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Gold(I) and Gold(III) Complexes of Expanded-Ring N-Heterocyclic Carbenes: Structure, Reactivity, and Catalytic Applications

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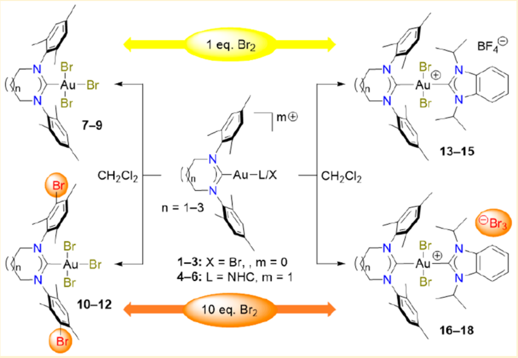
Supporting Information

ABSTRACT: The oxidative addition of bromine to homo- and heterobis(carbene) gold(I) complexes **1**−**6** containing expanded-ring N-heterocyclic carbene (erNHC) ligands was explored to prepare the first examples of gold(III) erNHC complexes. The use of stoichiometric amounts of bromine consistently gave clean gold-centered oxidations leading to the isolation of monocarbene and mixed carbene complexes of the type [AuBr$_3$(erNHC)] (**7**−**9**) and *trans*-[AuBr$_2$(^{i}Pr$_2$-bimy)(erNHC)]BF$_4$ (**13**−**15**), respectively. The use of excess bromine additionally led to ligand brominations in the monocarbene series affording [AuBr$_3$(erNHC^{Br2})] complexes (**10**−**12**), while in the case of the heterobis(carbene) series, tribromide complexes of the type *trans*-[AuBr$_2$(^{i}Pr$_2$-bimy)(erNHC)]Br$_3$ (**16**−**18**) were obtained instead. Comparison of the catalytic activities of all complexes in the hydroamination of alkynes revealed the superior performance of mono-erNHC complexes in all cases.



INTRODUCTION

N-Heterocyclic carbenes (NHCs) are state-of-the-art ligands in organometallic chemistry.[1−5] Most NHCs are derived from five-membered heterocycles, but expanded-ring NHCs (erNHCs) have also received an increasing amount of attention in recent years.[6−11] In general, erNHCs are more donating and bulkier compared to classical five-membered NHCs due to their larger N−C−N angles.[12−16] In this respect, we have reported a detailed stereoelectronic profiling of saturated erNHCs with ring sizes ranging from six to eight atoms using gold(I) and palladium(II).[17] Very recently, Hashmi and co-workers managed to prepare the first gold(I) complexes of nine- and ten-membered erNHCs as the largest members in this family.[18] These and other studies demonstrate that the coordination of erNHCs is well explored with gold(I) centers.[19,20] The resulting linear complexes are usually air- and moisture-stable and can be handled with ease, which should allow for further reactivity studies. One common reaction of electron-rich gold(I) NHC complexes is the oxidative addition of halogens, which usually affords the respective square-planar gold(III) NHC complexes.[21] Although erNHCs are known to be stronger donors than classical NHCs, it is surprising that gold(III) complexes of erNHCs are unknown so far. In a search for such compounds, we explored reactions of mono- and heterobis(carbene) gold(I) complexes containing erNHC ligands with stoichiometric and excess amounts of bromine. Herein, we report the preparation and characterization of the first gold(III) erNHC complexes. In addition, the catalytic activities of gold(I) and gold(III) erNHC complexes in the hydroamination of alkynes are compared.

RESULTS AND DISCUSSION

Gold(I) Complexes. The syntheses of Au^{I} NHC complexes **1**, **2**, **4**, and **5** containing the six- and seven-membered erNHCs 6-Mes and 7-Mes, respectively, have been reported recently by our group (Scheme 1).[17] Similarly, the eight-membered NHC complex [AuBr(8-Mes)] (**3**) has been prepared in a moderate yield of 64% by the reaction of salt **C** with [AuCl(tht)] in the presence of KHMDS starting at −78 °C with gradual warming to ambient temperature. The successful complex formation was evident from the absence of the NC*H*N resonance characteristic for ligand precursor **C** in the ^{1}H NMR spectrum of **3**, while a new gold-bound carbene resonance (Au NCN) is observed at 202.8 ppm in the ^{13}C NMR spectrum.

Single crystals of **3** suitable for X-ray diffraction studies were grown by slow evaporation of its saturated solution in CH$_3$CN. The molecular structure depicted in Figure 1 confirms the proposed composition of species **3** as a neutral and linear bromido-monocarbene gold(I) complex. Using this structure, a percentage of buried volume (%V_{bur}) of 46.5 was determined as an estimate for the steric bulk of the 8-Mes ligand. As expected, 8-Mes is bulkier than 7-Mes (43.1),[17] but smaller %V_{bur} values were also determined for 9-Mes (43.6) and 10-Mes (43.3) using their [AuCl(erNHC)] complexes.[18] As for other gold(I) erNHC complexes, ligand disproportionation[22,23] was not observed for complex **3** upon prolonged standing in solution.

Complex **3** provides access to the respective heterobis(NHC) complex [Au(^{i}Pr$_2$-bimy)(8-Mes)]BF$_4$ (**6**) in excellent

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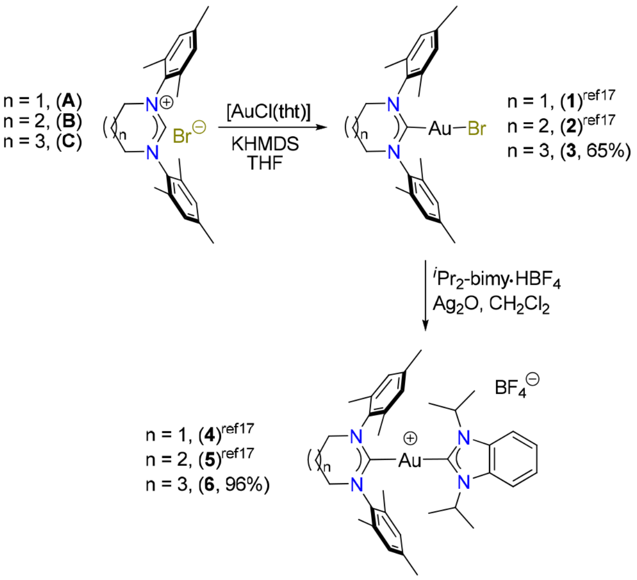
Scheme 1. Preparation of Expanded-Ring Au^I erNHC Complexes



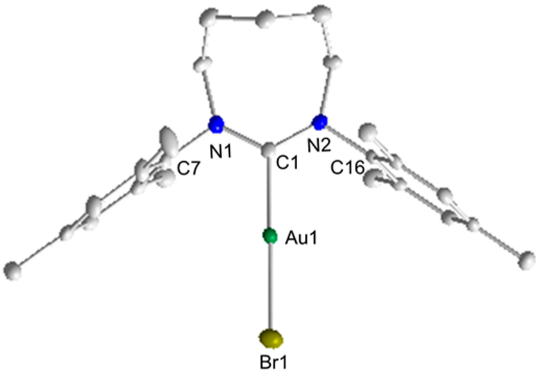
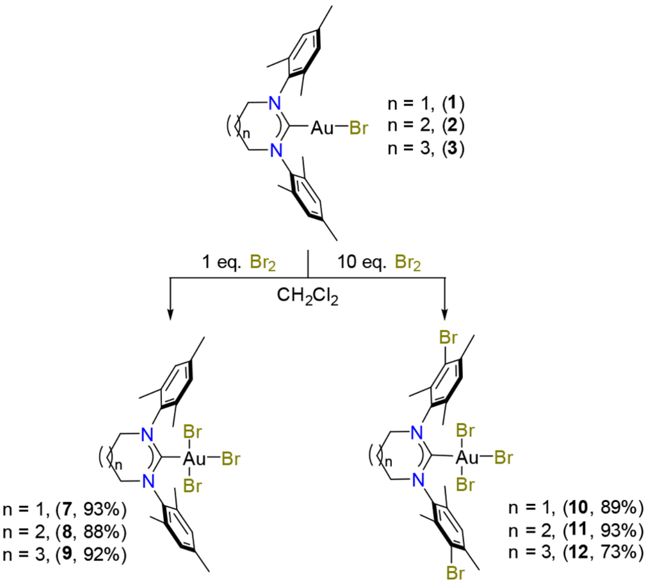


Figure 1. Molecular structures of complexes **3** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for the sake of clarity. Selected bond lengths (angstroms) and angles (degrees) for **3**: Au1−C1, 2.026(3); Au1−Br1, 2.417(1); C1−Au1−Br1, 179.62(8); N1−C1−N2, 123.4(3); C16−N2−C1, 116.2(2); C7−N1−C1, 116.3(2); Au1−C1−N2, 118.2(1); Au1−C1−N1, 118.4(2).

yields of 96% upon treatment with ${}^iPr_2$-bimy·HBF_4 and Ag_2O at ambient temperature in dichloromethane. Support for the formation of complex **6** was obtained by positive mode ESI MS, which shows a base peak for the respective $[Au({}^iPr_2\text{-bimy})(8\text{-Mes})]^+$ cation. ^1H NMR spectroscopy reveals the isopropyl methine signal of the ${}^iPr_2$-bimy ligand in complex **6** at 3.72 ppm, which is notably more upfield than those in the six- and seven-membered analogues **4** and **5**, respectively (i.e., 3.93 and 3.82 ppm, respectively).[17] This upfield shift is in line with the increased anisotropic effect of mesityl rings[24] due to the larger NCN angle of the eight-membered 8-Mes ligand in complex **6**. As anticipated, two distinct carbene signals are found in the ^{13}C NMR spectrum of this complex. The carbene atom of 8-Mes resonates at 209.6 ppm, while that for the ${}^iPr_2$-bimy is found at 186.5 ppm. A significant downfield shift of the former was noted compared to that in precursor complex **3** due to the coordination of a second strong NHC donor.[25]

Gold(III) Monocarbene Complexes. Gold(I) NHC complexes can easily undergo oxidative addition with halogens to afford the gold(III) NHC analogues.[21] This reaction is usually straightforward because NHCs are very good electron donors. It is therefore surprising that Au^{III} complexes of erNHCs are unknown thus far, although erNHCs are even stronger donors compared to their classical five-membered NHC counterparts. To explore such reactivity, the charge-neutral bromido-erNHC Au^I complexes **1**−**3** were treated with bromine in an initial trial (Scheme 2). Indeed, gold-centered oxidative additions occurred readily, and gold(III) monocarbene complexes of the formula $[AuBr_3(\text{erNHC})]$ (**7**−**9**) were obtained in good yields of 88−93% when 1 equiv of bromine was used. The notable upfield shifts of the carbene resonances to 169.0 ppm (**7**), 176.6 ppm (**8**), and 174.6 ppm (**9**) observed in the ^{13}C NMR spectra agree well with the formation of Au^{III} species.[21] The presence of dominant peaks for the $[M - Br]^+$ ions in positive mode ESI mass spectra provides additional support. Finally, their identities as tribromido-erNHC gold(III) complexes were corroborated by X-ray diffraction of single crystals obtained by slow evaporation of their concentrated solutions in acetonitrile.

