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# NHC−Gold(I) Complexes as Effective Catalysts for the Carboxylative Cyclization of Propargylamines with Carbon Dioxide

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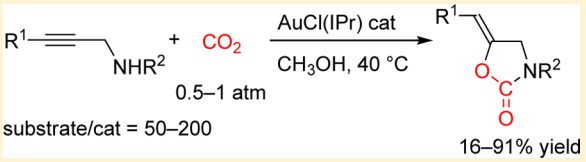
Supporting Information

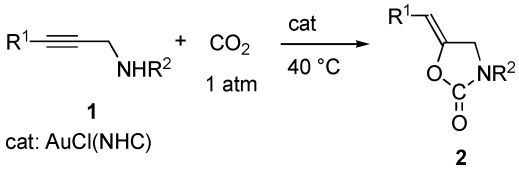
**ABSTRACT:** NHC−gold(I) complexes promote carboxylative cyclization of a range of propargylic amines to afford (*Z*)-5-alkylidene-1,3-oxazolidin-2-ones in methanol under neutral and mild conditions. The highly active and robust catalyst permits $CO_2$ utilization under a mixed gas atmosphere containing CO or $H_2$. As a key intermediate, a new alkenylgold(I) complex was successfully identified from a stoichiometric reaction of Au(OH)(IPr) and 1-methylamino-2-butyne in THF. The methanol solvent influences the formation of catalytically active cationic gold species and facilitates protodeauration from the alkenylgold complex to release the cyclic urethane product due to in situ generation of methylcarbonic acid in the presence of $CO_2$.




Transformation of carbon dioxide ($CO_2$) into value-added compounds has attracted significant attention as a principal approach to utilize an abundant, inexpensive, and renewable C1 resource.[1] As one of the reliable methods, conversion of thermodynamically less stable carbamic acid family into robust functionalized molecules has been broadly explored.[2] With regard to the facile formation of *N*,*N*-dialkylcarbamic acids from secondary amines in supercritical $CO_2$, we have reported effective $CO_2$ fixation protocols affording urethanes and ureas.[3,4] For example, carboxylative cyclization of propargylamines (**1**) with $CO_2$ has been successfully achieved under supercritical conditions even in the absence of catalysts to give 5-alkylidene-1,3-oxazolidin-2-ones (**2**).[3] Although the carboxylation proceeds regio- and stereoselectively through intramolecular addition of carbamic acids to C−C triple bonds, some drawbacks still remain concerning limited substrate scopes and severe pressurization conditions.[5]

From the intense research efforts in the field of catalysis with coinage metals, various addition reactions of protic functional groups to C−C multiple bonds have been developed.[6] Indeed, gold(I) catalysts effect intramolecular cyclization of alkynoic acids to give lactones.[7] The related carbamic acids derived from aminoalkynes and $CO_2$ have not been subjected to gold-catalyzed cyclizations, whereas the other triad metals, copper and silver, were employed for the urethane formation. Dimroth and Pasedach originally found, nearly a half century ago, that some copper compounds can catalyze the carboxylative cyclization of terminal propargylamines.[5a] Recently, Yamada and co-workers reported the effectiveness of silver acetate for synthesis of cyclic urethanes from aminoalkynes under mild conditions.[5f−h] Herein we disclose the carboxylative cyclization of propargylamines catalyzed by gold(I) complexes bearing an N-heterocyclic carbene (NHC) ligand under atmospheric pressure of $CO_2$ (Scheme 1) and identification of alkenylgold species relevant to the catalytic intermediates.

**Scheme 1. Carboxylative Cyclization of Propargylamines**




We initially examined the reaction of 1-methylamino-2-butyne (**1a**; $R^1 = R^2 = CH_3$) with 1 atm of $CO_2$ in the presence of group 11 metal compounds with a substrate/catalyst (S/C) ratio of 50 in methanol at 40 °C for 15 h (the standard conditions in Table 1). In contrast to the unsatisfactory results obtained with AuCl (entry 1), the NHC−gold complex AuCl(IPr) (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) was found to promote the carboxylation effectively to afford a 5-*exo*-*dig* cyclization product, 5-ethylidene-1,3-oxazolidin-2-one (**2a**), in 91% yield (entry 2).[8] The reaction proceeded independently of the $CO_2$ pressure above 1 atm. In our previous work on catalyst-free carboxylation under supercritical conditions,[3] such an alkyl-substituted internal propargylic amine could not be transformed into the urethane product. The $^1$H NMR spectrum of the reaction mixture clearly showed a quartet of triplets signal at 4.59 ppm ($^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 2.2 Hz) due to the olefinic proton, indicating that no other isomers were formed in the cyclization. The C−C double bond of **2a** was found to be in the *Z* configuration by NMR spectroscopy and X-ray crystallographic analysis (Supporting Information), indicating that addition of the carbamate moiety to the alkyne proceeded predominantly in an *anti* fashion, as seen in our previous report for the catalyst-free system.[3] The reaction even with the catalyst loading reduced to 0.5 mol %

