

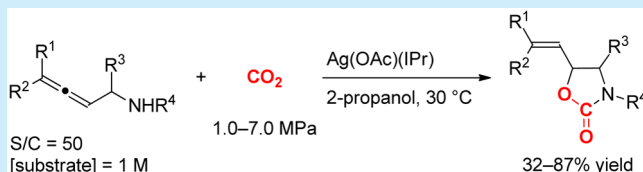
Highly Selective Carboxylative Cyclization of Allenylmethyllamines with Carbon Dioxide Using N-Heterocyclic Carbene-Silver(I) Catalysts

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S Supporting Information

ABSTRACT: Silver(I) carboxylate complexes promote the carboxylative cyclization of allenylmethyllamines to afford 5-alkenyl-1,3-oxazolidin-2-ones in 2-propanol. The use of an N-heterocyclic carbene ligand (IPr) under pressurized CO₂ is effective in suppressing the intramolecular hydroamination that leads to 2,5-dihydropyrroles. The mechanism involving a nucleophilic attack of the carbamate of the allene moiety and a subsequent protonation was realized on the basis of experimental and theoretical results involving a model intermediate, the allenylgold(I) complex, which was synthesized from Au(OH)(IPr) and 1-methylamino-2,3-butadiene.



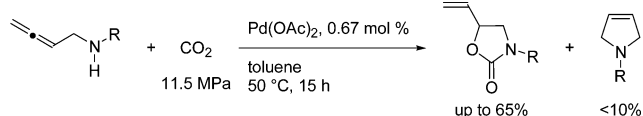
The formation of carbamic acids and their salts from carbon dioxide (CO₂) and amines is a fundamental step in the transformation of CO₂ into a range of urethanes and ureas as value-added compounds.¹ Among the possible reactions, the addition of carbamic acids to C–C multiple bonds has been regarded to be a simple and advantageous protocol for urethane synthesis in terms of operational simplicity and atom economy.^{2,3} We recently found that N-heterocyclic carbene (NHC)-gold(I) complexes serve as highly effective catalysts in alcoholic solvents for the carboxylative cyclization of propargylamines to yield 5-alkylidene-1,3-oxazolidin-2-ones with perfect regio- and stereoselectivities at ambient temperature and under atmospheric pressure of CO₂.⁴ At nearly the same time, Yamada and co-workers reported the promotion of similar carboxylation reactions by silver salts.^{3j,n–p}

The related addition to a C–C double bond has been less explored. In an original study reported in 1978 on a three-component reaction of secondary amines, CO₂, and enol ethers, the urethane product was obtained in only 11% yield.⁵ The cyclization of allylic and homoallylic amines with CO₂ was examined with the use of stoichiometric iodine compounds or catalytic amounts of guanidine bases.⁶ Very recently, Ca⁺ and co-workers reported the direct synthesis of 1,3-oxazolidin-2-one derivatives from CO₂ and electrophilic allyl amines attached to electron-withdrawing ester and aryl groups in a mixture of acetonitrile and methanol in supercritical CO₂.⁷ In a previous work, we established a palladium-catalyzed cyclization of allenylmethyllamines with dense CO₂ (Scheme 1);⁸ however,

an intramolecular hydroamination reaction competed with the formation of urethane. A 65/10 urethane/amine selectivity was attained, even under supercritical conditions (50 °C and 11.5 MPa). As an alternative means to access 5-alkenyl-1,3-oxazolidin-2-ones, Ma and co-workers successively reported the Pd-catalyzed three-component coupling reaction of allenylmethyllamines, aryl halides, and CO₂ in the presence of a stoichiometric amount of base and carboxylation of 2,3-allenamides using K₂CO₃ or Cs₂CO₃.⁹ Given the interesting catalytic properties of the above-mentioned group-11 metal catalysts, we sought to develop more active and selective catalysts that can operate under ambient conditions. Outlined herein are our findings on the efficient carboxylative cyclization promoted by silver(I) carboxylate complexes.

