Serendipitous Discovery of the Catalytic Hydroammoniumation and Methylamination of Alkynes

ARTICLE *in* ANGEWANDTE CHEMIE INTERNATIONAL EDITION · JANUARY 2010

Impact Factor: 11.26 · DOI: 10.1002/anie.200905341 · Source: PubMed

Published in final edited form as:
Angew Chem Int Ed Engl. 2010 ; 49(5): 942–945. doi:10.1002/anie.200905341.

Serendipitous Discovery of the Catalytic Hydroammoniumation and Methylamination of Alkynes**

Xiaoming Zeng, **Rei Kinjo**, **Bruno Donnadieu**, and **Guy Bertrand**
UCR-CNRS Joint Research Chemistry Laboratory (UMI 2957), Department of Chemistry, University of California Riverside, Riverside, CA 92521-0403 (USA), Fax: (+1)951-827-2725, guy.bertrand@ucr.edu, Homepage: http://research.chem.ucr.edu/groups/bertrand/guy-bertrandwebpage/

Keywords

alkynes; gold; homogeneous catalysis; hydroamination; methylamination

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 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 hydroammoniumation 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, 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

**We are grateful to the NIH (R01 GM 68825) and the DOE (DE-FG02-09ER16069) for the financial support of this work, and to the China Scholarship Council (X.Z.), and the Japan Society for the Promotion of Science (R.K.) for fellowships.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200905341.

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 allenoates, and the intramolecular hydroarylation of allenes, 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 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 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).

Following a brief investigation into the scope of this hydroammoniumation 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 hydroammoniumation of **4 f** 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 methylamination reaction: in the presence of 10 mol% of a 1:1 mixture of (CAAC)AuCl(**A**)/$KB(C_6F_5)_4$, 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 hydroammoniumation 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) δ =22.9 (*C*H_3), 23.0 (*C*H_3), 26.87 (*C*H_3), 26.90 (*C*H_3), 27.4 (*C*H), 28.4 (*C*H), 29.5 (*C*H × 2), 29.5 (C*C*H_3), 29.6 (C*C*H_3), 33.5 (N*C*H_3), 34.6 (*C*H_2 × 2), 35.4 (*C*H_2), 35.9 (*C*H_2), 37.39 (*C*H), 37.42 (*C*H), 39.1 (*C*H_2), 48.6 (*C*H_2), 64.6 (C^q), 67.1 (*C*(H)Au), 79.1 (C^q), 112.7 (*C*H), 122.1 (*C*H), 124.6 (br, C^q), 125.6 (*C*H), 125.8 (*C*H), 126.0 (*C*H), 126.2 (*C*H), 128.6 (C^q), 129.9 (C^mH × 2 and *C*H × 2), 131.0 (C^pH), 131.8 (*C*H), 134.0 (C^q), 135.7 (C^i), 136.9 (d, J_{CF} = 242.8 Hz, C^q), 138.9 (d, J_{CF} = 242.6 Hz, C^q), 140.8 (C^q), 145.1 (C^o), 145.8 (C^o), 148.8 (d, J_{CF} = 238.3 Hz, C^q), 164.4 (C^q), 242.7 ppm ($C_{carbene}$).

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, $CDCl_3$): δ = 23.0 (*C*H_3), 26.5 (*C*H_3), 27.0 (*C*H), 27.8 (*C*H), 29.0 (*C*H), 29.1 (*C*H_3), 34.2 (*C*H_2), 35.2 (*C*H_2), 37.1 (*C*H), 38.8 (*C*H_2), 48.4 (*C*H_2), 51.9 (*C*H_3), 65.1 (C^q), 77.9 (C^q), 115.5 (*C*H), 125.0 (*C*H), 127.7 (*C*H), 128.0 (*C*H), 129.3 (*C*H), 129.6 (*C*H), 130.3 (*C*H), 130.7 (*C*H), 132.2 (*C*H), 135.4 (C^q), 136.3 (d, J_{CF} = 246.6 Hz, C^q), 138.2 (d, $J_{C–F}$ = 245.4 Hz, C^q), 142.7 (C^q), 144.9 (C^q), 145.3 (C^q), 147.6 (C^q), 138.3 (d, $J_{C–F}$ = 239.5 Hz, C^q), 154.7 (C^q), 159.5 (C^q), 259.7 ppm ($C_{carbene}$).

