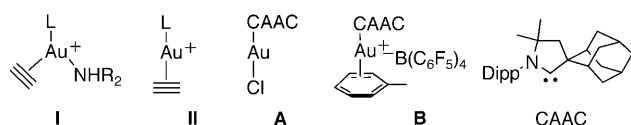


Serendipitous Discovery of the Catalytic Hydroammoniation and Methylation of Alkynes**

Xiaoming Zeng, Rei Kinjo, Bruno Donnadieu, and Guy Bertrand*

The transition-metal-catalyzed hydroamination reaction, that is, the addition of an N–H bond across a carbon–carbon multiple bond, has been widely studied.^[1,2] We have recently reported that cationic gold(I) complexes,^[3,4] supported by cyclic (alkyl)(amino)carbene (CAAC) ligands,^[5] readily catalyze the intermolecular hydroamination of alkynes with a variety of amines,^[6] including ammonia.^[6c] Based on preliminary mechanistic studies, we postulated that the key step of the catalytic cycle was the formation of a tricoordinate gold complex (**I**), which was followed by inner-sphere C–N bond formation, as first postulated by Tanaka et al.,^[7a] and Nishina and Yamamoto^[7b,c] (Scheme 1). However, for other gold

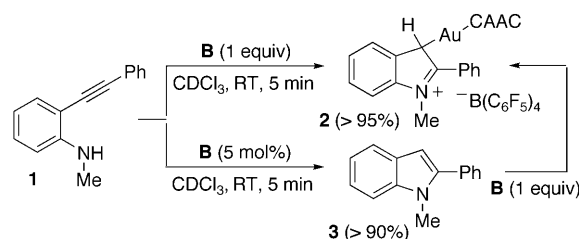


Scheme 1. Possible intermediates **I** and **II** in the gold-catalyzed hydroamination of alkynes, and the gold complexes **A** and **B** used in this study.

catalysts,^[8] Che et al.^[9a] and Li et al.^[9b] hypothesized an outer-sphere nucleophilic attack to the alkyne complex **II**, a mechanism widely accepted for palladium^[10] and platinum complexes.^[11] Herein, our attempts to isolate a gold(I) complex of type **I** have led to the structural characterization of two (CAAC)(η^1 -alkene)Au^I complexes, and to the discovery of two catalytic reactions: the intramolecular hydroamination using tertiary ammonium salts, and the aminomethylation of carbon–carbon triple bonds.

For obvious entropic reasons, intramolecular hydroamination reactions occur under much milder conditions than their intermolecular analogues, and therefore are better suited for characterizing reaction intermediates. We first chose N-methyl-2-(2-phenylethynyl)aniline (**1**), as the rigidity

of the phenyl spacer group places both the amino and the alkyne moieties in the ideal positions to coordinate to the metal center. The reaction of **1** with a stoichiometric amount of cationic gold(I) complex **B** at room temperature was monitored by multinuclear NMR spectroscopy. The instantaneous disappearance of both **1** and **B** was observed, along with the formation of a new complex, which was isolated in near quantitative yield. However, the spectroscopic data suggested that it was not the desired tricoordinate gold(I) complex of type **I**, but rather complex **2**, presumably formed from the coordination of the hydroamination product **3** to the metal (Scheme 2). Even by monitoring the reaction at -70°C ,



Scheme 2. Stoichiometric and catalytic gold(I)-catalyzed intramolecular hydroamination of **1**.

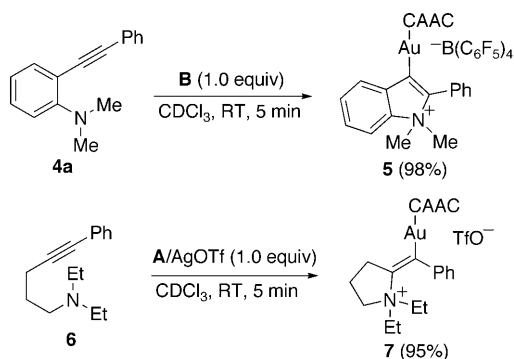
no trace of starting material **1** could be observed, the conversion into **2** being complete in a few seconds. The high catalytic activity was confirmed using 5 mol % of **B**; at room temperature, heterocycle **3** formed instantaneously in almost quantitative yield. As expected, addition of one equivalent of **B** to heterocycle **3** led cleanly to complex **2**.

