This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Journal Name

ARTICLE TYPE

Nickelalactones with Allyl Subunit – the Effect of Penta-Coordination on Structures and Stability[†]

Robert R. A. Freund,[a] **Helmar Görls**[a] **and Jens Langer***[a]

A series of allyl modified nickelalactone derivatives of the general formula [(L)$_n$Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] was synthesized _via_ ligand exchange reactions in order to investigate the influence of the neutral ligand L on structure and stability of these complexes. While the square planar 1,8-diazabicyclo[5,4,0]undec-7-ene ligated derivative **1** is stable in solid state and solution
10 at ambient temperature, the use of the chelating ligands 6-diphenylphosphino-1,8-diazabicyclo[5.4.0]undec-7-ene, 1,1-bis(dicyclohexylphosphino)methane and 1,2-bis(dicyclohexylphosphino)ethane (dcpe) led to square pyramidal derivatives **2**, **4**, and **5** with a novel ligand arrangement. In solution, these derivatives are fluxional and show increasing tendencies in the order **2**<**4**<**5** to decouple the nickelalactone moiety to 2,3-dimethylbutadiene (dmbd), CO$_2$ and zero-
15 valent nickel complexes. During the investigation of **5**, the tetrahedral complex [(dcpe)$_2$Ni] (**6**) and the trigonal planar derivative [(dcpe)Ni(dmbd)] (**7**) were observed as predominant decomposition products. In case of the application of 1,1-bis(diphenylphosphino)methane as neutral ligand, a dinuclear nickelalactone species [(μ-dppm)(Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO})$_2$] (**3**) was isolated in which the two nickel atoms realize different coordination geometries (SP-4 and SPY-5) in solid state. The complexes
20 were characterized by NMR techniques, single crystal X-ray diffraction measurements and infrared spectroscopy.

Introduction

Metal mediated reactions of unsaturated hydrocarbons and CO$_2$ offer a straightforward strategy to use CO$_2$ as a cheap and
25 nontoxic carbon source in organic synthesis.[1] In this context, the palladium catalyzed co-oligomerization of 1,3-butadiene and carbon dioxide to 3-ethylidene-6-vinyltetrahydro-2_H_-pyran-2-one, as one of the few examples of an selective and atom-economic catalysis in which carbon dioxide is utilized as such a
30 C1 building block under C–C carbon bond formation, might considered a chemist's dream reaction.[2] Consequently, this system has received considerable interest over decades,[2,3] although the reaction seems unfortunately limited to 1,3-butadiene as substrate. In contrast, CO$_2$ fixation _via_ coupling with
35 other 1,3-dienes is possible in presence of low-valent nickel complexes.[4] Although the latter reaction is not a catalytic transformation, the isolable products, allyl modified nickelalactones, are interesting synthons for the synthesis of a number of carboxylic acid derivatives in subsequent reactions.[5]
40 Depending on the neutral ligand present, allyl modified nickelalactones with square planar (SP-4, type **A**, chart 1)[6] or square pyramidal (SPY-5, type **C**)[4b,7] coordination sphere were isolated, while related derivatives which are formally derived by coupling of simple alkenes[7,8] and alkynes[7,8a,9] exclusively show
45 square planar geometries. In this type of reaction, the formation
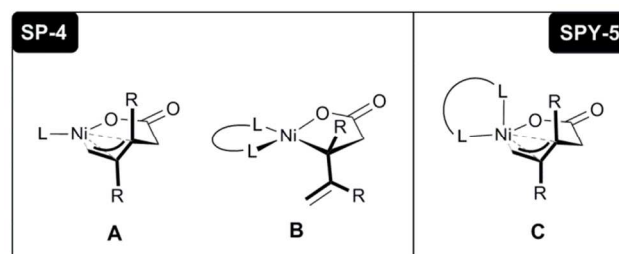

Chart 1 Known structural SP-4 and SPY-5 isomers of nickelalactones with allyl subunit.

of penta-coordinated nickel derivatives seems unique to 1,3-diene
50 substrates in presence of chelating ligands. So far, only two structurally characterized derivatives are known, containing the nitrogen donor ligands 2,2'-bipyridine (bipy)[7] and _N,N,N',N'_-tetramethylethylenediamine (tmeda)[4b]. In contrast, the utilization of the chelating ligand 2-[(diisopropylphosphino)methyl]pyridine
55 led to a rearrangement from a π-allyl to a σ-allyl structure and consequently to a square planar complex (type **B**, chart 1)[10] while the introduction of 1,2-bis(diphenylphosphino)ethane (dppe) resulted in decomposition of the nickelalactone.[6a]

Obviously the nature of the neutral ligand strongly affects the
60 structure, stability and reactivity of allyl modified nickelalactones but due to the limited data available the ligand influence is not fully understood. Since such information is crucial for the development of further applications of allyl-modified
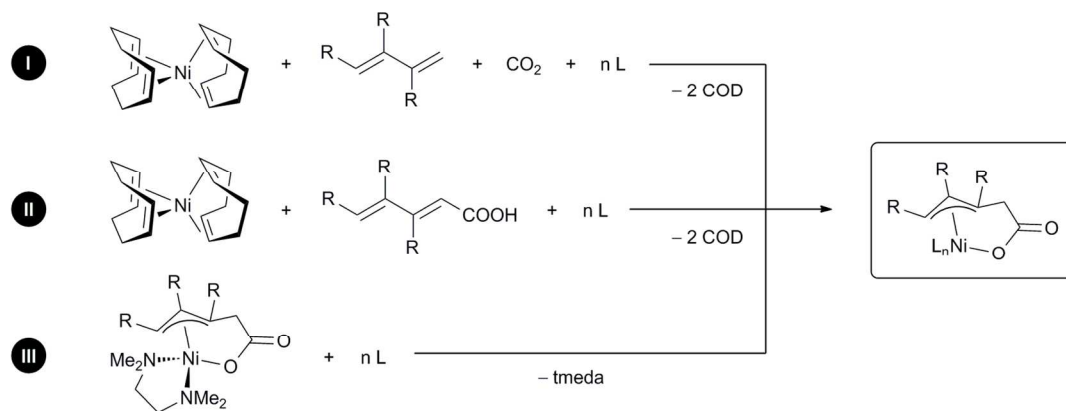
Scheme 1 Routes to nickelalactones with allyl subunit.

nickelalactones in organic synthesis, the effect of a series of neutral ligands, including 1,8-diazabicyclo[5,4,0]undec-7-ene 5 (dbu) and 1,2-bis(dicyclohexylphosphino)ethane (dcpe) as two ligands previously used to achieve the oxidative coupling of substituted 1,3-dienes and CO_2 at the zero-valent nickel center, was investigated.[4c,5d]

Results and Discussion

10 Different strategies for the synthesis of allyl modified nickelalactones of the formal composition $[(L)_nNi(RCHCR'CR''CH_2COO)]$ have been reported (see scheme 1). Beside the above mentioned route *via* oxidative coupling of 1,3-dienes and CO_2 in presence of the desired ligand 15 L at the zero-valent nickel center, the reaction of a 2,4-dienecarboxylic acid with appropriate nickel(0) complexes is an alternative pathway at least in presence of some selected neutral ligands.[6b] Additionally, ligand exchange reactions offer a third strategy with tmeda ligated complexes as suitable starting 20 materials.[6a,7,11] Its simplicity makes this last route very appealing for the study of the effect of different neutral ligands. Since most of the structurally characterized derivatives are formally derived from 2,3-dimethyl-1,3-butadiene (dmbd), the well-known complex $[(tmeda)Ni\{CH_2C(CH_3)C(CH_3)CH_2COO\}]$[4a-b] was 25 prepared *via* route I (see scheme 1) and used as staring material in subsequent ligand exchange reactions (route III) to allow a simple comparison to known derivatives. In an initial investigation the bicyclic amidine dbu was employed for the ligand exchange. Two equivalents of this base, which normally acts as a monodentate 30 ligand, were used for this purpose per nickel centre, since this stoichiometry was found in related dbu-ligated nickelalactones[8a,9d] derived by nickel mediated coupling of alkenes or alkynes and CO_2 and was also used in the *in situ* generation of diene derived derivatives *via* route I.[5d] However, 35 the isolated product $[(dbu)Ni\{CH_2C(CH_3)C(CH_3)CH_2COO\}]$ (**1**) contained only one equivalent of the ligand and underlined that a further uptake of neutral ligands which might lead to penta-coordination at nickel is unfavorable under the applied conditions.

40 In the ^1H NMR spectrum of **1**, two signals each were observed for the CH_2 group of the allyl subunit (δ_H = 1.34 and 1.99) and the neighboring diastereotopic CH_2 group (δ_H = 2.42 and 3.01) in addition to the expected eight signals of the CH_2 groups of the dbu ligand. The two singlets of the methyl groups at δ_H = 0.92

45 and 2.12 complete the spectrum. In the $^{13}C\{^1H\}$ spectrum, the allyl group shows resonances typical for a unsymmetrical η^3-coordination mode at δ_C = 41.1, 73.8 and 111.8 (see ESI, fig. S1).

A π-allyl structure was also confirmed in solid state by X-ray diffraction experiments (see fig. 1). While the application of 50 chelating nitrogen donor ligands such as tmeda and bipy resulted in derivatives with a more or less distorted square pyramidal coordination sphere around the nickel center,[4b,7] compound **1**, as the first structurally characterized complex of this type with an monodentate nitrogen donor ligand, contains the divalent nickel 55 cation in a distorted square planar environment formed by the nitrogen atom N1 of dbu, the carboxylic oxygen atom O1 and the carbon atoms C3 and C5 of the π-allyl group. A *trans*-arrangement of N1 and C3 is observed while O1 is positioned *trans* relative to C5. The CH_2COO group as the substituent with 60 the highest priority attached to the allyl group shows a *syn* orientation, while the
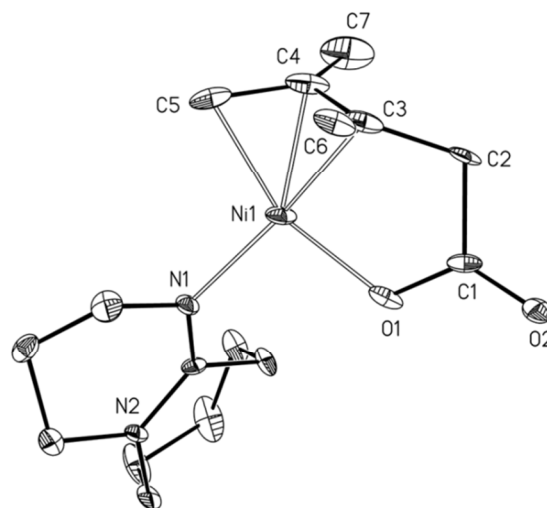

