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Synthesis of Propargyl-Functionalized NHC Gold Complexes

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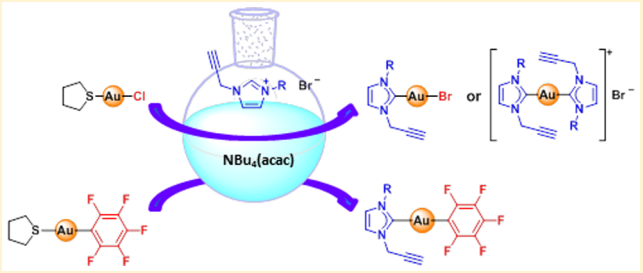
Supporting Information

ABSTRACT: A series of propargyl functionalized N-heterocyclic carbene gold(I) complexes have been synthesized from the corresponding imidazolium salts with tetrabutylammonium acetylacetonate in the presence of a gold(I) precursor in a one-pot reaction. Several complexes of different stoichiometries are described: [AuBr(NHC)], [Au(NHC)$_2$]Br and [Au(C_6F_5)(NHC)], and many of these have been characterized by X-ray diffraction studies. Aurophilic interactions are present in the compounds bearing less sterically hindered carbenes, and secondary interactions such as hydrogen bonds, $\pi-\pi$ stacking, or weak contacts of the gold center with the carbon of the propargyl unit have also been found. These complexes possess a high degree of water solubility, which makes them potentially useful for the synthesis of biologically active compounds or as gold catalysts in water. Activation of the propargyl unit in [AuBr(NHC)] complexes leads to the formation of interesting trimers with bridging bidentate C^C alkynyl-carbene ligands.



INTRODUCTION

N-heterocyclic carbenes (NHCs) are of ever-increasing interest due to the multiple and diverse applications of their corresponding transition metal complexes.[1] Their strong σ-donor capacity makes them excellent ligands, and generally they form very stable complexes. A huge variety of different substituents can be introduced at the nitrogen atoms, allowing both steric and electronic requirements to be fine-tuned for specific applications and giving them an incredibly versatile coordination chemistry.[2−5] They are currently among some of the most important ligands and are ubiquitous within organometallic chemistry.

NHC gold complexes were first isolated in 1989 by Bonati;[6] however the potential of these compounds was not realized until many years later. They now have numerous applications in catalysis,[7] medicine,[8] and luminescence.[9] NHC-Au(I) complexes are commonly used in homogeneous gold catalysis and are considered powerful synthetic tools in organic synthesis. They have unique catalytic activity because the strong σ-donor ability of the NHC ligand results in these complexes being more electron rich than other homogeneous gold catalysts. Since their first reported use by Herrmann and co-workers in 2003 for the gold-catalyzed hydration of 3-hexyne,[10] they have been successfully employed in a wide variety of organic transformations, including enyne cycloisomerizations, alkyne hydration, propargylic ester activation, alkene activation, alkane C−H bond activation, and cross-coupling reactions. However, the importance of NHC gold complexes in catalysis comes from not only their use as highly selective catalysts in directed organic synthetic strategies but also their ability to stabilize intermediates in catalytic reactions. Recent reports have described how the stabilization imparted by the NHC ligand allows the isolation of otherwise highly unstable intermediates, e.g. vinyl gold derivatives,[11] gold(I) hydrides,[12] and gold(I) or gold(III) intermediates in gold-only photoredox catalysis,[13] thus providing chemists with a better understanding of key steps in reaction mechanisms.

NHC gold complexes are also of biological importance. The strong gold−carbene bonds in NHC-Au(I) complexes cause them to be inert toward biologically important thiol groups and hence have potential medical applications. In 2004 the first report of the antimicrobial activity of NHC gold complexes was published by Çetinkaya, in which a series of gold bis-carbene complexes were found to be effective with a variety of both Gram-positive and Gram-negative bacteria.[14] Following this, significant contributions were made by Berners-Price and co-workers with studies of the mitochondrial permeability of NHC-Au(I) complexes.[15] The complexes were found to induce mitochondrial membrane permeabilization, a unique property which gives them the potential to be excellent anticancer agents, since when a cell undergoes apoptosis it will not harm the surrounding cells.

Another important property of NHC gold complexes is their luminescence. This was first reported in 1999 by Lin and co-workers, in which a series of NHC-Au(I) complexes bearing a benzimidazol-2-ylidene ligand were found to exhibit long-lived luminescence at room temperature, both in the solid state and in acetonitrile solutions.[16] More recently some NHC gold complexes have been found to have low-energy excitation and emission bands at suitable wavelengths for use in cellular distribution studies using fluorescence confocal microscopy.[17]

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Organometallics XXXX, XXX, XXX−XXX

NHC ligands have also been found to stabilize three-coordinate gold complexes incorporating a *nido*-carborane diphosphine.[18] These brightly luminescent complexes were found to have incredibly high quantum yields, giving them the potential for future practical applications such as in OLEDs. Simple changes in the structure of the NHC ligand result in changes in the emission of the NHC gold complexes, and hence ligand design can allow the luminescent properties to be fine-tuned for specific applications.

Propargyl-functionalized NHC gold complexes are of particular interest because of the amazing potential and versatility imparted by the propargyl unit. Propargyl-functionalized NHC complexes of silver are known to show biological activity,[19] and the propargyl unit also gives the complexes a degree of water solubility. Alkyne groups can be used in "click" reactions, and recently Cai and co-workers were able to create polymer-supported NHC silver complexes through the "click" reaction of propargyl-functionalized imidazolium salts.[20] Such supported NHC metal complexes are advantageous in catalysis due to their recyclability. For optical applications, the formation of polynuclear complexes is desirable and the propargyl unit can provide an additional coordination site with the potential for the formation of allenyl complexes. Recently, we found that allenyl gold complexes derived from propargyl-functionalized phosphonium salts exhibit an unusual regioselectivity dependent on the oxidation state of the gold,[21] where allenyl ligands substituted at the α or γ carbon were obtained for gold(I) or gold(III), respectively, and hence further studies on the reactions of propargyl-functionalized ligands with gold are of interest.

The recently reported use of tetrabutylammonium acetylacetonate for the preparation of NHC gold complexes was found to be an economical and incredibly versatile method.[22] This method is particularly advantageous when sterically smaller NHCs are used, as generally they are less stable and decomposition is observed when standard synthetic methods are employed. Since propargyl-functionalized NHCs are sterically small, this method is the ideal choice for the synthesis of their gold complexes. Furthermore, this method is suitable for poorly soluble imidazolium salts, as in this case.

Herein we report the synthesis of several new propargyl-functionalized NHC gold complexes using $NBu_4(acac)$ with reactions carried out at room temperature, in air, and with very short reaction times. Additionally, to demonstrate the reaction possibilities of these complexes, the synthesis of double alkynylcarbene species is described.