To prevent the hydroamination process, and thereby possibly characterize a putative tricoordinate gold(I) complex, we prepared the corresponding tertiary amine **4a**. A stoichiometric amount of cationic gold(I) complex **B** was added at room temperature to a solution of **4a** in CDCl_3 , and the reaction was monitored by NMR spectroscopy (Scheme 3). Once again, we observed the instantaneous disappearance of both **4a** and **B**, and the clean formation of a new complex **5**, which was isolated in 98% yield. Surprisingly, single-crystal X-ray diffraction^[12] revealed that **5** was a gold(I) η^1 -alkene complex resulting from the addition of the tertiary amino group to the coordinated alkyne (Figure 1, left). Complex **5** is structurally reminiscent of complexes recently isolated by Hammond et al.,^[13] and Gagné et al.,^[14] from the gold-promoted cyclization of allenates, and the intramolecular hydroarylation of allenates, respectively.^[15] Interestingly, the formation of gold(I) η^1 -alkene complexes of type **5** is not limited to the rigid 2-alkynyl-benzenamine **4a**. A mixture of (CAAC)AuCl(**A**)/AgOTf (1:1) instantaneously

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Scheme 3. Synthesis of complexes **5** and **7**.

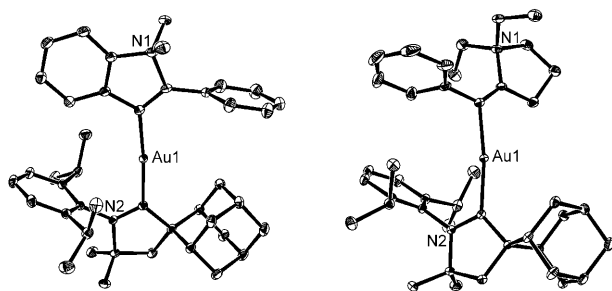
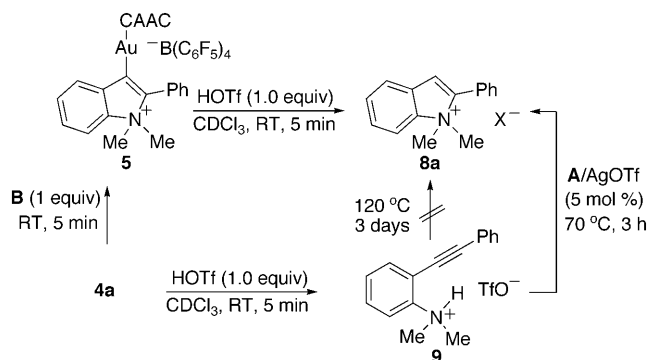


Figure 1. ORTEP of gold complexes **5** (left) and **7** (right); ellipsoids set at 50% probability. Hydrogen atoms, solvent molecules, and the corresponding counterions are omitted for clarity.

reacted stoichiometrically at room temperature with aliphatic *N,N*-diethylamino alkyne **6** to afford complex **7**, which was isolated in 95% yield and fully characterized (Figure 1, right).

Not surprisingly, treatment of complex **5** with one equivalent of trifluoromethanesulfonic acid induced immediate proto-deauration,^[2,16] affording the corresponding gold-free cyclic ammonium salt **8a** (Scheme 4). The stoichiometric two-step transformation of **4a** into **8a** (through **5**) led to the question of whether this process could be catalytic for gold, or if the presence of triflic acid would preferentially protonate the basic tertiary amine,^[7a,17] preventing the cyclization process. Addition of one equivalent of triflic acid to solution of alkynyl amine **4a** in chloroform readily gave rise to the corresponding acyclic ammonium salt **9**. In the absence of the



Scheme 4. Stoichiometric and catalytic syntheses of **8a**. X = TfO.

gold catalyst, no cyclization occurred, even under heating a CDCl_3 solution of **9** in a sealed tube at 120 °C for three days^[18] (Table 1, entry 1). In contrast, we were pleased to observe that in the presence of 5 mol% of a 1:1 mixture of (CAAC)AuCl(**A**)/AgOTf, derivative **9** underwent the desired cyclization to form **8a** in 98% yield after only 3 h at 70 °C (Table 1, entry 2).

