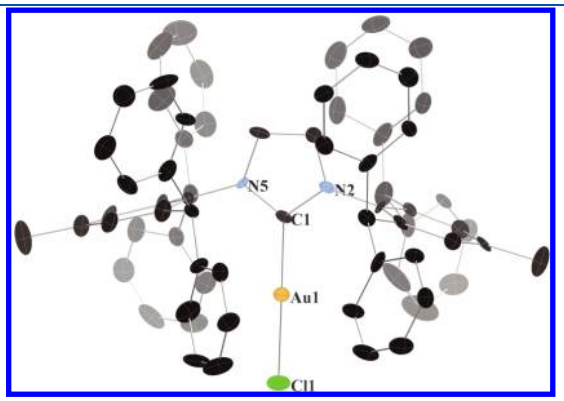


Figure 4. ORTEP representation for [Au(IPr*)Cl] showing 50% thermal ellipsoid probability. H atoms were omitted for clarity purposes. Selected bond distances (Å) and angles (deg): Au1−C1 1.987(7), Au1−Cl1 2.274(2), C1−N2 1.332(9), C1−N5 1.347(9), C1−Au1−Cl1 178.3(2), N2−C1−N5 106.3(6).

Computational studies using Sambvca[19] reveal that the $\%V_{Bur}$ of IPr* for [Au(IPr*)Cl] **C1** (50.4) and [Cu(IPr*)Cl] **3** (50.1) are smaller than that calculated for [Ag(IPr*)Cl] **2** (53.5).[13,20] The variation of $\%V_{Bur}$ of IPr* with different metals can be explained by the flexibility of the ligand, allowing it to adapt its shape to the metal center coordination environment. The results also explain the different $\%V_{Bur}$ for [Au(IPr*)Cl] calculated by us, in comparison to values provided by Glorius in his recent review on NHCs,[21] which were calculated using the closely related [Ag(IPr*)Cl] complex. The honorific title of "bulkiest NHC" based on $\%V_{Bur}$ still, to the best of our knowledge, belongs to the CAAC ligand reported by Bertrand *et al.*, with a $\%V_{Bur}$ of 51.2 (Figure 5).[22] Although extremely useful, it is recommended to compare $\%V_{Bur}$ for NHCs bound to the same metal center and calculate the values using the same parameters to prevent inconsistencies. The $\%V_{Bur}$ values are obtained from solid-state crystal structures; therefore they might not be completely representative of the actual coordination environment a metal center experiences in solution. The $\%V_{Bur}$ values should therefore be used to represent a trend rather than an absolute number and in any case should be interpreted with caution.

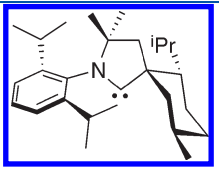
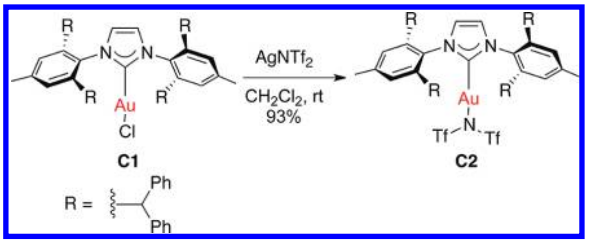


Figure 5. Bulkiest NHC on Au reported to date with a $\%V_{Bur}$ of 51.2.

Since silver salts are generally hygroscopic and light sensitive and have unpredictable catalytic activity, some protocols have been reported for Au-catalyzed organic reactions in the absence of silver additives.[23] The air-stable [Au(NHC)(NTf_2)] complexes, reported by Gagosz *et al.*,[23d] represent a very attractive and practical alternative to the use of protocols involving silver cocatalysts. The synthesis of [Au(IPr*)(NTf_2)] (**C2**) was attempted following the established procedure.[23d] Gratifyingly, the desired complex was isolated in 93% yield as a white microcrystalline solid (Scheme 2). A saturated solution of **C2** in toluene at 40 °C was prepared. Upon cooling to room temperature (rt), diffraction-quality crystals were obtained (Figure 6). As expected **C2** is a linear complex with a C1−Au1−Cl1 angle of 178.2(3)° and a Au1−C1 bond length of 1.986(7) Å. The Au1−C1 bond length is longer than the corresponding bond in Au complexes bearing IPr (1.969(2) Å) or IMes (1.976(3) Å) ligands, but within the normal range for [Au(NHC)(NTf_2)] complexes.[23d] As expected the $\%V_{Bur}$ of IPr* for **C2** (44.8) is smaller than for **C1** (50.1). This can be explained by the steric bulk of the ligand *trans* to the carbene, more significant for NTf_2 than for Cl.