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, $CDCl_3$): δ =9.7 (*C*H_3), 22.9 (*C*H_2), 23.4 (*C*H_3), 26.1 (*C*H_3), 27.2 (*C*H), 28.0 (*C*H), 29.1 (*C*H), 29.4 (*C*H_3), 34.5 (*C*H_2), 35.2 (*C*H_2), 36,3 (*C*H_2), 37.2 (*C*H), 39.0 (*C*H_2), 49.0 (*C*H_2), 60.6 (*C*H_2), 63.1 (*C*H_2), 64.7 (C^q), 77.9 (C^q), 121.0 (C^q, q, J_{CF} = 320.5 Hz), 123.1 (*C*H), 124.1 (*C*H), 125.0 (*C*H), 128.3 (*C*H), 129.6 (*C*H), 133.0 (C^q), 136.2 (C^q), 145.2 (C^q), 145.3 (C^q), 161.5 (C^q), 258.5 ppm ($C_{carbene}$).

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 $KB(C_6F_5)_4$ (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).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

References

1. For recent reviews on hydroamination reactions, see: a) Müller TE, Hultzsch KC, Yus M, Foubelo F, Tada M. Chem Rev 2008;108:3795–3892. [PubMed: 18729420] b) Severin R, Doye S. Chem Soc Rev 2007;36:1407–1420. [PubMed: 17660874] c) Aillaud I, Collin J, Hannedouche J, Schulz E. Dalton Trans 2007:5105–5118. [PubMed: 17985016] d) Matsunaga S. J Synth Org Chem Jpn 2006;64:778–779. e) Roesky PW. Z Anorg Allg Chem 2006;632:1918–1926. f) Odom AL. Dalton Trans 2005:225–233. [PubMed: 15616708] g) Hazari N, Mountford P. Acc Chem Res 2005;38:839–849. [PubMed: 16285707] h) Hartwig JF. Pure Appl Chem 2004;76:507–516. i) Hong S, Marks TJ. Acc Chem Res 2004;37:673–686. [PubMed: 15379583] j) Beller M, Seayad J, Tillack A, Jiao H. Angew Chem 2004;116:3448–3479.Angew. Chem. Int. Ed. 2004;43:3368–3398.
2. For recent reviews on gold-catalyzed hydroamination, see: a) Li Z, Brouwer C, He C. Chem Rev 2008;108:3239–3265. [PubMed: 18613729] b) Arcadi A. Chem Rev 2008;108:3266–3325. [PubMed: 18651778] c) Gorin DJ, Sherry BD, Toste FD. Chem Rev 2008;108:3351–3378. [PubMed: 18652511] d) Patil NT, Yamamoto Y. Chem Rev 2008;108:3395–3442. [PubMed: 18611054] e) Widenhoefer RA. Chem Eur J 2008;14:5382–5391. f) Krause N, Belting V, Deutsch C, Erdsack J, Fan HT, Gockel B, Hoffmann-Roder A, Morita N, Volz F. Pure Appl Chem 2008;80:1063–1069. g) Fürstner A, Davies PW. Angew Chem 2007;119:3478–3519.Angew Chem Int Ed 2007;46:3410–3449. h) Widenhoefer RA, Han X. Eur J Org Chem 2006:4555–4563.
3. a) Lavallo V, Frey GD, Kousar S, Donnadieu B, Bertrand G. Proc Natl Acad Sci USA 2007;104:13569–13573. [PubMed: 17698808] b) Frey GD, Dewhurst RD, Kousar S, Donnadieu B, Bertrand G. J Organomet Chem 2008;693:1674–1682. [PubMed: 19343084]
4. A few examples of similar cationic gold(I) complexes, bearing very bulky phosphine ligands, have been reported; see: Herrero-Gómez E, Nieto-Oberhuber C, López S, Benet-Buchholz J, Echavarren AM. Angew Chem 2006;118:5581–5585.Angew Chem Int Ed 2006;45:5455–5459.
5. a) Lavallo V, Canac Y, Präsang C, Donnadieu B, Bertrand G. Angew Chem 2005;117:5851–5855.Angew Chem Int Ed 2005;44:5705–5709. b) Lavallo V, Canac Y, DeHope A, Donnadieu B, Bertrand G. Angew Chem 2005;117:7402–7405.Angew Chem Int Ed 2005;44:7236–7239. c) Jazzar R, Dewhurst RD, Bourg JB, Donnadieu B, Canac Y, Bertrand G. Angew Chem 2007;119:2957–2960.Angew Chem Int Ed 2007;46:2899–2902. d) Jazzar R, Bourg JB, Dewhurst RD, Donnadieu B, Bertrand G. J Org Chem 2007;72:3492–3499. [PubMed: 17408289]
6. a) Zeng X, Frey GD, Kinjo R, Donnadieu B, Bertrand G. J Am Chem Soc 2009;131:8690–8696. [PubMed: 19456108] b) Zeng X, Frey GD, Kousar S, Bertrand G. Chem Eur J 2009;15:3056–3060. c) Lavallo V, Frey GD, Donnadieu B, Soleilhavoup M, Bertrand G. Angew Chem 2008;120:5302–5306.Angew Chem Int Ed 2008;47:5224–5228.
7. a) Mizushima E, Hayashi T, Tanaka M. Org Lett 2003;5:3349–3352. [PubMed: 12943424] b) Nishina N, Yamamoto Y. Angew Chem 2006;118:3392–3395.Angew Chem Int Ed 2006;45:3314–3317. c) Nishina N, Yamamoto Y. Tetrahedron 2009;65:1799–1808.
8. Labeling experiments that support trans addition have been reported for other gold-catalyzed reactions: a) Kennedy-Smith JJ, Staben ST, Toste FD. J Am Chem Soc 2004;126:4526–4527. [PubMed: 15070364] b) Hashmi ASK, Weyrauch JP, Frey W, Bats JW. Org Lett 2004;6:4391–4394. [PubMed: 15524491]

