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Research Paper

Cycloaddition of CO_2 to challenging *N*-tosyl aziridines using a halogen-free niobium complex: Catalytic activity and mechanistic insights

Sunatda Arayachukiat[a], Prapussorn Yingcharoen[a], Sai V.C. Vummaleti[b], Luigi Cavallo[b], Albert Poater[c,*], Valerio D'Elia[a,*]

[a] Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), 21210, Wang Chan, Thailand
[b] King Abdullah University of Science & Technology, KAUST Catalysis Center (KCC), 23955-6900 Thuwal, Saudi Arabia
[c] Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, c/Maria Aurèlia Capmany 6, 17003 Girona, Catalonia, Spain

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ABSTRACT

An efficient and facile approach to the regioselective synthesis of *N*-tosyloxazolidinones from the corresponding *N*-tosylaziridines and CO_2 was developed using dual catalytic systems involving an early transition metal coordination compound as a Lewis acid and a nucleophilic cocatalyst. Among the screened Lewis acids, halogen-free niobium pentaethoxide ($Nb(OEt)_5$) displayed the best catalytic activity when used in the presence of tetrabutylammonium iodide (TBAI). Systematic DFT calculations, supported by catalytic experiments, demonstrate that CO_2 insertion is the rate determining step for this process and it is highly dependent on the steric hindrance at the niobium center.

1. Introduction

Carbon dioxide is an important greenhouse gas and a renewable and ubiquitous C1 source for the synthesis of chemicals [1,2]. The latter approach is regarded as a potential strategy to contribute managing the excess anthropogenic emissions by sequestration of CO_2 into useful chemicals and fuels [3–6]. With the volume of CO_2 currently converted to chemicals representing just a tiny fraction of global emissions [7,8], the development of a diversified and versatile portfolio of products able to provide a long-term storage of CO_2 is highly desirable [9–15]. In this context, the products of cycloaddition of CO_2 to three-membered heterocycles such as cyclic organic carbonates[16–19] and oxazolidinones[20] are being widely investigated. Focusing on the latter family of compounds, *N*-aryl and *N*-alkyl oxazolidinones can be mainly prepared by the cycloaddition of CO_2 to aziridines [21–24], by the cycloaddition of isocyanates to epoxides[25–27] or by the one pot reaction of epoxides, amines and CO_2 [28–31]. The synthesis of *N*-tosyloxazolidinones from CO_2, being a class of compounds that can serve as key intermediates for the preparation of synthons and biologically active compounds [32–36], requires the cycloaddition reaction of CO_2 to *N*-tosylaziridines. Because of the presence of the electron-withdrawing sulfonyl group at the nitrogen atom, this reaction generally requires harsher reaction conditions than the synthesis of the cognate *N*-aryl and *N*-alkyl compounds and very few systematic attempts to develop an efficient catalyst for this reaction have been undertaken.

Beside the application of $Pd_2(dba)_3/PPh_3$/TBAT (dba: dibenzylideneacetone, TBAT: tetrabutylammonium difluorotriphenylsilicate) under mild conditions for the special case of *N*-tosyl-5-vinylaziridines [37], *in situ*-generated *N*-heterocyclic carbenes (NHCs) were reported to afford 5-aryl-3-tosyloxazolidin-2-ones in good yields at moderate temperatures and CO_2 pressure (80 °C, 20 bar) [38]. However, a high catalytic loading was required (20 mol% diisopropylphenylimidazolium chloride (NHC precursor) and 22 mol% KO*t*Bu). LiBr (20 mol%) is a readily available catalyst for the regioselective synthesis of the 4-aryl-3-tosyloxazolidin-2-ones

* Corresponding authors.
E-mail address: valerio.delia@vistec.ac.th (A. Poater).

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regioisomers in moderate yields, but cannot afford the 5-aryl-3-tosyloxazolidin-2-ones analogues [39].

Coordination compounds of early transition metal halides such as yttrium, niobium and zirconium are readily available inexpensive Lewis acids that do not require the synthesis of sophisticated ligand systems to harness the metal center that could have an impact on the costs, molecular weight and sustainability of the catalyst [16]. These compounds have shown the ability to catalyze the cycloaddition of CO_2 to epoxides under ambient conditions [40,41] even in the case when diluted CO_2 from flue gas was employed as an impure feedstock [42,43]. The mechanistic aspects of the cycloaddition reactions promoted by such catalysts have been investigated revealing intriguing details; a bimetallic cooperative mechanism for the activation of CO_2 between two niobium centers being identified in solution and on silica support [44,45]. Nevertheless, their application to the cycloaddition reactions of CO_2 has been, so far, limited to the synthesis of cyclic carbonates.