Scheme 2. Synthesis of [Au(IPr*)(NTf_2)]



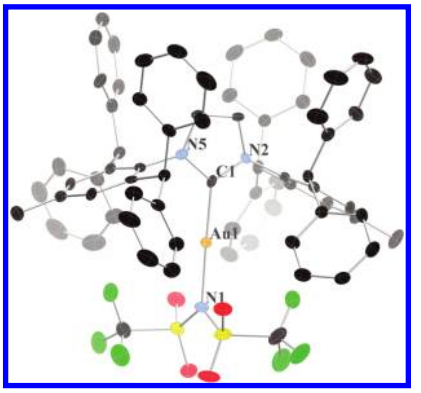


Figure 6. ORTEP representation for [Au(IPr*)(NTf_2)] showing 50% thermal ellipsoid probability. H atoms were omitted for clarity purposes. Selected bond distances (Å) and angles (deg): Au1−C1 1.986(7), Au1−N1 2.086(6), C1−N2 1.344(9), C1−N5 1.357(9), C1−Au1−N1 178.2(3), N2−C1−N5 105.9(6).

Catalytic Studies. Next, the catalytic activities of **C1** and **C2** were evaluated in several important organic transformations catalyzed by gold, such as the tandem alkoxylation/lactonization of γ-hydroxy-α,β-acetylenic esters,[24] the [3,3]-rearrangement of propargylic acetates leading to the formation of conjugated enones[25] and substituted indenes,[7a,26] and the rearrangement of allylic acetates.[7d] The Au complexes used for the catalytic studies are presented in Scheme 3. To avoid the use of silver salts in the reaction mixture, complex **C2** was preferably used instead of complex **C1** whenever possible.

Gold-Catalyzed Formation of Furanones. We have recently reported the base-free gold-catalyzed formation of several

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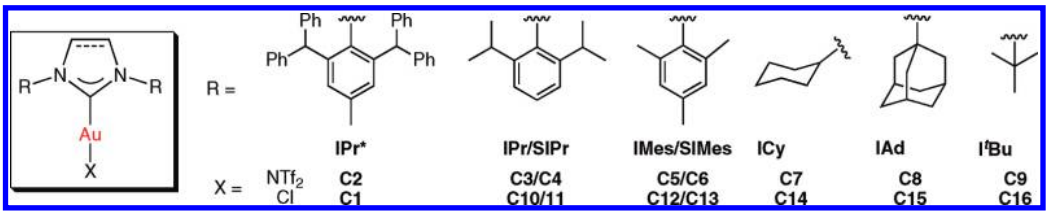
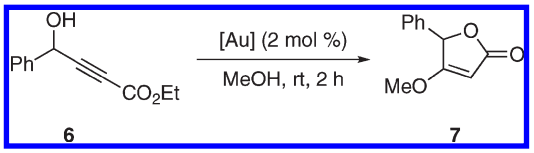
Scheme 3. Au Complexes Used in the Catalytic Studies



4-alkoxy-2(5*H*)-furanones from a variety of propargylic alcohols using a simple and straightforward procedure consisting in the use of **C3** (2 mol %) in MeOH at rt to afford the desired furanones in good yields (48−98%) within 2 h.[24] Initial catalytic studies revealed that **C3**, **C8**, and **C9** afforded compound **7** in good to excellent conversions (entries 2, 6, and 7; Table 1). For the reaction catalyzed by **C5** and **C6** no conversion could be determined due to the complexity of the mixture obtained (entries 4 and 5; Table 5). Unfortunately, **C2** showed poor catalytic activity for this transformation, allowing only 18% conversion of the desired furanone **7** (entry 1; Table 1). Interestingly, ^{1}H NMR analysis of the reaction mixture revealed a second unidentified intermediate species along with the expected (*E*)-ethyl 4-hydroxy-3-methoxy-4-phenylbut-2-enoate (**6a**),[27] suggesting a different reaction pathway when the reaction takes place in the presence of catalyst **C2**. This is presently being further explored.

