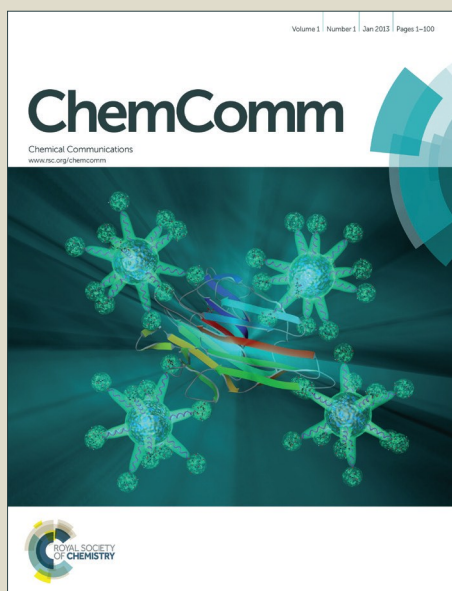


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## COMMUNICATION

Acrylate formation from CO<sub>2</sub> and ethylene: Catalysis with palladium and mechanistic insight

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**We report the first catalyst based on palladium for the reaction of CO<sub>2</sub>, ethylene and a base to form sodium acrylate and derivatives. A mechanism similar to a previously reported Ni(0)-catalyst is proposed based on stoichiometric in situ NMR experiments, isolated intermediates and a parent palladalactone. Our palladium catalyst was applied to the coupling of CO<sub>2</sub> with conjugated alkenes.**

The use of CO<sub>2</sub> as a cheap and abundant C<sub>1</sub> building block is of high interest and a hot topic of current academic and industrial research.<sup>1</sup> An attractive reaction with industrial relevance is the synthesis of sodium acrylate from CO<sub>2</sub> and ethylene, which allows for access to a different raw material base compared to the state of the art propylene route.<sup>2</sup> Initial work in the carboxylation of unsaturated hydrocarbons with CO<sub>2</sub> was done by Hoberg et al. in the 1980s. Several nickel complexes were identified to couple CO<sub>2</sub> and alkenes in a stoichiometric manner to form nickelalactones.<sup>3,4</sup> While the stoichiometric cleavage of those metallalactones has been rationalized and achieved over the years,<sup>5</sup> we recently reported the first one-pot catalytic reaction of sodium acrylate from CO<sub>2</sub>, ethylene, and a base using a nickel catalyst with TON > 100.<sup>6</sup> Extensive screening of bases identified sodium 2-fluorophenolate as the best base for the reported reaction conditions: The Brønsted basicity is sufficiently high,<sup>7</sup> and the nucleophilicity sufficiently low to deprotonate the nickelalactone, but extensive reactivity with CO<sub>2</sub> is avoided. This demonstrates the feasibility of the one-pot process, but opens questions regarding the fate of the catalyst and ways to improve turnover.

Since only nickel is known to be catalytically active in a one-pot system for the formation of sodium- or lithium acrylate<sup>8</sup> from CO<sub>2</sub>, ethylene, and a base, there is considerable interest in expanding the scope of metals used in catalysis. In the nickel system, nickelalactones have been identified as key intermediates.<sup>9</sup> This suggests that metals which form metallalactones may be candidates for the catalytic coupling of CO<sub>2</sub> and alkenes. A few examples of substituted palladalactones are known,<sup>10</sup> but none has been generated by the direct reaction of an alkene and CO<sub>2</sub>.

Yamamoto et al. formed substituted palladalactones upon oxidant addition of substituted cyclic acid anhydrides to (Ph<sub>3</sub>P)<sub>2</sub>Pd(styrene). Those lactones could be cleaved with CO or

acid.<sup>11</sup> A series of cationic palladium methylacrylate complexes release methylacrylate upon addition of ethylene or propylene as demonstrated by Aresta et al.<sup>12</sup> Heating the corresponding neutral compounds under CO<sub>2</sub> and ethylene pressure resulted in ethyl- and methylester formation with a molar ratio of 1.6 relative to Pd. Despite this initial work, no improvements with regards to TON or mechanistic insight have been reported.

