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

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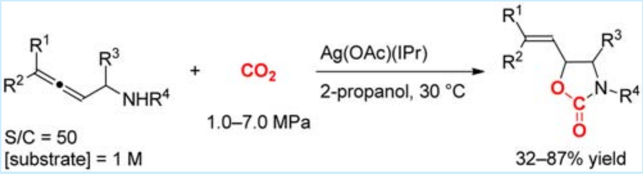
S *Supporting Information*

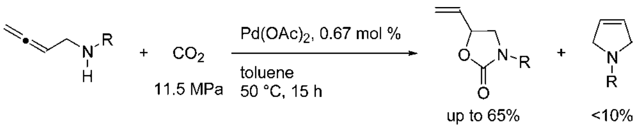
ABSTRACT: Silver(I) carboxylate complexes promote the carboxylative cyclization of allenylmethylamines to afford 5-alkenyl-1,3-oxazolidin-2-ones in 2-propanol. The use of an *N*-heterocyclic carbene ligand (IPr) under pressurized CO_2 is effective in suppressing the intramolecular hydroamination that 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 alkenylgold(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 (CO_2) and amines is a fundamental step in the transformation of CO_2 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 CO_2.[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, CO_2, and enol ethers, the urethane product was obtained in only 11% yield.[5] The cyclization of allylic and homoallylic amines with CO_2 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 CO_2 and electrophilic allylamines attached to electron-withdrawing ester and aryl groups in a mixture of acetonitrile and methanol in supercritical CO_2.[7] In a previous work, we established a palladium-catalyzed cyclization of allenylmethylamines with dense CO_2 (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 allenylmethylamines, aryl halides, and CO_2 in the presence of a stoichiometric amount of base and carboxylation of 2,3-allenamides using K_2CO_3 or Cs_2CO_3.[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.

Scheme 1. Pd-Catalyzed Carboxylative Cyclization



We initially examined the reaction of 1-(benzylamino)-2,3-butadiene (**1a**) and pressurized CO_2 (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 hydroamination[11] 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

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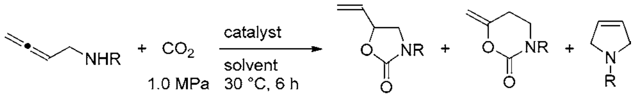
Table 1. Carboxylative Cyclization of 1a[a]



1a; R = $CH_2C_6H_5$ **2a** **3a** **4a**

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)(I^{t}Bu)	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_2Cl_2	50	3	4
13	Ag(OAc)(IPr)	CH_3OH	61	4	31
14	Ag(OAc)(IPr)	^{t}BuOH	71	6	4
15	Ag(OAc)(IPr)	CF_3CH_2OH	31	2	36
16[e]	Ag(OAc)(IPr)	2-propanol	77	5	7

[a] Standard 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 CO_2 at 30 °C for 6 h. [b] Determined by ^1H NMR analysis using durene as internal standard. [c] 40 °C, 7.0 MPa, 15 h. [d] 5.0 MPa. [e] 0.1 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 PPh_3 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 CH_2Cl_2 (entries 10–12), alcoholic solvents markedly accelerated the reaction (entries 1, 13, and 14), whereas the hydroamination product **4a** was competitively formed in CH_3OH and CF_3CH_2OH (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 CO_2, 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 CO_2, 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 product **4a** was almost suppressed. The positive pressure effect can be explained by the enhancement of CO_2 uptake by the amine substrate, thus more efficiently leading to the urethane product.[2d]

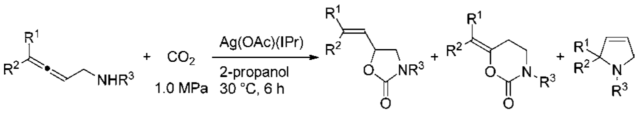
Table 2. Pressure Effect on Urethane Selectivity[a]

entry	pressure, MPa	% yield[b] 2a	3a	4a	% urethane selectivity
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

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

The silver catalyst was also applicable to the carboxylative cyclization of other allenylmethylamines at 30 °C under 1.0 MPa of CO_2, as summarized in Table 3. The substrate with a *p*-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 CO_2 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).