Table 1. Catalyst Screening for the Synthesis of Furanone 7[a]



entry	catalyst		7 (%)[b]
1	[Au(IPr*)(NTf$_2$)]	**C2**	18
2	[Au(IPr)(NTf$_2$)]	**C3**	67
3	[Au(SIPr)(NTf$_2$)]	**C4**	45
4[c]	[Au(IMes)(NTf$_2$)]	**C5**	nd
5[c]	[Au(SIMes)(NTf$_2$)]	**C6**	nd
6	[Au(IAd)(NTf$_2$)]	**C8**	85
7	[Au(I^{t}Bu)(NTf$_2$)]	**C9**	83

[a] Reaction conditions: propargylic alcohol **6** (245 μmol), [Au] (2 mol %), MeOH (2 mL). [b] Conversions determined by ^{1}H NMR as an average of 2 runs. [c] nd = not determined. Along with the desired product various side products were observed.

Gold-Catalyzed Isomerization of Propargylic Acetates into Enones and Indenes. The activity of gold(I) complexes **C1** and **C2** in the rearrangement of propargylic acetates was also studied. The rearrangement of propargylic acetate **8** can afford four different compounds depending on reaction conditions: (a) α,β-unsaturated ketone **9** under aqueous conditions,[25] (b) substituted indenes **10** (kinetic product)[7a] or **10b** (thermodynamic product) under anhydrous conditions,[26] and (c) depending on the gold complex, the reaction could be stopped at allene **11** (Scheme 4).[28]

Zhang[25a] and Nolan[25b] have independently reported the isomerization of **8** into **9** under mild conditions. Taking into account our reported catalytic protocol,[25b] the reaction procedure was slightly modified to study the activity of [Au(NHC)(NTf$_2$)] at shorter reaction times, allowing better comparison between catalysts (Table 2). In comparison to our previous results using [Au(NHC)Cl] complexes activated by $AgSbF_6$,[25b] [Au(NHC)(NTf$_2$)] complexes furnished diminished yields of **9** (e.g., from 98% with [Au(I^{t}Bu)Cl]/$AgSbF_6$ to 89% with [Au(I^{t}Bu)(NTf$_2$)]). Initial optimization studies indicated that sterically demanding ligands afforded **9** in better yields (entries 2, 3, and 8; Table 2). Unfortunately, rearrangement of propargylic acetate **8** in the presence of **C2** furnished disappointing conversions (entry 1; Table 2). A possible solvent effect was considered as the source of the problem, due to the ability of THF to coordinate to the gold center.[29] The reaction was therefore tested in benzene and 1,2-dichloroethane (DCE). In both cases a remarkable increase in the yield of **9** was observed (entries 4 and 6; Table 3). Noteworthy, reactions in benzene furnished a significant increase of allene **11** (entry 4; Table 3). The selective formation of allenes and inhibition of subsequent gold-catalyzed transformations was already reported by our group to be strongly dependent on the labile gold ligand. The allene **11** was selectivily formed in gold-catalyzed rearrangement of **9** applying several [Au(NHC)(L)]-[BF_4] complexes, with L = nitrogen-based ligand.[28] A similar effect induced by benzene acting as a labile ligand to stabilize the cationic gold center in the reaction mixture can rationalize the analogous observations in the current case.

Satisfyingly, **C2** performed better than **C3** (entries 5 and 6; Table 3) for reactions carried out in DCE. These results strongly support the hypothesis of coordinating solvents dampening the catalytic activity of **C2**, due to the effective steric protection of the gold center by both the NHC and the coordinating solvent, resulting in no coordination of substrate to the catalyst (see entries 2, 4, and 6; Table 3). The use of coordinating solvents was therefore avoided in the following reactions.

