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Article

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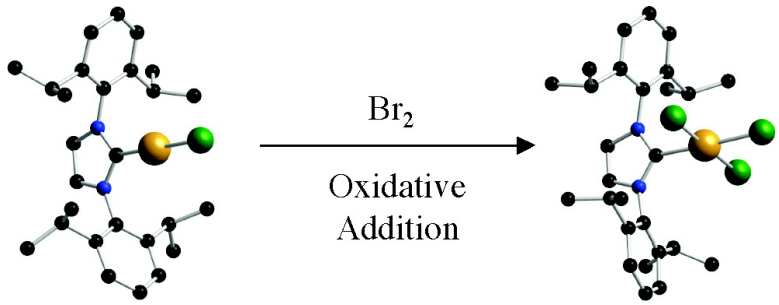


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# Synthesis, Characterization and Reactivity of *N*-Heterocyclic Carbene Gold(III) Complexes

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A series of (NHC)Au$^{I}$Cl (**1**, NHC = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr); **2**, NHC = *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes); **3**, NHC = *N*,*N*′-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene (SIPr); **4**, NHC = *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (SIMes); **5**, NHC = *N*,*N*′-dicyclohexylimidazol-2-ylidene (ICy); **6**, NHC = *N*,*N*′-diadamantylimidazol-2-ylidene (IAd); **7**, NHC = *N*,*N*′-di-*tert*-butylimidazol-2-ylidene (I$^{t}$Bu)) complexes were reacted with LiBr to generate [(IPr)AuBr] (**8**), [(IMes)AuBr] (**9**), [(SIPr)AuBr] (**10**), [(SIMes)AuBr] (**11**), [(ICy)AuBr] (**12**), [(IAd)-AuBr] (**13**), and [(I$^{t}$Bu)AuBr] (**14**). These (NHC)Au$^{I}$Br complexes undergo oxidative addition of elemental bromine, leading to the new Au(III) complexes [(IPr)AuBr$_3$] (**15**), [(IMes)AuBr$_3$] (**16**), [(SIPr)AuBr$_3$] (**17**), [(SIMes)AuBr$_3$] (**18**), [(ICy)AuBr$_3$] (**19**), [(IAd)AuBr$_3$] (**20**), and [(I$^{t}$Bu)AuBr$_3$] (**21**). Complete characterization by NMR spectroscopy and single-crystal X-ray diffraction were performed in order to discern structural differences between organogold(I/III) congeners. A preliminary study examining the activity of (NHC)Au$^{III}$ species on the addition of water to alkynes is also presented.

## Introduction

Although, historically, organogold complexes have been underutilized in organic synthesis, numerous publications have recently emphasized the beneficial role of gold(I) in catalysis.[1] Organic transformations such as skeletal rearrangements (cycloisomerizations),[2] carbene transfer reactions,[3] indanization,[4] oxidations,[5] and hydrosilylations[6] are examples of the diverse chemistry mediated by organogold catalysts. Such transformations have been achieved with low catalyst loading and high turnover numbers. The gold(I) center must have two coordination sites occupied to ensure stability of the complexes and thereby avoid reduction to gold(0).[7] The most commonly employed ligands so far have been phosphines ($PR_3$)[8] and, most recently, N-heterocyclic carbenes (NHC).[9] Both ligand families exhibit strong $\sigma$-donation, and coordination of such ligands results in good stability of the Au(I) complexes toward air, moisture, and thermolysis. It is interesting to note that gold has

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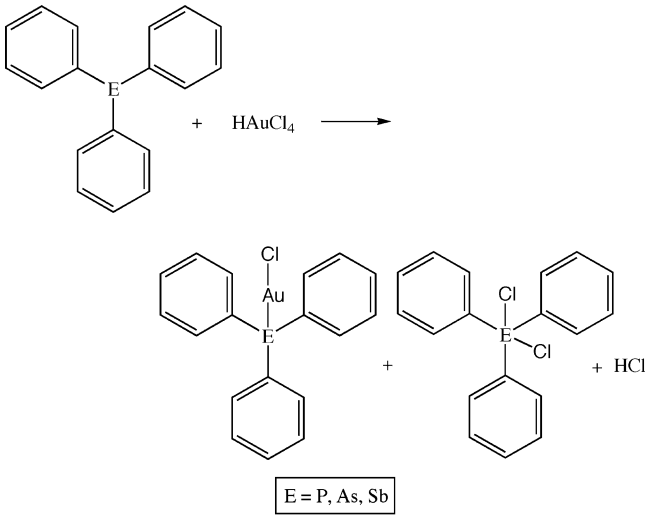
even a stronger affinity for *N*-heterocyclic carbene than for phosphine and other Fisher acyclic carbenes.[10] A broad range of catalyzed transformations by inorganic gold(III) salts has been reported in the literature; examples include hydroaminations,[11] [4 + 2] benzannulations,[12] functionalization of aromatic C−H bonds,[13] cycloisomerizations,[14] and addition reactions to heterocycles.[15] Most often $AuX_3$ (X = Cl, Br) salts are used directly[11−16] and only a limited number of examples of well-defined organogold(III) complexes acting as catalysts are known.[17] No catalysis mediated by $(PR_3)$- or $(NHC)Au^{III}$ complexes has been reported so far. This is quite surprising, since the chemistry of the arsine,[18] stilbine,[19] phosphine,[18b,c,20] and carbene[21] gold(III) complexes was first examined in the mid-1970s. Since these initial studies only a limited number of publications have focused on this chemistry. Notable exceptions are the extensive studies performed on gold(III) phosphine complexes by Schmidbaur *et al*.[22] Since then, *C*-tetrazolato,[23] bis(thiazolinylidene), and bis(NHC) gold(III) complexes bearing carbene moieties have been reported.[24] Nevertheless, no example of a mono(NHC) gold(III) complex has been reported, (4-methylthiazol-2-ylidene)$AuCl_3$ being the closest related complex reported so far.[24a] In order to expand the range of Au(III) complexes known and hopefully to provide access to novel Au(III) architectures, we reasoned that our prior expertise in NHC and Au(I) chemistry could be put to use in the synthesis of novel Au(III) complexes bearing the electron-rich NHC ligands.

**Scheme 1. Formation of Gold(I) Complexes by Reduction of $HAuCl_4$**




## Results and Discussion

To eventually develop a general synthetic route leading to a family of (NHC)$AuX_3$ (X = halide) complexes, we initially examined possible approaches to a single target compound: (IPr)$AuX_3$. Previously, chlorine gas had been used to convert (thiazolinylidene)AuCl to (thiazolinylidene)$AuCl_3$.[24] Because of the very aggressive nature of chlorine gas, liquid bromine was selected as a halogenation agent, as it does not require special safety equipment and allows for a fairly straightforward and general synthetic protocol.

We first attempted to generate a NHC−Au(III) complex from a gold(III) salt, by direct reaction of the free carbene IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with $AuCl_4^-$. The reaction led to the formation of yellow metallic gold(0). Study of the reaction mixture by $^1$H NMR spectroscopy showed extensive signs of decomposition of the carbene and formation of (IPr)AuCl, in a low yield (20%). This result is not surprising, as the gold(III) cation possesses a very strong oxidant character.[25] Indeed, reduction of tetrachloroauric acid ($HAuCl_4$) with a 2-fold excess of stibine, arsine, or phosphine ligands is known to generate the corresponding gold(I) complexes in good yield[25] (Scheme 1).

Oxidative addition of bromine by (IPr)AuCl (**1**) gave an orange powder in high yield. $^1$H NMR analysis provided a spectrum with the same pattern as that found for (IPr)AuCl, but with significant changes in the chemical shifts for all protons. We also noticed that the septuplet assigned to the protons from the diisopropyl group was split into two distinct multiplets at 2.99 and 2.96 ppm. We attribute this small splitting to the existence of two different complexes: (IPr)$AuBr_3$ and (IPr)$AuBr_2$-Cl. $^{13}$C NMR spectra also support this hypothesis, as two complexes with similar carbon skeletons and very similar signals are observed.

