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Ni-Catalyzed Site-Selective Dicarboxylation of 1,3-Dienes with CO₂

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Supporting Information Placeholder

ABSTRACT: A site-selective catalytic incorporation of multiple CO_2 molecules into 1,3-dienes en route to adipic acids is described. This protocol is characterized by its mild conditions, excellent chemo- and regioselectivity and ease of execution under CO_2 (1 atm), including the use of bulk butadiene and/or isoprene feedstocks.

The recent years have witnessed an emerging demand for catalytic techniques that forge multiple C–C bonds via the synergistic combination of chemical feedstocks.¹ Among various conceivable scenarios, a site-selective incorporation of carbon dioxide $(CO_2)^2$ into olefin feedstocks in the absence of stoichiometric organometallic reagents is of particular relevance,³ holding promise to streamline the synthesis of industrially-relevant carboxylic acids.⁴ Despite the elegant advances realized, these carboxylation protocols remain currently confined to *single* CO₂ insertions (Scheme 1, *paths a & b*).⁵ Therefore, the ability to expand the catalytic carboxylation portfolio of C=C bonds beyond *single* CO₂ insertions would be a worthwhile endeavour, opening up new strategies for preparing saturated polycarboxylic acids.⁶

Scheme 1. Carboxylation of Olefinic C=C Bonds.

state-of-the-art catalytic carboxylation of olefinic C=C bonds with CO₂



As part of our ongoing interest in CO₂,⁷ we questioned whether we could enable a catalytic, site-selective incorporation of *multiple* CO₂ motifs into abundant 1,3-dienes en route to adipic acids,⁸ building blocks of particular relevance in the production of plastics and adhesives.⁹ If successful, this pathway might also offer an opportunity

to complement recent catalytic difunctionalization of 1,3-dienes,¹⁰ as raw materials (CO₂) would be used as electrophilic carbon synthons in lieu of nucleophilic reagents.¹¹ However, such a scenario bears considerable risk and might seem counterintuitive at first sight due to (a) the proclivity of 1,3-dienes to trigger telomerization reactions¹² and (b) the fact that statistical mixtures of monocarboxylic acids were exclusively observed with hydrocarboxylation conditions previously employed for either alkynes¹³ or alkenes, ^{5b} reinforcing the notion that a multiple, yet controllable, CO₂ insertion event would be particularly problematic. We anticipated that a siteselective insertion of multiple CO2 units could be rationally controlled in the absence of hydride sources by exploiting the inherent carbogenic nucleophilicity of I (Scheme 1, *bottom*).¹⁴ Upon π - σ equilibration, the targeted adipic acids could be obtained by a subsequent regioselective CO_2 incorporation into I that precedes a final reduction to recover back the catalytic $Ni(0)L_n$ species. Herein, we report the successful realization of this goal, culminating in a mild method that operates at atmospheric pressure of CO₂ and is characterized by its chemo- and regioselectivity profile, including the ability to use of bulk butadiene and/or isoprene feedstocks.

Table 1. Optimization of the Reaction Conditions.^a



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^{*a*} **1a** (0.20 mmol), NiBr₄(TBA)₂ (5 mol%), **L7** (5 mol%), Mn (1.50 equiv), CO₂ (1 bar), DMA (0.5 M), 50 °C. ^{*b*} Z/E = 1.4:1 to 5:1. ^{*c*} ¹H-NMR yields using fluorene as internal standard. ^{*d*} Isolated yield. ^{*e*} with TBAB (10 mol%). TBAB: tetrabutylammonium bromide, TBA: tetrabutylammonium.

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We began our investigations by studying the reaction of 1a with CO_2 (1 atm). After some experimentation,¹⁵ a cocktail consisting of NiBr₄(TBA)₂, L7 and Mn as reductant in DMA at 50 °C furnished **2a** (Z/E = 2.4:1) in 74% isolated yield. It is worth noting that not even traces of 2a' or telomerization side-products were observed in the crude mixtures. Intriguingly, the absence of ammonium salts resulted in a markedly lower reactivity (entries 2 and 3).¹⁶ A detailed survey of nitrogen-donor ligands revealed that a seemingly trivial modification at C2 was critical for success (entries 4 vs 5-6). Unlike recent reductive carboxylations,¹⁷ the presence of substituents at both 2,2'-positions had a deleterious effect (entry 9 vs 1), thus showing the subtleties of our protocol. The use of other precatalysts (entries 2 and 3), solvents (entry 10) or reductants (entry 11) had a detrimental impact on reactivity.¹⁸ Notably, identical results were observed regardless of whether (E)-1a or (Z)-1a were used, constituting an additional bonus from a synthetic and practical standpoint.¹⁹ As expected, control experiments revealed no product formation when each parameter was omitted from the mixture (entry 12).¹⁵

Table 2. Ni-catalyzed 1,4-Dicarboxylation of 1,3-Dienes.^{*a,b*}



^{*a*} As Table 1 (entry 1), followed by exposure to TMSCHN₂ and Pd/C (5 mol%), B₂(OH)₄ (2 equiv) and H₂O (5 equiv) at rt. ^{*b*} Isolated yields, average of two independent runs, using 1,3-dienes as E/Z mixtures. ^{*c*} Using *E***-1a**. ^{*d*} dr = 1.5:1. ^{*e*} dr = 1:1. ^{*f*} 1 mmol scale. ^{*g*} Using H₂ and Pd/C as reductant. ^{*h*} NiBr₄(TBA)₂ (10 mol%) and **L7** (10 mol%).