The [3,3]-rearrangement/intramolecular hydroarylation of propargylic acetate **8** into indene **10** has also been reported by Nolan *et al.*[7a,26] In these studies, the conversion of the standard substrate **8** into **10** was accomplished in good yields after 5 min in CH_2Cl_2 using [Au(IPr)Cl)]/$AgBF_4$ (2 mol %) as the catalytic system. Initial studies revealed that complex **C2** was unsuitable for this transformation, as the hydroarylation of **11** does not occur under these reaction conditions. We had already observed formation of **10** under microwave heating in the presence of **C2** (see entries 5 and 6; Table 3). Encouraged by these results, the transformation of **8** into **10** was achieved using microwave irradiation in anhydrous DCE in order to avoid competing enone formation. The catalyst screening under these conditions revealed the superiority of complexes bearing bulky NHCs (entries 1, 2, 3, and 8; Table 4). A reasonable yield was afforded in the presence of complex **C9**; however good to excellent yields were achieved when the reaction was catalyzed by **C2**, **C3**, and **C4** (entries 1, 2, and 3; Table 4).

Finally, the rearrangement of allylic acetates was tested in order to study the potential of the new catalysts in reactions

Scheme 4. Rearrangement of Propargylic Acetates into Conjugated Enones or Substituted Indenes

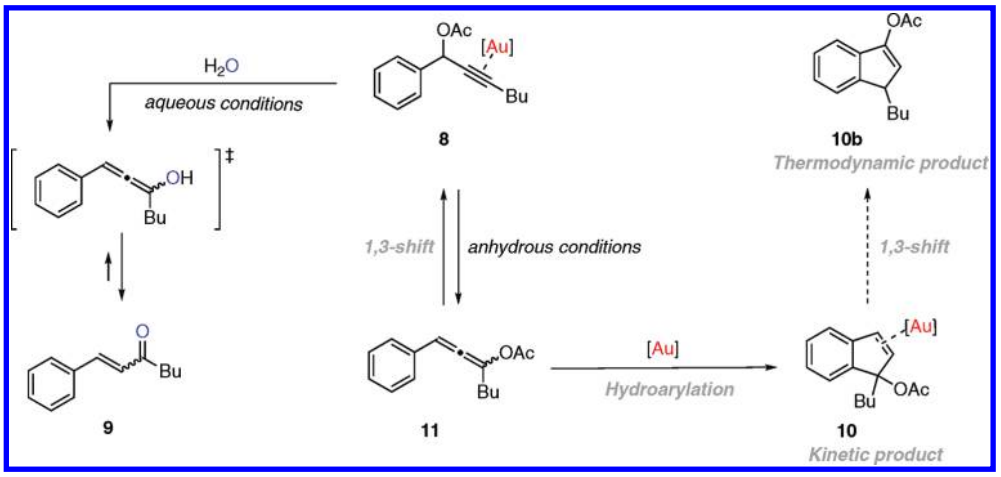
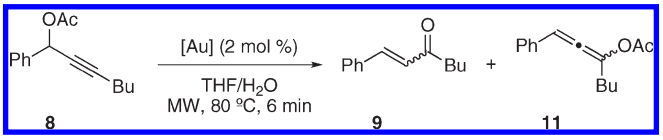


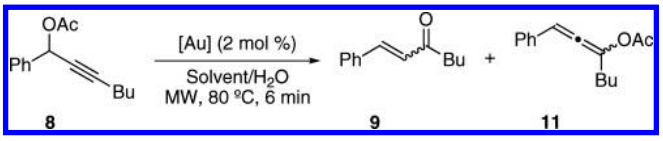
Table 2. Catalyst screening of the Isomerization of Propargylic Acetate 8 into α,β-Unsaturated Ketone 9[a]



entry	catalyst		9 (%)[b]	11 (%)
1	[Au(IPr*)(NTf_2)]	**C2**	8	18
2	[Au(IPr)(NTf_2)]	**C3**	79	17
3[c]	[Au(SIPr)(NTf_2)]	**C4**	83	13
4	[Au(IMes)(NTf_2)]	**C5**	38	33
5	[Au(SIMes)(NTf_2)]	**C6**	61	24
6	[Au(ICy)(NTf_2)]	**C7**	40	32
7	[Au(IAd)(NTf_2)]	**C8**	51	28
8	[Au(I^tBu)(NTf_2)]	**C9**	89	7

[a] Reaction conditions: propargylic acetate **8** (217 μmol), [Au] (2 mol %), THF (2 mL), H_2O (0.2 mL). [b] Yields determined by ^1H NMR as an average of at least 2 runs. [c] Average of 4 runs: 2 with 70% and 2 with 96% yield of **9**.