Therefore, we explore here the catalytic activity of group III–V transition-metal complexes in combination with nucleophilic co-catalysts, for the cycloaddition of CO_2 to *N*-tosylaziridines. Beside readily available metal halides, early transition metals alkoxides were employed in this study in order to identify greener and less corrosive halogen-free Lewis acids [46]. We show here that $Nb(OEt)_5$ is a readily available and efficient, halogen-free catalyst for the synthesis of 5-aryl-3-tosyloxazolidin-2-ones under mild conditions when used in the presence of co-catalytic amounts of TBAI (Tetrabutylammonium iodide). Furthermore, the mechanism of this reaction is investigated by DFT calculations demonstrating that the process of CO_2 insertion is the rate determining step of the whole reaction and that this step is highly dependent on the steric hindrance at the niobium center.

2. Experimental

General information, details on the computational methods and on the preparation of the aziridine substrates according to published procedures are provided in Appendix A (see Supplementary material).

2.1. Catalysis experiments

For a typical cycloaddition reaction, **1a** (273 mg, 1 mmol), $Nb(OEt)_5$ (21 mL, 0.08 mmol, 8 mol%) and TBAI (24 mg, 0.08 mmol, 8 mol%) were dissolved under a protective atmosphere in diethylether (3 mL) in a 50 mL stainless steel autoclave. CO_2 (30 bar) was added and the reaction vessel was heated to 80 °C. After stirring for 48 h, the reactor was cooled by an ice bath and the residual pressure was carefully vented. After withdrawal of an aliquot of the reaction for ^{1}H NMR analysis of the crude reaction, the reaction solvent was evaporated under reduced pressure and the product was purified by flash column chromatography (hexane/dichloromethane 8:2) yielding **1b** (288 mg, 0.91 mmol, 91%).

3. Results and discussion

3.1. Catalytic investigation

The initial catalysis study was performed at 80 °C under 30 bar CO_2 using 2-phenyl-*N*-tosyl aziridine (**1a**) as a benchmark substrate (Table 1). Diethyl ether (DEE) resulted as the best solvent for this reaction after an initial screening. In general, at the end of the reaction the formed **1b** isomer could be nearly completely isolated by column chromatography. Therefore, the large discrepancy between **1a** conversion and **1b** isolated yield observed In some cases (*i.e.* Table 1, Entries 4, 6, 10–12) is to attribute to the formation of various by-products as observed in the crude ^{1}H NMR of the reaction mixture.

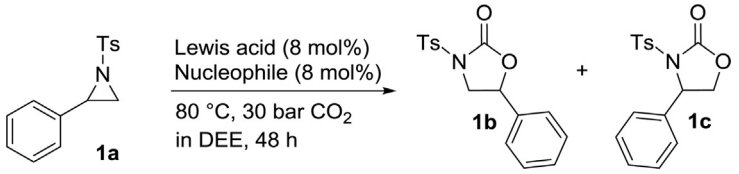
Among the selected early transition metal compounds, $Nb(OEt)_5$ (Table 1, Entry 8) showed complete **1a** conversion and the highest isolated yield of the target product **1b** with high regioselectivity. Niobium-based catalysts showed generally the best regioselectivity for **1b** *versus* its **1c** isomer. $NbCl_5$ (Table 1, Entry 7) afforded exclusively **1b**, albeit in moderate yields. $Nb(OEt)_5$ was selected for further investigation (Table 1, Entries 9–13) taking into account the use of different nucleophilic cocatalysts such as TBAC (tetrabutylammonium chloride), TBAB; (tetrabutylammonium bromide), pyridine bases of different nucleophilicity, DMAP (*N*,*N*-dimethylamino pyridine) and PPY (4-pyrrolidinopyridine) [47], and amidine base DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene). In agreement with previously published mechanistic studies on the cycloaddition of CO_2 to aziridines, the cocatalyst plays a crucial role by serving as a nucleophile for the ring-opening of the niobium-coordinated aziridine substrate and as a leaving group in the final step of cyclization following CO_2 activation (*vide infra* in the DFT section for a more detailed mechanistic picture) [21,48]. Furthermore, the regiochemistry of the initial nucleophilic attack of the cocatalyst on the aziridine determines the regioselectivity of the reaction [21,39].

This screening confirmed quaternary ammonium salts, and in particular TBAI, as the most suitable nucleophilic co-catalysts. Strong nitrogen nucleophiles such as DBU and PPY failed to produce any appreciable amount of product (Table 1, Entries 11, 13). In the case of PPY, the starting material was recovered unreacted. A possible explanation for this observation could be a stable interaction between strong aminopyridine nucleophiles and niobium complexes as suggested by previous studies. [41]. In the case of DBU, we observed complete conversion of the starting material but the target product was not formed. In the ^{1}H NMR spectrum of the reaction mixture a main by-product was observed displaying a downfield shift with respect to the aziridine protons of **1a**, but lower than expected for the formation of the oxazolidinone product. These signals are likely to arise from the formation of the intermediate product of aziridine-ring opening without the insertion of CO_2. The pair $Nb(OEt)_5$/DMAP, being a completely halogen-free system, produced **1b** in moderate yields but with low regioselectivity (Table 1, Entry 12) reflecting the higher tendency of the strong pyridine nucleophile to attack the less sterically hindered carbon atom of the aziridine ring [21]. Consistently, when exploring the effect of the counterion of the quaternary ammonium salt (Table 1, Entries 8–10), only a limited effect on the yield of the reaction was observed, however, the regioselectivity decreased in the order TBAI $\gg>$ TBAB $\gg>$ TBAC thus following the inverse trend of nucleophilicity ($Cl^- \gg> Br^- \gg> I^-$) of the halogen anion in the aprotic reaction medium [49]. Whereas the regioselectivity of the nucleophilic ring-opening of phenyl substituted three-membered heterocycles is generally directed to the phenyl-bearing carbon by the electronic effects of the aromatic ring [50], it is likely that the tendency to attack the least sterically hindered carbon increases when more nucleophilic species (TBAB, TBAC and DMAP) are used as cocatalysts leading to the observed decrease of regioselectivity.