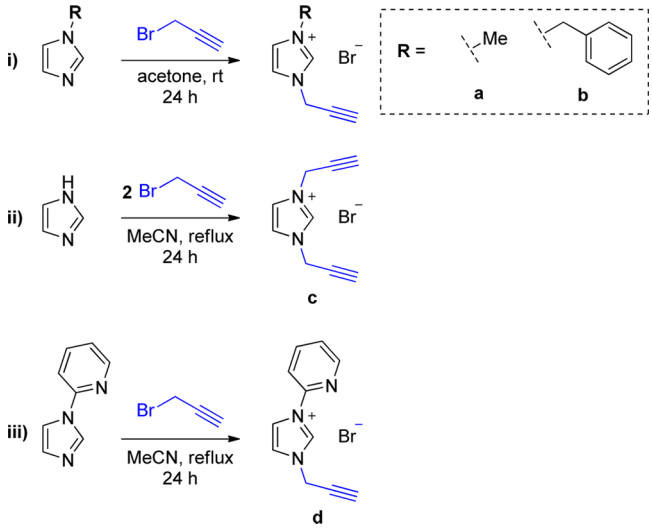
RESULTS AND DISCUSSION

Synthesis and Structural Characterization. A series of propargyl-functionalized imidazolium bromide salts were prepared by reaction of the imidazoles with propargyl bromide following a previously reported procedure for the methyl and benzyl derivatives (Scheme 1).[23]

The 1,3-dipropargylimidazolium bromide salt was prepared by another previously reported procedure,[24] and the pyridyl species is described for the first time. All, apart from the methyl derivative, were off-white solids at room temperature and were insoluble in all common organic solvents but soluble in water and alcohols. The methyl derivative was a pale yellow ionic liquid, immiscible with organic solvents but miscible with water and alcohols.

Addition of a stoichiometric amount of [AuCl(tht)] (tht = tetrahydrothiophene) to the imidazolium bromide salts in dichloromethane led to solutions of the [imidazolium][AuBrCl] salts. Subsequent addition of $NBu_4(acac)$ gave the [AuBr(NHC)] complexes with reaction times of just 1 h (Scheme 2). The complexes **1** could be separated from the NBu_4Cl formed in the reaction by a simple filtration through silica, giving the complexes in good yields (73−82%).

Scheme 1. Formation of Imidazolium Bromide Salts



Molecular structures of complexes **1a−d** were determined by single-crystal X-ray diffraction. Suitable crystals were obtained by the slow diffusion of pentane into solutions of the complexes in dichloromethane. In all of the complexes the carbon−carbon triple bond of the propargyl unit is maintained and no interaction with the gold center is observed.

Complex **1a** with the smallest substituent on the NHC, a methyl group, shows a structure in which intermolecular aurophilic interactions are present, with Au···Au distances of 3.324(1) Å (Figure 1). The propargyl substituent is orientated perpendicular to the coplanar Br−Au−NHC unit. The Au−C bond distance is 1.985(5) Å, which is the shortest described for an NHC−Au−Br complex and indicates a strong bond, as expected for strong σ-donor NHCs. The Au−Br distance of 2.4038(15) Å is longer than that reported by Meyer and co-workers[25] with an aryl-substituted carbene, 2.3904(4) Å. The C−C distances within the propargyl unit are C(5)−C(6) 1.472(6) Å and C(6)−C(7) 1.183(7) Å, which correspond to single and triple bonds, respectively. The gold center is in a linear geometry with a C(1)−Au(1)−Br(1) angle of 174.35(12)°.

The structures of complexes **1b−d** (Figure 2) show patterns similar to those found in **1a**, excluding the aurophilic interactions. The increase in the steric demand of the substituents on the nitrogen atom of the imidazole ring causes the disappearance of this intermolecular contact. As expected when changing to substituents with a weaker donor capacity, the Au−$C_{carbene}$ bond distances are slightly longer in these complexes, following the order Me < $CH_2C{\equiv}CH$ < $CH_2Ph \approx$ py, although the values for py and CH_2Ph are similar within the errors and the differences may not be significant. Additionally a concurrent decrease in the Au−Br distance is observed with increasing Au−$C_{carbene}$ bond distance.

When the reaction of the imidazolium bromide salts, [AuCl(tht)], and $NBu_4(acac)$ was carried out in THF, rather than dichloromethane, a white precipitate was observed in all

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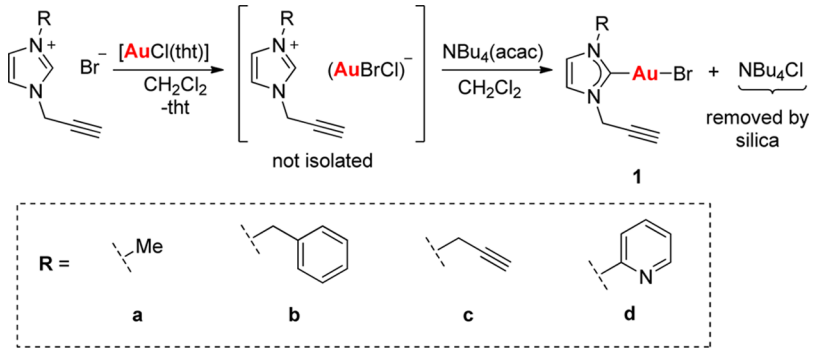
Organometallics XXXX, XXX, XXX−XXX

Scheme 2. Formation of [AuBr(NHC)] Complexes



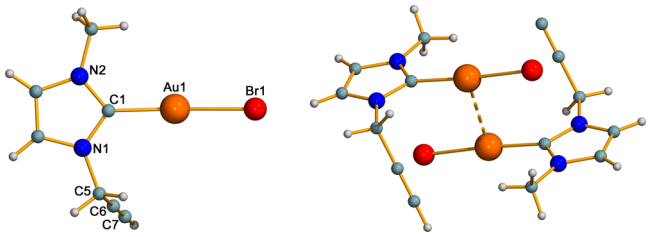


Figure 1. Molecular structure of complex **1a** and association in dimers through aurophilic interactions. Selected bond lengths (Å) and angles (deg): Au(1)−C(1) 1.985(5), Au(1)−Br(1) 2.4038(15), N(1)−C(1) 1.353(6), N(2)−C(1) 1.342(6), C(5)−C(6) 1.472(6), C(6)−C(7) 1.183(7), C(1)−Au(1)−Br(1) 174.35(12).