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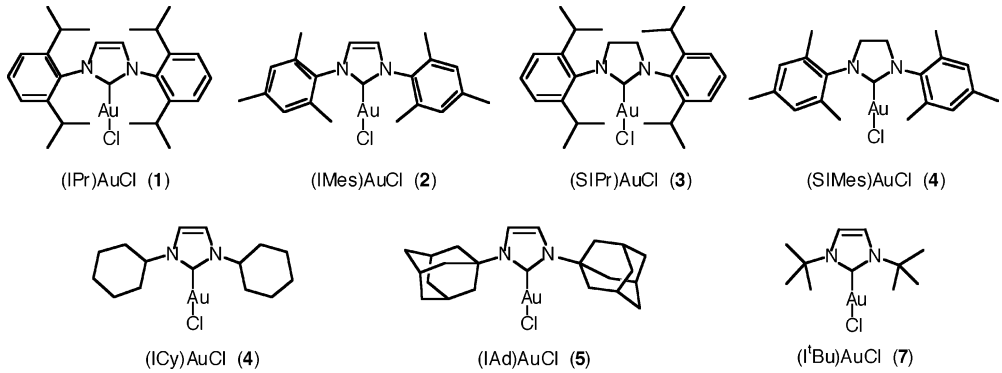


**Figure 1.** (NHC)Au$^I$Cl complexes used as starting materials in this study.

To exclude the formation of a mixture of (IPr)AuBr$_{3-x}$Cl$_x$, we proceeded to convert the reported[7a,26] (NHC)Au$^I$ chloride complexes (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)-gold(I) chloride (**1**; (IPr)AuCl[26]), (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)gold(I) chloride (**2**; (IMes)AuCl[26]), (1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene)gold(I) chloride (**3**; (SIPr)AuCl[26]), (1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene)gold(I) chloride (**4**; (SIMes)AuCl[26]), (1,3-bis(cyclohexyl)imidazol-2-ylidene)gold(I) chloride (**5**; (ICy)AuCl[26]), (1,3-bis(adamantyl)imidazol-2-ylidene)gold(I) chloride (**6**; (IAd)-AuCl[26]), and (1,3-bis(*tert*-butyl)imidazol-2-ylidene)gold(I) chloride (**7**; (I$^t$Bu)AuCl[7a]) (Figure 1) into their (NHC)Au$^I$ bromide relatives **8**−**14** by use of a metathetical reaction with LiBr. As the gold(I) cation is one of the softest available acids, we suspected that the bromide anion would easily replace the chloride anion.

The complexes (NHC)AuCl (**1**−**7**) were stirred with a large excess of lithium bromide, at room temperature, with acetone or THF as solvent. The reactions are not sensitive to air and provide the desired bromide complexes (IPr)AuBr (**8**), (IMes)-AuBr (**9**), (SIPr)AuBr (**10**), (SIMes)AuBr (**11**), (ICy)AuBr (**12**), (IAd)AuBr (**13**), and (I$^t$Bu)AuBr (**14**) as white powders (eq 1). The protocol furnishes the products in good yields after stirring for 24 h.

$$\text{(NHC)AuCl} + \text{LiBr} \xrightarrow{\text{acetone}} \text{(NHC)AuBr} + \text{LiCl} \qquad (1)$$

It is interesting to note that while these complexes are air-stable, the presence of water leads to rapid decomposition with appearance of purple colloidal gold(0) and formation of imidazolium salts. This trend is strongly accentuated for complexes bearing saturated carbene moieties (**10** and **11**). While Baker *et al.*[7a] reported a reaction time of 16 h to convert (I$^t$Bu)AuCl (**7**) into (I$^t$Bu)AuBr (**14**), we selected the longer reaction time of 24 h as a general reaction time, as we noticed that the metathesis reaction could require longer time to reach completion as a function of the NHC. This reaction time is then general and has not been optimized for each NHC employed. The $^1$H NMR spectra of complexes **8**, **9**, and **12**−**14** display a low-field singlet between 6.95 and 7.17 ppm, assigned to the two protons located on the unsaturated imidazole backbone. Spectra of complexes **10** and **11** display a more upfield singlet at 4.04 and 3.97 ppm, respectively, assigned to the four protons located on the saturated imidazole backbone. For all complexes, all signals expected for the *N*-aryl and *N*-alkyl chains are present. As expected, no significant change in the chemical shift (less than 0.1 ppm) is visible for the signals attributed to congeners of the (NHC)AuCl and (NHC)AuBr series. The substitution of a chloride by a bromide has a very small effect on the environment seen by the protons of the different complexes. $^{13}$C NMR spectra display resonances for the different carbenic carbons between 166.3 and 175.1 ppm for the unsaturated imidazole moieties and around 195 ppm for the saturated imidazole moieties (Table 1). The intensity of this resonance is weak, since the carbenic carbon is a quaternary center and is affected by the quadrupolar moment of the gold atom ($I = {}^3/_2$).

**Table 1. Chemical Shifts of the Carbenic Carbon in NMR for the Gold(I) Halide Complexes**

| (NHC)AuCl | $\delta_C$ (ppm) | (NHC)AuBr | $\delta_C$ (ppm) | $\Delta\delta_C$ (ppm) |
|---|---|---|---|---|
| (IPr)AuCl$^a$ (**1**) | 175.1 | (IPr)AuBr$^b$ (**8**) | 179.0 | +3.9 |
| (IMes)AuCl$^b$ (**2**) | 173.4 | (IMes)AuBr$^b$ (**9**) | 176.7 | +3.3 |
| (SIPr)AuCl$^b$ (**3**) | 196.1 | (SIPr)AuBr$^b$ (**10**) | 199.0 | +2.9 |
| (SIMes)AuCl$^b$ (**4**) | 195.0 | (SIMes)AuBr$^b$ (**11**) | 198.1 | +3.1 |
| (ICy)AuCl$^a$ (**5**) | 168.0 | (ICy)AuBr$^b$ (**12**) | 172.1 | +4.1 |
| (IAd)AuCl$^a$ (**6**) | 166.3 | (IAd)AuBr$^b$ (**13**) | 170.2 | +3.9 |
| (I$^t$Bu)AuCl$^a$ (**7**) | 168.2 | (I$^t$Bu)AuBr$^b$ (**14**) | 172.4 | +4.2 |

$^a$ NMR recorded in $CD_2Cl_2$. $^b$ NMR recorded in $CDCl_3$.

Herrmann *et al.*[27] have postulated that the chemical shift of the carbenic carbon can be correlated to the acidity of the metal to which the NHC is bound. Indeed, a free NHC ligand, with no electronic donation toward a Lewis acid, would have a very low-field signal, usually above 200 ppm, reflecting the availability of an excess of electron density on the carbene carbon. In contrast, a bond with a metal will displace the chemical shift to a higher field value when the electronic density from the carbene is partially transferred to the metal by $\sigma$ donation. By comparison of the chemical shifts of the carbenic carbon, between the chloride and the bromide series of the gold(I) complexes, a consistent shift of 3−4 ppm to lower field due to the halide exchange was observed that we attribute to a small variation of the acidity of the gold center. We reasoned that the metal acidity is less, due to the lower electronegativity of bromine versus that of chlorine. This result is in good agreement with the study published by Baker *et al.*[7a] Crystals of (IPr)-AuBr (**8**) were grown by slow diffusion in a mixture of DCM and hexane and allowed us to perform a single-crystal X-ray diffraction study (Figure 2).

The gold atom is two-coordinate, as is usual for gold(I) complexes, and exhibits a linear geometry with a C(1)−Au−Br bond angle value of 180.0°. The C(1)−Au bond length (1.975 Å) is in good agreement with those for reported NHC−gold(I) complexes.[7a,26,28] The Au−Br bond length (2.381 Å) is in the

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(27) Herrmann, W. A.; Runte, O.; Artus, G. *J. Organomet. Chem.* **1995**, *501*, C1−C4.

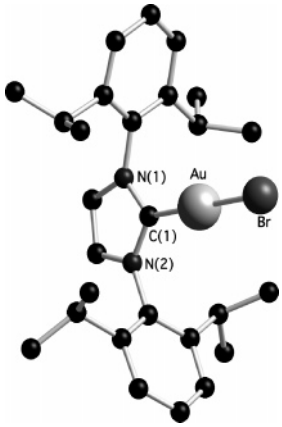


**Figure 2.** Ball-and-stick representation of (IPr)AuBr. Hydrogen atoms have been omitted for clarity.

range of those for known bromide gold(I) salts and complexes.[7a,29] The minimal Au···Au distance is 8.431 Å, excluding any aurophilic interactions, which require a distance shorter than 3.60 Å between gold(I) cations.[30] There is no major structural difference between (IPr)AuCl (**1**) and (IPr)AuBr (**8**). Crystals of other (NHC)AuBr complexes, described in this paper, can be grown in a mixture of DCM and heptane.