Table 1: Gold(I)-catalyzed intramolecular hydroammoniation of **4** with HOTf.^[a]

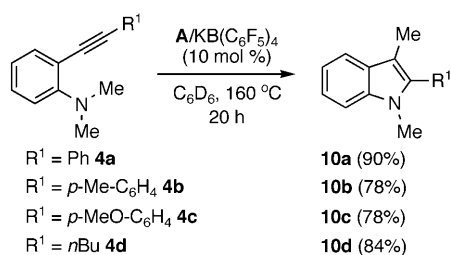
Entry	4	R ¹	R ²	R ³	T [°C]	t [h]	8	Yield [%] ^[b]
1	4a	Ph	Me	Me	120	72	8a	0 ^[c]
2	4a	Ph	Me	Me	70	3	8a	98
3	4b	<i>p</i> -Me-C ₆ H ₄	Me	Me	60	2.5	8b	99
4	4c	<i>p</i> -MeO-C ₆ H ₄	Me	Me	60	2.5	8c	99
5	4d	<i>n</i> Bu	Me	Me	60	2	8d	97
6	4e	Ph	Me	Et	60	7	8e	94
7	4f	Ph	Me	Ph	25	0.5	8f	99

[a] **A** (5 mol%), AgOTf (5 mol%), **4** (0.25 mmol), HOTf (0.25 mmol), CDCl_3 (0.4 mL). [b] Yields were determined by ¹H NMR spectroscopy using benzylmethyl ether as an internal standard. [c] No catalyst was used.

Following a brief investigation into the scope of this hydroammoniation reaction, we found that aryl or alkyl substituents were tolerated on the alkyne, and that the cyclization process occurred under milder conditions when a more weakly basic amine was used. For example, the hydroammoniation of **4f** readily occurred in a few minutes at room temperature (Table 1, entry 7).

Examples in the literature of the direct carboamination of alkynes (the addition of a carbon–nitrogen bond to a carbon–carbon triple bond) are very rare. Yamamoto et al.^[19] have reported the platinum- and palladium-catalyzed intramolecular C–N bond addition of amides and N,O-acetals, and Cacchi et al.^[20] reported the palladium-catalyzed cyclization of 2-alkynyl-*N*-allyl-*N'*-trifluoroacetyl benzenamine. Although the cleavage of a relatively weak carbon–nitrogen bond was involved in both cases, these results prompted us to investigate the related methylation reaction: in the presence of 10 mol% of a 1:1 mixture of (CAAC)AuCl(**A**)/KB(C₆F₅)₄, 2-alkynyl-*N,N'*-dimethyl-benzenamines **4a–d** was transformed into 2,3-disubstituted indoles **10a–d** in good to excellent yields after 20 h at 160 °C (Scheme 5). This rearrangement tolerates aryl or alkyl substituents on the alkyne. However, in the case of the *N*-ethyl-*N'*-methyl-benzenamine **4e**, loss of ethylene was observed, and the 3-unsubstituted indole **3** was cleanly formed.

These results suggest that, at least for the intramolecular variant, the gold-catalyzed hydroamination of alkynes does not involve a tricoordinate gold complex of type **I**. Importantly, cationic gold(I) complexes supported by CAAC ligands promote the intramolecular hydroammoniation



Scheme 5. First examples of catalytic methylamination of alkyne.

and methylamination reactions of alkynes. The scope of these catalytic reactions is under investigation.

Experimental Section

All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques.

Complex 2: A dried J-Young tube was loaded with gold complex **B** (0.10 g, 0.074 mmol), 2-alkynyl-*N*-methyl-benzenamine **1** (0.016 g, 0.075 mmol), and CD_2Cl_2 (0.5 mL). The reaction was monitored by NMR spectroscopy, and it had proceeded to completion after 5 min. Removal of the solvent under vacuum and washing with *n*-hexane gave gold complex **2** as a white solid (96% yield); m.p. 160 °C; ^{13}C NMR (126 MHz, CD_2Cl_2) $\delta = 22.9$ (CH_3), 23.0 (CH_3), 26.87 (CH_3), 26.90 (CH_3), 27.4 (CH), 28.4 (CH), 29.5 ($\text{CH} \times 2$), 29.5 (CCH_3), 29.6 (CCH_3), 33.5 (NCH_3), 34.6 ($\text{CH}_2 \times 2$), 35.4 (CH_2), 35.9 (CH_2), 37.39 (CH), 37.42 (CH), 39.1 (CH_2), 48.6 (CH_2), 64.6 (C^q), 67.1 ($\text{C}(\text{H})\text{Au}$), 79.1 (C^q), 112.7 (CH), 122.1 (CH), 124.6 (br, C^q), 125.6 (CH), 125.8 (CH), 126.0 (CH), 126.2 (CH), 128.6 (C^q), 129.9 ($\text{C}^m\text{H} \times 2$ and $\text{CH} \times 2$), 131.0 (C^pH), 131.8 (CH), 134.0 (C^q), 135.7 (C^q), 136.9 (d, $J_{\text{CF}} = 242.8$ Hz, C^q), 138.9 (d, $J_{\text{CF}} = 242.6$ Hz, C^q), 140.8 (C^q), 145.1 (C^q), 145.8 (C^q), 148.8 (d, $J_{\text{CF}} = 238.3$ Hz, C^q), 164.4 (C^q), 242.7 ppm ($\text{C}_{\text{carbene}}$).