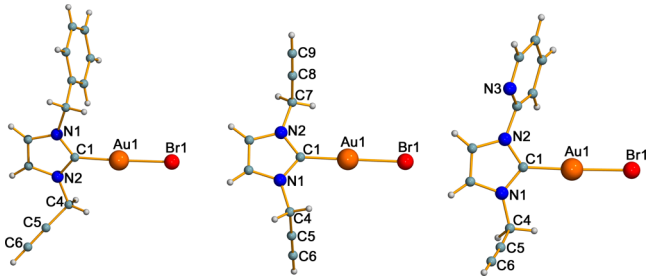


Figure 2. Molecular structures of complexes **1b−d**. Selected bond lengths (Å) and angles (deg): **1b**, Au(1)−C(1) 2.004(5), Au(1)−Br(1) 2.3927(7), N(1)−C(1) 1.341(6), N(2)−C(1) 1.327(6), C(4)−C(5) 1.453(7), C(5)−C(6) 1.179(7), C(1)−Au(1)−Br(1) 177.78(12); **1c**, Au(1)−C(1) 1.994(4), Au(1)−Br(1) 2.4057(4), N(1)−C(1) 1.337(5), N(2)−C(1) 1.346(5), C(5)−C(6) 1.176(7), C(8)−C(9) 1.172(6), C(1)−Au(1)−Br(1) 177.23(12); **1d**, Au(1)−C(1) 1.988(10), Au(1)−Br(1) 2.3967(10), N(1)−C(1) 1.347(12), N(2)−C(1) 1.354(11), C(4)−C(5) 1.478(13), C(5)−C(6) 1.191(15), C(8)−C(9) 1.172(6), C(1)−Au(1)−Br(1) 174.6(2).

cases except for that with the benzyl derivative **b** (Scheme 3). This was identified as the bis-carbene species $[Au(NHC)_2]Br$ (**2**), and its formation is likely favored in this case because of its insolubility in THF. Complexes **2** could be formed in excellent yields (82−95%) by reaction of 2 equiv of the imidazolium salt with 1 equiv of [AuCl(tht)] and 2 equiv of $NBu_4(acac)$ in THF with precipitation of the product (Scheme 3ii). Due to its solubility in THF, bis-carbene species **2b** was prepared by reaction in dichloromethane followed by washing with water to remove NBu_4Cl; however, **2b** also exhibits some water solubility and hence was only isolated in moderate yield (63%).

The molecular structures of bis-carbene complexes **2c,d** were obtained by single-crystal X-ray diffraction. Complex **2c** presents an almost ideal linear geometry with a C−Au−C angle of 178.6(5)° (Figure 3). The Au−C bond lengths are 2.011(13) and 2.015(12) Å, which as expected are longer than those in the [AuBr(NHC)] complexes. The molecules are associated in dimers with some secondary $\pi-\pi$ stacking contacts, resulting in a long Au···Au interaction of 3.797 Å between the gold centers. The distance between the centroids of the imidazolyl rings is 3.848 Å, although there are shorter contacts between the carbene carbon and the nitrogen atom of the other molecule. Additionally, a weak Au−C interaction of 3.243 Å is observed with the alkyne carbon. The bromide atoms form hydrogen bonds in an octahedral fashion with the protons of the propargyl units, most of which are above the sum of the van der Waals radii, the shortest value being 2.487 Å.

The structure of complex **2d** is shown in Figure 4. The molecule lies on a 2-fold axis, and therefore only half corresponds to the asymmetric unit. The Au−C distance of 2.21(8) Å is slightly longer than that found in complex **2c**, as expected for a less donating carbene.

The bromide makes weak hydrogen bonds of 2.522 and 2.594 Å with the alkyne protons, giving rise to a supramolecular structure with formation of squares (Figure 5).

Pentafluorophenyl derivatives were also prepared. In this case, reaction of the imidazolium bromide salts with $[Au(C_6F_5)(tht)]$ gave the $[imidazolium][AuBr(C_6F_5)]$ salts and subsequent addition of $NBu_4(acac)$ gave rise to the formation of the desired $[Au(C_6F_5)(NHC)]$ **3** (Scheme 4i). Initial NMR studies of the reaction showed the formation of small amounts of $NBu_4[Au(C_6F_5)_2]$, and washing the reaction mixture with water led to an increase in the ratio of this product compared to the desired $[Au(C_6F_5)(NHC)]$. This can be explained by the equilibrium shown in Scheme 4ii. Since the bis-carbene complexes **2** are soluble in water, washing the reaction mixture with water would result in removal of this product, forcing the equilibrium to produce more with concurrent formation of $NBu_4[Au(C_6F_5)_2]$.

Before washing with water the equilibrium lies far toward the side of the desired product **3**. Therefore, these complexes could be obtained cleanly in high yields by using an alternative purification method. Simply filtering the reaction mixture through silica led to removal of NBu_4Br and any of the byproducts formed as a result of the equilibrium of the products, thus leaving $[Au(C_6F_5)(NHC)]$ **3** in good yields.

The molecular structure of **3c** was obtained by single-crystal X-ray diffraction (Figure 6). The gold center is linearly coordinated with a C−Au−C angle of 175.79(19)°, to two different carbon donor ligands. The $C_{carbene}$−Au distance is 2.022(5) Å, while the $C_{pentafluorophenyl}$−Au distance is 2.048(5) Å.

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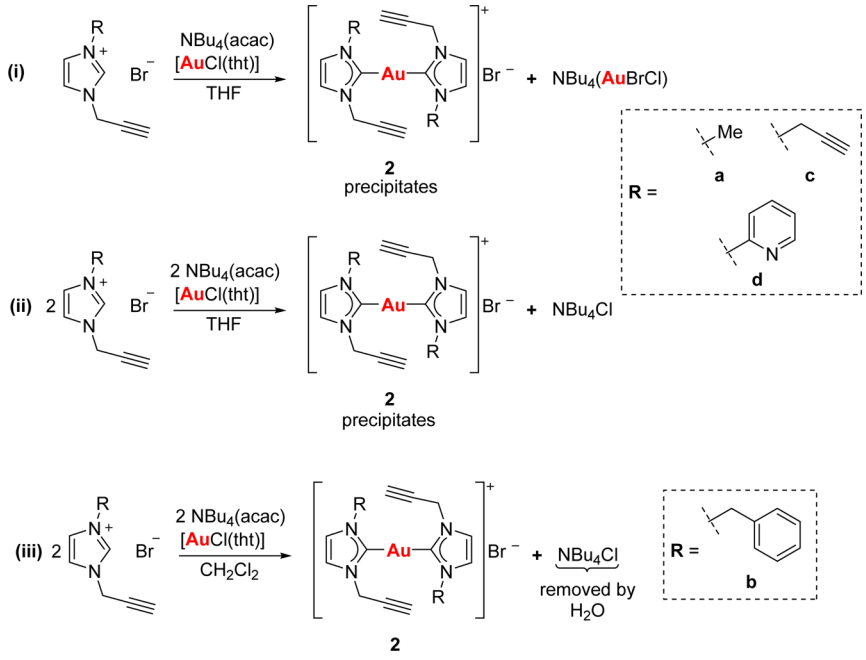
Scheme 3. Formation of [Au(NHC)$_2$]Br Compounds