Direct addition of a slight excess of elemental bromine ($Br_2$) to solutions of the complexes (IPr)AuBr (**8**), (IMes)AuBr (**9**), (SIPr)AuBr (**10**), (SIMes)AuBr (**11**), (ICy)AuBr (**12**), (IAd)AuBr (**13**), and (I$^t$Bu)AuBr (**14**) gives the desired complexes (IPr)$AuBr_3$ (**15**), (IMes)$AuBr_3$ (**16**), (SIPr)$AuBr_3$ (**17**), (SIMes)$AuBr_3$ (**18**), (ICy)$AuBr_3$ (**19**), (IAd)$AuBr_3$ (**20**), and (I$^t$Bu)$AuBr_3$ (**21**) in good yields, as yellow or orange powders stable in air (eq 2).

$$\text{(NHC)AuBr} + \text{Br}_2 \xrightarrow[\text{oxidative addition}]{\text{CH}_2\text{Cl}_2} \text{(NHC)AuBr}_3 \qquad (2)$$

Initially, the reactions were allowed to proceed overnight, but we noticed that the reactions were very fast at room temperature (even at −78 °C) and were complete in less than $^1/_2$ h. This is not surprising, since redox reactions involving metals are known to proceed with rapid kinetics. We did not observe any NHC−Au bond cleavage or rearrangement by using bulky carbenes, such as IAd and I$^t$Bu, as reported for the oxidation of sterically demanding gold(I) phosphines.[22b] Attempts to synthesize (IMes)$AuBr_3$ (**16**) and (SIMes)$AuBr_3$ (**18**) at room temperature failed and gave decomposition products with no trace of the desired complexes, even when a substoichiometric amount of bromine was used. At −78 °C, the reaction proceeded smoothly without any trace of decomposition product. These particular synthetic conditions for the complexes bearing the IMes and SIMes moieties again illustrate the difference in reactivity encountered with these two carbenes on the chemistry of metals from group 11[31] (Scheme 2).

The $^1$H NMR spectra of the complexes **15**, **16**, and **19**−**21** display a low-field singlet between 7.21 and 7.53 ppm, assigned to the two protons located on the unsaturated imidazole backbone. The chemical shifts are slightly shifted downfield, in comparison to the shifts for the (NHC)AuBr series, likely due to the double bond being less rich in electron density. It is reasonable to assume that gold(III), being more acidic than gold(I), induces a greater delocalization of the electronic density from the carbon−carbon double bond to the carbenic carbene, through the entire aromatic system. There is no sign of attack by the bromine on the double bond. $^1$H NMR spectra of **17** and **18** display more upfield singlets at 4.29 and 4.23 ppm, respectively, assigned to the four protons located on the saturated imidazole backbone. For all complexes, signals expected for the N-aryl and N-alkyl chains are present. $^{13}$C NMR resonances of the different carbenic carbons are characterized by a weak upfield signal between 132.9 and 146.2 ppm for the unsaturated imidazole moieties and around 173 ppm for the saturated imidazole moieties (Table 2).

Differences in the carbenic carbon shifts between the two series of gold bromide complexes are found to be between 24.9 and 38.3 ppm. However, the shifts are within the range for the oxidation of gold(I) thiazolinylidene chloride reported by Raubenheimer *et al.*[24] Expectedly, the differences indicate an increase of acidity of the gold atom associated with an increase in oxidation state (Table 2). It is reasonable to assume that a smaller upfield shift indicates an attenuated acidity of the gold atom, likely due to a better donation of the carbene moieties. If this is correct, the saturated SIPr and SIMes carbenes provide the greatest electronic density to the gold(III) cation. A comparison between unsaturated carbenes bearing aromatic and alkyl R groups is also possible. Interestingly, IPr and IMes appear to be better $\sigma$ donors than IAd, ICy, and I$^t$Bu. All NHC ligands display the same donor property trends as seen for the gold(I) complexes.[26] It is also interesting to note that the chemical shifts of the carbenic carbon in these gold(III) complexes, especially the complexes bearing the alkyl R group, are extremely close to the reported value for the imidazolium salts, with a difference of 0.9−2.3 ppm. Unfortunately, we cannot unequivocally quantify in an absolute sense the electronic effect associated with electronic density residing on the carbenic carbene, as the $-Au^{III}Br_3$ moiety is not isolobal with the acidic proton borne by imidazolium salts.[7a]

To unambiguously characterize all these new gold(III) complexes, X-ray-quality crystals were grown in a mixture of DCM and heptane. Ball-and-stick representations are provided in Figures 3−5, and crystallographic data are given in Table 5.

All (NHC)$AuBr_3$ complexes have a four-coordinate gold atom, in a square-planar environment, as expected for $d^8$ metals. The C(1)−Au−Br(2) and Br(1)−Au−Br(3) bonds are nearly linear, with angles between 173.73 and 178.66° (Table 3).

All C(1)−Au distances lie in the range of 2.01−2.05 Å, regardless of whether the gold center bears a saturated or unsaturated imidazole motif (Table 4). These metrical parameters are in close agreement with those of reported organogold(III) complexes[32] possessing carbon−gold bond lengths between 2.01 and 2.07 Å. There is no discernible correlation between the gold−carbon bond length and the electronic or steric parameters associated with the NHCs employed.

All Br−Au distances were found to be between 2.38 and 2.47 Å (Table 4). They are similar to those of reported Br−Au$^{III}$

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**Scheme 2. Reactivity of Complexes Bearing Different NHC Moieties**

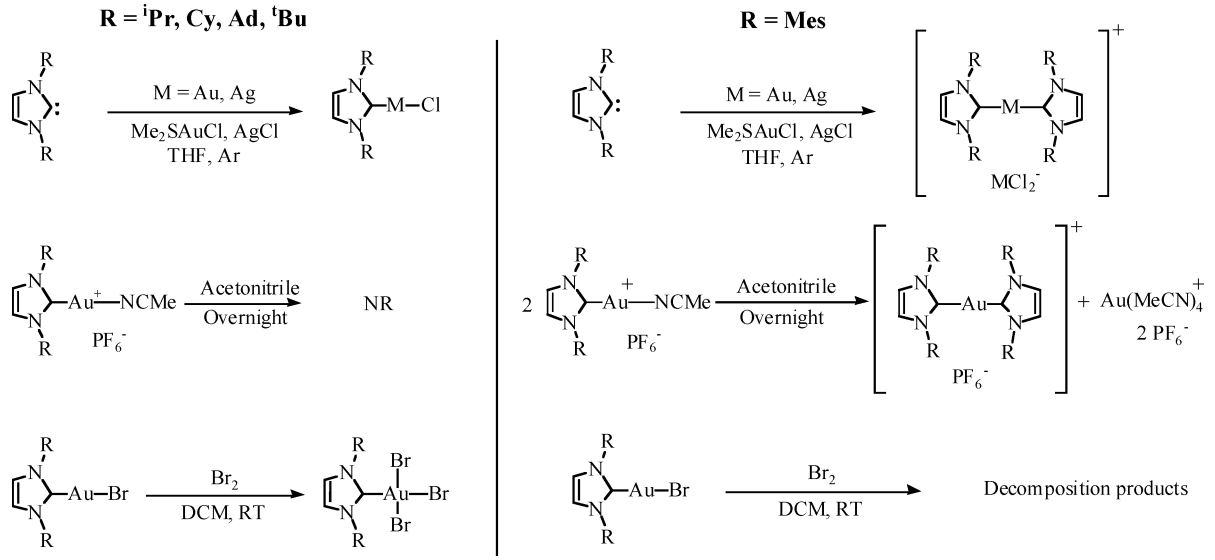


**Table 2. NMR Chemical Shifts of the Carbenic Carbon for the Au−Br Complexes**

| (NHC)AuBr | $\delta_C$ (ppm) | (NHC)AuBr$_3$ | $\delta_C$ (ppm) | $\Delta\delta_C$ (ppm) |
|---|---|---|---|---|
| (IPr)AuBr[a] (**8**) | 179.0 | (IPr)AuBr$_3$[a] (**15**) | 146.2 | −32.8 |
| (IMes)AuBr[a] (**9**) | 176.7 | (IMes)AuBr$_3$[a] (**16**) | 144.4 | −32.3 |
| (SIPr)AuBr[a] (**10**) | 199.0 | (SIPr)AuBr$_3$[a] (**17**) | 174.1 | −24.9 |
| (SIMes)AuBr[a] (**11**) | 198.1 | (SIMes)AuBr$_3$[a] (**18**) | 172.3 | −25.8 |
| (ICy)AuBr[a] (**12**) | 172.1 | (ICy)AuBr$_3$[a] (**19**) | 136.8 | −35.3 |
| (IAd)AuBr[a] (**13**) | 170.2 | (IAd)AuBr$_3$[a] (**20**) | 132.9 | −37.3 |
| (I$^t$Bu)AuBr[a] (**14**) | 172.4 | (I$^t$Bu)AuBr$_3$[a] (**21**) | 134.2 | −38.3 |

| (NHC)·HCl | $\delta_C$ (ppm) | $\Delta\delta_C$ (ppm) |
|---|---|---|
| (IPr)·HCl[b] | 132.2 | +14.0 |
| (IMes)·HCl[b] | 134.8 | +9.6 |
| (SIPr)·HCl[b] | 160.0 | +14.1 |
| (SIMes)·HCl[b] | 160.2 | +12.1 |
| (ICy)·HCl[b] | 134.5 | +2.3 |
| (IAd)·HCl[b] | 132.1 | +0.8 |
| (I$^t$Bu)·HCl[b] | 132.7 | +1.5 |

