

Homogeneous Catalytic Hydroamination of Alkynes and Allenes with Ammonia**

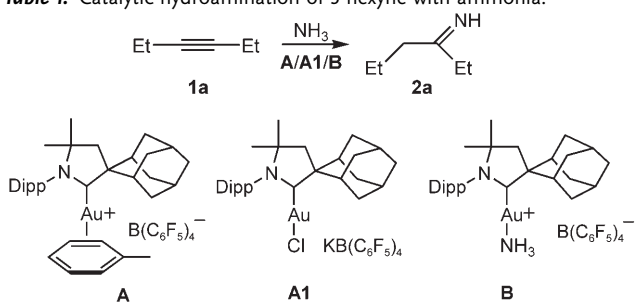
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Nitrogen–carbon bonds are ubiquitous in products ranging from chemical feedstock to pharmaceuticals. As ammonia is among the least expensive bulk chemicals produced in the largest volume, one of the greatest challenges of synthetic chemistry is to develop atom-efficient processes for the combination of NH_3 with simple organic molecules to create nitrogen–carbon bonds. Transition-metal complexes can readily render a variety of N–H bonds reactive enough to undergo functionalization, including those of primary and secondary amines. However, with a few exceptions,^[1,2] metals react with ammonia to afford supposedly inert Lewis acid–base complexes, as first recognized in the late 19th century by Werner.^[3] Consequently, the homogeneous catalytic functionalization of NH_3 remained elusive^[4] until the recent discovery by Shen and Hartwig^[5] and Surry and Buchwald^[6] of the palladium-catalyzed coupling of aryl halides with ammonia in the presence of a stoichiometric amount of a base. An even more appealing process would be the addition of NH_3 to carbon–carbon multiple bonds, a process that would occur ideally with 100 % atom economy.^[7] Although various homogeneous catalysts, including alkali metals,^[8] early^[9] and late transition metals,^[10] and d-^[11] and f-block elements,^[12] have been used to effect the so-called hydroamination reaction, none of them were reported to be effective when NH_3 is used as the amine partner.^[13] Herein we report that cationic gold(I) complexes supported by a cyclic (alkyl)(amino)carbene (CAAC)^[14] ligand readily catalyze the addition of ammonia to a variety of unactivated alkynes and allenes to provide a diverse array of linear and cyclic nitrogen-containing compounds.

We showed recently that the cationic CAAC–gold complex **A** was very robust and exhibited unusual catalytic reactivity towards alkynes.^[15] This discovery prompted us to investigate whether such a complex could activate alkynes sufficiently to enable the addition of NH_3 .^[16] Thus, excess

ammonia was condensed into a sealable NMR tube containing **A** (5 mol %), 3-hexyne, and deuterated benzene. Upon heating to 160 °C for 3.5 h, the clean addition of NH_3 afforded the primary imine **2a**, the expected tautomer of the corresponding enamine (Table 1).^[17]

Table 1: Catalytic hydroamination of 3-hexyne with ammonia.^[a]



Catalyst [mol %]	t [h]	T [°C]	Conv. [%]
5.0	3.5	160	95
1.0	14	160	95
0.1	17	160	58
0.1	20	200	93

[a] Dipp = 2,6-diisopropylphenyl.

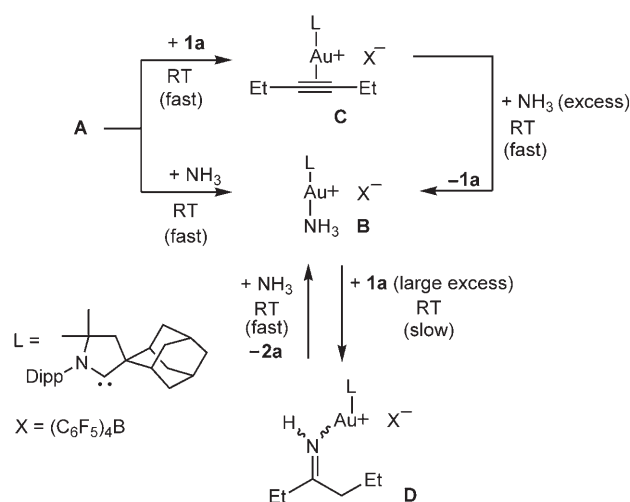
Complex **A** does not have to be isolated; when it was prepared in situ from an equimolar mixture of [(CAAC)AuCl]/KB(C₆F₅)₄ (**A1**), identical results were obtained. When the related silver complex [(CAAC)AgCl]/KB(C₆F₅)₄ or NH₄B(C₆F₅)₄ was used as the catalyst, no reaction was observed, which shows the importance of gold and rules out a Brønsted acid mediated reaction.^[18] Finally, as AuCl, AuCl/KB(C₆F₅)₄, and even [(CAAC)AuCl] do not induce the hydroamination, it is clear that the gold center can only catalyze the addition of NH_3 if it is coordinated by the CAAC ligand and rendered cationic by Cl abstraction.