Scheme 2. Synthetic Route to erNHC Au^{III} Complexes



The solid-state molecular structures of **7**−**9** depicted in Figure 2 reveal Au^{III} centers that are coordinated by three bromido ligands and one erNHC in a square-planar geometry. Au^{III}−C bond distances of 2.058(8) Å (**7**), 2.057(4) Å (**8**), and 2.072(4) Å (**9**) were found to be slightly longer than the respective distances of 2.003(3) Å (**1**), 2.004(3) Å (**2**), and 2.026(3) Å (**3**), respectively, in their Au^I precursors.[17] Supposedly, this bond elongation is due to enhanced crowding with the increase in the coordination number from two to four. On the other hand, N−C−N angles of 121.8(7)° (**7**), 122.9(3)° (**8**), and 124.6(3)° (**9**) differ only marginally from those of the parent Au^I complexes, i.e., 118.9(3)° (**1**), 119.8(2)° (**2**), and 123.4(3)° (**3**), respectively. Nevertheless, complex **9** exhibits the largest N−C−N angle among all reported Au−erNHC complexes, including those of nine- and ten-membered erNHCs.[18]

We found that stoichiometry control is very important in the formation of complexes **7**−**9**. The use of excess bromine additionally led to the bromination of the mesityl wing tips of

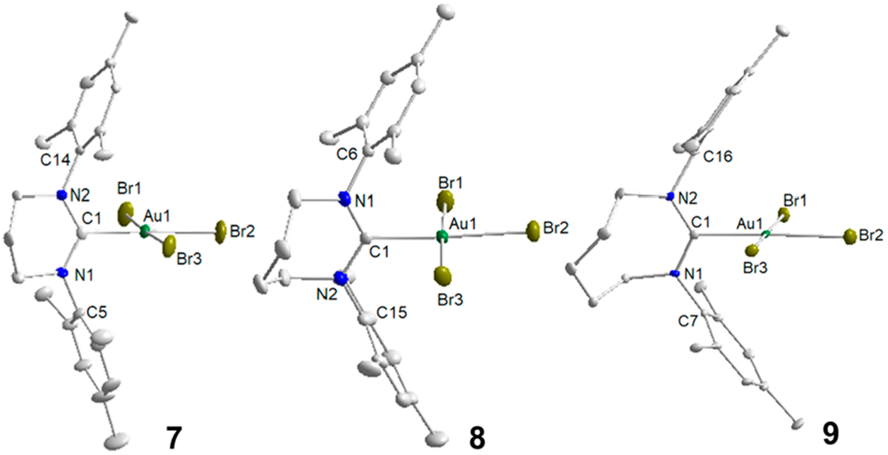


Figure 2. Molecular structures of complexes 7·0.5H_2O, **8**, and **9** showing 50% probability ellipsoids. Only one independent molecule is shown for **7**. Hydrogen atoms and solvent molecules have been omitted for the sake of clarity. Selected bond lengths (angstroms) and angles (degrees) for **7**: Au1−C1, 2.058(8); Au1−Br1, 2.415(1); Au1−Br2, 2.437(9); Au1−Br3, 2.421(1); C1−Au1−Br2, 175.4(2); Br1−Au1−Br3, 177.5(4); N2−C1−N1, 121.8(7). Selected bond lengths (angstroms) and angles (degrees) for **8**: Au1−C1, 2.057(4); Au1−Br1, 2.412(5); Au1−Br2, 2.456(4); Au1−Br3, 2.413(5); C1−Au1−Br2, 173.4(1); Br1−Au1−Br3, 176.2(2); N2−C1−N1, 122.9(3). Selected bond lengths (angstroms) and angles (degrees) for **9**: Au1−C1, 2.072(4); Au1−Br1, 2.423(5); Au1−Br2, 2.450(4); Au1−Br3, 2.422(4); C1−Au1−Br2, 176.8(1); Br1−Au1−Br3, 176.4(1); N2−C1−N1, 124.6(3).

the erNHC ligands by electrophilic substitution. Interestingly, the introduction of one bromo substituent deactivates each aryl ring for a second bromination, giving rise to gold(III) complexes of dibrominated erNHCs as the final products (Scheme 2). Because the reactions did not reach completion with 3 or 4 equiv of bromine, a 10-fold excess of bromine was used at ambient temperature instead. Under these conditions, the [$AuBr_3$(erNHC^{Br2})]-type complexes (**10**−**12**) were isolated in good yields of 73−93%. Notably, the bromination of the erNHC ligands leads to a reduced solubility of the respective complexes, and complexes **10**−**12** show very poor solubility in common organic solvents such as dichloromethane, chloroform, acetonitrile, and dimethyl sulfoxide.

Positive mode ESI MS shows strong [M − Br]$^+$ peaks for all three complexes due to loss of one bromido ligand. Upon bromination of the mesityl substituent, all methyl groups become inequivalent, and accordingly, three different methyl signals are observed in the ^{1}H NMR spectra of complexes **10**−**12**. The $^{13}C_{carbene}$ NMR signals detected at 169.6 ppm (**10**), 176.7 ppm (**11**), and 175.1 ppm (**12**) are in the same range as those of their nonbrominated analogues **7**−**9**, indicating that the remote brominations have little effect on the carbene donor. On the other hand, all aromatic carbon atoms of each mesityl ring become distinct, and an increase in the resonances in the aromatic region is expected. Moreover, the various degrees of backbone twisting of the erNHC ligands result in different orientations of the brominated wing tips relative to each other, which complicate the ^{13}C NMR spectra of the complexes further. Single crystals of [$AuBr_3$(7-Mes^{Br2})] (**11**) obtained from a concentrated solution in dichloromethane were found to be suitable for X-ray diffraction studies. Due to the many possible orientations of the highly flexible 7-Mes^{Br2} ligand, only highly disordered structures could be obtained despite several attempts. A best representative depiction of the molecular structure is shown in Figure 3, which in combination with other spectroscopic and spectrometric analytical methods can confirm the monobromination of each mesityl ring.

Gold(III) Heterobis(carbene) Complexes. To explore the structural diversity of gold(III) erNHC complexes further, the cationic heterobis(carbene) complexes [Au(^{i}Pr$_2$-bimy)(erNHC)]BF_4 (**4**−**6**) were also subjected to different amounts of bromine in dichloromethane at ambient temperature (Scheme 3). The addition of 1 equiv of bromine resulted in a clean oxidative addition at the gold(I) center giving the cationic gold(III) complexes [$AuBr_2$(^{i}Pr$_2$-bimy)(6-Mes)]BF_4 (**13**), [$AuBr_2$(^{i}Pr$_2$-bimy)(7-Mes)]BF_4 (**14**) and [$AuBr_2$(^{i}Pr$_2$-bimy)(8-Mes)]BF_4 (**15**) in high yields of >95%.

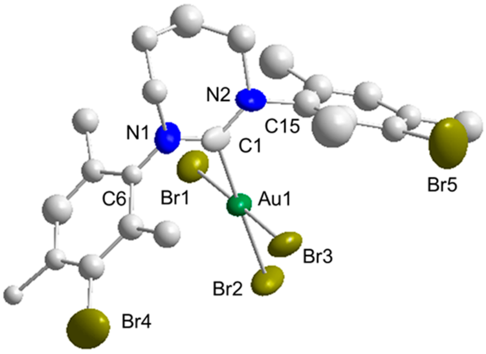


Figure 3. Molecular structures of complexes **11**·H_2O showing 50% probability ellipsoids. Disordered atoms of lower occupancy, the solvent molecule, and hydrogen atoms have been omitted for the sake of clarity. Selected bond lengths (angstroms) and angles (degrees) for **11**: Au1−C1, 2.071(2); Au1−Br1, 2.449(2); Au1−Br2, 2.411(2); Au1−Br3, 2.418(2); C1−Au1−Br2, 178.0(5); Br2−Au1−Br3, 179.3(1); N2−C1−N1, 123.7(1).

In all three cases, base peaks are observed at *m*/*z* 879 (**13**), *m*/*z* 893 (**14**), and *m*/*z* 907 (**15**) for the respective [$AuBr_2$(^{i}Pr$_2$-bimy)(erNHC)]$^+$ molecular cations in their positive mode ESI mass spectra. The erNHC carbene signals are found at 178.3 ppm (**13**), 187.7 ppm (**14**), and 184.1 ppm (**15**), while those for the benzimidazolin-2-ylidenes resonate at 155.6 ppm (**13**), 155.8 ppm (**14**), and 154.8 ppm (**15**). All of these carbene signals are significantly upfield-shifted relative to those in the gold(I) precursors **4**−**6**, clearly indicating an oxidation of the gold center from I to III.