We initially examined the reaction of 1-(benzylamino)-2,3-butadiene (**1a**) and pressurized CO₂ (1.0 MPa) in the presence of catalytic amounts of group-11 metal complexes (2.0 mol %) in 2-propanol at 30 °C for 6 h (the standard conditions are given in Table 1). The IPr-coordinated acetatosilver(I) complex Ag(OAc)(IPr)¹⁰ [IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene] underwent smooth carboxylation to afford the cyclic urethanes 3-benzyl-5-vinyl-1,3-oxazolidin-2-one (**2a**) and 3-benzyl-6-methylene-1,3-oxazinan-2-one (**3a**) in 86 and 6% yield, respectively, with a small amount (7%) of the hydroamination¹¹ product 1-benzyl-2,5-dihydropyrrole (**4a**) (entry 1). In contrast, Au(OAc)(IPr)¹² and Cu(OAc)(IPr)¹³ were found to have poor catalytic activity (entries 2 and 3). Switching the acetato ligand to benzoate did not affect the reaction outcome, but the addition of a chloro ligand significantly deteriorated the catalytic performance (entries 4 and 5), suggesting that the weakly coordinating nature of the carboxylato ligands rather than the chloro ligand will be crucial

Scheme 1. Pd-Catalyzed Carboxylative Cyclization



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Table 1. Carboxylative Cyclization of **1a**^a

entry	catalyst	solvent	% yield ^b		
			2a	3a	4a
1	Ag(OAc)(IPr)	2-propanol	86	6	7
2	Au(OAc)(IPr)	2-propanol	0	0	0
3	Cu(OAc)(IPr)	2-propanol	3	0	<1
4	Ag(OBz)(IPr)	2-propanol	85	6	7
5	AgCl(IPr)	2-propanol	7	<1	<1
6	AgOAc	2-propanol	71	1	26
7 ^c	Ag(OAc)(tBu)	2-propanol	69	2	26
8	Ag(OAc)(PPh ₃)	2-propanol	3	<1	3
9 ^d	Ag(OAc)[(S)-binap]	2-propanol	3	<1	3
10	Ag(OAc)(IPr)	toluene	2	<1	2
11	Ag(OAc)(IPr)	THF	5	<1	4
12	Ag(OAc)(IPr)	CH ₂ Cl ₂	50	3	4
13	Ag(OAc)(IPr)	CH ₃ OH	61	4	31
14	Ag(OAc)(IPr)	^t BuOH	71	6	4
15	Ag(OAc)(IPr)	CF ₃ CH ₂ OH	31	2	36
16 ^e	Ag(OAc)(IPr)	2-propanol	77	5	7

^aStandard conditions: the reaction was carried out with **1a** (1.0 mmol) and the catalyst (0.02 mmol, 2 mol %) in a solvent (1.0 mL) under 1.0 MPa of CO₂ at 30 °C for 6 h. ^bDetermined by ¹H NMR analysis using durene as internal standard. ^c40 °C, 7.0 MPa, 15 h. ^d5.0 MPa. ^e0.1 mol % of the catalyst for 96 h.

for generating active cationic silver species with a vacant reaction site. Notably, the catalytic use of a silver acetate salt resulted in the formation of **2a** in 71% yield accompanied by the side product **4a** in 26% yield (entry 6), which supports the important role of the IPr ligand in the enhancement of the urethane/amine selectivity. Although related acetatosilver complexes with other NHC ligands could also promote the reaction, the urethane/amine selectivity was lowered (entry 7). Silver acetate complexes bearing PPh₃ or BINAP ligands displayed limited activity for the cyclization (entries 8 and 9).

