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Mesoionic Carbene-Gold(I) Catalyzed Bis-Hydrohydrazination of Alkynes with Parent Hydrazine

Daniel R. Tolentino, Liqun Jin, Mohand Melaimi, and Guy Bertrand*[a]

Dedication ((optional))

Abstract: A novel synthetic route gives access to mesoionic carbene and cyclopropenylidene supported gold chloride complexes. The corresponding cationic MIC-gold complex obtained by chloride abstraction allows for the first transition metal-catalyzed functionalization of both nitrogens of parent hydrazine.

The hydroamination reaction is an atom-efficient route to carbon-nitrogen bond containing products starting from readily accessible materials.[1,2] Compounds featuring nitrogen-nitrogen bonds constitute an important family of molecules, many of which are natural products that display biological activity.[3] Thus, the hydroamination reaction, using parent hydrazine as a building block, is quite appealing, since it is by far more atom-efficient than known methods.[4] However, like ammonia, NH_2NH_2 readily forms Werner complexes, which are usually inert.[5] Hydrazine is also a strong reducing agent, which can induce the formation of inactive metal(0) particles[6] or lead to the formation of undesired side-products.[7] Despite these difficulties,[8] we have already shown that parent hydrazine can be used in the hydrohydrazination of unactivated alkynes and allenes using gold(I) chloride complexes supported by a cyclic (alkyl)(amino)carbene (CAAC)[9] and an *anti*-Bredt *N*-heterocyclic carbene (*pyr*NHC) (Figure 1).[10] Importantly, Hashmi *et al.* reported that the gold-catalyzed hydrohydrazination of terminal alkynes is even easier when a saturated abnormal N-heterocyclic carbene (*sa*NHC) is used as ancillary ligand.[11] CAACs,[12] *pyr*NHCs[13] and *sa*NHCs are recognized as strong σ-donating ligands,[14] but the π-accepting properties of the latter are by far weaker than the other two.[15] This analysis prompted us to consider the bis(diisopropylamino)cyclopropenylidene (BAC) **1**[15] and the 1,2,3-triazol-5-ylidene **2** [also named mesoionic carbene (MIC)],[17] as ligands.

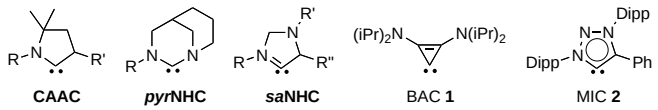

Figure 1. CAAC, *pyr*NHC and *sa*NHC ligands previously used in gold-catalyzed hydrohydrazination, and BAC **1** and MIC **2** considered in this study (Dipp: 2,6-diisopropylphenyl).

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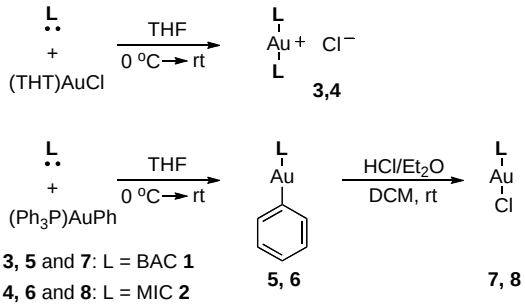
Preparation of (CAAC)AuCl complexes is readily achieved by the direct addition of free CAAC to (THT)AuCl (THT = tetrahydrothiophene).[18] Attempts to generalize this synthetic route to **1** and **2** resulted in the formation of [bis(carbene)Au]$^+$Cl$^-$ complexes **3** and **4**, probably because of the high basicity of the carbenes (Scheme 1). Such bis(carbene) complexes are known to be catalytically inactive,[19] and therefore we looked for an alternative synthetic route to access the desired mono(carbene) gold chloride complexes. We found that BAC **1** and MIC **2** could substitute triphenylphosphine in the Ph_3PAuPh complex, affording (**L**)AuPh **5** and **6**. Subsequent addition of HCl affords (**L**)AuCl complexes **7** and **8** in 74 and 91% yield, respectively. These highly air-stable complexes were characterized by NMR spectroscopy, and a crystal structure was obtained for the MIC complex **8** (Figure 2).[20] The carbene-Au bond length [1.991(6) Å] is comparable to those of the (CAAC)AuCl [1.973(4) Å][18] and (pyrNHC)AuCl [1.983(3) Å].[10]



Scheme 1. Synthesis of bis(carbene)Au$^+$Cl$^-$ **3** and **4**, and mono(carbene) gold chloride complexes **7** and **8**.

