Synthetic Methods

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Gold-Catalyzed Hydroamination of Alkynes and Allenes with Parent Hydrazine**

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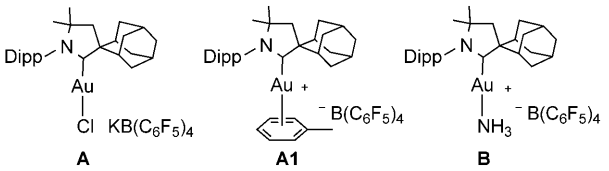
Acyclic and heterocyclic nitrogen-containing derivatives are common components of naturally occurring compounds,[1] agrochemicals, cosmetics, and pharmaceuticals; they are also useful intermediates in a number of industrial processes.[2] Because of the limitations in C–N bond formation with traditional methods, various homogeneous catalysts have been used to effect the so-called hydroamination reaction,[3] including alkali metals, early and late transition metals, and f-block elements. Although most of these catalysts are efficient with aryl amines, and to a lesser extent with primary and secondary alkyl amines, no hydroamination reaction involving hydrazine has been reported. More generally, despite the economic interest of the use of this small molecule, which is produced in bulk quantities, the recently disclosed palladium-catalyzed cross-coupling of aryl chlorides and tosylates with hydrazine[4] is the only example of the transition-metal-catalyzed functionalization of H_2NNH_2. The use of this reagent is hampered by several difficulties. Like ammonia, hydrazine readily forms Werner complexes, which are usually inert.[5] H_2NNH_2 is known as a strong reducing reagent[6] that can induce the formation of inactive metal(0) particles[7] and hydrogenate substrates to give saturated molecules.[8] The resulting products can undergo metal-mediated N–N bond cleavage to form undesired by-products.[9] To prevent such unfavorable processes, hydrazine derivatives, such as substituted hydrazines, hydrazones, and hydrazides, have been used as substrates,[10] although these surrogates are not ideal from the viewpoints of atom efficiency and economics.

Recently, we showed that gold(I) complexes[11] featuring a bulky cyclic (alkyl)(amino)carbene (CAAC)[12] as an ancillary ligand are very robust and efficiently promote the intermolecular addition of a variety of amines to non-activated carbon–carbon multiple bonds.[13,14] Importantly, **A** (Scheme 1), which is an equimolar mixture of a gold complex [(CAAC)AuCl] and $KB(C_6F_5)_4$, and the isolated cationic complexes **A1** and **B**, are the first homogeneous catalysts that enable the hydroamination of alkynes and allenes with ammonia.[13e] This discovery prompted us to investigate whether these catalysts would also be compatible with hydrazine. Herein we report that **A**, as well as the corresponding hydrazine complex **C** (Figure 1), readily catalyze the addition of H_2NNH_2 to a variety of non-activated alkynes and allenes to afford a diverse array of acyclic and cyclic nitrogen-containing compounds.



Scheme 1. CAAC–gold(I) catalysts **A**, **A1**, and **B** (Dipp = 2,6-diisopropylphenyl).

Gold–hydrazine complexes have not been described previously. Moreover, examples of the formation of gold particles by the reduction of gold chloride with hydrazine have been reported,[15] and cationic trinuclear phosphine–gold complexes of the type $[(LAu)_3(O)]^+X^-$ have been shown to promote the dehydrogenation of H_2NNH_2 to give N_2 complexes $[(LAu)_6(N_2)]^{2+}$.[16] Therefore, we first checked the compatibility of **A** with hydrazine, and found that the latter cleanly coordinates to the gold center to produce complex **C** in excellent yield (94%). In the ^1H NMR spectrum, two broad signals were observed at $\delta = 3.37$ and 4.72 ppm, which indicate that the two NH_2 groups are inequivalent in solution. The solid-state structure of **C** was determined by an X-ray diffraction study,[17] which confirmed that only one amino group coordinates to the cationic gold(I) center to give an η^1 Werner complex (Figure 1).

