

Saturated and unsaturated nickelalactones with N-heterocyclic carbene ligands: Synthesis and structures

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Abstract

Monomeric and dimeric nickelalactones with N-heterocyclic carbene ligands [(py)(im^{mes})Ni(CH₂CH₂COO)] (**1**), [(im^{mes})Ni(CH₂CH₂COO)]₂ (**2**), [(im^{t-but})Ni(C(Et)=C(Et)-COO)]₂ (**3**), [(im^{mes})Ni(C(Et)=C(Et)-COO)]₂ (**4**), and [(im^{mes})Ni(CH₂-C(CH₃)-C(CH₃)-CH₂-COO)] (**5**) (im^{mes}: 1,3-dimesitylimidazol-2-ylidene; im^{t-but}: 1,3-di-*t*-butylimidazol-2-ylidene) were synthesized and investigated by ¹H, ¹³C NMR and IR spectroscopic measurements. The solid-state structures of **1–3** and **5** were also elucidated by X-ray diffraction analyses of single crystals. In the compounds the Ni(II) ion has square-planar geometry. The metal centers in the dimers **2** and **3** are bridged by two endocyclic oxygen donor atoms of the carboxylate groups resulting in Ni₂O₂-four-membered rings. Reaction of [(im^{mes})Ni] with 2,3-dimethylbutadiene and CO₂ resulted in an oxidative coupling of the two dienes followed by insertion of CO₂ to form the dimeric complex **6**. The X-ray structure of **6** shows two substituted heptenoic acid dianions which connect the two Ni(II) centers. Each nickel atom is surrounded by a η³-allyl group, a monodentate carboxylate group and an im^{mes} ligand.

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1. Introduction

Nickelalactones (“nickelacyclic carboxylates”) are interesting organometallic building blocks for the organic synthesis of a variety of functionalized organic compounds [1–6] and for the self-organization to form nickelamacrocycles of different ring size [7]. Furthermore, they are discussed as possible intermediates in a hypothetical catalytic cycle to form acrylic acid from CO₂ and ethylene [8–11] and are suggested to be formed as intermediates in the catalytic formation of 2-pyrones from CO₂ and alkynes [12–15]. To date only nickelalactones with N-donor ligands or phosphines are known. In spite of the extraordinary properties of N-heterocyclic carbenes (NHCs) as stabilizing ligands for organometallics and as ancillary ligands for metal catalyzed reactions (for recent reviews see [16–19]) we were interested in investigating the hitherto unknown

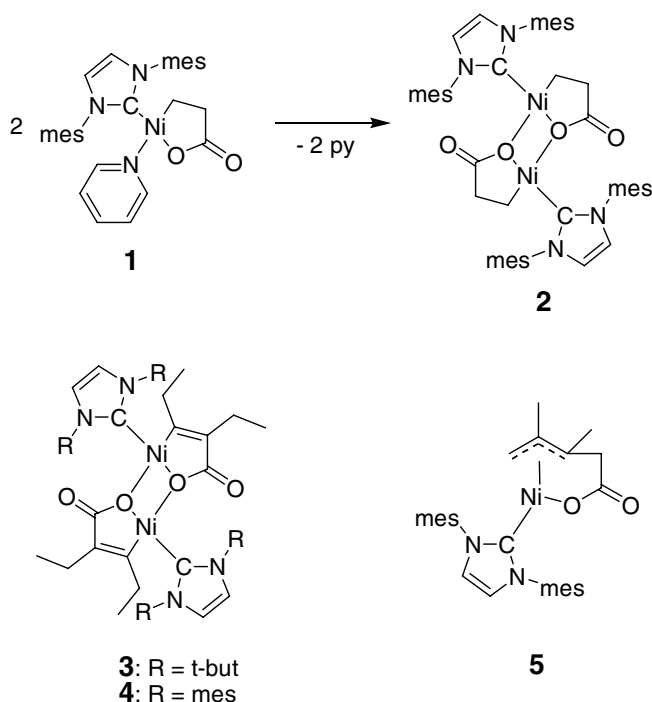
NHC-supported nickelalactones. We report herein the synthesis of the first representatives of these complexes and compare their structures with those of nickelalactones containing phosphine or N-donor ligand. This should allow gaining more information about the similarities and differences between these ligands.