Once we established the optimized reaction conditions, we next studied the generality of our catalytic dicar-boxylation of 1,3-dienes (Table 2).¹⁹ In situ protection of the carboxylic acid function as the methyl ester and reduction of the pending alkene was necessary to avoid unnecessary purification issues of the resulting adipic acid derivatives.²⁰ As expected, a host of 1,3-dienes substituted with either aliphatic (1n-1g) or aromatic backbones (1a-1m) reacted equally well with the $NiBr_4(TBA)_2/L7$ couple. Notably, the outcome of the latter was found to be insensitive to whether electronrich or electron-poor arenes were employed, even in the presence of ortho-substituents (1i-1k). The site-selective incorporation of multiple CO₂ motifs into 1,3-dienes was accompanied by an excellent chemoselectivity, as esters (3j, 3k), nitriles (3m), ketones (3p) or amides (3q) were well-tolerated. Interestingly, the presence of an organometallic reagent does not interfere with productive formation of **31**, thus demonstrating the complementarity of our technique with classical nucleophilic/electrophilic regimes.^{21,22} Likewise, the reaction could be applied in the presence of heterocyclic cores (3f). As illustrated by the successful preparation of 3g and 3h, the reaction could also be extended to disubstituted 1,3-dienes, albeit with lower diastereoselectivities. Although C-O electrophiles are inherently predisposed to nickel-catalyzed C-C bond-forming reactions,²³ we found that $3\mathbf{k}$ could be obtained in 89% yield, leaving ample room for further derivatization via cross-coupling technologies.

Scheme 2. Ni-catalyzed Carboxylation of Diene Feedstocks.



In light of these results, we wondered whether our protocol could be used for the valorization of butadiene, isoprene or piperylene, compounds that are obtained in bulk as byproducts of the steam cracking in the produc1

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tion of ethylene.²⁴ As shown in Scheme 2, this turned out to be the case, and 7a-9a were all obtained in good yields from the corresponding 1,3-diene feedstocks after a subsequent hydrogenolysis event. Strikingly, butadiene **4** resulted in a 93:7 regioselectivity pattern whereas the presence of a methyl group in either 5 or 6 had a nonnegligible effect on site-selectivity, with 5 providing the best regiochemical discrimination (8a).²⁵ Although the 1,4-ratio of 7a and 9a could partially be improved by using either L5 or L2 in lieu of L7, significant lower yields were observed in these cases.¹⁵ Taken together, the results summarized in Table 2 and Scheme 2 stand as a testament to the potential of this catalytic technology for enabling a site-selective incorporation of multiple CO₂ units into abundant 1,3-diene precursors.

as Table 1 (entry 1) CO₂Me CO₂Me - then ---> TMSCHN₂ MeO₂C MeO₂C 10 majo minor 60% vield trans-11 cis-12 (91:9)stoichiometric studies with Ni(0)(L7)_n Ni(COD)₂ (1 equiv) Me **L7** (1 equiv) N TBAB (1 equiv) Mn (1 equiv), 50 °C 56% (E:Z = 69:31)Ni-1 Me 1a 2a CO₂ (1 atm) Ni-1 (1 equiv) TBAB (1 equiv) Mn (1 equiv), 50 °C Ni-1 0% stoichiometric studies with Ni-2 L7 (1 equiv) Ph TBAB (1 equiv) Mn (1 equiv), 50 °C Cy₃P CO2 (1 atm) Ni-2 37% (E:Z = 36:64) Ni-2

Next, we decided to gather indirect evidence about the mechanism by studying the stereochemical course of 10 with CO₂ (Scheme 3, top). Interestingly, trans-11 was preferentially formed over cis-12, suggesting that the second CO₂ unit is inserted into the π -allyl complex I (Scheme 1) via formal backside attack.²⁶ This seemingly trivial interpretation, however, does certainly not rule out a rapid interconversion of the putative π -allyl nickel complexes upon exposure to Ni(0)(L7) prior to CO_2 insertion.²⁷ Although unraveling the mechanistic underpinnings of this reaction should await further investigations, we turned our attention to study the reactivity of Ni-1 (Scheme 3, *middle*). This complex was easily prepared by exposure of L7 and $Ni(COD)_2$ in benzene at 40 °C, the structure of which was univocally determined by X-ray crystallography.¹⁵ Interestingly, the reactivity of Ni-1 with 1a was not comparable to that observed with $Ni(COD)_2/L7$, with not even traces of 2a being observed

in the former.²⁸ While one might attribute this finding to the non-innocent role of COD,²⁹ the reluctance of coordinatively saturated Ni-1 to dissociate L7 prior to 1,3diene binding seems more likely. Unfortunately, the preparation of π -allyl complex I (Scheme 1) in pure analytical form bearing L7 as ligand proved to be particularly elusive. Gratifyingly, we could prepare structurally-related Ni-2, and the η^3 -hapticity of the allyl motif was finally revealed by X-ray structure analysis (bottom).¹⁵ Interestingly, we found that Ni-2 only furnished 2a in the presence of both L7 and Mn.^{15,30} Whether these results suggest that single-electron transfer processes come into play via putative Ni(I) species³¹ or invoke other mechanistic interpretations is the subject of ongoing studies.

In summary, we have documented a site-selective, catalytic incorporation of multiple CO2 molecules into abundant 1,3-dienes, thus giving access to adipic acids from simple and available precursors. The salient features of this method are its excellent regio- and chemoselectivity, mild conditions and ease of execution. Further extensions to other hydrocarbons, including asymmetric transformations, are currently in progress.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, crystallographic data and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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