Our study commenced with a preliminary screening of a one-pot procedure under ethylene and CO<sub>2</sub> pressure, analogous to our recently reported conditions for nickel (*cf.* Table 1).<sup>6</sup> A variety of palladium precursors were examined and (COD)PdCl<sub>2</sub> and (η<sup>5</sup>-Cp)Pd(η<sup>3</sup>-allyl) resulted in the highest catalytic activity. When (COD)PdCl<sub>2</sub> was used as a precursor, a reducing agent such as Zn(0) was necessary to form a Pd(0) species to enter the catalytic cycle. However, significant TON was demonstrated without metallic reductant for (η<sup>5</sup>-Cp)Pd(η<sup>3</sup>-allyl) and 1,2-bis(dicyclohexylphosphino)ethane (dcpe) as the most promising ligand (TON ~19, *cf.* supporting information). Given the relative stability and commercial availability of (COD)PdCl<sub>2</sub>, the reaction conditions were optimized with this precursor and dcpe.

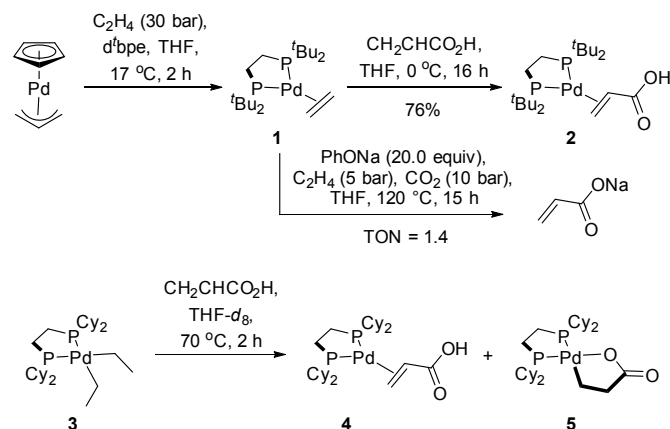
**Table 1** Pd-catalyzed formation of sodium acrylate from CO<sub>2</sub>, ethylene and a base under different conditions.

Entry	$\text{C=C} + \text{CO}_2 + \text{Base} \xrightarrow[\text{TON}]{(\text{COD})\text{PdCl}_2/\text{Zn}, \text{dcpe, temp.}} \text{C=C-CO}_2\text{ONa} + \text{HBase}$				
	(COD)PdCl <sub>2</sub> [mmol]	dcpe [mmol]	Base	Temp. [°C]	TON <sup>a</sup>
1	0.20	0.22	2-F-PhONa	100	9
2	0.20	0.22	2-F-PhONa	120	27
3	0.20	0.22	2-F-PhONa	145	24
4	0.20	0.22	NaHMDS	145	4
5	0.10	0.11	2-F-PhONa	145	29

<sup>a</sup> TON reported as (mmol product)/(mmol [Pd]) after 20 h using sodium 3-(trimethylsilyl)-2,2,3,3-*d*<sub>4</sub>-propionate as an internal standard. Reactions were performed using Zn (10 mmol), base (20 mmol), ethylene (10 bar), CO<sub>2</sub> (20 bar) and THF (30 mL), 20 h reaction time.

A TON of 9 for sodium acrylate was achieved by stirring 0.20 mmol (COD)PdCl<sub>2</sub>, 0.22 mmol dcpe, 20 mmol sodium 2-fluorophenolate, 10 mmol Zn under 10 bar ethylene, and 20 bar CO<sub>2</sub> at 100 °C and 300 rpm for 20 h in an autoclave. Increasing the temperature to 145 °C resulted in a TON of 24. Decreasing the catalyst loading to 0.10 resulted in a TON of 29 (see Table 1). The use of sodium 2-fluoro-phenolate gave a significant higher TON as compared to NaHMDS, similar to the reported nickel system.<sup>6</sup>

Demonstrating the feasibility of palladium in the catalytic formation of sodium acrylate from CO<sub>2</sub> and ethylene raised the question whether similar species are involved in the mechanism as in the nickel system: For nickel and 1,2-bis(di-*tert*-butylphosphino)ethane (d**t**bpe), the parent ethylene-complex, nickelalactone, acrylic acid and acrylate- $\pi$ -complexes were isolated. The reaction of d**t**bpe with ( $\eta^3$ -Cp)Pd( $\eta^3$ -allyl) and ethylene furnished (d**t**bpe)Pd( $\eta^2$ -CH<sub>2</sub>=CH<sub>2</sub>) (**1**), which was immediately reacted with acrylic acid to form (d**t**bpe)Pd( $\eta^2$ -CH<sub>2</sub>CHCO<sub>2</sub>H) (**2**) in 76% yield (Scheme 1). The solid state infrared spectrum of this compound shows a C=O stretch at 1634 cm<sup>-1</sup>, comparable to that reported for (d**t**bpe)Ni( $\eta^2$ -CH<sub>2</sub>CHCO<sub>2</sub>H) at 1627 cm<sup>-1</sup>.<sup>9</sup> While the nickel analogue decomposed to CO<sub>2</sub> and ethylene at 100 °C, (d**t**bpe)Pd( $\eta^2$ -CH<sub>2</sub>CHCO<sub>2</sub>) turned out to be stable at 100 °C for at least 17 h.