2. Results and discussion

The simplest way to prepare the NHC-stabilized nickelalactones **1–5** (Scheme 1) was found to be the displacement of pyridine in pyridine-supported nickelalactones [2] by NHC's. To generate the complexes **1** and **2**, [(py)₂Ni(C₂H₄COO)] was reacted with one eq. 1,3-dimesitylimidazol-2-ylidene (im^{mes}) in THF. The pyridine ligand could easily be replaced in a stepwise reaction. In the first step one pyridine ligand was substituted by the NHC resulting in the yellow mixed ligand complex **1** which was isolated in good yields as sparingly soluble product (Scheme 1). Its elemental analyses confirmed the composition [(im^{mes})(py)Ni(C₂H₄COO)]

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Scheme 1. The NHC complexes 1–5.

and its IR spectrum showed a strong $\nu_{as}(\text{C}=\text{O})$ band at 1617 cm^{-1} which is typical for a mononuclear nickelalactone. In principle, this exchange reaction could result in two geometric isomers, different in the positions of the carbene and pyridine ligands (*trans* or *cis* to the oxygen donor atom); however it was found that only one isomer was formed. The structure motif of **1** determined by X-ray crystallographic analysis (not depicted) undoubtedly confirmed that in **1** the NHC ligand adopts the *trans* position to the coordinated oxygen atom of the monodentate carboxylate group (Scheme 1); however the insufficient quality of the crystals prevented detailed information about bond lengths and angles. It is noteworthy that related mixed pyridine phosphine complexes form the same type of regioisomers [7].

^1H NMR spectroscopic investigations in $[D_7]\text{DMF}$ at 25°C showed that the pure complex **1** is in equilibrium with a second complex **2** which resulted from the elimination of the pyridine ligand.

The signals of complex **1** at 0.15 ppm (t, $^3J = 7.2$ Hz) and 1.58 ppm (t, $^3J = 7.2$ Hz) were assigned to the $\text{CH}_2\text{—CH}_2$ unit of the organometallic ring. In addition, coordinated NHC gave rise to the resonances at 2.24 (*o*- CH_3 mes), 2.40 (*p*- CH_3 mes), 7.18 (*m*-CH mes) and 7.48 ppm (CH). The coordinated pyridine ligand resonated at 7.14 (*m*-CH), 7.71 (*p*-CH) and 8.04 ppm (*o*-CH).

The second complex **2** showed a similar pattern for the coordinated NHC ligand (2.24 (*o*- CH_3 mes), 2.42 (*p*- CH_3 mes), 7.18 (*m*-CH mes) and 7.48 ppm) whereas the $\text{CH}_2\text{CH}_2\text{—}$ unit was more high-field shifted with signals at 0.00 (t, $^3J = 7.2$ Hz) and 1.46 ppm (t, $^3J = 7.2$ Hz). Furthermore uncoordinated pyridine was indicated by its typ-

ical signals at 7.40, 7.81 and 8.61 ppm. Also the ^{13}C NMR spectrum exhibited the two signal sets for **1** and **2** (see Section 4).

The pure complex **2** was isolated by reaction of the starting complex $[(\text{py})_2\text{Ni}(\text{C}_2\text{H}_4\text{COO})]$ with the NHC ligand in DMF followed by distillation of the solvent under reduced pressure, dissolution of the remaining orange oil in diethyl ether and crystallization of the compound. Its ^1H NMR spectrum was identical with the ^1H NMR pattern of the complex formed by pyridine elimination from **1** in solution. Single crystals suitable for an X-ray crystallographic analysis were grown from diethyl ether. Fig. 1 shows the molecular structure and lists relevant bond lengths and angles in the caption.

