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Nickelacyclic carboxylates derived from 3-hexyne and CO₂ and their application in the synthesis of a new muconic acid derivative

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ABSTRACT

The mononuclear unsaturated nickelalactones [Ni{C(Et)=C(Et)-COO}(DBU)₂] (1) and [Ni{C(Et)=C(Et)-COO}(dcpe)] (2) were synthesized by oxidative coupling of CO₂ and 3-hexyne at zero-valent nickel in presence of DBU or dpce, respectively. Attempts to use Cy₃P or dppe as ligands in this reaction gave the zero-valent complex [Ni(cy₃P)₂(η^2 -3-hexyne)] (3) and the well known [Ni(dppe)₂] instead. However, the dppe stabilized unsaturated nickelalactone [Ni{C(Et)=C(Et)-COO}(dppe)] (4) was synthesized from the corresponding 2,2'-bipyridine complex by ligand displacement with dppe. Complex 1 is a useful synthon for the synthesis of carboxylic acid derivatives, as shown by its reaction with NBS leading to 3-bromo-2-ethyl-pent-2-enoic acid in good yield. On the contrary, the reaction between [Ni{C(Et)=C(Et)-COO}(bipy)] and NBS gave the hitherto unknown 2-(2,3,4-triethyl-5-oxo-2,5-dihydrofuran-2-yl)butyric acid (5) as major product. Compounds 1–5 were structurally investigated by NMR and IR spectroscopy and in the solid state by X-ray diffraction analysis of single crystals.

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1. Introduction

The use of non-toxic carbon dioxide as building block in organic synthesis is highly attractive due to its low cost and abundance. In this context, efficient, atom economic catalytic transformations involving C–C bond formation between CO_2 and organic substrates are of particular interest. A reaction that fulfills all those criteria is the well-known nickel catalyzed co-oligomerisation of CO_2 and alkynes leading to 2*H*-pyran-2-one derivatives (see Scheme 1). This transformation, which was initially reported by Inoue and coworkers over 30 years ago [1,2], was later on optimized by Walther and Dinjus [3], who used monodentate phosphane ligands to achieve high selectivity towards pyranone formation, and Tsuda and coworkers who extended the substrate scope [4] and used this reaction e.g. in polymer synthesis [5].

A recent development is the use of *N*-heterocyclic carbenes as ligands for nickel catalysts, which allow much milder reaction conditions ($60 \degree$ C, 1 atm CO₂) [6–8].

The initial step of this catalysis is supposed to be the oxidative coupling of an alkyne and CO_2 at the zero-valent nickel center leading to unsaturated nickelalactones. The first derivative of this type, namely [Ni{C(Me)=C(Me)-COO}(tmeda)] was reported by Burkhart and Hoberg in 1982 [9]. These compounds are not only proposed intermediates in the catalysis mentioned above, but also in the nickel-catalyzed arylative and alkylative carboxylation of alkynes [10–12]. Additionally, they are also interesting synthons for the stoichiometric synthesis of carboxylic acids or their derivatives [13– 15]. In light of their importance it is surprising that only a few derivatives have been isolated and studied thoroughly yet [3,14,16–19].

While complexes with a variety of different ligands, ranging from phosphanes [20–23], *N*-heterocyclic carbenes (NHC's) [24], amines [16,25], amidines [26,27], imine [21] and pyridine derivatives [16,19,21,22,25] to even inorganic ligands [28] were isolated and structurally studied in case of their saturated analogues, only four derivatives of the unsaturated type have been characterized by X-ray diffraction experiments yet. Three of them contain nitrogen donor ligands [14,17,19], the fourth was stabilized by an NHC ligand. Interestingly, this NHC stabilized derivative was found to be a dinuclear complex [24].

However, little is known about such nickelacyclic carboxylates with other ligand classes. Since DBU (1,8-diazabicyclo[5.4.0] undec-7-ene) was successfully applied as ligand in the nickel catalyzed arylative and alkylative carboxylation of alkynes [10–12] and phosphanes are known to be suitable ligands for co-oligomerisation of alkynes and CO_2 by nickel [1–4], we investigated the coordination behavior of these ligands towards unsaturated nickelacyclic carboxylates.

2. Experimental

2.1. General procedures

¹H NMR and ¹³C NMR spectra were recorded at ambient temperature with a Bruker AC 200 or AC 400 MHz spectrometer. All



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Scheme 1. Proposed mechanism of the nickel catalyzed co-oligomerisation of alkynes and CO_2 .

spectra were referenced to TMS or the deuterated solvent as an internal standard. In the ¹H NMR spectra of compounds **1–3**, ill defined overlapping signals over a large range were observed due to the high number of only slightly different CH_2 groups. ¹H NMR data of these compounds is rather uninformative and therefore not given.

FAB-mass spectra were obtained using a Finnigan MAT SSQ 710 system (2,4-dimethoxybenzylalcohol as matrix), IR measurements were performed on a Perkin–Elmer System 2000 FT-IR. All manipulations were carried out by using Schlenk techniques under an atmosphere of argon. Prior to use, tetrahydrofuran and diethyl ether were dried over potassium hydroxide and distilled over Na/benzophenone. The starting complexes [Ni(cod)₂] and [(Ni{C(Et)=C(Et)-COO}(bipy)] were prepared according to known methods [3,29].

