

Table of Contents

Mechanistic Aspects of the Carboxylative Cyclization of Propargylamines and Carbon Dioxide Catalyzed by Gold(I) Complexes Bearing an *N*-Heterocyclic Carbene Ligand

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Supporting Information Placeholder

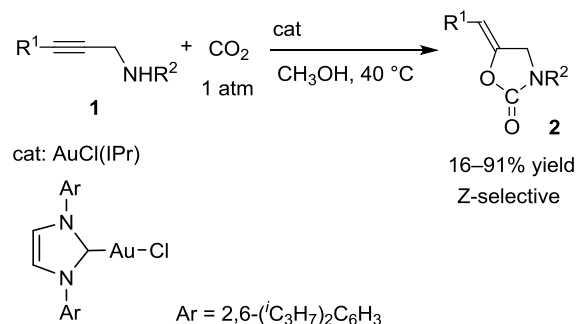
ABSTRACT: The carboxylative cyclization of a range of propargylic amines using carbon dioxide (CO₂) is promoted by IPr-gold(I) (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) complexes to afford (*Z*)-5-alkylidene-2-oxazolidones in methanol under mild conditions, even in the absence of additives such as silver salts and bases. Investigation of the substrate scope shows that the catalytic performance is markedly retarded by the introduction of aromatic substituents at the alkyne terminus. The formation of alkenylgold(I) complexes as catalytic intermediate models is demonstrated by the treatment of methyl- and phenyl-substituted propargylamines with AuOH(IPr) under a CO₂ atmosphere. A comparison of the reactivity of the alkenylgold(I) complexes clearly indicates that the alkenyl ligand attached to an alkyl group at the α position is more susceptible to protonolysis compared with that attached to a phenyl group. These results and kinetic experiments corroborate a catalytic cycle that involves the nucleophilic attack of carbamate at the C-C triple bond bound to the Au center and its subsequent protodeauration to release the cyclic urethane products. **KEYWORDS:** gold catalysis, carbon dioxide, carboxylative cyclization, alkenyl complex, cyclic urethane

INTRODUCTION

Catalytic CO₂ fixation into valuable compounds has received considerable attention as desirable chemical processes to utilize a ubiquitous C1 source.¹ Because 2-oxazolidones are versatile intermediates for the production of pharmaceuticals and fine chemicals and are also chiral auxiliaries, the CO₂-based dehydrative carboxylation of amino alcohols,² the cycloaddition of aziridines³ and the cyclization of alkynyl and alkenyl amines with CO₂ have been explored to construct the five-membered urethane ring structure.^{4–14} These effective CO₂ fixation protocols are based on the conversion of thermodynamically less stable carbamic acids generated from amines and CO₂ into robust urethanes.¹⁵

As a part of our research directed toward the development of addition reactions of CO₂ to unsaturated molecules,^{14,16} we recently observed that *N*-heterocyclic carbene-coordinated Au(I) complexes effectively promote the carboxylative cyclization of

propargylamines (**1**) under ambient CO₂ conditions to afford 5-vinylidene-2-oxazolidones (**2**) (Scheme 1).^{14b} An intensive comparative study on the choice of ligands and solvents revealed that the use of gold(I) chloride with a 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr) ligand in methanol was highly beneficial with respect to productivity and allowed the reaction to proceed even in the absence of cocatalysts such as silver salts. A recent computational study suggested that the ring formation by the nucleophilic attack of a carbamate anion at an (η^2 -alkyne)gold species is the rate-determining step and that the use of methanol as a solvent could stabilize the carbamate anion to lower the energy barrier for the transition state.¹⁷ Although the calculations indicated that the resulting cyclized intermediate is easy for the subsequent protonation, we successfully synthesized a model alkenylgold(I) complex with a five-membered urethane moiety from AuOH(IPr) with 1-methylamino-2-butyne (**1a**) and CO₂. In this paper, we disclose a full account of the 2-oxazolidone synthesis from a range of propargylic amines as well as the properties of the intermediate models, which helps provide further insight into the gold-catalyzed reaction mechanism. In particular, we observed that the reactivity of the amine substrate is markedly influenced by the substituents attached to the alkyne moiety, and that this influence originates from the susceptibility of the alkenylgold(I) intermediate to protonolysis to liberate the urethane products.



Scheme 1. Metal/NH Bifunctionality Based on the Interconversion Between the Amido and Amine Complexes.

RESULTS AND DISCUSSION

As evaluated by the screening of group 11 metal complexes in our previous paper,^{14b} AuCl(IPr)¹⁸ catalyzes efficiently under an atmospheric pressure of CO₂ with a substrate/catalyst ratio of 50 in methanol at 40 °C for 15 h (the standard conditions in Table 1). Various 5-alkylidene-2-oxazolidones were prepared from alkyl-substituted internal aminoalkynes, which could not be transformed under catalyst-free supercritical conditions.^{14a}

Using 1-(methylamino)-2-butyne (**1a**; R¹ = R² = CH₃; 2.0 mmol) as a substrate afforded Z-5-ethylidene-2-oxazolidone (**2a**) regioselectively as a 5-*exo-dig* cyclization product in 91% yield (entry 1). The ¹H NMR spectrum of the reaction mixture clearly indicates that no other regioisomers or stereoisomers were formed in the cyclization and that the *anti* addition of the carbamate anion to the alkyne moiety therefore occurred in a stereoselective manner.^{14b} The use of methanol as a solvent gave optimal results compared to CH₂Cl₂, toluene, or tetrahydrofuran, in which **1a** remained intact (*vide infra*).