Table 3. Ag(OAc)(IPr) Catalyzed Reaction of 1 with CO_2[a]



1 **2** **3** **4**

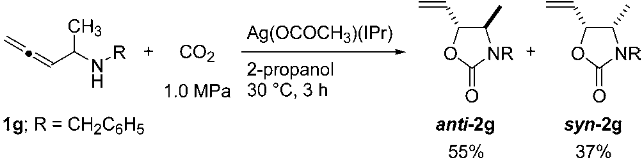
1b; R^1 = H, R^2 = H, R^3 = *p*-$CH_3OC_6H_4CH_2$
1c; R^1 = H, R^2 = H, R^3 = *p*-$NCC_6H_4CH_2$
1d; R^1 = H, R^2 = H, R^3 = *p*-$BrC_6H_4CH_2$
1e; R^1 = H, R^2 = H, R^3 = *p*-$FC_6H_4CH_2$
1f; R^1 = H, R^2 = H, R^3 = 3,4-$OCH_2OC_6H_3CH_2$
1h; R^1 = C_3H_7, R^2 = H, R^3 = CH_3
1i; R^1 = C_3H_7, R^2 = C_3H_7, R^3 = CH_3
1j; R^1 = R^2 = -$(CH_2)_5$-, R^3 = CH_3

entry	amine	% yield[b] 2	3	4
1	**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

[a] Reaction 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 CO_2 at 30 °C for 6 h. [b] Determined by ^1H NMR. [c] 5.0 MPa. [d] Not detected. [e] 7.0 MPa, 40 °C, 15 h. *E*/*Z* = 93/7.

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

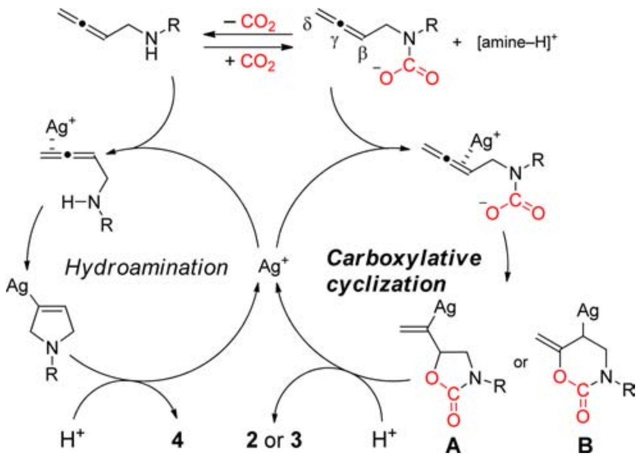
Scheme 2. Carboxylative Cyclization of 1g



hydroamination to give **4i** and **4j** in 40 and 61% yield, respectively, even under high pressure (7.0 MPa) of CO_2 (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 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 CO_2 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]

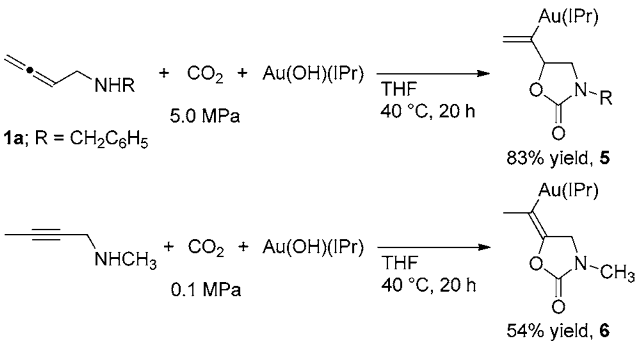
Scheme 3. Plausible Catalytic Cycles



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 CO_2 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 complex Au(OAc)(IPr) and **1a** in 2-propanol under CO_2 (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.

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



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 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 CO_2 that was synthesized in our previous work.[4] However, in the ^{13}C 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.

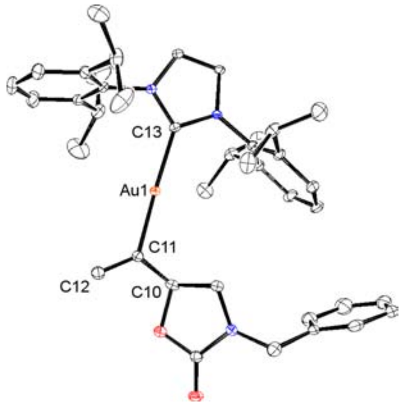


Figure 1. ORTEP diagram of **5**. Ellipsoids are shown at 30% probability. Hydrogen atoms are omitted for clarity.

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 allenylmethylamines and CO_2 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 CO_2 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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