2.2. Synthesis of $[Ni{C(Et)=C(Et)-COO}(DBU)_2]$ (1)

DBU (490 mg, 3.22 mmol) was added to $[Ni(cod)_2]$ (435 mg, 1.58 mmol) in THF (15 mL). Then 3-hexyne (148 mg, 1.80 mmol) was added to the mixture via syringe resulting in a color change of from yellow to red. Afterwards the formed solution was saturated with CO_2 at -10 °C and stirred for 2 h at room temperature. Storage of the reaction mixture at -40 °C over night resulted in precipitation of yellow needles (the solution tends to oversaturate and in some cases it was necessary to shake the cooled solution to initiate crystallization). The precipitate was collected on a cooled Schlenk frit, washed with precooled diethyl ether (15 mL) and dried in a vacuum. Yield: 495 mg (64%) yellow 1. Anal. Calc. for C₂₅H₄₂N₄O₂Ni (489.33 g/mol): C, 61.36; H, 8.65; N, 11.45. Found: C, 61.12; H, 8.28; N, 11.31%. ${}^{13}C{}^{1}H$ NMR (100 MHz, d₈-THF): δ 14.4 (2x CH₃), 15.0 (2x CH₃), 20.8 (2x CH₂-CH₃), 22.7 (2x CH₂ DBU), 23.9 (2x CH₂ DBU*), 24.9 (2x CH₂ DBU), 26.3 (2x CH₂-CH₃), 27.2 (2x CH₂ DBU*), 28.5 (2x CH₂ DBU), 29.6 (2x CH₂ DBU*), 30.4 (2x CH2 DBU), 30.7 (2x CH2 DBU*), 37.9 (2x CH2 DBU*), 41.15 (CH₂ DBU), 41.2 (CH₂ DBU), 45.2 (2x CH₂ DBU*), 47.5 (2x CH₂ DBU), 48.2 (2x CH₂ DBU), 49.0 (2x CH₂ DBU*), 53.2 (2x CH₂ DBU*), 54.26 (CH₂ DBU), 54.28 (CH₂ DBU), 135.3 (=C), 135.4 (=C), 158.4 (C=), 158.6 (C=), 159.8 (2x C=N DBU*), 164.5 (C=N), 164.7 (C=N), 175.95 (COO), 175.99 (COO) (Signals of not coordinated DBU are marked with an asterisk). IR (nujol, cm⁻¹): 1604vs (C=O). Suitable crystals of **1** for X-ray diffraction experiments were obtained by recrystallization in THF (room temperature to -20 °C). Recrystallization from toluene affords crystals of **1** 0.5toluene.

2.3. Synthesis of [Ni{C(Et)=C(Et)-COO}(dcpe)] (2)

Dcpe (753 mg, 1.78 mmol) was added to a stirred solution of [Ni(cod)₂] (466 mg, 1.69 mmol) in THF (15 mL). The reaction mixture was cooled to -20 °C and 3-hexyne (280 mg, 3.41 mmol was added to the pale yellow suspension obtained. Afterwards, the mixture was saturated with CO₂ at this temperature. Then it was allowed to slowly warm up to room temperature and stirred for 20 h. The resulting red solution was evaporated to drvness and the remaining oil was taken up in diethyl ether (40 mL) with rapid stirring, resulting in precipitation of the yellow product. The precipitate was collected by filtration, washed with diethyl ether (10 mL) and dried in a vacuum. Yield: 540 mg (0.88 mmol, 52%). Suitable crystals of 2.2THF for X-ray diffraction experiments were obtained by recrystallization in THF (room temperature to 4 °C). Recrystallization from a two to one mixture of toluene and THF (room temperature to 4 °C) affords crystals of **2** toluene. Anal. Calc. for C₃₃H₅₈NiO₂P₂·toluene (699.61 g/mol): C, 68.67; H, 9.51. Found: C, 68.38; H, 9.42%. ¹³C{¹H} NMR (150 MHz, d₈-THF): δ 15.4 (s, CH₃), 15.5 (s, CH₃), 17.5 (dd, J_{PC} = 21.2 Hz, J_{PC} = 9.7 Hz, P–CH₂), 22.8 (br, CH₂-CH₃), 23.2 (dd, J_{PC} = 27.8 Hz, J_{PC} = 21.8 Hz, P-CH₂), 27.0 (s, 2x CH₂), 27.1 (s, 2x CH₂), 27.95-28.25 (m, 6x CH₂), 28.5 (d, J_{PC} = 14.0 Hz, 2x CH₂), 29.7 (s, 2x CH₂), 30.20 (s, 2x CH₂), 30.21 (d, J_{PC} = 9.3 Hz, 2x CH₂), 32.2 (pseudo-t, J_{PC} = 6.5 Hz, CH₂-CH₃), 33.3 (d, J_{PC} = 5.7 Hz, 2x CH₂), 34.5 (d, J_{PC} = 16.2 Hz, 2x CH), 36.9 (d, J_{PC} = 20.3 Hz, 2x CH), 144.9 (s, =C), 166.8 (dd, J_{PC} = 83.2 Hz, J_{PC} = 23.1 Hz, Ni–C=), 182.7 (dd, J_{PC} = 17.3 Hz, J_{PC} = 2.3 Hz, COO). ³¹P{¹H} NMR (81 MHz, d₈-THF): δ 67.2 (d, ²J_{PP} = 19.8 Hz), 74.0 (d, ${}^{2}I_{PP}$ = 19.8 Hz). IR (nujol, cm⁻¹): 1621vs (C=O).

