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SHORT COMMUNICATION

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Platinum-Catalyzed Cyclization of *N*-Allyl Carbamates for the Synthesis of 5-Vinyloxazolidinones

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Platinum-catalyzed addition of the oxygen nucleophile of a carbamate to an allyl bromide was carried out to afford a range of biologically active 5-vinyl-substituted oxazolidinones in good yields. Over the course of the reaction, a platinum complex, $SnCl_2$, and the allyl bromide are assumed to generate an electrophilic allyl-platinum intermediate in the presence of carbamate oxygen nucleophiles. This method provides a wide range of 5-vinyloxazolidinones regardless of the substitution at the nitrogen and oxygen atoms.

Introduction

Oxazolidinone derivatives have been widely used as chiral building blocks for asymmetric reactions and as biologically active units; thus, selective and efficient synthesis of oxazolidinones has been intensively studied.[1] For example, reactions of 1,2-amino alcohols with phosgene, diethyl carbonate, isocyanates, and CO_2,[1,2] epoxide and aziridine ring opening reactions,[3] and electrolytic reactions of a propargylamine with CO_2[4] have been reported for the synthesis of oxazolidinones. In addition, the transition-metal-catalyzed reaction of amine compounds with CO_2,[5] Pd-catalyzed allylic substitution with amines,[6,7] and Au- and Cu-catalyzed cyclization of alkynyl carbamates[8] have been employed to prepare a range of oxazolidinone derivatives. By using different methods, different positions can be substituted and specific functional groups can be introduced.

Among the above-mentioned methods, reactions catalyzed by allyl-metal complexes have attracted our attention,[3f,6a,6c] as we have studied the catalytic generation and reactions of allyl-platinum complexes.[9] During a study of the reactivity of allyl-platinum intermediates, it was not clear whether the electronic properties of the allyl-platinum complex could be switched in the presence of a nucleophile and an electrophile. Furthermore, to extend the use of allyl-platinum-mediated reactions to the synthesis of useful building blocks, the platinum-catalyzed reaction of an allyl bromide with a nucleophile was attempted. In this study, we present the expanded reaction scope of electrophilic allyl-platinum complexes derived from an allyl bromide and a platinum complex,[9b,10] and the use of these complexes in the synthesis of synthetically and biologically useful 5-vinyloxazolidinones.[11,12] Although numerous examples of platinum-catalyzed reactions of allyl alcohols with amines and allyl acetates with carbon nucleophiles are known,[10] platinum-catalyzed reactions of allyl halides with fragmented carbamate oxygen nucleophiles are being reported here for the first time.

Results and Discussion

Table 1 lists the cyclization results for allyl carbamate **1a**. This allyl carbamate was subjected to the allyl-platinum forming conditions involving $PtCl_2$ (5 mol-%), phosphanes (10 mol-%), and $SnCl_2$ (25 mol-%) in dichloroethane (DCE) at 80 °C,[9b] and 5-vinyloxazolidinone **1b** was obtained in 38% yield with P(Ph-*p*CF_3)$_3$ and 32% yield with P(furyl)$_3$ (entries 1 and 2). The yield significantly increased to 89% when electron-rich phosphanes were used (entries 3–5). The stoichiometry of the phosphane ligand appears to be an important factor influencing the product yield (entry 6). Reduced loadings of $SnCl_2$ afforded a reasonable yield of **1b**; however, no reaction occurred in the absence of $SnCl_2$ (entries 7 and 8). As a platinum(II) source, $PtBr_2$ showed good catalytic activity, but Pt(acac)$_2$ did not induce cyclization at all (entries 9 and 10). In addition to platinum(II) complexes, $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, and $Ru(PPh_3)_3Cl_2$ were added to a solution of **1a**, and it was observed that only $Ru(PPh_3)_3Cl_2$ catalyzed the reaction to provide **1b** in 11% yield (entry 11).[13] When gold complexes $AuCl_3$ and $Au(PPh_3)Cl$, which were employed for the cyclization of alkynyl carbamates, were treated with **1a**, they afforded only *N*-Boc-deprotected compounds. This cyclization was also attempted in the absence of platinum catalysts, assuming that the cyclization of **1a** might occur by $SnCl_2$-assisted cleavage of the C–O bond in the carbamate followed by the

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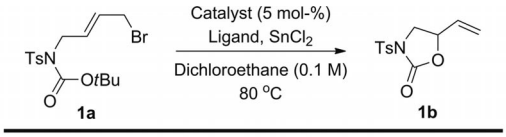
addition of the oxygen nucleophile to allyl bromide (S_N2' type reaction). In the presence of $SnCl_2$ (25 mol-% and 100 mol-%), most of **1a** underwent *N*-Boc deprotection initiated by $SnCl_2$-assisted C–O bond cleavage, and **1b** was formed with low yields (18% and 21%). Relative to the platinum–stannane catalysis conditions (entries 5 and 9), Lewis acid $SnCl_2$-mediated S_N2' type reaction and Ru-allyl-mediated cyclization (entry 11) provided **1b** in low yield. Thus, the combination of a platinum complex and $SnCl_2$ was chosen as the optimum catalyst for the formation of 5-vinyl oxazolidinones with high yield.

