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# Investigations on the catalytic carboxylation of olefins with CO<sub>2</sub> towards $\alpha$ , $\beta$ -unsaturated carboxylic acid salts: characterization of intermediates and ligands as well as substrate effects<sup>†</sup>

The carboxylation of olefins beyond ethylene towards  $\alpha$ , $\beta$ -unsaturated carboxylic acid salts and a detailed investigation on the critical steps in the catalysis are reported. The influence of two chelating phosphine ligands and several olefins on the elemental steps of the catalysis is shown. The work focusses on the formation of intermediate olefin complexes, lactone formation and base induced elimination of the lactone. The direct carboxylation of olefins is possible using nickel catalysts, which opens a new route towards the desired  $\alpha$ , $\beta$ -unsaturated carboxylic acid salts. The reaction works particularly well for 1,3-dienes and proceeds *via* the formation of allyl-carboxylates. The ability to form such allyl-type lactone complexes seems in this case to be the most challenging step towards satisfactory turnover numbers.

## Introduction

The carboxylation of olefins with  $CO_2$  in the presence of bases to the corresponding  $\alpha,\beta$ -unsaturated carboxylic acid salts provides atom efficient access to this class of compounds. The abundant and cheap  $CO_2$  can be used in this case as the  $C_1$ -building block.<sup>1</sup> This carboxylation to the desired acids or salts respectively, mediated by several metals, has been investigated over the last few decades, based on the early results of Hoberg *et al.*<sup>1b</sup> The transformations were thereby mainly limited to stoichiometric reactions with respect to the metal complexes to obtain  $\alpha,\beta$ -unsaturated carboxylic acids:<sup>2</sup> using nickel(0),  $CO_2$  and olefins followed by acidic workup or alkylation of cyclopentene,<sup>3</sup> styrene,<sup>4</sup> piperylene,<sup>5</sup> or ethylene.<sup>6</sup> Under similar conditions,  $\alpha,\beta$ -unsaturated carboxylic could not be obtained in many cases due to reduction of the double bond,<sup>7</sup> isomerization<sup>8</sup> or telomerisation.<sup>9</sup>

Despite this early work, by the catalytical method, only telomerisation reactions,<sup>10</sup> the use of Zn-alkyls<sup>11</sup> as reductants or the reductive carboxylation of allyl esters<sup>12</sup> were reported, whereby  $\alpha,\beta$ -saturated carboxylic acid salts are formed. The catalytic synthesis of the desired  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids based on olefins and CO<sub>2</sub> in the presence of a base has been achieved just recently by the appropriate choice of bases and ligands. The first catalytic carboxylation of ethylene to sodium acrylate was described by our laboratory using a twostage process with Ni-dtbpe (dtbpe = 1,2-bis(di-tert-butylphosphino)ethane) as the catalyst and NaOtBu as the base.<sup>13</sup> The two-stage mode was necessary because the lactone-formation and the acrylate-formation have to be separated in two steps, but is, in the overall reaction, catalytic towards the nickel. When the steps were repeated, roughly 10 turn-overs could be achieved by this method. Vogt et al. were able to achieve the catalytic formation of lithium acrylates in a single step catalysis by the use of LiI, an amine base, Zn as a reductant and a Ni-dcpp (dcpp = 1,3-bis(di-cyclohexylphosphino)propane) catalyst with a TON up to 21, but the reaction was not reported for other olefins (Scheme 1).<sup>14</sup>

By further variation of the base (to avoid carbonate formation) and change of the ligands, we were also able to achieve the formation of sodium acrylate in a single step

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Scheme 1 Catalytic carboxylation of ethylene to acrylates with CO2.

catalysis. In this system, Ni-BenzP\* (BenzP\* = (R,R)-1,2-bis(*tert*butyl-methyl-phosphino)benzene) as the catalyst and sodium-2-fluorophenolate as the base together with Zn were used to achieve a TON up to 107.<sup>15</sup> It was also possible to apply the reaction for the first time towards the synthesis of a series of  $\alpha$ , $\beta$ -unsaturated carboxylic acid salts *via* the catalytic carboxylation with CO<sub>2</sub> of olefins like styrenes, butadiene, piperylene, isoprene or cyclohexadiene. For a systematic improvement of the reaction, it is essential to understand the critical steps of the catalysis and we have investigated the carboxylation of olefins beyond ethylene in more detail. Herein, we report the influence of two chelating phosphines and several olefins on the elemental steps of the catalysis, mainly the formation of intermediate olefin complexes, lactone formation and the base induced elimination of the lactone.



Scheme 2 Main species in the catalytic cycle on the carboxylation of olefins with CO<sub>2</sub> towards  $\alpha$ , $\beta$ -unsaturated carboxylic acid salts.



Scheme 3 Synthesis of olefin complexes with the phosphine ligands dtbpe and dcpe.

#### Results and discussion

According to our previous work on the formation of sodium acrylate,<sup>13,15</sup> the main intermediates in the olefin carboxylation are the olefin complex, the lactone and the carboxylate complexes according to Scheme 2.

For a deeper understanding, we focused on the synthesis of the species shown in Scheme 2, in order to obtain insight into which the crucial steps are in the catalytic conversion with nickel as the catalyst while using different olefins like 1-hexene, 3-hexene, styrene, butadiene, methyl-2,4-pentadienoate, piperylene and *cis*-3-hexene.

In our previous work, we just reported the catalytic conversion of several olefins by using the Ni-BenzP\* catalyst, without any characterisation of intermediates or variation of the ligand. Within these more systematic investigations, we also focused on the use of the more common and easily available chelating phosphines dcpe (1,2-bis(dicyclohexylphosphino)ethane) and dtbpe (Scheme 3).

As given in Table 1, both ligands immediately formed the corresponding olefin complexes in clean reactions for the

 Table 1
 Synthesis of olefin complexes

	Alkene	1: d <i>t</i> bpe (conv. in %)	2: dcpe (conv. in %)
a		$100^{a}$	23 <sup>c</sup>
b		$100^a$	$100^a$
c		91 <sup><i>c</i></sup>	95 <sup><i>c</i></sup> mixture of isomers
d	OMe	94 <sup>b</sup>	97 <sup>b</sup>
e		95 <sup>c</sup> mixture of	5 <sup>c</sup>
f	Et	somers Only from (L)NiCl <sub>2</sub> and NaBHEt <sub>2</sub>	Only from (L)NiCl <sub>2</sub> and <i>N</i> -Selectride

<sup>*a*</sup> Ni(COD)<sub>2</sub> (0.1 mmol), ligand (0.1 mmol), olefin (0.3 mmol) at 60 °C, overnight in  $d_8$ -THF. <sup>*b*</sup> [Ni(COD)<sub>2</sub>] (0.1 mmol), ligand (0.1 mmol), olefin (0.3 mmol) at room temperature, overnight in  $d_8$ -THF. <sup>*c*</sup> Ni(COD)<sub>2</sub> (0.1 mmol), ligand (0.1 mmol), olefin (0.3 mmol) at 100 °C, overnight in  $d_8$ -THF (0.6 mL).



**Fig. 1** Molecular structure of  $[(dcpe)Ni(C_6H_5CHCH_2)]$  (2b). Ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–P1 2.159(1), Ni–P2 2.152(1), Ni–C1 1.959(5), Ni1–C2 1.981(4), C1–Ni1–C2 42.0(2), C1–Ni1–P1 154.3(2), P1–Ni1–P2 91.9(1).

entries a-e. The reactions of [Ni(COD)<sub>2</sub>]/dcpe with 1-hexene and 1,3-pentadiene were relatively slow even at elevated temperatures resulting in low yields after the chosen reaction time (overnight), whereas high conversions were obtained for the other olefin/ligand combinations. Almost all of these complexes were synthesized at higher temperatures, except for the olefin complexes of methyl-2,4-pentadienoate. Crystals of the  $[(dcpe)Ni(C_6H_5CHCH_2)]$  (2b) complex could be isolated by the NMR experiment in  $d_8$ -THF at ambient temperature (Fig. 1). These were characterised by X-ray analysis. By the use of [Ni(COD)<sub>2</sub>] as a convenient and commercially available precursor with either dtbpe or dcpe and cis-3-hexene, the substitution of the COD ligand was not possible. It should be noted that the synthesis of these complexes has been reported by Hoberg et al., however, it was only achieved starting from the labile 16 electron [Ni(CDT)] (CDT = all trans-1,5,9-cyclododecatriene) complex.16 In our case, the chelating COD is a far better ligand in comparison to 3-hexene, which makes the substitution difficult and the  $\pi$ -olefin complex inaccessible under these conditions. This was also reflected in the catalysis, where the carboxylation of cis-3-hexene could not be achieved under the conditions we have investigated. Under the conditions we used, we could also never observe any carboxylation products of the COD, which underlines that internal olefins are not accessible for the carboxylation in this system. Nevertheless, both complexes of 3-hexene (1f and 2f) could be synthesised independently in a reaction of (L)NiCl<sub>2</sub>, cis-3-hexene (5 equiv.) and NaBHEt<sub>3</sub>/N-selectride (3/2 equiv.) for dtbpe and dcpe respectively. These were tested in the lactone formation step of the overall reaction.

VT NMR experiments on the reaction of  $[Ni(COD)_2]/dcpe$  with 1,3-butadiene enabled us to distinguish between two different isomers of the [(dcpe)Ni(1,3-butadiene)] (2c) complex (Scheme 4).



Scheme 4 Proposed isomers for the [(dcpe)Ni(1,3-butadiene)] (2c) complex.

<sup>31</sup>P NMR of the mixture at RT shows an expected AB spin system ( $\delta_A$  = 77.5,  $\delta_B$  = 76.8,  ${}^2J_{AB}$  = 54.1 Hz) for the isomer where a 1,3-butadiene molecule is bonded in a single  $\eta^2$ -trans manner. Another isomer gives two broad signals, difficult to assign at room temperature. Upon reducing the temperature to -40 °C the two broad signals sharpen and move to a slightly lower field to give a set of doublets ( $\delta_{\rm A}$  = 52.6,  $\delta_{\rm B}$  = 78.1,  ${}^{2}J_{\rm AB}$  = 51.2 Hz). At an elevated temperature, the two sets of signals slowly broaden, eventually becoming a single line suggesting fluxional behaviour where most likely a  $\eta^2$ -trans butadiene molecule adopts a single *cis*-configuration *via*  $\eta^4$ -bonded butadiene. Such isomerisations are not uncommon and were observed previously for several transition metal butadiene complexes.<sup>16</sup> Therefore, while using the dienes in entries d and e, coordination on the nickel through the primary olefin bond was observed. Most likely, due to the presence of the methyl- and carboxylic methyl-ester groups, coordination through the primary olefin bond is favoured, which excludes further the formation of allyl-carboxylato type complexes. This reflects the poor reactivity of piperylene and methyl-2,4-pentadienoate in comparison to 1,3-butadiene.