Complex **2** is a dimer of the composition $[(\text{im}^{\text{mes}})\text{Ni}(\text{C}_2\text{H}_4\text{COO})]_2$ and contains two nickel centers in a square-planar environment. Both nickel atoms are bridged via two endocyclic oxygen donor atoms of the carboxylate groups resulting in a Ni_2O_2 four-membered ring. Bond lengths and angles lie within the usual range of nickelacyclic compounds [2,4,7]. As expected, the Ni–C–carbene bond of 1.845(3) Å is significantly shorter than the Ni–C bond of the nickelalactone unit (1.908(3) Å).

It is interesting to note that related mixed pyridine phosphine nickelalactones can eliminate pyridine as well; however in this case nickelamacrocycles of varying ring size are formed, depending on the bulkiness of the phosphine used [7]. Phosphines with bulky groups reacted under formation of cyclic tetramers using the exocyclic oxygen atom of the carboxylate group as bridging group. In contrast to the above NHC stabilized dimeric nickelalactons dimers

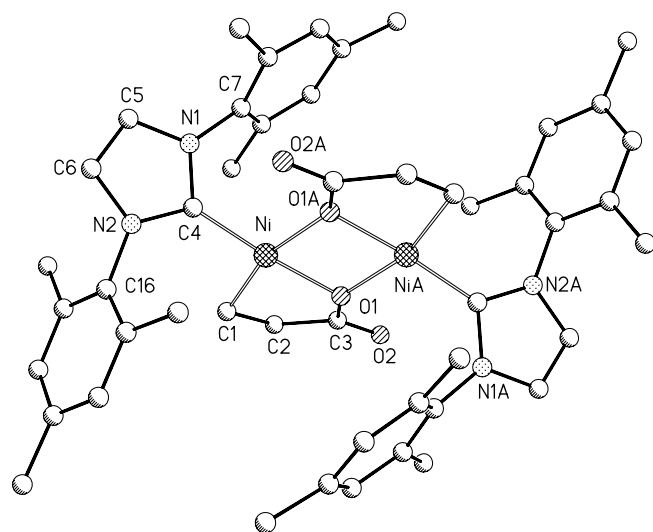


Fig. 1. X-ray structure of complex **2** (H-atoms are omitted for clarity). Selected bond distances (Å) and bond angles ($^\circ$): Ni–O1 1.909(2), Ni–O1A 1.971(2), Ni–C1 1.908(3), Ni–C4 1.844(3), C1–C2 1.524(4), C2–C3 1.516(4), C3–O1 1.321(3), C3–O2 1.219(3), C4–N1 1.366(4), C4–N2 1.369(3), N1–C5 1.389(4), N1–C7 1.446(4), N2–C6 1.393(4), N2–C16 1.443(4), C5–C6 1.340(4), C4–Ni–O1A 102.4(1), C4–Ni–C1 94.2(1), C4–Ni–O1 172.1(1), O1A–Ni–C1 163.2(1), O1A–Ni–O1 78.4(1), C1–Ni–O1 85.5(1), Ni–O1–NiA 101.60(9). Symmetry transformation used to generate equivalent atoms: A: $-X + 2, -Y + 1, -Z$.

containing phosphine ligands have never been isolated. This shows that the rules found for the structures of phosphine-containing nickelamacrocycles [7] cannot be transferred to NHC containing nickelalactones which have different ligand geometry.

As shown in Scheme 1 not only saturated NHC-nickelalactones can be synthesized but also compounds containing an unsaturated nickelalactone ring. The reaction with the ligand $\text{im}^{t\text{-but}}$ (1,3-di-*t*-butylimidazol-2-ylidene) resulted in the formation of the dimeric complex **3** in which the same type of bridging was found as in the saturated nickelalactones. However, monomeric nickelalactones with NHC ligands, postulated as intermediate in the homogeneous catalytic reaction of carbon dioxide and diines [14,15], were not isolated. Fig. 2 shows the X-ray structure of single crystals of **3** grown from DMF.