Table 3. Solvent Influence on the Catalyst Activity[a]



entry	solvent	catalyst		9 (%)[b]	11 (%)
1	THF	[Au(IPr)(NTf_2)]	**C3**	79	17
2	THF	[Au(IPr*)(NTf_2)]	**C2**	8	18
3	C_6H_6	[Au(IPr)(NTf_2)]	**C3**	48	32
4	C_6H_6	[Au(IPr*)(NTf_2)]	**C2**	23	67
5[c]	DCE	[Au(IPr)(NTf_2)]	**C3**	65	0
6[c]	DCE	[Au(IPr*)(NTf_2)]	**C2**	78	0

[a] Reaction conditions: propargylic acetate **8** (217 μmol), [Au] (2 mol %), solvent (2 mL), H_2O (0.2 mL). [b] Yields determined by ^1H NMR as an average of at least 2 runs. [c] Indene **10** was found in 31% yield in entry 5 and 22% yield in entry 6.

beyond alkyne activation. This classical skeletal rearrangement has been described to be catalyzed by several transition metals,[30] including gold.[7d] In the latter case, complete conversion of **12** into **13** after 12 min at 80 °C in DCE using microwave heating and [Au(IPr)Cl] (3 mol %)/$AgBF_4$ (2 mol %) as catalyst had been described by Nolan *et al.*[7d] Initial catalytic studies revealed

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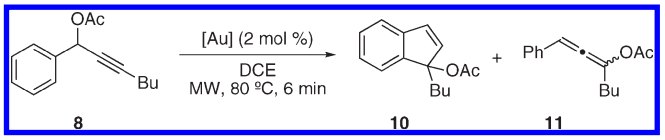
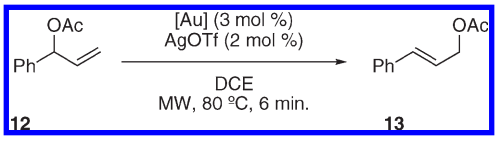
Table 4. Catalyst Screening for the Synthesis of Substituted Indenes 10[a]



entry	catalyst		10 (%)[b]	11 (%)
1	[Au(IPr*)(NTf$_2$)]	**C2**	72	11
2	[Au(IPr)(NTf$_2$)]	**C3**	85	0
3	[Au(SIPr)(NTf$_2$)]	**C4**	79	0
4	[Au(IMes)(NTf$_2$)]	**C5**	3	10
5	[Au(SIMes)(NTf$_2$)]	**C6**	8	28
6	[Au(ICy)(NTf$_2$)]	**C7**	5	50
7	[Au(IAd)(NTf$_2$)]	**C8**	17	35
8	[Au(I^{t}Bu)(NTf$_2$)]	**C9**	45	23

[a] Reaction conditions: propargylic acetate **8** (217 μmol), [Au] (2 mol %), DCE (2 mL). [b] Yields determined by ^{1}H NMR as an average of at least 2 runs. The formation of enone **9** (*E* and *Z*) due to the presence of water was observed.

Table 5. Catalyst Screening for the Rearrangement of Allylic Acetate 12[a]



entry	catalyst		12 (%)[b]
1	[Au(IPr*)Cl]	**C1**	79
2	[Au(IPr)Cl]	**C10**	84
3	[Au(SIPr)Cl]	**C11**	55
4	[Au(IAd)Cl]	**C15**	68
5	[Au(I^{t}Bu)Cl]	**C16**	76

[a] Reaction conditions: allylic acetate **12** (284 μmol), [Au] (3 mol %), AgOTf (2 mol %), DCE (5 mL). [b] Conversions determined by GC as an average of 2 runs.