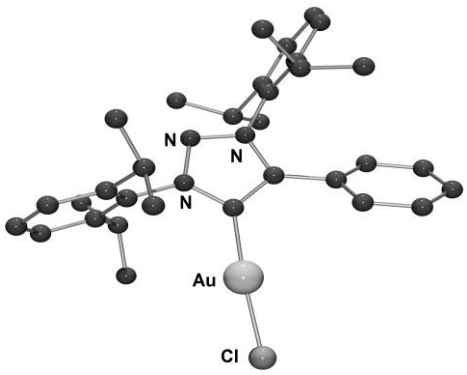
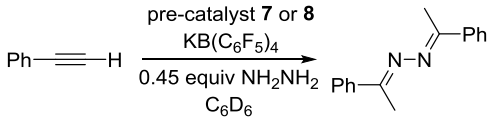


Figure 2. X-ray structure of **8**. Hydrogen atoms are omitted for clarity; Selected bond lengths [Å] and angles [°]: C-Au 1.991(6), Au-Cl 2.2761(17); C-Au-Cl 174.20(17).

Initial catalytic studies were conducted at 100 °C, using 1 mol% of a stoichiometric mixture of (**L**)AuCl (**7** and **8**) with $KB(C_6F_5)_4$ as chloride scavenger, and a 1/1 mixture of parent hydrazine and phenylacetylene as a model substrate. The reactions were monitored by ^1H NMR spectroscopy using benzyl methyl ether as internal standard. The BAC-gold complex **7** showed minimal activity, only a small amount of hydrazone (≈12%) was obtained after 61 hours (Table 1, entry 1). In marked contrast, when MIC complex **8** was used, total conversion of the acetylene was observed after 12 hours. Surprisingly, in addition to the mono-hydrohydrazinated derivative, we also observed the formation of the corresponding azine (Table 1, entry 2). Since such a bis-hydrohydrazination reaction has no precedent, we explored this new avenue towards the formation of molecules with N-N bonds. By using 0.45 equivalent of hydrazine with respect to phenylacetylene, full conversion of NH_2NH_2 was observed, and the azine was obtained in 84% yield after 12 hours (Table 1, Entry 2). Complex **8** displays excellent activity, even at catalyst loadings as low as 0.5 and 0.1 mol% (Table 1, Entries 3 and 4). It is even able to facilitate the bis-hydrohydrazination of phenylacetylene in good yield at 60 °C with 1 mol% loading (Table 1, Entry 5).

Previous reports on the hydroamination and hydrohydrazination with (carbene)AuCl precatalysts have led to the conclusion that the active species is likely a cationic gold coordinated by one carbene,[18b] while the resting state is the $[(carbene)Au(NH_3)]^+X^-$ and $[(carbene)Au(N_2H_4)]^+X^-$ complex, respectively.[9,10,21] Similarly, we found that the gold chloride complex **8** is inactive in the absence of chloride scavenger, and that the air-stable and storable $[(\mathbf{2})Au(N_2H_4)]^+B(C_6F_5)_4^-$ complex performed similarly to **8**/$KB(C_6F_5)_4$ and is certainly the resting state of the catalyst (Table 1, entry 6). Lastly, to rule out the formation of active gold nanoparticles, the reaction was carried out in the presence of elemental mercury (Table 1, entry 7) and catalysis still proceeded, which is consistent with homogeneous catalysis.[22]

Table 1. Optimization of reaction conditions with phenylacetylene.