As expected, the bond length C1–C2 (1.354(5) Å) in the unsaturated nickelalactone **3** is significantly shorter than the bond length C1–C2 (1.525(4) Å) in the saturated complex **1**. $[(\text{py})_2\text{Ni}(\text{C}(\text{Et})=\text{C}(\text{Et})-\text{COO})]$ reacted also with im^{mes} to form the nickelalactone **4** which has the same composition and very similar spectral properties as found for **3**. Therefore, **4** may also have a dimeric structure. For example, the expected seven signals for the carbons of the metalacyclic ring appeared in the ^{13}C NMR spectrum, assigned to two signals of the CH_3 groups, two resonances of the CH_2 groups, two resonances of the $\text{C}=\text{C}$ carbons and one signal belonging to the carboxylate carbon. Also, all resonances for the carbene ligand were found.

In connection with the catalytic formation of 2-pyrones via an unsaturated nickelalactone, stabilized by NHCs, we suggest that dimeric carbene-stabilized nickelalactones may play an important role during the catalytic cycle. Even if an additional equivalent of NHC was added to the dimeric complex **3** no monomeric derivative could be isolated. Possibly, the formation of the highly soluble dimeric complexes is crucial for this catalysis. Furthermore, it is noteworthy that monodentate phosphines which are the only other capable ligands for this type of catalysis form oligomeric nickelacyclic carboxylates [7].

Another type of unsaturated nickelalactones, complex **5**, was formed if the product of the oxidative coupling of CO_2 with 2,3-dimethyl-butadiene at the complex fragment $(\text{tmeda})\text{Ni}(0)$ in THF was reacted with im^{mes} (Scheme 1). Crystallization from diethyl ether resulted in orange crystals containing diethyl ether which was partially eliminated by drying. The X-ray analysis of **5** is displayed in Fig. 3 and contains relevant bond lengths and angles in the caption. Nickel has a slightly disordered square planar geometry and the bond lengths and angles lie within typical values. The most interesting feature is that **5** is a monomeric compound with a η^3 -allyl group occupying two coordination positions. Since in the crystals of **5** there are two enantiomers the allyl groups are disordered.

The ^1H NMR spectrum of **5** in $[D_8]\text{THF}$ at room temperature is in agreement with the structure found in the solid state. Two resonances for both the *meta* protons (at

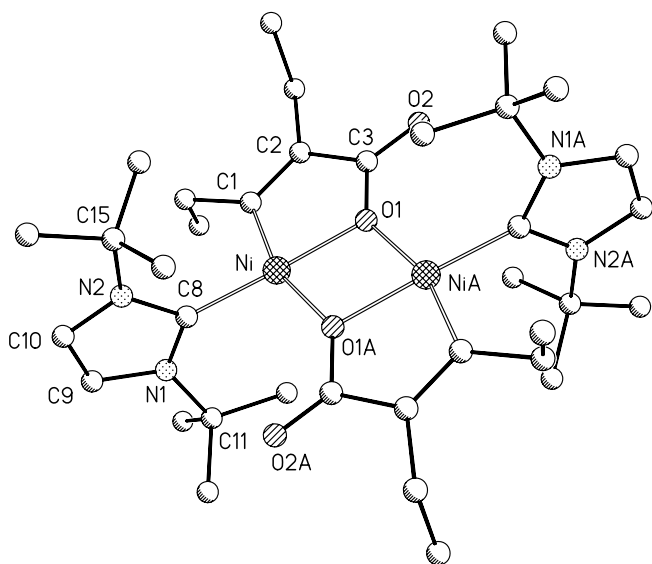


Fig. 2. X-ray structure of complex **3** (H-atoms are omitted for clarity). Selected bond distances (Å) and bond angles ($^\circ$): Ni–O1 1.890(2), Ni–O1A 1.960(2), Ni–C1 1.890(4), Ni–C8 1.859(3), C1–C2 1.354(5), C2–C3 1.482(5), C3–O1 1.327(4), C3–O2 1.220(4), C8–N1 1.368(4), C8–N2 1.375(4), N1–C9 1.392(4), N1–C11 1.498(5), N2–C10 1.387(4), N2–C15 1.507(5), O1–Ni–O1A 77.5(1), O1–Ni–C1 85.2(1), O1–Ni–C8 177.6(1), O1A–Ni–C1 162.6(1), O1A–Ni–C8 102.9(1), C1–Ni–C8 94.3(1), O1–NiA–O1A 77.5(1), Ni–O1–NiA 102.5(1). Symmetry transformation used to generate equivalent atoms: A: $-X+2, -Y+2, -Z+1$.