Table 1. Carboxylative Cyclization with AuCl(IPr) Catalyst^a

entry	amine	R ¹	R ²	time/h	% yield ^b
1	1a	CH ₃	CH ₃	15	91
2 ^c	1a	CH ₃	CH ₃	48	85
3	1b	C ₂ H ₅	CH ₃	15	83
4	1c	(CH ₃) ₂ CH	CH ₃	15	87
5	1d	(CH ₃) ₃ C	CH ₃	15	81
6	1e	H	CH ₃	15	9
7	1f	(CH ₃) ₃ Si	CH ₃	48	7(2f), 16(2e)
8	1g	CH ₃	CH ₂ C ₆ H ₅	15	83
9	1i	C ₆ H ₅	CH ₃	48	76
10	1j	4-CH ₃ C ₆ H ₄	CH ₃	48	75(69)
11	1k	4-CH ₃ OC ₆ H ₄	CH ₃	48	53
12	1l	4-NCC ₆ H ₄	CH ₃	48	45
13	1m	4-FC ₆ H ₄	CH ₃	48	59
14	1n	4-ClC ₆ H ₄	CH ₃	48	56(55)
15	1o	4-BrC ₆ H ₄	CH ₃	48	43(40)
16	1p	C ₆ H ₅	H	48	47

^aReaction conditions: the reaction was carried out with **1** (2.0 mmol) and AuCl(IPr) (0.04 mmol) in CH₃OH (2.0 mL) under CO₂ (1 atm) at 40 °C. ^bIsolated yield in parentheses. ^cThe reaction was conducted with AuCl(IPr) (0.01 mmol) under otherwise identical conditions.

The time-course of the conversion of **1a** into **2a** under the standard conditions indicates that no marked induction period occurs at the early stage of the carboxylation and that the yield of **2a** reaches 77% within 6 h (Figure 1). The reaction with a reduced catalyst loading of 0.5 mol% from 2 mol% proceeded smoothly to give **2a** in 85% yield after 48 h (entry 2). Notably, the high efficiency of the gold catalysts was maintained under a mixed-gas atmosphere; i.e., the reaction of **1a** proceeded smoothly to yield the desired product in comparable yields, even when the CO₂ was diluted with O₂, H₂, CO, ethylene, NO or N₂O, as shown in Table 2.

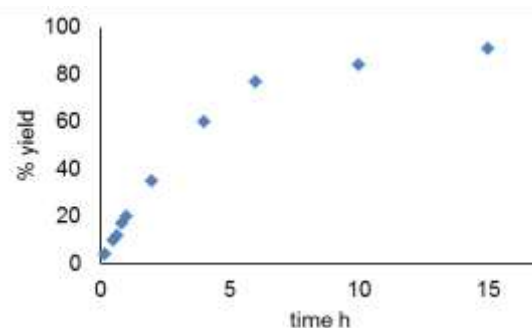


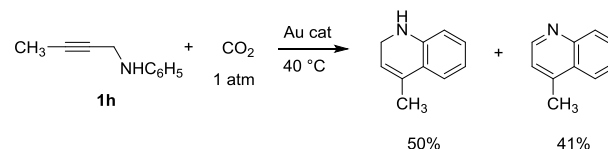
Figure 1. Time dependence on the yield **2a** from **1a** under the standard conditions described in the footnote of Table 1.

Table 2. Catalytic activities under mixed gas atmospheres^a

entry	mixed gas	% yield ^b
1	CO ₂	91
2	CO ₂ /O ₂	80
3	CO ₂ /CO	80
4	CO ₂ /H ₂	75
5	CO ₂ /C ₂ H ₄	77
6	CO ₂ /NO	59
7	CO ₂ /N ₂ O	78

^aReaction conditions: the reaction was carried out with **1** (2.0 mmol) and catalyst (0.04 mmol) in CH₃OH (2.0 mL) under a gaseous mixture containing CO₂ (50% vol) at 40 °C for 15 h. ^bDetermined by ¹H NMR using durene as an internal standard.

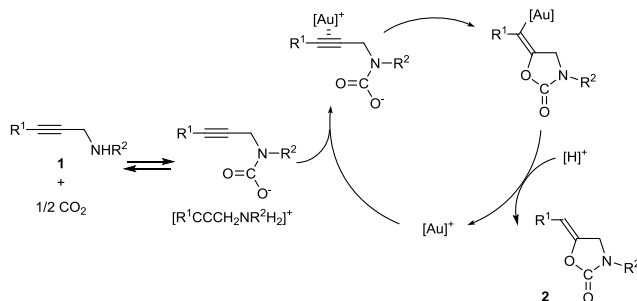
Under the optimized reaction conditions and in the presence of 2 mol% of AuCl(IPr) in methanol, aliphatic *N*-methylaminoalkyne substrates (**1b-1d**; R¹ = alkyl) were fully converted into the analogous Z-products (**2b-2d**) in yields of 85–91% (entries 3–5). A substrate with a terminal alkyne unit, *N*-methylpropargylamine (**1e**), gave only 9% yield with recovery of 91%, possibly because of the *in-situ* formation of a gold acetylide as a less catalytically active species (entry 6). The incorporation of a trimethylsilyl group at the alkyne terminus was ineffective and resulted in the formation of the desilylated product **2e** coupled with **2f** in 16% and 7% yields, respectively, after 48 h (entry 7). Whereas the desired Z-5-ethylidene-2-oxazolidone product (**2g**) was obtained in 83% yield from 1-benzylamino-2-butyne (**1g**; entry 8), *N*-propargylated aniline (**1h**) gave a mixture of 1,2-dihydroquinoline and quinoline derivatives in 50% and 41% yields, respectively. These products were formed via 6-*endo-dig* cycloisomerization¹⁹ without CO₂ incorporation, as shown in Scheme 2.



Scheme 2. Reaction of 1-anilino-2-butyne **1h**.

When a series of substrates (**1i-1p**; $R^1 = \text{aryl}$) containing aromatic groups attached to the alkyne moiety were subjected to the reaction, the *anti*-addition products were obtained in moderate to good yields and with perfect stereoselectivities (Table 2, entries 9–16). Changing the R^1 group from alkyls to aryls resulted in retardation of the gold-catalyzed carboxylation; in contrast, aminoalkynes substituted with electrophilic functional groups are rather susceptible to reaction in scCO_2 without any catalysts.^{14a} The amine conversion was significantly reduced even at elongated reaction times. A primary amine **1p** was also transformed into the urethane in a reasonable yield (entry 16).