Fig. 1 Molecular structure and numbering scheme of $[(dbu)Ni\{CH_2C(CH_3)C(CH_3)CH_2COO\}]\cdot0.5\ C_6H_6$ (**1**). The ellipsoids 65 represent a probability of 40%. H atoms and co-crystallized benzene are omitted for clarity. Selected bond lengths (Å): Ni1–C3 2.003(7), Ni1–C4 1.961(7), Ni1–C5 1.992(7), Ni1–O1 1.935(5), Ni1–N1 1.944(5), O1–C1 1.282(8), O2–C1 1.229(8), C1–C2 1.539(10), C2–C3 1.536(11), C3–C4 1.400(11), C3–C6 1.518(10), C4–C5 1.430(12), C4–C7 1.537(12); angles 70 (deg.): N1–Ni1–O1 99.4(2), N1–Ni1–C3 161.1(3), N1–Ni1–C4 143.1(3), N1–Ni1–C5 102.5(3), O1–Ni1–C3 84.9(3), O1–Ni1–C4 116.5(3), O1–Ni1–C5 158.0(3), C3–Ni1–C4 41.3(3), C3–Ni1–C5 73.7(3), C4–Ni1–C5 42.4(3), C3-C4–C5 115.8(7).
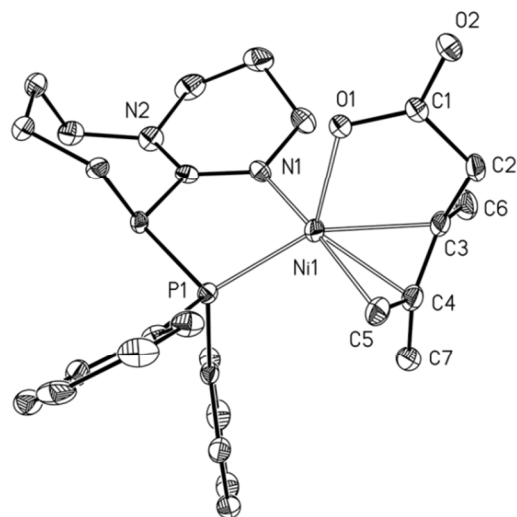
Fig. 2 Molecular structure and numbering scheme of [(dbuP)Ni{CH₂C(CH₃)C(CH₃)CH₂COO}] (**2ᵃ**). The ellipsoids represent a probability of 40%. H atoms are omitted for clarity. Selected bond lengths (Å): Ni1–C3 2.215(5), Ni1–C4 2.031(5), Ni1–C5 1.991(5), Ni1–O1 2.106(3), Ni1–P1 2.0968(12), Ni1–N1 1.977(4), O1–C1 1.266(5), O2–C1 1.248(5), C1–C2 1.532(7), C2–C3 1.527(7), C3–C4 1.377(7), C3–C6 1.526(8), C4–C5 1.441(7), C4–C7 1.507(7); angles (deg.): P1–Ni1–N1 84.27(11), P1–Ni1–O1 122.47(10), P1–Ni1–C3 151.78(14), P1–Ni1–C4 115.58(15), P1–Ni1–C5 94.28(16), N1–Ni1–O1 92.90(14), N1–Ni1–C3 107.25(19), N1–Ni1–C4 129.19(19), N1–Ni1–C5 168.7(2), O1–Ni1–C3 84.41(16), O1–Ni1–C4 110.14(17), O1–Ni1–C5 97.29(18), C3–Ni1–C4 37.5(2), C3–Ni1–C5 69.3(2), C4–Ni1–C5 42.0(2), C3–C4–C5 116.7(5).

methyl group at C3 is consequently found in *anti* position. Similar arrangements were found for related derivatives containing the monodentate phosphanes Ph₃P, Cy₃P[6a] or the *N*-heterocyclic carbene 1,3-dimesitylimidazol-2-ylidene (IMes)[6c] as neutral ligands (see table 1). As judged by comparison of the NMR data (see ESI, table S1), the structurally not characterized pyridine complex [(py)Ni{CH₂C(CH₃)C(CH₃)CH₂COO}][7] has a comparable structure, too.

As mentioned above, complexes such as **1** show little tendency to take up an additional monodentate neutral donor ligand. Therefore, the employment of chelating ligands is necessary to study the effect of an enhancement of the coordination number at nickel. In order to elucidate how the enforced introduction of such a second neutral donor alters the structure and reactivity of the resulting nickelalactone, ligands with two different donor atoms seemed preferable, since they might allow additional conclusions about preferred donor atoms and arrangements at the nickel center. The selection of a ligand with a P,N donor set was obvious, not only because of the overwhelming number of known nickelalactones containing ligands with at least one of these two donor atoms, but also because ligands with this donor set are known to trigger subsequent reactions like π-σ rearrangements[10] or even initiate cascade reactions[12] in related complexes. Application of the dbu-derived racemic chelating ligand 6-diphenylphosphino-1,8-diazabicyclo[5.4.0]undec-7-ene (dbuP), recently developed by Braunstein and co-workers,[13] in a ligand exchange reaction additionally ensured a high degree of comparability to complex **1**. The isolated red product of this reaction is sparingly soluble in THF, toluene and benzene, but the addition of small amounts of methanol enhanced its solubility and allowed recrystallization of the product from toluene. Subsequent removal of methanol induced crystallization and resulted in red crystals of [(dbuP)Ni{CH₂C(CH₃)C(CH₃)CH₂COO}] (**2**) as judged by single crystal X-ray diffraction experiments and elemental analysis. The solid state structure of a racemic crystal containing the enantiomeric pair **2ᵃ/2ᵃ'** (see chart 2) was determined and the molecular structure of **2ᵃ** is depicted in figure 2.
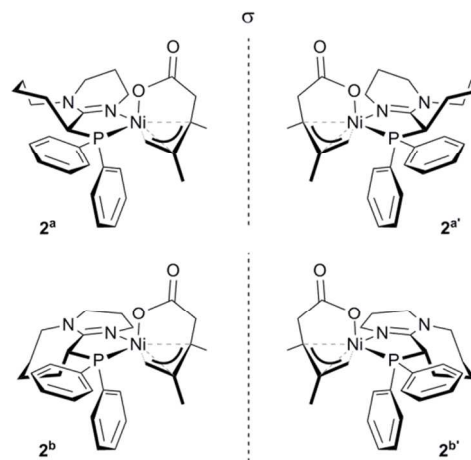

Chart 2 Two enantiomeric pairs of **2** forming diastereomers.

Table 1 Comparison of selected structural parameters of the nickelalactone moieties of [(L)Ni{C⁵H₂C⁴(CH₃)C³(CH₃)C²H₂C¹OO}].

| L | Coordination geometry | Bond lengths [Å] | | | | | | Ref. |
		Ni–C³	Ni–C⁴	Ni–C⁵	Ni–O	C³–C⁴	C⁴–C⁵	
tmeda	SPY-5	1.978(10)	1.940(9)	2.018(12)	1.966(6)	1.41(1)	1.44(1)	[4b]
bipy	SPY-5	1.955(6)	1.915(6)	2.003(7)	1.971(4)	1.383(9)	1.458(10)	[7]
dbu	SP-4	2.003(7)	1.961(7)	1.992(7)	1.935(5)	1.400(11)	1.430(12)	–
IMesᵃ⁾	SP-4	2.045(6)	1.948(6)	1.981(5)	1.917(3)	1.465(8)	1.492(7)	[6c]
Ph₃P	SP-4	2.012(5)	1.970(6)	2.010(6)	1.898(5)	1.323(9)	1.436(9)	[6a]
Cy₃P	SP-4	2.025(3)	1.968(3)	1.994(3)	1.889(2)	1.401(4)	1.412(5)	[6a]
dbuP	SPY-5	2.215(5)	2.031(5)	1.991(5)	2.106(3)	1.377(7)	1.441(7)	–
dcpmᵇ⁾	SPY-5	2.096(6)	2.001(5)	2.099(8)	2.114(4)	1.360(7)	1.460(9)	–
dppmᶜ⁾	SP-4/	2.008(8)/	1.983(8)/	1.999(9)/	1.919(6)/	1.416(13)/	1.400(13)/	–
	SPY-5	2.020(8)	1.953(8)	2.004(8)	1.927(6)	1.424(12)	1.405(12)	

ᵃ⁾ Data suffers from a disorder of the allyl subunit. ᵇ⁾ Data suffers from a positional disorder of the nickel atom. The data related to the dominantly occupied position is listed. ᶜ⁾ The dinuclear compound **3** contains a bridging dppm ligand.

In compound **2^a**, the central nickel atom is penta-coordinated (assuming that the allyl ligand occupies two coordination sites). The coordination sphere is formed by the oxygen atom of the carboxylate function, the nitrogen and phosphorus donor atom of the dbuP ligand and the carbon atoms C3 and C5 of the allyl subunit. The angular parameter τ,[14] derived from the two largest angles α and β observed around nickel (N1–Ni–C5 168.7° and P1–Ni–C3 151.8°), was calculated [$\tau = (\alpha - \beta)/60°$] in order to distinguish between a square pyramidal (SPY-5; $\tau = 0$) and a trigonal bipyramidal (TBPY-5; $\tau = 1$) ligand arrangement. The observed value of 0.28 allows a description of **2^a** as a distorted square pyramidal complex. However, the ligand arrangement in **2^a** is strikingly different from the one observed in the closely related tmeda and bipy ligated complexes.[4b,7] While the chelating nitrogen donor ligands adopt one basal and the apical position of the pyramid, the dbuP ligand blocks two basal coordination sites. The apical position is taken by the oxygen atom O1 of the carboxylate group. The resulting distance Ni1–O1 of 2.106(3) Å is longer than observed in related derivatives with deviating geometry (see table 1). In contrast to compound **1**, the nitrogen donor atom is now found in *trans* position to the carbon atom C5. Within the nickelalactone, the orientation of the substituents of the allyl subunit changed and an *anti* alignment of the CH$_2$COO group is now observed. The finding indicates that a π-σ-π rearrangement of the allyl group is part of the occurring rearrangement induced by the ligand exchange.

While the crystalline appearance, the elemental analysis and the observation of a single absorption for the asymmetric stretching mode of the carboxylate group at 1579 cm^{-1} in the infrared spectrum of solid **2** suggest a uniform compound in solid state, the ^{31}P NMR data of a crystalline sample of **2** in a mixture of C$_6$D$_6$ and CD$_3$OD clearly indicates that a mixture of substances is present in solution. Beside a rather sharp singlet at $\delta_P = 40.7$ as the dominating signal of the spectrum, another small singlet was observed at $\delta_P = 41.0$ and tentatively assigned to another diastereomer of **2** (see chart 2).