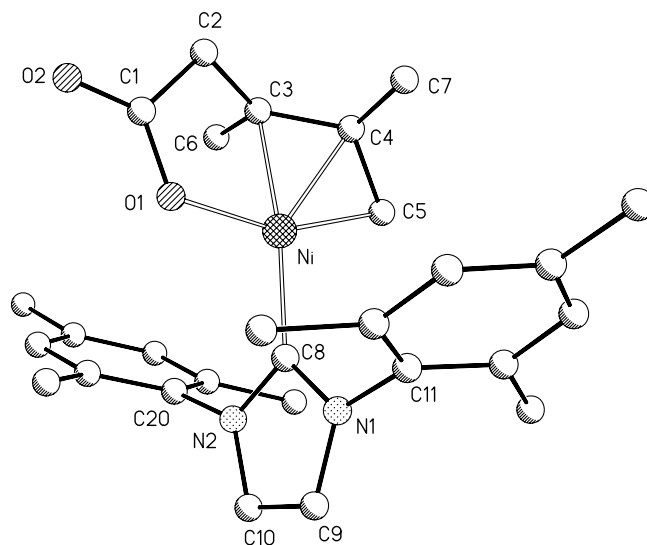


Fig. 3. X-ray structure of complex **5** (H-atoms are omitted for clarity). Selected bond distances (Å) and bond angles ($^\circ$): Ni–O1 1.917(3), Ni–C3 2.045(6), Ni–C4 1.948(6), Ni–C5 1.981(5), Ni–C8 1.892(3), C1–O1 1.297(4), C1–O2 1.221(4), C1–C2 1.539(5), C2–C3 1.428(7), C3–C4 1.465(8), C4–C5 1.492(7), C3–C6 1.507(9), C4–C7 1.421(12), C8–N1, 1.358(4), C8–N2 1.359(4), N1–C9 1.392(4), N1–C11 1.439(4), N2–C10 1.384(4), N2–C20 1.446(4), C9–C10 1.338(5), O1–Ni–C3 82.2(2), O1–Ni–C4 112.7(2), O1–Ni–C5 156.7(2), O1–Ni–C8 100.7(1), C3–Ni–C4 43.0(2), C3–Ni–C5 75.6(2), C3–Ni–C8 164.4(2), C4–Ni–C5 44.8(2), C4–Ni–C8 143.3(2), C5–Ni–C8 102.6(2). Symmetry transformation used to generate equivalent atoms: A: $-X+3, -Y+2, -Z+1$.

7.02 and 7.06 ppm) and the *ortho* methyl protons (2.08 und 2.17 ppm) of the carbene ligand were found whereas the *para* methyl protons and the two protons of the imidazole ring gave only one signal. This suggests a hindered rotation of the mesityl substituents in the coordinated NHC. The two protons of the η^3 -allyl group resonated at 1.04 and 1.72 ppm, and the protons of the two CH₂ groups appeared at 1.88 and 2.52 ppm. In addition, the chemical shifts for the methyl groups were 0.43 and 1.47 ppm. Compared with related phosphine stabilized nickelalactones, which have the same molecular structure [20] the protons of the nickelalactone ring in **5** are high-field shifted.

In order to proof the reactivity of NHC-stabilized nickel(0) complexes in oxidative coupling reactions (im_2^{mes})Ni [21] was reacted with an excess of 2,3-dimethylbuta(1,3)diene under CO₂ pressure (6 bar) in toluene at room temperature. From the reaction mixture a sparingly soluble white precipitate could be isolated which was identified as the known carboxylation product of the N-heterocyclic carbene, [$\text{im}^{\text{mes}+} - \text{CO}_2^-$] [22,23]. Upon workup the orange complex **6** crystallized. Scheme 2 shows the products formed in this reaction and the X-ray structure is displayed in Fig. 4.