As listed in Table 1, the solvent had a pronounced effect on both the conversion and product selectivity. Compared to aprotic solvents such as toluene, THF, and CH₂Cl₂ (entries 10–12), alcoholic solvents markedly accelerated the reaction (entries 1, 13, and 14), whereas the hydroamination product **4a** was competitively formed in CH₃OH and CF₃CH₂OH (entries 13 and 15). These acidic alcohols would activate **1a**, making the allene unit more susceptible to attack by the amino group. Even at a catalyst loading as low as 0.1 mol %, the carboxylation steadily proceeded in 2-propanol to give **2a** in 77% yield when the reaction time was increased to 96 h (entry 16). A similar beneficial role of methanol was demonstrated in the Au-catalyzed carboxylative cyclization of propargylamines, where a half-ester of carbonic acid,¹⁴ generated from alcohol and CO₂, facilitated the product-releasing step, i.e., the protonolysis of the Au–C bond.

As shown in Table 2, Ag(OAc)(IPr) exhibited sufficient catalytic activity, even under atmospheric pressure of CO₂, with a good urethane selectivity of 81% (entry 1). Further improvement in the urethane yield was successfully achieved when the reaction was conducted under higher pressure. The yields of **2a** and **3a** reached 89 and 6%, respectively, under the condition of 7.0 MPa, and the formation of the hydroamination

Table 2. Pressure Effect on Urethane Selectivity^a

entry	pressure, MPa	% yield ^b			% urethane selectivity
		2a	3a	4a	
1	0.1	70	7	18	81
2	1.0	82	5	10	90
3	3.0	85	5	5	95
4	5.0	88	5	4	96
5	7.0	89	6	1	99

^aReaction conditions: **1a** (1.0 mmol), Ag(OAc)(IPr) (0.02 mmol), 2-propanol (1.0 mL) at 40 °C for 15 h. ^bDetermined by ¹H NMR.

product **4a** was almost suppressed. The positive pressure effect can be explained by the enhancement of CO₂ uptake by the amine substrate, thus more efficiently leading to the urethane product.^{2d}

The silver catalyst was also applicable to the carboxylative cyclization of other allenylmethylamines at 30 °C under 1.0 MPa of CO₂, as summarized in Table 3. The substrate with a *p*-

Table 3. Ag(OAc)(IPr) Catalyzed Reaction of **1** with CO₂^a

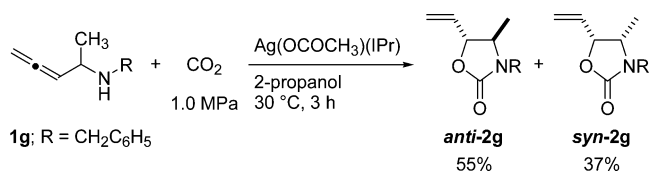
entry	amine	% yield ^b		
		2	3	4
1b	1b	82	5	5
2 ^c	1c	82	5	7
3	1d	80	6	9
4	1e	81	4	8
5	1f	83	5	5
6	1h	87	n.d. ^d	n.d. ^d
7 ^e	1i	41	n.d. ^d	40
8 ^e	1j	32	n.d. ^d	61

^{1b}: R¹ = H, R² = H, R³ = *p*-CH₃OC₆H₄CH₂
^{1c}: R¹ = H, R² = H, R³ = *p*-NCC₆H₄CH₂
^{1d}: R¹ = H, R² = H, R³ = *p*-BrC₆H₄CH₂
^{1e}: R¹ = H, R² = H, R³ = *p*-FC₆H₄CH₂
^{1f}: R¹ = H, R² = H, R³ = 3,4-OCH₂OC₆H₃CH₂
^{1h}: R¹ = C₃H₇, R² = H, R³ = CH₃
¹ⁱ: R¹ = C₃H₇, R² = C₃H₇, R³ = CH₃
^{1j}: R¹ = R² = -(CH₂)₅-, R³ = CH₃