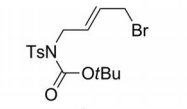
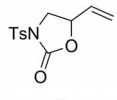
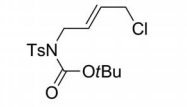
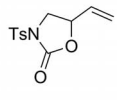
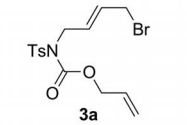
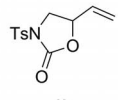
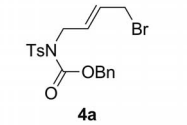
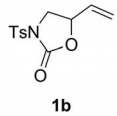
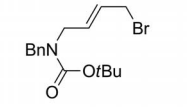
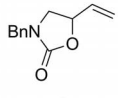
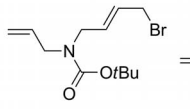
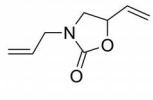
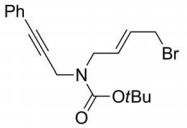
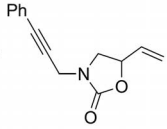
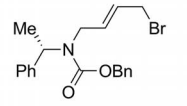
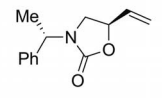
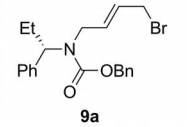
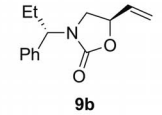
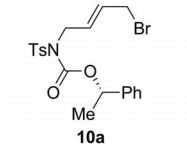
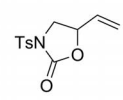
Table 1. Optimization of the cyclization of **1a**.



	Catalyst	Ligand	$SnCl_2$	Yield (**1b**)
1	$PtCl_2$	P(Ph-*p*CF_3)$_3$ (10 mol-%)	25 mol-%	38%
2	$PtCl_2$	P(2-furyl)$_3$ (10 mol-%)	25 mol-%	32%
3	$PtCl_2$	P(Ph-*p*OMe)$_3$ (10 mol-%)	25 mol-%	56%
4	$PtCl_2$	P(Ph-*o*OMe)$_3$ (10 mol-%)	25 mol-%	65%
5	$PtCl_2$	P(Ph-OMe$_3$)$_3$ (10 mol-%)	25 mol-%	89%
6	$PtCl_2$	P(Ph-OMe$_3$)$_3$ (5 mol-%)	25 mol-%	65%
7	$PtCl_2$	P(Ph-OMe$_3$)$_3$ (10 mol-%)	10 mol-%	68%
8	$PtCl_2$	P(Ph-OMe$_3$)$_3$ (10 mol-%)	–	–
9	$PtBr_2$	P(Ph-OMe$_3$)$_3$ (10 mol-%)	25 mol-%	93%
10	$Pt(acac)_2$	P(Ph-OMe$_3$)$_3$ (10 mol-%)	25 mol-%	–
11	$RuCl_2(PPh_3)_3$	–	–	11%

A range of substrates were evaluated under the standard cyclization conditions by using $PtCl_2$ (5 mol-%), P(Ph-OMe$_3$)$_3$ (10 mol-%), and SnX_2 (X = Cl, Br) in dichloroethane (DCE) at 80 °C (Table 2). To assess the leaving group, an allyl chloride derivative was used in the reaction to afford **1b** in lower yield than that in the reaction of **1a** (entries 1 and 2). Instead of allyl halides, an allyl-acetate-substituted compound was subjected to the standard cyclization conditions, and there was no product formation. The cyclization yield varied dramatically with a change in the allyl substituent. Next, to check the effect of substituents on the carbamate oxygen atom, allyl- and benzyl-substituted carbamates were tested (**3a** and **4a**). Surprisingly, in the presence of Pt catalysts, the allyl group on **3a** and the benzyl group on **4a** underwent fragmentation and cyclization to afford **1a** in good yields (entries 3 and 4). Next, the *p*-toluenesulfonyl group on nitrogen was replaced by benzyl and allyl groups in compounds **5a** and **6a** (entries 5 and 6). In the presence of 10 mol-% $SnCl_2$, substrates **5a** and **6a** underwent cyclization to afford products in good yields (93% and 66%). On the basis of the cyclization results for compound **6b**, it was inferred that the carbamate oxygen reacted with the allyl bromide selectively over the alkene. The competition between the allyl bromide and the alkyne in **7a** led to the preference of the addition of the carbamate to the allyl bromide over the reaction with the alkyne (entry 7). In the case of chiral compounds **8a** and **9a** (entries 8 and 9, Table 2), cyclization occurred successfully, but, disappointingly, a low diastereomeric ratio was observed (*trans*/*cis* = 1:1 and 1.7:1). The diastereomers are separable by silica gel chromatography. Presumably, the chirality of the amine in the tether of **8a** and **9a** was not transferred to the newly formed C–O bond. Substrate **10a**, which possesses a chiral unit bound to the carbamate oxygen, participated in the reaction to afford a cyclized product **1b** in 90% yield with 0% enantiomeric excess (*ee*) (entry 10, Table 2). When the