To gain insight into the catalytic process, we performed a number of experiments: The addition of excess NH_3 to complex **A** gave the Werner complex **B** instantaneously; the addition of 3-hexyne (**1a**; 1 equiv) to complex **A** gave the η^2 -bound alkyne complex **C** instantaneously (Scheme 1). Upon the exposure of a solution of **C** in benzene to excess NH_3 , 3-hexyne was immediately displaced from the gold center, and the Werner complex **B** was isolated in quantitative yield. This result suggests that NH_3 does not add to the alkyne through an outer-sphere mechanism. Importantly, when a solution of complex **B** in benzene was treated at room temperature for 24 h with a large excess of 3-hexyne, the imine complex **D** was obtained quantitatively, even when the reaction vessel was open to a glovebox atmosphere. This

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Scheme 1. Experiments to probe the reaction mechanism. The results suggest that an insertion process is involved, and that **B** is the resting state of the catalyst.

experiment implies that NH_3 does not dissociate from the metal by a simple ligand exchange with the alkyne. Therefore, an insertion mechanism, similar to that proposed by Tanaka and co-workers^[19] and Nishina and Yamamoto^[20] for gold-catalyzed hydroamination with aryl amines, is quite likely. Finally, the addition of excess NH_3 to **D** liberated the imine **2a** and regenerated complex **B**. From the results of these experiments, it can be concluded that the Werner complex **B** is the resting state of the catalyst. Indeed, **B** exhibits identical catalytic activity to that of **A/A1**. Consequently, the robust and readily available complex **B** (Figure 1)^[21] was used in subsequent experiments.

To test the scope of the reaction, the terminal alkyne **1b** and the diaryl alkyne **1c** were treated with NH_3 in the presence of a catalytic amount of complex **B** (Scheme 2). With **1b**, the reaction took place even at 110 °C to afford the Markovnikov imine **2b** exclusively in 60% yield. When diphenyl acetylene (**1c**) was used, the 2-aza-1,3-diene **3c** was

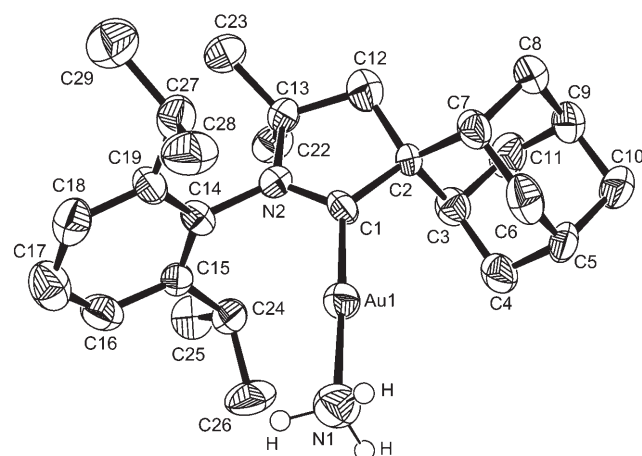
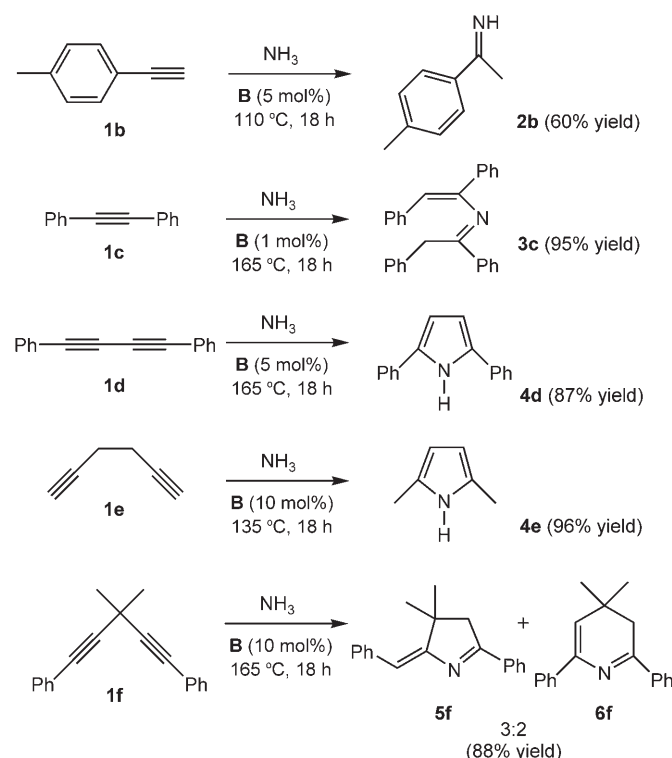