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**Table 1. Carboxylative Cyclization of 1a and $CO_2$[a]**

| entry | catalyst | solvent | yield, %[b] |
|---|---|---|---|
| 1 | AuCl | $CH_3OH$ | 0 |
| 2 | AuCl(IPr) | $CH_3OH$ | 91 |
| 3 | AuCl(IPr)[c] | $CH_3OH$ | 85 |
| 4 | AuCl(IMes)[d] | $CH_3OH$ | 89 |
| 5 | AuCl($I^tBu$)[e] | $CH_3OH$ | 83 |
| 6 | AuCl[$P(C_6H_5)_3$] | $CH_3OH$ | 41 |
| 7 | AuCl[$P(OC_2H_5)_3$] | $CH_3OH$ | 61 |
| 8 | AuCl[$P(C_2H_5)_3$] | $CH_3OH$ | 70 |
| 9 | AuBr(IPr) | $CH_3OH$ | 84 |
| 10 | AuI(IPr) | $CH_3OH$ | 71 |
| 11 | AgCl(IPr) | $CH_3OH$ | 52 |
| 12 | CuCl(IPr) | $CH_3OH$ | 19 |
| 13 | $I^tBu-CO_2$[f] | $CH_3OH$ | 0 |
| 14 | AuCl(IPr) | 2-propanol | 55 |
| 15 | AuCl(IPr) | $CH_3CN$ | 15 |
| 16 | AuCl(IPr) | THF | 0 |
| 17 | AuCl(IPr) | $CH_2Cl_2$ | 0 |
| 18 | AuCl(IPr) | toluene | 0 |

[a]Standard conditions: the reaction was carried out with **1a** (2.0 mmol) and catalyst (0.04 mmol) in solvent (2.0 mL) under a $CO_2$ atmosphere at 40 °C for 15 h. [b]Determined by the $^1H$ NMR method, using durene as an internal standard. [c]The reaction was conducted with catalyst (0.01 mmol) for 48 h under otherwise identical conditions. [d]IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene. [e]$I^tBu$ = 1,3-di-*tert*-butylimidazol-2-ylidene. [f]$I^tBu$-$CO_2$ = 1,3-di-*tert*-butylimidazolium-2-carboxylate.

from 2 mol % proceeded smoothly to give **2a** in 85% yield in 48 h, indicating the IPr−Au catalyst is stable enough for the carboxylation (entry 3).

Further screening tests using a series of Au catalysts under the same conditions revealed that similar levels of catalytic activity (89% and 83% yields) were attained with the related NHC complexes (entries 4 and 5), whereas Au complexes bearing $P(C_6H_5)_3$, $P(OC_2H_5)_3$, and $P(C_2H_5)_3$ ligands were found to have lower catalyst activities (41−70% yield; entries 6−8). The halide ligand also delicately influenced the product yield (84% and 71% in entries 9 and 10). Changing the central metal to Ag and Cu caused a decrease in the yield to 52% and 19%, respectively (entries 11 and 12), even though several NHC−Cu complexes have been realized as efficient catalysts for $CO_2$ fixations.[9] We have also developed $CO_2$-fixation reactions catalyzed by isolated NHC molecules or these $CO_2$ adducts;[10] however, the carboxylation with a catalytic amount of 1,3-di-*tert*-butylimidazolium-2-carboxylate ($I^tBu$-$CO_2$) resulted in the recovery of **1a** (entry 13).

The outcome of the carboxylation was strongly influenced by the solvent used. The use of methanol gave beneficial results in comparison with 2-propanol or acetonitrile, and **1a** remained intact after the reaction in $CH_2Cl_2$, toluene, or THF (entries 2 and 14−18).

The NHC−Au(I) catalyst paved the way to a variety of five-membered cyclic urethanes from propargylic amines, as summarized in Table 2. With the optimized reaction conditions using 2 mol % of AuCl(IPr) in methanol, aliphatic *N*-methylaminoalkyne substrates (**1b−d**; $R^1$ = alkyl) were smoothly converted into the analogous *Z* products (**2b−d**) in yields of 85−91% (entries 1−3). The reaction of a substrate having a terminal alkyne unit, *N*-methylpropargylamine (**1e**), gave the product **2e** in 16% yield, possibly due to in situ formation of a gold acetylide as a less catalytically active species