that no rearrangement was promoted by the [Au(NHC)(NTf$_2$)] complexes. In this context, **C1**, along with AgOTf, was chosen as catalytic system for the initial screening instead of using **C2**. Moreover, the reaction time was reduced to 6 min to allow a better comparison between catalysts. As shown in Table 5, **C10** exhibited the best catalytic performance, achieving 84% conversion (entry 2; Table 5). Unfortunately, **C11** and **C15**, which allowed almost full conversion under the initial conditions, were not very active at shorter reaction times (entries 3 and 4; Table 5). We were pleased to see that **C1** promoted the reaction in excellent conversions (79%), showing similar catalytic activity to **C10**, the best catalyst in our previous report (entries 1, 2, and 5; Table 5).[7d]

CONCLUSION

The syntheses of carbene **1** and complexes [Au(IPr*)Cl] (**C1**) and [Au(IPr*)(NTf$_2$)] (**C2**) have been performed in high yields. The %V_{Bur} of IPr* for **C1** and **C2** was evaluated, revealing it as the second bulkiest NHC on [Au(NHC)Cl] complexes reported to date. The catalytic activity of **C1** and **C2** in several reactions typically catalyzed by Au^I complexes was investigated, revealing a strong solvent effect. DCE has been shown to be the solvent of choice, allowing for good activity of [Au(IPr*)(L)] complexes. The screening of **C1** and **C2** demonstrated a catalytic activity similar to [Au(NHC)(L)] complexes bearing bulky NHCs such as IPr (**C3**/**C10**) and SIPr (**C4**/**C11**). Further studies aimed at extending and exploring the catalytic effect of the bulky IPr* in gold and other metal-mediated transformations are ongoing in our laboratories.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all solvents and reagents were used as purchased and all reactions were performed under air. Dry solvents were obtained from a solvent purification system. NMR spectra were recorded on 400 and 300 MHz spectrometers at room temperature in $CDCl_3$. Chemical shifts are given in parts per million (ppm) with respect to TMS. Reactions under microwave irradiation were performed in a single-mode microwave apparatus, producing controlled irradiation at 2450 MHz. Reaction times refer to hold times at the indicated temperature and not total irradiation times with constant cooling *via* propelled air flow at a set power of 200 W. Elemental analysis was carried out by the analytical services of London Metropolitan University. Compounds **4**,[13] **6**,[24] **8**,[7a] and **12**[7d] were synthesized according to literature procedures.

Synthesis of Free IPr* (1). As the free NHC is the foundation of this study, a detailed synthetic protocol is provided here. In a glovebox (under Ar atmosphere), NaH (8.48 mmol, 203 mg, 1.50 equiv) was added to a suspension of **5** (5.65 mmol, 5.65 g, 1.00 equiv) in anhydrous THF (150 mL). A tip of a spatula of KO^{t}Bu was added. The reaction mixture was stirred overnight at rt. The mixture was filtered over a pad of Celite and was concentrated *in vacuo*. The resulting solid was then dissolved in the minimum amount of THF, and the product was precipitated by the addition of hexane. It was then collected by filtration to afford **1** (3.50 mmol, 3.19 g, 62%) as a white powder. ^{1}H NMR (400 MHz; C_6H_6): δ 7.36 (m, 8H, CH_{Ar}), 7.10−7.08 (m, 8H, CH_{Ar}), 7.03−6.92 (m, 28H, CH_{Ar}), 6.03 (s, 4H, CHPh$_2$), 5.78 (s, 2H, C$H^{4,5}$), 1.85 (s, 6H, CH_3). ^{13}C NMR (101 MHz; C_6H_6): δ 220.02 (C_{carb}), 145.0 (C_{Ar}), 143.9 (C_{Ar}), 142.0 (C_{Ar}), 138.4 (C_{Ar}), 138.3 (C_{Ar}), 130.2 (CH_{Ar}), 130.0 (CH_{Ar}), 129.9 (CH_{Ar}), 128.6 (CH_{Ar}), 128.5 (CH_{Ar}), 126.5 (CH_{Ar}), 126.5 (CH_{Ar}), 122.6 (C$H^{4,5}$), 51.5 (CHPh$_2$), 21.4 (CH_3). Anal. Calcd for $C_{69}H_{56}N_2$ (913.20): C, 90.75; H, 6.18; N, 3.07. Found: C, 90.65; H, 6.04; N, 3.14.