9. a) Zhou CY, Chan PWH, Che CM. Org Lett 2006;8:325–328. [PubMed: 16408906] b) Zhang Y, Donahue JP, Li CJ. Org Lett 2007;9:627–630. [PubMed: 17286370]
10. a) Cao H, McNamee L, Alper H. Org Lett 2008;10:5281–5284. [PubMed: 18950190] b) Patil NT, Wu H, Yamamoto Y. J Org Chem 2007;72:6577–6579. [PubMed: 17636960] c) Bajracharya GB, Huo Z, Yamamoto Y. J Org Chem 2005;70:4883–4886. [PubMed: 15932337] d) Lutete LM, Kadota I, Yamamoto Y. J Am Chem Soc 2004;126:1622–1623. [PubMed: 14871079] e) Penzien J, Su RQ, Müller TE. J Mol Catal A 2002;183:489–498. f) Su RQ, Müller TE. Tetrahedron 2001;57:6027–6033. g) Müller TE, Berger M, Grosche M, Herdtweck E, Schmidtchen FP. Organometallics 2001;20:4384–4393. h) Takaya J, Hartwig JF. J Am Chem Soc 2005;127:5756–5757. [PubMed: 15839651] i) Tobisch S. Chem Eur J 2007;13:4884–4894. j) Müller C, Koch R, Doye S. Chem Eur J 2008;14:10430–10436. k) Nettekoven U, Hartwig JF. J Am Chem Soc 2002;124:1166–1167. [PubMed: 11841274] l) Cochran BM, Michael FE. J Am Chem Soc 2008;130:2786–2792. [PubMed: 18254623]
11. a) Patil NT, Kavthe RD, Raut VS, Reddy VVN. J Org Chem 2009;74:6315–6318. b) McBee JL, Bell AT, Tilley TD. J Am Chem Soc 2008;130:16562–16571. [PubMed: 19554728]
12. CCDC 748500 (**5**) and 748501 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
13. Liu L, Xu B, Mashuta MS, Hammond GB. J Am Chem Soc 2008;130:17642–17643. [PubMed: 19055329]
14. Weber D, Tarselli MA, Gagné MR. Angew Chem 2009;121:5843–5846.Angew Chem Int Ed 2009;48:5733–5736.
15. See also: a) Seidel G, Mynott R, Fürstner A. Angew Chem 2009;121:2548–2551.Angew Chem Int Ed 2009;48:2510–2513. b) Akana JA, Bhattacharyya KX, Miller P, Sadighi JP. J Am Chem Soc 2007;129:7736–7737. [PubMed: 17547409]
16. a) Gorin DJ, Toste FD. Nature 2007;446:395–403. [PubMed: 17377576] b) Hashmi ASK, Hutchings GJ. Angew Chem 2006;118:8064–8105.Angew Chem Int Ed 2006;45:7896–7936.
17. a) Bender CF, Widenhoefer RA. Chem Commun 2008:2741–2743. b) Hashmi ASK. Catal Today 2007;122:211–214. c) Kovács G, Ujaque G, Lledós A. J Am Chem Soc 2008;130:853–864. [PubMed: 18166047]
18. A few examples of acid-catalyzed hydroaminations have been reported; see: a) Schlummer B, Hartwig JF. Org Lett 2002;4:1471–1474. [PubMed: 11975606] b) Motokura K, Nakaagiri N, Mori K, Mizugaki T, Ebitani K, Jitsukawa K, Kaneda K. Org Lett 2006;8:4617–4620. [PubMed: 16986964] c) Rosenfeld DC, Shekhar S, Takemiya A, Utsunomiya M, Hartwig JF. Org Lett 2006;8:4179–4182. [PubMed: 16956181] d) Anderson LL, Arnold J, Bergman RG. J Am Chem Soc 2005;127:14542–14543. [PubMed: 16231885] e) Lapis AAM, DaSilveira Neto BA, Scholten JD, Nachtigall FA, Eberlin MN, Dupont J. Tetrahedron Lett 2006;47:6775–6779. f) Li ZG, Zhang JL, Brouwer C, Yang CG, Reich NW, He C. Org Lett 2006;8:4175–4178. [PubMed: 16956180]
19. a) Nakamura I, Mizushima Y, Yamagishi U, Yamamoto Y. Tetrahedron 2007;63:8670–8676. b) Shimada T, Nakamura I, Yamamoto Y. J Am Chem Soc 2004;126:10546–10547. [PubMed: 15327305]
20. a) Cacchi S. J Organomet Chem 1999;576:42–64. b) Cacchi S, Fabrizi G, Pace P. J Org Chem 1998;63:1001–1011.