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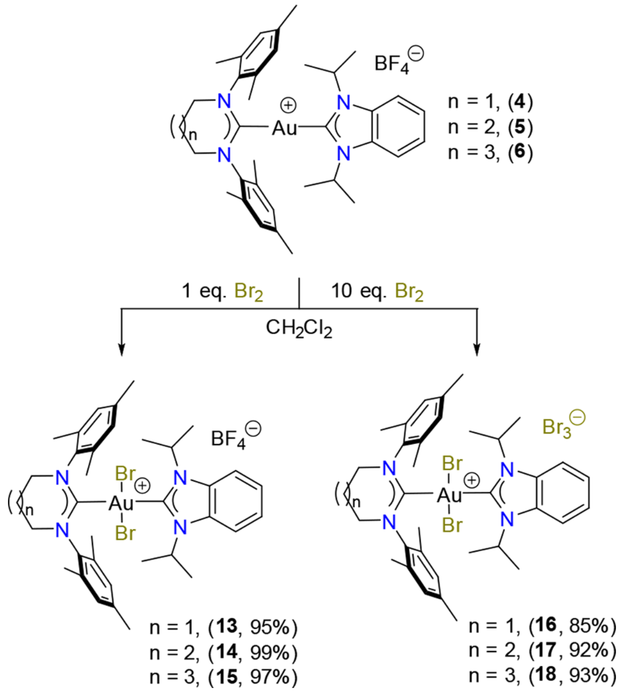
Scheme 3. Synthetic Route to Hetero-Bis(carbene) Au^{III} Complexes



Another interesting observation is that the signals for the isopropyl methine protons shift stepwise upfield from 3.51 ppm (**13**) to 3.47 ppm (**14**) and finally to 3.39 ppm (**15**) with increasing ring sizes of the erNHC ligands. We have previously observed this phenomenon in isoelectronic and isostructural palladium(II) complexes as well as in the gold(I) heterobis(carbene) complexes **4** and **5** and ascribed it to the increasing anisotropic effects of the mesityl substituents in the erNHC ligands.[17] Single-crystal X-ray diffraction studies confirm the identities of all three gold(III) heterobis(carbene) complexes (see the Supporting Information).

The reactions of cationic Au^{I} heterobis(carbene) complexes **4**−**6** with 10 equiv of bromine show a very different outcome compared to those of the charge-neutral monocarbene complexes **1**−**3**. In these cases, no wing-tip brominations took place at all after the gold-centered oxidations. Instead, the excess of bromine led to the formation of tribromides, which replaced the tetrafluoroborate counteranions, and the new gold(III) complexes [AuBr$_2$(^{i}Pr$_2$-bimy)(6-Mes)]Br$_3$ (**16**), [AuBr$_2$(^{i}Pr$_2$-bimy)(7-Mes)]Br$_3$ (**17**), and [AuBr$_2$(^{i}Pr$_2$-bimy)(8-Mes)]Br$_3$ (**18**) were obtained in good yields of >85%. Supposedly, electrophilic substitution of the mesityl groups is prevented by the positive charge of complexes **4**−**6**. Complexes **13**−**15** and **16**−**18** show very similar analytical characteristics, because they differ in only the counteranion. However, complete replacement of the tetrafluoroborate anions is supported by the lack of any fluorine signals in the ^{19}F NMR spectra of complexes **16**−**18**.

The molecular structures of all heterobis(carbene) gold(III) complexes (**13**−**18**) were also established by single-crystal X-ray diffraction, and those of **16**−**18** are depicted in Figure 4. All complexes are square planar, in which the Au^{III} centers are coordinated by two different NHCs and two bromido ligands in an exclusively *trans* arrangement. The Au^{III}−erNHC bond distances in the range of 2.072−2.105 Å are notably longer

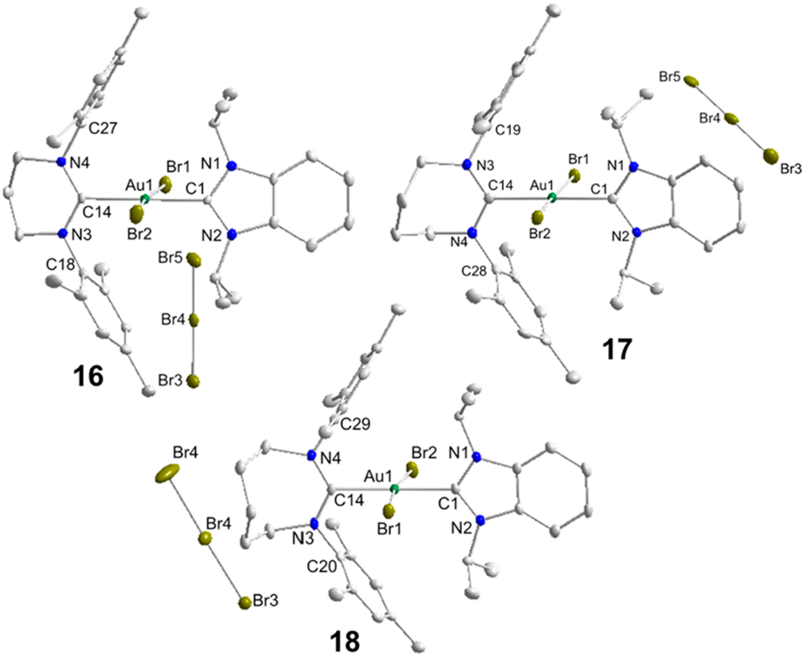


Figure 4. Molecular structures of complexes **16**·CHCl$_3$, **17**·CHCl$_3$, and **18** showing 50% probability ellipsoids. Hydrogen atoms and the solvent molecule have been omitted for the sake of clarity. Selected bond lengths (angstroms) and angles (degrees) for **16**: Au1−C1, 2.033(4); Au1−C14, 2.076(4); Au1−Br1, 2.426(1); Au1−Br2, 2.420(1); C14−Au1−C1, 176.3(2); Br1−Au1−Br2, 170.8(2); N4−C14−N3, 120.6(3). Selected bond lengths (angstroms) and angles (degrees) for **17**: Au1−C1, 2.041(3); Au1−C14, 2.085(3); Au1−Br1, 2.416(1); Au1−Br2, 2.420(1); C14−Au1−C1, 176.7(1); Br1−Au1−Br2, 173.7(1); N4−C14−N3, 121.6(3). Selected bond lengths (angstroms) and angles (degrees) for **18**: Au1−C1, 2.043(2); Au1−C14, 2.105(2); Au1−Br1, 2.422(3); Au1−Br2, 2.422(3); C14−Au1−C1, 178.2(1); Br1−Au1−Br2, 170.5(1); N4−C14−N3, 124.9(2).

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than the Au^{III}−^{i}Pr$_2$-bimy bond lengths ranging from 2.034 to 2.053 Å, possibly indicating the increased strengths of the latter. Specifically, the Au^{III}−erNHC distances of 2.084(5) Å in **14** and 2.085(3) Å in **17** were found to be larger than the distance of 2.035(4) Å for the respective bond found in their common parent Au^I complex **5**, which can be ascribed to an increase in the coordination number (vide supra).

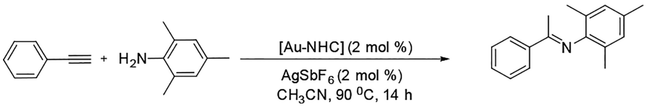
To the best our knowledge, complexes **7**−**18** are the first examples of Au^{III} complexes bearing erNHC ligands.

Hydroamination of Alkynes with Primary Amines. The gold-catalyzed hydroamination reaction of alkynes and amines represents a good example for a simple one-step conversion of inexpensive and readily available substrates, which is 100% atom efficient.[26−33] Thus, we were interested in examining and comparing the catalytic efficiencies of all of our synthesized Au erNHC complexes in this important reaction. In a preliminary study, all Au erNHC complexes **1**−**18** have been tested as precatalysts for the hydroamination of alkynes and primary amines as a standard test reaction. Initially, the simplest precatalyst [AuBr(6-Mes)] (**1**) was chosen for the exploration of reaction conditions. The complex was found to catalyze the hydroamination of phenylacetylene and mesitylamine at 50 °C using AgBF$_4$ as a bromide scavenger and gave 52% conversion (by GC/GC-MS) after 24 h with respect to the mesitylamine, which was chosen as the limiting substrate in this reaction (Table S1, entry 1). The use of AgSbF$_6$ gave better product conversion [73% (Table S1, entry 2)] under the same reaction condition. The performance was further improved at 90 °C, which allowed for shorter reaction times (Table S1, entries 3 and 5). Among the different halide scavengers (AgPF$_6$, AgOAc, NaBF$_4$, and KBF$_4$), AgSbF$_6$ was found to be the most suitable for the present reaction condition in acetonitrile (Table S1, entries 3−8). Solvents other than CH$_3$CN were found to be less suitable for the reaction (Table S1, entries 9−13). Exceptionally, comparable conversion was observed in 1,4-dioxane. However, acetonitrile gave cleaner reactions. Finally, poor hydroamination activity was noted in the absence of any gold complex. The very low yield in this case is attributed to a low background catalytic activity of AgSbF$_6$ (Table S1, entry 14).

With optimized reaction conditions in hand, the remaining complexes **2**−**18** were benchmarked against complex **1** to evaluate their catalytic efficiency in the hydroamination of phenyl acetylene with mesitylamine.