Further investigation was dedicated to the study of the influence of the reaction parameters (temperature and pressure) on the catalytic efficiency of $Nb(OEt)_5$/TBAI in the cycloaddition of CO_2 to **1a**. When the reaction temperature was varied under 30 bar CO_2 pressure (Fig. 1a) a low yield of **1b** was observed at 50 °C. Nevertheless, moderate yields of the target product were obtained already at 60 °C whereas for $T \geq 70$ °C high to quantitative yields of **1b** were afforded.

The reaction yield appears to be strongly dependent on CO_2 pressure (Fig. 1b). Indeed, despite the catalyst displaying some

Table 1
Application of various early transition metal coordination compounds as catalysts for the cycloaddition of CO_2 to aziridine 1a in the presence of nucleophilic cocatalysts.[a]



Entry	Lewis acid	Nucleophile	**1a** Conversion (%)[b]/**1b** Isolated yield (%)[c]	(**1b**:**1c**)[b]	TOF(h^{-1})[d]
1		TBAI	77/43	87:13	0.11
2	YCl_3	TBAI	83/69	88:12	0.18
3	$ScCl_3$	TBAI	93/63	89:11	0.16
4	$ZrCl_4$	TBAI	53/27	93:3	0.07
5	$Zr(OEt)_4$	TBAI	89/87	88:12	0.23
6	$Ti(OEt)_4$	TBAI	64/33	88:12	0.09
7	$NbCl_5$	TBAI	50/43	100	0.11
8	$Nb(OEt)_5$	TBAI	100/91	92:8	0.24
9	$Nb(OEt)_5$	TBAB	99/79	87:13	0.20
10	$Nb(OEt)_5$	TBAC	92/58	77:23	0.15
11	$Nb(OEt)_5$	DBU	100/0	–	–
12	$Nb(OEt)_5$	DMAP	100/45	57:43	0.12
13	$Nb(OEt)_5$	PPY	0/0	–	–

[a] Using **1a** (1 mmol), catalyst (0.08 mmol, 8 mol%), nucleophile (0.08 mmol, 8 mol%) in 3 mL DEE at 80 °C, 30 bar CO_2 for 48 h.
[b] Regioselectivity and **1a** conversion determined by ^1H NMR analysis of the crude reaction mixture.
[c] Isolated yield of **1b** after column chromatography.
[d] Values relative to the isolated yield of **1b**.

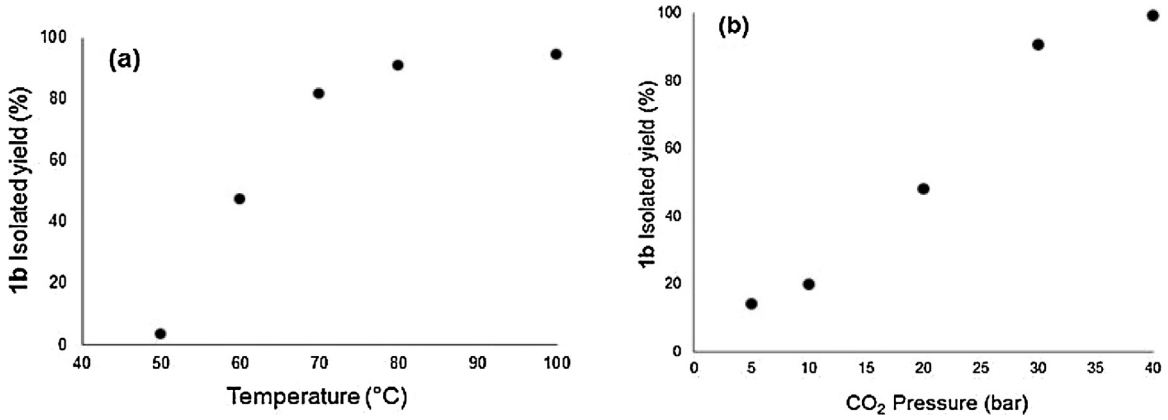


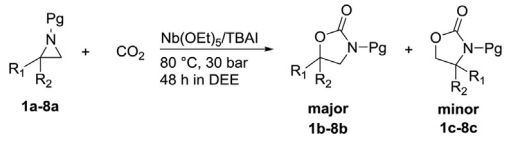
Fig. 1. (a) Dependency of **1b** isolated yield on the reaction temperature under 30 bar CO_2 pressure using $Nb(OEt)_5$ (8 mol%) and TBAI (8 mol%) as a catalyst (Reaction time 48 h); (b) dependency of **1b** isolated yield on the CO_2 pressure at 80 °C using $Nb(OEt)_5$ (8 mol%) and TBAI (8 mol%) as a catalyst (Reaction time 48 h).