[a] NMR recorded in $CDCl_3$. [b] NMR recorded in DMSO-$d_6$.

complexes, where the bromide−gold(III) bond lengths are between 2.38 and 2.65 Å.[22b,33] The carbene ligands (except IPr and IAd) induce a trans influence with a lengthening of the Au−Br(2) bond. This effect is less pronounced than that observed for the phosphine−$AuBr_3$ complexes described by Schmidbaur *et al*.[22b] It is surprising to observe that, while there is no visible trans effect for the complex (IAd)$AuBr_3$ (**20**), the three different Au−Br bonds are slightly longer than expected when compared to our other gold(III) complexes. There is no close contact between gold atoms. This is not surprising, since aurophilic interactions only apply for $d^{10}$ gold(I) cations.[34] There is no insertion of bromine in the crystal lattices, as reported for some gold(III) phosphine tribromide complexes.[22b]

We were interested in testing the catalytic activity of our new well-defined gold(III) complexes to mediate the addition of water to alkynes. As gold(I) and gold(III) salts are known to catalyze this reaction, we used a reported work[35] as reference to gauge the catalytic activity of our system. Of the many Au(III) complexes synthesized, (IPr)$AuBr_3$ displays the best catalytic activity (Table 6).

The solvent screening indicates that an alcohol is required for the catalysis to proceed efficiently (Table 7). There is no trace of enol ethers or acetals resulting from the addition of alcohol to the alkynes as a competing reaction.

The present complexes were inefficient with internal alkynes, confirming the likely formation of a gold(III) vinyl secondary carbocation as an early reaction intermediate[14d,35] (Table 8).

However, the most dramatic result is the acceleration obtained when 1 equiv of a silver(I) salt is added as cocatalyst. This permits the rapid and quantitative formation of products while reducing catalyst loading from 10 to 2 mol % (Table 9).

These initial catalytic observations raise many questions in term of mechanism of activation and nature of the true catalytic species. Ongoing studies in our laboratories are aimed at answering these questions.

## Conclusion

We report the synthesis of the first series of well-defined (NHC)$Au^{III}$ complexes. Their straightforward synthesis can be carried out under aerobic conditions by oxidative addition of elemental bromine to the corresponding (NHC)$Au^{I}$ precursor. NMR and crystallographic data provide detailed information concerning the steric constraints and electronic effects produced by the different carbene environments around the Au(III) center. We also report the first use of a (NHC)$Au^{III}$ complex to catalyze an organic transformation. While the initial catalytic tests provide modest results, addition of a silver salt as a cocatalyst allowed the formation of a very efficient catalytic system. We are currently investigating the possible mechanism at play in this and related reactions.

## Experimental Section

**General Considerations.** All reactions using (NHC)AuCl or (NHC)AuBr as starting material were carried out in air. All alkynes were used as received (Aldrich, Acros). All reactions were carried out open to air unless indicated otherwise. Solvents for NMR spectroscopy were dried over molecular sieves. NMR spectra were collected on a 500 or 400 MHz Varian Gemini spectrometer. Flash

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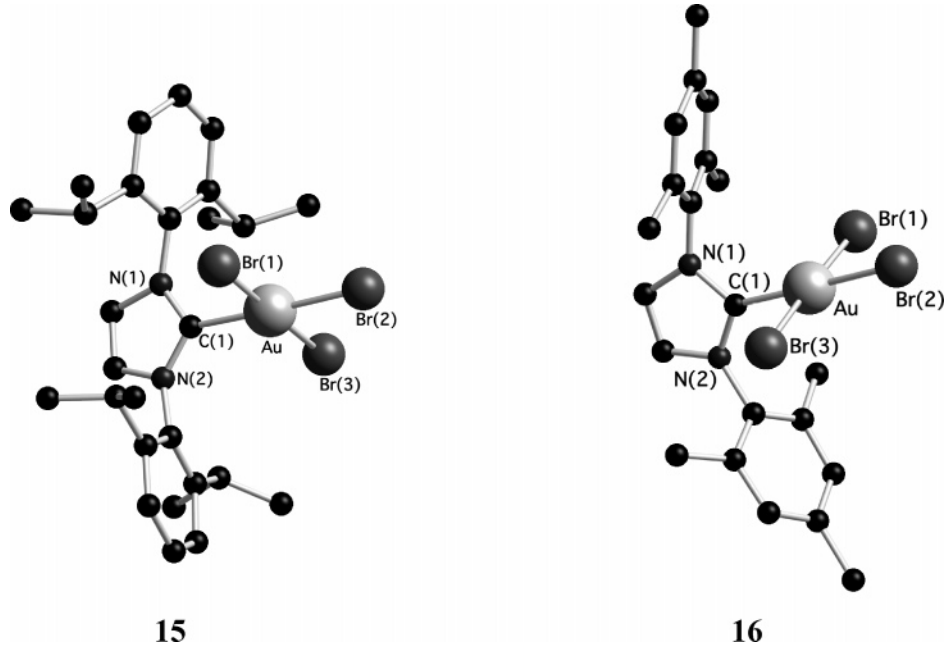



**Figure 3.** Ball-and-stick representations of (IPr)$AuBr_3$ (**15**) and (IMes)$AuBr_3$ (**16**). Hydrogen atoms have been omitted for clarity.

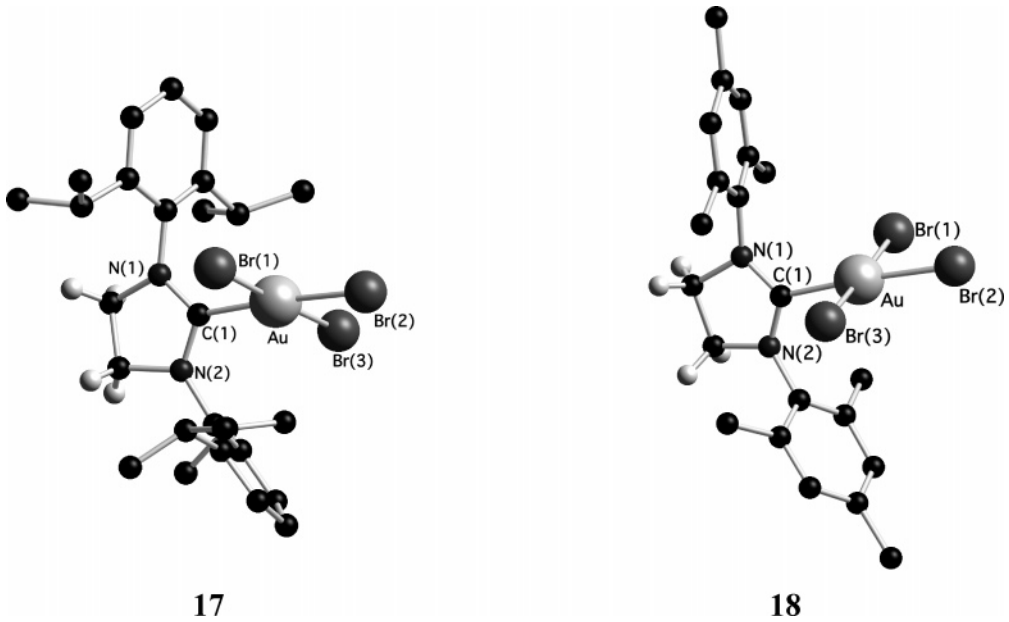



**Figure 4.** Ball-and-stick representations of (SIPr)$AuBr_3$ (**17**) and (SIMes)$AuBr_3$ (**18**). Most hydrogen atoms have been omitted for clarity.