The seven-membered erNHC complex **2** was found to be more active than its six-membered analogue **1** and yielded 96% conversion (Table 1, entry 2). Within the same series, the eight-membered erNHC complex **3** gave the best results with 98% conversion (Table 1, entry 3). Au^{III} complexes **7**−**12** with a single erNHC ligand are all active but are inferior to their Au^I counterparts **1**−**3** (Table 1, entries 4−9). Moreover, a decrease in conversion was observed with complexes **10**−**12** containing the electron-poorer, bromo-substituted erNHCs ligands. Notably, all cationic heterobis(carbene) complexes were inactive regardless of the gold oxidation state, the nature of the counteranion, and the presence of the halide scavenger (Table 1, entries 10−19). The inactivity of these complexes could be rationalized by the lack of binding sites for incoming substrates due to the presence of two strong Au−NHCs bonds and the increased steric bulk. Overall, charge-neutral Au^I complexes with larger and supposedly stronger donating erNHCs ligands gave rise to better precatalysts in this reaction.

Table 1. Catalyst Screening[a]



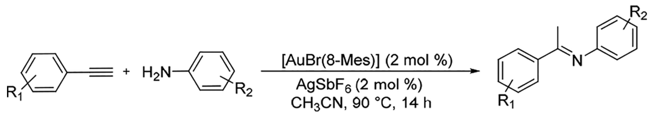
entry	Au NHC	Ag salt	conversion[b]/yield[c]
1	[AuBr(6-Mes)] (**1**)	AgSbF$_6$	91
2	[AuBr(7-Mes)] (**2**)	AgSbF$_6$	96
3	[AuBr(8-Mes)] (**3**)	AgSbF$_6$	98/94
4	[AuBr$_3$(6-Mes)] (**7**)	AgSbF$_6$	86
5	[AuBr$_3$(7-Mes)] (**8**)	AgSbF$_6$	88
6	[AuBr$_3$(8-Mes)] (**9**)	AgSbF$_6$	90
7	[AuBr$_3$(6-Mes^{Br})] (**10**)	AgSbF$_6$	80
8	[AuBr$_3$(7-Mes^{Br})] (**11**)	AgSbF$_6$	74
9	[AuBr$_3$(8-Mes^{Br})] (**12**)	AgSbF$_6$	80
10	[Au(^{i}Pr$_2$-bimy)(6-Mes)]BF$_4$ (**4**)	–	0
11	[Au(^{i}Pr$_2$-bimy)(7-Mes)]BF$_4$ (**5**)	–	0
12	[Au(^{i}Pr$_2$-bimy)(8-Mes)]BF$_4$ (**6**)	–	0
13	[Au(^{i}Pr$_2$-bimy)(6-Mes)]BF$_4$ (**4**)	AgSbF$_6$	13
14	[AuBr$_2$(^{i}Pr$_2$-bimy)(6-Mes)]BF$_4$ (**13**)	AgSbF$_6$	0
15	[AuBr$_2$(^{i}Pr$_2$-bimy)(7-Mes)]BF$_4$ (**14**)	AgSbF$_6$	0
16	[AuBr$_2$(^{i}Pr$_2$-bimy)(8-Mes)]BF$_4$ (**15**)	AgSbF$_6$	0
17	[AuBr$_2$(^{i}Pr$_2$-bimy)(6-Mes)]Br$_3$ (**16**)	AgSbF$_6$	0
18	[AuBr$_2$(^{i}Pr$_2$-bimy)(7-Mes)]Br$_3$ (**17**)	AgSbF$_6$	0
19	[AuBr$_2$(^{i}Pr$_2$-bimy)(8-Mes)]Br$_3$ (**18**)	AgSbF$_6$	0

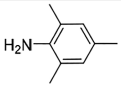
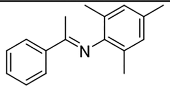
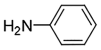
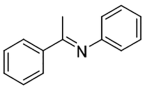
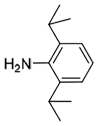
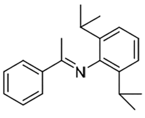
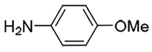
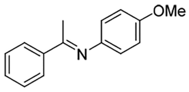
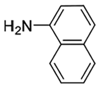
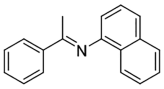
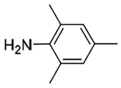
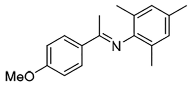
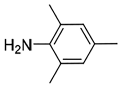
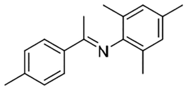
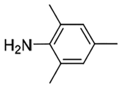
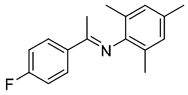
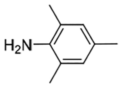
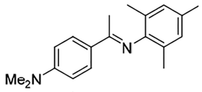
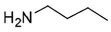
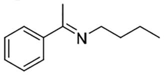
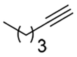
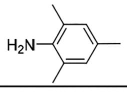
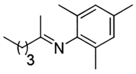
[a]Reaction conditions: phenylacetylene (0.3 mmol, 1.5 equiv), mesitylamine (0.2 mmol, 1 equiv), AgSbF$_6$ (0.004 mmol, 2 mol %), Au NHC (0.004 mmol, 2 mol %) in CH$_3$CN (~1 mL) heated at 90 °C in a screw cap tube under air. [b]GC/GC-MS conversion to product. [c]Isolated yield.

With [AuBr(8-mes)] (**3**) having been identified as the most active precatalyst, a small substrate scope study was conducted with different alkynes and amines. Notably, various substituted anilines and phenylacetylenes were found to undergo hydroaminations, giving the desired products in excellent yields (Table 2). In particular, sterically demanding mesitylamine and 2,6-diisopropylaniline showed very good reactivity (>99%) and gave addition products to phenylacetylene in excellent yields (Table 2, entries 1 and 3). The parent aniline also reacted very well (Table 2, entry 2). 4-Methoxyphenylamine and 1-naphthylamine gave excellent reaction product conversion (Table 2, entries 4 and 5). Phenylacetylenes with electron-donating substituents, e.g., 4-methoxyphenylacetylene, 4-methylphenylacetylene, and 4-(dimethylamino)-phenylacetylene, or with electron-withdrawing substituents, e.g., 4-fluorophenylacetylene, gave excellent reaction outcomes under standard reaction condition (Table 2, entries 6−9). However, the aliphatic butylamine was found to be unreactive. Likewise, the aliphatic 1-hexyne also gave poor conversion when reacted with mesitylamine under this reaction condition (Table 2, entries 10 and 11).

In general, the catalytic efficiency of our most active precatalyst **3** compares well with those of other reported Au^I NHC complexes for the intermolecular hydroamination of terminal alkynes and primary amines. However, a fair comparison is often not possible due to the application of different reaction conditions and times, varying additives, and varying catalyst loadings. Nevertheless, precatalyst **3** gave better results than 1,2,4-triazole- and imidazole-derived Au^I complexes under similar reaction conditions.[26] Similarly, precatalyst **3** shows far better reactivity than pyrazole-

Table 2. Substrate Scope Study[a]



Entry	R₁	Amine	Product	Conv.[b]/Yield[c]
1	H			>99/94
2	H			98[d]
3	H			>99/98
4	H			>99[d]
5	H			>99/55[d]
6	4-OMe			>99/98
7	4-Me			>99/98
8	4-F			>99/97
9	4-NMe₂			>99/92
10	H			NR
11				11/-

[a]Reaction conditions: alkyne (0.75 mmol, 1.5 equiv), amine (0.5 mmol, 1 equiv), $AgSbF_6$ (0.01 mmol, 2 mol %), Au NHC (0.01 mmol, 2 mol %) in CH_3CN (~1 mL) heated at 90 °C in a screw cap tube under air. [b]GC/GC-MS conversion to product. [c]Isolated yield. [d]Decomposition of the product during column chromatography.

functionalized imidazole-derived Au^{I} and Au^{III} NHC complexes.[31] Dinuclear Au NHC complexes and [AuCl(IPr)] showed results comparable to those for complex **3** under neat conditions.[30] Finally, some hexaazatriphenylene-bridged,[34] benzoferrocenyl-fused,[35] and polyaromatic-annulated[36] NHC complexes outperformed precatalyst **3** and were more active at comparatively lower catalyst loadings. However, these precatalysts contain much more complicated ligand systems.

To gain insight into the catalytically active species generated by the Au^{I} and Au^{III} precatalysts, detailed ^{13}C NMR studies have been performed. Thus, the most active precatalyst **3** and its direct Au^{III} analogue **9** were chosen for catalytic NMR monitoring experiments at 50 mol % loading in CD_3CN to ensure decent resolution of the NMR spectra. Precatalyst **3** was first heated with an equimolar amount of $AgSbF_6$ at 90 °C. Halide abstraction should lead to formation of a CD_3CN adduct, which leads to an expected upfield shift of the $^{13}C_{carbene}$ resonance (see Figure S82B). Addition of 2 equiv of aniline and phenylacetylene yielded the hydroamination product almost immediately, and three carbene resonances for three distinct Au^{I} erNHC adducts {e.g., [Au(erNHC)L]SbF_6, where L = $PhNH_2$, PhCCH, or CD_3CN} were observed in the ^{13}C NMR spectrum (Figure S82C). Further heating of the reaction mixture indicated the presence of only Au^{I} erNHC species, while no signals for Au^{III} erNHC species could be observed. The study was repeated with Au^{III} precatalyst **9**, which, however, showed poor solubility in CD_3CN, and the initial ^{13}C NMR spectrum was not very conclusive (Figure S83A). However, addition of an equimolar amount of $AgSbF_6$ led to the formation of two new species by the presence of two new methylene carbon signals (Figure S83B). The introduction of substrates resulted in product formation; new Au^{I}−erNHC adducts were also observed in the ^{13}C NMR spectra, while Au^{III} species were absent (Figure S83C). In conclusion, this study supports the notion that the Au^{III} precatalyst **9** is reduced to an Au^{I} erNHC adduct as the likely active species (Figure S84). Supposedly, this can occur via reductive elimination of Br$_2$.