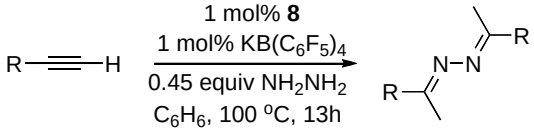


Entry	Pre-catalyst (mol%)	Temp. (°C)	Time (h)	Yield (%)[a]
1	**7** (1.0)	100	61	12[b]
2	**8** (1.0)	100	12	84
3	**8** (0.5)	100	13	82
4	**8** (0.1)	100	13	78
5	**8** (1.0)	60	13	81
6	$[(\mathbf{2})AuN_2H_4]^+B(C_6F_5)_4^-$ (1.0)[c]	100	13	81
7	**8** (1.0) + Hg	100	13	84

[a] Determined by ^1H NMR with benzyl methyl ether as an internal standard. [b] Percent yield refers to hydrazone product; no azine was observed. [c] No addition of $KB(C_6F_5)_4$.

We then briefly explored the substrate scope of the gold-catalyzed bis-hydrohydrazination (Table 2). Terminal alkynes were converted efficiently. The ^1H NMR spectra of the crude products were very clean after evaporation of volatiles, and the azines were isolated in reasonable yields. However, no clean reactions were observed with internal alkynes.

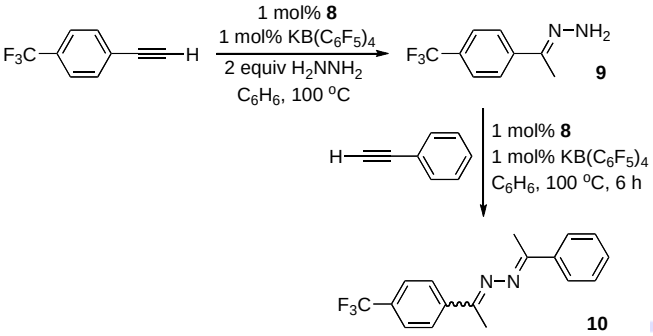
Table 2. Bis-hydrohydrazination of terminal alkynes.



Entry	R	% Yield[a]
1	4-Methoxyphenyl	95 (21)
2	4-trifluoromethylphenyl	92 (67)
3	Cyclohexyl	88 (50)
4	1-Cyclohexenyl	100 (94)

[a] Determined by ^1H NMR with benzyl methyl ether as an internal standard; isolated yield in parentheses.

To illustrate the synthetic potential of this bis-hydrohydrazination reaction, two different alkynes were sequentially reacted to give an unsymmetrical azine (Scheme 2). First, 4-trifluoromethylphenyl acetylene was converted to hydrazone **9** using an excess of hydrazine; then phenyl acetylene was added to give **10**, which was isolated as a 50/50 mixture of stereoisomers in 61% yield.



Scheme 2. Step-wise preparation of unsymmetrical azine.

In summary, a novel synthetic route allows for the preparation of a gold chloride complex bearing a mesoionic carbene as ancillary ligand. In the presence of a chloride scavenger, this complex promotes the catalytic functionalization of both nitrogens of parent hydrazine with terminal alkynes. Current investigations are directed towards understanding ligand effects leading to the bis-functionalization.

Experimental Section

All reactions were performed under an atmosphere of argon using standard Schlenk or dry box techniques; solvents were dried over sodium or CaH_2. ^1H, ^{13}C, and ^{19}F NMR spectra were obtained with Bruker Advance 300 and Varian VX 500 spectrometers at 298K. Chemical shifts (δ) are reported in parts per million (ppm) and were referenced to the residual solvent peak. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal.

Preparation of L_2Au^+Cl 3[23] **and 4:** (THT)AuCl (0.43 g, 1.33 mmol) and MIC **2** (1.24 g, 2.66 mmol) were added to a flame-dried Schlenk flask and cooled to 0 °C. Anhydrous THF (20 mL) was added, and the mixture was slowly warmed to room temperature and stirred for 16 hours. Volatiles were removed *in vacuo*. Washing the solid residue with anhydrous benzene afforded **4** as an off-white solid in 93% yield. ^1H NMR (300 MHz,