2.4. Synthesis of $[Ni(Cy_3P)_2(3,4-\eta^2-hex-3-yne)]$ (3)

Cy₃P (3.02 g, 10.76 mmol) was added to a stirred suspension of yellow [Ni(cod)₂] (1.48 g, 5.38 mmol) in THF (25 mL). While the starting materials dissolved, a color change to orange was observed. 3-Hexyne (0.53 g, 6.45 mmol) were added and the formed red solution was stirred for 12 h at room temperature. Afterwards the solution was kept at -20 °C for four days, resulting in precipitation of a pale yellow solid, which was isolated by filtration and dried in a vacuum. A second crop of the product was obtained from the mother liquor after evaporation to dryness in vacuo and uptake of the residue in diethyl ether (15 mL). Combined yield: 2.6 g (69%) pale yellow 3. Anal. Calc. for C₄₂H₇₆P₂Ni (701.711 g/mol): C, 71.89; H, 10.92. Found: C, 70.86; H, 10.30%. ¹³C{¹H} NMR (50 MHz, d₈-THF): δ 15.9 (s, 2x CH₃ hexyne), 23.3 (t, ${}^{3}J_{CP}$ = 6.8 Hz, 2x CH₂ hexyne), 27.6 (s, 6x CH₂ Cy₃P), 28.9 (pt, ${}^{3}J_{CP}$ = 4.1 Hz, 12x CH₂ Cy₃P), 31.0 (s, $12x CH_2 Cy_3P$), 36.7 (br, $6x CH Cy_3P$), 130.2 (dd, ${}^{2}J_{CP}$ = 18.9 Hz, ${}^{2}J_{CP}$ = 49.2 Hz, 2x C hexyne). ${}^{31}P{}^{1}H$ NMR (81 MHz, d₈-THF): δ 58.6 (s).

2.5. Synthesis of [Ni{C(Et)=C(Et)-COO}(dppe)] (4)

Solid dppe (0.76 g, 1.91 mmol) was added to a stirred suspension of orange red [Ni{C(Et)=C(Et)-COO}(bipy)] in THF (20 mL). While the starting materials dissolved, the precipitation of a pale yellow solid occurred. The stirring was continued for additional 30 min. Afterwards the precipitate was isolated by filtration, washed with diethyl ether (10 mL) and dried in a vacuum. Yield:

0.98 g (92%) pale yellow **4**. ¹H NMR (d_6 -DMSO): δ -0.05 (3H, t, ${}^{3}I_{HH}$ = 7.3 Hz, Ni–C–CH₂–CH₃), 0.83 (3H, t, ${}^{3}I_{HH}$ = 7.3 Hz, CH₃), 1.60 $(2H, m, Ni-C-CH_2-CH_3)$, 1.90 $(2H, q, {}^{3}I_{HH} = 7.3 \text{ Hz}, CH_2)$, 2.08 $(2H, q, {}^{3}I_{HH} = 7.3 \text{ Hz})$ m, CH₂ dppe), 2.35 (2H, m, CH₂ dppe), 7.45-7.57 (12H, m, m-CH + *p*-CH dppe), 7.88 (8H, m, *o*-CH dppe). ¹³C{¹H} NMR (100 MHz, d₆-DMSO): δ 13.4 (CH₃), 14.8 (CH₃), 21.8 (CH₂), 21.8 (CH₂* dppe), 30.5 (CH₂*), 31.0 (CH₂* dppe), 128.4 (2x *i*-C), 128.9 (d, ${}^{3}J_{PC}$ = 9.5 Hz, 4x *m*-CH dppe), 129.0 (d, ${}^{3}J_{PC}$ = 10.2 Hz, 4x *m*-CH dppe), 130.5 (2x *i*-C), 130.8 (2x *p*-CH dppe), 131.5 (2x *p*-CH dppe), 132.7 (d, ${}^{2}J_{PC}$ = 11.2 Hz, 4x o-CH dppe), 133.4 (d, ${}^{2}J_{PC}$ = 11.4 Hz, 4x o-CH dppe), 143.1 (C=*), 167.7 (C=*), 182.3 (COO*). The signals marked with an asterisk were observed via HMBC and HSQC experiments. ³¹P{¹H} NMR (d_6 -DMSO): δ 43.7 (d, ²J_{PP} = 15.6 Hz), 62.3 (d, $^{2}J_{PP}$ = 15.6 Hz). IR (nujol, cm⁻¹): 1620vs (C=O). Suitable crystals of 4 CH₂Cl₂ for X-ray diffraction experiments were obtained by recrystallization in CH_2Cl_2 (room temperature to -20 °C).

2.6. Reaction of 1 with N-bromosuccinimide

Solid N-bromosuccinimide (260 mg, 1.46 mmol) was added to a stirred orange colored solution of $[Ni{C(Et)=C(Et)-COO}(DBU)_2]$ (690 mg, 1.40 mmol) in THF (30 mL). While the added starting material dissolved, a color change to yellowish brown was observed. The reaction mixture was stirred over night and reduced to dryness afterwards. Thereafter, the residue was hydrolyzed with diluted hydrochloric acid (2 M, 15 mL) (further workup did not require inert handling). The aqueous phase was extracted twice with chloroform (15 mL). The organic phases were extracted with saturated, aqueous sodium carbonate solution (2x·20 mL). Then the combined aqueous phases were acidified (HCl) and extracted with chloroform (3x 20 mL). These organic layers were dried with anhydrous sodium sulfate and the solvent was removed in vacuum to give the crude product as pale yellow oil (257 mg). This crude product consists of a seven to one mixture of (Z)-3-bromo-2-ethylpent-2-enoic acid and succinimide besides minor amounts of 5. Analytical data of (*Z*)-3-bromo-2-ethylpent-2-enoic acid: ¹H NMR (200 MHz, CDCl₃): δ 1.07 (3H, t, ${}^{3}J_{HH}$ = 7.6 Hz, CH₃), 1.14 (3H, t, ${}^{3}J_{\text{HH}}$ = 7.4 Hz, CH₃), 2.36 (2H, q, ${}^{3}J_{\text{HH}}$ = 7.5 Hz, CH₂), 2.55 (2H, q, ${}^{3}J_{\text{HH}}$ = 7.4 Hz, CH₂), 10.98 (1H, br, COOH). ${}^{13}C{}^{1}H$ NMR (50 MHz, CDCl₃): δ 12.7 (CH₃), 12.9 (CH₃), 24.2 (CH₂), 30.8 (CH₂), 130.0 (Br-C=), 133.8 (=C), 173.4 (COO).