^aReaction conditions: the reaction was carried out with **1** (1.0 mmol) and Ag(OAc)(IPr) (0.02 mmol) in 2-propanol (1.0 mL) under 1.0 MPa of CO₂ at 30 °C for 6 h. ^bDetermined by ¹H NMR. ^c5.0 MPa. ^dNot detected. ^e7.0 MPa, 40 °C, 15 h. E/Z = 93/7.

methoxybenzyl group on the amine nitrogen provided the desired five-membered urethane in 82% yield (**1b**, entry 1). An electron-withdrawing CN group was also applicable to the carboxylative cyclization to afford the corresponding urethane **2c** in 82% yield under a higher CO₂ pressure of 5.0 MPa. Other substituents on the aryl group, including bromide, fluoride, and acetal, were tolerated under the reaction conditions to give **2c**–**2f** in yields greater than 80% (entries 2–5).

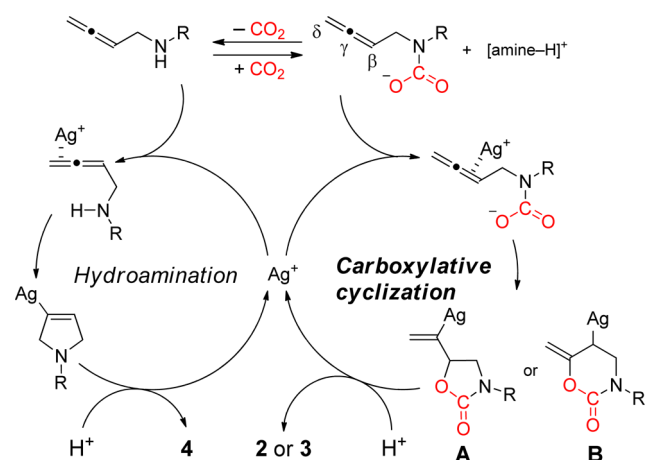
The attachment of a methyl group at the α-position to the amine facilitated the formation of the 5-membered cyclic urethane **2g** in 92% yield as a mixture of diastereomers (*anti*/*syn* = 60/40), as shown in Scheme 2. The reaction of an internal aminomethylallene (**1h**) containing an alkyl group at the allene terminal also furnished the desired urethane **2h** in 87% yield as a mixture of *E*/*Z* (93/7) isomers under similar conditions (entry 6, Table 3). On the other hand, 1,1,3-trisubstituted allenes, such as **1i** and **1j**, gave the urethanes in moderate yields and competitively underwent intramolecular

Scheme 2. Carboxylative Cyclization of **1g**

hydroamination to give **4i** and **4j** in 40 and 61% yield, respectively, even under high pressure (7.0 MPa) of CO₂ (entries 7 and 8, Table 3).

Following the related catalytic hydrofunctionalization of allenes,¹⁵ we propose two catalytic cycles induced by a cationic species through the facile dissociation of the acetate ligand on the silver complex in a polar alcoholic solvent (Scheme 3). In

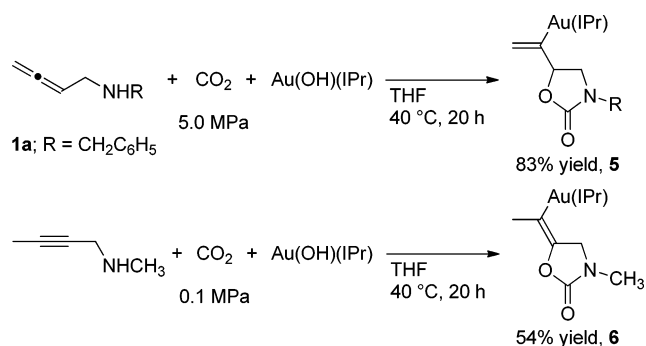
Scheme 3. Plausible Catalytic Cycles



the case of intramolecular hydroamination, the mechanism involves the initial formation of a cationic π -allene complex by the coordination of the γ,δ -double bond of the amine substrates followed by 5-*endo*-cyclization via an outer sphere attack of the amino group. For the carboxylative cyclization, the nucleophilic attack of the carbamate moiety generated from CO₂ and the amine substrate on another π -allene complex coordinated by the β,γ -unsaturated bond probably leads to the corresponding neutral alkenylsilver intermediates (**A**, **B**). Proton exchange between the reaction medium or the carbamic acid and the organosilvers regenerates the cationic species and liberates the urethane products. These steps are deducible from our previous study on the Au(I)-catalyzed carboxylative cyclization of propargylamines.⁴