According to the catalytic cycle, the formation of the lactone from the olefin-complex with  $CO_2$  follows in the olefin carboxylation. In the cases where the synthesis of the olefin complex starting form  $[Ni(COD)_2]$  was not successful, we attempted the one-pot lactone formation from  $[Ni(COD)_2]/ligand/olefin under CO_2-pressure.$ 

The oxidative coupling of ethylene and  $CO_2$  using Ni(0) systems has been reported for both dcpe and dtbpe ligands.<sup>7d,13</sup> However, whereas the ethylene complexes could be easily converted to the desired nickelalactones in good to excellent yields depending on the ligand, the subsequent reaction of the olefin complexes with  $CO_2$  seems to be not that straightforward (Scheme 5). Experiments were performed under  $CO_2$  pressure (5 bar) with [Ni(COD)<sub>2</sub>] (0.1 mmol), ligand (0.1 mmol) and olefin (0.3 mmol) at 100 °C overnight. While



the dcpe/Ni(0) butadiene complex is being carboxylated under  $CO_2$  pressure to give the nickelalactone [(dcpe)Ni(OC(=O)  $C_4H_6$ )] in a straightforward and fast reaction even at RT, only traces of the lactone could be detected in the <sup>31</sup>P NMR spectra in the case of d*t*bpe/Ni(0) systems with 1-hexene and methyl-2,4-pentadienoate. The carboxylation reaction on the other olefin complexes was not successful under these conditions.

As expected, the coupling of 1,3-butadiene with  $CO_2$  in nickel(0) does not proceed *via* a cyclic nickelalactone complex, but rather yields an allyl-carboxylato complex. This is not surprising, as several allyl-nickel complexes obtained *via* carboxylation of 1,3-butadiene and 1,3-piperylene were described before.<sup>5*a*</sup> It seems that the selectivity for such allyl-type complexes is dependent on the ligand used in the system.<sup>17</sup> In the molecular structure, the remaining carbon atoms of the unsaturated butadiene unit form an  $\eta^3$ -allylic structure with the nickel atom. These findings were confirmed with X-ray analysis of [(dcpe)Ni(OC(=O)C\_4H\_6)] obtained in THF at ambient temperature. Due to disorder in the molecule, we abstained from a quantitative discussion of the bond length in the molecule (Fig. 2).

Unable to access many of the compounds using the previously described direct route, we investigated the stoichiometric reaction of  $[Ni(COD)_2]$  and the ligand with *trans*cinnamic acid, 2-heptenoic acid as well as 2,4-pentadienoic acid (Scheme 6). These reactions were performed in order to obtain insights into the mechanism and an idea about the stability of the intermediates towards decarboxylation in the overall reaction as well as to check, if the lack of lactone formation is preventing the catalysis.

The reactions were monitored by <sup>31</sup>P NMR spectroscopy (Fig. 3). It can be seen that the reactions with both *trans*-cinnamic and 2-heptenoic acid are slow at room temperature, yielding a mixture of nickelalactone and  $\pi$ -carboxylic acid complex (Fig. 4). However, at temperatures above 40 °C the complexes resulted from the reaction with *trans*-cinnamic acid decarboxylate to give the  $\pi$ -styrene [(dcpe)Ni(0)] (**2b**) complex.



**Fig. 2** Molecular structure of  $[(dcpe)Ni(OC(=O)C_4H_6)]$  (**4c**). Ellipsoids represent 50% probability. Hydrogen atoms and carbon ellipsoids in the ligand are omitted for clarity.



Scheme 6 Stoichiometric reaction of [Ni(COD)<sub>2</sub>]/ligand with cinnamic acid, 2-heptenoic acid and 2,4-pentadienoic acid.

In order to avoid the formation of the decarboxylated product, the reaction was also performed under 3 bar of CO<sub>2</sub>. Although the decarboxylation was disfavoured, less formation of the lactones was detected. On increasing the temperature to 80 °C under the same CO<sub>2</sub> pressure, the decarboxylated product was also formed as the major product. In this case, it seems that the insufficient lactone stability towards the reverse reaction can be an explanation for the lack of catalytic activity in the styrene carboxylation while using Ni-dcpe. Heating the reaction mixture with 2-heptenoic acid at 40 °C for 1 day leads to decomposition of the  $\pi$ -complex, suggesting that the nickelalactone is the more stable species. Also in this case, performing the reaction under a  $CO_2$  atmosphere (3 bar) inhibits the formation of the nickelalactone. Cooling down the mixture again, only the signals for the nickelalactone complex could be assigned, indicating simple decarboxylation of the  $\pi$ -carboxylic acid complex and excluding temperature dependent equilibrium between the two species.

Performing the reaction with cinnamic acid and  $[Ni(COD)_2]/BenzP^*$ , one could observe that the cinnamic acid complex and the nickelalactone bearing this ligand are much more stable and decarboxylate only after heating at 100 °C. This most likely explains why this ligand is much more active in the catalysis with 1,3-butadiene (TON 116) and also suitable for the carboxylation of other olefins.<sup>15</sup>

Adding a slight excess (2 equiv.) of 2,4-pentadienoic acid to [Ni(COD)]/ligand gives quantitatively a allyl-carboxylato  $[(dcpe)-Ni(OC(=O)C_4H_6)]$  complex (4c). The reaction includes hydrogen migration from the Ni-atom to the  $\alpha$ -C atom of the carboxylate. Such oxidative additions have been described before for Ni(0) and Pd(0).<sup>18,19</sup> The compound shows the same spectral features as the coupling product of [(dcpe)Ni(1,3-butadiene)] with carbon dioxide. While dcpe gives exclusively one product, the reaction with *dt*bpe results in the formation of two different compounds, presumably two isomeric nickelalac-



**Fig. 3** Time and temperature dependence in the reaction of [Ni(COD)<sub>2</sub>]/ dcpe with 2-heptenoic acid (top) and *trans*-cinnamic acid (bottom).

tones. The small  $J_{\rm PP}$  coupling constants of 9 and 10 Hz respectively, excludes the presence of a Ni(0) species and suggests again an oxidative addition of the doubly unsaturated acid, followed by a hydrogen migration step. Unfortunately, separating and purifying these two species was unsuccessful and distinguishing between species in the <sup>1</sup>H NMR is really difficult due to overlapping regions with  $CH_3$  groups from dtbpe. Therefore, assuming that these isomers have a similar structures to 4c (due to the corresponding chemical shift range and similar  $J_{\rm PP}$  coupling constants), we have calculated the relative energies for various isomers such as  $\eta^{1}$ - and  $\eta^{3}$ -allylic structures as well as 4- and 5-membered cyclic ethers for both dtbpe and dcpe (Fig. 6; details in the ESI<sup>†</sup>). Surprisingly, for dtbpe, a 4-membered  $\beta$ -nickelalactone seems to be the most stable isomer. As expected,  $\eta^3$ -allylic carboxylates are also low in energy, whereas the five-membered cyclic ethers, where the



Fig. 4 Molecular structure of  $[(dcpe)Ni(C_6H_5CHCHCO_2H)]$  (5b). Ellipsoids represent 50% probability. Hydrogen atoms (except for H1) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–P1 2.174(3), Ni–P2 2.168(4), Ni–C1 1.976(7), Ni1–C2 1.991(7), C1–Ni1–C2 43.1(2), C2–C3–O2 122.7(7), O2–C3–O1 120.6(7).



Fig. 5 <sup>31</sup>P{H} NMR spectra of lactone complexes synthesised from 2,4pentadienoic acid and [Ni(COD)<sub>2</sub>]/ligand: dcpe (left) and dtbpe (right).

alkene rest is located at  $\alpha$ - or  $\beta$ -position with respect to the carbonyl group, seems to be thermodynamically less favourable.

The reaction mixtures depicted in Fig. 5 were used without purification in a subsequent reaction with a base and the olefin (1,3-butadiene) to show the feasibility of the next steps in the catalytic cycle: deprotonation (II) and olefin exchange (III). In order to obtain any catalysis, the choice of the base is also crucial: the base should not irreversibly react with  $CO_2$  to form carbonates, but should be basic enough to allow cleavage of the lactone to form sodium acrylate. Sodium-



Fig. 6 Relative energies of different isomeric nickelalactones for 3c calculated in kJ mol<sup>-1</sup> (ligand = dtbpe).



Scheme 7 Base-mediated cleavage of [(dcpe)Ni(lactone)] into a carboxylate complex [(dcpe)Ni(RCH=CHCO<sub>2</sub>Na)] and a *in situ* exchange reaction with olefin.

2-fluorophenolate was identified to be an appropriate base for this reaction (Scheme 7).<sup>15</sup> However, sodium-2-fluorophenolate did not give a clean reaction. For this reason, NaO*t*Bu was used as a stronger base, to determine whether the lactone could be cleaved at all.

By adding a base, the coordinated sodium carboxylate can be formed by reductive elimination of the lactone. The stability and the reactivity of the investigated nickelalactones are rather surprising. The allyl-carboxylato (dcpe)Ni( $\pi$ ) complex underwent an exchange reaction with NaOtBu to give, by <sup>31</sup>P NMR spectroscopy, a characteristic broadening that could be assigned as a  $\pi$ -butadiene Ni(0) complex with only one equivalent of olefin present in the mixture. In contrast, the mixture of isomeric (dtbpe)Ni( $\pi$ ) complexes mainly remained unreacted even with an excess of base/olefin.

In the earlier studies on the catalytic reaction of ethylene and CO<sub>2</sub> with the BenzP\* ligand, the addition of finely powdered Zn proved to be beneficial for the coupling (TON 69 *vs.* 39), most likely reducing Ni( $\pi$ ) intermediates formed during the reaction.<sup>15</sup> A similar behaviour was observed in the catalytic carboxylation of 1,3-butadiene with BenzP\* (TON 137 *vs.* 117) and dcpe (TON 37 *vs.* 22). Taking our standard conditions into consideration, we assume that Ni( $\pi$ ) species such as the phenoxide complex [(L)Ni(OC<sub>6</sub>H<sub>4</sub>F)<sub>2</sub>] and the carbonate complex [(L)Ni(O<sub>2</sub>CO)] (Fig. 7) can be formed during this reaction and elemental Zn is regenerating the active catalytic species from these complexes in the catalysis. These two com-





Scheme 8 Reduction of Ni(u) complexes with elemental Zn in the presence of styrene.

pounds were therefore synthesized separately, isolated and used in the catalysis of butadiene and  $CO_2$  with the dcpe/ d*t*bpe ligand systems, in order to evaluate the role of Zn. Prior to that, we performed stoichiometric reactions with these two complexes, Zn (10 equiv.) and olefin (styrene/10 equiv.) under standard conditions (THF, 20 h, 100 °C) and investigated the reduction of Ni(0) species (Scheme 8).