2.7. Synthesis of 2-(2,3,4-triethyl-5-oxo-2,5-dihydrofuran-2-yl)butyric acid (**5**)

Solid N-bromosuccinimide (0.39 g, 2.23 mmol) was added to a stirred red solution of [Ni{C(Et)=C(Et)-COO}(bipy)] (0.76 g, 2.23 mmol) in DMF (35 mL). A color change to yellow brown was observed while the starting material dissolved. The resulting solution was stirred over night. Afterwards the now green solution was reduced to dryness at 40 °C under reduced pressure and the remaining sticky residue was dried at that temperature in a vacuum. Thereafter, the residue was hydrolyzed with diluted hydrochloric acid (2 M, 15 mL) (further workup did not require inert handling). The aqueous phase was extracted twice with chloroform (15 mL). The organic phases were extracted with saturated, aqueous sodium carbonate solution (2x·20 mL). Then the combined aqueous phases were acidified (HCl) and extracted with chloroform (3x 20 mL). These organic layers were dried with anhydrous sodium sulfate and the solvent was removed in vacuum to give the product as colorless oil which transforms upon storage at 4 °C into a waxy solid. Yield: 210 mg crude product, containing 5 (90% purity; mixture of diastereomers, ratio of enantiomeric pairs: ca. 2:1) besides (Z)-3-bromo-2-ethylpent-2-enoic acid as major impurity. Suitable crystals for X-ray diffraction experiments and elemental analysis were obtained by slow evaporation of a solution of **5** in a heptane/THF mixture at room temperature.

Anal. Calc. for C₁₄H₂₂O₄ (254.33 g/mol): C, 66.12; H, 8.72. Found: C, 66.06; H, 8.45%. ¹H NMR (400 MHz, CDCl₃): major pair of enantiomers: δ 0.69 (3H, t, ${}^{3}J_{HH}$ = 7.4 Hz, CH₃), 0.92 (3H, t, ${}^{3}J_{HH}$ = 7.6 Hz, CH₃), 1.03 (3H, t, ${}^{3}J_{HH}$ = 7.5 Hz, CH₃), 1.14 (3H, t, ${}^{3}J_{HH}$ = 7.6 Hz, CH₃), 1.50–1.80 (3H, m, CHH' + CHH'), 2.14 (1H, m, ³J_{HH} = 7.2 Hz, CHH'), 2.20–2.40 (4H, m, CH₂), 2.64 (1H, dd, ${}^{3}J_{HH}$ = 11.4 Hz, ${}^{3}J_{HH}$ = 3.6 Hz, CH), 7.3–8.5 (1H, br, COOH). minor pair of enantiomers: δ 0.63 (3H, t, ${}^{3}J_{HH} = 7.4$ Hz, CH₃), 0.87 (3H, t, ${}^{3}J_{HH} = 7.2$ Hz, CH₃), 1.08 (3H, t, ${}^{3}J_{HH} = 7.4$ Hz, CH₃), 1.14 (3H, t, ${}^{3}J_{HH} = 7.6$ Hz, CH₃), 1.10– 1.25 (1H, m, ³*J*_{HH} = 2.8 Hz, CHH'), 1.63 (1H, m, CHH'), 1.82 (1H, m, ${}^{3}J_{\text{HH}}$ = 7.2 Hz, CHH'), 1.99 (1H, m, ${}^{3}J_{\text{HH}}$ = 7.2 Hz, CHH'), 2.15–2.35 (4H, m, CH₂), 2.57 (1H, dd, ${}^{3}J_{HH}$ = 11.8 Hz, ${}^{3}J_{HH}$ = 3.0 Hz, CH), 8.2–.3 (1H, br, COOH). ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃): major pair of enantiomers: δ 6.9 (CH₃), 12.0 (CH₃), 12.2 (CH₃), 12.7 (CH₃), 17.1 (CH₂), 19.7 (CH₂), 20.2 (CH₂), 26.5 (CH₂), 53.8 (CH), 89.4 (C), 131.9 (>C=), 163.2 (=C<), 173.4 (COO), 177.4 (COO). Minor pair of enantiomers: δ 6.9 (CH₃), 11.7 (CH₃), 12.0 (CH₃), 12.9 (CH₃), 17.3 (CH₂), 19.2 (CH₂), 19.6 (CH₂), 27.1 (CH₂), 53.7 (CH), 89.4 (C), 132.1 (>C=), 162.4 (=C<), 173.2 (COO), 177.1 (COO). IR (as methyl ester) (gas phase, cm⁻¹): major pair of enantiomers: 2979m, 2951m, 1782vs (C=O), 1746m (C=O), 1464w, 1352w, 1169m, 1080w. Minor pair of enantiomers: 2979m, 2951m, 1782vs (C=O), 1745m, (C=O), 1464w, 1351w, 1240w, 1160w, 1083w. MS (DEI): m/z (%) = 255 [M+1]⁺ (94), 167 [M-C₄H₇O₂]⁺ (100), 139 (20), 111 (18), 74 (23).