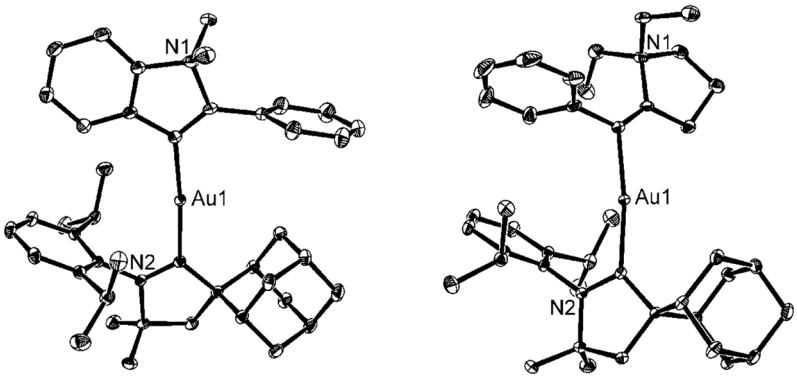
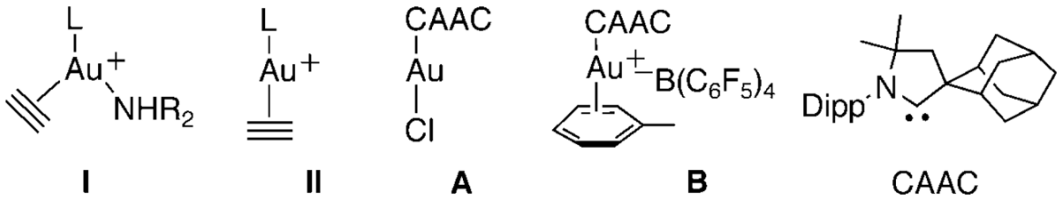
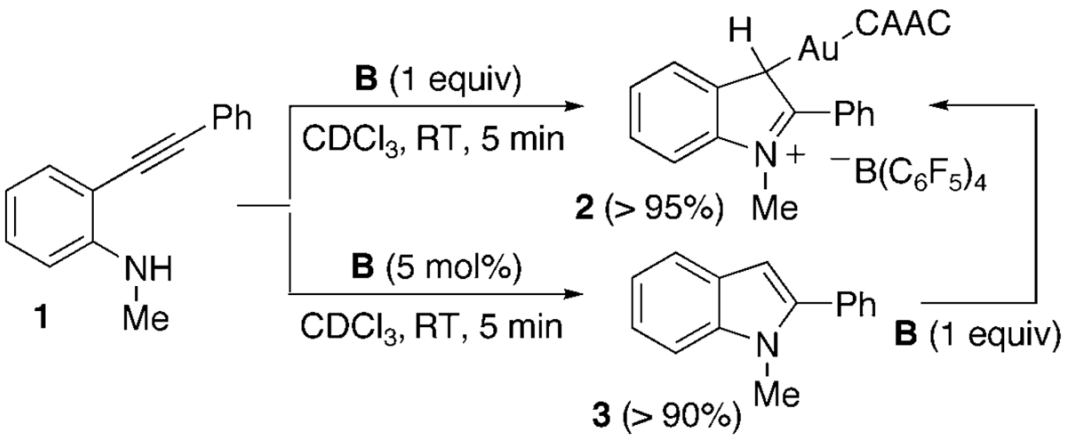