 $[(dcpe)Ni(OC_6H_4F)_2]$  was easily reduced, affording the desired olefin complex (65% conversion after 20 h by <sup>31</sup>P NMR). The  $[(dtbpe)Ni(O_2CO)]$  carbonate complex however, was not reduced with Zn under these conditions, suggesting that its formation could be one deactivation pathway of the catalysis. With these assumptions, the next step was testing the complexes in the catalysis using styrene with and without Zn (Scheme 9). In the reactions without Zn, both complexes showed minor activity and very low turnovers were achieved:  $[(dcpe)Ni-(OC_6H_4F)_2]$  gave a TON of 1 and  $[(dtbpe)Ni(O_2CO)]$ gave a TON of 3. After the addition of powdered Zn, slightly higher TONs were observed: 5 vs. 1 for [(dcpe)Ni(OC<sub>6</sub>H<sub>4</sub>F)<sub>2</sub>] and 4 vs. 3 for  $[(dtbpe)Ni(O_2CO)]$ . One could argue that these results are in agreement with the stoichiometric reactions and that possibly Zn has a role of a reductant, at least in the case of  $[(dcpe)Ni-(OC_6H_4F)_2]$ . However, the very low TON values and the given error make these arguments questionable. Therefore, despite the certain beneficial effect of the powdered Zn in the catalytic reactions, the mechanism of its reactivity is still not very clear. This opens a further question, how necessary are such large quantities of Zn in the reaction medium and is it worth pursuing the advantages of having a homogeneous system for a process development, albeit the slightly lower turnover numbers.

Catalysis was performed with  $[Ni(COD)_2]$  (0.1 mmol), ligand (0.11 mmol), 2-F-phenoxide (300 mmol), Zn (100 mmol), CO<sub>2</sub> (20 bar) and the corresponding olefin in THF (30 mL) at 100 °C overnight. The reaction under CO<sub>2</sub> pressure (20 bar),



Fig. 7 Molecular structure of [(dtbpe)Ni(O<sub>2</sub>CO)]. Ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–P1 2.177(7), Ni–P2 2.165(7), Ni–O1 1.882(2), Ni1–O2 1.889(2), O1–Ni1–O2 70.0(8), O1–Ni1–P2 98.4(6).

Scheme 9 Catalytic carboxylation of olefins to acrylates with CO<sub>2</sub> towards  $\alpha$ , $\beta$ -saturated carboxylic acid salts.

1,3-butadiene (300 equiv.) with sodium 2-fluorophenoxide (300 equiv.) and dcpe as the ligand gave a TON of 37. A low TON of 3 could be observed using dtbpe, a result consistent with the earlier observations, in which it was shown that the corresponding nickelalactone is not accessible under these conditions. Both ligands showed a low activity in the catalytic reaction with 1,3-pentadiene (100 equiv. of olefin) giving 4 and 11 turnovers respectively. A similar reaction was observed in the case of methyl-2,4-pentadienoate, where both ligands gave a comparably low TON of 3 (100 equiv. of olefin). Assuming that the allyl-nickel(II) complex is not only an intermediate in the C-C coupling reaction between butadiene and CO<sub>2</sub>, but also a catalytically active species, the complex was used in the catalysis under standard conditions to give 33 turnovers, which is comparable to the TON achieved using the  $[Ni(COD)_2]/$ dcpe/1,3-butadiene system. Unlike the coupling of ethylene with CO<sub>2</sub>, where the cleavage of nickelalactones [(L)Ni- $(CH_2CH_2CO_2)$ ] to form acrylate  $\pi$ -complexes  $[(L)Ni(\eta^2 -$ CH2=CHCO2R)] is considered the most challenging step in the catalytic cycle,<sup>13</sup> it appears that in the case of substituted alkenes, the lactone formation is a crucial step that influences the outcome of the overall reaction.

### Conclusions

We have shown that the direct carboxylation of olefins is possible using a nickel catalyst, which opens a new route towards the desired  $\alpha,\beta$ -unsaturated carboxylic acid salts. The reaction works particularly well for 1,3-dienes and proceeds *via* the formation of allyl-carboxylates. Investigations showed that the ability to form such allyl-type lactone complexes represents in this case the most challenging step towards satisfactory turnover numbers.

#### **Experimental**

#### **General considerations**

All manipulations were performed under an inert atmosphere of dry argon by using Schlenk techniques or by working in the glovebox. All autoclave reactions were performed under an inert atmosphere of argon by working in a glovebox. Solvents were purchased from Sigma-Aldrich. <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectra were recorded on Bruker Avance 200, 400, 500, or 600 MHz spectrometers and were referenced to the residual proton (<sup>1</sup>H) or carbon (<sup>13</sup>C) resonance peaks of the solvent. Chemical shifts ( $\delta$ ) are expressed in ppm. <sup>31</sup>P NMR was referenced to triphenylphosphine oxide as an internal standard. Elemental analyses were recorded by the analytical service of the chemistry department of the University of Heidelberg. Bis(di-*tert*-butylphosphino)ethane<sup>17b</sup> and [(dcpe)NiCl<sub>2</sub>]<sup>20</sup> were synthesised following reported procedures. X-ray structures were solved by direct methods and refined against  $F^2$  with a full-matrix least squares algorithm by using the SHELXTL (Version 2008/4) software package.<sup>21</sup> Intensities were corrected

for Lorentz and polarisation effects.<sup>22</sup> CCDC 1052343 (**2b**), 1052344 (**4c**), 1052345 (**5b**) and 1052346 (Ni-dtbpe carbonate) contain the supplementary crystallographic data for this paper.

Formation of olefin complexes 1a–f and 2a–f, NMR experiments.  $[Ni(COD)_2]$  (27.5 mg, 0.1 mmol), phosphine ligand (0.1 mmol, 1 equiv., dcpe 42.2 mg, dtbpe 38.2 mg) and olefin (0.3 mmol, 3 equiv.) were dissolved in d<sub>8</sub>-THF (0.6 mL) and placed in a J-young NMR tube. The mixture was heated (60–100 °C for 24 h accordingly) to form the desired olefin complex. After the time had elapsed, the mixture was cooled down to room temperature and the reaction was studied by NMR spectroscopy.

[(dtbpe)Ni(1-hexene)] (1a). <sup>31</sup>P NMR spectroscopic yield: 100%. <sup>1</sup>H NMR (600 MHz,  $d_8$ -THF):  $\delta$  0.88 (t, 3H,  $CH_3$ ,  $J_{HH}$  = 7.2 Hz), 1.20 (m, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 1.40 (m, 4H, CH), 1.66 (ddd, 1H, CH, J = 3.4, 6.7, 12.6 Hz), 1.72 (m, 4H, PCH<sub>2</sub>CH<sub>2</sub>P), 1.88 (m, 1H, CH), 1.95 (tdd, 1H, CH, J = 3.9, 5.9, 9.7 Hz), 2.18 (m, 1H, CH), 2.59 (m, 1H, CH);  $^{13}$ C NMR (151 MHz,  $d_8$ -THF)  $\delta$  13.7 (s, CH<sub>3</sub>), 22.7 (dd, PCH<sub>2</sub>CH<sub>2</sub>P, J<sub>CP</sub> = 11.8, 18.8 Hz), 24.0 (dd,  $PCH_2CH_2P$ ,  $J_{CP} = 13.8$ , 21.8 Hz), 29.2 (t,  $CH_3$ ,  $J_{CP} = 7.36$  Hz), 29.8 (d,  $C(CH_3)_3$ ,  $J_{CP} = 6.6$  Hz), 30.0 (d,  $C(CH_3)_3$ ,  $J_{CP} = 6.8$  Hz), 30.2 (d,  $C(CH_3)_3$ ,  $J_{CP}$  = 7.6 Hz), 30.3 (d,  $C(CH_3)_3$ ,  $J_{CP}$  = 7.6 Hz), 30.9 (dd,  $CH_3$ ,  $J_{CP}$  = 9.2, 13.4 Hz), 34.1 (m,  $CH_3$ ), 34.2 (m,  $CH_3$ ), 34.1 (d,  $CH_2$ ,  $J_{CP}$  = 4.9 Hz), 36.6 (d,  $CH_2$ ,  $J_{CP}$  = 8.3 Hz), 37.0 (t,  $CH_2$ ,  $J_{CP}$  = 2.7 Hz), 38.9 (dd,  $CH_2$  from 1-hexene,  $J_{CP}$  = 3.5, 19.3 Hz), 49.9 (dd, CH from 1-hexene,  $J_{CP}$  = 2.5, 23.3 Hz); <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF)  $\delta$  91.0 (d,  ${}^{3}J_{PP}$  = 75.1 Hz), 88.6 (d,  ${}^{3}J_{PP}$  = 75.1 Hz) ppm; IR after evaporation of all volatiles ( $\nu$ , cm<sup>-1</sup>): 660 (w, P-C), 728 (m), 912 (s), 1073 (s), 1179 (w), 1261 (w), 1380 (m), 1461 (s, C-H aliph.), 1974 (w), 2364 (w), 2872 (vs, C-H aliph.), 2959 (s, C-H aliph.).

[(dcpe)Ni(1-hexene)] (2a). <sup>31</sup>P NMR spectroscopic yield: 23%. <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF)  $\delta$  62.3 (d, <sup>3</sup> $J_{PP}$  = 72.2 Hz), 57.7 (d, <sup>3</sup> $J_{PP}$  = 71.8 Hz) ppm.