The stereochemical outcome of the cyclization has a clear consonance with a catalytic cycle involving the intramolecular addition of carbamates to the alkyne moiety in an *anti* fashion, as depicted in Scheme 3. The chlorogold(I) precursor can form a catalytically active cationic species via dissociation of the anion in a polar medium. The alkyne moiety on the propargylic carbamate formed from the amine substrate and CO_2 is activated on the cationic gold(I) center. The carbamate anion attacks the C–C triple bond to generate the corresponding neutral alkenylgold intermediate. After protonolysis, the resulting gold intermediate releases the urethane product and regenerates the cationic active species.



Scheme 3. A possible catalytic cycle of the carboxylative cyclization of propargylamines promoted by IPr–Au complexes.

To account for the catalytic cycle, the kinetic aspects of the catalytic urethane formation were analyzed. We determined the relative rates of the urethane formation by measuring the initial rates of the reaction of **1a** and CO_2 (1 atm) in methanol (2.0 mL) at 40 °C. Under the standard conditions of a substrate/catalyst ratio of 50 (i.e., $[\mathbf{1a}] = 1.0 \text{ mol dm}^{-3}$, $[\text{cat}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$), the formation of **2a** was not influenced by an increase of the CO_2 pressure to greater than 0.1 MPa (see Supporting Information). A linear relationship was observed between the rates and the concentrations of the gold catalyst, which ranged from 1.0×10^{-2} to $4.0 \times 10^{-2} \text{ M}$, as shown in Figure 2. In contrast, the rate increased nonlinearly with increasing concentration of **1a**. The slopes of the $\log[\text{rate}]$ vs. $\log[\mathbf{1a}]$ plots reveal that the rate obeys a three-fourths-order relationship with $[\mathbf{1a}]$, as illustrated in Figure 3. On the basis of the fact that the reaction rate was not affected by the CO_2 concentration and followed first order kinetics with respect to the gold catalyst, the formation of ammonium carbamate from **1** and CO_2 should be relatively fast. We postulated that the coordination of the ammonium carbamate is the rate-determining step under a lower concentration of the amine substrate. The non-integer reaction order with $[\mathbf{1a}]$ was possibly observed because the protonation of the alkenylgold(I) intermediate becomes sluggish with the increase in $[\mathbf{1a}]$.

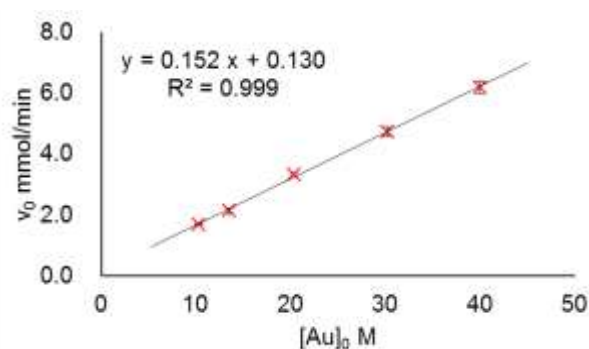


Figure 2. Plots of rate against gold concentration under the conditions of CO_2 (1 atm) and $[\mathbf{1a}] = 1.0 \text{ M}$ in methanol (2.0 mL) at 40 °C.

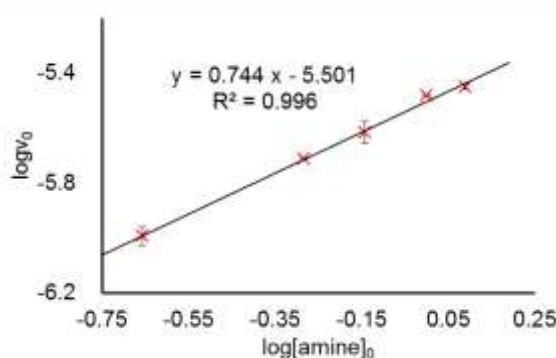
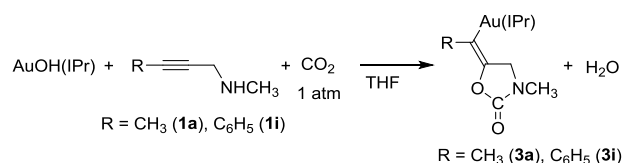


Figure 3. Plots of $\log(\text{rate})$ against $\log([\mathbf{1a}])$ under the conditions of CO_2 (1 atm) and $[\text{cat}] = 2.0 \times 10^{-2} \text{ M}$ in methanol (2.0 mL) at 40 °C.

We envisioned that the treatment of the IPr–Au(I) complex with propargylic amines under aprotic and non-acidic conditions could suppress the protodeauration and will permit confirmation of the formation of alkenylgold species containing cyclic urethane units. Actually, the alkenylgold complexes (**3a**^{14b} and **3i**) were isolated from a stoichiometric reaction of $\text{AuOH}(\text{IPr})^{20}$ with 1-(methylamino)-2-butyne (**1a**) or 1-methylamino-3-phenyl-2-propyne (**1i**) under a CO_2 atmosphere at 40 °C in dry THF (Scheme 4). Recrystallization by the slow diffusion of *n*-pentane into a THF solution of **3a** or **3i** gave colorless crystals in 54% or 16% yield, respectively. These complexes were fully characterized by NMR spectroscopy, elemental analysis and X-ray crystallography. The Au(I) atom is bound to the NHC carbene and alkenyl carbons in a typical linear two-coordinate geometry. As observed from Figures 4 and 5, no apparent structural difference exists between **3a**^{14b} and **3i**. The gold-carbon (alkenyl and IPr) bond lengths are in the range of 2.021–2.049 Å, which are typical values for related alkenylgold compounds.²¹ The alkylidene-carbamate scaffold that includes the five-membered ring is virtually planar, and the geometry is almost identical to that of the Z-urethanes, **2**. These structural data suggest that the cyclization proceeds via the attack of the carbamate at the alkyne unit coordinated to the gold center to form the *anti* addition product.



Scheme 4. Synthesis of alkenylgold(I) complexes **3** as model intermediates in the carboxylative cyclization.