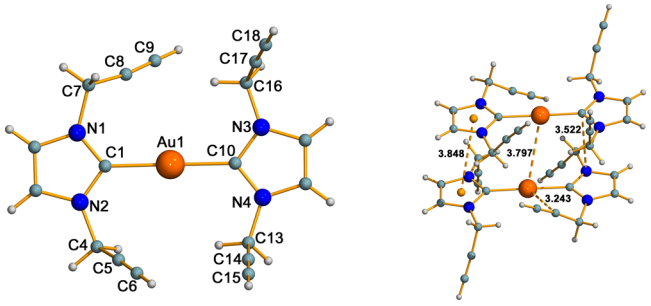


Figure 3. Molecular structure of complex **2c** and associated dimers through different secondary interactions. Selected bond lengths (Å) and angles (deg): Au(1)−C(10) 2.011(13), Au(1)−C(1) 2.015(12), N(1)−C(1) 1.342(15), N(2)−C(1) 1.353(15), N(3)−C(10) 1.368(16), N(4)−C(10) 1.351(17), C(4)−C(5) 1.469(18), C(5)−C(6) 1.185(19), C(7)−C(8) 1.457(17), C(8)−C(9) 1.182(19), C(13)−C(14) 1.489(18), C(14)−C(15) 1.18(2), C(16)−C(17) 1.466(19), C(17)−C(18) 1.19(2), C(10)−Au(1)−C(1) 178.6(5).

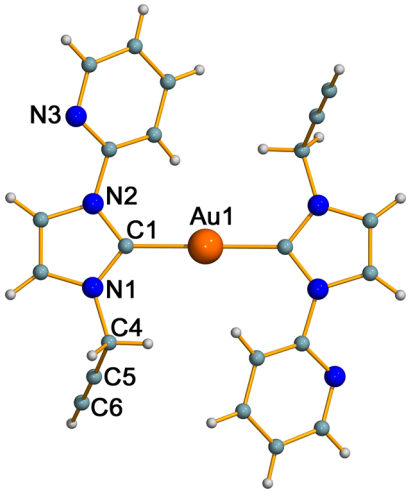


Figure 4. Molecular structure of complex **2d**. Selected bond lengths (Å) and angles (deg): Au(1)−C(1) 2.021(8), C(5)−C(6) 1.176(14), C(5)−C(4) 1.463(15), C(1)#1−Au(1)−C(1) 179.997(1). Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1/2, -y + 1/2, -z$.

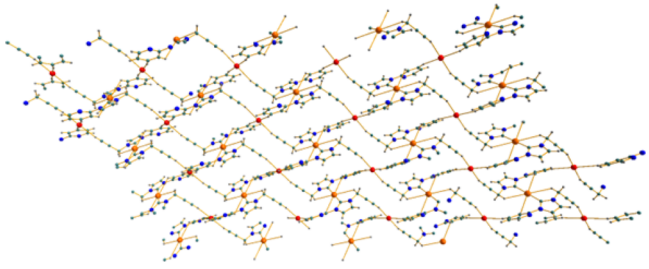


Figure 5. Formation of a supramolecular structure by Br···H interactions in complex **2d**.

The molecules of **3c** are associated in dimers with a weak intermolecular Au···Au interaction of 3.3506(8) Å, together with some slipped $\pi-\pi$ stacking interactions between the imidazolyl and the pentafluorophenyl rings; the shortest contacts are 3.386 and 3.420 Å.

To illustrate the reactivity of these propargyl-functionalized NHC gold complexes, we aimed to deprotonate the alkyne moiety and coordinate to an additional gold center. The reaction of complexes [AuBr(NHC)] (**1**) with HN^{i}Pr$_2$ in the presence of CuI as a catalyst led to the elimination of both the alkyne proton and the bromide ligand bound to gold to afford the sparingly soluble trinuclear complexes **4** (Scheme 5).

The elimination of the alkyne proton has been confirmed by NMR spectroscopy and the formation of trimers by HRMS-(ESI-QTOF), with spectra showing the presence of the molecular peaks $[M + Na]^+$ as the most intense peaks. The IR spectra of these new complexes **4** lack the C≡C−H vibration present in the starting products **1** at around 3260 cm^{-1}, while the −C≡C− vibration mode at around 2160 cm^{-1} is maintained.

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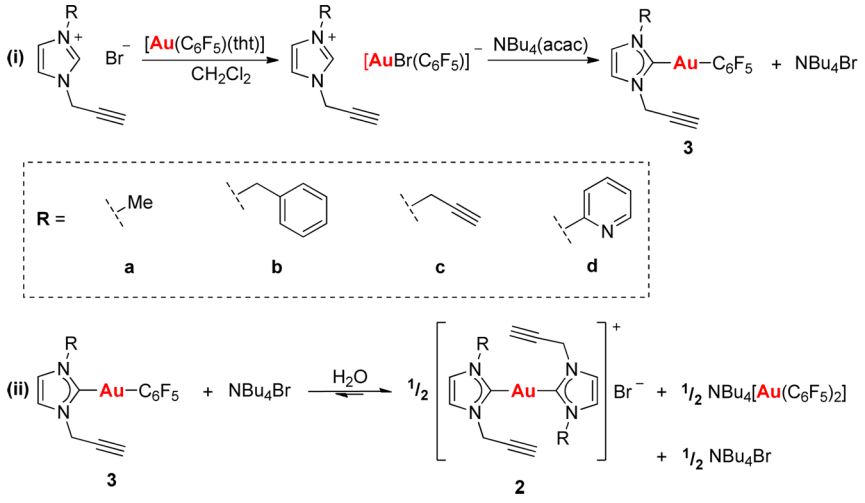
Organometallics XXXX, XXX, XXX−XXX

Scheme 4. Formation of [Au(C_6F_5)(NHC)] Species and Their Equilibrium in Water



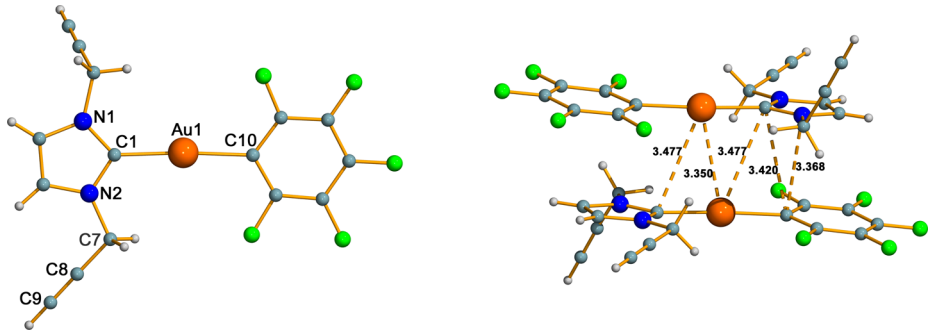
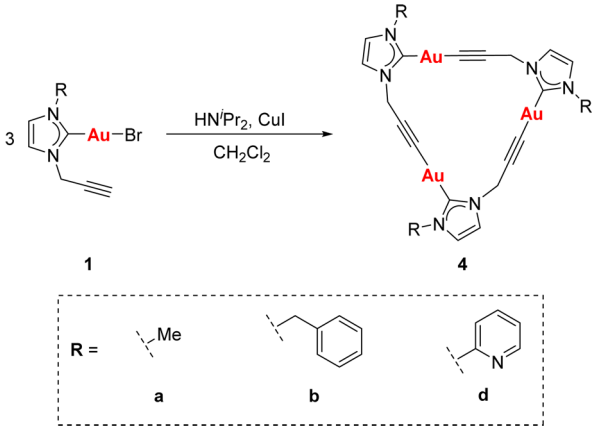