[(dtbpe)Ni(styrene)] (1b). <sup>31</sup>P NMR spectroscopic yield: 100%. <sup>1</sup>H NMR (600 MHz,  $d_8$ -THF):  $\delta$  1.15 (m, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 1.64 (m, 4H,  $PCH_2CH_2P$ ), 2.19 (td, 2H,  $CH_2$ , J = 4.8, 9.7 Hz), 3.53 (qt, 1H, CH, J = 14.7, 29.3 Hz), 6.95 (m, 5H, CH); <sup>13</sup>C NMR (151 MHz,  $d_8$ -THF)  $\delta$  20.9 (dd, PCH<sub>2</sub>CH<sub>2</sub>P,  $J_{CP}$  = 13.6, 18.1 Hz), 21.7 (dd, PCH<sub>2</sub>CH<sub>2</sub>P, J<sub>CP</sub> = 14.1, 20.1 Hz), 27.4 (t, CH<sub>3</sub>,  $J_{\rm CP}$  = 7.0 Hz), 27.7 (d,  $C({\rm CH}_3)_3$ ,  $J_{\rm CP}$  = 7.2 Hz), 28.0 (d,  $C({\rm CH}_3)_3$ ,  $J_{\rm CP}$  = 6.3 Hz), 28.3 (d,  $C({\rm CH}_3)_3$ ,  $J_{\rm CP}$  = 7.0 Hz), 28.6 (d,  $C({\rm CH}_3)_3$ ,  $J_{\rm CP}$  = 7.0 Hz), 29.1 (dd,  $CH_3$ ,  $J_{\rm CP}$  = 9.4, 14.1 Hz), 32.2 (dd,  $CH_2$ from styrene,  $J_{CP}$  = 3.4, 21.9 Hz), 32.4 (dd,  $CH_3$ ,  $J_{CP}$  = 5.4, 8.7 Hz), 35.5 (dd,  $CH_3$ ,  $J_{CP}$  = 4.1, 8.3 Hz), 48.2 (dd, CH from styrene, J<sub>CP</sub> = 2.08, 19.2 Hz), 118.3 (d, CH<sup>Ph</sup>, J<sub>CP</sub> = 2.3 Hz), 122.1 (d,  $CH^{Ph}$ ,  $J_{CP}$  = 2.1 Hz), 125.5 (d,  $CH^{Ph}$ ,  $J_{CP}$  = 1.7 Hz), (148.8 (dd, *ipso-C*<sup>Ph</sup>,  $J_{CP}$  = 1.6, 5.6 Hz); <sup>31</sup>P NMR (81 MHz, THF)  $\delta$  95.1 (d,  ${}^{3}J_{PP}$  = 68.2 Hz), 84.4 (d,  ${}^{3}J_{PP}$  = 68.2 Hz) ppm; IR after evaporation of all volatiles ( $\nu$ , cm<sup>-1</sup>): 658 (m, P-C), 911 (s), 1070 (s), 1177 (m), 1364 (m), 1459 (s, C-H aliph.), 1967 (w), 2082 (m), 2235 (m), 2682 (m), 2860 (vs, C-H aliph.), 2974 (vs, C-H aliph.).

[(*dcpe*)Ni(*styrene*)] (2b). <sup>31</sup>P NMR spectroscopic yield: 100%. <sup>1</sup>H NMR (600 MHz,  $d_8$ -THF):  $\delta$  1.34 (m, 44H, CH and CH<sub>2</sub> (Cy)),

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1.96 (m, 4H, PCH<sub>2</sub>CH<sub>2</sub>P), 2.21 (m, 2H, CH<sub>2</sub>), 3.81 (m, 1H, CH), 6.91 (m, 5H, CH); <sup>13</sup>C NMR (151 MHz,  $d_8$ -THF)  $\delta$  19.9 (ddd, PCH<sub>2</sub>CH<sub>2</sub>P, J<sub>CP</sub> = 25.8, 38.1, 26.7 Hz), 24.2–28.4 (m, CH<sub>2</sub> from Cy), 31.9 (dd, CH from Cy,  $J_{CP}$  = 4.5, 13.3 Hz), 33.1 (m, CH from Cy), 33.1 (d, CH<sub>2</sub> from styrene overlapping with CH from Cy,  $J_{CP} = 14.4$  Hz), 33.6 (dd, CH from Cy,  $J_{CP} = 3.7$ , 15.6 Hz), 47.7 (d, CH from styrene,  $J_{CP}$  = 17.9 Hz), 117.8 (d, CH<sup>Ph</sup>,  $J_{CP}$  = 2.1 Hz), 121.7 (d,  $CH^{Ph}$ ,  $J_{CP}$  = 2.5 Hz), 125.4 (d,  $CH^{Ph}$ ,  $J_{CP}$  = 1.8 Hz), 147.6 (dd, *ipso-C*<sup>Ph</sup>,  $J_{CP} = 1.4$ , 5.6 Hz); <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF)  $\delta$  68.7 (d,  ${}^{3}J_{PP}$  = 64.4 Hz), 56.2 (d,  ${}^{3}J_{PP}$  = 64.4 Hz) ppm; IR after evaporation of all volatiles ( $\nu$ , cm<sup>-1</sup>): 657 (m, P–C), 911 (s), 1069 (s), 1178 (m), 1364 (m), 1459 (s, C-H aliph.), 1812 (w), 1967 (w), 2083 (m), 2235 (m), 2682 (m), 2862 (vs, C-H aliph.), 2977 (s, C-H aliph.). Elemental analysis of the crystals isolated from the NMR experiment calcd C 69.75%, H 9.64; found C 70.46%, H 9.75%. Single crystals suitable for X-ray analysis were isolated from the NMR experiment. Orange crystals (polyhedron), dimensions  $0.20 \times 0.15 \times 0.15$  mm<sup>3</sup>, crystal system monoclinic, space group  $P2_1/c$ , Z = 4, a = 10.6643(18) Å, b =9.5838(16) Å, c = 31.345(6) Å,  $\beta = 97.564(5)^{\circ}$ , V = 3175.7(9) Å<sup>3</sup>,  $\rho = 1.224 \text{ g cm}^{-3}$ , T = 200(2) K,  $\theta_{\text{max}} = 25.090^{\circ}$ , radiation Mo K<sub>a</sub>,  $\lambda = 0.71073$  Å,  $0.5^{\circ} \omega$  scans with a CCD area detector, covering the asymmetric unit in reciprocal space; reflections: 17 547 measured, 5635 unique ( $R_{int} = 0.0606$ ), 4308 observed  $(I > 2\sigma(I)); \mu = 0.73 \text{ mm}^{-1}, \min/\max \text{ transmission: } 0.77/0.92,$ 346 parameters refined, hydrogen atoms were treated using appropriate riding models, except for the olefinic ones, which were refined isotropically, goodness of fit: 1.10 for observed reflections, final residual values  $R_1(F) = 0.058$ , w $R(F^2) = 0.088$ for observed reflections, residual electron density -0.37 to  $0.45 \text{ e} \text{ Å}^{-3}$ .

[(dtbpe)Ni(1,3-butadiene)]<sup>17c</sup> (1c). <sup>31</sup>P NMR spectroscopic yield: 91%. <sup>1</sup>H NMR (600 MHz,  $d_8$ -THF):  $\delta$  1.04 (m, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 1.56 (dd, 4H, PCH<sub>2</sub>CH<sub>2</sub>P, J = 7.0, 15.5 Hz), 3.00 (d, 1H, CH<sub>2</sub>, J<sub>HH</sub> = 8.6 Hz), 3.16 (d, 1H, CH<sub>2</sub>, J<sub>HH</sub> = 13.4 Hz), 4.46 (m, 1H, CH), 4.93 (d, 1H, CH, J<sub>HH</sub> = 9.4 Hz), 5.05 (d, 1H, CH<sub>2</sub>, J<sub>HH</sub> = 15.5 Hz), 6.16 (m, 1H, CH); <sup>13</sup>C NMR (151 MHz,  $d_8$ -THF)  $\delta$  20.8 (t, PCH<sub>2</sub>CH<sub>2</sub>P, J<sub>CP</sub> = 16.6 Hz), 26.8 (t, CH<sub>3</sub>, J<sub>CP</sub> = 7.3 Hz), 27.7 (d, C(CH<sub>3</sub>)<sub>3</sub>, J<sub>CP</sub> = 6.9 Hz), 28.6 (dd, CH<sub>3</sub>, J<sub>CP</sub> = 9.0, 13.7 Hz), 30.4 (t, CH<sub>2</sub> from 1,3-butadiene, J<sub>CP</sub> = 3.4 Hz), 31.8 (t, CH from 1,3-butadiene, J<sub>CP</sub> = 5.8 Hz); <sup>31</sup>P NMR (162.0 MHz,  $d_8$ -THF, -40 °C)  $\delta$  90.7 (d, <sup>3</sup>J<sub>PP</sub> = 68.6 Hz), 83.8 (d, <sup>3</sup>J<sub>PP</sub> = 68.6 Hz) ppm; IR after evaporation of all volatiles ( $\nu$ , cm<sup>-1</sup>): 657 (m, P–C), 733 (m), 913 (s), 1067 (s), 1168 (s), 1364 (m), 1459 (s, C–H aliph.), 1601 (w), 1808 (w), 1967 (m), 2082 (s), 2235 (s), 2682 (m), 2862 (vs, C–H aliph.), 2971 (vs, C–H aliph.).

[(dcpe)Ni(1,3-butadiene)]<sup>17c</sup> (2c). <sup>31</sup>P NMR spectroscopic yield: 95%. <sup>1</sup>H NMR (600 MHz,  $d_8$ -THF):  $\delta$  1.27 (m, 44H, CH and CH<sub>2</sub> (Cy)), 1.51 (d, 4H, PCH<sub>2</sub>CH<sub>2</sub>P, J = 8.7 Hz), 1.66 (d, 4H, PCH<sub>2</sub>CH<sub>2</sub>P, J = 10.9 Hz), 2.78 (d, 1H, CH<sub>2</sub>, J<sub>HH</sub> = 12.6 Hz), 2.86 (d, 1H, CH<sub>2</sub>, J<sub>HH</sub> = 7.3 Hz), 4.71 (m, 1H, CH), 5.05 (d, 1H, CH<sub>2</sub>, J<sub>HH</sub> = 8.9 Hz), 5.17 (d, 1H, CH, J<sub>HH</sub> = 15.4 Hz), 6.32 (m, 1H, CH); <sup>13</sup>C NMR (151 MHz,  $d_8$ -THF)  $\delta$  19.9 (t, PCH<sub>2</sub>CH<sub>2</sub>P, J<sub>CP</sub> = 19.94 Hz), 24.6–27.5 (m, CH<sub>2</sub> from Cy), 30.2 (t, CH<sub>2</sub> from 1,3butadiene, J<sub>CP</sub> = 3.5 Hz), 33.2 (dd, CH from Cy, J<sub>CP</sub> = 4.2, 14.5 Hz), 76.7 (t, CH from 1,3-butadiene, J<sub>CP</sub> = 2.6 Hz); <sup>31</sup>P NMR (162.0 MHz, THF, -40 °C)  $\delta$  76.1 (d,  ${}^{3}J_{PP}$  = 54.8 Hz), 75.4 (d,  ${}^{3}J_{PP}$  = 54.8 Hz),  $\delta$  78.12 (d,  ${}^{3}J_{PP}$  = 51.2 Hz), 52.6 (d,  ${}^{3}J_{PP}$  = 51.2 Hz) ppm. IR after evaporation of all volatiles ( $\nu$ , cm<sup>-1</sup>): 657 (m, P–C), 912 (s), 1074 (s), 1180 (s), 1364 (m), 1458 (s, C–H aliph.), 1810 (w), 1967 (m), 2084 (w), 2235 (w), 2361 (w), 2681 (m), 2856 (vs, C–H aliph.), 2973 (vs, C–H aliph.).