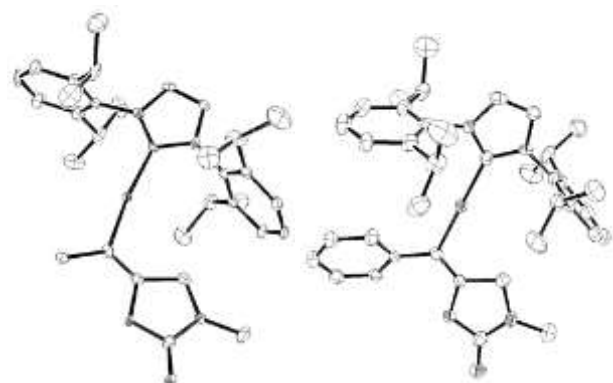


Figure 4. ORTEP diagram of alkenylgold complexes **3a** (left) and **3i** (right) with 50% probability ellipsoids; hydrogen atoms are omitted for clarity.

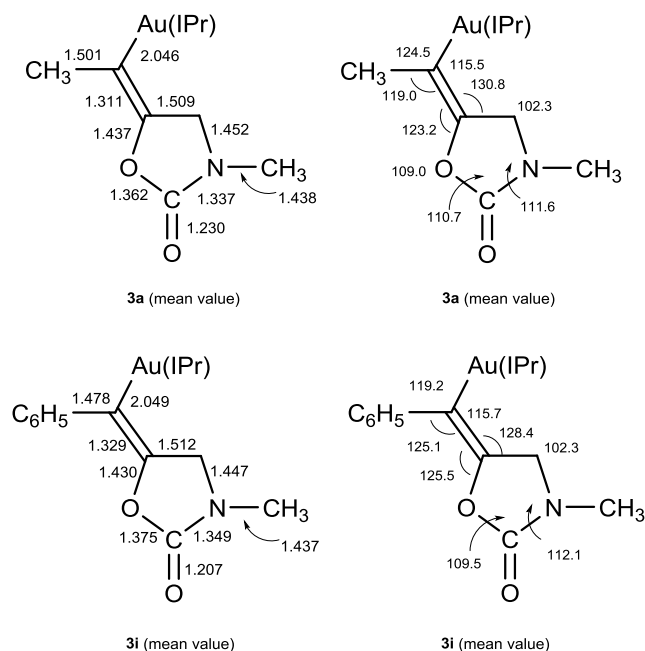


Figure 5. Selected bond lengths (Å) and angles (°) for **3a**^{14b} and **3i**.

To corroborate the catalytic mechanism involving the alkenylgold species, the carboxylative cyclizations of **1a** and **1i** were conducted in the presence of **3a** and **3i**, respectively, for 15 h under the standard catalytic conditions (Table 3). The isolated methyl-substituted complex **3a** exhibited catalytic activity (90% yield) comparable with that of AuCl(IPr) in the reaction of **1a** (entries 1 and 2). The lower reactivity of **1i** compared to that of **1a** was reproduced in the carboxylation using the phenyl-substituted complex **3i** (48% yield), as shown in entries 4 and 5.

Table 3. Comparison of catalytic activities in the presence of **3a** and **3i**^a

entry	substrate	Au catalyst	% yield ^b
1	1a	AuCl(IPr)	91
2	1a	3a	90
3	1a	AuOH(IPr)	83
4	1i	AuCl(IPr)	53
5	1i	3i	48

^aReaction conditions: the reaction was carried out with **1** (2.0 mmol) and catalyst (0.04 mmol) in CH₃OH (2.0 mL) under CO₂ (1 atm) at 40 °C for 15 h. ^bDetermined by ¹H NMR using durene as an internal standard.

The stoichiometric reaction of AuOH(IPr) with **1a** in THF gave the alkenylgold complex **3a** and H₂O as a co-product; this complex lacks sufficient acidity to cleave the alkenyl–Au bond (Scheme 4). Nevertheless, AuOH(IPr) was also active for catalytic carboxylation in CH₃OH under catalytic conditions (entry 3). These results suggest that some acidic compounds such as methylcarbonic acid²² (CH₃OCO₂H; *vide infra*) might be generated during the carboxylation in CH₃OH for the protonolysis of the alkenylgold intermediate, as shown in Scheme 3. In fact, the isolated complex **3a** was smoothly deaurated upon the addition of an equimolar amount of acetic acid in CD₃OD at room temperature to give **2a** in 83% yield within 1 h, as shown in Figure 6. In contrast, the phenyl-substituted complex **3i** gave **2i** in only 15% yield under identical conditions. The substituents on the alkenyl carbon proximal to the gold center in **3a** and **3i** clearly affect the relative ease of protodeauration; hence, the strong correlation between the reactivities of the isolated complexes and the catalytic reaction rates of **1a** and **1i** was realized.

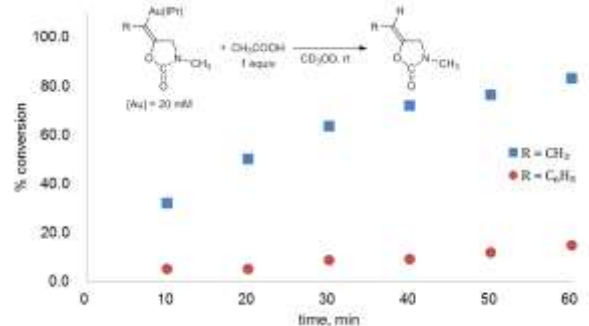


Figure 6. Conversion versus time curve for the reactions of **3a** (■) and **3i** (●) with equimolar amounts of acetic acid in CD₃OD at room temperature.

When the alkenyl complexes were treated in CD₃OD under an argon atmosphere (Table 4), 91% of the **3a** was remained untouched and **3i** was mostly recovered after 24 h (entries 1 and 2). Although the alkenyl–Au bond proved to be more stable than expected, the protodeauration of **3a** was significantly facilitated by the exposure to atmospheric CO₂ to furnish **2a** in 95% yield after 9 h (entry 3), possibly because the combination of methanol and CO₂ results in the formation of methylcarbonic acid. The acceleration due to the CO₂-mediated protonation was also confirmed by the reaction of **3i** in methanol; however, the phenyl substituent diminishes the carbanionic character of the alkenyl groups, leading to a limited yield of **2i** (13 %; entry 4).