Synthesis of [Cu(IPr*)Cl] (3). In a microwave vial, inside a glovebox (under Ar atmosphere), **4** (263 μmol, 250 mg, 1.00 equiv) and Cu_2O (175 μmol, 25.0 mg, 0.66 equiv) were dissolved in anhydrous toluene (1 mL). The vial was then removed from the glovebox and heated in a microwave reactor at 150 °C for 15 min, affording a white crystalline solid in solution. The crude product was dissolved in CH_2Cl_2 (10 mL) and filtered through Celite to remove the excess Cu_2O. The pad of Celite was washed with CH_2Cl_2 (3 × 10 mL), and solvent evaporated *in vacuo*, affording complex **3** as a white solid (258 μmol, 261 mg, 98%). ^{1}H NMR (300 MHz; CD_2Cl_2): δ 7.16−7.21 (m, 24H, CH_{Ar}), 7.02−7.05 (m, 8H, CH_{Ar}), 6.92 (s, 4H, CH_{Ar}), 6.88−6.91 (m, 8H, CH_{Ar}), 5.87 (s, 2H, C$H^{4,5}$), 5.21 (s, 4H, CHPh$_2$), 2.25 (s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.7 (C_{carb}), 143.3 (C_{Ar}), 143.0 (C_{Ar}), 141.4 (C_{Ar}), 140.6 (C_{Ar}), 134.6 (C_{Ar}), 130.5 (CH_{Ar}), 130.0 (CH_{Ar}), 129.7 (CH_{Ar}), 129.0 (CH_{Ar}), 128.8 (CH_{Ar}), 127.1 (CH_{Ar}), 127.0 (CH_{Ar}), 123.7 (C$H^{4,5}$), 51.6 (CHPh$_2$), 21.9 (CH_3). Anal. Calcd for $C_{69}H_{56}ClCuN_2$ (1012.20): C, 81.88; H, 5.58; N, 2.77. Found: C, 81.73; H, 5.44; N, 2.65.

Synthesis of IPr*·HBF$_4$ (5). To a stirred suspension of **4** (3.95 mmol, 3.75 g, 1.00 equiv) in water (250 mL) was added aqueous HBF_4 (5.90 mmol, 0.58 mL, 1.50 equiv). The mixture was stirred for 3 h at rt. It was then extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic

layers were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The resulting solid was dissolved in a minimum amount of CH_2Cl_2, precipitated by the addition of Et_2O, and collected by filtration to afford **5** (3.38 mmol, 3.39 g, 86%) as an off-white powder. ^{1}H NMR (300 MHz; $CDCl_3$): δ 10.13 (t, ^4J = 1.5 Hz, 1H, H^2), 7.28−7.13 (m, 24H, CH_{Ar}), 7.04 (m, 8H, CH_{Ar}), 6.82−6.79 (m, 12H, CH_{Ar}), 5.65 (d, ^4J = 1.5 Hz, 2H, $CH^{4,5}$), 5.05 (s, 4H, $CHPh_2$), 2.21 (s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.5 (C_{Ar}), 142.0 (C_{Ar}), 141.5 (C_{Ar}), 140.6 (C_{Ar}), 140.3 (CH^2) 130.9 (CH_{Ar}), 129.8 (CH_{Ar}), 129.3 (CH_{Ar}), 128.9 (CH_{Ar}), 128.8 (CH_{Ar}), 127.2 (CH_{Ar}), 127.1 (CH_{Ar}), 124.3 ($CH^{4,5}$), 51.5 ($CHPh_2$), 22.0 (CH_3). ^{19}F NMR (282 MHz; $CDCl_3$): δ −150.50, −150.56. Anal. Calcd for $C_{69}H_{57}BF_4N_2$ (1001.01): C, 82.79; H, 5.74; N, 2.80. Found: C, 82.87; H, 5.59; N, 2.71.