activity already under just 5 bar CO_2, only low to moderate yields of **1b** could be obtained for CO_2 pressures below 30 bar. Under 40 bar CO_2 a quantitative yield of **1b** could be obtained. The observed trend suggests that the CO_2 concentration in the reaction mixture is a crucial factor for high reaction yields and that the step of insertion/activation of CO_2 might constitute the rate determining step of the reaction (*vide infra* for DFT calculations). The application of $Nb(EtO)_5$ in the presence of quaternary ammonium salts could be extended to other *N*-tosylaziridines (**1a–4a**) to yield the corresponding 5-aryl-3-tosyloxazolidin-2-ones with high regioselectivity (Table 2). Aziridines **1a**-**3a** bearing no substituents or electron withdrawing groups on the phenyl substituent could be quantitatively converted to the target products (Table 2, Entries 1–3). In the case of aziridine **4a**, bearing a methyl group on the phenyl ring, only moderate conversion to the target oxazolidinone was achieved (Table 2, Entry 4). This observation could be tentatively attributed to the effect of the increased electronic density at the phenyl ring on the step of aziridine ring-opening by the combined action of the Lewis acid and of the iodide anion [39]. A control experiment using aziridine **5a** (Table 2, Entry 5), displaying a quaternary carbon at the functionalized aziridine ring, shows that this substrate could not be converted to the corresponding oxazolidinone as expected on the basis of the observed regioselectivity of the reaction that implies a nucleophilic attack of the iodide anion at the aziridine ring carbon bearing the aryl substituent (*vide infra* for the DFT calculations). Furthermore, the use of $Nb(OEt)_5$ as a Lewis acid could be extended also to *N*-aryl and *N*-alkyl aziridines (**6a–8a**, Table 2, Entries 5–8). For this different family of substrates a new optimization of the reaction conditions had to be carried out resulting in a slightly modified reaction protocol under comparable reaction conditions (T = 60–100 °C, 30 bar CO_2) as for the *N*-tosylaziridines. The highest reaction yields were generally obtained using TBAB as a nucleophile and THF (tetrahydrofuran) as a solvent. Moreover, the catalyst loading could be reduced. Under the optimized reaction conditions the same regioselectivity as for the *N*-tosylaziridines was observed.

3.2. DFT studies

There are only very few examples of DFT investigations for the cycloaddition of CO_2 to aziridines in the literature and only for the case of *N*-aryl or *N*-alkyl aziridines [21,48,51]. In order to gain

Table 2
Cycloaddition of CO_2 to several aziridines catalyzed by $Nb(OEt)_5$/TBAI.[a]



Entry	Substrate	Yield (%)[b]	Regioselectivity (**b**:**c**)[c]	TOF (h^{-1})
1		91	92:8	0.24
2		94	100	0.24
3		92	92:8	0.24
4		40	94:6	0.10
5		0		–
6[d]		85 (traces)[e]	94:6	0.44
7[f]		80 (73)[e]		1.67
8[g]		78	88:12	0.41

[a] Using aziridines **1a–8a** (1 mmol), $Nb(OEt)_5$ (0.08 mmol, 8 mol%), TBAI (0.08 mmol, 8 mol%) in DEE (3 mL) at 80 °C, 30 bar CO_2 for 48 h.
[b] Isolated yield of the most abundant regioisomer.
[c] Determined by ^{1}H NMR analysis of the crude reaction mixture.
[d] Using $Nb(OEt)_5$ (4 mol%), TBAB (8 mol%) at 100 °C.
[e] Refers to the outcome of the reaction carried out under identical conditions as per the *N*-tosylaziridines.
[f] Using $Nb(OEt)_5$ (2 mol%), TBAB (4 mol%) in THF at 100 °C for 24 h.
[g] Using $Nb(OEt)_5$ (4 mol%), TBAB (8 mol%) in THF at 60 °C for 48 h.