Compound **6** was a dimeric compound in which the two Ni centers are connected by two bridging dianions of two substituted heptenoic acid chains. The allyl groups at the ends of these chains are η^3 -coordinated to one Ni atom, and the carboxylate groups at the other end are monodentately bound to the other nickel atom. The geometry around the metals can be described as distorted square-planar with one carbene ligand in *cis* position to the oxygen atom of the carboxylate group. Thus, the coordination sphere is comparable with that in **5** with similar bond lengths and angles, however the Ni–O bond length in **6** (1.894(2) Å), is slightly shorter than in **5** (1.917(3) Å), whereas the Ni–C3 bond length in **6** (2.131(4) Å) is remarkably elongated compared with that of complex **5** (Ni–C3 2.045(6) Å).

The ¹H NMR spectrum of **6** in [D₈]THF at room temperature is rather complicated due to dynamic processes which result in broad signals for the coordinated carbene ligands. The presence of η^3 -coordinated allyl groups was confirmed by the signals of the terminal protons at 0.74

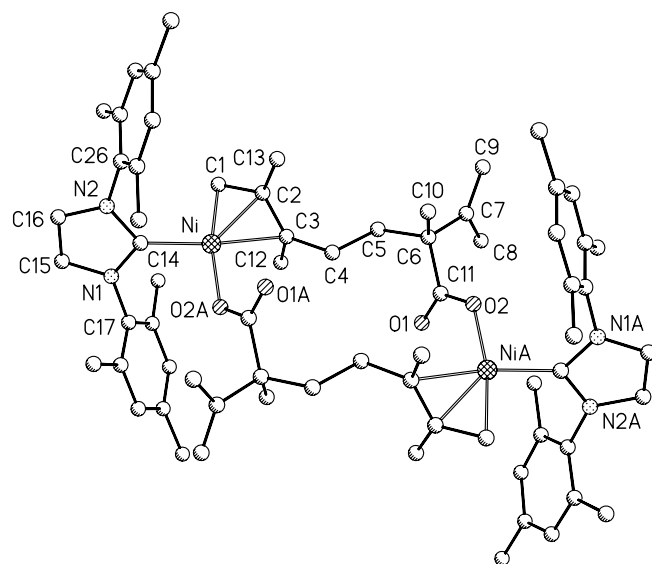
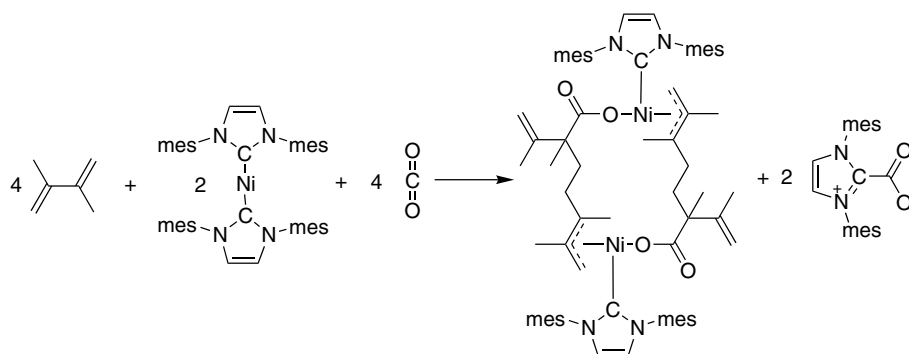


Fig. 4. X-ray structure of complex **6** (H-atoms are omitted for clarity). Selected bond distances (Å) and bond angles (°): Ni–O2A 1.894(2), Ni–C1 1.960(3), Ni–C2 1.987(3), Ni–C3 2.133(3), Ni–C14 1.902(3), C1–C2 1.413(5), C2–C3 1.374(5), C2–C13 1.529(6), C3–C4 1.517(5), C3–C12 1.529(5), C4–C5 1.535(5), C5–C6 1.548(4), C7–C8 1.416(7), C7–C9 1.357(7), C6–C10 1.571(6), C6–C11 1.552(5), C11–O1 1.225(4), C11–O2 1.282(4), C14–N1 1.367(4), C14–N2 1.364(4), N1–C15 1.387(4), N1–C17 1.438(4), N2–C16 1.392(4), N2–C26 1.447(4), O2A–Ni–C1 166.1(1), O2A–Ni–C2 127.4(1), O2A–Ni–C3 95.3(1), O2A–Ni–C14 98.8(1), C1–Ni–C2 41.9(1), C1–Ni–C3 71.1(1), C1–Ni–C14 93.7(1), C2–Ni–C3 38.7(1), C2–Ni–C14 132.8(1), C3–Ni–C14 160.5(1).