We first used the Werner complex **C** to investigate the catalytic hydroamination of *p*-methoxyphenylacetylene (**1a**) with hydrazine. Excess anhydrous hydrazine was introduced into a sealable NMR tube containing **C** (5.0 mol%), alkyne **1a**, and deuterated chloroform or benzene. Upon heating at 100 °C for 30 min, a clean addition of H_2NNH_2 was observed to afford hydrazone **2a**, the expected tautomer of the enamine resulting from a Markovnikov addition (Table 1, entry 1). A similar result was obtained when complex **C** was generated in situ from **A** (Table 1, entry 2). Even with just 0.1 mol% of **A**, 95% conversion was observed when the reaction mixture was heated at 150 °C for 6 h (Table 1, entry 5). In the absence of a catalyst[18] (Table 1, entry 6), or in the presence of AuCl, AuCl/$KB(C_6F_5)_4$, or even [(CAAC)AuCl], no reaction occurred. Therefore, as previously observed with ammonia and various amines,[13] the gold center can only catalyze the hydroamination reaction when it is cationic and coordinated by the CAAC ligand.

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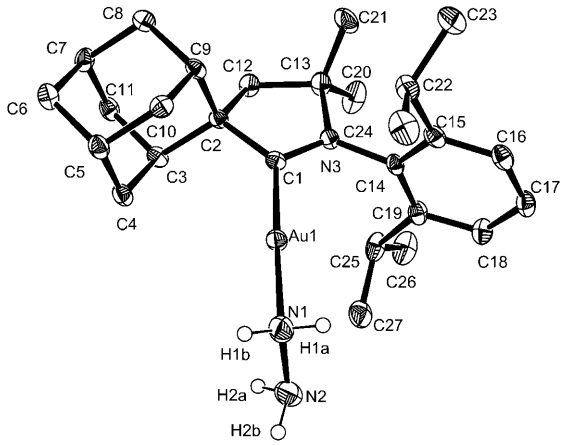
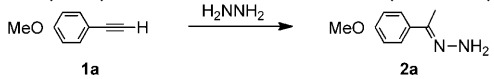


Figure 1. Molecular structure of complex **C** in the solid state. Hydrogen atoms, except for those at N1 and N2, and $B(C_6F_5)_4^-$ have been omitted for clarity; ellipsoids are drawn at 30% probability.

Table 1: Catalytic hydroamination of a terminal alkyne with hydrazine.



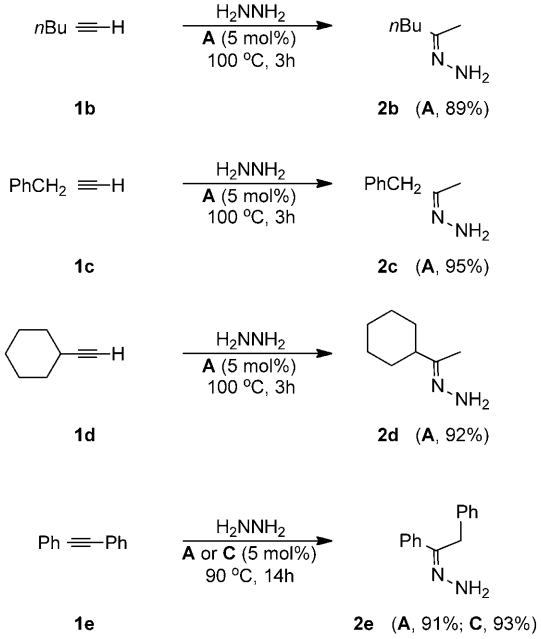
1a **2a**

Entry	Catalyst (mol%)	*t* [h]	*T* [°C]	Conversion [%][a]
1	**C** (5.0)	0.5	100	95
2	**A** (5.0)	0.5	100	95
3	**A** (1.0)	2	100	95
4	**A** (0.1)	5	100	32
5	**A** (0.1)	6	150	95
6	–	14	150	0