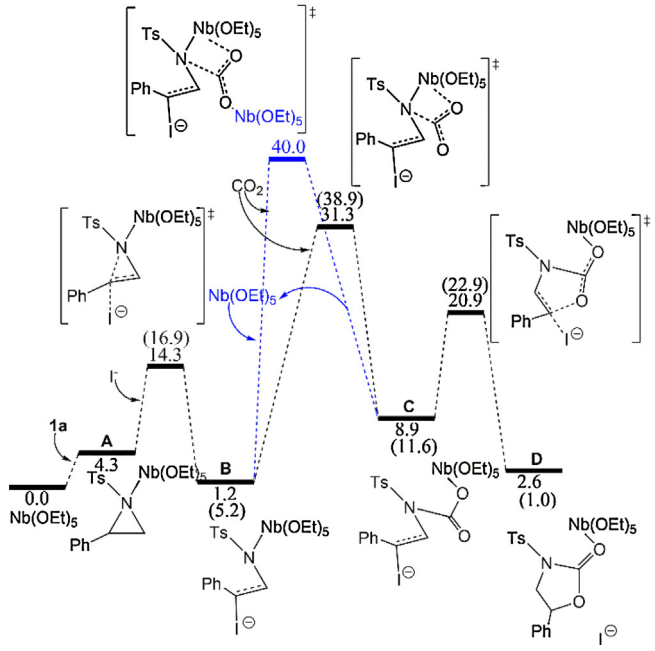


Fig. 2. Reaction mechanism for the cycloaddition of CO_2 to aziridine **1a** catalyzed by $Nb(OEt)_5$/TBAI (The values in brackets refer to the steps leading to the minor regioisomer and starting with the nucleophilic attack at the least substituted carbon atom of the aziridine; Gibbs free energies in solvent are given in kcal/mol, the reaction barrier in blue (see web version of the paper) refers to a bimetallic pathway of CO_2 insertion).

deeper insight on the mechanism of the reaction, that could be crucial for the development of more active catalysts, the cycloaddition of CO_2 to **1a** was investigated using the M06/TZVP ~ sdd//BP86-D3/SVP ~ sdd computational scheme (See Appendix A for details in Supplementary material). We calculated the whole reaction pathway of the cycloaddition of CO_2 to aziridine **1a** catalyzed by $Nb(OEt)_5$/TBAI (Fig. 2) leading to 5-aryl-3-tosyloxazolidin-2-one (**1b**). For the sake of comparison we studied also the same reaction catalyzed by $NbCl_5$/TBAI and $Nb(OMe)_5$/TBAI (See Appendix A, Fig. S1 in Supplementary material). The mechanism considered is represented by the steps of aziridine ring-opening at the phenyl-substituted methine carbon atom by the cooperative action of $Nb(OEt)_5$ and TBAI, CO_2 insertion and ring-closure to afford the desired product. This mechanism is analogous to that accepted for the synthesis of cyclic carbonates from CO_2 and epoxides [52,53] and is supported experimentally by the lack of reactivity of aziridine **5a** (Table 2, Entry 5). For the sake of completeness we also studied the attack of the iodide anion at the least substituted carbon atom of the aziridine ring to clarify the origin of the observed regioselectivity. Moreover, prompted by the cooperative effect observed between atoms of niobium for the activation of CO_2 when investigating its cycloaddition to epoxides [44,45], we considered the possibility of a bimetallic mechanism in the step of CO_2 insertion. Following the formation of intermediate **A** by coordination of $Nb(OEt)_5$ by the nitrogen atom of the aziridine, its ring-opening proceeds *via* C—N bond cleavage by the nucleophilic attack of the iodide anion on the carbon atom bearing the phenyl ring and requires an energy barrier of 10.0 kcal/mol (the total energy barrier for the step of ring-opening is therefore 14.3 kcal/mol). The insertion of CO_2 in the Nb—N bond of the ring-opened intermediate **B** was found to be highly energy demanding, with a barrier of 30.1 kcal/mol and leading to intermediate **C**. Cyclization of the latter intermediate *via* C—O bond formation proceeds through a transition state of 12.0 kcal/mol. The calculated Gibbs free energy of cyclized intermediate **D**, that still bears the Nb moiety, confirms that the process starting from intermediate **A** is exergonic, by 1.7 kcal/mol.