chromatography was performed on silica gel (230−400 mesh; Natland International Corp.). Elemental analyses were performed by Robertson Microlit Laboratories. (NHC)AuCl complexes were synthesized according to literature procedures.[26]

**Synthesis of [(IPr)AuBr] (8).** In a flask, (IPr)AuCl (**1**; 1.00 g, 1 equiv, 1.61 mmol) was dissolved in 5 mL of acetone with LiBr (1.19 g, 8.5 equiv, 13.70 mmol) and the solution was stirred at room temperature for 24 h. The acetone was removed by vacuum and 2 mL of DCM added to the residue. The organic phase was dried over $MgSO_4$, since LiBr is extremely hygroscopic. The solution was filtered over a plug of silica gel (3 g). After reduction of the volume of DCM to 0.5 mL, 5 mL of pentane was added, which led to the appearance of a white precipitate. This precipitate was filtered, washed with 5 mL of cold pentane, and dried to afford the desired complex. Yield: 0.94 g (87%). $^1$H NMR ($CDCl_3$): $\delta$ 7.50 (t, $J$ = 8.0 Hz, 2H, C*H* aromatic), 7.28 (d, $J$ = 8.0 Hz, 4H, C*H* aromatic), 7.17 (s, 2H, C*H* imidazole), 2.56 (septet, $J$ = 7.0 Hz, 4H, C*H*($CH_3$)$_2$), 1.34 (d, $J$ = 7.0 Hz, 12H, CH ($CH_3$)$_2$), 1.22 (d, $J$ = 7.0 Hz, 12H, CH ($CH_3$)$_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 179.0 (s, *C* carbene), 145.8 (s, *C*H aromatic), 134.2 (s, *C*H aromatic), 131.0 (s, *C*H aromatic), 124.5 (s, *C*H imidazole), 123.3 (s, *C*H aromatic), 29.0 (s, *C*H ($CH_3$)$_2$), 24.7 (s, CH ($CH_3$)$_2$), 24.2 (s, CH ($CH_3$)$_2$). Anal. Calcd for $C_{27}H_{36}N_2AuBr$ (665.21): C, 48.74; H, 5.41; N, 4.21. Found: C, 48.68; H, 5.17; N, 3.94.

**Synthesis of [(IMes)AuBr] (9).** A protocol similar to that used for **8** gave **9** (from 0.90 g, 1.68 mmol, of **2**) as a white solid. Yield: 0.780 g (80%). $^1$H NMR ($CDCl_3$): $\delta$ 7.09 (s, 2H, C*H* imidazole), 6.98 (s, 4H, C*H* aromatic), 2.33 (s, 6H, C$H_3$), 2.10 (s, 12H, C$H_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 176.7 (s, *C* carbene), 139.7 (s, *C*H aromatic), 134.6 (s, *C*H aromatic), 134.5 (s, *C*H aromatic), 129.4 (s, *C*H aromatic), 122.0 (s, *C*H imidazole), 21.1 (s, C$H_3$), 17.7 (s, C$H_3$). Anal. Calcd for $C_{21}H_{24}N_2AuBr$ (581.02): C, 43.39; H, 4.16; N, 4.82. Found: C, 43.51 H, 3.88; N, 4.66.

**Synthesis of [(SIPr)AuBr] (10).** In a flask (SIPr)AuCl (**3**; 1.00 g, 1 equiv, 1.61 mmol) was dissolved in 5 mL of acetone, and LiBr (1.19 g, 8.5 equiv, 13.70 mmol) was added. This solution was stirred at room temperature for 48 h. The acetone was removed by vacuum and replaced by DCM. This solution was filtered over

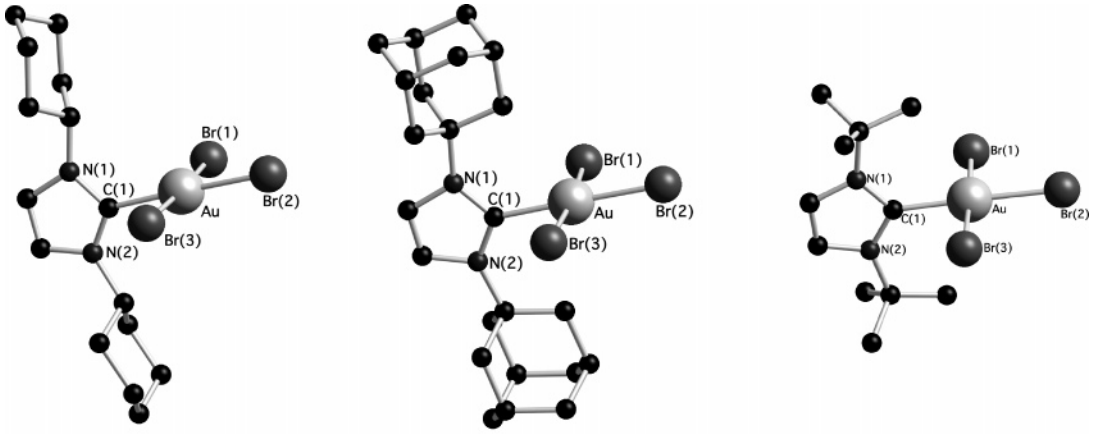



**Figure 5.** Ball-and-stick representations of (ICy)$AuBr_3$ (**19**), (IAd)$AuBr_3$ (**20**), and (I$^t$Bu)$AuBr_3$ (**21**). Hydrogen atoms have been omitted for clarity.

**Table 3. Selected Bond Angle Values (deg) for (NHC)$AuBr_3$ Complexes**

| (NHC)$AuBr_3$ | C(1)−Au−Br(1) | C(1)−Au−Br(2) | C(1)−Au−Br(3) | Br(1)−Au−Br(2) | Br(1)−Au−Br(3) | Br(2)−Au−Br(3) |
|---|---|---|---|---|---|---|
| (IPr)$AuBr_3$ (**15**) | 92.3(5) | 178.2(5) | 88.8(5) | 87.66(15) | 178.79(12) | 91.21(16) |
| (IMes)$AuBr_3$ (**16**) | 91.4(2) | 178.0(2) | 89.1(2) | 89.69(7) | 177.78(5) | 89.83(6) |
| (SIPr)$AuBr_3$ (**17**) | 88.0(4) | 174.9(4) | 93.0(4) | 89.89(7) | 177.76(4) | 89.28(7) |
| (SIMes)$AuBr_3$ (**18**) | 91.0(4) | 175.9(4) | 90.9(4) | 88.71(7) | 176.60(7) | 89.66(7) |
| (ICy)$AuBr_3$ (**19**) | 89.2(6) | 178.3(6) | 86.4(6) | 91.92(11) | 175.45(11) | 92.51(10) |
| (IAd)$AuBr_3$ (**20**) | 87.80(15) | 178.66(16) | 85.93(15) | 93.53(2) | 173.73(3) | 92.73(2) |
| (I$^t$Bu)$AuBr_3$ (**21**) | 90.69(14) | 177.97(14) | 87.16(14) | 91.32(2) | 177.82(2) | 90.83(3) |

**Table 4. Selected Au−X Bond Distances (Å) in (NHC)$AuBr_3$ Complexes**

| (NHC)$AuBr_3$ | Au−C(1) | Au−Br(1) | Au−Br(2) | Au−Br(3) |
|---|---|---|---|---|
| (IPr)$AuBr_3$ (**15**) | 2.048(19) | 2.384(3) | 2.386(4) | 2.397(3) |
| (IMes)$AuBr_3$ (**16**) | 2.009(8) | 2.4156(15) | 2.4224(12) | 2.4123(14) |
| (SIPr)$AuBr_3$ (**17**) | 2.042(13) | 2.405(2) | 2.4452(18) | 2.408(2) |
| (SIMes)$AuBr_3$ (**18**) | 2.052(13) | 2.4108(15) | 2.4468(17) | 2.4169(17) |
| (ICy)$AuBr_3$ (**19**) | 2.04(2) | 2.405(3) | 2.444(3) | 2.410(3) |
| (IAd)$AuBr_3$ (**20**) | 2.052(6) | 2.4465(8) | 2.4496(7) | 2.4426(7) |
| (I$^t$Bu)$AuBr_3$ (**21**) | 2.015(5) | 2.4209(6) | 2.4403(6) | 2.4638(6) |