Additionally, very broad signals at $\delta_P = 25.7, 38.3$ and 44.0 are also present. Two possible explanations for this observation are (i) the formation of different species in equilibrium in solution from a uniform crystalline batch due to the well-known fluxionality of penta-coordinated species and/or a π-σ (and reverse) rearrangement of the allyl group or (ii) the formation of different aggregates in solution due to hydrogen bond formation between the nickelalactones and CD$_3$OD.[15] Although we tend to option (i), we were not able to clearly rule one of them out as the absence of methanol makes compound **2** insoluble in commonly used solvents such as toluene, benzene or THF. The utilization of more polar solvents like CD$_2$Cl$_2$ enhanced the solubility of **2** but led to its subsequent decomposition in solution. Additionally, temperature dependent NMR measurements were performed to gain further information about the system but were uninformative. Nevertheless, the dominant species present in solution clearly is a nickelalactone with typical signals in the ^{13}C NMR spectrum (see ESI, table S1).

In order to evaluate if such fluxional behavior in solution is typical for the penta-coordinated compounds under investigation, we additionally included chelating phosphane ligands in subsequent experiments, although the widely used
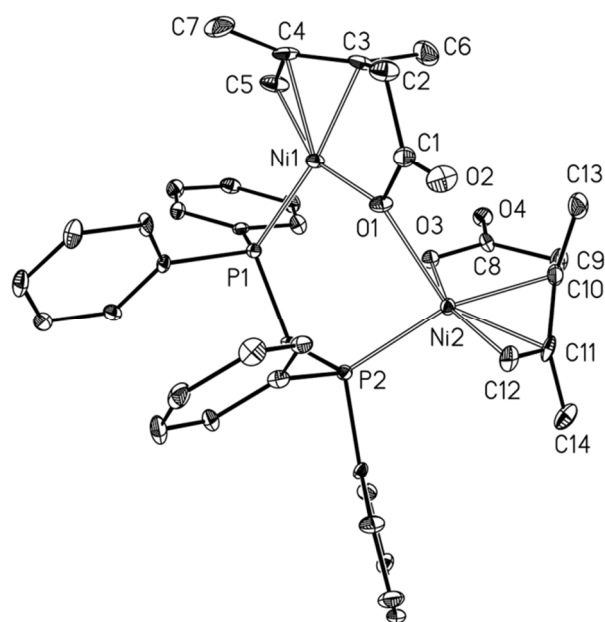

Fig. 3 Molecular structure and numbering scheme of [(μ-dppm-1κP;2κP')Ni$_2${CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO-1κ^{3}C;1:2κO}{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO-2κ^{3}C;2κO}] Et$_2$O (**3**). The ellipsoids represent a probability of 40%. H atoms and the co-crystallized diethyl ether are omitted for clarity. Selected bond lengths (Å): Ni1–C3 2.008(8), Ni1–C4 1.983(8), Ni1–C5 1.999(9), Ni1–O1 1.919(6), Ni1–P1 2.212(2), O1–C1 1.319(10), O2–C1 1.228(11), C1–C2 1.522(12), C2–C3 1.522(13), C3–C4 1.416(13), C3–C6 1.512(14), C4–C5 1.400(13), C4–C7 1.518(14), Ni2–C10 2.020(8), Ni2–C11 1.953(8), Ni2–C12 2.004(8), Ni2–O1 2.372(6), Ni2–O3 1.927(6), Ni2–P2 2.205(2), O3–C8 1.303(10), O4–C8 1.231(10), C8–C9 1.521(11), C9–C10 1.541(12), C10–C11 1.424(12), C10–C13 1.505(13), C11–C12 1.405(12), C11–C14 1.517(13); angles (deg.): P1–Ni1–O1 107.53(18), P1–Ni1–C3 168.6(3), P1–Ni1–C4 128.0(3), P1–Ni1–C5 95.6(3), O1–Ni1–C3 83.8(3), O1–Ni1–C4 119.1(3), O1–Ni1–C5 156.8(3), C3–Ni1–C4 41.6(4), C3–Ni1–C5 73.0(4), C4–Ni1–C5 41.2(4), C3–C4–C5 115.7(9), P2–Ni2–O1 88.84(15), P2–Ni2–O3 97.33(18), P2–Ni2–C10 162.7(3), P2–Ni2–C11 123.5(3), P2–Ni2–C12 100.5(3), O1–Ni2–O3 87.8(2), O1–Ni2–C10 108.4(3), O1–Ni2–C11 133.1(3), O1–Ni2–C12 105.8(3), O3–Ni2–C10 85.7(3), O3–Ni2–C11 116.5(3), O3–Ni2–C12 157.7(3), C10–Ni2–C11 42.0(4), C10–Ni2–C12 73.3(4), C11–Ni2–C12 41.6(4), C10–C11–C12 116.3(8).

1,2-bis(diphenylphosphino)ethane (dppe) was reported to trigger the decomposition of allyl modified nickelalactones and led to formation of [Ni(dppe)$_2$].[6a] A chelating phosphane ligand which is known to result in unique reactivity and structures[8c,16e] when introduced as neutral ligand in nickelalactones and therefore might spare the nickelalactone under investigation the fate of the dppe ligated derivative, is the closely related 1,1-bis(diphenylphosphino)methane (dppm).

Initial experiments performed with equimolar amounts of dppm and [(tmeda)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] led to complicated product mixtures from which considerable amounts of dppm were regained even after complete removal of the liberated tmeda ligand from the system. The reason therefore was sought in the weak chelating ability of dppm due to the almost parallel alignment of the lone pairs of the two phosphorus atoms which often leads to bridging or even monodentate coordination modes of dppm in related zero-valent and divalent nickel compounds.[8c,16] When dppm was consequently considered as an assembly of two independent monodentate phosphanes rather than a chelating ligand and consequently a stoichiometry of 0.5

dppm per nickel center was applied, an orange colored solid was obtained. This solid consisted mainly of [(μ-dppm)(Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}$_2$)$_2$] (**3**). A few well-shaped crystals of **3** were obtained of the ethereal mother liquor of the reaction at -20 °C. The molecular structure of **3**·Et$_2$O is depicted in figure 3 along with selected bond lengths and angles of the molecule.

In **3**, two crystallographically independent nickel atoms Ni1 and Ni2 were observed, both incorporated in nickelalactone moieties in which the CH$_2$COO groups occupy the *syn* positions at the allylic carbon atoms C3 and C10, respectively. While the nickel atom Ni1 is found in a square planar coordination environment closely related to the situation in **1** and known derivatives containing monodentate phosphane ligands, the coordination number of Ni2 is enhanced to five and a square pyramidal coordination sphere is formed due to an additional contact between this nickel center and the endocyclic oxygen atom of the carboxylate moiety of the neighboring nickelalactone. The additional oxygen donor occupies the apical position of the resulting pyramid. The extremely long nickel oxygen bond Ni2–O1 of 2.372(6) Å points to a rather weak interaction. Similarly, the bonding of the tmeda ligand in [(tmeda)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] is strongly asymmetric with a much longer bond between the nickel center and the nitrogen atom in apical position [Ni–N2 2.314(8) Å] than in basal position [Ni–N1 2.064(7) Å].[4b]

Although the formation of oligomeric nickelalactones *via* bridging carboxylate groups is not without precedence and for instance derivatives of the general formula [(L)Ni(CH$_2$CH$_2$COO)]$_n$ (*n* = 2,4,6) with monodentate phosphane[17] and *N*-heterocyclic carbene donor ligands[6c] L are known, these derivatives usually contain the nickel cation in square planar coordination sphere. To the best of our knowledge, the formation of oligonuclear square pyramidal nickelalactones such as **3**, interconnected *via* the carboxylate group, was not observed before. The isolation of such a compound is rather surprising given the unwillingness of compound **1** to take up an additional ligand. Its formation is clearly linked to the use of dppm which acts as a bridging ligand and enforces close proximity of neighboring nickelalactones. The formation of a central six-membered ring, consisting of the methylene carbon atom and the two phosphorus atoms of dppm, the two nickel atoms and the bridging oxygen atom of one carboxylate group, stabilizes the emerging molecule. The bond lengths and angles within the two nickelalactone moieties of **3** are very similar despite the deviating coordination number of the nickel atoms and comparable to those observed in related derivatives with a *syn* orientation of the CH$_2$COO group (see table 1).

The presence of two different carboxylate groups in solid **3** is also observable by infrared spectroscopy where two distinct vibrational bands at $\tilde{v}$ = 1656 and 1634 cm^{-1} for the asymmetric carboxylate stretching vibration were observed (see table 2). In solution, the solid state structure is not preserved. Here, the dominating species which contains 0.5 equivalents of dppm per nickelalactone, is a symmetric species with a single signal in the ^{31}P{^{1}H} NMR spectrum at δ_P = 13.0. The ^{13}C{^{1}H} NMR data obtained is unremarkable and shows typical chemical shifts for the carbon atoms of the nickelalactone moiety (see ESI, table S1).

Table 2 Comparison of the asymmetric carboxylate stretching bands of [(L)Ni{C^{5}H$_2$C^4(CH$_3$)C^3(CH$_3$)C^{2}H$_2$C^{1}OO}] in solid state.

L	Coordination geometry	Alignment of CH$_2$COO	v_{as}(COO)	Ref.
py	SP-4	*syn*	1636	[7]
dbu	SP-4	*syn*	1626	–
IMes	SP-4	*syn*	1639	[6c]
Cy$_3$P	SP-4	*syn*	1648	[6a]
Ph$_3$P	SP-4	*syn*	1650	[6a]
½ dppm	SP-4/SPY-5	*syn*	1656/1634	–
tmeda	SPY-5	*syn*	1618	[4b]
dbuP	SPY-5	*anti*	1579	–
dcpm	SPY-5	*anti*	1599	–
dcpe[a]	SPY-5	*anti*	1584	–

[a] The appearance of a weaker second band at 1607 cm^{-1} indicate the presence of another isomer.

Only a slight downfield shift of the CH$_2$ groups of the allyl subunit to δ_C = 48.1 was detected. Additionally, the signal of the allylic carbon atom in *trans* position to phosphorus at δ_C = 83.0 as well as the signal of the carboxylate carbon at δ_C = 183.7 were observed as pseudo-triplets, most likely due to virtual coupling in an AA'X (or ABX) spin system (A, A', B = phosphorus, X = carbon). These observations indicate that the solution structure of **3** is dominantly those of a SP-4 complex and penta-coordinated species play a minor role under these conditions. Nevertheless, such interactions do exit as highlighted by the solid state structure of **3**. However, a second weaker and incomplete signal set of another nickelalactone was observed in both, the ^{13}C and ^{1}H NMR spectra. Attempts to remove this impurity by recrystallization were unsuccessful. The too high carbon content determined by elemental analysis points towards the initially envisioned nickelalactone [(dppm)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] as the impurity, while unreacted tmeda-containing starting material could be excluded because the product contained no nitrogen.