■ CONCLUSIONS

We have reported the preparation and full characterization of the first gold(III) complexes bearing expanded-ring NHCs (erNHCs) by simple oxidative addition of bromine to the respective gold(I) erNHC precursors. Using this approach, charge-neutral [AuBr$_3$(erNHC)] or cationic [AuBr$_2$(^{i}Pr$_2$-bimy)(erNHC)]$^+$ complexes derived from six- to eight-membered heterocycles were obtained in generally high yields. Stoichiometry control was found to be important, because an excess of bromine led to different side reactions depending on the precursor complex used. In the case of the neutral monocarbene complexes, ligand brominations were observed, while the formation of tribromide counteranions was noted for cationic bis(carbene) complexes. Finally, the catalytic performance of 18 gold erNHC complexes in the hydroamination of alkynes was compared, which revealed that monocarbene complexes consistently performed better than their bis(carbene) counterparts. The [AuBr(8-Mes)] complex **3** bearing the bulkiest erNHC was identified as the best precatalyst, which was used for a small substrate scope study generally revealing good performance. Overall, this study diversifies the applications of erNHC ligands in organometallic chemistry. The isolation of the first gold(III) erNHC complexes could pave the way for new potential applications of this class of nonclassical N-heterocyclic carbenes.

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out using standard Schlenk techniques. ^{i}Pr$_2$-bimy·HBF$_4$ was prepared according to a literature procedure.[37] The ligand precursors **A**−**C** were synthesized according to modified literature procedures.[38,39] ^{1}H, ^{13}C{^{1}H}, and ^{19}F{^{1}H} NMR spectra were recorded on Bruker 400 MHz or Bruker 500 MHz NMR spectrometers. ^{1}H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), broad (br), doublet of doublets (dd), multiplet (m), and septet (sept). ESI mass spectra were measured using a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on an Elementar Vario Micro Cube elemental analyzer at the Department of Chemistry, National University of Singapore. X-ray data for **3**, **7**−**9**, **11**, and **13**−**18** were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation with the SMART suite of programs,[40] and refinement parameters are summarized in Tables S2−S4.

[AuBr(8-Mes)] (3). A mixture of 8-Mes·HBr (**C**) (0.431 g, 1.00 mmol) and [AuCl(tht)] (0.320 g, 1.00 mmol) was dried under vacuum for 30 min in a Schlenk tube. Then, dry THF (~30 mL) was added to the mixture under an argon atmosphere, and the solution was cooled to −78 °C. KHMDS (0.91 M in THF, 1.10 mL, 1.2 mmol) was added via a syringe, and the reaction mixture was stirred at −78 °C for a further 30 min. The cooling bath was removed, and the reaction mixture was allowed to stir at ambient temperature for 3 h. The reaction mixture was filtered through Celite, and drying under vacuum gave the crude product as a brown solid. The latter was redissolved in CH$_2$Cl$_2$ and filtered through Celite. The solvent of the filtrate was removed, and the residue was washed with hexane (3 × 3 mL). Drying under vacuum gave the product an air-stable, white solid (0.409 g, 65%). Single crystals of **3** were grown from evaporation of a concentrated solution in CH$_3$CN: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.90 (s, 4 H, Ar−H), 4.08 (br, 4 H, CH$_2$), 2.33 (s, 12 H, CH$_3$), 2.26 (s, 6 H, CH$_3$). 2.06 (br, 6 H, CH$_2$); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 202.8 (C$_{8\text{-Mes}}$), 147.2, 138.3, 134.4, 130.7 (Ar−C), 53.6, 29.1, 22.8 (CH$_2$), 21.7, 19.5 (CH$_3$); MS (ESI) m/z calcd for $C_{48}H_{64}BrN_4Au_2$ [2 M − Br]$^+$ 1171, found 1171. Anal. Calcd for $C_{24}H_{22}BrN_2Au$: C, 46.09; H, 5.16; N, 4.48. Found: C, 46.40; H, 5.18; N, 4.88.

[Au(^{i}Pr$_2$-bimy)(8-Mes)]BF$_4$ (6). A mixture of [AuBr(8-Mes)] (**3**) (0.160 g, 0.255 mmol), ^{i}Pr$_2$-bimy·HBF$_4$ (0.074 g, 0.255 mmol), and Ag$_2$O (0.059 g, 0.255 mmol) was allowed to stir in CH$_2$Cl$_2$ (40 mL) at ambient temperature for 1 h. Then, the reaction mixture was filtered through Celite, and the solvent of the filtrate was removed under vacuum to give the crude product as a white solid, which was purified by washing with hexane (~3 × 5 mL) to give a white solid (0.204 g, 96%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.48 [dd, ^3J(H,H) = 6 Hz, 2 H, Ar−H], 7.25 [dd, ^3J(H,H) = 6 Hz, 2 H, Ar−H], 6.98 (s, 4 H, Ar−H), 4.19 (br, 4 H, CH$_2$), 3.72 [sept, ^3J(H,H) = 7 Hz, 2 H, C*H*(CH$_3$)$_2$], 2.40 (s, 12 H, CH$_3$), 2.32 (s, 6 H, CH$_3$), 2.08 (br, 6 H, CH$_2$), 1.27 [d, ^3J(H,H) = 7 Hz, 12 H, CH(C*H*$_3$)$_2$]; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 209.6 (C$_{8\text{-Mes}}$), 186.5 (C$_{\text{probe}}$), 146.6, 138.3, 135.2, 132.8, 130.7, 124.6, 114.2 (Ar−C), 54.8 (CH$_2$), 54.4 [CH(CH$_3$)$_2$], 29.1, 22.3 (CH$_2$), 21.8, 21.8, 19.4 (CH$_3$); ^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ −154.21 (s, ^{10}BF$_4$), −154.26 (s, ^{11}BF$_4$); MS (ESI) m/z calcd for $C_{37}H_{50}N_4Au$ [M − BF$_4$]$^+$ 747, found 747. Anal. Calcd for $C_{37}H_{50}BF_4N_4Au$: C, 53.25; H, 6.04; N, 6.71. Found: C, 52.67; H, 6.53; N, 5.70. The elemental analysis remains unsatisfactory despite repeated purification and analysis, possibly because of solvation.

[AuBr$_3$(6-Mes)] (7). Bromine (~10 μL, 0.201 mmol) was added dropwise to a stirred solution of [AuBr(6-Mes)] (**1**) (0.120 g, 0.201 mmol) in CH$_2$Cl$_2$ (~5 mL) at ambient temperature, and the reaction mixture was allowed to stir for a further 30 min. Then, volatiles were removed under vacuum, and the residue was washed with diethyl ether. Finally, the residue was dried under vacuum to give the product as an orange solid (0.141 g, 93%). Single crystals of **7** were grown from evaporation of a concentrated solution in CH$_3$CN: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.92 (s, 4 H, Ar−H), 3.74 [t, ^3J(H,H) = 6 Hz, 4 H, CH$_2$], 2.50 (s, 12 H, CH$_3$), 2.47−2.44 (m, 2 H, CH$_2$), 2.27 (s, 6 H, CH$_3$); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 169.0 (C$_{6\text{-Mes}}$), 140.4, 139.4, 136.1, 130.9 (Ar−C), 50.9, 21.7 (CH$_2$), 21.3, 20.9 (CH$_3$); MS (ESI) m/z calcd for $C_{22}H_{28}Br_2N_2Au$ [M − Br]$^+$ 677, found 677. Anal. Calcd for $C_{22}H_{28}Br_3N_2Au$: C, 34.90; H, 3.73; N, 3.70. Found: C, 34.98; H, 3.73; N, 4.52.

[AuBr$_3$(7-Mes)] (8). Complex **8** was prepared in analogy to compound **7** using bromine (~10 μL, 0.201 mmol) and [AuBr(7-Mes)] (**2**) (0.120 g, 0.197 mmol) and isolated as an orange solid (0.135 g, 88%). Single crystals of **8** were grown from evaporation of a concentrated solution in CH$_3$CN: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.93 (s, 4 H, Ar−H), 4.10 (br, 4 H, CH$_2$), 2.58 (s, 12 H, CH$_3$), 2.35 (br, 4 H, CH$_2$), 2.27 (s, 12 H, CH$_3$); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 176.6 (C$_{7\text{-Mes}}$), 141.0, 140.3, 135.9, 131.2 (Ar−C), 58.7, 24.7 (CH$_2$), 21.8, 21.7 (CH$_3$); MS (ESI) m/z calcd for $C_{23}H_{30}Br_2N_2Au$ [M − Br]$^+$ 691, found 691. Anal. Calcd for $C_{23}H_{30}Br_3N_2Au$: C, 35.82; H, 3.92; N, 3.63. Found: C, 35.86; H, 3.84; N, 3.81.

[AuBr$_3$(8-Mes)] (9). Complex **9** was prepared in analogy to compound **7** using bromine (~11 μL, 0.224 mmol) and [AuBr(8-Mes)] (**3**) (0.140 g, 0.224 mmol) and isolated as an orange solid (0.165 g, 92%). Single crystals of **9** were grown from evaporation of a concentrated solution in CH$_3$CN: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.94 (s, 4 H, Ar−H), 4.12−4.10 (m, 4 H, CH$_2$), 2.58 (s, 12 H, CH$_3$), 2.27 (s, 10 H, CH$_3$ and CH$_2$), 1.96−1.92 (m, 2 H, CH$_2$); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 174.6 (C$_{8\text{-Mes}}$), 141.7, 140.3, 135.9, 131.4 (Ar−C), 59.5, 26.6, 25.1 (CH$_2$), 22.6, 21.6 (CH$_3$); MS (ESI) m/z calcd for $C_{24}H_{32}Br_2N_2Au$ [M − Br]$^+$ 705, found 705. Anal. Calcd for $C_{24}H_{32}Br_3N_2Au$: C, 36.71; H, 4.11; N, 3.57. Found: C, 36.58; H, 4.00; N, 3.70.

