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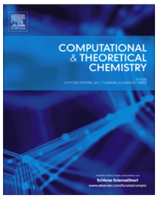

Theoretical study on the nickel(0)-mediated coupling of carbon dioxide and benzylidenecyclopropane: Mechanism and selectivity

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ABSTRACT

Density functional theory (DFT) calculations have been conducted to gain insights into the mechanism and chemoselectivity of the Ni(0)-mediated carboxylation reactions of benzylidenecyclopropane with CO_2. The experimentally observed selectivity of reaction products may be explained through the formation of a common π-complex $Ni(L)_2(\eta^2\text{-}C_2H_4C{=}CHPh)$, which can undergo a direct nucleophilic cyclic addition with CO_2 or an isomerization to four-membered nickelacycle complex followed by the CO_2 insertion. All possible pathways to afford the product precursor five/six-membered cyclic Ni–carboxylates species are examined, and their corresponding energetics are demonstrated. Among the various reaction pathways, we have found that the formation of five-membered cyclic Ni–carboxylate (**2**) via the bisligand route I_A, leading to the target product cyclopropane derivative **A**, has a lower reaction barrier and is the most preferred in the polarity weaker solvent (toluene), which is very in good agreement with the experimental finding. As for the formation process of six-membered cyclic Ni–carboxylates (**4** and **5**), the rate-determining step is associated with the ring-opening of benzylidenecyclopropane to give a four-membered metallacyclic intermediate. In acetonitrile and using DBU as ligands, the monoligand route II_B is competitive with the bisligand route II_B because the activation barrier difference for the ring-opening benzylidenecyclopropane is small (1.34 kcal/mol) and the energy barrier of CO_2 insertion into the Ni—C(sp^2) bond is lower. The monoligand cyclic Ni–carboxylate **4B′d**, generated from the CO_2 insertion into the Ni—C(sp^2) bond of the proposed four-membered intermediate **2B′d**, is predicted to be the most probable species leading to the branched α,β-unsaturated ester **B**.

1. Introduction

The efficient transformation of carbon dioxide (CO_2) into useful organic compounds has attracted much attention in the content of carbon management due to its environmental effects and economic benefits [1–3]. Many synthetic reactions incorporating CO_2 are mediated by various transition metals that are able to activate CO_2 or its coupling partner, resulting in the formation of new C—C, C—N, C—O, or C—H bonds [4–11]. It is worth noting that the carboxylation of carbon nucleophiles using cheap and abundant CO_2 as the electrophilic carbon source represents an excellent opportunity for conversion of CO_2 to industrially valuable products [12–16].

During the past few years, research has been particularly in areas that focus on low-valent nickel-mediated coupling of CO_2 with various unsaturated hydrocarbons under mild conditions [17–23]. For example, Hoberg et al. [17] reported reactions of alkenes with carbon dioxide mediated by Ni(0)-complexes as early as 1982. In particular, recent studies on the carboxylation reactions of methylenecyclopropanes with carbon dioxide showed interesting observations of product distribution in response to reaction conditions, such as reaction solvent and the amine ligand employed (Eqs. (1)–(3)) [24]. Cyclopropane derivative **A** was the major product along with minor α,β-unsaturated ester **B** when diazabicyclo[5.4.0]undec-7-ene (DBU) was used as the amine ligand in toluene solvent (Eq. (1)). In contrast, the use of more polar solvent CH_3CN favored the formation of the branched α,β-unsaturated ester **B** (Eq. (2)) accompanied with **A** as minor product. Surprisingly, the use of 7-methyl-1,5,7-triazabicyclo-[4.4.0]dec-5-ene (MTBD) instead of DBU exclusively afforded the linear γ,δ-unsaturated ester **C** (Eq. (3)). These experimental results implied that there are diverse reaction pathways controlled by reaction conditions (solvent and ligand). However, since none of intermediates was detected, the details of the reaction mechanism are still ambiguous so far. Moreover, for the design of more efficient and selective promoters or catalysts, deeper understanding of the mechanistic details is required.