It is noteworthy that the selectivity in the coordination of the allene substrates directly affects the amine/urethane ratios. Namely, in the competition between the hydroamination and carboxylative cyclization cycles in the reaction of the 1,1,3-trisubstituted allenes **1i** and **1j**, the more electron-rich double bond on the allene substrates will favor coordination to the metal center and will be more susceptible to attack by the amino group.¹⁶

To provide corroborative evidence of the nucleophilic attack on the allene, stoichiometric reactions using NHC-Au(I) complexes were investigated. The treatment of Au(OH)(IPr) with an equimolar amount of **1a** under a CO₂ atmosphere in dehydrated THF at 40 °C afforded the alkenylgold complex **5** in 83% yield after recrystallization from acetone/*n*-pentane (Scheme 4). Moreover, **5** was similarly formed from the acetate

Scheme 4. Synthesis of Alkenylgold(I) Complexes **5** and **6** as Model Intermediates in the Carboxylation Reaction

complex Au(OAc)(IPr) and **1a** in 2-propanol under CO₂ (1.0 MPa) in 89% yield without furnishing the free urethane **2**, indicating that the catalytic inefficiency of acetatogold is ascribable to the poor reactivity of **5** toward protons.

The colorless complex **5** was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. The crystal structure (Figure 1) shows that the gold atom is

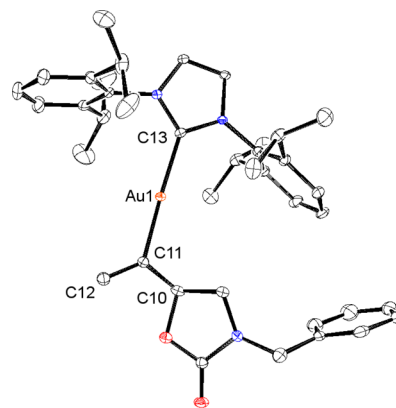


Figure 1. ORTEP diagram of **5**. Ellipsoids are shown at 30% probability. Hydrogen atoms are omitted for clarity.

bound to an NHC-carbene and an alkenyl carbon in a linear geometry. The gold–carbon bond lengths are 2.036 and 2.023 Å, which are within the typical range for related alkenylgold complexes.¹⁷ Complex **5** displays a similar structure to the gold complex **6** derived from 1-methylamino-2-butyne and CO₂ that was synthesized in our previous work.⁴ However, in the ¹³C NMR spectra, the chemical shift of complex **5** (δ 175.4), attributed to the alkenyl carbon adjacent to the gold center, was found to be significantly shifted downfield compared to that of **6** (δ 130.4). These spectroscopic data suggest that complexes **5** and **6** show divergent reactivity toward electrophiles.

The clear differences in electronic structure of these complexes as well as the enhanced electrophilicity of the silver variant were supported by DFT calculations (see the Supporting Information). These experimental and theoretical results confirm that the polarized metal–carbon bond is crucial for accomplishing the carboxylative cyclization.

In conclusion, we have demonstrated that NHC-Ag(I) carboxylate complexes serve as efficient catalysts, providing 1,3-oxazolidin-2-one derivatives from allenylmethanamines and CO₂ under relatively mild conditions with excellent selectivities. The superiority of the Ag catalyst over the Au catalyst is in line

with the fact that the alkenylgold complex derived from **1a** and CO₂ was less susceptible to the protonolysis reaction relevant to the product-releasing step.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedure and analytical data for new compounds. 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.

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