**Scheme 1** Synthesis of (d**t**bpe)Pd(CH<sub>2</sub>=CH<sub>2</sub>) (**1**), (d**t**bpe)Pd(CH<sub>2</sub>CHCO<sub>2</sub>H) (**2**), (dcpe)Pd(CH<sub>2</sub>CHCO<sub>2</sub>H) (**4**) and (dcpe)Pd(-CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>-) (**5**).

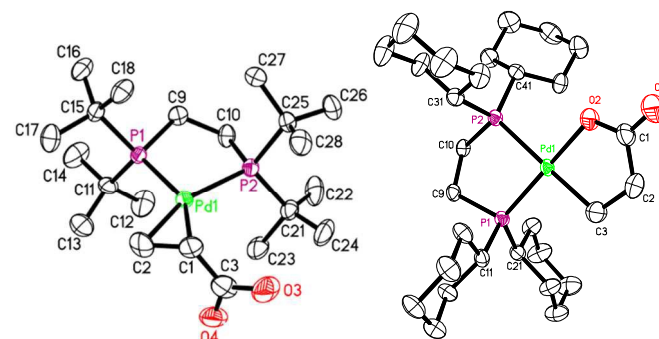
In the solid state the C(1)-C(2) bond length in (d**t**bpe)Pd( $\eta^2$ -CH<sub>2</sub>CHCO<sub>2</sub>H) (**2**) is comparable to its nickel analogue (1.424(8) vs. 1.417(3) Å, *cf.* Figure 1).<sup>9</sup> The palladium-ligand bond lengths of Pd(1)-C(2) and Pd(1)-C(1) are longer than those for nickel (2.089(6) and 2.144(5) Å vs. 1.942(2) and 1.988(2) Å, respectively) due to the palladium centre. Efforts to synthesize a d**t**bpe-ligated palladalactone either directly by addition of CO<sub>2</sub> and ethylene or indirectly by addition of  $\beta$ -propiolactone to ( $\eta^5$ -Cp)Pd( $\eta^2$ -allyl) failed. Reductive routes from palladium(II)dihalides were not met with success either.

Alternative routes towards a palladalactone were explored with various palladium precursors and ligands: (Dialkyl)Pd(II)-complexes are prone to undergo reductive elimination, either thermally or acid-induced.<sup>14</sup> Indeed, (dcpe)Pd(CH<sub>2</sub>CH<sub>2</sub>) (**3**),<sup>15</sup> which was synthesized starting from Pd(OAc)<sub>2</sub> and Et<sub>3</sub>Al in 50% yield, formed (dcpe)Pd(H<sub>2</sub>C=CH<sub>2</sub>)<sup>15,16</sup> upon heating (70 °C, THF-*d*<sub>8</sub>, 2 h).

Synthesis of the elusive palladalactone **5** was finally achieved from acrylic acid and (dcpe)Pd(CH<sub>2</sub>CH<sub>2</sub>) (**3**) upon heating in THF-*d*<sub>8</sub> (70 °C, 2 h, *cf.* Scheme 1). In solution, a mixture of palladalactone **5** and acrylic acid-complex **4** formed (ratio **4**:**5** ca. 1:1).

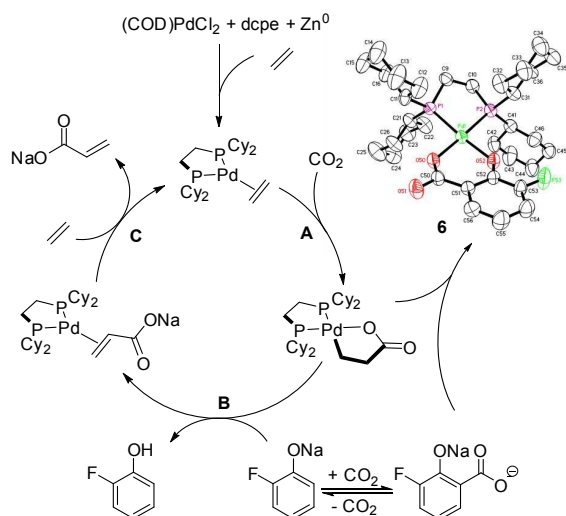
Recrystallization at -35 °C yielded crystals of palladalactone (dcpe)Pd(-CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>-) (**5**) suitable for crystallographic

characterization (Figure 1). The Pd(1)-O(2) and Pd(1)-C(3) bond lengths compare well with in Yamamoto's methyl-substituted palladalactone, (PPh<sub>3</sub>)<sub>2</sub>Pd(-CH<sub>2</sub>CHCH<sub>3</sub>CO<sub>2</sub>-) (2.059(4) and 2.068(5) Å vs. 2.064(7) and 2.070(9) Å, respectively).<sup>10a</sup>