Unfortunately, the inability to obtain a pure derivative of the type [(L)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] which contains dppm as a chelating ligand leaves the initial question concerning the stability and structure of such chelate phosphane ligated nickelalactones unanswered. In a second attempt, the closely related 1,1-bis(dicyclohexylphosphino)methane (dcpm) was employed. The ligand exchange reaction between [(tmeda)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] and dcpm takes another course than in case of dppm and it was possible to isolate a 1 to 1 adduct. Since the ligand that was used shows superior σ-donor capacity relative to dppm, a stable product was expected. However, the crude product, obtained at ambient temperature, was observed to be a mixture which already contained decomposition products beside the desired nickelalactone [(dcpm)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] (**4**). Therefore recrystallization and meanwhile handling and storage of the solutions at low temperatures (–40 °C) was necessary to isolate a pure substance (see experimental section). Nevertheless, only the addition of small portions of methanol and further recrystallization yielded suitable crystals for X-ray diffraction analysis. In solid state, compound **4**·MeOH resembles the dbuP ligated derivate **2** with respect to the general conformation of molecule, but in this case one molecule of methanol per
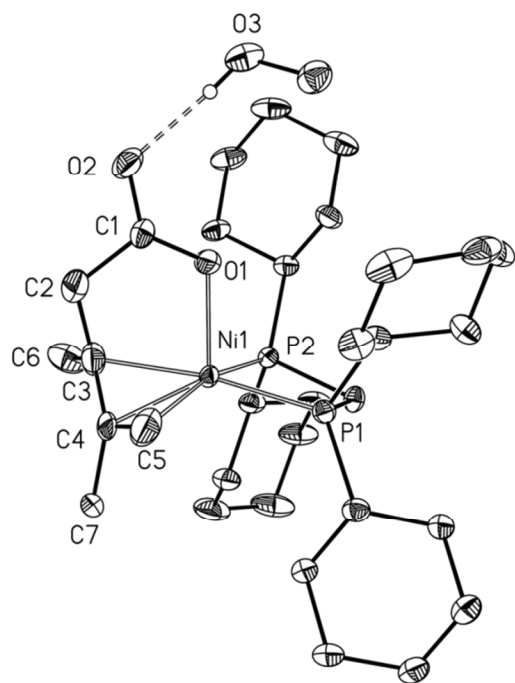
Fig. 4 Molecular structure and numbering scheme of [(dcpm)Ni{CH₂C(CH₃)C(CH₃)CH₂COO}]·CH₃OH (**4**). The ellipsoids represent a probability of 40 %. H atoms (except the one at O3) and a
5 disorder of the nickel atom are omitted for clarity. Selected bond lengths (Å): Ni–C3 2.096(6), Ni1–C4 2.001(5), Ni1–C5 2.099(8), Ni1–O1 2.114(4), Ni1–P1 2.134(4), Ni1–P2 2.305(6), O1–C1 1.226(5), O2–C1 1.248(5), C1–C2 1.502(7), C2–C3 1.564(8), C3–C4 1.360(7), C3–C6 1.453(8), C4–C5 1.460(9), C4–C7 1.588(8), O2···O3 2.702(9); angles
10 (deg.): P1–Ni1–P2 75.79(7), P1–Ni1–O1 102.3(2), P1–Ni1–C3 171.6(2), P1–Ni1–C4 133.1(3), P1–Ni1–C5 102.7(3), P2–Ni1–O1 99.35(16), P2–Ni1–C3 108.5(4), P2–Ni1–C4 129.1(4), P2–Ni1–C5 164.2(2), O1–Ni1–C3 84.3(2), O1–Ni1–C4 109.6(2), O1–Ni1–C5 96.3(3), C3–Ni1–C4 38.7(2), C3–Ni1–C5 71.2(2), C4–Ni1–C5 41.6(2), C3–C4–C5 119.9(6).

15 nickelalactone, which forms a hydrogen bond to the exocyclic oxygen atom of the nickel complex, was found within the crystal. This finding underlines that the derivatives under investigation are rather stable against protolysis in agreement with the results obtained for related derivatives of the type
20 [(L)$_n$Ni(CH₂CH₂COO)] which also form stable hydrogen bonds with alcohols[8c,15,17] and amines[18]. The molecular structure of **4**·MeOH is shown in figure 4.

The preference of the less basic exocyclic oxygen atom of **4** for adduct formation results from steric shielding of the
25 endocyclic oxygen atom by the dcpm ligand. With compound **4**, a second square pyramidal nickelalactone derivative is available in which the carboxylate group occupies the apical position of the pyramid. Comparison of its properties with previously investigated derivatives allowed the identification of the
30 asymmetric stretching vibration of the carboxylate group as a valid criterion to simply distinguish this isomeric form from others. Both known examples, compounds **2** and **4**, show this band at remarkably low wavenumber (**2**: 1579 cm⁻¹; **4**: 1599 cm⁻¹) while for all other derivatives higher values were found (see table
35 2). The observed values indicate an increased degree of charge delocalization within the carboxylate group and increased contribution of resonance form **b** (see scheme 2) to the overall structure of the molecule. Expectedly, hydrogen bond formation
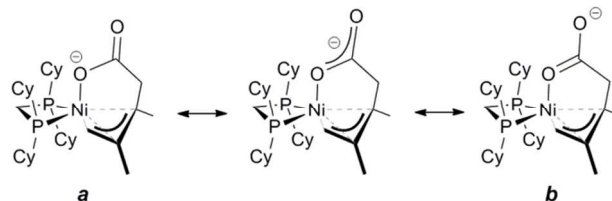
40 **Scheme 2** Resonance forms *a* and *b* of **4**.

fortified this effect and measurement of crystals of **4**·MeOH gave a value of 1577 cm⁻¹.

In solution, compound **4** is neither uniform nor stable at ambient temperature. ¹H and ¹³C spectra show the presence of at
45 least two different nickelalactones as indicated for instance by the presence of two different signals of the carboxylate group at δ_C = 183.7 (major isomer) and 175.8. Additionally, the isomers as penta-coordinated molecules can be fluxional themselves as observed for the major isomer in solution. In the ³¹P{¹H}
50 spectrum this compound gave rise to a broadened singlet at δ_P = 10.6 due to rapid exchange of the positions of the two non-equivalent phosphorus nuclei. The situation is further complicated by slow decomposition of **4** to unknown nickel containing products. The simultaneous occurrence of typical
55 signals of liberated 2,3-dimethylbutadiene at δ_C = 20.6, 113.1 and 144.1 is an indication that decoupling of the nickelalactone subunit occurred as one of the decomposition pathways. Nevertheless, with the help of two-dimensional HMBC and HSQC NMR experiments it was possible to identify and assign
60 all ¹³C NMR signals of the nickelalactone subunit of the dominant species in solution (see ESI, table S1).

The unexpected destabilization of the investigated nickel derivative upon utilization of dcpm needed some additional considerations. The use of highly basic chelate phosphanes like
65 dcpm, dcpe and 1,2-bis(dicyclopentylphosphino)ethane as ligands usually led to stable, structurally characterized saturated[8c,19] and unsaturated[9d] nickelalactones (without allyl moiety) which do not decouple spontaneously into CO₂ and the parent hydrocarbon (alkene, alkyne) at ambient temperature.
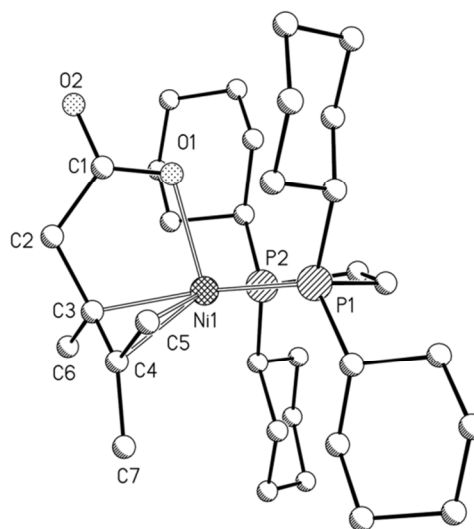
70

Fig. 5 Structural motif of [(dcpe)Ni{CH₂C(CH₃)C(CH₃)CH₂COO}]·0.5 THF (**5**). The H atoms, co-crystallized THF and a disorder of C2, C3, C5, C6, O1 and O2 are omitted for clarity.

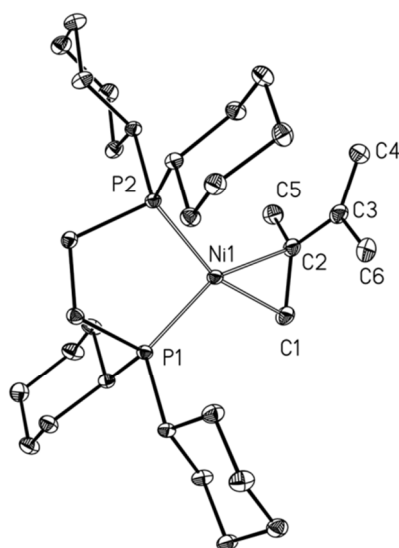**Fig. 6** Molecular structure and numbering scheme of [(dcpe)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$}] (**7**). The ellipsoids represent a probability of 40 %. H atoms are omitted for clarity. Selected bond
5 lengths (Å)[values of **7**·0.5THF added in square brackets]: Ni1–C1 1.954(3) [1.954(3)], Ni1–C2 1.997(3) [2.009(3)], Ni1–P1 2.1361(7) [2.1420(7)], Ni1–P2 2.1565(7) [2.1571(7)], C1–C2 1.437(4) [1.440(4)], C2–C3 1.476(4) [1.481(4)], C2–C5 1.515(4) 1.508(4)], C3–C4 1.351(4) [1.341(5)], C3–C6 1.495(5) [1.504(5)]; angles (deg.): P1–Ni1–P2
10 91.92(3) [92.25(3)], P1–Ni1–C1 108.47(9) [108.11(9)], P1–Ni1–C2 150.23(9) [150.30(9)], P2–Ni1–C1 159.35(9) [158.87(10)], P2–Ni1–C2 116.70(9) [116.52(9)], C1–C2–C3 121.0(3) [119.5(3)], C1–C2–C5 117.8(3) [118.4(3)].