$CDCl_3$): δ = 7.52-7.45 (m, 4H, Ar), 7.28 (m, 2H, Ar), 7.18 (m, 9H, Ar), 7.01 (m, 7H, Ar), 2.18 (septet, *J* = 6.0 Hz, 4H), 2.08 (septet, *J* = 6.0 Hz, 4H), 1.02 (d, *J* = 6.0 Hz, 12H), 0.99 (d, *J* = 6.0 Hz, 12H), 0.96 (d, *J* = 6.0 Hz, 12H), 0.86 (d, *J* = 6.0 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.3, 149.8, 144.8, 134.6, 132.5, 131.8, 130.2, 130.0, 128.9, 128.6, 128.3, 125.4, 124.8, 124.3, 29.3, 28.9, 25.3, 24.2, 24.0, 22.4. HR-MS (m/z): $[M]^+$ calcd. for $C_{64}H_{78}AuN_6^+$, 1127.5949; $[M\text{-}Cl]^+$ found, 1127.5948. m.p. = 315 °C (decomposition).

Preparation of (L)AuPh 5 and 6: Free carbene **1** or **2** (1.28 mmol) and PPh_3AuPh (0.690 g, 1.28 mmol) were added to a flame-dried Schlenk flask and cooled to 0°C. Anhydrous THF (15 mL) was added, and the mixture was allowed to warm to room temperature while stirring for 1 hour. Volatiles were removed *in vacuo*, and the residue was washed with anhydrous hexane to afford L-AuPh as solids in 74-91% yield. **5:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (m, 2H, Ar), 7.20 (m, 2H, Ar), 6.98 (m, 1H, Ar), 3.82 (br, 4H), 1.57 (br, 12H), 1.29 (br, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 170..2, 159.6, 146.5, 140.8, 127.3, 124.6, 54.2, 48.9, 21.9, 21.5. **6:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (m, 2H), 7.57 (m, 2H), 7.34 (m, 9H), 7.12 (m, 2H), 6.94 (m, 1H), 2.61 (septet, *J* = 6.0 Hz, 2H), 2.40 (septet, *J* = 6.0 Hz, 2H), 1.48 (d, *J* = 6.0 Hz, 6H), 1.19 (d, *J* = 6.0 Hz, 6H), 1.15 (d, *J* = 6.0 Hz, 6H), 0.98 (d, *J* = 6.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 182.5, 169.9, 148.8, 145.1, 144.9, 140.6, 135.5, 134.0, 133.8, 131.9, 131.3, 131.0, 129.5, 128.9, 128.4, 126.8, 124.6, 123.9, 29.0, 28.9, 25.1, 24.3, 24.2, 22.4.

Preparation of (L)AuCl 7 and 8: A 2.0 M solution of HCl in diethyl ether (4 mL, excess) was added to a stirred dichloromethane solution (10 mL) of (carbene)AuPh complex (1.28 mmol). The reaction was stirred for 1 hour at room temperature, then dried *in vacuo* to afford (carbene)AuCl as a solid in quantitative yield. **7:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (br, 4H), 1.51 (br, 12H), 1.29 (br, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 144.1, 133.9, 54.4, 48.8, 21.8, 21.3. m.p. = 198 °C (decomposition). **8:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64-7.29 (m, 11H, Ar), 2.48 (septet, *J* = 6.0 Hz, 2H), 2.34 (septet, *J* = 6.0 Hz, 2H), 1.42 (d, *J* = 6.0 Hz, 6H), 1.17 (d, *J* = 6.0 Hz, 6H), 1.13 (d, *J* = 6.0 Hz, 6H), 0.98 (d, *J* = 6.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 161.1, 148.0, 145.2, 144.9, 135.0, 132.2, 131.5, 130.8, 130.1, 128.9, 128.7, 125.8, 124.7, 124.3, 29.2, 29.0, 25.3, 24.3, 24.2, 22.4. m.p. = 235 °C (decomposition).