The upper reaction barrier is located at 31.3 kcal/mol for the step of CO_2 insertion that, therefore, represents the rate determining step of the process. This barrier is consistent with the experimentally observed requirement of at least 60 °C for a significant but slow conversion of the substrate. Going into further detail on this mechanism, we observed the lack of cooperativity of a second $Nb(OEt)_5$ moiety in the step of CO_2 insertion with the barrier of this process increasing by 8.7 kcal/mol when a bimetallic mechanism was taken into account (see blue dashed lines in Fig. 2) [54,55], basically due to sterical reasons that do not allow access to an optimal conformation for bending the entering CO_2 [56], whereas the increase of entropy here is lower with just one niobium moiety. Second, we investigated the formation of the minor regioisomer arising from the ring-opening of the aziridine ring at the less sterically crowded methylene carbon (See values in brackets in Fig. 2). The step of ring-opening was found to be 2.6 kcal/mol higher in energy than for the major regioisomer since, electronically, the NBO charge on the methylene carbon is lower by 0.182 e, thus less electrophilic [57]. Importantly, also all the other steps of the calculated mechanism for the minor regioisomer (**1c**) were found to be more energy demanding than for the formation of **1b** with the rate-determining step of CO_2 insertion being over 7 kcal/mol higher in energy. Switching to the $NbCl_5$/TBAI system (See Fig. S1a), no qualitative differences were observed, but, quantitatively, the corresponding transition state **A** → **B** appeared more facile with a barrier of 6.6 just kcal/mol. This barrier was significantly higher for the aziridine ring opening at the methylene carbon (9.9 kcal/mol) thus explaining the perfect regioselectivity observed for this catalyst (Table 1, Entry 7). However, the CO_2 insertion step became much more challenging with a barrier of 37.7 kcal/mol (thus 7.6 kcal/mol higher in energy with respect to the corresponding barrier for $Nb(OEt)_5$). This observation, consistent with the difference in catalytic activity found experimentally, suggests the importance of the steric hindrance at niobium center to facilitate the insertion of CO_2 by favoring the Nb-N bond cleavage. Indeed, when $Nb(OEt)_5$ is used as a catalyst, this distance elongates by 0.128 Å with respect to the case of $NbCl_5$ (Fig. 3). At the same time the distance between the nitrogen atom and the carbon atom of CO_2 is 0.197 Å shorter for $Nb(OEt)_5$. Also for the case of $NbCl_5$, the cooperativity by a second niobium atom in the step of CO_2 insertion was found to be disfavored, but only by 1.3 kcal/mol. Last, the reaction profile was recalculated using

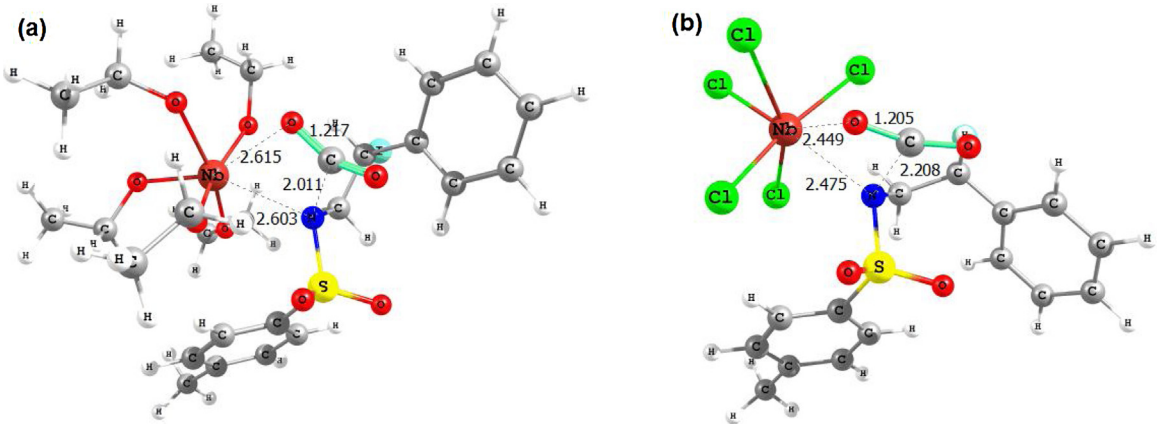


Fig.3. Molecular structures of the computed transition state **B** → **C** for (a) $Nb(OEt)_5$ and (b) $NbCl_5$ (selected distances are given in Å).

$Nb(OMe)_5$/TBAI as a catalyst to understand, and at the same time, remove the potential noise due to the alkyl chains, which might rotate freely at the experimental conditions (See Fig. S1b). Apart from other minimal energy differences in the calculated pathway with respect to $Nb(OEt)_5$, the rate determining barrier for the step of CO_2 insertion increased by 2.6 kcal/mol in the case of $Nb(OMe)_5$; the **B** → **C** transition state displays a N···C distance that is 0.167 Å shorter than for the case of $NbCl_5$ but still 0.030 Å longer than for $Nb(OEt)_5$. This trend confirms the importance of the steric hindrance at the niobium center in facilitating the step of CO_2 insertion.

4. Conclusions

we developed an efficient and readily available dual catalyst based on halogen-free $Nb(OEt)_5$ for the regioselective synthesis of 5-aryl-3-tosyloxazolidin-2-ones by cycloaddition of CO_2 to the parent *N*-tosylaziridines under mild conditions. The method could be also applied to the conversion of different kinds of aziridines. DFT investigation was carried out unravelling the whole reaction pathway. The step of CO_2 insertion was generally found as the rate determining step. Contrarily to recent work on the synthesis of cyclic organic carbonates, the potential occurrence of a bimetallic mechanism between two atoms of niobium was not found to assist in the insertion of CO_2. Investigation of the latter insertion mechanism considering a series of niobium-based catalysts, led to the intriguing conclusion that this crucial step might be facilitated by an increase of the steric hindrance at the niobium center. Furthermore, the provided calculations justify the observed regioselectivity of the reaction.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2017.10.023.