Additionally, dcpe is a ligand which is commonly used in the
15 synthesis of such nickel derivatives *via* oxidative coupling of CO$_2$ and unsaturated substrates[8a,19] including 1,3-dienes.[4c] The observed instability of the dcpm ligated derivative **4** does not seem to fit the reactivity scheme although it is in line with the reported behavior[6a] of the dppe derivative. Clearly, the dcpe
20 stabilized compound [(dcpe)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] (**5**) would be the perfect candidate to decide whether chelate phosphane ligands *per se* have a destabilizing effect on the investigated nickelalactones or dcpm is an exception due to the formation of an unfavorable four membered chelate ring at nickel
25 which already led to the isolation of the unusual derivative **3** in case of dppm. Initial ligand exchange reactions at ambient temperature using dcpe led to a slow color change from red to yellow and the precipitation of a pale yellow substance which was identified as the well-known zero-valent nickel complex
30 [(dcpe)$_2$Ni][20] (**6**) by comparison of the NMR data and additional X-ray diffraction analysis (see ESI, fig. S4). The isolation of **6** underlines that chelating diphosphane ligands indeed have a destabilizing effect on the allyl modified nickelalactones under investigation. Nevertheless the isolation of the dcpe ligated
35 nickelalactone **5** is possible due to its low solubility in THF *via* crystallization, when the initial reaction mixture was rapidly cooled to –10 °C in order to avoid the decoupling of the nickelalactone. The red crystalline product obtained in this manner showed two asymmetric carboxylate stretching vibrations
40 in the infrared spectrum, a stronger one at $\tilde{v} = 1584$ and a weaker at $\tilde{v} = 1607\,cm^{-1}$, as an indication that two slightly different isomers or conformers of **5** are present in solid state (table 2). For the major form, a structure in analogy to the

complexes **2** and **4** was confirmed by X-ray diffraction analysis.
45 Due to the rather low quality of the obtained crystals only a structural motif of **5** (see fig. 5) is available which was sufficient to establish the connectivity of the atoms but precludes further discussion of bond lengths and angles. Despite several attempts, no suitable crystals of the other form of **5** were found and
50 therefore its conformation remains uncertain although the IR data might point to a square pyramidal complex with a ligand alignment in analogy to the known tmeda derivative[4b] Limited NMR data of **5** was obtained in THF-d_8 under a CO$_2$ atmosphere, applied to suppress decomposition *via* decoupling of the
55 nickelalactone to CO$_2$ and 2,3-dimethylbutadiene. Unfortunately, under these conditions, only a useful ^{31}P{^{1}H} spectrum of **5**, consisting of two singlet at $\delta_P = 63.8$ and 74.0 of equal intensity, is accessible while the ^{1}H NMR spectrum is uninformative due to broad overlapping signals and a meaningful ^{13}C NMR spectrum
60 is prevented by the very limited solubility of **5** under these condition.

If compound **5** is kept in contact with the tmeda containing mother liquor of the reaction for an enhanced time span at low temperature, the solid product becomes more and more
65 contaminated with the above mentioned [(dcpe)$_2$Ni] in crystalline form. In contrast, isolated **5** dissolves readily in THF at ambient temperature without an CO$_2$ atmosphere, but rapid decoupling and predominant formation of the zero-valent nickel derivative [(dcpe)Ni{η^2-CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$}] (**7**) besides minor
70 amounts of **6** were observed. Related complexes of nickel with 1,3-butadiene ligands are known and different coordination modes of the diene ligand including η^2-; η^4- and μ$_2$-η^2:η^2-coordination were reported.[21] While in case of the closely related 1,3-butadiene complex [(dcpe)Ni{CH$_2$CHCHCH$_2$}] a η^4-
75 coodination mode was found in solid state[21b], 2,3-dimethylbutadiene as a slightly more electron-rich and sterically demanding ligand prefers η^2-coordination in **7** as confirmed by X-ray analysis. As depicted in figure 6, the diene ligand adopts an s-trans conformation in this distorted trigonal planar nickel
80 complex. Coordination to nickel leads to a lengthening of the double bond between C1 and C2 [1.437(4)] by 0.086 Å relative to the undisturbed double bond between C3 and C4 [1.351(4) Å].

The presence of **6** as an impurity and its ongoing slow formation besides liberated 2,3-dimethylbutadiene and other
85 unidentified products in solution indicate that compound **7** has a lower stability than the related 1,3-butadiene derivative. The straightforward synthesis of pure **7** was attempted by the reaction of equimolar amounts of dcpe and [Ni(cod)$_2$] (cod = *cis,cis*-1,5-cyclooctadiene) in presence of a tenfold excess of 2,3-
90 dimethylbutadiene but only led to isolation of [(dcpe)Ni(cod)][22] (**8**) in good yield. (The same product was obtained in absence of 2,3-dimethylbutadiene; see experimental section and ESI, figure S6.) Nevertheless, the formation of minor amounts of **7** in equilibrium were detected *via* NMR investigation of the reaction
95 mixture.

The structurally characterized derivatives **7** and **8** are two potential intermediates on route to the nickelalactone derivative **5** *via* coupling of 2,3-dimethylbutadiene and CO$_2$ by the system dcpe/[Ni(cod)$_2$] in analogy to the reactions with 1,3-butadiene
100 and isoprene.[4c] Additionally, their formation in the above described experiments underlines the obstacles on this known

pathway to allyl modified nickelalactones and during their utilization. First of all, substitution of the cod ligand by electron rich diene derivatives is unfavorable and therefore often an excess of the diene component is necessary to achieve satisfying reaction rates. Furthermore, an excess of CO_2 is not only beneficial to shift the equilibrium between complexes like **7** and CO_2 towards the desired products but might also help to prevent the reversion of their formation in subsequent reactions in order to make these derivative utilizable in organic synthesis. The investigation especially of the dcpm and dcpe ligated derivatives **4** and **5** indicate that this decoupling reaction is a serious threat in solution.

Conclusion and Perspective

In contrast to the nickelalactones derived *via* coupling of CO_2 and alkenes or alkynes, the stability of allyl modified nickelalactones derived from dienes does not benefit from the application of chelating ligands. Especially the use of widely applied bidentate chelate phosphane ligands has a destabilizing effect on these species. This deviating reactivity is closely related to the penta-coordinated nature of derivatives such as [(dcpm)Ni{CH_2C(CH_3)C(CH_3)CH_2COO}] (**4**) and [(dcpe)Ni{CH_2C(CH_3)C(CH_3)CH_2COO}] (**5**) which seems to significantly lower the activation barriers for decoupling reactions. This activating effect of penta-coordination, although in context of other reactions, is well-documented in the chemistry of related d^8-systems of iridium(I)[23] and ascribed to the formation of highly distorted tetra-coordinated intermediates from the preferred penta-coordinated species which leads to a significant lowering of the overall activation energies of the investigated processes. However, the assumption that the observed destabilization in case of the investigated nickelalactones is closely related to the hitherto unknown conformation of the derivatives **4** and **5** and not the result of the enhanced coordination number alone can be ruled out. The starting material [(tmeda)Ni{CH_2C(CH_3)C(CH_3)CH_2COO}], which shares the coordination number of the compounds **4** and **5** but has another alignment of the ligands around the nickel center, also showed slow decomposition when handled in solution without additional CO_2 present. The stability of dinuclear [(µ-dppm)(Ni{CH_2C(CH_3)C(CH_3)CH_2COO})_2] (**3**) exceeds those of the dcpm and dcpe ligated derivatives, most likely because this compound is a predominantly tetra-coordinated species in solution although penta-coordination of one of the two nickel centers was observed in solid state. Among the penta-coordinated derivates investigated, the dbuP ligated compound [(dbuP)Ni{CH_2C(CH_3)C(CH_3)CH_2COO}] (**2**) shows the lowest tendency for the decoupling of the nickelalactone moiety and might indicate that chelating ligands with P,N donor set are superior for the stabilization of these derivatives. However, subsequent investigations with additional ligands of this type are necessary to clarify this point. In contrast to the penta-coordinated derivatives, the square planar compound [(dbu)Ni{CH_2C(CH_3)C(CH_3)CH_2COO}] (**1**) is perfectly stable in solution at ambient temperature.

It can be concluded from the obtained results, that tetra-coordinated allyl modified nickelalactones containing a single highly basic monodentate neutral ligand show superior long term stability in solution and therefore are the systems of choice for the exploration of these derivatives as organometallic reagents in organic synthesis. Since it is commonly accepted that for the coupling process of a diene and CO_2 at the nickel center itself, the presence of two monodentate ligands or of a bidentate chelate ligand per nickel center is required, isolation of the product (in case of monodenate ligands) or the subsequent exchange of the chelate ligand by a monodentate one are further measures to ensure the stability of the complexes in following reactions. It should be noted that even the presence of a second non-coordinated ligand in solution was proven counterproductive in related systems.[24] Additionally, a CO_2 atmosphere might be beneficial as well in order to further suppress the impending decoupling of the nickelalactone in succeeding transformations.

Experimental

General comments

All manipulations were carried out under an inert argon atmosphere using standard Schlenk techniques. THF, THP, toluene, diethyl ether and heptanes (mixture of isomers) were dried over KOH and distilled over sodium/benzophenone in an argon atmosphere; deuterated THF and benzene were dried over sodium, degassed, and saturated with argon. Acetone was dried over B_2O_3. The yields given are not optimized. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AC 400, or AC 600 spectrometers. Chemical shifts are reported in parts per million relative to Me_4Si as an external standard. The residual signals of THF-d_8 or C_6D_6 were used as an internal standard in the ^1H and ^{13}C NMR spectra. The following abbreviations are used for the NMR data: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad and IR data: s = strong, m = medium. The pseudo-triplets observed are most likely the result of virtual coupling phenomena. [Ni(cod)_2][25] and [(tmeda)Ni{CH_2C(CH_3)C(CH_3)CH_2COO}][4a] were prepared according to known procedures. Dppm, dcpm and dcpe were purchased from Strem Chemical, Inc. and used as received.

Synthesis of [(dbu)Ni{CH_2C(CH_3)C(CH_3)CH_2COO}] (1)

Dbu (0.44 mL, 448 mg, 2.94 mmol) was added dropwise to a stirred solution of [(tmeda)Ni{CH_2C(CH_3)C(CH_3)CH_2COO}] (440 mg, 1.47 mmol) in toluene (10 mL) at ambient temperature *via* syringe. The red reaction mixture was stirred for two hours followed by removal of the solvent under reduced pressure at ambient temperature. The resulting viscous red oil was dispersed in diethyl ether (15 mL) whereupon the product precipitated as orange yellow solid. The compound was isolated by filtration and dried in a vacuum. Yield: 249 mg (50%). Anal. Calcd. for $C_{16}H_{26}N_2NiO_2$ (337.08): C, 57.01; H, 7.77; N, 8.31; found: C, 57.07; H, 7.82; N, 8.23%; Selected IR (ATR): $\tilde{\nu}$ = 1626(s, $\nu_{as,COO}$), 1592(s, $\nu_{C=N}$) cm^{-1}; ^1H NMR (600.1 MHz, C_6D_6): δ 3.24 (br s, 2H, C=N–CH_2), 3.01 (d, 1H, $^2J_{H,H}$ = 15.9 Hz, O_2C–C(H_{eq})H_{ax}), 2.91 (br s, 2H, N=C–CH_2), 2.70 (br s, 2H, N=C–(CH_2)_4CH_2), 2.65 (br s, 2H, C=N–(CH_2)_2CH_2), 2.42 (d, 1H, $^2J_{H,H}$ = 15.9 Hz, O_2C–C(H_{eq})H_{ax}), 2.12 (s, 3H, C$H_{3(meso)}$), 1.99 (s, 1H, C(H_{anti})H_{syn}), 1.47 (br s, 2H, N=C–CH_2CH_2), 1.35–1.36 (m, 3H, C=N–CH_2CH_2, + C(H_{anti})H_{syn}), 1.29 (br s, 2H, N=C–(CH_2)_2CH_2), 1.10 (br s, 2H, N=C–(CH_2)_3CH_2), 0.92 (s, 3H, C$H_{3(anti)}$). $^{13}C\{^1H\}$ NMR (150.9 MHz, C_6D_6): δ 182.4 (*C*OO),

163.9 (C=N), 111.8 (C–CH$_{3(meso)}$), 73.9 (C–CH$_{3(anti)}$), 53.1 (N=C–(CH$_2$)$_4$$CH_2$), 47.7 (C=N–(CH$_2$)$_2$$CH_2$), 47.2 (C=N–$CH_2$), 44.4 (O$_2$C–$CH_2$), 41.1 ($CH_2$), 38.9 (N=C–$CH_2$), 29.2 (N=C–(CH$_2$)$_2$$CH_2$), 28.0 (N=C–(CH$_2$)$_3$$CH_2$), 25.3 (N=C–$CH_2CH_2$), 22.1 (C=N–CH$_2$$CH_2$), 21.7 ($CH_{3(anti)}$), 20.1 ($CH_{3(meso)}$). Crystals of **1**·0.5 benzene suitable for X-ray diffraction experiments were obtained by cooling a saturated solution of **1** in a mixture of *n*-heptane and benzene from ambient temperature to 0 °C.