[AuBr$_3$(6-Mes^{Br2})] (10). Bromine (~40 μL, 0.840 mmol) was added dropwise to a stirred solution of [AuBr(6-Mes)] (**1**) (0.050 g, 0.084 mmol) in CH$_2$Cl$_2$ (~5 mL) at ambient temperature, and the reaction mixture was allowed to stir for a further 2 h. Then, the volatiles were removed under vacuum, and the residue was washed with diethyl ether followed by drying under vacuum to give the product as an orange solid (0.69 g, 89%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.13 (s, 4 H, Ar−H), 3.73 (br, 4 H, CH_2), 2.57 (s, 6 H, CH_3), 2.50 (s, 8 H, CH_3 and CH_2), 2.43 (s, 6 H, CH_3); ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ 169.6 ($C_{6\text{-Mes}}^{Br2}$), 141.1, 140.2, 136.8, 135.3, 135.2, 136.6, 126.6 (Ar−C), 51.3 (CH_2), 24.3, 23.8 (CH_3), 21.0 (CH_2), 20.8 (CH_3); MS (ESI) *m/z* calcd for $C_{22}H_{26}Br_4N_2Au$ [M − Br]$^+$ 835, found 834. Anal. Calcd for $C_{22}H_{26}Br_5N_2Au$: C, 28.88; H, 2.86; N, 3.06. Found: C, 28.42; H, 2.76; N, 3.60.

[AuBr$_3$(7-Mes^{Br2})] (11). Complex **11** was prepared in analogy to compound **10** using bromine (~40 μL, 0.840 mmol) and [AuBr(7-Mes)] (**2**) (0.050 g, 0.082 mmol) and isolated as an orange solid (0.071 g, 93%). Single crystals of **11** were grown from evaporation of a concentrated solution in CD_2Cl_2: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.12 (s, 4 H, Ar−H), 4.10 (br, 4 H, CH_2), 2.65 (s, 6 H, CH_3), 2.56 (s, 6 H, CH_3), 2.42 (s, 6 H, CH_3), 2.37 (br, 4 H, CH_2); ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ 176.7 ($C_{7\text{-Mes}}^{Br2}$), 142.0, 140.8, 136.5, 136.5, 135.0, 135.0, 131.8, 131.7, 126.8, 126.7 (Ar−C), 59.3, 59.2 (CH_2), 24.5, 24.2 (CH_3), 24.2, 24.2 (CH_2), 21.5, 21.5 (CH_3); MS (ESI) *m/z* calcd for $C_{23}H_{28}Br_4N_2Au$ [M − Br]$^+$ 849, found 848. Anal. Calcd for $C_{23}H_{28}Br_5N_2Au$: C, 29.74; H, 3.04; N, 3.02. Found: C, 30.17; H, 3.05; N, 3.26.

[AuBr$_3$(8-Mes^{Br2})] (12). Complex **12** was prepared in analogy to compound **10** using bromine (~99 μL, 1.91 mmol) and [AuBr(8-Mes)] (**3**) (0.120 g, 0.191 mmol) and isolated as an orange solid (0.132 g, 73%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.12 (s, 4 H, Ar−H), 4.12 (br, 4 H, CH_2), 2.62 (s, 6 H, CH_3), 2.53 (s, 6 H, CH_3), 2.42 (s, 6 H, CH_3), 2.25 (br, 4 H, CH_2), 1.95 (br, 4 H, CH_2); ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ 175.1 ($C_{8\text{-Mes}}^{Br2}$), 142.8, 140.8, 136.6, 136.6, 135.1, 135.1, 132.0, 132.0, 127.0 (Ar−C), 60.2, 26.2 (CH_2), 25.1, 25.0 (CH_3), 24.6 (CH_2), 24.3, 22.3, 22.3 (CH_3); MS (ESI) *m/z* calcd for $C_{24}H_{30}Br_4N_2Au$ [M − Br]$^+$ 863, found 862. Anal. Calcd for $C_{24}H_{30}Br_5N_2Au$: C, 30.57; H, 3.21; N, 2.97. Found: C, 30.69; H, 3.19; N, 3.20.

[AuBr$_2$(^{i}Pr$_2$-bimy)(6-Mes)]BF$_4$ (13). Bromine (~13 μL, 0.248 mmol) was added dropwise to a stirred solution of [Au(^{i}Pr$_2$-bimy)(6-Mes)]BF$_4$ (**4**) (0.200 g, 0.248 mmol) in CH_2Cl_2 (~5 mL) at ambient temperature, and the reaction mixture was allowed to stir for 30 min. The volatiles were removed under vacuum, and the residue was washed with diethyl ether. Finally, the residue was dried under vacuum to give the product as a yellow solid (0.201 g, 95%). Single crystals of **13** were grown from evaporation of a concentrated solution in $CHCl_3$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 [dd, ^3J(H,H) = 6 Hz, 2 H, Ar−H], 7.35 [dd, ^3J(H,H) = 6 Hz, 2 H, Ar−H], 7.02 (s, 4 H, Ar−H), 3.85 [t, ^3J(H,H) = 5 Hz, 4 H, CH_2], 3.51 [sept, ^3J(H,H) = 7 Hz, 2 H, C*H*(CH_3)$_2$], 2.61 (br, 2 H, CH_2), 2.60 (s, 12 H, CH_3), 2.38 (s, 6 H, CH_3), 1.34 [d, ^3J(H,H) = 7 Hz, 12 H, CH(C*H*$_3$)$_2$]; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 178.3 ($C_{6\text{-Mes}}$), 155.6 (C_{probe}), 139.8, 139.6, 137.6, 133.5, 130.6, 125.3, 114.7 (Ar−C), 54.7 (CH_2), 50.1 [$CH(CH_3)_2$], 22.0 (CH_2), 21.0, 20.8, 20.6 (CH_3); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −154.09 (s, $^{10}BF_4$), −154.15 (s, $^{11}BF_4$); MS (ESI) *m/z* calcd for $C_{35}H_{46}Br_2N_4Au$ [M − Br$_3$]$^+$ 879, found 879. Anal. Calcd for $C_{35}H_{46}Br_2BF_4N_4Au\cdot CHCl_3$: C, 43.50; H, 4.80; N, 5.80. Found: C, 43.57; H, 4.79; N, 6.20.

[AuBr$_2$(^{i}Pr$_2$-bimy)(7-Mes)]BF$_4$ (14). Complex **14** was prepared in analogy to compound **13** using bromine (~3 μL, 0.062 mmol) and [Au(^{i}Pr$_2$-bimy)(7-Mes)]BF$_4$ (**5**) (0.053 g, 0.062 mmol) and isolated as a yellow solid (0.061 g, 99%). Single crystals of **14** were grown from evaporation of a concentrated solution in $CHCl_3$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 [dd, ^3J(H,H) = 8 Hz, 2 H, Ar−H], 7.33 [dd, ^3J(H,H) = 8 Hz, 2 H, Ar−H], 7.01 (s, 4 H, Ar−H), 4.19 (br, 4 H, CH_2), 3.47 [sept, ^3J(H,H) = 7 Hz, 2 H, C*H*(CH_3)$_2$], 2.60 (s, 12 H, CH_3), 2.45 (br, 4 H, CH_2), 2.37 (s, 6 H, CH_3), 1.33 [d, ^3J(H,H) = 7 Hz, 12 H, CH(C*H*$_3$)$_2$]; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 187.7 ($C_{7\text{-Mes}}$), 155.8 (C_{probe}), 141.4, 139.7, 137.3, 133.4, 130.8, 125.2, 114.8 (Ar−C), 57.7 (CH_2), 54.6 [$CH(CH_3)_2$], 25.1 (CH_2), 21.9, 21.4, 20.8 (CH_3); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −154.16 (s, $^{10}BF_4$), −154.21 (s, $^{11}BF_4$); MS (ESI) *m/z* calcd for $C_{36}H_{48}Br_2N_4Au$ [M − BF$_4$]$^+$ 893, found 893. Anal. Calcd for $C_{36}H_{48}Br_2BF_4N_4Au$: C, 44.10; H, 4.94; N, 5.71. Found: C, 43.32; H, 4.82; N, 5.92.

[AuBr$_2$(^{i}Pr$_2$-bimy)(8-Mes)]BF$_4$ (15). Complex **15** was prepared in analogy to compound **13** using bromine (~4 μL, 0.091 mmol) and [Au(^{i}Pr$_2$-bimy)(8-Mes)]BF$_4$ (**6**) (0.076 g, 0.091 mmol) and isolated as a yellow solid (0.089 g, 97%). Single crystals of **15** were grown from evaporation of a concentrated solution in $CHCl_3$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 [dd, ^3J(H,H) = 8 Hz, 2 H, Ar−H], 7.33 [dd, ^3J(H,H) = 8 Hz, 2 H, Ar−H], 7.02 (s, 4 H, Ar−H), 4.29 (br, 4 H, CH_2), 3.39 [sept, ^3J(H,H) = 7 Hz, 2 H, C*H*(CH_3)$_2$], 2.59 (s, 12 H, CH_3), 2.38 (s, 6 H, CH_3), 2.24 (br, 4 H, CH_2), 2.06 (br, 2 H, CH_2), 1.33 [d, ^3J(H,H) = 7 Hz, 12 H, CH(C*H*$_3$)$_2$]; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 184.1 ($C_{8\text{-Mes}}$), 154.8 (C_{probe}), 143.3, 139.5, 137.2, 133.4, 131.1, 125.2, 114.8 (Ar−C), 58.6 (CH_2), 54.4 [$CH(CH_3)_2$], 28.3, 23.4 (CH_2), 22.3, 21.9, 20.8 (CH_3); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −153.93 (s, $^{10}BF_4$), −153.99 (s, $^{11}BF_4$); MS (ESI) *m/z* calcd for $C_{37}H_{50}Br_2N_4Au$ [M − BF$_4$]$^+$ 907, found 907. Anal. Calcd for $C_{37}H_{50}Br_2BF_4N_4Au\cdot 0.5CHCl_3$: C, 42.73; H, 4.83; N, 5.32. Found: C, 43.11; H, 4.92; N, 5.56.