Figure 6. Molecular structure of complex **3c** and formation of dimers through secondary bonds. Selected bond lengths (Å) and angles (deg): Au(1)–C(1) 2.022(5), Au(1)–C(10) 2.048(5), Au(1)–Au(1)#1 3.3506(8), N(1)–C(1) 1.353(7), C(4)–C(5) 1.462(7), C(5)–C(6) 1.181(8), C(7)–C(8) 1.455(8), C(8)–C(9) 1.184(8), C(1)–Au(1)–C(10) 175.79(19).

Scheme 5. Formation of Trimers 4



CONCLUSIONS

Several new propargyl-functionalized NHC gold complexes have been prepared. The recently reported procedure for the synthesis of gold NHC complexes from their corresponding imidazolium salts and NBu_4(acac) has been used with reactions carried out at room temperature in air and using standard reagent grade solvents. All reaction times are under 1 h, and only very basic purification is needed to obtain the pure products in good to excellent yields. These propargyl derivatives show interesting structural features because of the presence of different secondary bonds, including aurophilic interactions for the sterically small NHC complexes, hydrogen bonds between the bromide and the alkyne protons, slipped $\pi-\pi$ interactions between the imidazole rings or between the imidazole and pentafluorophenyl rings, and some close Au–C contacts with the propargyl unit.

These new propargyl-functionalized gold NHC complexes have great potential due to the versatility of the propargyl unit, which may be used as an additional coordination site for the formation of polynuclear complexes, or may be functionalized itself. This is exemplified by the synthesis of interesting trinuclear derivatives with the propargyl-carbene ligand acting as bidentate C^C ligands. Many of the complexes are soluble in water, which could be of significance in the development of biologically active gold complexes or in the development of water-soluble gold catalysts.

EXPERIMENTAL SECTION

Instrumentation. ^{1}H and $^{13}C\{^1H\}$ NMR, including 2D experiments, were recorded at room temperature on a Bruker AVANCE 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100.6 MHz) or on a Bruker AVANCE II 300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75.5 MHz), with chemical shifts (δ, ppm) reported relative to the solvent peaks of the deuterated solvent.[26]

Starting Materials. The starting materials [AuCl(tht)][27] and [Au(C_6F_5)(tht)],[27] 1-pyridylimidazole,[28] and the imidazolium salts[23] were prepared according to published procedures. All other reagents

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Organometallics XXXX, XXX, XXX–XXX

were commercially available. Solvents were used as received without purification or drying.

1,3-Bis(2-propyn-1-yl)-1*H*-imidazol-3-ium Bromide (c). To a solution of imidazole (0.2723 g, 4.0 mmol) in acetonitrile (30 mL) was added propargyl bromide (0.86 mL, 8.0 mmol, 80 wt % solution in toluene) and the mixture heated to reflux for 24 h. After the mixture was cooled to room temperature, solvent was removed in vacuo to leave an oily solid, which was recrystallized in acetonitrile/Et_2O, washed with further Et_2O, and vacuum-dried to give the product as a beige solid (0.2851 g, 32%).

Spectral data are in agreement with those previously reported in the literature.

1-Pyridyl-3-(2-propyn-1-yl)-1*H*-imidazol-3-ium Bromide (d). To a solution of 1-pyridylimidazole (0.7259 g, 5.0 mmol) in acetonitrile (50 mL) was added propargyl bromide (1.1 mL, 10.0 mmol, 80 wt % solution in toluene) and the mixture heated to reflux for 24 h. A pale yellow precipitate formed, which was collected by vacuum filtration, washed with Et_2O, and vacuum-dried to give the product (0.9504 g, 72%).

^{1}H NMR (300 MHz, DMSO): δ 10.20 (s, 1H, N−C*H*−N, imidazole), 8.65 (dd, $^3J_{HH}$ = 4.8, $^4J_{HH}$ = 1.0 Hz, 1H, Py), 8.60 (m, 1H, C*H*), 8.27−8.18 (m, 1H, Py), 8.16−8.05 (m, 2H, Py and C*H*), 7.72−7.60 (m, 1H, Py), 5.35 (d, $^4J_{HH}$ = 2.6 Hz, 2H, CH_2), 3.92 (t, $^4J_{HH}$ = 2.6 Hz, 1H, C≡C*H*). ^{13}C APT (75 MHz, DMSO): δ 149.25 (s, *C*H (Py)), 146.29 (s, *ipso-Py*), 140.63 (s, *C*H (Py)), 135.13 (s, N−*C*−N), 125.39 (s, *C*H (Py)), 123.38 (s, *C*H), 119.74 (s, *C*H), 114.49 (s, *C*H (Py)), 79.30 (s, C≡*C*H), 75.85 (s, *C*≡CH), 39.24 (s, *C*H$_2$−C≡CH).

Synthesis of [AuBr(NHC)] (1). *Complex **1a**.* 1-Methyl-3-(2-propyn-1-yl)-1*H*-imidazol-3-ium bromide (0.0402 g, 0.2 mmol) and [AuCl(tht)] (0.0641 g, 0.2 mmol) were mixed in CH_2Cl_2 (10 mL) until a colorless solution formed (5 min). NBu_4(acac) (0.0683 g, 0.2 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colorless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid, which was collected and vacuum-dried to give the product (0.0646 g, 82%). ^{1}H NMR (400 MHz, DMSO): δ 7.53 (d, $^3J_{HH}$ = 1.9 Hz, 1H, C*H*), 7.48 (d, $^3J_{HH}$ = 1.9 Hz, 1H, C*H*), 5.00 (d, $^4J_{HH}$ = 2.5 Hz, 2H, CH_2), 3.76 (s, 3H, CH_3), 3.59 (t, $^4J_{HH}$ = 2.5 Hz, 1H, C≡C*H*). ^{13}C APT (75 MHz, DMSO): δ 172.52 (s, N−*C*−N), 123.16 (s, *C*H), 121.35 (s, *C*H), 78.21 (s, *C*≡CH), 77.30 (s, C≡*C*H), 39.88 (s, *C*H$_2$) 37.79 (s, *C*H$_3$).