[(dtbpe)Ni(Me-2,4-pentadienoate)] (1d). <sup>31</sup>P NMR spectroscopic vield: 94%. <sup>1</sup>H NMR (600 MHz,  $d_8$ -THF):  $\delta$  1.10 (m, 36H,  $C(CH_3)_3$ , 1.55 (m, 4H,  $PCH_2CH_2P$ ), 1.69 (m, 2H,  $CH_2$ ), 1.93 (m, 1H, CH), 3.32 (s, 3H, OCH<sub>3</sub>), 3.52 (m, 1H, CH), 4.84 (m, 1H, CH); <sup>13</sup>C NMR (151 MHz,  $d_8$ -THF)  $\delta$  21.5 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 26.8 (t,  $CH_3$ ,  $J_{CP}$  = 7.2 Hz), 27.6 (m,  $C(CH_3)_3$ ), 28.5 (dd, CH3,  $J_{CP}$  = 8.9, 13.6 Hz), 32.5 (m, CH<sub>3</sub>), 33.2 (m, CH<sub>3</sub>), 35.2 (m, CH<sub>2</sub> from Me-2,4-pentadienoate), 46.3 (s, OCH<sub>3</sub>), 48.1 (m, CH from Me-2,4-pentadienoate), CH from Me-2,4-pentadienoate could not be located. 169.5 (m, C=O);  ${}^{31}$ P NMR (81 MHz,  $d_8$ -THF)  $\delta$  93.4 (d,  ${}^{3}J_{PP} = 53.7$  Hz), 88.5 (d,  ${}^{3}J_{PP} = 57.4$  Hz) ppm; IR after evaporation of all volatiles ( $\nu$ , cm<sup>-1</sup>): 660 (m, P–C), 749 (m), 842 (m), 911 (s), 1069 (s), 1160 (m), 1268 (s, C-O), 1365 (m, -CH<sub>3</sub>), 1460 (s), 1583 (w), 1681 (m, -C=C-), 1723 (m, C=O), 1885 (w), 1970 (w), 2083 (s), 2235 (s), 2682 (w), 2863 (vs, C-H aliph.), 2976 (vs, C-H aliph.).

[(dcpe)Ni(Me-2,4-pentadienoate)] (2d). <sup>31</sup>P NMR spectroscopic yield: 97%. <sup>1</sup>H NMR (600 MHz,  $d_8$ -THF):  $\delta$  1.66 (m, 44H, CH<sub>2</sub> (Cy)), 1.61 (m, 4H, PCH<sub>2</sub>CH<sub>2</sub>P), 2.65 (m, 1H, CH), 3.00 (m, 2H, CH<sub>2</sub>), 3.33 (s, 3H, OCH<sub>3</sub>), 3.52 (m, 1H, CH), 4.58 (m, 1H, CH); <sup>13</sup>C NMR (151 MHz,  $d_8$ -THF)  $\delta$  13.3 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 24.2-27.9 (m, CH<sub>2</sub> from Cy), 32.2 (m, CH from Cy), 32.5 (m, CH from Cy), 33.3 (m, CH from Cy), 33.9 (m, CH from Cy), CH<sub>2</sub> from Me-2,4-pentadienoate overlapping with CH from Cy, 46.7 (s, OCH<sub>3</sub>), 48.6 (m, CH from Me-2,4-pentadienoate), 81.0 (br. s, CH from Me-2,4-pentadienoate), 94.5 (br. s, CH from Me-2,4pentadienoate), 168.2 (s, C=O); <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF)  $\delta$ 80.0 (d,  ${}^{3}J_{PP}$  = 29.2 Hz), 60.0 (d,  ${}^{3}J_{PP}$  = 31.0 Hz) ppm; IR after evaporation of all volatiles ( $\nu$ , cm<sup>-1</sup>): 655 (m, P–C), 747 (m), 842 (m), 911 (s), 1069 (s), 1163 (m), 1268 (m, C-O), 1364 (m), 1459 (s), 1667 (m, -C=C-), 1723 (m, C=O), 1968 (w), 2082 (s), 2235 (s), 2682 (m), 2859 (vs, C-H aliph.), 2974 (vs, C-H aliph.).

[(dtbpe)Ni(piperylene)] (1e). <sup>31</sup>P NMR spectroscopic yield: 95%. <sup>1</sup>H NMR (600 MHz,  $d_8$ -THF):  $\delta$  1.11 (m, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 1.31 (d, 3H, CH<sub>3</sub>, J<sub>HH</sub> = 8.3 Hz), 2.19 (m, 2H, CH<sub>2</sub>), 3.42 (m, 1H, CH), 4.66 (m, 1H, CH), 5.25 (m, 1H, CH); PCH<sub>2</sub>CH<sub>2</sub>P bridge could not be assigned due to overlapping with signals from the unreacted starting material; <sup>13</sup>C NMR (151 MHz,  $d_8$ -THF)  $\delta$  15.3 (s,  $CH_3$  from 1,3-pentadiene), 18.6 (t,  $PCH_2CH_2P$ ,  $J_{CP} = 21.2$  Hz), 19.8 (t,  $PCH_2CH_2P$ ,  $J_{CP} = 19.8$  Hz), 24.5-27.8 (m, C(CH<sub>3</sub>)<sub>3</sub>), 30.2 (t, CH from 1,3-pentadiene,  $J_{\rm CP}$  = 3.4 Hz), 32.1 (m, CH<sub>3</sub>), 32.7 (m, CH<sub>3</sub>), 33.4 (t, CH<sub>2</sub> from 1,3-pentadiene,  $J_{CP}$  = 7.4 Hz), 76.6 (t, CH from 1,3-pentadiene,  $J_{\rm CP}$  = 2.3 Hz); <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF)  $\delta$  98.8 (d, <sup>3</sup> $J_{\rm PP}$  = 53.7 Hz), 97.5 (d,  ${}^{3}J_{PP}$  = 53.1 Hz),  $\delta$  89.6 (d,  ${}^{3}J_{PP}$  = 71.7 Hz), 86.5 (d,  ${}^{3}J_{PP}$  = 71.6 Hz) ppm; IR after evaporation of all volatiles  $(\nu, \text{ cm}^{-1})$ : 655 (m, P–C), 747 (m), 909 (s), 1069 (s), 1177 (s), 1364 (m), 1459 (s, C-H aliph.), 1817 (w), 1967 (m), 2083 (s), 2235 (s), 2682 (m), 2860 (vs, C-H aliph.), 2975 (s, C-H aliph.).

[(dcpe)Ni(piperylene)] (2e). <sup>31</sup>P NMR spectroscopic yield: 5%. <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF)  $\delta$  63.6 (d, <sup>3</sup> $J_{PP}$  = 61.5 Hz), 57.2 (d, <sup>3</sup> $J_{PP}$  = 61.5 Hz) ppm.

[(dtbpe)Ni(cis-3-hexene)] (1f). A solution of NaBHEt<sub>3</sub> in THF (300 µL, 1 M, 0.3 mmol) was added at room temperature to a suspension of (dtbpe)NiCl<sub>2</sub> (44.8 mg, 0.1 mmol) and cis-3hexene (42.0  $\mu$ L, 0.5 mmol) in 0.6 mL of d<sub>8</sub>-THF. The color changed from red to brown and release of gas was observed. The mixture was stirred (the reaction vessel was open to an Ar line) at room temperature for 1 hour. <sup>31</sup>P NMR spectroscopic yield: 65%. <sup>1</sup>H NMR (600 MHz,  $d_8$ -THF):  $\delta$  1.08 (t, 3H, CH<sub>3</sub>,  $J_{\rm HH}$  = 7.3 Hz), 1.21 (m, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 1.49 (m, 2H, PCH<sub>2</sub>CH<sub>2</sub>P), 1.65 (m, 4H, CH<sub>2</sub>), 2.17 (m, 2H, PCH<sub>2</sub>CH<sub>2</sub>P), 2.68 (m, 2H, CH); <sup>13</sup>C NMR (151 MHz,  $d_8$ -THF)  $\delta$  15.3 (t, CH<sub>3</sub> from *cis*-3-hexene,  $J_{\rm CP}$  = 4.9 Hz), 20.8 (t, CH<sub>2</sub> from *cis*-3-hexene, overlapping with *C*H<sub>2</sub> of d*t*bpe), 20.9 (t, *PC*H<sub>2</sub>*C*H<sub>2</sub>P, *J*<sub>CP</sub> = 16.7 Hz), 27.3 (t, *C*H<sub>3</sub>,  $J_{\rm CP}$  = 3.6 Hz), 28.1 (m,  $C({\rm CH}_3)_3$ ), 31.9 (m,  $C{\rm H}_3$ ), 54.5 (t,  $C{\rm H}_3$ ) from *cis*-3-hexene,  $J_{CP}$  = 9.4 Hz); <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF)  $\delta$ 83.5 ppm, (s); IR after evaporation of all volatiles ( $\nu$ , cm<sup>-1</sup>): 662 (w, P-C), 748 (m), 841 (s), 910 (s), 1048 (s), 1100 (s), 1160 (s), 1385 (m), 1460 (m, C-H aliph.), 1596 (w), 1885 (w), 2083 (s), 2235 (s), 2794 (m, C-H aliph.), 2850 (s, C-H aliph.), 2892 (s, C-H aliph.), 2929 (s, C-H aliph.).

 $[(dcpe)Ni(cis-3-hexene)]^{16}$  (2f). A solution of Na selectride in THF (40 µL, 1 M, 0.04 mmol) was added at room temperature to a suspension of (dcpe)NiCl<sub>2</sub> (11.3 mg, 0.02 mmol) and *cis*-3-hexene (12.6 µL, 0.1 mmol) in 0.6 mL of d<sub>8</sub>-THF. NMR analysis after 15 min at RT showed full conversion of the starting materials and selective formation of the desired complex. <sup>31</sup>P NMR spectroscopic yield: 20%. <sup>31</sup>P NMR (81 MHz, *d*<sub>8</sub>-THF)  $\delta$  58.0 ppm (s).