Figure 1.
ORTEP of gold complexes **5** (left) and **7** (right); ellipsoids set at 50% probability. Hydrogen atoms, solvent molecules, and the corresponding counterions are omitted for clarity.

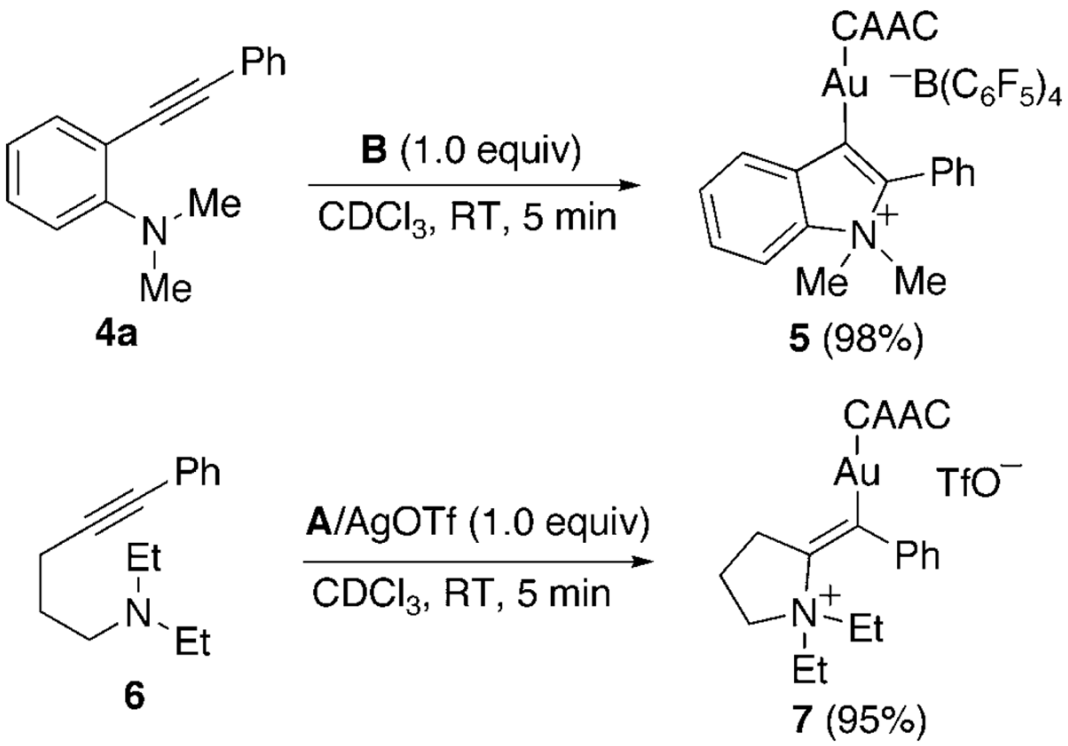


Scheme 1.