*Complex **1b**.* 1-Benzyl-3-(2-propyn-1-yl)-1*H*-imidazol-3-ium bromide (0.0554 g, 0.2 mmol) and [AuCl(tht)] (0.0641 g, 0.2 mmol) were mixed in CH_2Cl_2 (10 mL) until a colorless solution formed (5 min). NBu_4(acac) (0.0683 g, 0.2 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colorless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid, which was collected and vacuum-dried to give the product (0.0696 g, 74%). ^{1}H NMR (300 MHz, DMSO): δ 7.60 (d, $^3J_{HH}$ = 2.0 Hz, 1H, C*H*), 7.57 (d, $^3J_{HH}$ = 2.0 Hz, 1H, C*H*), 7.42−7.27 (m, 5H, *Ph*), 5.36 (s, 2H, CH_2−Ph), 5.03 (d, $^4J_{HH}$ = 2.5 Hz, 2H, CH_2-C≡CH), 3.60 (t, $^4J_{HH}$ = 2.5 Hz, 1H, C≡*C*H). ^{13}C APT (75 MHz, DMSO): δ 172.55 (s, N−*C*−N), 136.44 (s, *ipso-Ph*), 128.78 (s, *m-Ph*), 128.18 (s, *p-Ph*), 127.65 (s, *o-Ph*), 122.10 (s, *C*H), 121.87 (s, *C*H), 78.02 (s, *C*≡CH), 77.39 (s, C≡*C*H), 53.85 (s, CH$_2$−Ph), 40.03 (s, CH$_2$−C≡CH).

*Complex **1c**.* 1,3-Bis(2-propyn-1-yl)-1*H*-imidazol-3-ium bromide (0.0450 g, 0.2 mmol) and [AuCl(tht)] (0.0641 g, 0.2 mmol) were mixed in CH_2Cl_2 (10 mL) until a colorless solution formed (5 min). NBu_4(acac) (0.0683 g, 0.2 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colorless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid, which was collected and vacuum-dried to give the product (0.0616 g, 73%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.29 (s, 2H, C*H*), 5.04 (d, $^4J_{HH}$ = 2.6 Hz, 4H, CH_2), 2.63 (t, $^4J_{HH}$ = 2.6 Hz, 1H, C≡C*H*). ^{13}C APT (75 MHz, CD_2Cl_2): δ 175.44 (s, N−*C*−N), 121.09 (s, CH), 76.22 (s, C≡CH), 41.48 (s, CH$_2$−C≡CH).

*Complex **1d**.* 1-Pyridyl-3-(2-propyn-1-yl)-1*H*-imidazol-3-ium bromide (0.0528 g, 0.2 mmol) and [AuCl(tht)] (0.0641 g, 0.2 mmol) were mixed in CH_2Cl_2 (10 mL) until a colorless solution formed (5 min). NBu_4(acac) (0.0683 g, 0.2 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colorless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid, which was collected and vacuum-dried to give the product (0.0718 g, 78%). ^{1}H NMR (300 MHz, DMSO): δ 8.63 (m, 1H, Py), 8.20 (dd, $^3J_{HH}$ = 7.1, $^4J_{HH}$ = 1.0 Hz, 1H, Py), 8.17−8.09 (m, 1H, Py), 8.03 (d, $^3J_{HH}$ = 2.1 Hz, 1H, C*H*), 7.82 (d, $^3J_{HH}$ = 2.1 Hz, 1H, C*H*), 7.61 (m, 1H, Py), 5.17 (d, $^4J_{HH}$ = 2.5 Hz, 2H, CH_2), 3.69 (t, $^4J_{HH}$ = 2.5 Hz, 1H, C≡C*H*). ^{13}C APT (75 MHz, DMSO): δ 171.96 (s, N−*C*−N), 150.28 (s, *ipso-Py*), 149.17 (s, *C*H (Py)), 139.61 (s, *C*H (Py)), 124.75 (s, *C*H (Py)), 122.43 (s, *C*H), 121.50 (s, *C*H), 118.07 (s, *C*H (Py)), 77.87 (s, *C*≡CH), 77.80 (s, C≡*C*H), 40.91 (s, *C*H$_2$−C≡CH).

Synthesis of [Au(NHC)$_2$]Br (2). *Complex **2a**.* 1-Methyl-3-(2-propyn-1-yl)-1*H*-imidazol-3-ium bromide (0.0804 g, 0.4 mmol) and [AuCl(tht)] (0.0641 g, 0.2 mmol) were mixed in THF (10 mL) until a colorless solution formed (5 min). NBu_4(acac) (0.1366 g, 0.4 mmol) was added and the mixture stirred. After approximately 30 min a white precipitate formed. The mixture was stirred for 12 h and then the precipitate collected by vacuum filtration and dried to give the product (0.0848 g, 82%). ^{1}H NMR (300 MHz, DMSO): δ 7.60 (d, $^3J_{HH}$ = 1.8 Hz, 1H, C*H* imidazole), 7.55 (d, $^3J_{HH}$ = 1.8 Hz, 1H, C*H* imidazole), 5.13 (d, $^4J_{HH}$ = 2.5 Hz, 2H, CH_2), 3.90 (s, 3H, Me), 3.65 (t, $^4J_{HH}$ = 2.5 Hz, 1H, C≡C*H*). ^{13}C APT (75 MHz, DMSO): δ 183.28 (s, N−*C*−N), 123.51 (s, *C*H), 122.05 (s, *C*H), 78.60 (s, *C*≡CH), 77.45 (s, C≡*C*H), 39.69 (s, CH$_2$−C≡CH), 37.75 (s, CH$_3$). HRMS (ESI/QTOF) m/z: [M]$^+$ calcd for $C_{14}H_{16}AuN_4$ 437.1035; found 437.1049.

*Complex **2b**.* 1-Benzyl-3-(2-propyn-1-yl)-1*H*-imidazol-3-ium bromide (0.1109 g, 0.4 mmol) and [AuCl(tht)] (0.0641 g, 0.2 mmol) were mixed in CH_2Cl_2 (10 mL) until a colorless solution formed (5 min). NBu_4(acac) (0.1366 g, 0.4 mmol) was added and the mixture stirred for 1 h. The solution was washed with H_2O (3 × 25 mL) and dried over Na_2SO_4. The solution was evaporated to minimum volume under reduced pressure and pentane added to precipitate a white solid, which was collected and vacuum-dried to give the product (0.0803 g, 63%). ^{1}H NMR (300 MHz, DMSO): δ 7.70 (s, 1H, C*H*), 7.66 (s, 1H, C*H*), 7.34 (m, 5H, *Ph*), 5.44 (s, 2H, CH_2-Ph), 5.13 (d, $^4J_{HH}$ = 1.9 Hz, 2H, CH_2-C≡CH), 3.64 (s, 1H, C≡C*H*). ^{13}C APT (75 MHz, DMSO): δ 182.89 (s, N−*C*−N), 136.68 (s, *ipso-Ph*), 128.79 (s, *m-Ph*), 128.15 (s, *p-Ph*), 127.63 (s, *o-Ph*), 122.75 (s, *C*H), 122.49 (s, *C*H), 78.36 (s, *C*≡CH), 77.54 (s, C≡*C*H), 53.82 (s, CH$_2$−Ph), 39.96 (s, *C*H$_2$−C≡CH). HRMS (ESI/QTOF) m/z: [M]$^+$ calcd for $C_{26}H_{24}AuN_4$ 589.1661; found 589.1634.