Synthesis of [Au(IPr*)Cl] (C1). In a glovebox (under Ar atmosphere), a slight excess of [Au(DMS)Cl] (662 μmol, 605 mg, 1.01 equiv) was added to a solution of **1** (656 μmol, 194 mg, 1.00 equiv) in anhydrous THF (250 mL). A fast color change to purple was observed. The reaction was stirred for 3 h at rt and removed from the glovebox. To the reaction mixture was added a spatula of charcoal, and it was stirred for 20 min. Then, it was filtered over a pad of silica and concentrated *in vacuo*. The resulting solid was then dissolved with a minimum of CH_2Cl_2 and precipitated by the addition of pentane. The precipitate was collected by filtration to afford **C1** (538 μmol, 616 mg, 82%) as a white solid. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.19−7.13 (m, 24H, CH_{Ar}), 7.10−7.07 (m, 8H, CH_{Ar}), 6.89−6.84 (m, 12H, CH_{Ar}), 5.81 (s, 2H, $CH^{4,5}$), 5.26 (s, 4H, $CHPh_2$), 2.23 (s, 6H, CH_3). ^{13}C NMR (75 MHz; $CDCl_3$): δ 175.2 (C_{carb}), 143.0 (C_{Ar}), 142.3 (C_{Ar}), 140.9 (C_{Ar}), 140.2 (C_{Ar}), 133.8 (C_{Ar}), 130.3 (CH_{Ar}), 129.7 (CH_{Ar}), 129.4 (CH_{Ar}), 128.5 (CH_{Ar}), 128.4 (CH_{Ar}), 126.7 (CH_{Ar}), 126.7 (CH_{Ar}), 123.2 ($CH^{4,5}$), 51.2 ($CHPh_2$), 21.9 (CH_3). Anal. Calcd for $C_{69}H_{56}AuClN_2$ (1145.62): C, 72.39; H, 4.93; N, 2.45. Found: C, 72.49; H, 4.84; N, 2.36.

Synthesis of [Au(IPr*)(NTf$_2$)] (C2). To a stirred solution of **C1** (174 μmol, 200 mg, 1.00 equiv) in anhydrous CH_2Cl_2 (2 mL) was added $AgNTf_2$ (183 μmol, 71.0 mg, 1.05 equiv). Immediate formation of a white precipitate was observed. The reaction was stirred for 1 h at rt and then filtered over a pad of silica. The solution was then reduced *in vacuo* to a minimum of CH_2Cl_2, and the product was precipitated by the addition of pentane. The precipitate was collected by filtration to afford **C2** (162 μmol, 225 mg, 93%) as a white powder. ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.27−7.20 (m, 12H, CH_{Ar}), 7.17−7.11 (m, 20H, CH_{Ar}), 6.83−6.80 (m, 12H, CH_{Ar}), 5.49 (s, 2H, $CH^{4,5}$), 5.27 (s, 4H, $CHPh_2$), 2.23 (s, 6H, CH_3). ^{13}C NMR (101 MHz; $CDCl_3$): δ 168.0 (C_{carb}), 142.9 (C_{Ar}), 142.4 (C_{Ar}), 141.1 (C_{Ar}), 140.6 (C_{Ar}), 133.2 (C_{Ar}), 130.3 (CH_{Ar}), 129.9 (CH_{Ar}), 129.3 (CH_{Ar}), 128.7 (CH_{Ar}), 128.5 (CH_{Ar}), 127.02 (CH_{Ar}), 126.9 (CH_{Ar}), 123.9 ($CH^{4,5}$), 120.7 (C_{Ar}), 117.5 (C_{Ar}), 51.7 ($CHPh_2$), 21.9 (CH_3). ^{19}F NMR (376 MHz; $CDCl_3$): δ −76.4. Anal. Calcd for $C_{71}H_{56}AuF_6N_3O_4S_2$ (1390.01): C, 61.24; H, 4.06; N, 3.02. Found: C, 61.50; H, 3.89; N, 2.87.

■ ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Parameters used for SambVca calculations: (a) 3.50 Å was selected as the value for the sphere radius, (b) 2.00 Å was considered as distances for the metal−ligand bond, (c) usually irrelevant in crystallography, hydrogen atoms were omitted, and (d) Bondi radii scaled by 1.17 were used.

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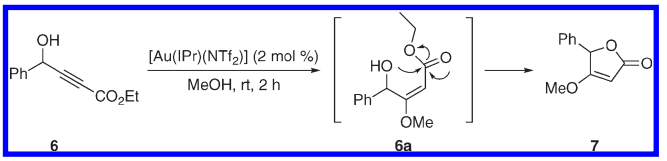
(27) Expected intermediate for the formation of furanone **7**:



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