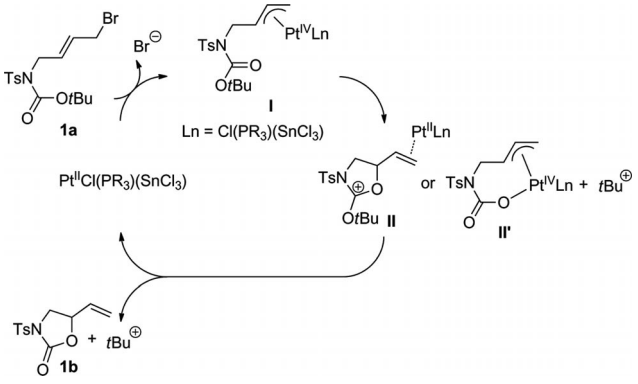
Table 2. Substrate scope.

Entry	Reactant	Product	Yield
1	 **1a**	 **1b**	89%[a]
2	 **2a**	 **1b**	18%[a] 30%[b]
3	 **3a**	 **1b**	92%[c]
4	 **4a**	 **1b**	90%[a]
5	 **5a**	 **5b**	93%[c]
6	 **6a**	 **6b**	66%[c]
7	 **7a**	 **7b**	69%[c]
8	 **8a**	 **8b**	87 %[c] d.r. 1:1
9	 **9a**	 **9b**	69 %[c] d.r. 1.7:1
10	 **10a**	 **1b**	90 %[a] 0% *ee*

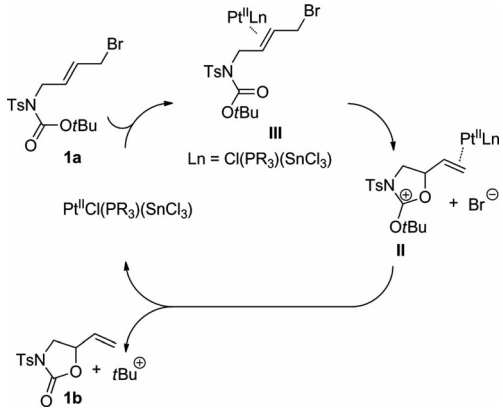
[a] $SnCl_2$ (25 mol-%). [b] $SnBr_2$ (25 mol-%). [c] $SnCl_2$ (10 mol-%).

cyclization occurs, the chiral unit of **10a** is too far from the reaction center, or the cleavage of the carbamate C–O bond takes place prior to the ring closing.

On the basis of the results in Table 2, plausible catalytic cycles are proposed in Schemes 1 and 2. Both catalytic cycles begin with the formation of the platinum–stannane complex from $PtCl_2$, phosphane, and $SnCl_2$, which is assumed to react with **1a**.[9b,14] The role of $SnCl_2$ in both mechanisms is speculated as a promoter for the cleavage of the C–O bond in the carbamate as well as a catalyst activator.[15]



Scheme 1. The catalytic cycle mediated by the allyl-platinum complex.

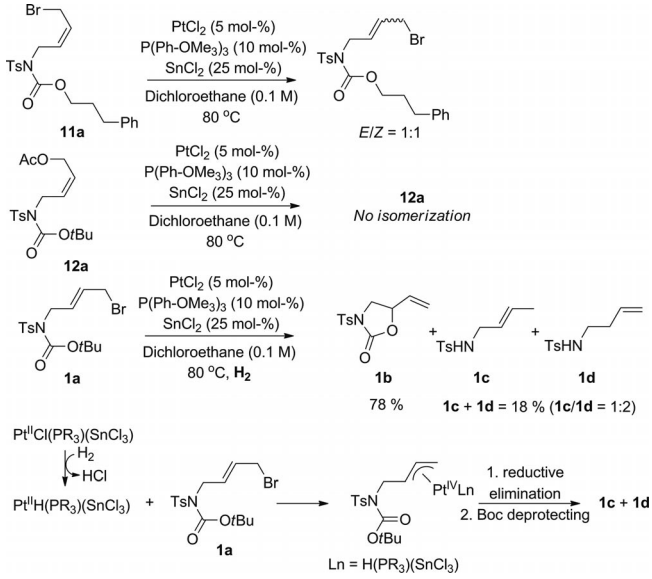


Scheme 2. The catalytic cycle including a platinum-coordinated alkene intermediate.