*Complex **2c**.* 1,3-Bis(2-propyn-1-yl)-1*H*-imidazol-3-ium bromide (0.0900 g, 0.4 mmol) and [AuCl(tht)] (0.0641 g, 0.2 mmol) were mixed in THF (10 mL) until a colorless solution formed (5 min). NBu_4(acac) (0.1366 g, 0.4 mmol) was added and the mixture stirred. After approximately 30 min a white precipitate formed. The mixture was stirred for 12 h and then the precipitate collected by vacuum filtration and dried to give the product (0.1074 g, 95%). ^{1}H NMR (300 MHz, DMSO): δ 7.68 (s, 1H, C*H*), 5.20 (d, $^4J_{HH}$ = 2.5 Hz, 2H, CH_2), 3.66 (t, $^4J_{HH}$ = 2.5 Hz, 1H, C≡C*H*). ^{13}C APT (75 MHz, DMSO): δ 183.12 (s, N−*C*−N), 122.32 (s, *C*H), 78.27 (s, *C*≡CH), 77.64 (s, C≡*C*H), 40.13 (s, *C*H$_2$−C≡CH). HRMS (ESI/QTOF) m/z: [M]$^+$ calcd for $C_{18}H_{16}AuN_4$ 485.1035; found 485.1044.

*Complex **2d**.* 1-Pyridyl-3-(2-propyn-1-yl)-1*H*-imidazol-3-ium bromide (0.1056 g, 0.4 mmol) and [AuCl(tht)] (0.0641 g, 0.2 mmol) were mixed in THF (10 mL) until a colorless solution formed (5 min). NBu_4(acac) (0.1366 g, 0.4 mmol) was added and the mixture stirred. After approximately 30 min a white precipitate formed. The mixture was stirred for 12 h and then the precipitate collected by vacuum filtration and dried to give the product (0.1159 g, 90%). ^{1}H NMR (300 MHz, DMSO): δ 8.54 (m, 1H, Py), 8.15 (d, $^3J_{HH}$ = 2.0 Hz, 1H, C*H*), 8.13 (d, $^3J_{HH}$ = 5.3 Hz, 1H, Py), 8.01 (m, 1H, Py), 7.91 (d, $^3J_{HH}$ = 2.0 Hz, 1H, C*H*), 7.59 (m, 1H, Py), 5.27 (d, $^4J_{HH}$ = 2.4 Hz, 2H, CH_2), 3.69 (t, $^4J_{HH}$ = 2.4 Hz, 1H, C≡C*H*). ^{13}C APT (75 MHz, DMSO): δ 181.34 (s, N−*C*−N), 150.01 (s, *ipso-Py*), 148.95 (s, *C*H (Py)), 139.67 (s, *C*H (Py)), 124.65 (s, *C*H (Py)), 123.10 (s, *C*H), 121.71 (s, *C*H), 117.53 (s, *C*H (Py)), 77.96 (s, *C*≡CH), 77.83 (s,

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Organometallics XXXX, XXX, XXX−XXX

C≡CH), 40.87 (s, CH_2−C≡CH). HRMS (ESI/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{18}AuN_6$ 563.1253; found 563.1247.

Synthesis of [Au(C_6F_5)(NHC)] (3). *Complex **3a**.* 1-Methyl-3-(2-propyn-1-yl)-1*H*-imidazol-3-ium bromide (0.0804 g, 0.4 mmol) and [Au(C_6F_5)(tht)] (0.1809 g, 0.4 mmol) were mixed in CH_2Cl_2 (10 mL) until a colorless solution formed (5 min). NBu_4(acac) (0.1366 g, 0.4 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colorless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid, which was collected and vacuum-dried to give the product (0.1466 g, 76%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.23 (d, $^3J_{HH}$ = 1.9 Hz, 1H, C*H*), 7.02 (d, $^3J_{HH}$ = 1.9 Hz, 1H, C*H*), 5.09 (d, $^4J_{HH}$ = 2.6 Hz, 2H, CH_2), 3.90 (s, 3H, CH_3), 2.61 (t, $^4J_{HH}$ = 2.6 Hz, 1H, C≡C*H*). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −116.54 to −116.86 (m, 2F, *o*-C_6F_5), −160.80 (t, $^3J_{FF}$ = 19.8 Hz, 1F, *p*-C_6F_5), −163.61 to −163.89 (m, 2F, *m*-C_6F_5). ^{13}C APT (75 MHz, CD_2Cl_2): δ 188.06 (s, N−*C*−N), 122.90 (s, *C*H), 120.73 (s, *C*H), 76.90 (s, *C*≡CH), 75.73 (s, C≡*C*H), 40.90 (s, CH_2−C≡CH), 38.51 (s, CH_3).

*Complex **3b**.* 1-Benzyl-3-(2-propyn-1-yl)-1*H*-imidazol-3-ium bromide (0.1109 g, 0.4 mmol) and [Au(C_6F_5)(tht)] (0.1809 g, 0.4 mmol) were mixed in CH_2Cl_2 (10 mL) until a colorless solution formed (5 min). NBu_4(acac) (0.1366 g, 0.4 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colorless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid, which was collected and vacuum-dried to give the product (0.1758 g, 78%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.49−7.32 (m, 5H, Ph), 7.25 (d, $^3J_{HH}$ = 1.9 Hz, 1H, C*H*), 7.03 (d, $^3J_{HH}$ = 1.9 Hz, 1H, C*H*), 5.43 (s, 2H, CH_2-Ph), 5.11 (d, $^4J_{HH}$ = 2.6 Hz, 1H, CH_2-C≡CH), 2.61 (t, $^3J_{HH}$ = 2.6 Hz, 1H, C≡C*H*). ^{19}F NMR (282 MHz, CD_2Cl_2): δ −115.78 to −117.58 (m, 2F, *o*-C_6F_5), −160.81 (t, $^3J_{FF}$ = 19.8 Hz, 1F, *p*-C_6F_5), −163.16 to −165.55 (m, 2F, *m*-C_6F_5). ^{13}C APT (75 MHz, CD_2Cl_2): δ 187.70 (s, N−*C*−N), 136.19 (s, *ipso-Ph*), 129.56 (s, *m-Ph*), 129.21 (s, *p-Ph*), 128.75 (s, *o-Ph*), 121.64 (s, *C*H), 121.16 (s, *C*H), 76.76 (s, *C*≡CH), 75.89 (s, C≡*C*H), 55.63 (s, CH_2−Ph), 41.09 (s, CH_2−C≡CH).