All olefin complexes were used in the next step of reaction without being isolated and without further purification. Due to low conversion or instability, [(dcpe)Ni(1-hexene)], [(dcpe)Ni-(piperylene)] and [(dcpe)Ni(*cis*-3-hexene)] were identified only by <sup>31</sup>P NMR spectroscopy.

Formation of nickelalactones 3a–f and 4a–f in an highpressure (HP) NMR experiments.  $[Ni(COD)_2]$  (27.5 mg, 0.1 mmol), phosphorus ligand (0.1 mmol, 1 equiv., dcpe 42.2 mg, dtbpe 38.2 mg) and olefin (0.3 mmol, 3 equiv.) were dissolved in d<sub>8</sub>-THF (0.6 mL) and placed in a HP NMR tube. The mixture was heated for 24 h accordingly, to form the desired olefin complex. After the time had elapsed, the mixture was cooled down to room temperature and the NMR tube was consecutively pressurized with CO<sub>2</sub> (5 bar, 15 min equilibration time). The mixture was heated at 100 °C for an additional 24 h, except in the case of 1,3-butadiene where the reaction proceeds at RT. The reaction was studied by <sup>31</sup>P NMR spectroscopy.

[(dtbpe)Ni(OC(=O)C<sub>6</sub>H<sub>12</sub>)] (3a). <sup>31</sup>P NMR spectroscopic yield: 6%. <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF)  $\delta$  83.5 (d, <sup>3</sup>J<sub>PP</sub> = 9.1 Hz), 79.5 (d, <sup>3</sup>J<sub>PP</sub> = 8.7 Hz) ppm. [(dcpe)Ni(OC(=O)C\_4H\_6)] (4c): <sup>31</sup>P NMR spectroscopic yield: 100%. <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF)  $\delta$  77.1 (d, <sup>3</sup>J<sub>PP</sub> = 6.4 Hz), 71.4 (d, <sup>3</sup>J<sub>PP</sub> = 6.4 Hz) ppm. [(dcpe)Ni(OC(=O)C\_5H\_5OMe)] (4d): <sup>31</sup>P NMR spectroscopic yield: 4%. <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF)  $\delta$  78.2 (d, <sup>3</sup>J<sub>PP</sub> = 10.6 Hz), 71.5 (d,  ${}^{3}J_{PP} = 10.9 \text{ Hz}$ ) ppm. Due to very low conversion, the formed lactones [(d*t*bpe)Ni(OC(=O)C\_4H\_6)] and [(dcpe)Ni(OC(=O)C\_5H\_5OMe)] could not be isolated and further characterised. For [(dcpe)Ni(OC(=O)C\_4H\_6)] a dedicated synthesis was achieved.

 $[(dcpe)Ni(OC(=O)C_4H_6)]$  (4c).  $[Ni(COD)_2]$  (0.36 mmol, 100 mg) and dcpe (0.36 mmol, 153 mg) were suspended in THF (30 mL). A solution of 1,3-butadiene (1.08 mmol, 360 µL) was added in toluene (20 wt%). The mixture was added in an autoclave and stirred (300 rpm) at 100 °C for 24 h. When the time had elapsed, the mixture was cooled down to room temperature and pressurised with  $CO_2$  (20 bar, 15 min equilibration time) at 25 °C. The mixture was stirred (300 rpm) at RT for additional 20 h. When the time had elapsed, the pressure was released and the autoclave was opened under an inert argon atmosphere in the glove box. The solution which was concentrated and precipitated by addition of pentane (10 mL) yielded the compound as a fine red solid. Yield: 146 mg, 70%. <sup>1</sup>H NMR (400 MHz, d<sub>8</sub>-THF) δ 1.58 (m, 44H, CH and CH<sub>2</sub>, Cy), 2.70 (m, 2H, CH<sub>2</sub> next to carbonyl), 3.51 (m, 1H, CH), 4.55 (m, 2H,  $CH_2$ ), 4.84 (m, 1H, CH); <sup>13</sup>C NMR (151 MHz,  $d_8$ -THF)  $\delta$  20.7 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 21.8 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 25.4-29.4 (m, CH<sub>2</sub> from Cy), 33.6 (t, CH from Cy,  $J_{CP}$  = 11.5 Hz), 35.0 (dd, CH from Cy,  $J_{CP}$  = 4.4, 14.2 Hz), 37.8 (d, CH,  $J_{CP}$  = 3.4 Hz), 58.7 (d, CH,  $J_{CP}$  = 21.9 Hz), 60.0 (d, CH, J<sub>CP</sub> = 15.3 Hz), 70.3 (d, CH<sub>2</sub>, J<sub>CP</sub> = 17.7 Hz), 177.4 (d, *C*==O,  $J_{\rm CP}$  = 11.4 Hz); <sup>31</sup>P NMR (162.0 MHz,  $d_8$ -THF)  $\delta$ 77.1 (d,  ${}^{3}J_{PP} = 6.4$  Hz), 71.3 (d,  ${}^{3}J_{PP} = 6.4$  Hz) ppm; IR ( $\nu$ , cm<sup>-1</sup>): 658 (m, P-C), 910 (s), 1069 (s), 1181 (m), 1364 (m), 1459 (s, C-H aliph.), 1621 (m, C=O), 1804 (w), 1967 (m), 2364 (w), 2682 (m), 2861 (vs, C-H aliph.), 2977 (vs, C-H aliph.). Elemental analysis calcd C 64.56%, H 9.39; found C 65.10%, H 9.32%. Crystals suitable for X-ray analysis could be obtained from concentrated THF solution at RT. Orange crystals (polyhedron), dimensions  $0.13 \times 0.12 \times 0.10 \text{ mm}^3$ , crystal system orthorhombic, space group Pnma, Z = 8, a = 31.6368(16) Å, b =21.6435(12) Å, c = 9.1291(4) Å, V = 6251.0(5) Å<sup>3</sup>,  $\rho = 1.231$  g cm<sup>-3</sup>, T = 200(2) K,  $\theta_{\text{max}} = 24.984^{\circ}$ , radiation Mo K $\alpha$ ,  $\lambda =$ 0.71073 Å, 0.5°  $\omega$ -scans with a CCD area detector, covering the asymmetric unit in reciprocal space; reflections: 40 500 measured, 4469 unique ( $R_{int} = 0.0843$ ), 2880 observed  $(I > 2\sigma(I)); \mu = 0.73 \text{ mm}^{-1}, \min/\max \text{ transmission: } 0.88/0.94,$ 409 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit: 1.08 for observed reflections, final residual values  $R_1(F) = 0.076$ ,  $wR(F^2) = 0.173$ for observed reflections, residual electron density -0.56 to  $0.53 \text{ e} \text{ Å}^{-3}$ .

Stoichiometric reactions between [Ni(COD)]/ligand with  $\alpha$ ,β-unsaturated carboxylic acids. [Ni(COD)<sub>2</sub>] (27.5 mg, 0.1 mmol), ligand (0.1 mmol, 1 equiv., dcpe 42.2 mg, dtbpe 38.2 mg), 2-heptenoic acid (12.8 mg, 0.1 mmol)/cinnamic acid (14.8 mg, 0.1 mmol)/2,4-pentadienoic acid (24.9 mg, 0.3 mmol) were dissolved in d<sub>8</sub>-THF (0.6 mL) in a NMR tube. The mixtures was analysed by <sup>31</sup>P NMR spectroscopy after given times and at given temperatures. The reactions with *trans*-cinnamic acid and 2-heptenoic acid are very slow and the conversions to lactones and acid-π-complexes are very low in

comparison to the unreacted [(dcpe)Ni(COD)] complex For these reasons, it was extremely difficult to separate the mixtures, and the compounds were identified only by <sup>31</sup>P NMR spectroscopy. Due to low solubility, it was possible to isolate the [(dcpe)Ni(*trans*-cinnamic acid)] (**5b**) complex from the reaction mixture and have it fully characterised. [(dcpe)Ni((C<sub>4</sub>H<sub>9</sub>)-C-CC(=O)O)] (**4a**): <sup>31</sup>P NMR (81 MHz, *d*<sub>8</sub>-THF)  $\delta$  69.6 (d, <sup>3</sup>*J*<sub>PP</sub> = 8.0 Hz), 63.3 (d, <sup>3</sup>*J*<sub>PP</sub> = 8.4 Hz) ppm.

[(dcpe)Ni(2-heptenoic acid)] (5a). <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF)  $\delta$  64.3 (d, <sup>3</sup> $J_{PP}$  = 55.5 Hz), 59.0 (d, <sup>3</sup> $J_{PP}$  = 56.1 Hz) ppm.