References

[1] I. Omae, Coord. Chem. Rev. 256 (2012) 1384–1405.
[2] Q.-W. Song, Z.-H. Zhou, L.-N. He, Green Chem. 19 (2017) 3707–3728.
[3] M. Cokoja, C. Bruckmeier, B. Rieger, W.A. Herrmann, F.E. Kühn, Angew. Chem. Int. Ed. 50 (2011) 8510–8537.
[4] G. Centi, E.A. Quadrelli, S. Perathoner, Energy Environ. Sci. 6 (2013) 1711.
[5] M. Aresta, A. Dibenedetto, A. Angelini, Chem.Rev 114 (2014) 1709–1742.
[6] A. Goeppert, M. Czaun, J.-P. Jones, G.K. Surya Prakash, G.A. Olah, Chem. Soc. Rev. 43 (2014) 7995–8048.
[7] M. North, P. Styring, Faraday Discuss. 183 (2015) 489–502.
[8] A.W. Kleij, M. North, A. Urakawa, ChemSusChem 10 (2017) 1036–1038.
[9] W. Guo, J. Gónzalez-Fabra, N.A.G. Bandeira, C. Bo, A.W. Kleij, Angew. Chem. Int. Ed. 54 (2015) 11686–11690.
[10] S. Manzini, A. Cadu, A.-C. Schmidt, N. Huguet, O. Trapp, R. Paciello, T. Schaub, ChemCatChem 9 (2017) 2269–2274.
[11] S.Y.T. Lee, A.A. Ghani, V. D'Elia, M. Cokoja, W.A. Herrmann, J.-M. Basset, F.E. Kühn, New J. Chem. 37 (2013) 3512.
[12] A. Tlili, E. Blondiaux, X. Frogneux, T. Cantat, Green Chem. 17 (2015) 157–168.
[13] C.C. Chong, R. Kinjo, ACS Catal. 5 (2015) 3238–3259.
[14] Z. He, H. Liu, H. Liu, Q. Qian, Q. Meng, Q. Mei, B. Han, ChemCatChem 9 (2017) 1947–1952.
[15] J.-F. Wu, S.-M. Yu, W.D. Wang, Y.-X. Fan, S. Bai, C.-W. Zhang, Q. Gao, J. Huang, W. Wang, J. Am. Chem. Soc. 135 (2013) 13567–13573.
[16] V. D'Elia, J.D.A. Pelletier, J.-M. Basset, ChemCatChem 7 (2015) 1906–1917.
[17] C. Martín, G. Fiorani, A.W. Kleij, ACS Catal. 5 (2015) 1353–1370.
[18] J.W. Comerford, I.D.V. Ingram, M. North, X. Wu, Green Chem. 17 (2015) 1966–1987.
[19] H. Büttner, L. Longwitz, J. Steinbauer, C. Wulf, T. Werner, Top. Curr. Chem. 375 (2017).
[20] Z.-Z. Yang, L.-N. He, J. Gao, A.-H. Liu, B. Yu, Energy Environ. Sci. 5 (2012) 6602.
[21] D. Adhikari, A.W. Miller, M.-H. Baik, S.T. Nguyen, Chem. Sci. 6 (2015) 1293–1300.
[22] V.B. Saptal, B.M. Bhanage, ChemSusChem 9 (2016) 1980–1985.
[23] H. Zhou, G.-X. Wang, W.-Z. Zhang, X.-B. Lu, ACS Catal. 5 (2015) 6773–6779.
[24] K.R. Roshan, B.M. Kim, A.C. Kathalikkattil, J. Tharun, Y.S. Won, D.W. Park, Chem. Commun. 50 (2014) 13664–13667.
[25] J.A. Castro-Osma, A. Earlam, A. Lara-Sánchez, A. Otero, M. North, ChemCatChem 8 (2016) 2100–2108.
[26] P. Wang, J. Qin, D. Yuan, Y. Wang, Y. Yao, ChemCatChem 7 (2015) 1145–1151.
[27] R.L. Paddock, D. Adhikari, R.L. Lord, M.-H. Baik, S.T. Nguyen, Chem. Commun. 50 (2014) 15187–15190.
[28] U.R. Seo, Y.K. Chung, Green Chem. 19 (2017) 803–808.
[29] B. Xu, P. Wang, M. Lv, D. Yuan, Y. Yao, ChemCatChem 8 (2016) 2466–2471.
[30] B. Wang, E.H.M. Elageed, D. Zhang, S. Yang, S. Wu, G. Zhang, G. Gao, ChemCatChem 6 (2014) 278–283.
[31] B. Wang, Z. Luo, E.H.M. Elageed, S. Wu, Y. Zhang, X. Wu, F. Xia, G. Zhang, G. Gao, ChemCatChem 8 (2016) 830–838.
[32] S.G. Davies, A.L.A. Figuccia, A.M. Fletcher Paul, M. Roberts, J.E. Thomson, J. Org. Chem. 81 (2016) 6481–6495.
[33] Z. Li, Y. Shi, Org. Lett. 17 (2015) 5752–5755.
[34] X. Ariza, J. Cornellà, M. Font-Bardia, J. Garcia, J. Ortiz, C. Sánchez, X. Solans, Angew. Chem. Int. Ed. 48 (2009) 4202–4205.
[35] K.J. Fraunhoffer, M.C. White, J. Am. Chem. Soc. 129 (2007) 7274–7276.
[36] S. Nicolai, C. Piemontesi, J. Waser, Angew. Chem. Int. Ed. 50 (2011) 4680–4683.
[37] F. Fontana, C.C. Chen, V.K. Aggarwal, Org. Lett. 13 (2011) 3454–3457.
[38] J. Seayad, A.M. Seayad, J.K.P. Ng, C.L.L. Chai, ChemCatChem 4 (2012) 774–777.
[39] A. Sudo, Y. Morioka, F. Sanda, T. Endo, Tetrahedron Lett. 45 (2004) 1363–1365.
[40] A. Monassier, V. D'Elia, M. Cokoja, H. Dong, J.D.A. Pelletier, J.-M. Basset, F.E. Kühn, ChemCatChem 5 (2013) 1321–1324.