Table 4 Protodeauration of alkenyl complexes **3a and **3i** in CD₃OD^a**

entry	Au complex	atmosphere	time/h	% yield of 2^b
1	3a	Ar	24	9
2	3i	Ar	24	<1
3	3a	CO ₂	9	95
4	3i	CO ₂	24	13

^aReaction conditions: the reaction was carried out with **3a** or **3i** (0.020 mmol) in CD₃OD (1.0 mL) at room temperature.

^bDetermined by ¹H NMR using durene as an internal standard.

To further investigate the rate enhancement in acidic reaction media, a 1:1 mixture of methanol and water was employed as the solvent in the catalytic reaction involving the less reactive substrate **1i**; however, only a trace amount of the desired 2-oxazolidone **2i** was obtained. Presumably, the preferential formation of ammonium hydrogen carbonate, [RR'NH₂]⁺[HCO₃]⁻, from the amine substrate, water and CO₂ prevented the carbamate-induced cyclization. However, the catalytic carboxylation was accelerated in 2,2,2-trifluoroethanol to give **2i** in 71% yield under conditions otherwise identical to the standard conditions. The positive effect of the acidic alcohol intimates that the product-releasing protodeauration of the alkenylgold intermediates governs the overall catalyst performance as the rate-determining step.

CONCLUSIONS

We have demonstrated that IPr-Au(I) complexes serve as efficient catalysts that provide 2-oxazolidones from propargylamines and CO₂. This gold catalyst system exhibits considerable versatility with respect to the substrate scope, operational simplicity, and ambient reaction conditions. In particular, the catalytic intermediates can be successfully isolated as alkenylgold(I) complexes by treatment of AuOH(IPr) with an equimolar amount of propargylamines under a CO₂ atmosphere in aprotic THF. The experimental results obtained from kinetic experiments as well as stoichiometric reactions using the model intermediates support the validity of the catalytic cycle shown in Scheme 3 and are congruent with the dramatic CO₂-mediated acceleration of the product-releasing protodeauration step.

EXPERIMENTAL SECTION

Materials. Solvents were purchased from Kanto Chemical Co., Inc. or Nacalai Tesque, Inc., and dried by refluxing over sodium benzophenone ketyl (toluene, THF, ether), P₂O₅ (CH₂Cl₂, *n*-pentane) or CaH₂ (methanol) and distilled under argon. Carbon dioxide (99.999%) was purchased from Showa Tansan. Other reagents were used as delivered. (IPr)AuCl¹⁸ and (IPr)Au(OH)²⁰ were prepared according to literatures. Aliphatic internal propargylamines (**1a-1d** and **1f-1h**) were prepared by propargylation of primary amines by treatment with the propargyl chlorides or bromides in the presence of base.^{14b} Aromatic internal propargylamines (**1i-1p**) were prepared by Sonogashira reaction of the corresponding aryl halides and terminal propargylamines.²³

Analytical methods. ¹H(300.40 and 399.78 MHz), ¹³C(100.53 MHz) NMR were recorded with JEOL JNM-LA300 and

JNM-ECX400 spectrometers. The NMR chemical shifts were referenced to SiMe₄ by using residual protio impurities in the deuterated solvent. Abbreviations for ¹H NMR are as follows: s = singlet, d = doublet, t = triplet, q = quartet or m = multiplet. Elemental analyses were carried out using a PE2400 Series II CHNS/O Analyser (Parkin Elmer) or a MICRO CORDER JM10 instrument. IR spectra were recorded on a JASCO FT/IR-610 spectrometer. Mass spectra (MS) were obtained with a JEOL JMS-SX102A instrument. Recyclable preparative high-performance liquid chromatography was performed on a Japan Analytical Industry LC-9225 NEXT system equipped with JAIGEL-1H and -2H columns using CHCl₃ as an eluent at a flow rate of 14 mL min⁻¹.

General procedure for the catalytic carboxylative cyclization. Propargylamines (2.0 mmol) were added to a methanol (2.0 mL) suspension of AuCl(IPr) (0.04 mmol) in a 20 mL Schlenk flask under an Ar atmosphere. The flask was charged with 2.0 L of CO₂ through a balloon and stirred at 40 °C. After evaporation of the resulting mixture under reduced pressure, the product yield was determined by ¹H NMR using durene as an internal standard. The characterization data for **2a-2e**, **2g**, **2i**, and **2p** were described in our previous paper.^{14b}

Kinetic experiments. AuCl(IPr) (0.01-0.04 mmol) and durene (an internal standard for NMR analysis; 0.08 mmol) were dissolved in methanol (1.0 mL) in a 20 mL Schlenk flask under an Ar atmosphere. The flask was sealed with a septum, charged with 2.0 L of CO₂ through a balloon and stirred at 40 °C. **1a** (0.2-1.2 mmol) was added to the solution. A portion of the reaction mixture was collected every 5 or 10 min and diluted with CDCl₃ (0.5 mL) for determination of the product yield by ¹H NMR.

Synthesis of alkenylgold complex **3i.** To a THF (7 mL) solution of AuOH(IPr) (0.50 mmol) in a 20 mL Schlenk flask, 1-methylamino-3-phenyl-2-propyne (**1i**, 0.50 mmol) was added under an Ar atmosphere. The Schlenk flask was charged with CO₂ and stirred at 40 °C for 48 h. The resulting mixture was evaporated to dryness, and the residue was washed with ether and then recrystallized from THF and *n*-pentane to give **3i** as colorless crystals in 16% yield (62 mg). ¹H NMR (399.78 MHz, THF-*d*₈, rt, δ/ppm): 1.21 (d, ³J_{HH} = 6.7 Hz, 12H, (CH₃)₂CH), 1.31 (d, ³J_{HH} = 6.7 Hz, 12H, (CH₃)₂CH), 2.61 (s, 3H, NCH₃), 2.67 (sept, ³J_{HH} = 6.7 Hz, 4H, (CH₃)₂CH), 3.40 (s, 2H, CH₂), 6.70 (t, ³J_{HH} = 7.3 Hz, 1H, Ar), 6.80 (t, ³J_{HH} = 7.6 Hz, 2H, Ar), 7.06 (d, ³J_{HH} = 7.3 Hz, 2H, Ar), 7.37 (d, ³J_{HH} = 7.8 Hz, 4H, Ar), 7.54 (t, ³J_{HH} = 7.8 Hz, 2H, Ar), 7.58 (s, 2H, NCH=CHN); ¹³C NMR (100.53 MHz, THF-*d*₈, rt, δ/ppm): 23.3, 23.8, 28.8, 29.2, 51.8, 123.0, 123.4, 123.8, 126.3, 130.0, 130.4, 135.2, 135.6, 139.5, 144.9, 146.1, 156.6 (C=O), 195.5 (NCN). Anal. Calcd for C₃₈H₄₆N₃O₂Au: C, 58.99; H, 5.99; N, 5.43. Found: C, 58.81; H, 5.93; N, 5.19.