Complex 5: A dried J-Young tube was loaded with gold complex **B** (0.15 g, 0.112 mmol), amino alkyne **4a** (0.025 g, 0.112 mmol), and CDCl_3 (0.4 mL). After 5 min, the solvent was removed under vacuum, and the solid residue washed with *n*-hexane to give complex **5** as a white solid (98% yield). Single crystals were obtained by recrystallization from a CH_2Cl_2 /*n*-hexane/toluene (10:20:1) solution at -20 °C; m.p. 243 °C; ^{13}C NMR (75 MHz, CDCl_3): $\delta = 23.0$ (CH_3), 26.5 (CH_3), 27.0 (CH), 27.8 (CH), 29.0 (CH), 29.1 (CH_3), 34.2 (CH_2), 35.2 (CH_2), 37.1 (CH), 38.8 (CH_2), 48.4 (CH_2), 51.9 (CH_3), 65.1 (C^q), 77.9 (C^q), 115.5 (CH), 125.0 (CH), 127.7 (CH), 128.0 (CH), 129.3 (CH), 129.6 (CH), 130.3 (CH), 130.7 (CH), 132.2 (CH), 135.4 (C^q), 136.3 (d, $J_{\text{CF}} = 246.6$ Hz, C^q), 138.2 (d, $J_{\text{CF}} = 245.4$ Hz, C^q), 142.7 (C^q), 144.9 (C^q), 145.3 (C^q), 147.6 (C^q), 138.3 (d, $J_{\text{CF}} = 239.5$ Hz, C^q), 154.7 (C^q), 159.5 (C^q), 259.7 ppm ($\text{C}_{\text{carbene}}$).

Complex 7: Complex **A** (0.043 g, 0.071 mmol) and AgOTf (0.021 g, 0.071 mmol) were loaded in a dried J-Young tube; CDCl_3 (0.4 mL) and **6** (0.015 g, 0.071 mmol) were added, and the tube was sealed. The reaction was monitored by NMR spectroscopy. After removing the solvent under vacuum, the residue was washed with *n*-hexane to give gold complex **7** as a white solid (95% yield). Single crystals were obtained by recrystallization from a CHCl_3 /*n*-hexane (1:1) solution at -20 °C; m.p. 199 °C; ^{13}C NMR (126 MHz, CDCl_3): $\delta = 9.7$ (CH_3), 22.9 (CH_2), 23.4 (CH_3), 26.1 (CH_3), 27.2 (CH), 28.0 (CH), 29.1 (CH), 29.4 (CH_2), 34.5 (CH_2), 35.2 (CH_2), 36.3 (CH_2), 37.2 (CH), 39.0 (CH_2), 49.0 (CH_2), 60.6 (CH_2), 63.1 (CH_2), 64.7 (C^q), 77.9 (C^q), 121.0 (C^q , q, $J_{\text{CF}} = 320.5$ Hz), 123.1 (CH), 124.1 (CH), 125.0 (CH), 128.3 (CH), 129.6 (CH), 133.0 (C^q), 136.2 (C^q), 145.2 (C^q), 145.3 (C^q), 161.5 (C^q), 258.5 ppm ($\text{C}_{\text{carbene}}$).

General procedure for the catalytic hydroammoniumation reaction: CAAC(AuCl) complex **A** (0.008 g, 0.0125 mmol) and AgOTf (0.003 g, 0.0125 mmol) were loaded in a dried J-Young tube; CDCl_3

(0.4 mL), the internal standard (benzyl methyl ether), derivatives **4** (0.25 mmol), and HOTf (37 mg, 0.25 mmol) were added, the tube was sealed, placed in an oil bath, and heated at the specified temperature (Table 1). The reaction was monitored by NMR spectroscopy.

General procedure for the catalytic methylamination of **4**: CAAC(AuCl) complex **A** (0.030 g, 0.05 mmol) and $\text{KB}(\text{C}_6\text{F}_5)_4$ (0.036 g, 0.05 mmol) were loaded in a dried J-Young-Tube. C_6D_6 (0.5 mL) and **4a–d** (0.5 mmol) were then added. The tube was sealed, placed in an oil bath, and heated at 160 °C for 20 h. Heterocycle **10a–d** was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane 5:95).

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