a plug of silica gel and dried over $MgSO_4$. After filtration and reduction of the volume of DCM to 0.5 mL, 5 mL of pentane was added until appearance of a white precipitate. This precipitate was filtered, washed with pentane, and dried to afford the desired complex. It is worthy of note that washing the complex with water leads to its decomposition to the corresponding imidazolium salt. Yield: 0.610 g (57%). $^1$H NMR ($CDCl_3$): $\delta$ 7.41 (t, $J$ = 7.5 Hz, 2H, C*H* aromatic), 7.23 (d, $J$ = 7.5 Hz, 4H, C*H* aromatic), 4.04 (s, 4H, C$H_2$ imidazole), 3.05 (septet, $J$ = 6.5 Hz, 4H, C*H*($CH_3$)$_2$), 1.41 (d, $J$ = 6.5 Hz, 12H, CH(C$H_3$)$_2$), 1.33 (d, $J$ = 6.5 Hz, 12H, CH-(C$H_3$)$_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 199.0 (s, *C* carbene), 146.7 (s, *C*H aromatic), 134.1 (s, *C*H aromatic), 130.2 (s, *C*H aromatic), 124.8 (s, *C*H aromatic), 53.7 (s, *C*$H_2$ imidazole), 29.2 (s, *C*H($CH_3$)$_2$), 25.3 (s, CH(*C*$H_3$)$_2$), 24.3 (s, CH(*C*$H_3$)$_2$). Anal. Calcd for $C_{27}H_{38}N_2$-AuBr (667.14): C, 48.58; H, 5.74; N, 4.20. Found: C, 48.60; H, 5.60; N, 4.05.

**Synthesis of [(SIMes)AuBr] (11).** A protocol similar to that used for **10** provided **11** (from 1.00 g, 1.86 mmol, of **4**) as a white solid. Yield: 0.780 g (72%). $^1$H NMR ($CDCl_3$): $\delta$ 6.93 (s, 4H, C*H* aromatic), 3.97 (s, 4H, C$H_2$ imidazole), 2.31 (s, 12H, C$H_3$), 2.29 (s, 6H, C$H_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 198.1 (s, *C* carbene), 139.1 (s, *C*H aromatic), 135.7 (s, *C*H aromatic), 134.7 (s, *C*H aromatic), 130.0 (s, *C*H aromatic), 50.9 (s, *C*$H_2$ imidazole), 21.3 (s, C$H_3$), 18.2 (s, C$H_3$). Anal. Calcd for $C_{21}H_{26}N_2$AuBr (583.08): C, 43.24; H, 4.49; N, 4.80. Found: C, 43.14 H, 4.22; N, 4.69.

**Synthesis of [(ICy)AuBr] (12).** A protocol similar to that used for **8** gave **12** (from 1.15 g, 2.47 mmol, of **5**) as a white solid. Yield: 0.980 g (78%). $^1$H NMR ($CDCl_3$): $\delta$ 6.95 (s, 2H, C*H* imidazole), 4.57 (m, 2H, NC*H* cyclohexyl), 2.07 (m, 4H, C$H_2$), 1.86 (m, 4H, C$H_2$), 1.73 (m, 2H, C$H_2$), 1.56 (m, 4H, C$H_2$), 1.43 (m, 4H, C$H_2$), 1.22 (m, 2H, C*H*). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 172.1 (s, *C* carbene), 117.3 (s, *C*H imidazole), 61.0 (s, N*C*H cyclohexyl), 34.3 (s, *C*$H_2$), 25.5 (s, *C*$H_2$), 25.3 (s, *C*$H_2$). Anal. Calcd for $C_{15}H_{24}N_2$AuBr (509.20): C, 35.38; H, 4.75; N, 5.50. Found: C, 35.50; H, 4.73; N, 5.30.

**Synthesis of [(IAd)AuBr] (13).** A protocol similar to that used for **8** gave **13** (from 1.00 g, 1.76 mmol, of **6**) as a white solid. Yield: 0.590 g (55%). $^1$H NMR ($CDCl_3$): $\delta$ 7.08 (s, 2H, C*H* imidazole), 2.56 (m, 14H, C$H_2$ adamantyl), 2.26 (m, 6H, C$H_2$ adamantyl), 1.75 (m, 10H, C$H_2$ adamantyl). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 170.2 (*C* carbene), 115.2 (s, *C*H imidazole), 59.2 (s, N*C*H adamantyl), 44.0 (s, *C*$H_2$), 35.7 (s, *C*$H_2$), 29.8 (s, *C*$H_2$). Anal. Calcd for $C_{23}H_{32}N_2$AuBr (613.10): C, 45.04; H, 5.26; N, 4.57. Found: C, 44.97; H, 5.01; N, 4.44.

**Synthesis of [(I$^t$Bu)AuBr][7a] (14).** A protocol similar to that used for **8** gave **14** (from 1.00 g, 2.42 mmol, of **7**) as a white solid. Yield: 0.810 g (73%). $^1$H NMR ($CDCl_3$): $\delta$ 7.09 (s, 2H, C*H* imidazole), 1.87 (s, 18H, C(C$H_3$)$_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 172.4 (s, *C* carbene), 116.4 (s, *C*H imidazole), 59.2 (s, *C*($CH_3$)$_3$), 31.9 (s, C(*C*$H_3$)$_3$).

**Synthesis of [(IPr)$AuBr_3$] (15).** In a flask (IPr)AuBr (**8**; 0.840 g, 1 equiv, 1.262 mmol) was dissolved in 5 mL of DCM with bromine (0.240 g, 1.2 equiv, 1.514 mmol). The solution was stirred at room temperature for 1 h. The volume of DCM was reduced to 0.5 mL by vacuum, at the same time removing the excess bromine. Then 5 mL of pentane was added to produce an orange precipitate. This solid was collected on a filter, washed with 5 mL of pentane, and dried to afford the desired complex. Yield: 0.870 g (84%). $^1$H NMR ($CDCl_3$): $\delta$ 7.54 (t, $J$ = 7.5 Hz, 2H, C*H* aromatic), 7.35 (d, $J$ = 7.5 Hz, 4H, C*H* aromatic), 7.35 (s, 2H, C*H* imidazole), 2.99 (septet, $J$ = 6.5 Hz, 4H, C*H*($CH_3$)$_2$), 1.41 (d, $J$ = 6.5 Hz, 12H, CH(C$H_3$)$_2$), 1.13 (d, $J$ = 6.5 Hz, 12H, CH(C$H_3$)$_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 146.2 (s, *C* carbene), 145.8 (s, *C*H aromatic), 132.6 (s, *C*H aromatic), 131.6 (s, *C*H aromatic), 126.1 (s, *C*H

**Table 5. Crystallographic Data for Complexes 8 and 15−21**

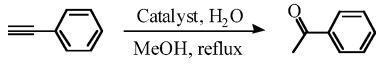
| | 8 | 15 | 16 | 17 |
|---|---|---|---|---|
| formula | $C_{27}H_{36}N_2AuBr$ | $C_{27.50}H_{37}N_2AuBr_3$ | $C_{21}H_{24}N_2AuBr_3$ | $C_{28}H_{40}N_2AuBr_3Cl_2$ |
| $M_r$ | 665.45 | 867.74 | 741.12 | 912.22 |
| cryst syst | orthorhombic | monoclinic | orthorhombic | monoclinic |
| space group | *Pccn* | $P2_1/n$ | $P2_12_12_1$ | $P2_1/c$ |
| cell constants | | | | |
| *a* (Å) | 10.9117(6) | 16.950(2) | 10.6845(6) | 10.677(2) |
| *b* (Å) | 12.6771(7) | 19.403(3) | 14.2833(8) | 16.593(4) |
| *c* (Å) | 19.9643(10) | 20.417(3) | 15.7115(9) | 19.306(4) |
| α (deg) | 90.00 | 90.00 | 90.00 | 90.00 |
| *β* (deg) | 90.00 | 110.421(3) | 90.00 | 99.664(4) |
| *γ* (deg) | 90.00 | 90.00 | 90.00 | 90.00 |
| *V* (Å$^3$) | 2761.6 (3) | 6293.0(15) | 2397.7(2) | 3371.5(12) |
| *Z* | 4 | 8 | 4 | 4 |
| *λ* (Å) | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 |
| *ρ*(calcd) (g/cm$^3$) | 1.601 | 1.832 | 2.053 | 1.797 |
| *μ* (mm$^{-1}$) | 6.789 | 8.588 | 11.143 | 8.096 |
| *F*(000) | 1304 | 3336 | 1392 | 1760 |
| *T* (K) | 295(2) | 295(2) | 295(2) | 295(2) |
| $2\theta_{max}$ (deg) | 55.04 | 52.774 | 46.718 | 53.004 |
| no. of rflns measd | 17 717 | 39 800 | 25 184 | 16 323 |
| no. of indep rflns | 3140 | 8206 | 3137 | 4009 |
| $R_{int}$ | 0.0505 | 0.0574 | 0.0410 | 0.0820 |
| no. of data/restraints/params | 2026/0/146 | 5509/563/638 | 2891/705/330 | 2934/335/377 |
| $R_w$ ($F^2$ all rflns) | 0.0758 | 0.0967 | 0.0701 | 0.0992 |
| $R$ ($F$, $>4\sigma(F)$) | 0.0321 | 0.0495 | 0.0300 | 0.0589 |
| max, min Δ*ρ* (e Å$^{-3}$) | +0.928, −0.986 | +0.925, −1.413 | +0.744, −0.530 | +1.130, −0.775 |