**Table 2. Carboxylative Cyclization Catalyzed by AuCl(IPr)[a]**

| entry | substrate | $R^1$ | $R^2$ | *t*, h | yield, %[b] |
|---|---|---|---|---|---|
| 1 | **1b** | $C_2H_5$ | $CH_3$ | 15 | 83 |
| 2 | **1c** | $(CH_3)_2CH$ | $CH_3$ | 15 | 87 |
| 3 | **1d** | $(CH_3)_3C$ | $CH_3$ | 15 | 81 |
| 4 | **1e** | H | $CH_3$ | 15 | 16 |
| 5 | **1f** | $CH_3$ | $C_2H_5$ | 48 | 85 |
| 6 | **1g** | $CH_3$ | $C_3H_7$ | 48 | 86 |
| 7 | **1h** | $CH_3$ | $CH_2C_6H_5$ | 15 | 83 |
| 8 | **1i** | $CH_3$ | $(CH_3)_2CH$ | 66 | 27 |
| 9 | **1j** | $C_6H_5$ | $CH_3$ | 48 | 76 |
| 10 | **1k** | $C_6H_5$ | H | 48 | 47 |

[a]Reaction conditions: the reaction was carried out with **1a** (2.0 mmol) and catalyst (0.04 mmol) in $CH_3OH$ (2.0 mL) under $CO_2$ (1 atm) at 40 °C. [b]Determined by $^1H$ NMR. [c]Isolated yield in parentheses.

(entry 4). The carboxylative cyclization of other 1-amino-2-butynes (**1f−h**) with alkyl and benzyl substituents on the nitrogen atom also afforded (*Z*)-5-ethylidene-1,3-oxazolidin-2-ones (**2f−h**) in 83−86% yields (entries 5−7), although sterically congested amino groups required a longer reaction time of 48 h. A sharp drop in the catalytic activity was observed for the reaction of a bulky *N*-isopropyl variant (**1i**), furnishing the desired product only in 27% yield after 66 h (entry 8). The amine conversion was obviously reduced by replacement of the $R^1$ group from alkyls to phenyl, even at elongated reaction times (entry 9). Moreover, the primary amine **1k**, which was hardly carboxylated in the preceding reports, was applicable to the present Au system, resulting in a comparable yield (entry 10).

Notably, the reaction of **1a** under mixed gas conditions proceeded smoothly to give the urethane product in a reasonable yield. As shown in Table 3, the high efficiency

**Table 3. Carboxylative Cyclization of 1a under a Mixed $CO_2$ Atmosphere[a]**

| entry | mixed gas | v/v, % | *t*, h | yield, %[b] |
|---|---|---|---|---|
| 1 | $CO_2$ | | 15 | 91 |
| 2 | $CO_2$/Ar | 50/50 | 15 | 85 |
| 3 | $CO_2$/Ar | 10/90 | 15 | 24 |
| 4 | $CO_2$/air | 50/50 | 48 | 75 |
| 5 | $CO_2$/CO | 50/50 | 15 | 80 |
| 6 | $CO_2$/$H_2$ | 50/50 | 15 | 75 |

[a]Reaction conditions: the reaction was carried out with **1a** (2.0 mmol) and catalyst (0.04 mmol) in $CH_3OH$ (2.0 mL) under $CO_2$ (1 atm) at 40 °C. [b]Determined by $^1H$ NMR.

was maintained in the case of a 1:1 mixture of $CO_2$ with argon, whereas further dilution resulted in retardation of the process (entries 1−3). A mixture with air was also usable, although a prolonged reaction time was needed to provide a similar level of productivity (entry 4). Unexpectedly, the gold catalyst tolerated the presence of CO or $H_2$ gas as well (entries 5 and 6) and hence offers potential for $CO_2$ utilization directly from exhaust combustion gas.

In order to gain mechanistic insight into the carboxylation, stoichiometric reactions using an NHC−Au(I) complex under aprotic and nonacidic conditions were evaluated. The treatment of AuOH(IPr)[11] with an equimolar amount of **1a** under a $CO_2$ atmosphere in dehydrated THF at 40 °C afforded the alkenylgold complex **3a**, which was isolated in 54% yield after


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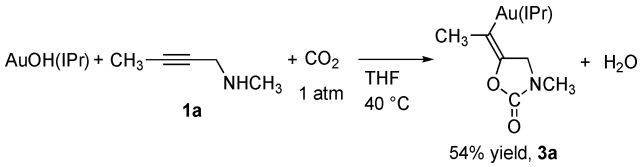
recrystallization from THF/*n*-pentane (Scheme 2). The colorless complex **3a** was unambiguously characterized by

**Scheme 2. Synthesis of the Alkenylgold(I) Complex 3a as a Model Intermediate in Carboxylative Cyclization**




NMR spectroscopy, elemental analysis, and X-ray crystallography. The crystal structure (Figure 1) shows that the Au(I)