[41] B. Dutta, J. Sofack-Kreutzer, A.A. Ghani, V. D'Elia, J.D.A. Pelletier, M. Cokoja, F.E. Kühn, J.-M. Basset, Catal. Sci. Technol. 4 (2014) 1534–1538.
[42] M.J. Kelly, A. Barthel, C. Maheu, O. Sodpiban, F.-B. Dega, S.V.C. Vummaleti, E. Abou-Hamad, J.D.A. Pelletier, L. Cavallo, V. D'Elia, J.-M. Basset, J. CO2 Util. 20 (2017) 243–252.
[43] A. Barthel, Y. Saih, M. Gimenez, J.D.A. Pelletier, F.E. Kühn, V. D'Elia, J.-M. Basset, Green Chem. 18 (2016) 3116–3123.
[44] V. D'Elia, A.A. Ghani, A. Monassier, J. Sofack-Kreutzer, J.D.A. Pelletier, M. Drees, S.V.C. Vummaleti, A. Poater, L. Cavallo, M. Cokoja, J.-M. Basset, F.E. Kühn, Chem. Eur. J. 20 (2014) 11870–11882.
[45] V. D'Elia, H. Dong, A.J. Rossini, C.M. Widdifield, S.V.C. Vummaleti, Y. Minenkov, A. Poater, E. Abou-Hamad, J.D.A. Pelletier, L. Cavallo, L. Emsley, J.-M. Basset, J. Am. Chem. Soc. 137 (2015) 7728–7739.
[46] I.D.V. Ingram, M. North, X. Wu, Halide-free synthesis of cyclic and polycarbonates, in: P. Tundo, L.-N. He, E. Lokteva, C. Mota (Eds.), Chemistry Beyond Chlorine, Springer International Publishing, Switzerland, 2016, pp. 413–434.
[47] Tandon, T. Unzner, T.A. Nigst, N. De Rycke, P. Mayer, B. Wendt, O.R.P. David, H. Zipse, Chem. Eur. J. 19 (2013) 6435–6442.
[48] W.-H. Mu, G.A. Chasse, D.-C. Fang, J. Phys. Chem. A 112 (2008) 6708–6714.
[49] W.M. Weaver, J.D. Hutchison, J. Am. Chem. Soc. 86 (1964) 261–265.
[50] F. Castro-Gómez, G. Salassa, A.W. Kleij, C. Bo, Chem. Eur. J. 19 (2013) 6289–6298.
[51] W. Li, D. Huang, Y. Lv, RSC Adv. 4 (2014) 17236–17244.
[52] C.J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E.C. Escudero-Adán, C. Bo, A.W. Kleij, Chem. Eur. J. 20 (2014) 2264–2275.
[53] S. Arayachukiat, C. Kongtes, A. Barthel, S.V.C. Vummaleti, A. Poater, S. Wannakao, L. Cavallo, V. D'Elia, ACS Sustain. Chem. Eng. 5 (2017) 6392–6397.
[54] S.V.C. Vummaleti, G. Talarico, S.P. Nolan, L. Cavallo, A. Poater, Org. Chem. Front. 3 (2016) 19–23.
[55] S.V.C. Vummaleti, G. Talarico, S.P. Nolan, L. Cavallo, A. Poater, Eur. J. Inorg. Chem. (2015) 4653–4657.
[56] L. Falivene, R. Credendino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano, L. Cavallo, Organometallics 35 (2016) 2286–2293.
[57] A. Poater, A. Gallegos, R. Carbó-Dorca, J. Poater, M. Solà, L. Cavallo, A.P. Worth, J. Comput. Chem. 30 (2009) 275–284.