| | 18 | 19 | 20 | 21 |
|---|---|---|---|---|
| formula | $C_{21.50}H_{27.01}N_2AuBr_3Cl_{1.01}$ | $C_{15.50}H_{25}N_2AuBr_3Cl$ | $C_{23}H_{32}N_2AuBr_3$ | $C_{11}H_{20}N_2AuBr_3$ |
| $M_r$ | 785.90 | 711.52 | 773.20 | 616.99 |
| cryst syst | monoclinic | orthorhombic | monoclinic | monoclinic |
| space group | $P2_1/c$ | *Pccn* | $P2_1/c$ | $P2_1/c$ |
| cell constants | | | | |
| *a* (Å) | 8.7226(8) | 15.0878(9) | 16.4445(16) | 9.2947(5) |
| *b* (Å) | 16.0470(15) | 19.9495(13) | 11.1131(10) | 15.3944(8) |
| *c* (Å) | 19.7576(18) | 14.6881(9) | 12.9782(12) | 12.1528(7) |
| α (deg) | 90.00 | 90.00 | 90.00 | 90.00 |
| *β* (deg) | 95.611(2) | 90.00 | 90.044(2) | 96.7460(10) |
| *γ* (deg) | 90.00 | 90.00 | 90.00 | 90.00 |
| *V* (Å$^3$) | 2752.3(4) | 4421.0(5) | 2371.8(4) | 1726.86(16) |
| *Z* | 4 | 8 | 4 | 4 |
| *λ* (Å) | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 |
| *ρ*(calcd) (g/cm$^3$) | 1.897 | 2.138 | 2.165 | 2.373 |
| *μ* (mm$^{-1}$) | 9.808 | 12.198 | 11.270 | 15.445 |
| *F*(000) | 1485 | 2664 | 1472 | 1136 |
| *T* (K) | 295(2) | 295(2) | 295(2) | 295(2) |
| $2\theta_{max}$ (deg) | 61.21 | 58.484 | 46.718 | 52.846 |
| no. of rflns measd | 39 906 | 36 155 | 21 229 | 21 428 |
| no. of indep rflns | 3600 | 2892 | 3429 | 3569 |
| $R_{int}$ | 0.0603 | 0.0586 | 0.0494 | 0.0418 |
| no. of data/restraints/params | 3197/240/278 | 2609/186/217 | 2888/280/390 | 3107/491/235 |
| $R_w$ ($F^2$ all rflns) | 0.1291 | 0.1339 | 0.0725 | 0.0548 |
| $R$ ($F$, $>4\sigma(F)$) | 0.0490 | 0.0438 | 0.0295 | 0.0259 |
| max, min Δ*ρ* (e Å$^{-3}$) | +1.610, -0.797 | +0.778, −1.198 | +1.244, −1.443 | +1.127, −0.907 |

aromatic), 124.7 (s, *C*H imidazole), 29.1 (s, *C*H($CH_3$)$_2$), 26.5 (s, CH(*C*H$_3$)$_2$), 23.0 (s, CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{27}H_{36}N_2AuBr_3$ (825.27): C, 39.30; H, 4.40; N, 3.39. Found: C, 39.26; H, 4.12; N, 3.28.

**Synthesis of [(IMes)AuBr$_3$] (16).** In a flask (IMes)AuBr (**9**; 0.100 g, 1 equiv, 0.179 mmol) was dissolved in 1 mL of DCM and cooled to −78 °C, and then bromine (0.040 g, 1.2 equiv, 0.214 mmol) was added and the solution was stirred for 20 min. The excess bromine was removed by vacuum while the temperature was slowly raised to room temperature. Then 0.5 mL of DCM was added, followed by 5 mL of pentane, until the appearance of an orange precipitate. This suspension was filtered and the solid washed with pentane and dried to afford the desired complex. Yield: 0.120 g (94%). $^1$H NMR ($CDCl_3$): *δ* 7.32 (s, 2H, C*H* imidazole), 7.06 (s, 4H, C*H* aromatic), 2.37 (s, 6H, C$H_3$), 2.29 (s, 12H, C$H_3$). $^{13}$C NMR ($CDCl_3$): *δ* (ppm) 144.4 (s, *C* carbene), 140.9 (s, *C*H aromatic), 135.2 (s, *C*H aromatic), 132.8 (s, *C*H aromatic), 130.1 (s, *C*H aromatic), 125.9 (s, *C*H$_2$ imidazole), 21.3 (s, C$H_3$), 19.7 (s, C$H_3$). Anal. Calcd for $C_{21}H_{24}N_2AuBr_3$ (740.82): C, 34.03; H, 3.26; N, 3.78. Found: C, 34.13; H, 3.49; N, 3.52.

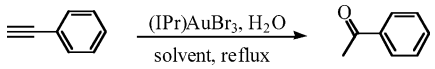
**Table 6. Screening of (NHC)AuBr$_3$ Complexes in Addition of Water to Alkynes[a]**




| entry | catalyst | time (h) | yield (%)[b] |
|---|---|---|---|
| 1 | − | − | NR |
| 2 | IPr | − | NR |
| 3 | $AuCl_3$ | 24 | 94 |
| 4 | (IPr)$AuBr_3$ | 24 | 95 |
| 5 | (IMes)$AuBr_3$ | 24 | 91 |
| 6 | (IAd)$AuBr_3$ | 48 | 35 |
| 7 | (ItBu)$AuBr_3$ | 48 | 92 |

[a] Reaction conditions: 10 mol % of catalyst, 0.5 mL of $H_2O$, 0.5 mL of methanol, 1 mmol of phenylacetylene. [b] GC yields, an average of two runs. NR = no reaction.

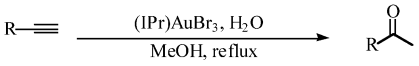
**Table 7. Solvent Screening in Addition of Water to Alkynes[a]**

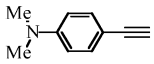
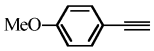
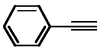
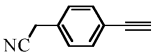
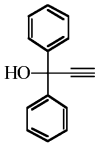
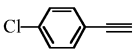
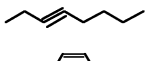
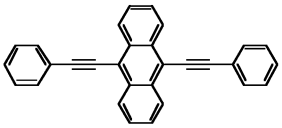



| entry | solvent | time (h) | yield (%)[b] |
|---|---|---|---|
| 1 | MeOH | 24 | 95 |
| 2 | IPA | 36 | 47 |
| 3 | $H_2O$ | 48 | 62[c] |
| 4 | MeCN | | NR |
| 5 | THF | | NR |

[a] Reaction conditions: 10 mol % of catalyst, 0.5 mL of $H_2O$, 0.5 mL of methanol, 1 mmol of phenylacetylene. [b] GC yields, an average of two runs. NR = no reaction. [c] Small amount of acetone added to solubilize the catalyst.

**Table 8. Various Alkynes Screened in Addition of Water to Alkynes[a]**



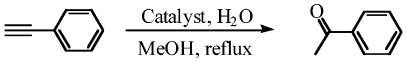

| entry | alkyne | cat. loading | time (h) | yield (%)[b] |
|---|---|---|---|---|
| 1 |  | 10 mol% | 1 | 100 (92)[c] |
| 2 |  | 10 mol% | 6 | 96 (90) |
| 3 |  | 10 mol% | 24 | 95 (88) |
| 4 |  | 10 mol% | 36 | 92 (86) |
| 5 |  | 10 mol% | 3 | 40 (36) |
| 6 |  | 10 mol% | 36 | 80 (77) |
| 7 |  | 10 mol% | - | NR |
| 8 |  | 20 mol% | - | NR |

[a] Reaction conditions: 0.5 mL of $H_2O$, 0.5 mL of methanol, 1 mmol of alkyne. [b] GC yields, isolated yields in parentheses, an average of two runs. NR = no reaction. [c] Temperature 25 °C.