2.8. Structure determinations

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo K α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects [30,31].

The structures were solved by direct methods (SHELXS [32]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [32]). The hydrogen atoms of the carboxylic acid groups from the two independent molecules of **5** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [32]. Crystallographic data as well as structure solution and refinement details are summarized in Table 1. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

3. Results and discussion

3.1. Synthesis and characterization of the nickel complexes

In principle, two ways are known to prepare this type of unsaturated five-membered nickelalactones. Besides ligand exchange reactions, the straightforward synthesis by oxidative coupling of an alkyne and CO₂ in presence of a suitable zero-valent nickel compound succeeds, if strongly basic ligands are used. It is known that nitrogen donor ligands like 2,2'-bipyridine (bipy) [3], N,N,N',N'tetramethylethylendiamine (tmeda) [9] or amidine ligands [13,33] are applicable for this reaction. One of the most efficient and therefore frequently used ligands is 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU). Although the formation of unsaturated nickelalactones in presence of DBU was investigated by quantum chemical calculations, these complexes have not been isolated yet [34,35]. In this investigation, 3-hexyne was chosen as a model substrate to ensure comparability to the known derivatives.

Initial attempts to synthesize a well-defined DBU stabilized nickel alkyne precursor, starting from [Ni(cod)₂], DBU and 3-hex-

C 1	1. 1	C .	1 . 11 .	.1 .7			4	C . 1			-
Crystal	data and	refinement	details for	r the X-ray	/ crystal	structure	determinations	of the	compounds	1-:	5.

Compound	1	1.0.5toluene	2 ·2THF	2-toluene	3	4	5
Compound Formula Formula weight $(g \mod^{-1})$ $T (^{\circ}C)$ Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å ³) Z ρ (g·cm ⁻³) μ (mm ⁻¹) Measured data Data with $l > 2\sigma(l)$	$\begin{array}{c} \textbf{1} \\ \hline \\ C_{25}H_{42}N_4NiO_2 \\ 489.34 \\ -90(2) \\ monoclinic \\ P2_1/c \\ 10.1391(3) \\ 12.7123(4) \\ 19.4762(5) \\ 90 \\ 99.560(2) \\ 90 \\ 2475.45(12) \\ 4 \\ 1.313 \\ 8.12 \\ 9956 \\ 4168 \end{array}$	$\begin{array}{c} 1.0.5 toluene \\ \hline C_{25}H_{42}N_4NiO_2 \ 0.5C_7H_8 \\ 535.40 \\ -90(2) \\ monoclinic \\ P2_1/n \\ 11.5645(7) \\ 15.3234(8) \\ 16.2987(9) \\ 90 \\ 106.614(2) \\ 90 \\ 2767.7(3) \\ 4 \\ 1.285 \\ 7.33 \\ 10067 \\ 3582 \\ \end{array}$	$\begin{array}{c} \textbf{2.2THF} \\ \hline C_{33}H_{58}NiO_2P_2\ 2C_4H_8O \\ 751.65 \\ -140(2) \\ monoclinic \\ P2_1/c \\ 11.5442(3) \\ 17.9407(3) \\ 20.3550(5) \\ 90 \\ 103.551(1) \\ 90 \\ 4098.90(16) \\ 4 \\ 1.218 \\ 5.89 \\ 24962 \\ 7842 \end{array}$	2.toluene C ₃₃ H ₅₈ NiO ₂ P ₂ C ₇ H ₈ 699.58 -140(2) monoclinic P2 ₁ /c 11.4715(2) 14.0123(2) 23.3296(3) 90 95.889(1) 90 3730.26(10) 4 1.246 6.39 21058 7361	$\begin{array}{c} \textbf{3} \\ \hline C_{42}H_{76}\text{NiP}_2 \\ -90(2) \\ orthorhombic \\ Pbca \\ 18.7832(2) \\ 10.0580(1) \\ 43.5820(5) \\ 90 \\ 90 \\ 90 \\ 8233.57(15) \\ 8 \\ 1.132 \\ 5.75 \\ 34531 \\ 6326 \end{array}$	$\begin{array}{c} \textbf{4} \\ \hline \\ C_{33}H_{34}NiO_2P_2\ CH_2Cl_2 \\ 668.18 \\ -90(2) \\ orthorhombic \\ Pna2_1 \\ 28.0005(7) \\ 11.5745(2) \\ 9.6567(2) \\ 90 \\ 90 \\ 90 \\ 3129.66(12) \\ 4 \\ 1.418 \\ 9.23 \\ 6767 \\ 4942 \\ \end{array}$	$\begin{array}{c} \textbf{5} \\ \hline C_{14}H_{22}O_4 \\ 254.32 \\ -90(2) \\ monoclinic \\ P2_1/c \\ 14.6232(3) \\ 7.1437(2) \\ 26.5888(8) \\ 90 \\ 90 \\ 91.636(1) \\ 90 \\ 2776.43(13) \\ 8 \\ 1.217 \\ .88 \\ 15609 \\ 3994 \\ \end{array}$
Data with $I > 2\sigma(I)$ Unique data (R_{int}) wR_2 (all data, on F^2) ^a	4168 5650/0.0356 0.0944	3582 6083/0.0619 0.1727	7842 9359/0.0449 0.1237	7361 8538/0.0368 0.0943	6326 9346/0.1129 0.1449	4942 6767/0.0000 0.1188	3994 6321/0.0469 0.1324
$R_1 (I > 2\sigma(I))^a$ S^b Recidual density (e Å ⁻³)	0.0344 0.0371 1.011 0.335/_0.358	0.0717 1.030 0.436/_0.320	0.0505 1.118 0.395/_0.535	0.0405 1.046 0.416/_0.323	0.0531 1.025 0.834/_0.733	0.0538 1.012 0.751/_0.679	0.0519 0.997 0.202/ 0.218
Absorption method CCDC No.	none 818501	none 818502	none 818503	none 818504	none 818505	none 818506	none 818507

^a Definition of the *R* indices: $R_1 = (\Sigma ||F_o| - |F_c||\Sigma |F_o|; wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2 (F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \text{Max}(F_o^2)/3]$. ^b $s = \{\Sigma [w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.