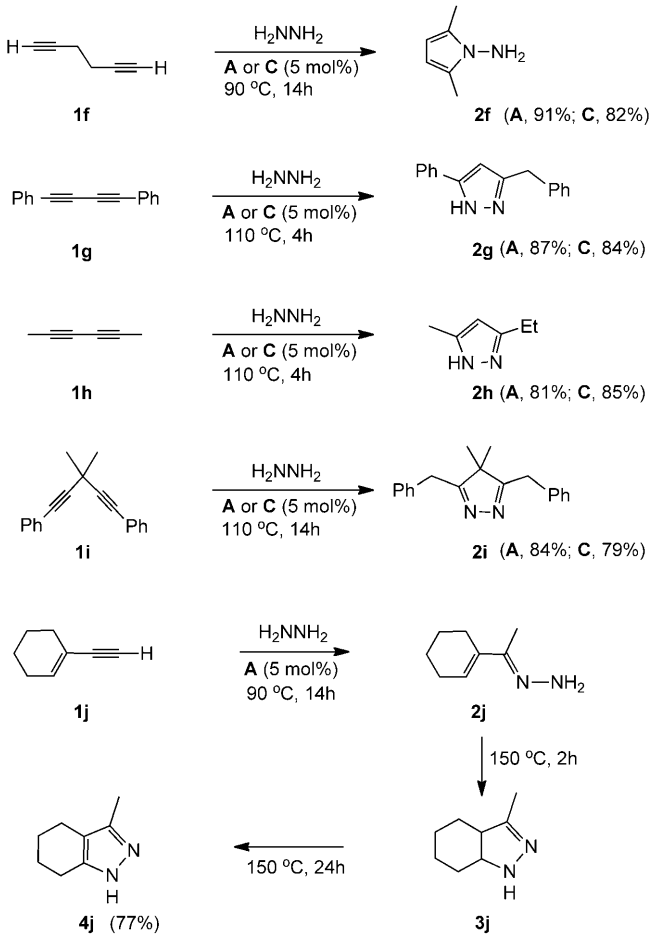
[a] Conversion was determined by ^{1}H NMR spectroscopy with 1,4-di-*tert*-butylbenzene as an internal standard.

To test briefly the scope of the reaction, alkynes **1b–e** were treated with hydrazine in the presence of the gold complex **A** or **C** (5 mol%; Scheme 2). With terminal alkynes **1b–d**, the reaction took place at 100°C to afford after 3 h hydrazones **2b–d** resulting from Markovnikov addition in good to excellent yields. Similarly, the internal alkyne **1e** was converted into hydrazone **2e** in high yield, although a longer reaction time was necessary.

We then turned our attention to the direct synthesis of heterocycles from diynes (Scheme 3). We were pleased to observe that the treatment of 1,5-hexadiyne (**1f**) with hydrazine led to the 1-aminopyrrole derivative **2f**, which was isolated in 91% yield when catalyst **A** was used and in 82% yield with **C**. This heterocycle arises from two consecutive Markovnikov hydroaminations involving a single NH_2 group, followed by aromatization. In contrast, when 1,4-diphenylbuta-1,3-diyne (**1g**) and 2,4-hexadiyne (**1h**) were used, both amino groups were involved in the reaction, which led to pyrazole derivatives **2g**[19] and **2h** in more than 80% yield. Similarly, 1,5-diphenyl-3,3-dimethylbuta-1,4-diyne (**1i**) reacted with hydrazine to produce the 4*H*-pyrazole **2i** in 79 or 84% yield, depending on the gold complex used. As expected, these results show that the formation of five-membered heterocycles is largely favored over the formation of their six-membered-ring isomers. Finally, we expanded the scope of



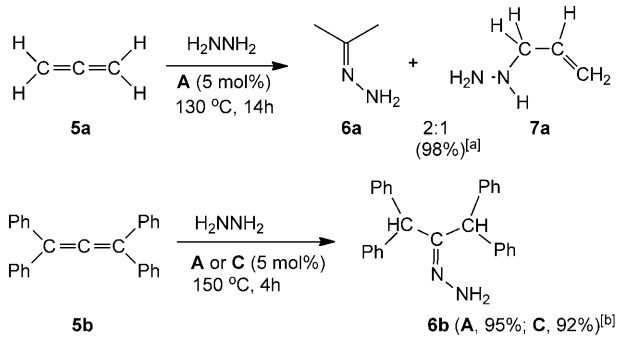
Scheme 2. Catalytic hydroamination of terminal and internal alkynes with hydrazine (yields refer to the isolated product).



Scheme 3. Catalytic hydroamination of diyne and enyne derivatives with hydrazine (yields refer to the isolated product).

these cyclization processes to enyne **1j**. The first step, a Markovnikov hydroamination of the triple bond, took place at 90 °C to yield the corresponding hydrazone **2j**. Then, as observed by Nakhai and Bergman,[20] **2j** could be thermally converted (150 °C, 2 h) into the indazole derivative **3j**. Interestingly, further heating at 150 °C for 24 h without an oxidant induced the aromatization of **3j** by dehydrogenation and afforded 4,5,6,7-tetrahydro-3-methyl-1*H*-indazole (**4j**), which was isolated in good yield (77 %).