Figure 1. Molecular structure of complex **B** in the solid state. (Hydrogen atoms, except those at N1, and the $(C_6F_5)_4B$ anion are omitted for clarity; ellipsoids are drawn at 50% probability).



Scheme 2. Catalytic hydroamination of various alkynes with ammonia.

formed cleanly in 95% yield. The different outcome of the reaction of **1c** with respect to the results with substrates **1a,b** can be rationalized by the presence of acidic benzylic hydrogen atoms in the imine. These acidic hydrogen atoms favor the formation of the enamine tautomer, which can then react further with a second molecule of the alkyne to afford **3c**.

Nitrogen heterocycles are an important class of compounds that occur widely in natural products and often display potent biological activity. On the basis of the results described above, we attempted the direct synthesis of heterocycles from diynes and NH_3 . When 1,4-diphenylbuta-1,3-diyne (**1d**) and hexa-1,5-diyne (**1e**) were used, the corresponding 2,5-disubstituted pyrroles **4d** and **4e** were produced in 87 and 96% yield, respectively. Both products result from the Markovnikov addition of NH_3 , followed by ring-closing hydroamination.^[22,23] The treatment of the 1,4-diyne **1f** with NH_3 under similar conditions led to a 3:2 mixture of the five- and six-membered heterocycles **5f** and **6f** in 88% yield. The six-membered ring **6f** arises from two consecutive Markovnikov hydroamination reactions, whereas the formation of **5f** involves an anti-Markovnikov addition of NH_3 or ring-closing step.

To expand the scope of the hydroamination reaction with NH_3 , we next tested allenes as substrates. When 1,2-propadiene (**7a**) was used, a mixture of mono- (**8a**), di- (**9a**) and triallylamine (**10a**) was obtained in excellent yield. Allyl amines are among the most versatile intermediates in synthesis and are of industrial importance. For example, the parent compound **8a**, which is produced commercially from ammonia and allyl chloride, is used in antifungal preparations

and the synthesis of polymers. By varying the NH_3 /allene ratio it is possible to control the selectivity of this reaction significantly (Table 2). In particular, the parent allylamine (**8a**) and triallylamine (**10a**) can be obtained with 86 and 91 %

Table 2: Catalytic hydroamination of allenes with ammonia.

	R	$\text{NH}_3/7$	B [mol %]	t [h]	T [°C]	Conv. [%]	8/9/10
a	H	1.4:1	1.2	22	175	98	1:4.3:3.7
		40:1	4.3	16	175	96	6.2:1:–
		1.4:5	1.4	36	165	91	1:6:73
b	Me	0.8:1	1.3	22	155	87	1:18:47

selectivity, respectively, and further optimization of the conditions should be possible. The addition of NH_3 to 1,2-dienes is not restricted to the parent allene **7a**. The dialkyl-substituted derivative **7b** was also converted into the corresponding allyl amines **8b–10b**, with exclusive addition of the NH_2 group at the less-hindered terminus; however the selectivity of this reaction for the mono-, di-, or trisubstituted amine product needs some improvement. Interestingly, even the tetrasubstituted allene **7c** underwent hydroamination with ammonia. Probably because of steric factors, a different regioselectivity was observed, and only the monohydroamination product **11c** was formed.^[24]

The results outlined herein demonstrate that (CAAC)-gold(I) cations readily catalyze the addition of NH_3 to non-activated alkynes and allenes. This reaction leads to reactive nitrogen-containing compounds, such as imines, enamines, and allyl amines, and is therefore an ideal initial step for the preparation of simple bulk chemicals, as well as rather complex molecules, as illustrated by the preparation of heterocycles **4–6**. This study paves the way for the discovery of catalysts that mediate the addition of ammonia to simple alkenes, a process considered to be one of the ten greatest challenges for catalytic chemistry.^[25]

Experimental Section

All manipulations were performed under an inert atmosphere of argon by using standard Schlenk techniques. Water- and oxygen-free solvents were employed.