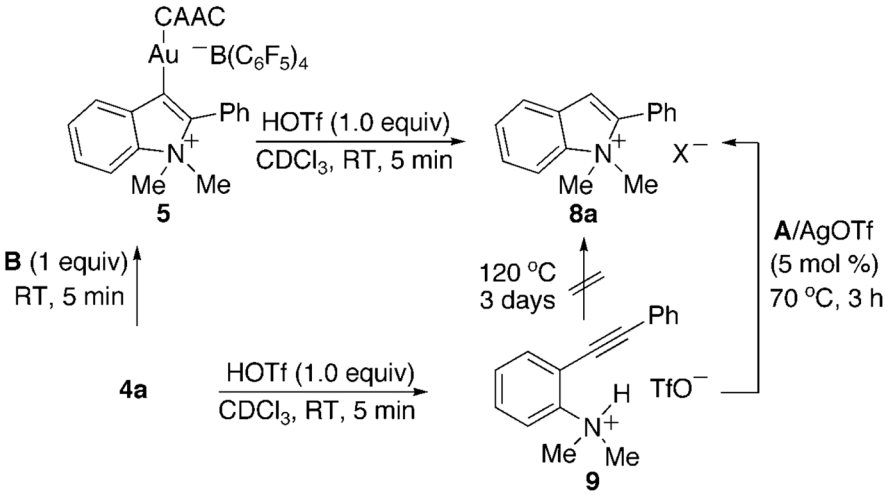
Possible intermediates **I** and **II** in the gold-catalyzed hydroamination of alkynes, and the gold complexes **A** and **B** used in this study.



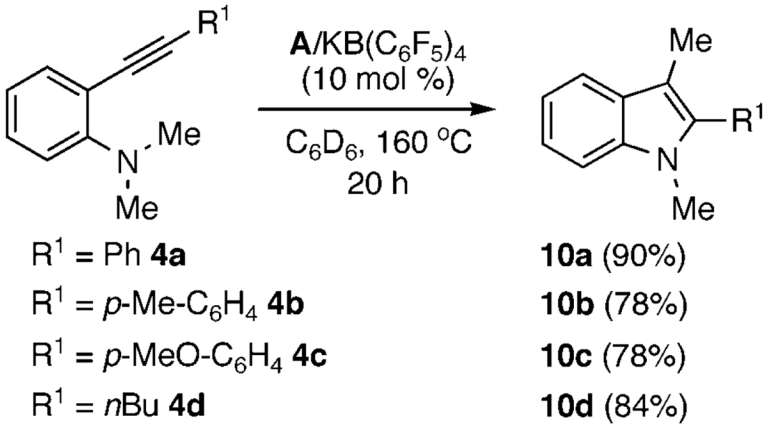
Scheme 2.
Stoichiometric and catalytic gold(I)-catalyzed intramolecular hydroamination of **1**.



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



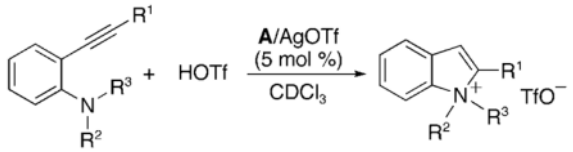
Scheme 4.
Stoichiometric and catalytic syntheses of **8a**. X=TfO.



Scheme 5.
First examples of catalytic methylamination of alkyne.

Table 1

Gold(I)-catalyzed intramolecular hydroammoniumation of **4** with HOTf.[a]



4a-f **8a-f**

Entry	4	R^1	R^2	R^3	*T* [°C]	*t* [h]	8	Yield [%][b]
1	**4 a**	Ph	Me	Me	120	72	**8 a**	0[c]
2	**4 a**	Ph	Me	Me	70	3	**8 a**	98
3	**4 b**	*p*-Me-C_6H_4	Me	Me	60	2.5	**8 b**	99
4	**4 c**	*p*-MeO-C_6H_4	Me	Me	60	2.5	**8 c**	99
5	**4 d**	nBu	Me	Me	60	2	**8 d**	97
6	**4 e**	Ph	Me	Et	60	7	**8 e**	94
7	**4 f**	Ph	Me	Ph	25	0.5	**8 f**	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.