Preparation of $[(2)AuN_2H_4]^+B(C_6F_5)_4^-$: 8 (60 mg, 0.086 mmol) and $KB(C_6F_5)_4$ (62 mg, 0.086 mmol) were added to a flame-dried Schlenk flask and anhydrous $CHCl_3$ (5 mL) was added. Anhydrous hydrazine (22 µL, 0.70 mmol) was added and the reaction was stirred at room temperature for 1 hour. The mixture was then filtered and the filtrate dried *in vacuo* to yield the hydrazine complex as an air-stable solid in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (m, 2H, Ar), 7.49 (m, 2H, Ar), 7.35 (m, 7H, Ar), 5.00 (s, 2H, br), 3.64 (s, 2H, br), 2.42 (septet, *J* = 6.0 Hz, 2H), 2.30 (septet, *J* = 6.0 Hz, 2H), 1.37 (d, *J* = 6.0 Hz, 6H), 1.21 (d, *J* = 6.0 Hz, 6H), 1.16 (d, *J* = 6.0 Hz, 6H), 1.01 (d, *J* = 6.0 Hz, 6H). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$): 154.3, 149.1, 144.9, 134.4, 132.7, 132.1, 131.0, 129.0, 128.8, 124.9, 124.5, 29.4, 29.1, 25.3, 24.3, 22.2.

Optimization of Bis-hydrohydrazination: C_6D_6 (0.4 mL), phenylacetylene (100 µL, 0.91 mmol), anhydrous hydrazine (13 µL, 0.41 mmol), and the internal standard benzyl methyl ether (15 µL, 0.12 mmol) were added to a mixture of pre-catalyst (1 mol% with respect to phenylacetylene) and $KB(C_6F_5)_4$ (1 mol% with respect to phenylacetylene) in a dry J-Young NMR tube. For experiments with a low catalyst loading (0.5 mol%, 0.1 mol%), a stock solution was prepared by dissolving (**2**)AuCl (100 mg) in methylene chloride (5 mL). The appropriate amount added to the NMR tube, and the solvent removed under vaccum. Then, the other reagents and the solvent were added. The tube was sealed, and placed in an oil bath and heated at the specified temperature. The reaction was monitored by ^{1}H NMR spectroscopy.

General Procedure for Bis-Hydrohydrazination of Alkynes: 8 (5.0 mg, 0.007 mmol, 1 mol% with respect to. alkyne) and $KB(C_6F_5)_4$ (5.0 mg, 0.007 mmol, 1 mol% with respect to alkyne) were introduced in a Teflon sealed Schlenk tube. Anhydrous benzene (0.4 mL), the desired alkyne (0.7 mmol), and anhydrous hydrazine (10 µL, 0.319 mmol) were added in this order. The solution was then heated to 100 °C for 13 hours, after which the reaction was cooled to room temperature and the volatiles removed *in vacuo.* The crude product was then passed through a short column of dry florisil silica gel (benzene or CH_2Cl_2 eluent). **1,2-bis(1-phenylethylidene)hydrazine:** ^{1}H NMR (300 MHz, C_6D_6): δ = 7.94 (m, 2H), 7.20 (m, 8H), 2.15 (s, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 158.3, 139.0, 129.7, 128.5, 127.0, 14.7. HR-MS (m/z): $[M+H]^+$ calcd. for $C_{16}H_{17}N_2$, 237.1384; $[M+H]^+$ found, 237.1384. **1,2-bis(1-(4-methoxyphenyl)ethylidene)hydrazine:**[24] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 9.0 Hz, 4H), 6.95 (d, *J* = 9.0 Hz, 4H), 3.86 (s, 6H), 2.33 (s, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 160.7, 157.8, 131.2, 128.0, 113.6, 55.3, 14.8. **1,2-bis(1-(4-trifluoromethyl)phenyl)ethylidene)hydrazine:** ^{1}H NMR (300 MHz, C_6D_6): δ = 7.71 (d, *J* = 9.0 Hz, 4H), 7.41 (d, *J* = 9.0 Hz, 4H), 1.98 (s, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 157.1, 141.6, 127.2, 125.4, 14.6. $^{19}F\{^1H\}$ NMR (282 MHz, C_6D_6): δ -62.5. HR-MS (m/z): $[M+H]^+$ calcd. for $C_{18}H_{15}F_6N_2$, 373.1134; $[M+H]^+$ found, 373.1136. **1,2-bis(1-cyclohexylethylidene)hydrazine:** ^{1}H NMR (300 MHz, C_6D_6): δ = 2.17-1.14 (br, m, cyclohexyl, 22H), 1.75 (s, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 164.4, 47.1, 30.7, 26.6, 26.5, 15.1. HR-MS (m/z): $[M+H]^+$ calcd. for $C_{16}H_{29}N_2$, 249.2325; $[M+H]^+$ found, 249.2327. **1,2-bis(1-(cyclohex-1-en-1-yl)ethylidene)hydrazine:** ^{1}H NMR (300 MHz, C_6D_6): δ = 6.09 (m, 2H), 2.68 (m, 2H), 2.00 (s, 6H), 1.60 (m, 2H), 1.49 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 158.1, 138.5, 26.3, 25.1, 23.1, 22.7, 12.9. HR-MS (m/z): $[M+H]^+$ calcd. for $C_{16}H_{2h}N_2$, 245.2012; $[M+H]^+$ found, 245.2014.