Fig. 1. Molecular structure of complex **1** (H-atoms are omitted for clarity. Values in square brackets correspond to **1**·0.5toluene). The ellipsoids represent a probability of 40%. Selected bond distances (Å) and bond angles (°): Ni–O1 1.8681(13) [1.881(3)], Ni–C1 1.900(2) [1.899(4)], Ni–N1 1.9128(16) [1.911(4)], Ni–N3 1.9907(16) [1.997(4)], C1–C2 1.345(3) [1.360(7)], C2–C3 1.482(3) [1.481(7)], C3–O1 1.303(2) [1.298(5)], C3–O2 1.238(2) [1.240(6)], C1–Ni–O1 85.37(8) [84.96(17)], N1–Ni–N3 87.95(7) [87.27(15)], N1–Ni–C1 97.62(8) [97.02(18)], N3–Ni–O1 89.11(6) [91.15(14)].

yne, failed since the equilibrium of this reaction is on the side of starting materials. Therefore, the *in situ* system was exposed to a CO_2 atmosphere at room temperature. Under these conditions the formation of the desired nickelalactone [Ni{C(Et)=C(Et)-COO}(DBU)_2] (1) proceeds smoothly and the product was crystallized at -40 °C and isolated by filtration in good yield.

 Table 2

 Selected structural data of unsaturated nickelacyclic carboxylates [Ni{C(Et)=C(Et)-C(OO)(L)n]m (bond lengths [Å]).

		-					
Ligand L	n	т	Ni–C	Ni-O	Ni-L	C1-C2	References
dppe	1	1	1.963	1.886	2.135 (P1)	1.337	-
					2.235 (P2)		
dcpe	1	1	1.961	1.892	2.150 (P1)	1.346	-
					2.210 (P2)		
tmeda	1	1	1.944	1.855	1.987 (N1)	1.341	[17]
					2.010 (N2)		
bipy	1	1	1.926	1.848	1.903 (N1)	1.346	[14]
					1.953 (N2)		
ру	2	1	1.909	1.864	1.895 (N1)	1.344	[19]
					1.997 (N2)		
DBU	2	1	1.900	1.874	1.912 (N1)	1.352	-
					1.994 (N3)		
ItBu	1	2	1.890	1.890	1.859 (C4)	1.354	[24]
					1.960 (03)		

Recystallization of **1** in either THF or toluene led to crystals of **1** (or **1**·0.5toluene) suitable for X-ray diffraction experiments (see Section 2). The molecular structures of both compounds are rather similar, however, a different conformation of the seven-membered ring of the DBU ligand in *trans* position to the Ni–C bond was observed. The molecular structure of **1** is shown in Fig. 1.

For the following structure discussion the average values from both structure determinations are used. As expected, compound **1** contains the nickel atom in a square planar environment. Since the use of strongly basic DBU as ligand leads to an electron-rich nickel centre, a rather short Ni–C1 bond of 1.900 Å and a slightly elongated C1–C2 bond of 1.352 Å were observed. This indicates enhanced backbonding of electrons of the nickel atom into the empty π^* -orbital of the C1–C2 double bond when compared to related complexes with N-donor ligands (see Table 2). The Ni–N bond lengths of 1.912 Å (Ni–N1) and 1.994 Å (Ni–N3) vary due to the differing *trans* influence of C1 and O1. Compared to the calculated structure of [Ni{C(Me)=CH-COO}(DBU)₂] optimized at the B3LYP level of density functional theory [40], significant deviations around the nickel center were observed. Especially the observed Ni–N3 bond length of 1.994 Å is much shorter than the calculated

Table 3	
¹³ C NMR data of the nickelacyclic moiety in 1 , 2 , 4 and related complexes.	

Compound	Solvent	δ Ni–C=	δ C=C-COO	δ COO	References
[Ni{C(Et)=C(Et)-COO}(dppe)]	d ₆ -DMSO	167.7	143.1	183.3	-
[Ni{C(Et)=C(Et)-COO}(dcpe)]	d ₈ -THF	166.8	144.9	182.7	-
$[Ni{C(Et)=C(Et)-COO}(py)_2]$	d ₆ -DMSO	159.0	139.0	178.9	[19]
$[Ni{C(Et)=C(Et)-COO}(DBU)_2]$	d ₈ -THF	158.5	135.4	176.0	-
[Ni{C(Et)=C(Et)-COO}(IMes)] ₂	d ₇ -DMF	158.6	141.5	178.5	[24]
[Ni(CH=CH-COO)(dcpe)]	CDCl ₃	161.2	139.0	186.3	[16]



Fig. 2. Molecular structure of complex **2**·2THF (H-atoms and co-crystallized THF are omitted for clarity). The ellipsoids represent a probability of 40%.Values in square brackets correspond to **2**-toluene. Selected bond distances (Å) and bond angles (°): Ni-O1 1.8943(17) [1.8904(13)], Ni-C1 1.965(2) [1.9561(19)], Ni-P1 2.1485(7) [2.1525(5)], Ni-P2 2.2145(6) [2.2054(5)], C1-C2 1.342(3) [1.349(3)], C2-C3 1.499(3) [1.495(3)], C3-O1 1.307(3) [1.308(2)], C3-O2 1.227(3) [1.231(2)], C1-Ni-O1 85.78(9) [86.04(7)], P1-Ni-P2 87.61(2) [87.49(2)], P1-Ni-C1 98.70(7) [99.44(6)], P2-Ni-O1 87.70(5) [87.11(4)].

value of 2.070 Å. Similar, but less pronounced deviations occurred between the calculated und observed molecular structures of the related bipyridine complexes [14,35].