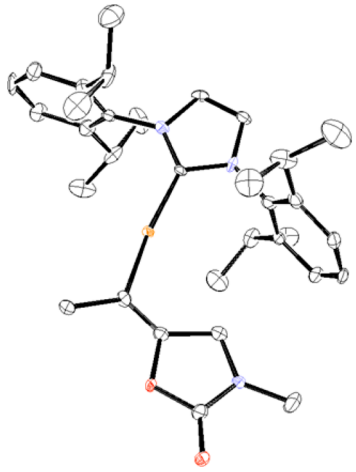


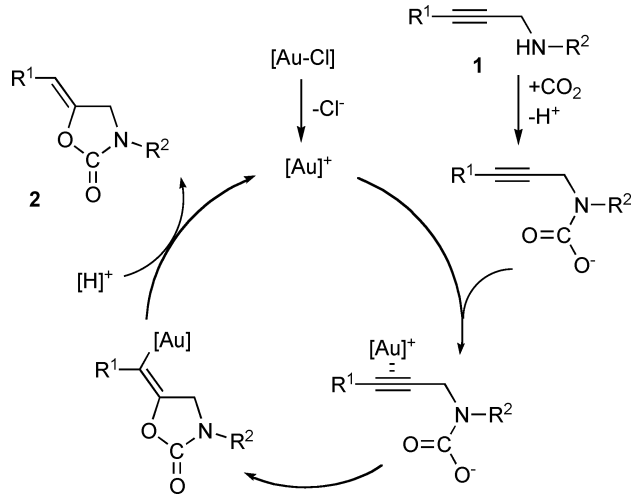
**Figure 1.** ORTEP diagram of **3a** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are given in the Supporting Information.

atom is bound to the NHC carbene and alkenyl carbons in a typical linear two-coordinate geometry. The gold−carbon bond lengths are 2.029 and 2.046 Å (mean values), which are within the typical range for related alkenylgold compounds.[12,13] The alkylidenecarbamate scaffold including the five-membered ring is virtually planar, and the geometry is almost identical with that of the liberated product **2a** (see the Supporting Information). These structural data suggest that the cyclization of the amine−$CO_2$ adduct will be promoted by coordination of the C−C triple bond to the Au(I) center to form the *anti* addition product exclusively.

Since the coproduct $H_2O$ does not have enough acidity to cleave the alkenyl−Au bond, the intermediate **3a** is obtainable from the stoichiometric reaction. The isolable complex **3a** was smoothly deaurated upon equimolar addition of acetic acid in $CD_3OD$ at room temperature to give **2a** in 83% yield within 1 h. In contrast, 91% of **3a** remained in a $CD_3OD$ solution under neutral conditions even after 24 h; thus, the alkenyl−Au bond proved to be more stable than expected. Of particular note is that the protodeauration of **3a** was significantly accelerated by exposure with atmospheric $CO_2$ to furnish **2a** in 54% yield after 3 h. Presumably, the combination of methanol and $CO_2$ will lead to marginal formation of methylcarbonic acid ($CH_3OCO_2H$),[14] which facilitates the protodeauration step in the catalytic carboxylative cyclization.

It is noteworthy that catalytic use of the isolated complex **3a** showed a comparable activity (90% yield of **2a**) with AuCl(IPr) under the standard reaction conditions mentioned above. On the basis of the experimental results on **3a**, a mechanism involving the alkenylgold(I) species is proposed (Scheme 3).

**Scheme 3. Proposed Mechanism of Carboxylative Cyclization of Propargylamines Catalyzed by the NHC−Au Complexes**




The chlorogold(I) precursor can form a catalytically active cationic species via facile dissociation of the anionic ligand in a polar methanol medium. The alkyne moiety on propargylic carbamate formed through a spontaneous carboxylation of the amine substrate is activated on the cationic gold(I) center. The carbamate anion attacks nucleophilically on the triple bond in an *anti* fashion to generate the corresponding neutral alkenylgold intermediate, as typified by **3a**. The presence of $CO_2$ in $CH_3OH$ enhances the following protodeauration in which the cationic species is regenerated with liberation of the urethane **2**.

In summary, we have demonstrated that NHC−Au(I) complexes serve as efficient catalysts, providing 1,3-oxazolidin-2-ones from propargylamines and $CO_2$ under mild conditions. Moreover, we have successfully identified a key alkenylgold(I) intermediate in the catalytic carboxylative cyclization and realized unique advantages of methanol to drive the catalytic cycle, especially with regard to the $CO_2$-mediated acceleration in the product-releasing step.

## ■ ASSOCIATED CONTENT

### Supporting Information

Text, figures, tables, and a CIF file giving experimental and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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