[AuBr$_2$(^{i}Pr$_2$-bimy)(6-Mes)]Br$_3$ (16). Bromine (~96 μL, 1.86 mmol) was added dropwise to a stirred solution of [Au(^{i}Pr$_2$-bimy)(6-Mes)]BF$_4$ (**4**) (0.150 g, 0.186 mmol) in CH_2Cl_2 (~5 mL) at ambient temperature, and the reaction mixture was allowed to stir for 2 h. The volatiles were removed under vacuum, and the residue was washed with diethyl ether followed by drying under vacuum to give the product as a yellow solid (0.178 g, 85%). Single crystals of **16** were grown from evaporation of a concentrated solution in $CHCl_3$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 [dd, ^3J(H,H) = 6 Hz, 2 H, Ar−H], 7.34 [dd, ^3J(H,H) = 6 Hz, 2 H, Ar−H], 7.02 (s, 4 H, Ar−H), 3.88 [t, ^3J(H,H) = 5 Hz, 4 H, CH_2], 3.51 [sept, ^3J(H,H) = 7 Hz, 2 H, C*H*(CH_3)$_2$], 2.62 (br, 2 H, CH_2), 2.55 (s, 12 H, CH_3), 1.33 [d, ^3J(H,H) = 7 Hz, 12 H, CH(C*H*$_3$)$_2$]; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 178.3 ($C_{6\text{-Mes}}$), 155.8 (C_{probe}), 139.9, 139.7, 137.6, 133.5, 130.6, 125.3, 114.8 (Ar−C), 54.7 (CH_2), 50.2 [$CH(CH_3)_2$], 22.0 (CH_2), 21.3, 21.1, 20.9 (CH_3); MS (ESI) *m/z* calcd for $C_{35}H_{46}Br_2N_4Au$ [M − Br$_3$]$^+$ 879, found 879. Anal. Calcd for $C_{35}H_{46}Br_5N_4Au\cdot CHCl_3$: C, 34.91; H, 3.82; N, 4.52. Found: C, 34.65; H, 3.77; N, 4.62.

[AuBr$_2$(^{i}Pr$_2$-bimy)(7-Mes)]Br$_3$ (17). Complex **17** was prepared in analogy to compound **16** using bromine (~44 μL, 0.851 mmol) and [Au(^{i}Pr$_2$-bimy)(7-Mes)]BF$_4$ (**5**) (0.070 g, 0.085 mmol) and isolated as a yellow solid (0.088 g, 92%). Single crystals of **17** were grown from evaporation of a concentrated solution in $CHCl_3$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 [dd, ^3J(H,H) = 6 Hz, 2 H, Ar−H], 7.34 [dd, ^3J(H,H) = 8 Hz, 2 H, Ar−H], 7.03 (s, 4 H, Ar−H), 4.24 (br, 4 H, CH_2), 3.48 [sept, ^3J(H,H) = 7 Hz, 2 H, C*H*(CH_3)$_2$], 2.62 (s, 12 H, CH_3), 2.49 (br, 4 H, CH_2), 2.38 (s, 6 H, CH_3), 1.34 [d, ^3J(H,H) = 7 Hz, 12 H, CH(C*H*$_3$)$_2$]; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 185.8 ($C_{7\text{-Mes}}$), 155.8 (C_{probe}), 141.4, 139.8, 137.3, 133.5, 130.9, 125.3, 114.8 (Ar−C), 58.0 (CH_2), 54.6 [$CH(CH_3)_2$], 25.2 (CH_2), 22.0, 21.7, 20.8 (CH_3); MS (ESI) *m/z* calcd for $C_{36}H_{48}Br_2N_4Au$ [M − Br$_3$]$^+$ 893, found 893. Anal. Calcd for $C_{36}H_{48}Br_5N_4Au$: C, 38.15; H, 4.27; N, 4.94. Found: C, 38.03; H, 4.20; N, 5.03.

[AuBr$_2$(^{i}Pr$_2$-bimy)(8-Mes)]Br$_3$ (18). Complex **18** was prepared in analogy to compound **16** using bromine (~123 μL, 2.39 mmol) and [Au(^{i}Pr$_2$-bimy)(8-Mes)]BF$_4$ (**6**) (0.200 g, 0.239 mmol) and isolated as a yellow solid (0.265 g, 93%). Single crystals of **17** were grown from evaporation of a concentrated solution in $CHCl_3$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 [dd, ^3J(H,H) = 6 Hz, 2 H, Ar−H], 7.33 [dd, ^3J(H,H) = 6 Hz, 2 H, Ar−H], 7.03 (s, 4 H, Ar−H), 4.36 (br, 4 H, CH_2), 3.41 [sept, ^3J(H,H) = 7 Hz, 2 H, C*H*(CH_3)$_2$], 2.61 (s, 12 H, CH_3), 2.39 (s, 6 H, CH_3), 2.27 (br, 4 H, CH_2), 2.10 (br, 2 H, CH_2), 1.34 [d, ^3J(H,H) = 7 Hz, 12 H, CH(C*H*$_3$)$_2$]; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 184.0 ($C_{8\text{-Mes}}$), 155.1 (C_{probe}), 143.4, 137.3, 133.5, 131.2, 125.2, 114.8 (Ar−C), 59.0 (CH_2), 54.3 [$CH(CH_3)_2$], 28.4, 23.5 (CH_2), 22.6, 22.0, 20.9 (CH_3); MS (ESI) *m/z* calcd for $C_{37}H_{50}Br_2N_4Au$ [M − Br$_3$]$^+$ 907, found 907. Anal. Calcd for $C_{37}H_{50}Br_5N_4Au$: C, 38.73; H, 4.39; N, 4.88. Found: C, 38.50; H, 4.26; N, 5.25.

General Procedure for the Optimization of Hydroamination Reactions and Catalyst Screening. A mixture of phenylacetylene

(0.3 mmol, 1.5 equiv), mesitylamine (0.2 mmol, 1 equiv), Ag, K, or Na salt (0.004 mmol, 2 mol %), and the respective Au NHC complex (0.004 mmol, 2 mol %) was heated in acetonitrile (~1 mL) in a screw cap tube under air. The reaction temperatures and times are summarized in Table 1 and Table S1. The reaction mixture was cooled to ambient temperature, and an aliquot was diluted with ethyl acetate and analyzed by GC/GC-MS.

General Procedure for the Substrate Scope Study. A mixture of alkyne (0.75 mmol, 1.5 equiv), amine (0.5 mmol, 1 equiv), $AgSbF_6$ (0.010 mmol, 2 mol %), and [AuBr(8-Mes)] (**3**) (0.010 mmol, 2 mol %) was heated in acetonitrile (~1 mL) at 90 °C in a screw cap tube under air for 14 h. The volatiles were removed under vacuum to give the crude product. Conversion to products was determined by GC/GC-MS, and isolated yields were obtained by column chromatography using a mixture of petroleum ether and EtOAc as the eluent.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00718.

> Characterization data for catalysis products, optimization of catalytic conditions, molecular structures of **13**–**15**, selected crystallographic data, NMR spectra, and ESI mass spectra (PDF)

Accession Codes

CCDC 1951134–1951139, 1951141–1951143, 1951847, and 1952089 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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■ REFERENCES

(1) Huynh, H. V. *The Organometallic Chemistry of N-heterocyclic Carbenes*; John Wiley & Sons, Ltd.: Chichester, U.K., 2017.

(2) Danopoulos, A. A.; Simler, T.; Braunstein, P. N-Heterocyclic Carbene Complexes of Copper, Nickel, and Cobalt. *Chem. Rev.* **2019**, *119*, 3730–3961.

(3) Gan, M. M.; Liu, J. Q.; Zhang, L.; Wang, Y. Y.; Hahn, F. E.; Han, Y. F. Preparation and Post-Assembly Modification of Metallosupramolecular Assemblies from Poly (N-Heterocyclic Carbene) Ligands. *Chem. Rev.* **2018**, *118*, 9587–9641.

(4) Nesterov, V.; Reiter, D.; Bag, P.; Frisch, P.; Holzner, R.; Porzelt, A.; Inoue, S. NHCs in Main Group Chemistry. *Chem. Rev.* **2018**, *118*, 9678–9842.

(5) Vivancos, A.; Segarra, C.; Albrecht, M. Mesoionic and Related Less Heteroatom-Stabilized N-Heterocyclic Carbene Complexes: Synthesis, Catalysis, and Other Applications. *Chem. Rev.* **2018**, *118*, 9493–9586.

(6) Sebest, F.; Dunsford, J. J.; Adams, M.; Pivot, J.; Newman, P. D.; Diez-Gonzalez, S. Ring-Expanded N-Heterocyclic Carbenes for Copper-Mediated Azide-Alkyne Click Cycloaddition Reactions. *ChemCatChem* **2018**, *10*, 2041–2045.

(7) Hall, J. W.; Unson, D. M. L.; Brunel, P.; Collins, L. R.; Cybulski, M. K.; Mahon, M. F.; Whittlesey, M. K. Copper-NHC-Mediated Semihydrogenation and Hydroboration of Alkynes: Enhanced Catalytic Activity Using Ring-Expanded Carbenes. *Organometallics* **2018**, *37*, 3102–3110.