Synthesis of [(dbuP)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] (2)

Solid dbuP (400 mg, 1.17 mmol) was added in one portion to a stirred solution of [(tmeda)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] (341 mg, 1.14 mmol) in THF (26 mL) at ambient temperature. After dissolution of the dbuP the red reaction mixture was cooled to 5 °C and stored at this temperature. After three days at this temperature the precipitated orange red crude product (336 mg, 56%) was collected by filtration and dried in a vacuum. Thereafter the compound was suspended in toluene (8 mL) and methanol was added dropwise with rapid stirring until a clear red solution was obtained. Afterwards the added methanol was slowly removed in a vacuum until the crystallization of the product started. Then the mixture was allowed to stand at –10 °C for 24 hours to complete crystallization. The red crystals formed were separated by decantation, washed with toluene (3 mL) and dried in a vacuum. Yield: 214 mg (36%). Anal. Calcd. for C$_{28}$H$_{35}$N$_2$NiO$_2$P (521.27): C, 64.52; H, 6.77; N, 5.37; found: C, 64.85; H, 6.66; N, 5.34; selected IR (ATR): ṽ = 1579 cm^{-1} (s, $v_{as,COO}$); ^{1}H NMR (400.1 MHz, C$_6$D$_6$ + CD$_3$OD): major species in solution: δ 7.52 (m, 2H, CH Ph), 7.4-7.1 (m, 8H, CH Ph), 3.4-2.3 (m, 7H, 3×CH$_2$+CH dbuP), 2.51 (m, 1H, O$_2$C–CH*H'*), 2.40 (m, 1H, O$_2$C–C*H*H'), 1.87 (br, 1H, CH*H'*), 1.80 (m, 1H, C*H*H'), 1.5-0.9 (m, 8H, 4×CH$_2$ dbuP), 1.49 (s, 3H, CH$_3$), 1.36 (d, 3H, J = 7.8 Hz, CH$_3$); ^{13}C{^{1}H} NMR (150.9 MHz, C$_6$D$_6$ + CD$_3$OD): incomplete signal set of the major species in solution: δ 179.2 (d, $^3J_{C,P}$ = 9.8 Hz, COO), 166.4 (d, $^2J_{C,P}$ = 18.7 Hz, C=N), 116.5 (d, $^2J_{C,P}$ = 2.4 Hz, C–CH$_{3(meso)}$), 94.9 (d, $^2J_{C,P}$ = 22.9 Hz, C–CH$_{3(syn)}$), 54.0 (s, CH$_2$ dbuP), 53.8 (s, CH$_2$ dbuP), 48.5 (d, $^1J_{C,P}$ = 2.1 Hz, CH dbuP), 48.3 (s, CH$_2$ dbuP), 46.2 (d, $^3J_{C,P}$ = 3.4 Hz, O$_2$C–CH_2), 39.2 (d, $^2J_{C,P}$ = 5.0 Hz, CH$_2$ allyl), 29.0 (s, CH$_2$ dbuP), 28.2 (d, $^2J_{C,P}$ = 8.7 Hz, CH$_2$ dbuP), 26.5 (s, CH$_2$ dbuP), 23.9 (d, $^3J_{C,P}$ = 2.7 Hz, CH$_3$), 22.4 (s, CH$_2$ dbuP), 21.1 (s, CH$_3$), the assignment of the signals of the Ph groups is uncertain and therefore not given. ^{31}P{^{1}H} NMR (162.0 MHz, C$_6$D$_6$ + CD$_3$OD): major species: δ 40.7 (s). The crystal, obtained as described above, are suitable for X-ray diffraction analysis.

Synthesis of [(μ-dppm)(Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO})$_2$] (3)

Solid dppm (180 mg, 0.48 mmol) was added in one portion to a stirred red solution of [(tmeda)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] (280 mg, 0.93 mmol) in THF (10 mL) at ambient temperature. The resulting orange red reaction mixture was stirred for 15 min and then toluene (10 mL) was added. Thereafter, the solvents were slowly removed by distillation in a vacuum. The remaining orange colored residue was taken up in diethyl ether (10 mL) resulting in the precipitation of the orange colored product. The solid was isolated by filtration, washed with diethylether (3 mL) and thoroughly dried in a vacuum. Yield: 272 mg (78%, crude product). Anal. Calcd. for C$_{39}$H$_{42}$Ni$_2$O$_4$P$_2$ (754.095): C, 62.11; H,

5.61; found: C, 64.37; H, 5.53; selected IR (ATR): ṽ = 1656 (m, $v_{as,COO}$), 1634 cm^{-1} (s, $v_{as,COO}$); ^{1}H NMR (400.1 MHz, THF-d_8): major species in solution: δ 7.86 (br, 4H, CH Ph), 7.38 (br, 4H, CH Ph), 7.35-7.05 (m, 12H, CH Ph), 3.39 (t, 2H, $^2J_{H,P}$ = 10.9 Hz, PCH$_2$P), 3.11 (br. d, 2H, $^2J_{H,H}$ = 16.3 Hz, O$_2$C–CH*H'*), 2.53 (br. d, 2H, $^2J_{H,H}$ = 16.3 Hz, O$_2$C–C*H*H'), 2.05 (br, 2H, CH*H'*), 1.97 (br, 2H, C*H*H'), 1.73 (br, 6H, CH$_{3(meso)}$), 1.14 (br, 6H, CH$_{3(anti)}$); ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8): major species in solution: δ 183.7 (pseudo-t, 2C, COO), 135.5 (br, 4C, *i*-C Ph), 134.6 (pseudo-t, 4C, CH Ph), 133.3 (pseudo-t, 4C, CH Ph), 130.1 (br s, 4C, CH Ph), 128.9 (pseudo-t, 4C, CH Ph), 128.8 (br, 4C, CH Ph), 128.5 (pseudo-t, 4C, CH Ph), 115.5 (s, 2C, C–CH$_{3(meso)}$), 83.0 (pseudo-t, 2C, C–CH$_{3(anti)}$), 48.1 (s, 2C, CH$_2$ allyl), 44.6 (s, 2C, O$_2$C–CH_2), 28.1 (t, $^1J_{C,P}$ = 6.5 Hz, 1C, PCH$_2$P), 23.4 (s, 2C, CH$_3$), 20.2 (s, 2C, CH$_3$); ^{31}P{^{1}H} NMR (162.0 MHz, THF-d_8): major species: δ 13.0 (s). Suitable crystals for X-ray diffraction analysis were obtained by cooling the mother liquor of the reaction from ambient temperature to –20 °C.

Synthesis of [(dcpm)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] (4)

Solid dcpm (264 mg, 0.65 mmol) was added in one portion to a stirred red solution of [(tmeda)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] (193 mg, 0.64 mmol) in THF (15 mL) at ambient temperature. After 5 min of stirring, the resulting brownish red reaction mixture was reduced to half of its original volume and stored for 3 days at –20 °C. Thereafter, a compact layer of a red solid had formed at the wall of the Schlenk tube. This crude product (237 mg) was isolated by decantation and dried in a vacuum. Afterwards it was suspended in heptanes (5 mL) and THP was slowly added until a clear solution was observed (the amount of THP necessary slightly varies from batch to batch). Storage of the resulting solution at –40 °C for one week resulted in the formation of **4**·THP as an amorphous orange red solid. The compound was isolated by filtration and dried in a vacuum. Prolonged drying was necessary to remove the co-crystallized THP. Yield: 169 mg (44%). Anal. Calcd. for C$_{32}$H$_{56}$NiO$_2$P$_2$ (593.407): C, 64.77; H, 9.51; found: C, 64.83; H, 9.74; selected IR (ATR): ṽ = 1599 (s, $v_{as,COO}$); Compound **4** decomposes in THF-d_8 at ambient temperature; ^{31}P{^{1}H} NMR (162.0 MHz, THF-d_8): δ –11.5 (s, *), 10.6 (br s, compound **4**, major species), 15.1 (s, *), 31.0 (s, *), 31.3 (s, *) + further minor signals (* = unidentified product). Selected ^{13}C{^{1}H} NMR data (100.6 MHz, THF-d_8): nickelalactone moiety of **4**: δ 183.7 (pseudo-t, 1C, COO), 115.6 (s, 1C, C–CH$_{3(meso)}$), 88.7 (pseudo-t, 1C, C–CH$_{3(syn)}$), 43.8 (s, 1C, CH$_2$) 42.2 (s, 1C, CH$_2$ allyl), 22.2 (s, 1C, CH$_3$), 20.5 (s, 1C, CH$_3$). Suitable crystals of **4**·MeOH for X-ray diffraction analysis were obtained by cooling a solution of **4** in a mixture of heptanes, THF and a few drops of methanol from ambient temperature to –20 °C.

Synthesis of [(dcpe)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] (5)

Solid dcpe (561 mg, 1.33 mmol) was added in one portion to a stirred red solution of [(tmeda)Ni{CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$COO}] (380 mg, 1.27 mmol) in THF (30 mL) at ambient temperature. Immediately after dissolution of all solids, the resulting dark red reaction mixture was cooled to 0 °C and stored for twelve hours at this temperature. The red crystals of **5**·0.5THF formed were isolated by filtration and dried in a vacuum. The compound slowly lost the co-crystallized THF upon prolonged drying.