[(dcpe)Ni(PhC-CC(=0)O)] (4b). <sup>31</sup>P NMR (81 MHz, THF)  $\delta$ 69.7 (d,  ${}^{3}J_{PP}$  = 2.6 Hz), 61.9 (d,  ${}^{3}J_{PP}$  = 2.7 Hz) ppm; [(dcpe)Ni-(*trans*-cinnamic acid)] (5b): <sup>1</sup>H NMR (600 MHz,  $d_8$ -THF)  $\delta$  1.37 (m, 44H, CH and CH<sub>2</sub> (Cy)), 3.39 (m, 1H, CH), 4.05 (m, 1H, CH), 6.80 (m, 1H, CH), 6.95 (m, 2H, CH), 7.02 (m, 2H, CH), 9.30 (s, 1H, COOH); <sup>13</sup>C NMR (151 MHz,  $d_8$ -THF)  $\delta$  19.1 (dd, PCH<sub>2</sub>CH<sub>2</sub>P, *J*<sub>CP</sub> = 20.1 Hz), 19.7 (dd, PCH<sub>2</sub>CH<sub>2</sub>P, *J*<sub>CP</sub> = 20.7 Hz), 23.5–28.6 (m,  $CH_2$  from Cy), 31.3 (dd, CH from Cy,  $J_{CP}$  = 4.8, 16.0 Hz), 31.6 (dd, CH from Cy,  $J_{CP}$  = 4.7, 15.1 Hz), 33.0 (dd, CH from Cy,  $J_{CP}$  = 1.8, 17.9 Hz), 33.7 (dd, CH from Cy,  $J_{CP}$  = 1.9, 17.9 Hz), 39.5 (d, CH, J<sub>CP</sub> = 15.1 Hz), 47.8 (d, CH, J<sub>CP</sub> = 20.7 Hz), 119.3 (s, CH<sup>Ph</sup>), 122.6 (d, CH<sup>Ph</sup>, J<sub>CP</sub> = 1.9 Hz), 125.7 (s,  $CH^{Ph}$ ), 145.8 (d, *ipso-C*<sup>Ph</sup>,  $J_{CP} = 5.7$  Hz), 172.5 (d,  $C(=O)OH, J_{CP} = 3.6); {}^{31}P$  NMR (81 MHz,  $d_8$ -THF)  $\delta$  65.5 (d,  ${}^{3}J_{PP} = 50.5$  Hz), 62.6 (d,  ${}^{3}J_{PP} = 50.3$  Hz) ppm; IR after evaporation of all volatiles ( $\nu$ , cm<sup>-1</sup>): 657 (m, P–C), 910 (s), 1068 (s), 1180 (s), 1364 (m), 1459 (s, C-H aliph.), 1802 (w), 1967 (m), 2363 (w), 2682 (m), 2862 (vs, C-H aliph.), 2977 (vs, C-H aliph.). Elemental analysis of the crystals isolated from the NMR experiment calcd C 66.78%, H 8.97%; found C 66.95%, H 8.87%. Single crystals suitable for X-ray analysis were isolated from the NMR experiment. Yellow crystals (needle), dimensions  $0.14 \times 0.08 \times 0.06 \text{ mm}^3$ , crystal system monoclinic, space group  $P2_1/c$ , Z = 4, a = 16.78(3) Å, b = 8.692(16) Å, c = 27.13(5) Å,  $\beta = 103.38(3)^{\circ}$ , V = 3850(13) Å<sup>3</sup>,  $\rho =$ 1.210 g cm<sup>-3</sup>, T = 200(2) K,  $\theta_{max} = 22.463^{\circ}$ , radiation Mo Ka,  $\lambda = 0.71073$  Å,  $0.5^{\circ}$   $\omega$ -scans with a CCD area detector, cover the asymmetric unit in reciprocal space; reflections: 18748 measured, 5010 unique ( $R_{int} = 0.1386$ ), 2827 observed  $(I > 2\sigma(I)); \mu = 0.62 \text{ mm}^{-1}, \text{ min/max transmission } 0.86/0.98;$ 410 parameters refined, hydrogen atoms were treated using appropriate riding models, except for H1 of the carboxy group, which was refined isotropically, goodness of fit of 1.02 for observed reflections, final residual values of  $R_1(F) = 0.066$ ,  $wR(F^2) = 0.127$  for observed reflections, and residual electron density -0.31 to 0.62 e Å<sup>-3</sup>. [(dcpe)Ni(OC(=O)C\_4H\_6)] (4c):  $^{31}$ P NMR (81 MHz,  $d_8$ -THF)  $\delta$  77.1 (d,  $^{3}J_{\rm PP}$  = 6.4 Hz), 71.4 (d,  ${}^{3}J_{PP}$  = 6.4 Hz) ppm. Full characterisation of this compound has been described in the previous section.

[(*dtbpe*)Ni(OC(=O)C<sub>4</sub>H<sub>6</sub>)] (3c). <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF)  $\delta$  98.1 (d, <sup>3</sup>J<sub>PP</sub> = 10.1 Hz), 91.2 (d, <sup>3</sup>J<sub>PP</sub> = 10.1 Hz),  $\delta$  93.0 (d, <sup>3</sup>J<sub>PP</sub> = 8.6 Hz), 88.4 (d, <sup>3</sup>J<sub>PP</sub> = 8.6 Hz) ppm.

The same reactions were also performed under a  $CO_2$  atmosphere (3 bar) in a pressure NMR-tube. Under these conditions, the formation of the nickelalactone is inhibited. The acid- $\pi$ -complexes were observed and decarboxylation occurred

at 80 °C for the *trans*-cinnamic acid complex whereas the 2-heptenoic acid complex did not decompose.

Stoichiometric reactions between [Ni(COD)]/ligand with 2,4-pentadienoic acid and a subsequent reaction with a base. [Ni(COD)<sub>2</sub>] (27.5 mg, 0.1 mmol), ligand (0.1 mmol, 1 equiv., dcpe 42.2 mg, dtbpe 38.2 mg), 2,4-pentadienoic acid (24.9 mg, 0.3 mmol) were dissolved in d8-THF (2 mL) in a pressure NMR tube and reacted at RT for 2 hours to give [(dtbpe)Ni(OC(=O)- $C_4H_6$ ] (3c), [(dcpe)Ni(OC(=O)C\_4H\_6)] (4c) respectively as described in the previous section. 1 equivalent of base (Na-2fluorophenoxide (0.1 mmol, 13.4 mg)/NaOtBu (0.1 mmol, 9.8 mg)) and 1 equivalent of 1,3-butadiene (16 wt% solution in toluene, 30 µL) were added and the reaction mixtures were analysed by <sup>31</sup>P NMR.  $[(dtbpe)Ni(OC(=O)C_4H_6)]$  (3c) gives no reaction with sodium 2-fluorophenoxide/NaOtBu and 1,3-butadiene and only signals for 3c could be observed in the <sup>31</sup>P NMR spectra. [(dcpe)Ni(OC(=O)C<sub>4</sub>H<sub>6</sub>)] (4c): The reaction of 4c with sodium 2-fluorophenoxide/1,3-butadiene results in decomposition. The reaction of 4c with NaOtBu/1,3-butadiene gives a broad signal that corresponds to [(dcpe)Ni(1,3butadiene)]<sup>17c</sup> (2c): <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF, 25 °C)  $\delta$ 70.0 ppm, br s.

[(dcpe)Ni(OC<sub>6</sub>H<sub>4</sub>F)<sub>2</sub>]. [(dcpe)NiCl<sub>2</sub>] (55.2 mg, 0.1 mmol) and sodium-2-fluorophenoxide (27 mg, 0.2 mmol) were suspended in THF (1 mL). The orange suspension turned red within 15 min and was stirred for an additional hour. The formed NaCl was filtered off and the bright red solution was dried under vacuum yielding the phenoxide complex as a fine red powder. <sup>1</sup>H NMR (300 MHz,  $d_8$ -THF)  $\delta$  1.64 (m, 44H, CH and CH<sub>2</sub> (Cy)), 5.92 (m, 1H, CH), 6.39 (m, 2H, CH), 6.96 (m, 1H, CH); <sup>13</sup>C NMR (151 MHz,  $d_8$ -THF)  $\delta$  18.6 (t, PCH<sub>2</sub>CH<sub>2</sub>P,  $J_{CP}$  = 19.5 Hz), 24.1 (s, CH<sub>2</sub> from Cy), 25.1 (m, CH<sub>2</sub> from Cy), 26.4 (s, CH<sub>2</sub> from Cy), 27.1 (s, CH<sub>2</sub> from Cy), 31.9 (t, CH from Cy,  $J_{CP}$  = 11.2 Hz), 109.6 (d,  $CH^{Ph} J_{CP}$  = 6.5 Hz), 111.6 (d,  $CH^{Ph}$ ,  $J_{CP}$  = 19.7 Hz), 120.8 (dd,  $CH^{Ph}$ ,  $J_{CP}$  = 2.8, 39.4), 152.6 (d,  $CH^{Ph}$ ,  $J_{CP}$  = 11.2 Hz), 153.0 (s, C<sup>Ph</sup>-O), 155.4 (C<sup>Ph</sup>-F); <sup>31</sup>P NMR (162.0 MHz,  $d_8$ -THF)  $\delta$  69.6 ppm (s); <sup>19</sup>F (282 MHz,  $d_8$ -THF)  $\delta$  –138.6 ppm (s); IR ( $\nu$ , cm<sup>-1</sup>): 657 (m, P–C), 910 (s), 1069 (s), 1181 (m), 1364 (m), 1459 (s, C-H aliph.), 1597 (w, C-C arom.), 1800 (w), 1967 (m), 2364 (w), 2682 (m), 2861 (vs, C-H aliph.), 2976 (vs, C-H aliph.). Elemental analysis calcd C 64.88%, H 8.02%; found C 64.84%, H 8.10%.

Reduction reactions with Zn. [(dcpe)Ni(OC<sub>6</sub>H<sub>4</sub>F)<sub>2</sub>] (10 mg, 0.014 mmol), Zn powder (9 mg, 0.14 mmol) and styrene (16 µL, 0.14 mmol) were suspended in  $d_8$ -THF (1 mL) and heated at 100 °C. After 20 h, the mixture was filtered to remove the excess of Zn and characterised by <sup>31</sup>P NMR spectroscopy. The product was identified as a [(dcpe)Ni(styrene)] complex. <sup>31</sup>P NMR (81 MHz,  $d_8$ -THF)  $\delta$  68.7 (d, <sup>3</sup>J<sub>PP</sub> = 64.4 Hz), 56.2 (d, <sup>3</sup>J<sub>PP</sub> = 64.4 Hz) ppm. The conversion was 65%.