*Complex **3c**.* 1,3-Bis(2-propyn-1-yl)-1*H*-imidazol-3-ium bromide (0.0900 g, 0.4 mmol) and [Au(C_6F_5)(tht)] (0.1809 g, 0.4 mmol) were mixed in CH_2Cl_2 (10 mL) until a colorless solution formed (5 min). NBu_4(acac) (0.1366 g, 0.4 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colorless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid, which was collected and vacuum-dried to give the product (0.1768 g, 87%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.29 (s, 2H, C*H*), 5.10 (d, $^4J_{HH}$ = 2.6 Hz, 2H, CH_2), 2.63 (t, $^4J_{HH}$ = 2.6 Hz, 1H, C≡C*H*). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −116.09 to −116.87 (m, 2F, *o*-C_6F_5), −160.34 (t, $^3J_{FF}$ = 19.8 Hz, 1F, *p*-C_6F_5), −163.26 to −163.61 (m, 2F, *m*-C_6F_5). ^{13}C APT (75 MHz, CD_2Cl_2): δ 187.87 (s, N−*C*−N), 121.18 (s, *C*H), 76.55 (s, *C*≡CH), 76.03 (s, C≡*C*H), 41.19 (s, CH_2−C≡CH).

*Complex **3d**.* 1-Pyridyl-3-(2-propyn-1-yl)-1*H*-imidazol-3-ium bromide (0.1056 g, 0.4 mmol) and [Au(C_6F_5)(tht)] (0.1809 g, 0.4 mmol) were mixed in CH_2Cl_2 (10 mL) until a colorless solution formed (5 min). NBu_4(acac) (0.1366 g, 0.4 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colorless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid, which was collected and vacuum-dried to give the product (0.1911 g, 87%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.77 (d, $^3J_{HH}$ = 8.2 Hz, 1H, Py), 8.62−8.41 (m, 1H, Py), 8.01−7.85 (m, 2H, Py and C*H*), 7.51−7.19 (m, 2H, Py and C*H*), 5.28 (d, $^4J_{HH}$ = 2.6 Hz, 2H, CH_2), 2.68 (t, $^4J_{HH}$ = 2.6 Hz, 1H, C≡C*H*). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −116.43 to −116.65 (m, 2F, *o*-C_6F_5), −160.56 (t, $^3J_{FF}$ = 19.8 Hz, 1F, *p*-C_6F_5), −163.56 to −163.82 (m, 2F, *m*-C_6F_5). ^{13}C APT (75 MHz, CD_2Cl_2): δ 186.66 (s, N−*C*−N), 149.29 (s, *C*H (Py)), 139.37 (s, *C*H (Py)), 124.52 (s, *C*H (Py)), 121.22 (s, *C*H), 121.08(s, CH), 120.13(s, *ipso-Py*), 117.69 (s, *C*H (Py)), 76.19 (s, C≡*C*H), 75.23(*C*≡CH), 42.00 (s, CH_2−C≡CH).

Synthesis of [Au(RImCH$_2$C≡C)]$_3$ (4). *Complex **4a**.* To a solution of **1a** (0.0397 g, 0.1 mmol) in CH_2Cl_2 (5 mL) were added diisopropylamine (0.0350 mL, 0.25 mmol) and CuI (2 mg), and the mixture was stirred for 2 h. A pale yellow precipitate formed, which was collected by vacuum filtration, washed with distilled water (20 mL) and acetone (20 mL), and vacuum-dried to give the product (0.0242 g, 77%). ^{1}H NMR (400 MHz, DMSO): δ 7.52 (s, 1H, C*H*), 7.45 (s, 1H, C*H*), 5.14 (s, 2H, CH_2), 3.85 (s, 3H, CH_3). ^{13}C APT (75 MHz, DMSO): δ 182.74 (s, N−*C*−N), 122.45 (s, *C*H), 122.18 (s, *C*H), 102.90(s, *C*≡CH), 43.29 (s, CH_2), 38.01 (s, CH_3). HRMS (ESI-QTOF) m/z: $[M + 3MeOH + Na]^+$ calcd for $C_{24}H_{33}Au_3N_6O_3Na$ 1067.1503; found 1067.1523.

*Complex **4b**.* To a solution of **1b** (0.0473 g, 0.1 mmol) in CH_2Cl_2 (5 mL) were added diisopropylamine (0.0350 mL, 0.25 mmol) and CuI (2 mg), and the mixture was stirred for 2 h. A white precipitate formed, which was collected by vacuum filtration, washed with distilled water (20 mL) and acetone (20 mL), and vacuum-dried to give the product (0.0255 g, 65%). ^{1}H NMR (400 MHz, DMSO): δ 7.54−7.28 (m, 7H, 2C*H* + Ph), 5.30 (s, 2H, CH_2), 5.17 (s, 2H, CH_2). The compound was too insoluble to obtain a ^{13}C NMR spectrum. HRMS (ESI-QTOF) m/z: $[M + Na]^+$ calcd for $C_{39}H_{33}Au_3N_6Na$ 1199.1655; found 1199.1721.

*Complex **4d**.* To a solution of **1d** (0.0460 g, 0.1 mmol) in CH_2Cl_2 (5 mL) were added diisopropylamine (0.0350 mL, 0.25 mmol) and CuI (2 mg), and the mixture was stirred for 2 h. A white precipitate formed, which was collected by vacuum filtration, washed with distilled water (20 mL) and acetone (20 mL), and vacuum-dried to give the product (0.0311 g, 82%). The compound was too insoluble to obtain NMR spectra. HRMS (ESI-QTOF) m/z: $[M + Na]^+$ calcd for $C_{33}H_{24}Au_3N_9Na$ 1160.1043; found 1160.1031.

Crystallography. Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of a Xcalibur Oxford Diffraction diffractometer equipped with a low-temperature attachment. Data were collected using monochromated Mo Kα radiation (λ = 0.71073 Å). Scan type ω. An absorption correction based on multiple scans was applied using spherical harmonics implemented in the SCALE3 ABSPACK[29] scaling algorithm. The structures were solved by direct methods and refined on F^2 using the program SHELXL-97.[30] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in some cases in calculated positions and refined using a riding model but in other cases were localized in the Fourier map. Refinements were carried out by full-matrix least squares on F^2 for all data. Further details of the data collection and refinement are given in Tables S1−S7 in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00012.

X-ray crystallographic data for complexes **1a−d**, **2c,d**, and **3c** (CCDC reference numbers 1517836−1517842) and NMR spectra for all of the compounds (PDF)
Crystallographic data (CIF)
Crystallographic data (CIF)
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Notes

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Organometallics XXXX, XXX, XXX−XXX

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