Protonolysis of the alkenylgold complexes with acetic acid. Acetic acid (10 mmol) was added to a CD₃OD (0.5 mL) solution of alkenylgold complex **3a** or **3i** (10 mmol) in a NMR tube. The reaction was monitored via ¹H NMR spectroscopy at room temperature.

Reaction of the alkenylgold complexes in deuterated methanol under CO₂. Alkenylgold complex **3a** or **3i** (20 mmol) was dissolved in CD₃OD (1.0 mL) in a 20 mL Schlenk flask under an Ar atmosphere. The flask was sealed with a septum, charged with 2.0 L of CO₂ through a balloon and stirred at room temperature. The reaction was monitored via ¹H NMR spectroscopy.

ASSOCIATED CONTENT

Supporting Information

Analytical data for new compounds, supplementary data for catalytic results, and X-ray scrytallographic data for **3i**. 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 interests.

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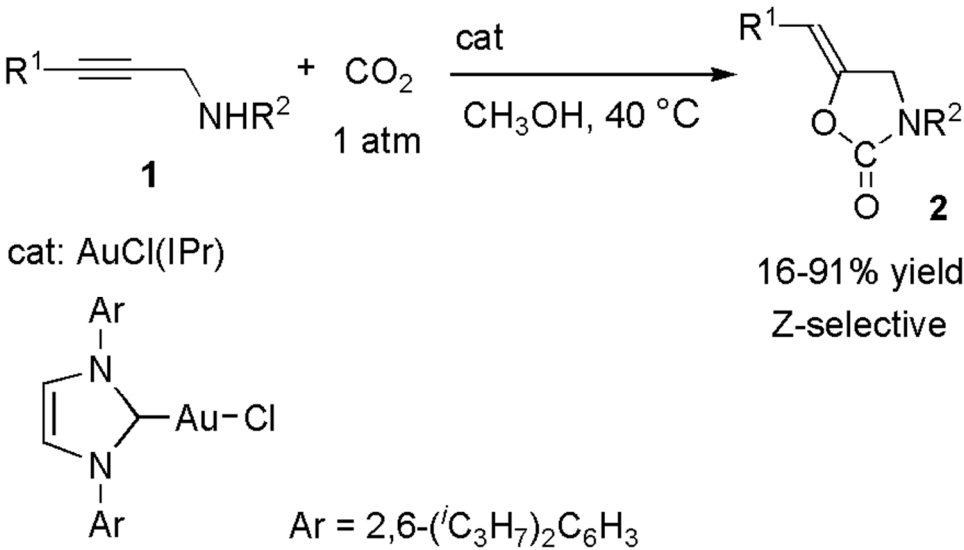
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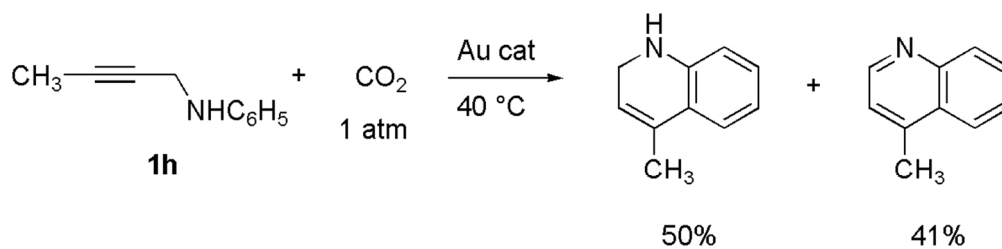
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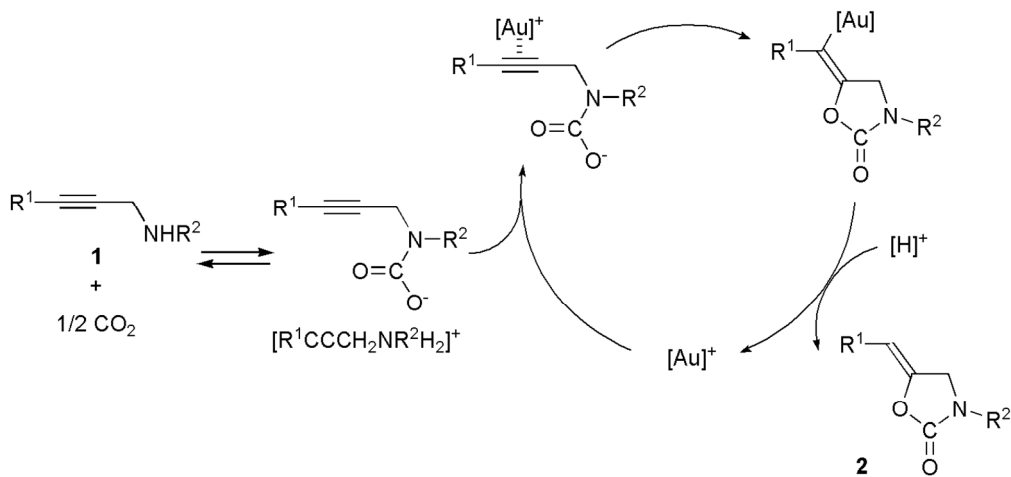
Scheme 1

77x52mm (300 x 300 DPI)