 $[(dtbpe)Ni(O_2CO)]^{23}$  [Ni(COD)<sub>2</sub>] (120 mg, 0.43 mmol) and dtbpe (137 mg, 0.43 mmol) were suspended in DMF (10 mL). The mixture was placed in an autoclave under an inert atmosphere in the glovebox. Outside the glovebox, the autoclave was pressurised with ethylene (5 bar, 15 min equilibration time) and CO<sub>2</sub> (35 bar, 15 min equilibration time) at 25 °C. The

mixture was stirred (300 rpm) and heated at 65 °C for 2 h. After the time had elapsed, the mixture was cooled down to room temperature and the pressure was released. The autoclave was carefully opened under an argon flow and degassed water (5 mL) was added to the mixture. The autoclave was closed under an argon atmosphere and pressurised again with ethylene (5 bar, 15 min equilibration time) and CO<sub>2</sub> (35 bar, 15 min equilibration time) at 25 °C. The mixture was stirred (300 rpm) and heated at 100 °C for 18 h. After the time had elapsed, the mixture was cooled down to room temperature and the pressure was released. The autoclave was carefully opened in the glove box and the mixture was transferred in a Schlenk flask. All solvents were evaporated and the orangebrown oily residue was washed with pentane  $(3 \times 10 \text{ mL})$  yielding the carbonate complex as an orange fine powder. Yield: 130 mg, 74%. <sup>1</sup>H NMR (600 MHz,  $d_8$ -THF)  $\delta$  1.36 (m, 36H,  $C(CH_3)_3$ , 1.62 (m, 4H, PCH<sub>2</sub>CH<sub>2</sub>P); <sup>13</sup>C NMR (151 MHz,  $d_8$ -THF)  $\delta$  19.7 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 20.6 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 27.3 (t, CH<sub>3</sub>,  $J_{CP}$  = 7.3 Hz), 27.6 (m,  $C(CH_3)_3$ ), 29.1 (dd,  $CH_3$ ,  $J_{CP}$  = 9.5, 14.1 Hz), 33.4 (dd, CH<sub>3</sub>, J<sub>CP</sub> = 6.8, 9.3 Hz), 34.0 (dd, CH<sub>3</sub>, J<sub>CP</sub> = 8.5, 15.5 Hz), 162.5 (d, C=O,  $J_{CP}$  = 4.1 Hz); <sup>31</sup>P NMR (243.0 MHz,  $d_8$ -THF)  $\delta$  90.3 ppm (s). IR ( $\nu$ , cm<sup>-1</sup>): 658 (m, P–C), 912 (s), 1068 (s), 1181 (m), 1364 (m), 1459 (s, C-H aliph.), 1563 (w), 1627 (w), 1636 (m, C=O), 1967 (m), 2682 (m), 2870 (vs, C-H aliph.), 2970 (vs, C-H aliph.). Crystals suitable for X-ray analysis could be obtained from concentrated THF solution at RT. Yellow crystals (plate), dimensions  $0.17 \times 0.07 \times 0.04 \text{ mm}^3$ , crystal system monoclinic, space group  $P2_1/c$ , Z = 4, a = 9.9880(9) Å, b = 14.3032(12) Å, c = 16.3855(13) Å,  $\beta = 106.4993(14)^{\circ}$ , V =2244.4(3) Å<sup>3</sup>,  $\rho = 1.294$  g cm<sup>-3</sup>, T = 200(2) K,  $\theta_{\text{max}} = 29.612^{\circ}$ , radiation Mo K $\alpha$ ,  $\lambda = 0.71073$  Å,  $0.5^{\circ} \omega$ -scans with a CCD area detector, covering the asymmetric unit in reciprocal space; reflections: 19 179 measured, 6295 unique (R<sub>int</sub> = 0.0581), 4243 observed  $(I > 2\sigma(I)); \mu = 1.02 \text{ mm}^{-1}, \text{min/max transmission:}$ 0.86/0.96, 238 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit: 1.04 for observed reflections, final residual values  $R_1(F) = 0.050$ ,  $wR(F^2) = 0.098$  for observed reflections, residual electron density -0.38 to  $0.53 \text{ e} \text{ Å}^{-3}$ .

General procedure for catalytic synthesis of acrylate derivatives. Ni precursor (0.1 mmol, [Ni(COD)<sub>2</sub>] 27.5 mg, [(dcpe)Ni-(OC<sub>6</sub>H<sub>4</sub>F)<sub>2</sub>] 70.3 mg, [(dtbpe)Ni(O<sub>2</sub>CO)] 43.7 mg) ligand (0.1 mmol, 1 equiv., dcpe 42.2 mg, dtbpe 38.2 mg), sodium 2-fluorophenolate (30.0 mmol, 300 equiv.), Zn (10.0 mmol, 100 equiv.) and alkene (30.0 mmol, 300 equiv.) were introduced into the autoclave together with 30 mL of THF under an argon atmosphere in the glove box. Outside the glovebox, the autoclave was pressured with  $CO_2$  (20 bar, 15 min equilibration time) at 25 °C. The reaction mixture was therefore stirred (300 rpm) at 100 °C for 20 h. When the time had elapsed, the autoclave was cooled down to room temperature and pressure was released. It was opened and the reaction crude was transferred to a 100 mL glass bottle. D<sub>2</sub>O (15 mL) was used to wash the autoclave and added to the reaction mixture. 3-(Trimethylsilyl)propionic-2,2,3,3-d<sub>4</sub> acid sodium salt (0.125 mmol) was dissolved in  $D_2O$  (5 mL) and added to the

reaction mixture as an internal standard. The vial was washed with additional  $D_2O$  (5 mL). Then, the reaction mixture was layered with Et<sub>2</sub>O (40 mL) and the aqueous phase (2 mL) was centrifuged to improve the phase separation. The corresponding sodium salt was then quantified by <sup>1</sup>H-NMR (200 MHz, 70 scans) and the turnover number (TON) was calculated accordingly.

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#### Notes and references

- Selected reviews containing transformations of olefins with CO<sub>2</sub>: (a) B. Yu, Z. F. Diao, C. X. Guo and L. N. He, J. CO<sub>2</sub> Util., 2013, 1, 60; (b) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kühn, Angew. Chem., Int. Ed., 2011, 50, 8510; (c) P. Braunstein, D. Matt and D. Nobel, Chem. Rev., 1988, 88, 747; (d) Y. Tsuji and T. Fujihara, Chem. Commun., 2012, 48, 9956.
- 2 Acrylate formation of metal complexes: (a) R. Alvarez, E. Carmona, D. J. Cole-Hamilton, A. Galindo, E. Gutierrez-Puebla, A. Monge, M. L. Poveda and C. Ruiz, J. Am. Chem. Soc., 1985, 107, 5529; (b) A. Galindo, A. Pastor, P. Pérez and E. Carmona, Organometallics, 1993, 12, 4443; (c) R. Fischer, J. Langer, A. Malassa, D. Walther, H. Görls and G. Vaughan, Chem. Commun., 2006, 2510; (d) D. Jin, P. G. Williard, N. Hazari and W. H. Bernskoetter, Chem. Eur. J., 2014, 20, 3205.
- 3 A. Hoberg, A. Ballesteros, A. Signan, C. Jegat and A. Milchereit, *Synthesis*, 1991, 395.
- 4 H. Hoberg, Y. Peres and A. Milchereit, *J. Organomet. Chem.*, 1986, **307**, C38.
- 5 (a) H. Hoberg, D. Schaefer and B. W. Oster, *J. Organomet. Chem.*, 1984, 266, 313; (b) H. Hoberg and S. Schaefer, *J. Organomet. Chem.*, 1983, 255, C15.
- 6 (a) S. Y. T. Lee, M. Cokoja, M. Drees, Y. Li, J. Mink,
  W. A. Herrmann and F. E. Kühn, *ChemSusChem*, 2011, 4, 1275; (b) C. Bruckmeier, M. W. Lehenmeier, R. Reichardt,
  S. Vagin and B. Rieger, *Organometallics*, 2010, 29, 2199.
- 7 (a) H. Hoberg and D. Schaefer, J. Organomet. Chem., 1982,
  236, C28; (b) H. Hoberg, K. Jenni, C. Krüger and E. Raabe,
  Angew. Chem., Int. Ed. Engl., 1986, 98, 819; (c) H. Hoberg
  and K. Jenni, J. Organomet. Chem., 1987, 322, 193;
  (d) H. Hoberg and D. Schaefer, J. Organomet. Chem., 1983,
  251, C51; (e) A. Behr and U. Kanne, J. Organomet. Chem.,
  1986, 317, C41; (f) M. Takimoto and M. Mori, J. Am. Chem.
  Soc., 2001, 123, 2895.
- 8 H. Hoberg, A. Ballesteros and A. Signan, J. Organomet. Chem., 1991, 403, C19.
- 9 (a) H. Hoberg, Y. Peres, A. Milchereit and S. Gross, J. Organomet. Chem., 1988, 345, C17; (b) H. Hoberg, Y. Peres,

C. Krüger and Y. H. Tsay, *Angew. Chem., Int. Ed. Engl.*, 1987, **99**, 799; (c) H. Hoberg and D. Bärhausen, *J. Organomet. Chem.*, 1989, **379**, C7; (d) H. Hoberg, Y. Peres and A. Milchereit, *J. Organomet. Chem.*, 1986, **307**, C41.

- 10 H. Hoberg, S. Groß and A. Milchreit, *Angew. Chem.*, 1987, 99, 567.
- 11 C. M. Willimas, J. B. Johnson and T. Rovis, *J. Am. Chem. Soc.*, 2008, **130**, 14936.
- 12 T. Moragas, J. Cornella and R. Martin, J. Am. Chem. Soc., 2014, 136, 17702.
- M. L. Lejkowski, R. Lindner, T. Kageyama, G. É. Bódizs, P. N. Plessow, I. B. Müller, A. Schäfer, F. Rominger, P. Hofmann, C. Futter, S. A. Schunk and M. Limbach, *Chem. – Eur. J.*, 2012, **18**, 14017.
- 14 C. Hendriksen, E. A. Pidko, G. Yang, B. Schäffner and D. Vogt, *Chem. – Eur. J.*, 2014, 20, 12037.
- 15 N. Huguet, I. Jevtovikj, A. Gordillo, M. L. Lejkowski, R. Linder, M. Bru, A. Y. Khalimon, F. Rominger, S. A. Schunk, P. Hofmann and M. Limbach, *Chem. – Eur. J.*, 2014, 20, 1.
- 16 H. Hoberg, D. Schaefer, G. Burkhart, C. Krüger and M. J. Romao, J. Organomet. Chem., 1984, 266, 203.

- (a) A. Döhring, R. Goddard, G. Hopp, P. W. Jolly, N. Kokel and C. Krüger, *Inorg. Chim. Acta*, 1994, 222, 179;
  (b) R. Benn, P. W. Jolly, T. Joswig, R. Mynott and K.-P. Schick, *Z. Naturforsch., B: Chem. Sci.*, 1986, 41, 680;
  (c) R. Benn, P. Betz, R. Goddard, P. W. Jolly, N. Kokel, C. Krüger and I. Topalović, *Z. Naturforsch., B: Chem. Sci.*, 1991, 46, 1395.
- 18 P. S. Schulz, O. Walter and E. Dinjus, Appl. Organomet. Chem., 2005, 19, 1176.
- T. Yamamoto, K. Sano, K. Osakada, S. Komiya, A. Yamamoto, Y. Kushi and T. Tada, *Organometallics*, 1990, 9, 2396.
- 20 I. Bach, R. Goddard, C. Kopiske, K. Seevogel and K.-R. Pörschke, *Organometallics*, 1999, **18**, 10.
- 21 Software package SHELXTL 2008/4 for structure solution and refinement, see: G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.
- 22 Program SADABS 2008/1 for absorption correction, see: G. M. Sheldrick, *Bruker Analytical X-ray Division*, Madison, Wisconsin, 2008.
- 23 L. Gonzáles-Sebastián, M. Flores-Alamo and J. J. García, *Organometallics*, 2012, **31**, 8200.