**Synthesis of [(SIPr)AuBr$_3$] (17).** A protocol similar to that used for **15** gave **17** (from 0.280 g, 0.448 mmol, of **10**) as a orange solid. Yield: 0.360 g (97%). $^1$H NMR ($CDCl_3$): $\delta$ 7.43 (t, $J$ = 7.0 Hz, 2H, C*H* aromatic), 7.26 (d, $J$ = 7.0 Hz, 4H, C*H* aromatic), 4.29 (s, 4H, C$H_2$ imidazole), 3.41 (septet, $J$ = 6.5 Hz, 4H, C*H*(CH$_3$)$_2$), 1.46 (d, $J$ = 6.5 Hz, 12H, CH(C$H_3$)$_2$), 1.25 (d, $J$ = 6.5 Hz, 12H, CH(C$H_3$)$_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 174.1 (s, *C* carbene), 147.0 (s, *C*H aromatic), 132.9 (s, *C*H aromatic), 131.1 (s, *C*H aromatic), 125.4 (s, *C*H aromatic), 55.0 (s, *C*H$_2$ imidazole), 29.3 (s, *C*H(CH$_3$)$_2$), 27.4 (s, CH(*C*H$_3$)$_2$), 24.2 (s, CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{27}H_{38}N_2AuBr_3$ (827.94): C, 39.20; H, 4.63; N, 3.39. Found: C, 39.52; H, 4.66; N, 3.32.

**Synthesis of [(SIMes)AuBr$_3$] (18).** A preparation similar to that used for **9** gave **18** (from 0.100 g, 0.185 mmol, of **11**) as a orange solid. Yield: 0.128 g (94%). $^1$H NMR ($CDCl_3$): $\delta$ 6.96 (s, 4H, C*H* aromatic), 4.23 (s, 4H, C$H_2$ imidazole), 2.54 (s, 12H, C$H_3$), 2.31 (s, 6H, C$H_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 172.3 (s, *C* carbene), 140.1 (s, *C*H aromatic), 135.8 (s, *C*H aromatic), 132.1 (s, *C*H aromatic), 130.3 (s, *C*H aromatic), 53.3 (s, *C*H$_2$ imidazole), 21.2 (s, C$H_3$), 20.3 (s, C$H_3$). Anal. Calcd for $C_{21}H_{26}N_2AuBr_3$ (742.88): C, 33.94; H, 3.53; N, 3.77. Found: C, 34.19; H, 3.57; N, 3.66.

**Table 9. Effect of a Silver Salt on Catalytic Addition of Water to Alkynes[a]**




| loading mol% | catalyst | time (h) | yield[b] |
|---|---|---|---|
| 10 | (IPr)AuBr$_3$ | 24 | 95% |
| 2 | (IPr)AuBr$_3$+AgPF$_6$ | 1 | 99% |
| 10 | AgPF$_6$ | 24 | NR |

| loading (mol %) | catalyst | time (h) | yield (%)[b] |
|---|---|---|---|
| 10 | (IPr)AuBr$_3$ | 24 | 95 |
| 2 | (IPr)AuBr$_3$ + AgPF$_6$ | 1 | 99 |
| 10 | AgPF$_6$ | 24 | NR |

[a] Reaction conditions: 0.5 mL of $H_2O$, 0.5 mL of methanol, 1 mmol of phenylacetylene. [b] GC yields, an average of two runs. NR = no reaction.

**Synthesis of [(ICy)AuBr$_3$] (19).** A protocol similar to that used for **15** gave **19** (from 0.365 g, 0.789 mmol of **12**) as a yellow solid. Yield: 0.470 g (89%). $^1$H NMR ($CDCl_3$): $\delta$ 7.21 (s, 2H, C*H* imidazole), 4.50 (m, 2H, NC*H* cyclohexyl), 2.24 (m, 4H, C$H_2$), 1.90 (m, 4H, C$H_2$), 1.77 (m, 2H, C$H_2$), 1.51 (m, 4H, C$H_2$), 1.46 (m, 4H, C$H_2$), 1.21 (m, 2H, C*H*). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 136.8 (s, *C* carbene), 120.5 (s, *C*H imidazole), 61.1 (s, N*C*H cyclohexyl), 33.4 (s, *C*H$_2$), 25.3 (s, *C*H$_2$), 25.1 (s, *C*H$_2$). Anal. Calcd for $C_{15}H_{24}N_2AuBr_3$ (668.82): C, 26.93; H, 3.63; N, 4.19. Found: C, 26.89; H, 3.56; N, 3.99.

**Synthesis of [(IAd)AuBr$_3$] (20).** A procedure similar to that used for **15** gave **20** (from 0.185 g, 0.325 mmol, of **13**) as a yellow solid. Yield: 0.240 g (95%). $^1$H NMR ($CDCl_3$): $\delta$ 7.53 (s, 2H, C*H* imidazole), 2.57 (m, 14H, C$H_2$ adamantyl), 2.32 (m, 6H, C$H_2$ adamantyl), 1.75 (m, 10H, C$H_2$ adamantyl). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) = 132.9 (*C* carbene), 121.4 (s, *C*H imidazole), 63.8 (s, N*C*H adamantyl), 44.1 (s, *C*H$_2$), 35.6 (s, *C*H$_2$), 30.2 (s, *C*H$_2$). Anal. Calcd for $C_{23}H_{32}N_2AuBr_3$ (778.93): C, 35.73; H, 4.17; N, 3.62. Found: C, 35.43; H, 4.05; N, 3.54.

**Synthesis of [(I$^t$Bu)AuBr$_3$] (21).** A protocol similar to that used for **15** gave **21** (from 0.360 g, 871 mmol, of **14**) as a yellow solid. Yield: 0.500 g (93%). $^1$H NMR ($CDCl_3$): $\delta$ 7.49 (s, 2H, C*H* imidazole), 1.92 (s, 18H, C(C$H_3$)$_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 134.2 (s, *C* carbene), 122.7 (s, *C*H imidazole), 62.6 (s, *C*(CH$_3$)$_3$), 32.2 (s, C(*C*H$_3$)$_3$). Anal. Calcd for $C_{11}H_{20}N_2AuBr_3$ (616.78): C, 21.41; H, 3.27; N, 4.54. Found: C, 21.59; H, 3.28; N, 4.47.

**Screening of Substrates in Catalytic Addition of Water to Terminal Alkynes.** Into a reaction vessel equipped with a magnetic stirring bar and a reflux condenser were placed the catalyst ((IPr)-AuBr$_3$; 10 mol %, 83 mg), distilled water (0.5 mL), and methanol (5 mL). A 1 mmol portion of the indicated alkyne was then added. The resulting mixture was refluxed and stirred using a magnetic plate in an oil bath for the indicated time. The reactions were monitored by gas chromatography. After reaching maximum conversion, the reaction mixture was cooled to room temperature. Prior to workup, the reaction mixture was passed through a short silica column. The resulting filtrate was concentrated under reduced pressure and the residue diluted with methyl *tert*-butyl ether or diethyl ether and washed with brine. The ethereal solution was dried over magnesium sulfate. The solvent was then evaporated in vacuo. When necessary, the product was purified by flash chromatography on silica gel with hexanes or a 2−10% mixture of ethyl acetate in hexanes.

**Isolated Products. 1-(4-(Dimethylamino)phenyl)ethanone[36] (Table 7, Entry 1).** The procedure afforded 133 mg (92%) of the product.

**1-(4-Methoxyphenyl)ethanone[37] (Table 7, Entry 2),** The procedure afforded 118 mg (90%) of the product.

**1-Phenylethanone[38] (Table 7, Entry 3),** The procedure afforded 105 mg (88%) of the product.

**(4-Acetylphenyl)acetonitrile[39] (Table 7, Entry 4).** The procedure afforded 121 mg (86%) of the product.

**1-Hydroxy-1,1-diphenylpropan-2-one[40] (Table 7, Entry 5).** The procedure afforded 74 mg (36%) of the product.

**1-(4-Chlorophenyl)ethanone[41] (Table 7, Entry 6).** The procedure afforded 118 mg (77%) of the product.

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**Supporting Information Available:** Crystallographic information files (CIF) of the complexes **8** and **15**−**21**. This material is available free of charge via the Internet at http://pubs.acs.org. These files have also been deposited with the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers 621434−621442.

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