Yield: 366 mg (47%). Anal. Calcd. for $C_{33}H_{58}NiO_2P_2$ (607.47): C, 65.25; H, 9.62; found: C, 64.71; H, 9.73; selected IR (ATR): $\tilde{v} = 1607$ (m, $v_{as,COO}$), 1584 cm^{-1} (s, $v_{as,COO}$); $^{31}P\{^1H\}$ NMR (242.9 MHz, THF-d_8, CO_2 atmosphere): δ 74.0 (s, 1P), 63.8 (s, 1P). The crystals obtained directly from the reaction mixture were used to determine the structural motif of **5** *via* X-ray diffraction experiments.

Formation of [(dcpe)$_2$Ni] (6) and [(dcpe)Ni{η^2-CH$_2$C(CH$_3$)C(CH$_3$)CH$_2$}] (7)

Complex **5** (274 mg, 0.45 mmol) was dissolved in THF (12 mL). The resulting solution was heated to 40 °C for 30 minutes. Afterwards, the solvent was removed *in vacuo* leaving a solidifying foam behind. This residue was taken up in acetone (10 mL) leading to precipitation of a yellow substance. The solid was isolated by filtration and dried in a vacuum. Yield: 133 mg [crude product, mixture of **6** (minor component) und **7** (major component)]. Analytical data of **6**: ^1H NMR (600.1 MHz, THF-d_8, 298 K): δ 2.21 (br, 8H, CH Cy), 1.90–1.05 (m, 88H, CH$_2$ dcpe); $^{13}C\{^1H\}$ NMR (150.9 MHz, THF-d_8, 298 K): δ 38.8 (br, 8C, CH Cy), 30.9 (br, 8C, CH$_2$ Cy), 29.1 (s, 8C, CH$_2$ Cy), 28.8 (s, 8C, CH$_2$ Cy), 28.6 (s, 8C, CH$_2$ Cy), 27.5 (s, 8C, CH$_2$ Cy), 22.5 (m, 4C, P–CH$_2$); $^{31}P\{^1H\}$ NMR (242.9 MHz, THF-d_8, 298 K): δ 43.7(s). Analytical data of **7**: ^1H NMR (600.0 MHz, THF-d_8, 298 K): δ 3.00 (s, 2H, =CHH'), 2.97 (s, 2H, =CHH'), 1.60-1.90 (m, 32H, CH Cy + CH$_2$ Cy + CH$_3$ dmbd), 1.53 (m, 4H, P-CH$_2$), 1.35-1.15 (m, 18H, CH$_2$ Cy); $^{13}C\{^1H\}$ NMR (150.9 MHz, THF-d_8, 298K): δ 105.7 (br, 2C, =C<), 66.4 (br, 2C, =CH$_2$), 36.0 (dd, $^1J_{C,P}$ = 13.8 Hz, $^4J_{C,P}$ = 4.6 Hz, 4C, P–CH), 29.9 (d, $J_{C,P}$ = 4.6 Hz, 4C, CH$_2$ Cy), 29.7 (s, 4C, CH$_2$ Cy), 28.03 (d, $J_{C,P}$ = 8.3 Hz, 4C, CH$_2$ Cy), 27.97 (d, $J_{C,P}$ = 5.7 Hz, 4C, CH$_2$ Cy), 27.2 (s, 4C, CH$_2$ Cy), 24.6 (s, 2C, CH$_3$ dmbd), 22.4 (pseudo-t, 2C, P–CH$_2$); $^{31}P\{^1H\}$ NMR (162.0 MHz, THF-d_8, 298 K): δ 65 (very br, 1P), 50 (very br, 1P); $^{31}P\{^1H\}$ NMR (162.0 MHz, THF-d_8, 253 K): δ 67.8 (br d, $^2J_{P,P}$ = 61.2 Hz, 1P), 47.9 (d, $^2J_{P,P}$ = 63.2 Hz, 1P). Suitable crystals of **6** for X-ray diffraction experiments were obtained during the attempted synthesis of **5** at ambient temperature directly from the reaction mixture. In case of **7,** crystals were obtained by recrystallization (ambient temperature to –20°) of the crude product in THF (**7**·0.5THF) or THP.

Synthesis of [(dcpe)Ni(cod)] (8)

Solid dcpe (406 mg, 0.96 mmol) was added in one portion to a stirred yellow solution of [Ni(cod)$_2$] (264 mg, 0.96 mmol) in THF (10 mL) at ambient temperature. After dissolution of the dcpe the yellow reaction mixture was stored for two days at –10 °C. Afterwards, the formed big bright yellow crystals of **8**·THF were isolated by decantation, washed with heptanes (5 mL) and briefly dried in a vacuum. Yield: 545 mg (86%). Anal. Calcd. for $C_{38}H_{68}NiOP_2$ (661.60): C, 68.99; H, 10.36; found: C, 69.06; H, 10.40; ^1H NMR (600.1 MHz, THF-d_8): δ 4.07 (br, 4H, CH cod), 3.62 (m, 4H, OCH$_2$ THF), 2.36 (m, 4H, CHH' cod), 2.12 (m, 4H, CHH' cod), 1.89-1.64 (m, 28H, CH$_2$ THF+CH/CH$_2$ Cy), 1.41 (m, 4H, P–CH$_2$), 1.33-1.16 (m, 20H, CH$_2$ Cy); $^{13}C\{^1H\}$ NMR (150.9 MHz, THF-d_8): δ 79.3 (pseudo-t, 4C, CH cod), 68.0 (s, 2C, OCH$_2$ THF), 36.1 (pseudo-t, 4C, CH Cy), 32.8 (pseudo-t, 4C, CH$_2$ cod), 29.9 (pseudo-t, 4C, CH$_2$ Cy), 28.4 (s, 4C, CH$_2$ Cy), 28.2 (pseudo-t, 4C, CH$_2$ Cy), 28.1 (pseudo-t, 4C, CH$_2$ Cy), 27.5 (s, 4C, CH$_2$ Cy), 26.2 (s, 2C, CH$_2$ THF), 21.4 (pseudo-t, 2C, P–CH$_2$); $^{31}P\{^1H\}$ NMR (162.0 MHz, THF-d_8): δ 59.9 (s).

Structure Determinations

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects[26,27].

The structures were solved by direct methods (SHELXS)[28] and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97)[28]. The hydrogen atoms of compound **7** (except of the methyl group at C6) and **8** (except of the hydrogen atoms of the co-crystallized thf molecule) as well as the hydrogen atoms bound to C1 and C4 of **7**·0.5THF were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. The crystal of **3** was a non-merohedral twin. The twin law was determined by PLATON[29] to (–1.0/0.0/0.0) (0.0/–1.0/0.0) (–0.485/–0.815/1.0). The contribution of the main component was refined to 0.302(3). The crystals of **1** and **6** contain large voids, filled with disordered solvent molecules. The size of the voids are 615 Å^3/unit cell (**1**) and 161 Å^3/unit cell (**6**), respectively. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON,[29] resulting in 97 electrons/unit cell (**1**) and 20 electrons/unit cell (**6**), respectively.

The crystals of **5** were extremely thin and of low quality, resulting in a substandard data set. However, the structure is sufficient to show connectivities and geometry despite the high final R value. We will only publishing the conformation of compound **5** and its crystallographic data. We will not deposit the data of **5** in the Cambridge Crystallographic Data Centre.

All non-disordered, non-hydrogen atoms were refined anisotropically.[28] Crystallographic data as well as structure solution and refinement details are summarized in Table 3. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Dalton Transactions

ARTICLE TYPE

Table 3 Crystal data and refinement details for the X-ray structure determinations of the compounds **1–5.**

Compound	1	2	3	4	5
formula	$C_{16}H_{26}N_2NiO_2$	$C_{28}H_{35}N_2NiO_2P$	$C_{39}H_{42}Ni_2O_4P_2$, $C_4H_{10}O$	$C_{32}H_{56}NiO_2P_2$, CH_4O	$C_{33}H_{58}NiO_2P_2$, 0.5 C_4H_8O
fw /g·mol^{-1}	337.10[a]	521.26	828.21	625.46	643.50
T/°C	−140(2)	−140(2)	−140(2)	−140(2)	−140(2)
crystal system	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic
space group	I m a 2	P 2$_1$/n	P $\bar{1}$	P 2$_1$/n	P 2$_1$/c
a/Å	28.090(2)	13.8132(5)	10.9306(3)	9.6594(4)	11.1546(11)
b/Å	13.7216(9)	12.2553(4)	11.3308(3)	32.5695(15)	34.917(3)
c/Å	10.9264(7)	14.9680(4)	18.4592(5)	10.9054(5)	9.3693(8)
α/°	90	90	72.221(1)	90	90
β/°	90	97.186(2)	76.133(1)	101.745(1)	95.371(3)
γ/°	90	90	67.433(1)	90	90
V/Å^3	4211.4(5)	2513.95(14)	1990.74(9)	3359.0(3)	3633.2(6)
Z	8	4	2	4	4
ρ/g·cm^{-3}	1.063[a]	1.377	1.382	1.237	1.176
μ/cm^{-1}	9.33[a]	8.64	10.70	7.03	6.51
measured data	4286	24526	7238	16775	11475
data with I > 2σ(I)	3643	4441	6342	5704	4494
unique data (R$_{int}$)	4286/0.0491	5761/0.0426	7238/0.0626	6726/0.0492	6681/0.0765
wR_2 (all data, on F^2)[b]	0.2185	0.1194	0.2196	0.1642	0.4215
R_1 (I > 2σ(I))[b]	0.0802	0.0516	0.0971	0.0774	0.1601
S[c]	1.045	1.047	1.231	1.130	1.110
Res. dens./e·Å^{-3}	1.104/−1.199	0.656/−0.413	1.315/−1.127	1.371/−0.680	1.667/−0.790
Flack-parameter	0.097(15)	–	–	–	–
CCDC No.	1002896	1002897	1002898	1002899	motif

cont. Table 3 Crystal data and refinement details for the X-ray structure determinations of the compounds **6–8.**

Compound	6	7	7·0.5THF	8
formula	$C_{52}H_{96}NiP_4$	$C_{32}H_{58}NiP_2$	$C_{32}H_{58}NiP_2$, 0.5 C_4H_8O	$C_{34}H_{60}NiP_2$, C_4H_8O
fw /g·mol^{-1}	903.88[a]	563.43	599.49	661.57
T/°C	−140(2)	−140(2)	−140(2)	−140(2)
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	P 2/n	P $\bar{1}$	P $\bar{1}$	P 2$_1$/n
a/Å	13.2538(3)	10.1055(3)	10.5810(2)	11.7198(2)
b/Å	9.9914(2)	11.0712(3)	12.3040(2)	20.4120(3)
c/Å	21.0848(3)	14.8446(4)	13.7385(2)	15.3870(2)
α/°	90	104.247(2)	97.923(1)	90
β/°	103.144(1)	92.999(1)	106.776(1)	100.370(1)
γ/°	90	103.896(2)	101.793(1)	90
V/Å^3	2718.98(9)	1551.63(8)	1638.94(5)	3620.75(9)
Z	2	2	2	4
ρ/g·cm^{-3}	1.104[a]	1.206	1.215	1.214
μ/cm^{-1}	5.05[a]	7.47	7.12	6.52
measured data	6212	9680	11318	27930
data with I > 2σ(I)	5382	6124	6759	7490
unique data (R$_{int}$)	6212/0.0305	6983/0.0221	7307/0.0214	8240/0.0271
wR_2 (all data, on F^2)[b]	0.1793	0.1065	0.1873	0.0801
R_1 (I > 2σ(I))[b]	0.0640	0.0505	0.0606	0.0318
S[c]	1.052	1.135	1.097	1.053
Res. dens./e·Å^{-3}	2.156/−0.802	0.950/−0.607	1.777/−1.161	0.461/−0.699
CCDC No.	1002900	1002901	1002902	1002903