General procedure: The catalyst **B** (15 mg) and the appropriate amount (see Tables 1 and 2 and Scheme 2.) of an alkyne or allene

were loaded into a Wilmad QPV thick-walled (1.4 mm) NMR tube. C_6D_6 (0.4 mL) and the internal standard benzyl methyl ether (5 mg) were added to the mixture. For experiments with a low catalyst loading (0.1 mol %), 3 mg of the catalyst and 0.1 mL of C_6D_6 were used. The NMR tube was connected to a high-vacuum manifold, and excess NH_3 (typically 3–6 equivalents) was carefully condensed at -60°C . For experiments with 1,2-propadiene, the allene was first condensed, with the subsequent addition of NH_3 . The tube was sealed, placed in an oil bath behind a blast shield, and heated at the specified temperature. (**Caution:** Sealed NMR tubes containing NH_3 and/or 1,2-propadiene are under high pressure and pose an explosion hazard. Only new tubes with a wall thickness of at least 1.4 mm should be used).

B: Excess NH_3 (approximately 1 mL) was condensed into a solution of **A** (1.00 g, 0.74 mmol) in toluene (3 mL) at -50°C . The mixture was stirred for 1 min and then removed from the cold bath. The excess NH_3 was removed, hexane (50 mL) was added, and the upper portion of the biphasic mixture was removed with a canula. The oily residue was dried under a high vacuum to afford complex **B** (0.90 g, 95 %) as a colorless solid. M.p.: $112\text{--}114^\circ\text{C}$; ^1H NMR (300 MHz, C_6D_6): $\delta = 1.19$ (d, $^3J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.22 (d, $^3J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.30 (s, 6H, $\text{C}(\text{CH}_3)_2$), 1.70–1.97 (m, 12H), 2.31 (s, 2H, CH_2), 2.53 (br s, 3H, NH_2), 2.60 (sept, $^3J = 6.7$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 3.50 (d, $^2J = 12.0$ Hz, 2H, CH_2), 7.18 (d, $J = 7.7$ Hz, 2H), 7.35 ppm (t, $J = 7.7$ Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 22.8$, 26.8, 27.4, 28.5, 28.8, 29.4, 34.4 (CH_2), 35.9 (CH_2), 37.3, 39.1 (CH_2), 48.1 (CH_2), 64.2 (C^q), 78.7 (NC^q), 125.6 (CH^m), 131.0 (CH^p), 135.5 (C^i), 135.6 (m, B– C^{Ar}), 137.4 (m, B– C^{Ar}), 138.9 (m, B– C^{Ar}), 140.8 (m, B– C^{Ar}), 145.1 (C^o), 147.9 (m, B– C^{Ar}), 151.1 (m, B– C^{Ar}), 236.7 ppm ($\text{C}_{\text{carbene}}$); HRMS (ESI; CH_3CN): m/z calcd for $\text{C}_{29}\text{H}_{42}\text{AuN}_2$: 615.3008 [(M– NH_3 + CH_3CN)] $^+$; found: 615.3010; m/z calcd for $\text{C}_{28}\text{H}_{40}\text{AuN}_2$: 601.2857 [(M– NH_3 +H CN)] $^+$; found: 601.2856.