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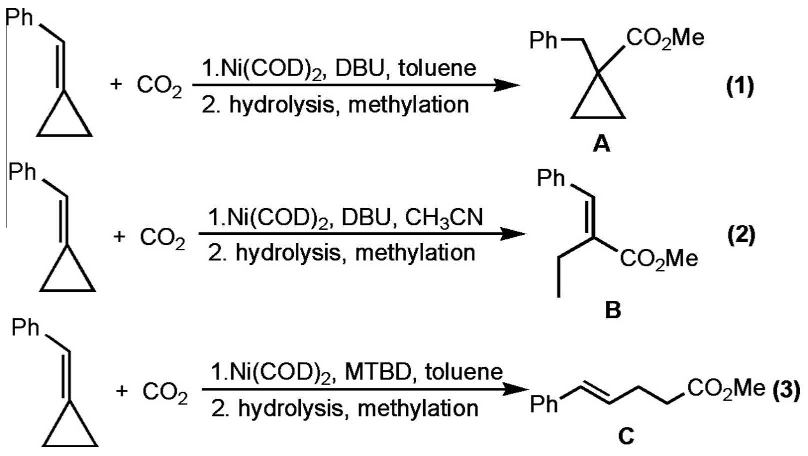
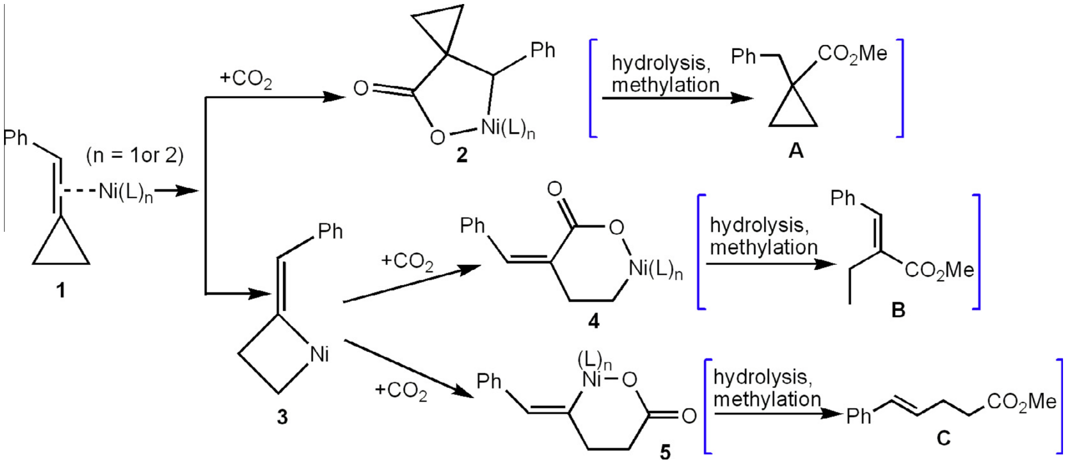


We note that a number of transition-metal-catalyzed coupling reactions involving CO_2 have been investigated from the theoretical side [25–32], and these computational studies proved to be quite useful and feasible in understanding the catalytic process. The theoretical research done by Pápai et al. [25] showed that the oxidative coupling of CO_2 and C_2H_4 catalyzed by nickel(0) did not involve CO_2 coordination, it corresponds to a one step C—C coupling process from $NiL_2(C_2H_4)$ and CO_2 resulting in a cyclic metalla–carboxylate intermediate. Lin et al. [33] put forward that the cyclic metalla–carboxylate intermediates are very important for affording α- or β-unsaturated carboxylic acids in reactions of terminal alkynes with CO_2 mediated by $Ni(DBU)_2$ complexes. As shown in Scheme 1, the formation of product **A** may proceed through the direct hydrolysis of the nickelacycle **2**, which is afforded from the oxidative cyclization between methylenecyclopropane and CO_2 in the presence of Ni promoter. Compounds **B** and **C** come from the proximal $C(sp^2)$—$C(sp^3)$ bond cleavage of cyclopropane, where the $C(sp^2)$—$C(sp^3)$ bond breaking may be triggered through their unique C=C bond coordination to the Ni center, as reported for other low-valent transition metals [34]. The polarity of solvent is expected to influence the C=C bond addition and $C(sp^2)$—$C(sp^3)$ bond cleavage of methylenecyclopropane; while the ancillary ligands will affect the CO_2 insertion into the Ni—$C(sp^2)$ or Ni—$C(sp^3)$ bond of the proposed intermediate **3**.

In this paper, we are interested in not only detailed mechanisms but also ligand effects and solvent effects for the formation of products **A**, **B**, and **C** (Eqs. (1)–(3)), as experimentally obtained [24]. In Murakami's experimental work [24], the products **A**, **B** and **C** were formed via two processes (as shown in Eqs. (1)–(3)), including stirring a solution of benzylidenecyclopropane (1.1 equiv), $Ni(COD)_2$ (1 equiv, COD = cycloocta-1,5-diene) and an amine ligand (2.2 equiv) for 4 h under an atmosphere of carbon dioxide, and then the reactions were quenched by protonolysis with DCl/D_2O and methylation with Me_3SiCHN_2. The reaction is stoichiometric and there is no regeneration of the active site and no turnover of $Ni(COD)_2$. Our attentions are focused on the process 1 that is the formation of possible nickelacycle intermediates **2**, **4**, and **5**. Thus, the second process in square brackets was not investigated. The crucial steps (Scheme 1) and energetics for the coupling of benzylidenecyclopropane with CO_2 mediated by $Ni(0)L_n$ to give five/six-membered cyclic metalla–carboxylates species were investigated by means of DFT calculations, where the real ligands DBU and MTBD were employed in calculations. New mechanisms are proposed based on the experimentally observed selectivity of the reaction. On the basis of present results, we will provide a rationale for the experimental observations and expect the mechanistic insights facilitate the design of efficient promoters or catalysts, thereby improving the chemoselectivity and the yields.



Scheme 1. Simplified pathways for the Ni-mediated carboxylation reaction of benzylidenecyclopropane; ancillary ligands omitted for clarity.