[a] Derived parameters do not contain the contribution of the disordered solvent. [b] Definition of the R indices: $R_1 = (\Sigma ||F_o| - |F_c||)/\Sigma |F_o|$;

$_5$ w$R_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \text{Max}(F_o^2)]/3$. [c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

Acknowledgement

References

[a] Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University Jena, Am Steiger 3 Haus 4, D-07743 Jena, Germany. Fax: $_{15}$ +4936419132; Tel: +493641948126; E-mail: j.langer@uni-jena.de

† Electronic Supplementary Information (ESI) available: NMR spectra of **1**, **6** and **8**, ^{31}P NMR spectra of **7** used for the determination of the coalescence temperature and ORTEP plots of **6** and **8**. Crystallographic data (excluding structure factors) has been deposited with the Cambridge

Dalton Transactions Accepted Manuscript

1 for a review see: (a) W. Leitner, *Coord. Chem. Rev.*, 1996, **153**, 257–284; (b) X. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27–59; (c) M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975–2992; (d) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kühn, *Angew. Chem. Int. Ed.*, 2011, **50**, 8510–8537; (e) K. Huang, C.-L. Sun and Z.-J. Shi, *Chem. Soc. Rev.*, 2011, **40**, 2435–2452.

2 (a) A. Behr and K.-D. Juszak, *J. Organomet. Chem.*, 1983, **255**, 263–268; (b) A. Behr, K.-D. Juszak and W. Keim, *Synthesis*, 1983, **7**, 574.

3 (a) A. Behr and U. Kanne, *J. Organomet. Chem.*, 1986, **309**, 215–223; (b) P. Braunstein, D. Matt and D. Nobel, *J. Am. Chem. Soc.*, 1988, **110**, 3207–3212; (c) E. Dinjus and W. Leitner, *Appl. Organometal. Chem.*, 1995, **9**, 43–50; (d) N. Holzhey, S. Pitter and E. Dinjus, *J. Organomet. Chem.*, 1997, **541**, 243–248; (e) A. Behr and M. Becker, *Dalton Trans.*, 2006, 4607–4613; (f) Y. Dai, X. Feng, B. Wang, R. He and M. Bao, *J. Organomet. Chem.*, 2012, **696**, 4309–4314.

4 (a) D. Walther and E. Dinjus, *Z. Chem.*, 1982, **22**, 228–229; (b) D. Walther, E. Dinjus, J. Sieler, N. N. Thanh, W. Schade and I. Leban, *Z. Naturforsch.*, 1983, **38b**, 835–840; (c) H. Hoberg, D. Schaefer and B. W. Oster, *J. Organomet. Chem.*, 1984, **266**, 313–320.

5 (a) H. Hoberg and B. Apotecher, *J. Organomet. Chem.*, 1984, **270**, C15-C17; (b) R. Fischer, D. Walther, G. Bräunlich, B. Undeutsch, W. Ludwig and H. Bandmann, *J. Organomet. Chem.*, 1992, **427**, 395–407; (c) G. Bräunlich, D. Walther, H. Eibisch and B. Schönecker, *J. Organomet. Chem.*, 1993, **453**, 295–298; (d) M. Takimoto and M. Mori, *J. Am. Chem. Soc.*, 2001, **123**, 2895–2896.

6 (a) D. Walther, E. Dinjus, H. Görls, J. Sieler, O. Lindqvist and L. Andersen, *J. Organomet. Chem.*, 1985, **286**, 103–113; (b) P. S. Schulz, O. Walter and E. Dinjus, *Appl. Organometal. Chem.*, 2005, **19**, 1176–1179; (c) J. Langer, D. Walther and H. Görls, *J. Organomet. Chem.*, 2006, **691**, 4874–4881.

7 J. Langer, R. Fischer, H. Görls and D. Walther, *J. Organomet. Chem.*, 2004, **689**, 2952–2962.

8 (a) H. Hoberg, D. Schaefer, G. Burkhart, C. Krüger and M. J. Romão, *J. Organomet. Chem.*, 1984, **266**, 203-224; (b) H. Hoberg, Y. Peres, C. Krüger and Y.-H. Tsay, *Angew. Chem Int. Ed. Engl.*, 1987, **26**, 771–773; (c) R. Fischer, J. Langer, A. Malassa, D. Walther, H. Görls and G. Vaughan, *Chem. Commun.*, 2006, 2510–2512.

9 (a) G. Burkhart and H. Hoberg, *Angew. Chem.*, 1982, **94**,75; (b) D. Walther, G. Bräunlich, R. Kempe and J. Sieler, *J. Organomet. Chem.*, 1992, **436**, 109-119; (c) J. Langer, M. Gärtner, H. Görls and D. Walther, *Synthesis*, 2006, 2697-2706; (d) J. Langer, H. Görls and D. Walther, *Polyhedron*, 2012, **32**, 60–67.

10 P. Schulz, *Wissenschaftliche Berichte - Forschungszentrum Karlsruhe*, 2002, FZKA 6785, 1–146.

11 D. Walther and E. Dinjus, *Z. Chem.*, 1984, **24**, 63.

12 J. Langer, H. Görls, G. Gillies and D. Walther, *Z. Anorg. Allg. Chem.*, 2005, **631**, 2719–2726.

13 M. O'Reilly, R. Pattacini and P. Braunstein, *Dalton Trans.*, 2009, 6092–6095.

14 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349–1356.

15 (a) B. Hipler, M. Döring, C. Dubs, H. Görls, T. Hübler and E. Uhlig, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1329–1335.

16 (a) X. L. R. Fontaine, S. J. Higgins, B. L. Shaw, M. Thornton-Pett and W. Yichang, *J. Chem. Soc., Dalton Trans.*, 1987, 1501-1507; (b) L. Manojlovic-Muir, H. A. Mirza, N. Sadiq and R. J. Puddephatt, *Inorg. Chem.*, 1993, **32**, 117-119; (c) J. D. Heise, J. J. Nash, P. E. Fanwick and C. P. Kubiak, *Organometallics*, 1996, **15**, 1690-1696; (d) J. Langer, R. Fischer, H. Görls and Dirk Walther, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2008, **64**, m412; (e) J. Langer, H. Görls and M. Westerhausen, *Inorg. Chem. Commun.*, 2010, **13**, 488–490; (f) A. Sousa-Pedrares, J. A. Viqueira, J. Antelo, E. Labisbal, J. Romero, A. Sousa, O. R. Nascimento and J. A. García-Vázquez, *Eur. J. Inorg. Chem.*, 2011, 2273–2287; (g) T. S. Lobana, P. Kumari, G. Hundal, R. J. Butcher, A. Castineiras and T. Akitsu, *Inorg. Chim. Acta*, 2013, **394**, 605–615.

17 J. Langer, H. Görls, R. Fischer and D. Walther, *Organometallics*, 2005, **24**, 272–279.

18 J. Langer, D. Walther, A. Malassa, M. Westerhausen and H. Görls, *Eur. J. Inorg. Chem.* 2010, 275–281.

19 D. Jin, P. G. Williard, N. Hazari and W. H. Bernskoetter, *Chem. Eur. J.*, 2014, **20**, 3205–3211.

20 (a) P. Mastrorilli, G. Moro, C. F. Nobile and M. Latronico, *Inorg. Chim. Acta*, 1992, **192**, 183–187; b) A. Sacco and P. Mastrorilli, *J. Chem. Soc., Dalton Trans.*, 1994, 2761–2764.

21 (a) W. Schröder and K.-R. Pörschke, *J. Organomet. Chem.*, 1987, **322**, 385–392; (b) R. Benn, P. Betz, R. Goddard, P. W. Jolly, N. Kokel, C. Krüger and I. Topalović, *Z. Naturforsch.*, 1991, **46b**, 1395–1405; (c) K.-R. Pörschke, C. Pluta, B. Proft, F. Lutz and C. Krüger, *Z. Naturforsch.*, 1993, **48b**, 608–626; (d) E. Dreher, B. Gabor, P. W. Jolly, C. Kopiske, C. Krüger, A. Limberg and R. Mynott, *Organometallics*, 1995, **14**, 1893–1900.

22 This compound was mentioned earlier, but no analytical data was reported: (a) H. Schwager, C. Krueger, R. Neidlein and G. Wilke, *Angew. Chem.*, 1987, **99**, 72-73; (b) R. Benn, P. W. Jolly, T. Joswig, R. Mynott and K. P. Schick, *Z. Naturforsch.*, 1986, **41b**, 680-691.

23 M. Martín, O. Torres, E. Oñate, E. Sola and L. A. Oro, *J. Am. Chem. Soc.*, 2005, **127**, 18074–18084.

24 S. Ogoshi, K.-I. Tonomori, M.-A. Oka and H. Kurosawa, *J. Am. Chem. Soc.*, 2006, **128**, 7077–7086.

25 B. Bogdanović, M. Kröner and G. Wilke, *Justus Liebigs Ann. Chem.*, 1966, **699**, 1–23.

26 R. Hooft, *COLLECT DataCollection Software for Nonius KappaCCD*, Nonius B. V., Delft, The Netherlands, 1998.

27 Z. Otwinowski and W. Minor, in *Methods in Enzymology*, eds. C. W. Carter and R. M. Sweet, Academic Press, 1997, vol. 276, pp. 307–326.

28 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.

29 A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2009, **65**, 148–155.

Dalton Transactions

For Table of Contents Entry only:
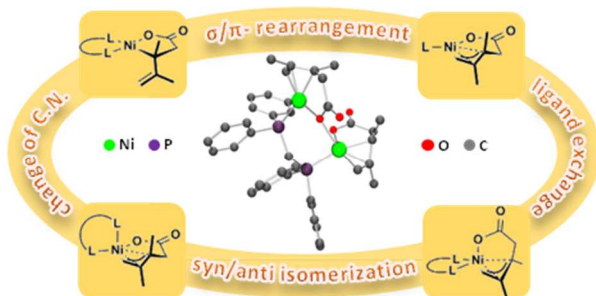
Nickelalactone derivatives with allyl subunit with different mono- and bidentate ligands were synthesized and characterized. The introduced neutral ligands strongly affect the structures of these versatile molecules and can be used to modulate their stabilities.