The bonding situation in the nickelalactone subunit of **1** is quite similar to the related NHC complex $[Ni{C(Et)=C(Et)-COO}(IMes)]_2$ [24]; however, **1** is a mononuclear compound. Those similarities are remarkable in light of the differing reactivity of these compounds. DBU stabilized nickel complexes are not known to catalyze the co-oligomerisation of CO₂ and alkynes (although they efficiently promote the initial oxidative coupling of alkynes with CO₂), in contrast to the combination NHC ligand/[Ni(cod)₂], which is so far the most active catalytic system for this reaction [6,7].

While the solid state structure of **1** is in agreement with other nitrogen donor substituted nickelalactones [14,17,19], the NMR spectroscopic investigation of **1** in d_8 -THF at 25 °C strongly indicates, that this structure is not maintained in solution. Dissolution of a crystalline sample results in the liberation of approximately half of the DBU, and the well known signals of the non coordinated DBU was observed in the ¹H and ¹³C NMR spectra. However, the nickelalactone subunit remains intact. Therefore this behavior can either be interpreted as displacement of DBU by THF or more likely as an oligomer formation. Oligomeric nickelalactones are so far only known for NHC and phosphane stabilized systems [20,24], but in case of related nickel compounds derived by oxida-

tive coupling of imines and CO₂ also imine ligands trigger such an oligomerisation [36]. In our case, there have to be two slightly different oligomers or at least two stable conformations, since a doubled signal set for the carbon atoms of the nickelacyclic moiety at δ 158.6 and 158.7 (Ni–C=), 135.47 and 135.54 (=C–) as well as 175.95 and 175.99 (COO) was observed. Additionally, two of the eight CH₂ groups of the coordinated DBU show two slightly different singlets each, while the others only gave one singlet per CH₂ group.

Besides the major signals, another incomplete signal set was observed *via* NMR measurement which might corresponds to the species observed in the solid state. Table 3 summarizes selected NMR data of **1** and related complexes.

In order to gain further inside into the solution behavior and solid state structures of such unsaturated nickelalactones, the synthesis of phosphane stabilized complexes was attempted. It is known that the use of monodentate phosphanes as ligands results in active catalysts for the co-oligomerisation of CO_2 and alkynes [3], although more forcing conditions are required to achieve satisfying yields. Additionally, related saturated nickelalactones are known to form different types of oligomers [20].

In contrast, the use of chelating diphosphane ligands give systems of poor catalytic activity [2], although some of them mediate the oxidative coupling of alkynes and CO₂ at the nickel center under mild conditions [16,18].1,2-Bis(dicyclohexylphosphino)ethane (dcpe), 1,2-bis(diphenylphosphino)ethane (dppe) and tricyclohexylphosphane (cy₃P) were chosen as representative ligands and their reactions with zero-valent nickel were carried out in analogy to the synthesis of **1**. While dcpe promotes the oxidative coupling of 3-hexyne and CO₂ to the desired nickelalactone **2** under these conditions as well, dppe or cy₃P did not lead to the envisioned products, even when prolonged reaction times were used. Instead, the zero-valent nickel complexes [Ni(cy₃P)₂(η^2 -3-hexyne)] **3** (see Fig. 3) and [Ni(dppe)₂] [37,38] were isolated yield from the reaction mixtures (see Scheme 2).

Recrystallization of **2** in THF or toluene affords suitable crystals for X-ray diffraction experiments of the composition $2 \cdot (\text{THF})_2$ and **2**-toluene, respectively. The molecular structures determined did not differ significantly from each other (see Fig. 2). The average values of bond lengths and angles are given in Table 2. A comparison to related complexes shows the influence of the chelating diphosphane ligand on the overall structure of such nickelalactones. Due to the slightly altered π -backbonding capacity of this ligand class, a diminished backbonding into the nickelalactone itself was observed leading to a rather long Ni–C bond of 1.961 Å in **2** (**1**: Ni– C: 1.900 Å) together with an insignificant shortening of the C=C bond.

The solid state structure is maintained in solution as indicated by the sharp doublets observed at δ 43.7 and 62.3 for the complex in the ³¹P NMR spectra.

Ligand exchange reactions offer an alternative strategy to obtain the desired nickelalactones. Complex **2** was independently prepared by addition of dcpe to a solution of **1** in THF; however, the observed product contained DBU as impurity after workup. In case of dppe, the easily accessible complex $[Ni{C(Et)=C(Et)-COO}(bipy)]$



Scheme 2. Synthesis of 1-3.