We also investigated the hydroamination of allenes with hydrazine (Scheme 4). When 1,2-propadiene (**5a**) was treated with H_2NNH_2, the formation of a 2:1 mixture of hydrazone **6a** and allylhydrazine (**7a**) was observed (98 % conversion after 14 h at 130 °C). The addition of hydrazine to 1,2-dienes is not restricted to the parent allene **5a**. Tetraphenyl-1,2-propadiene (**5b**) underwent hydroamination to afford the hydrazone derivative **6b** in more than 90 % yield after 4 h at 150 °C; the observed regioselectivity is probably due to steric factors.



Scheme 4. Catalytic hydroamination of allenes with hydrazine. [a] The yield was estimated by ^{1}H NMR spectroscopy. [b] Yield of the isolated product.

The results outlined herein demonstrate that the strong σ-donor and π-acceptor properties of cyclic (alkyl)(amino)carbenes enable the preparation of very robust gold–hydrazine complexes, which are nevertheless catalytically active. Since gold complexes display excellent functional-group tolerance as well as low air and moisture sensitivity, these reactions should be ideal initial steps for the synthesis of acyclic and heterocyclic bulk chemicals. This study conquers the difficulties associated with the use of hydrazine and opens an avenue for extensive applications.

Experimental Section

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

Synthesis of complex **C**: The [(CAAC)AuCl] complex (0.305 g, 0.5 mmol), $KB(C_6F_5)_4$ (0.359 g, 0.5 mmol), anhydrous hydrazine (0.128 g, 4.0 mmol), and $CHCl_3$ (12 mL) were placed in a Schlenk tube. The mixture was stirred for 30 min at ambient temperature, and then potassium chloride was filtered off. Removal of the solvent and excess hydrazine under vacuum gave the gold complex **C** as a white solid (94 % yield). M.p.: 120 °C; ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.49$ (d, $J = 7.7$ Hz, 1H, CH), 7.32 (d, $J = 7.7$ Hz, 2H, CH), 4.72 (br s, 2H, NH_2), 3.58–3.62 (m, 2H), 3.37 (br s, 2H, NH_2), 2.73 (sept, $J = 6.6$ Hz, 2H, $CH(CH_3)_2$), 2.44 (s, 2H, CH_2), 2.11–1.83 (m, 12H), 1.43 (s, 6H, CH_3), 1.35 (d, $J = 6.6$ Hz, 6H, $CH(CH_3)_2$), 1.34 ppm (d, $J = 6.6$ Hz, 6H, $CH(CH_3)_2$); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 237.8$ ($C_{carbene}$), 147.8 (d, $J_{C,F} = 232.9$ Hz, C_{quat}), 144.7 (*o*-C), 138.0 (d, $J_{C,F} = 236.3$ Hz, C_{quat}), 135.9 (d, $J_{C,F} = 253.6$ Hz, C_{quat}), 135.2 (C_{ipso}), 130.0 (*p*-CH), 124.9 (*m*-CH), 78.2 (C_{quat}), 63.8 (C_{quat}), 47.9 (CH_2), 38.4 (CH_2), 36.7 (CH), 35.4 (CH_2), 33.9 (CH_2), 28.8 (CH and CH_3), 27.7 (CH), 26.5 (CH), 26.3 (CH_3), 22.5 (CH_3).

General hydroamination procedure: $CDCl_3$ or C_6D_6 (0.4 mL), the alkyne or allene (0.5 mmol), anhydrous hydrazine (0.064 g, 2.0 mmol), and the internal standard 1,4-di-*tert*-butylbenzene (10 mg, 0.05 mmol) were added to either complex **C** (0.032 g, 0.025 mmol) or a mixture of the [(CAAC)AuCl] complex (0.015 g, 0.025 mmol) and $KB(C_6F_5)_4$ (0.018 g, 0.025 mmol) in a dried J Young NMR tube. For experiments with a low catalyst loading (0.1 mol %), 0.3 mg of the [(CAAC)AuCl] complex and 0.4 mg of $KB(C_6F_5)_4$ were used. The tube was sealed, placed in an oil bath behind a blast shield, and heated at the temperature specified. The reaction was monitored by NMR spectroscopy. Products **2a–i** and **4j** were purified by column chromatography on florisil. Product **6b** was purified by recrystallization from $CHCl_3$.

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