(8) Morozov, O. S.; Gribanov, P. S.; Asachenko, A. F.; Dorovatovskii, P. V.; Khrustalev, V. N.; Rybakov, V. B.; Nechaev, M. S. Hydrohydrazination of Arylalkynes Catalyzed by an Expanded Ring N-Heterocyclic Carbene (er-NHC) Gold Complex Under Solvent-Free Conditions. *Adv. Synth. Catal.* **2016**, *358*, 1463–1468.

(9) Yang, B. M.; Xiang, K.; Tu, Y. Q.; Zhang, S. H.; Yang, D. T.; Wang, S. H.; Zhang, F. M. Spiro-fused six-membered N-heterocyclic carbene: a new scaffold toward unique properties and activities. *Chem. Commun.* **2014**, *50*, 7163–5.

(10) Kumar, A.; Katari, M.; Ghosh, P. Understanding the lability of a trans bound pyridine ligand in a saturated six-membered N-heterocyclic carbene based (NHC)$PdCl_2$(pyridine) type complex: A case study. *Polyhedron* **2013**, *52*, 524–529.

(11) Teng, Q.; Wu, W.; Duong, H. A.; Huynh, H. V. Ring-expanded N-heterocyclic carbenes as ligands in iron-catalysed cross-coupling reactions of arylmagnesium reagents and aryl chlorides. *Chem. Commun.* **2018**, *54*, 6044–6047.

(12) Huynh, H. V. Electronic Properties of N-Heterocyclic Carbenes and Their Experimental Determination. *Chem. Rev.* **2018**, *118*, 9457–9492.

(13) Davies, C. J.; Page, M. J.; Ellul, C. E.; Mahon, M. F.; Whittlesey, M. K. Ni(I) and Ni(II) ring-expanded N-heterocyclic carbene complexes: C-H activation, indole elimination and catalytic hydrodehalogenation. *Chem. Commun.* **2010**, *46*, 5151–3.

(14) Hauwert, P.; Dunsford, J. J.; Tromp, D. S.; Weigand, J. J.; Lutz, M.; Cavell, K. J.; Elsevier, C. J. Zerovalent [Pd(NHC)(Alkene)1,2] Complexes Bearing Expanded-Ring N-Heterocyclic Carbene Ligands in Transfer Hydrogenation of Alkynes. *Organometallics* **2013**, *32*, 131–140.

(15) Morozov, O. S.; Lunchev, A. V.; Bush, A. A.; Tukov, A. A.; Asachenko, A. F.; Khrustalev, V. N.; Zalesskiy, S. S.; Ananikov, V. P.; Nechaev, M. S. Expanded-ring N-heterocyclic carbenes efficiently stabilize gold(I) cations, leading to high activity in pi-acid-catalyzed cyclizations. *Chem. - Eur. J.* **2014**, *20*, 6162–70.

(16) Iglesias, M.; Beetstra, D. J.; Stasch, A.; Horton, P. N.; Hursthouse, M. B.; Coles, S. J.; Cavell, K. J.; Dervisi, A.; Fallis, I. A. First Examples of Diazepanylidene Carbenes and Their Late-Transition-Metal Complexes. *Organometallics* **2007**, *26*, 4800–4809.

(17) Kumar, A.; Yuan, D.; Huynh, H. V. Stereoelectronic Profiling of Expanded-Ring N-Heterocyclic Carbenes. *Inorg. Chem.* **2019**, *58*, 7545–7553.

(18) Cervantes-Reyes, A.; Rominger, F.; Rudolph, M.; Hashmi, A. S. K. Gold(I) Complexes Stabilized by Nine- and Ten-Membered N-Heterocyclic Carbene Ligands. *Chem. - Eur. J.* **2019**, *25*, 11745–11757.

(19) Dunsford, J. J.; Cavell, K. J.; Kariuki, B. M. Gold(I) Complexes Bearing Sterically Imposing, Saturated Six- and Seven-Membered Expanded Ring N-Heterocyclic Carbene Ligands. *Organometallics* **2012**, *31*, 4118–4121.

(20) Sampford, K. R.; Carden, J. L.; Kidner, E. B.; Berry, A.; Cavell, K. J.; Murphy, D. M.; Kariuki, B. M.; Newman, P. D. Twisting the arm: structural constraints in bicyclic expanded-ring N-heterocyclic carbenes. *Dalton trans.* **2019**, *48*, 1850–1858.

(21) Huynh, H. V.; Guo, S.; Wu, W. Detailed Structural, Spectroscopic, and Electrochemical Trends of Halido Mono- and

Bis(NHC) Complexes of Au(I) and Au(III). *Organometallics* **2013**, *32*, 4591−4600.

(22) Guo, S.; Bernhammer, J. C.; Huynh, H. V. 1,2,4-Triazole-derived carbene complexes of gold: characterization, solid-state aggregation and ligand disproportionation. *Dalton trans.* **2015**, *44*, 15157−15165.

(23) Sivaram, H.; Jothibasu, R.; Huynh, H. V. Gold Complexes of an Alicyclic Indazole-Derived N-Heterocyclic Carbene: Syntheses, Characterizations, and Ligand Disproportionation. *Organometallics* **2012**, *31*, 1195−1203.

(24) Huynh, H. V.; Wu, J. Rotamers of palladium complexes bearing IR active N-heterocyclic carbene ligands: Synthesis, structural characterization and catalytic activities. *J. Organomet. Chem.* **2009**, *694*, 323−331.

(25) Teng, Q.; Huynh, H. V. A unified ligand electronic parameter based on ^{13}C NMR spectroscopy of N-heterocyclic carbene complexes. *Dalton trans.* **2017**, *46*, 614−627.

(26) Dash, C.; Shaikh, M. M.; Butcher, R. J.; Ghosh, P. Highly convenient regioselective intermolecular hydroamination of alkynes yielding ketimines catalyzed by gold(I) complexes of 1,2,4-triazole based N-heterocyclic carbenes. *Inorg. Chem.* **2010**, *49*, 4972−4983.

(27) Katari, M.; Rao, M. N.; Rajaraman, G.; Ghosh, P. Computational Insight into a Gold(I) N-Heterocyclic Carbene Mediated Alkyne Hydroamination Reaction. *Inorg. Chem.* **2012**, *51*, 5593−5604.

(28) Michon, C.; Gilbert, J.; Trivelli, X.; Nahra, F.; Cazin, C. S. J.; Agbossou-Niedercorn, F.; Nolan, S. P. Gold(i) catalysed regio- and stereoselective intermolecular hydroamination of internal alkynes: towards functionalised azoles. *Org. Biomol. Chem.* **2019**, *17*, 3805−3811.

(29) Cacchi, S.; Fabrizi, G.; Fochetti, A.; Ghirga, F.; Goggiamani, A.; Iazzetti, A. Stereo- and regioselective gold(i)-catalyzed hydroamination of 2-(arylethynyl)pyridines with anilines. *Org. Biomol. Chem.* **2019**, *17*, 527−532.

(30) Baron, M.; Battistel, E.; Tubaro, C.; Biffis, A.; Armelao, L.; Rancan, M.; Graiff, C. Single-Step Synthesis of Dinuclear Neutral Gold(I) Complexes with Bridging Di(N-heterocyclic carbene) Ligands and Their Catalytic Performance in Cross Coupling Reactions and Alkyne Hydroamination. *Organometallics* **2018**, *37*, 4213−4223.

(31) Nair, A. G.; McBurney, R. T.; Gatus, M. R. D.; Binding, S. C.; Messerle, B. A. Gold(III) NHC Complexes for Catalyzing Dihydroalkoxylation and Hydroamination Reactions. *Inorg. Chem.* **2017**, *56*, 12067−12075.

(32) Hashmi, A. S. K. Gold-Catalyzed Organic Reactions. *Chem. Rev.* **2007**, *107*, 3180−3211.

(33) Mizushima, E.; Hayashi, T.; Tanaka, M. Au(I)-Catalyzed Highly Efficient Intermolecular Hydroamination of Alkynes. *Org. Lett.* **2003**, *5*, 3349−3352.

(34) Ibanez, S.; Poyatos, M.; Peris, E. A D3h-symmetry hexaazatriphenylene-tris-N-heterocyclic carbene ligand and its coordination to iridium and gold: preliminary catalytic studies. *Chem. Commun.* **2017**, *53*, 3733−3736.

(35) Ibáñez, S.; Poyatos, M.; Dawe, L. N.; Gusev, D.; Peris, E. Ferrocenyl-Imidazolylidene Ligand for Redox-Switchable Gold-Based Catalysis. A Detailed Study on the Redox-Switching Abilities of the Ligand. *Organometallics* **2016**, *35*, 2747−2758.

(36) Ibáñez, S.; Poyatos, M.; Peris, E. Gold Catalysts with Polyaromatic-NHC ligands. Enhancement of Activity by Addition of Pyrene. *Organometallics* **2017**, *36*, 1447−1451.

(37) Guo, S.; Sivaram, H.; Yuan, D.; Huynh, H. V. Gold and Palladium Hetero-Bis-NHC Complexes: Characterizations, Correlations, and Ligand Redistributions. *Organometallics* **2013**, *32*, 3685−3696.

(38) Dunsford, J. J.; Cavell, K. J. Expanded ring N-heterocyclic carbenes: a comparative study of ring size in palladium (0) catalysed Mizoroki-Heck coupling. *Dalton trans* **2011**, *40*, 9131−5.

(39) Lu, W. Y.; Cavell, K. J.; Wixey, J. S.; Kariuki, B. First Examples of Structurally Imposing Eight-Membered-Ring (Diazocanylidene) N-Heterocyclic Carbenes: Salts, Free Carbenes, and Metal Complexes. *Organometallics* **2011**, *30*, 5649−5655.

(40) *APEX suite of crystallographic software, APEX 2*, version 2008.4; Bruker AXS Inc.: Madison, WI, 2008.

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