**Figure 1** Solid state structures of (d**t**bpe)Pd(CH<sub>2</sub>CHCO<sub>2</sub>H) (**2**) (left, second molecule in unit cell omitted) and (dcpe)Pd(-CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>-) (**5**) (right, one molecule of THF omitted) at 50% probability. H atoms omitted for clarity.

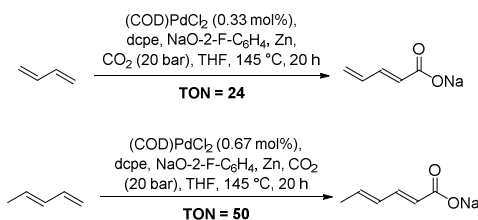
In situ prepared Pd(0)-complex **1** afforded under catalytic conditions (10 bar CO<sub>2</sub>, 5 bar ethylene, 20 equiv. NaOPh, THF, 120 °C, 15 h) indeed sodium acrylate in slightly over-stoichiometric amounts (TON 1.4).



**Figure 2** Proposed catalytic cycle for Pd catalyzed coupling of CO<sub>2</sub> and ethylene to form sodium acrylate.

We have not been able to isolate a palladalactone or other potential catalytic intermediates such as **1** or **4** from a crude reaction mixture, these findings lead us to the assumption of the catalytic cycle proposed in Figure 2. However, in the crude reaction mixture of a catalytic experiment, both sodium 2-fluorophenolate and 2-fluorophenol were identified by <sup>1</sup>H NMR spectroscopy, and the palladium complex (dcpe)Pd(-OPhCO<sub>2</sub>-) (**6**) was crystallized after aqueous work-up as a minor side product (<1% of phosphine species by <sup>31</sup>P NMR, see supporting information). The formation of Pd(II)-complex **6** can be rationalized if one assumes that in the presence of CO<sub>2</sub> sodium 2-fluorophenolate is susceptible to a Kolbe-Schmitt reaction and forms salicylates, which are capable to trap Pd(0). Thus, Zn(0) has a twofold function: Generation of catalytically active Pd(0) species from Pd(II) precursors and the reduction of any Pd(II) species such as **6** formed during catalysis.

Once the coupling of CO<sub>2</sub> and ethylene with palladium was optimized, preliminary investigations with conjugated alkenes were conducted. Reaction of 1,3-butadiene with (COD)PdCl<sub>2</sub>, dcpe, sodium 2-fluorophenolate and Zn under CO<sub>2</sub> (20 bar, THF, 145 °C, 20 h) resulted in a TON of 24 relative to Pd for the single CO<sub>2</sub> insertion product sodium (*E*)-penta-2,4-dionate (Scheme 2). The conformation was based on its characteristic <sup>1</sup>H NMR coupling constant of *J* = 15.4 Hz.<sup>4</sup> Under similar conditions the reaction of (*E*)-piperylene gave a TON of 50 for sodium sorbate relative to Pd.



**Scheme 2** Catalytic formation of acrylates from dienes.

In conclusion, we have found a palladium catalyst for the catalytic synthesis of sodium acrylates or  $\alpha,\beta,\gamma,\delta$ -unsaturated carboxylates from CO<sub>2</sub>, alkenes or 1,3-dienes and a base characterized by a TON > 20 relative to Pd and TOF > 24/day. Efforts are currently underway to further elucidate the catalytic cycle and optimize the system, which in its present form is still less efficient than the best reported Nickel catalyst. However, this work represents, to our knowledge, the first example of a catalytic coupling of CO<sub>2</sub> with ethylene or other alkenes at a palladium catalyst, and the first crystallographically characterized parent palladalactone.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental and X-ray crystallographic data. CCDC 1050643 (2), CCDC 1050644 (3), CCDC 1050645 (5) and CCDC 1050646 (6). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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The first palladium catalyst for the reaction of CO<sub>2</sub>, alkenes and a base to acrylates is reported (TON up to 50).