Fig. 3. Molecular structure of complex **3** (H-atoms are omitted for clarity). The ellipsoids represent a probability of 40%. Selected bond distances (Å) and bond angles (°): Ni-C1 1.902(3), Ni-C2 1.895(3), Ni-P1 2.1934(7), Ni-P2 2.1848(7), C1-C2 1.269(4), C2-C3 1.502(4), C1-C5 1.498(4), P1-Ni-P2 115.26(3), P1-Ni-C1 101.66(9), P2-Ni-C2 104.38(8), C1-Ni-C2 39.04(11), C1-C2-C3 139.8(3), C2-C1-C5 141.3(3).

was used as starting material, in analogy to known procedures [39] resulting in $[Ni{C(Et)=C(Et)-COO}(dppe)]$, isolated as pale yellow solid in excellent yield (92%). Fig. 4 shows the molecular structure

of **4**, determined by X-ray diffraction experiments. Bond lengths and angles are comparable to the values observed for **2** and therefore do not need further discussion.

3.2. Reactivity towards N-bromosuccinimide

Unsaturated nickelalactones like **1** are not only of interest as proposed intermediates in catalysis but are also valuable starting materials for the synthesis of organic fine chemicals.

Not surprising, the reaction of **1** with *N*-bromosuccinimide in THF resulted in the formation of 3-bromo-2-ethyl-pent-2-enoic acid as major product after hydrolysis. Similar procedures using related titanium or zirconium complexes are known. However, the addition of CuI in case of the zirconium derivatives was necessary [40–42]. Interestingly, the reaction route dramatically changes if the related 2,2'-bipyridine stabilized complex [Ni{C(Et)=C(Et)-COO}(bipy)] was used as starting material. The initial orange red suspension of this adduct in THF changed to beige upon addition of NBS. Due to the lower solubility of the bipyridine complexes, a clear solution was never observed during the reaction. After hydrolytic workup the hitherto unknown 2-(2,3,4-triethyl-5-oxo-2,5-dihydrofuran-2-yl)butyric acid (**5**) was isolated as the main product from the reaction mixture beside minor amounts of 3-bromo-2-ethyl-pent-2-enoic acid (see Scheme 3).

In order to elucidate the influence of the biphasic reaction conditions in case of $[Ni{C(Et)=C(Et)-COO}(bipy)]$ on the outcome of the reaction, the synthesis of **5** was repeated in DMF, in which the starting materials are well soluble. Again, **5** was isolated as major product upon workup. The constitution of **5** was undoubtedly confirmed by X-ray diffraction experiments. The molecular structure determined is shown in Fig. 5.

Compound **5** was obtained as mixture of diasteriomers, with a ratio between the enantiomeric pairs being approximately two to



Scheme 3. Ligand influence on the outcome of the reaction with NBS.



Fig. 4. Molecular structure of complex $4 \cdot CH_2Cl_2$ (H-atoms and co-crystallized CH_2Cl_2 are omitted for clarity). The ellipsoids represent a probability of 40%. Selected bond distances (Å) and bond angles (°): Ni–O1 1.886(3), Ni–C1 1.963(4), Ni–P1 2.1350(12), Ni–P2 2.2348(12), C1–C2 1.337(6), C2–C3 1.487(6), C3–O1 1.299(5), C3–O2 1.228(5), C1–Ni–O1 85.46(16), P1–Ni–P2 86.58(5), P1–Ni–C1 97.31(13), P2–Ni–O1 90.63(10).



Fig. 5. Molecular structure of compound **5** (H-atoms except O–H are omitted for clarity, molecule A of two independent molecules). The ellipsoids represent a probability of 40%. Selected bond distances (Å) and bond angles (°): 01A–C1A 1.364(2), C1A–C2A 1.475(2), C1A–02A 1.207(2), C2A–C3A 1.337(2), C3A–C4A 1.512(2), C4A–C11A 1.558(2), C4A–01A 1.4507(18), C11A–C14A 1.513(2), C14A–03A 1.294(2), C14A–04A 1.2418(19), 01A–C1A–02A 121.46(16), 01A–C1A–C1A–108.97(13), C1A–C2A–C3A–108.11(15), C2A–C3A–C4A 109.41(14), C3A–C4A–01A 103.93(12), 03A–C14A–04A 122.77(16).

one. Although the mechanism of the formation of the muconic acid derivative **5** is not fully understood yet, the observed product

points toward a radical pathway leading to a nickel coordinated *cis,cis*-tetraethylhexa-2,4-diendioate anion. Hydrolysis would result in the corresponding *cis,cis*-tetraethylhexa-2,4-diendioic acid which is supposed to form **5** by cyclization under acidic conditions. Similar behavior was reported for related hexa-2,4-diendioic acids. Depending on the substitution pattern of the muconic acid derivative, more or less harsh conditions were required to enforce lactonization [43,44].

4. Conclusion

The new unsaturated nickelalactons **1** and **2** are easily accessible by oxidative coupling of CO_2 and 3-hexyne at the zero-valent nickel center. While their solid state structures are similar, **1** partially liberates DBU in solution and most likely forms oligomeric aggregates. The nickelalactones **1** and [Ni{C(Et)=C(Et)-COO}(bipy)] are useful starting materials in the synthesis of highly substituted carboxylic acids. The predominant formation of either 3-bromo-2-ethyl-pent-2-enoic acid or 2-(2,3,4-triethyl-5-oxo-2,5-dihydrofuran-2-yl)butyric acid (**5**) was observed in the reaction with NBS, depending on the neutral ligand present. Hence, this nickel mediated reaction sequence offers a simple strategy towards new muconic acid derivatives from the corresponding alkynes and CO_2 . Scope and limitations of this reaction are subjects of ongoing studies.

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Appendix A. Supplementary data

CCDC 818501, 818502, 818503, 818504, 818505, 818506, 818507 contains the supplementary crystallographic data for 1, 1·0.5toluene, 2·2THF, 2·toluene, 3, 4, 5. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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