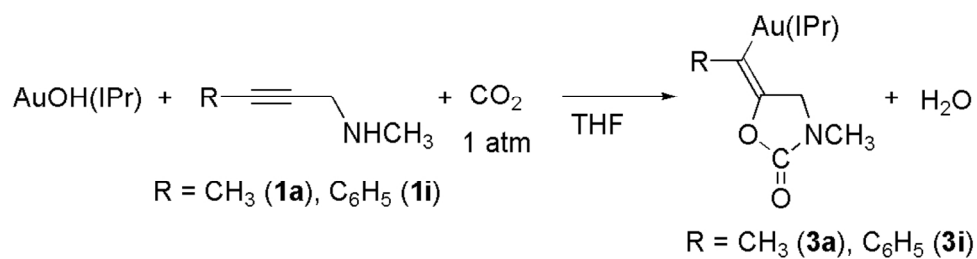
Scheme 2

100x32mm (300 x 300 DPI)



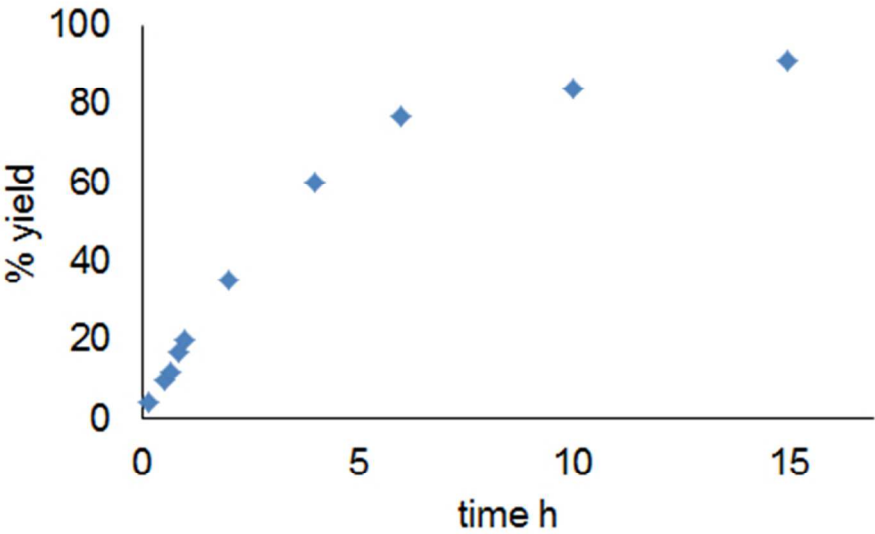
Scheme 3

125x134mm (300 x 300 DPI)

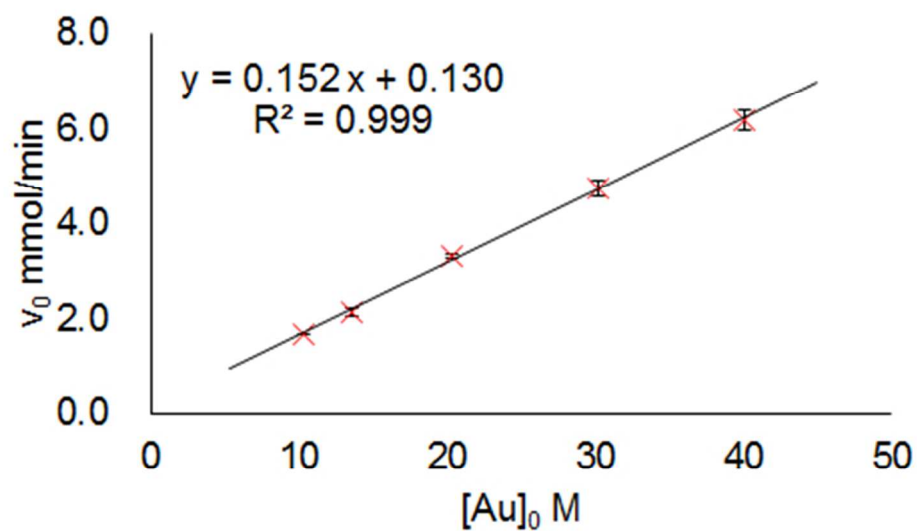


Scheme 4

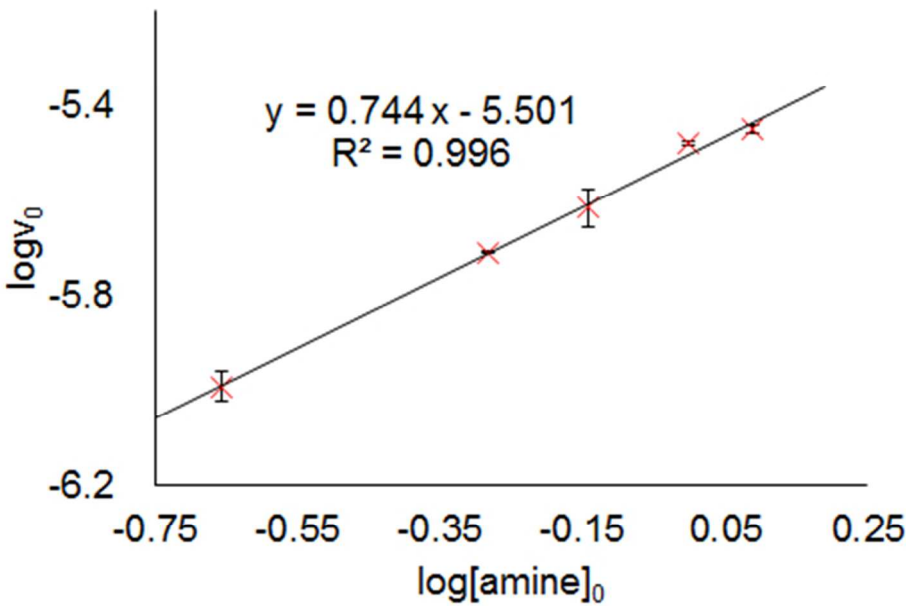
100x33mm (300 x 300 DPI)