C: 3-Hexyne (1 equiv) was added to a solution of **A** (1.00 g, 0.74 mmol) in toluene (3 mL). The mixture was stirred for 1 min, and then hexane (50 mL) was added. The upper portion of the biphasic mixture was removed with a canula, and the oily residue was dried under a high vacuum to afford complex **C** (0.95 g, 96 %) as a colorless solid. M.p.: $183\text{--}184^\circ\text{C}$; ^1H NMR (300 MHz, C_6D_6): $\delta = 0.93$ (t, $^3J = 7.5$ Hz, 6H, CH_2CH_3), 1.24 (d, $^3J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.26 (d, $^3J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.37 (s, 6H, $\text{C}(\text{CH}_3)_2$), 1.73–1.98 (m, 12H), 2.12 (q, $^3J = 7.5$ Hz, 4H, CH_2CH_3), 2.38 (s, 2H, CH_2), 2.69 (sept, $^3J = 6.7$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 3.33 (d, $^2J = 12.7$ Hz, 2H, CH_2), 7.26 (d, $J = 7.7$ Hz, 2H), 7.41 ppm (t, $J = 7.7$ Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 13.7$ (CH_2CH_3), 15.4 (CH_2CH_3), 23.2, 26.5, 27.3, 28.4, 28.9, 29.5, 34.2 (CH_2), 36.5 (CH_2), 37.3, 38.8 (CH_2), 48.5 (CH_2), 65.2 (C^q), 79.9 (NC^q), 87.5 ($\text{C}\equiv\text{C}$), 126.2 (CH^m), 131.3 (CH^p), 135.9 (m, B– C^{Ar}), 135.8 (C^i), 137.5 (m, B– C^{Ar}), 139.1 (m, B– C^{Ar}), 141.0 (m, B– C^{Ar}), 145.3 (C^o), 148.0 (m, B– C^{Ar}), 151.1 (m, B– C^{Ar}), 243.9 ppm ($\text{C}_{\text{carbene}}$); HRMS (ESI; CH_3CN): m/z calcd for $\text{C}_{29}\text{H}_{42}\text{AuN}_2$: 615.3008 [(M– C_6H_{10} + CH_3CN)] $^+$; found: 615.3011.

D: 3-Hexyne (6.47 g, 78.7 mmol) was added to a solution of **B** (0.50 g, 0.39 mmol) in benzene (3 mL). The mixture was stirred for 24 h, and then hexane (100 mL) was added. The upper portion of the biphasic mixture was removed with a canula, and the oily residue was dried under a high vacuum to afford complex **D** (0.50 g, 99 %; *cis/trans* 55:45) as a colorless solid. ^1H NMR (300 MHz, CDCl_3): $\delta = 0.80$ (t, $J = 7.1$ Hz, 3H, CH_3), 0.88 (t, $J = 7.8$ Hz, 3H, CH_3), 0.89 (t, $J = 7.8$ Hz, 3H, CH_3), 1.07 (t, $J = 7.1$ Hz, 3H, CH_3), 1.29 (d, $^3J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.30 (d, $^3J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.33 (br d, $^3J = 7.1$ Hz, 12H, $\text{C}(\text{CH}_3)_2$), 1.41 (s, 6H, $\text{C}(\text{CH}_3)_2$), 1.42 (s, 6H, $\text{C}(\text{CH}_3)_2$), 1.45–1.55 (br m, $J = 7.2$ Hz, 4H, CH_2), 1.75–2.18 (m, 24H), 2.29 (t, $J = 8.2$ Hz, 4H, $\text{HNC}(\text{CH}_2\text{CH}_2\text{CH}_3)$), 2.40 (q, $J = 7.1$ Hz, 4H, $\text{HNC}(\text{CH}_2\text{CH}_3)$), 2.42 (s, 4H, CH_2), 2.76 (sept, $^3J = 6.7$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 3.50–3.75 (br m, 4H), 7.30 (d, $J = 7.7$ Hz, 4H), 7.46 (t, $J = 7.7$ Hz, 2H), 8.30–8.40 ppm (br s, 2H, NH); ^{13}C NMR (75 MHz, CDCl_3): $\delta = 8.6$ (CH_2CH_3), 11.1 (CH_2CH_3), 13.1 (CH_2CH_3), 13.8 (CH_2CH_3), 18.5 (CH_2CH_3), 20.2 (CH_2CH_3), 23.0, 23.1, 26.6, 26.7, 26.9, 27.9, 29.2, 29.4,

32.5 (CH₂), 33.8 (CH₂), 34.3 (CH₂), 35.7 (CH₂), 37.2, 38.8 (CH₂), 40.7 (CH₂), 42.4 (CH₂), 48.5 (CH₂), 64.3 (C^q), 64.4 (C^q), 78.6 (2 × NC^q), 125.5 (CH^m), 130.5 (CH^p), 130.6 (CH^p), 134.9 (m, B–C^{Ar}), 135.8 (br, c^q), 136.8 (m, B–C^{Ar}), 138.0 (m, B–C^{Ar}), 140.0 (m, B–C^{Ar}), 145.0 (c^o), 145.1 (c^o), 146.6 (m, B–C^{Ar}), 150.1 (m, B–C^{Ar}), 199.6 (C=N), 200.2 (C=N), 238.1 (C_{carbene}), 238.6 (C_{carbene}).

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