Once the platinum–stannane complex is formed, oxidative insertion of the platinum complex into allyl bromide takes place along with the release of a bromide ion (Scheme 1).[16] Subsequently, the oxygen nucleophile of the carbamate is added to the allyl-platinum intermediate, and the removal of the *tert*-butyl group from **II** provides the desired product **1b**. Alternatively, the *tert*-butyl group might be released before the ring is closed, as shown in intermediate **II′**. Although the proposed catalytic cycle involving allyl-platinum(IV) **I** is inconclusive, the cyclization mediated by allyl-platinum(II) complexes derived from allyl bromide and in situ generated platinum(0) complexes is less favorable under our reaction conditions. In platinum-catalyzed coupling of allyl alcohols with nucleophiles,[10] platinum(0) complexes are formed from platinum(II) complexes during the oxidation of allyl alcohols by Pt^{II} complexes at the initial stage; however, allyl bromide in our reaction cannot undergo oxidation to form platinum(0) species.

As an alternative mechanism, platinum-catalyzed S_N2' allyl bromide substitution with an adjacent carbamate was considered (Scheme 2). The platinum complex may coordinate to allyl bromide, and the neighboring carbamate attacks the coordinated olefin moiety (**III**). At the end of the cycle, product **1b** is formed along with the release of *tert*-butyl cations. The formation of isobutylene and H^+ from *tert*-butyl cations was not checked; however, in the case of benzyl-substituted **4a**, benzyl bromide was observed, which was derived from the benzyl cation and the bromide ion.

To probe the mechanism, the following experiments were conducted (Scheme 3): (*Z*)-allyl carbamate **11a** was subjected to standard conditions to provide a mixture of (*E*) and (*Z*) alkenes without ring formation. In the presence of a non-fragmented rigid carbamate group, the platinum complex promotes alkene isomerization via the allyl-platinum intermediate.[17] The isomerization of **11a** via a zwitterionic intermediate formed by activation of the alkene by Pt^{II} may not occur, according to the results of **12a**. (*Z*)-Allyl acetate **12a** was exposed to the reaction conditions to recover **12a** without isomerization and cyclization. Accordingly, the platinum catalyst in this study does not promote simple isomerization via a zwitterionic intermediate, and the formation of the allyl-platinum intermediate is crucial for the cyclization. Under the hydrogenation atmosphere, the cyclization was attempted to trap the allyl intermediate. Gratifyingly, in the presence of hydrogen, the desired 5-vinyl oxazolidinone **1b** was obtained in good yield (78%) along with **1c** and **1d** (18% yield). Compounds **1c** and **1d** are formed from reductive elimination of the allyl-platinum intermediate in the presence of the hydride ligand around the platinum ion.[9b] On the basis of the above-mentioned



Scheme 3. Control experiments.

experimental results, it appears that an allyl-platinum intermediate is formed via allylic oxidative insertion of the platinum–stannane complex, leading to the desired cyclization.

Conclusions

We have discovered that a platinum complex can be utilized for the synthesis of synthetically and biologically important 5-vinyl oxazolidinones by cyclization of allyl carbamates. A variety of substrates possessing tosyl-, benzyl-, allyl-, and propargyl-substituted amines participate in the reaction to afford 5-vinyloxazolidinones. As a substituent at the carbamate oxygen, benzyl and allyl groups as well as the *tert*-butyl group undergo fragmentation to promote the desired cyclization. Regarding the working mechanism, the formation of the allyl-platinum intermediate and interaction of the platinum metal ion and the oxygen nucleophile are key factors that promote the efficient cyclization.

Experimental Section

Representative Experimental Procedure for Cyclization of *N*-Allyl Carbamates: To a premixed solution of $PtCl_2$ (5 mol-%), phosphane (10 mol-%), and $SnCl_2$ (25 mol-%) under N_2 in dichloroethane was added the starting material at room temperature. The resulting mixture was allowed to react at 80 °C until the starting material was completely consumed. The representative experimental procedure was applied to compound **1a** (101.0 mg, 0. 25 mmol) to yield product **1b** (59.4 mg, 89%). Compound **1b** has previously been reported.[18]

Supporting Information (see footnote on the first page of this article): Spectroscopic data for new compounds.

Acknowledgments

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