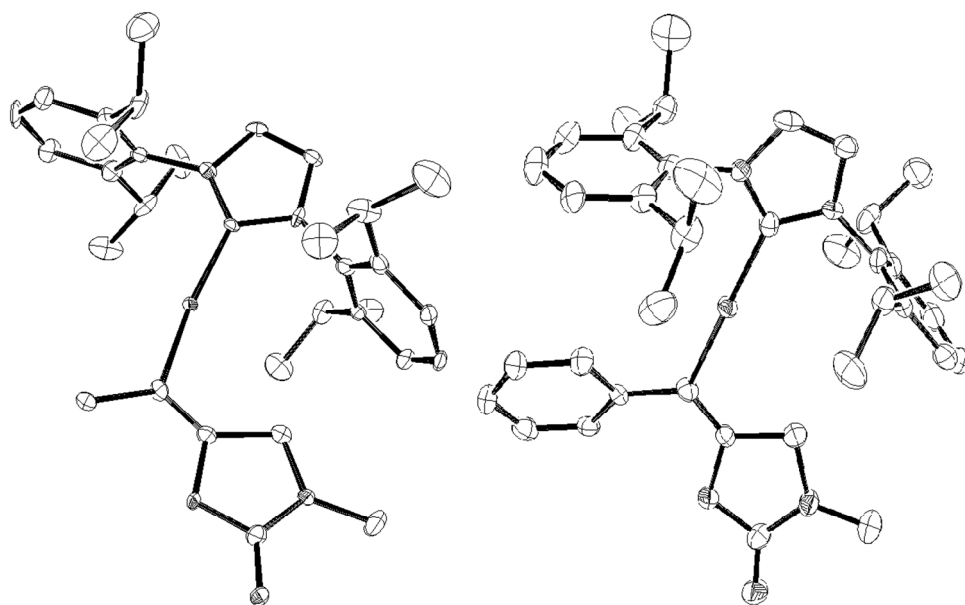
127x76mm (96 x 96 DPI)



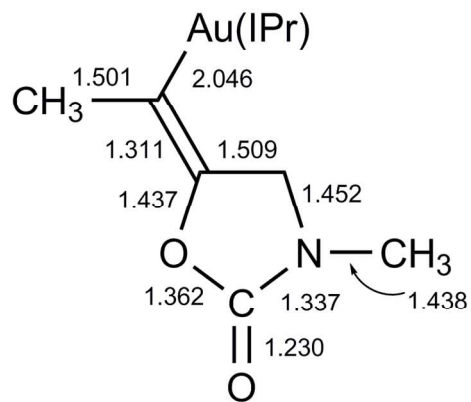
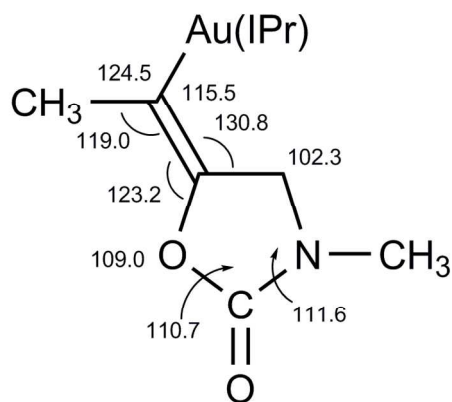
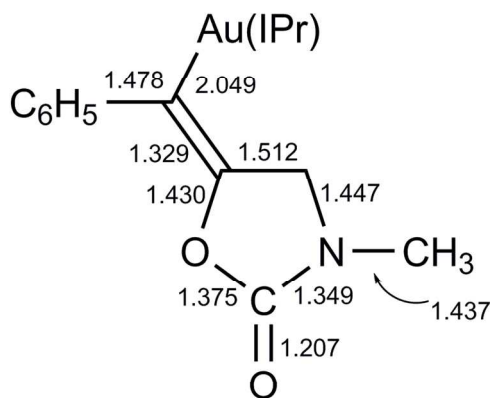
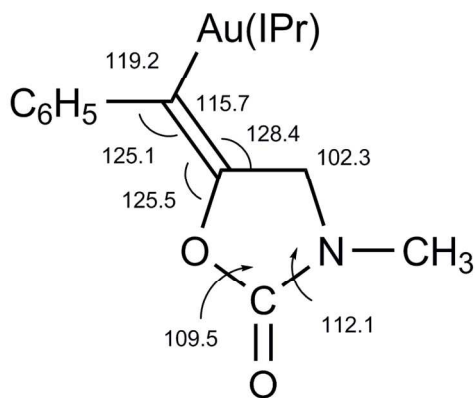
128x74mm (96 x 96 DPI)



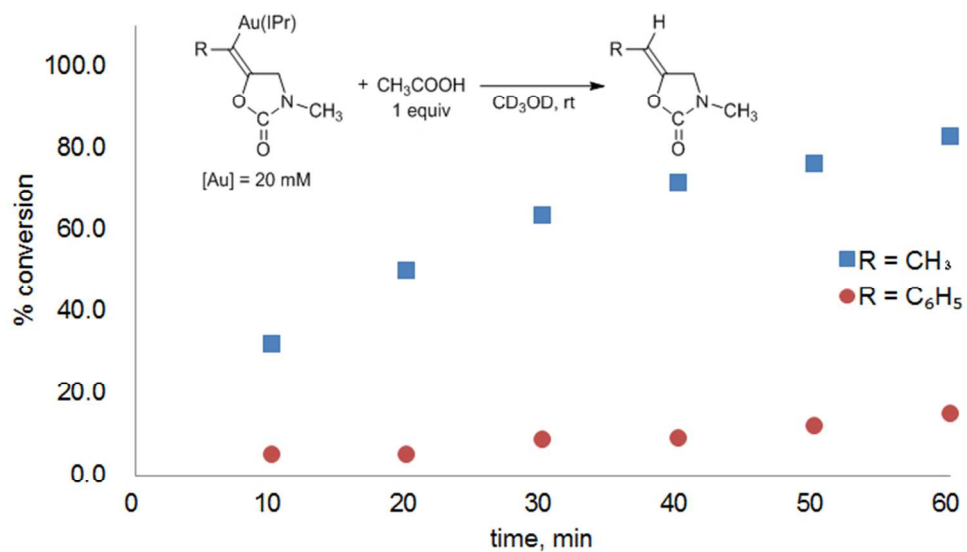
128x87mm (96 x 96 DPI)



350x215mm (96 x 96 DPI)

**3a** (mean value)**3a** (mean value)**3i** (mean value)**3i** (mean value)

144x146mm (300 x 300 DPI)



196x112mm (96 x 96 DPI)