Unsymmetrical azine: 8 (0.007 mmol) and $KB(C_6F_5)_4$ (0.007 mmol) were introduced in a flame-dried Schlenk tube, and anhydrous benzene (0.4 mL) was added. 1-ethynyl-4-(trifluoromethyl)benzene (0.72 mmol) and anhydrous hydrazine (1.43 mmol) were added, and the mixture was stirred for 13 hours at 100 °C under argon. The reaction was then cooled to room temperature and volatiles removed *in vacuo*. The crude product was dissolved in benzene and passed through dry florisil silica gel to afford **9** as a solid in 76% yield.[11b] ^{1}H NMR (300 MHz, C_6D_6): δ = 7.54 (d, *J* = 9 Hz, 2H), 7.37 (d, *J* = 9 Hz, 2H), 4.92 (s, 2H, br), 1.44 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 143.5, 126.1, 125.7, 125.6, 125.5, 10.6. $^{19}F\{^1H\}$ NMR (282 MHz, C_6D_6): δ -62.1. Phenylacetylene (0.82 mmol), **9** (0.54 mmol), **8** (0.006 mmol), $KB(C_6F_5)_4$ (0.006 mmol), and anhydrous benzene (1 mL) were added to a dry Schlenk tube. The tube was sealed and heated to 100 °C for 6 hours, cooled to room temperature, and the volatiles removed *in vacuo*. The crude product was dissolved in benzene and passed through dry florisil silica gel to afford **10** as a white solid in 61% yield. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.89 (m, 2H), 7.71 (m, 2H), 7.40 (m, 2H), 7.19 (m, 3H), 2.13 (d, 12 Hz, 3H), 2.02 (d, 12 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 158.6, 158.2, 157.1, 156.9, 142.0, 141.6, 138.9, 138.6, 130.0, 128.5, 127.1, 125.4, 14.6. $^{19}F\{^1H\}$ NMR (282 MHz, C_6D_6): δ -62.4. HR-MS (m/z): $[M+H]^+$ calcd. for $C_{17}H_{16}F_3N_2$, 305.1263; $[M+H]^+$ found, 305.1260.

Acknowledgements

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Keywords: gold • hydroamination • hydrazine • mesoionic carbene • cyclopropenylidene

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Layout 2:

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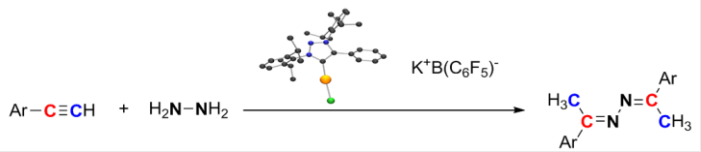

Twice is better than once! An original synthetic route gives access to a mesoionic carbene supported gold(I) complex, which is not only able to promote the hydrohydrazination of terminal alkynes, but also the bis(hydrohydrazination), giving access to azines.

*Daniel R. Tolentino, Liqun Jin, Mohand Melaimi, and Guy Bertrand**

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Mesoionic Carbene-Gold(I) Catalyzed Bis-Hydrohydrazination of Alkynes with Parent Hydrazine