(overlapping with a signal of a methyl group and therefore integrating to four protons) and 1.16 ppm (see Section 4).

In principle, two pathways for the formation of **6** may be discussed. The first would start with the oxidative coupling between CO₂ and a molecule dimethylbutadiene at the nickel(0) center to form **5**, followed by insertion of a second molecule dimethylbutadiene into the Ni–allyl bond and subsequent dimerization of the monomeric complex. However, this way can be excluded because the structure of **6** is not consistent with this route.

The second pathway starts with the oxidative coupling of two molecules 2,3-dimethylbutadiene at the carbene nickel(0) complex resulting in a bis(allyl)nickel complex in which an equilibrium between η^3 -allyl-Ni and η^1 -allyl-Ni



Scheme 2. Formation of the NHC complex **6**.

species can be assumed. Subsequent insertion of CO₂ into the η^1 -allyl-Ni bond formed between C3 and Ni followed by dimerization of two nickel species may then result in the formation of **6** containing a 14-membered nickelamacrocyclic ring.

The formation of such types of macrocycles by phosphine-supported reactions of nickel(0) is already known. Independently on the steric demand of the phosphines such ring systems were formed in the presence of Me₃P (with butadiene/CO₂) or in the presence of Cy₃P (with isoprene/CO₂) [24]. In other words, phosphines and the NHC ligand behave similar in these reactions and form the same molecular architectures.

3. Conclusion

In conclusion, we have shown that the new NHC-stabilized nickelalactones are easily accessible by simple displacement reactions of pyridine or tmeda in the corresponding starting complexes by N-heterocyclic carbenes. As well monomeric complexes as dimeric compounds could be isolated. In the latter compounds four-membered Ni₂O₂ rings are formed – in contrast to related phosphine complexes where nickelamacrocycles are built up. This is the result of the different ligand geometry of the NHCs compared with steric bulky phosphines. NHC-stabilized η^3 -allyl-carboxylate complexes **5** and **6**, however, have the same structure as described for phosphine-supported complexes.

4. Experimental

4.1. General procedures

¹H NMR and ¹³C NMR spectra were recorded at ambient temperature on a Bruker AC 200 or AC 400 MHz spectrometer. All spectra were referenced to TMS or deuterated solvent as an internal standard. FAB-mass spectra were obtained on a Finnigan MAT SSQ 710 system (2,4-dimethoxybenzylalcohol as matrix), IR measurements were carried out 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. DMF was distilled over CaH₂.

The starting complexes [(py)₂Ni(C₂H₄COO)], [(py)₂Ni(C(Et)=C(Et)-COO)], and [(tmeda)Ni(CH₂=C(Me)-C(Me)-CH₂-COO)] were prepared as recently described [2,25], the N-heterocyclic carbenes were prepared according to known methods [26] from the corresponding imidazolium chlorides.

4.2. [(py)(*im*^{mes})Ni(CH₂CH₂COO)] (**1**)

A solution of 0.14 g (0.46 mmol) 1,3-dimesitylimidazol-2-ylidene (*im*^{mes}) in 10 ml THF was treated with 0.13 g

(0.45 mmol) of the solid nickelalactone [(py)₂Ni(C₂H₄COO)] and stirred for 20 min. The suspension turned from initial green to a yellow-brown clear solution from which a pale-yellow solid crystallized. After 20 min the solid was filtered and dried; yield: 0.19 g (82%). C₂₉H₃₃N₃O₂Ni (514.29): Calc.: C 67.72, H 6.47, N 8.17; Found: C 67.58, H 6.46, N 8.07%; IR (nujol, cm⁻¹) ν_{CO} 1617 (s). The ¹H NMR spectrum in [*D*₇]DMF showed an equilibrium between **1** and **2**. Assignment for **1** (200 MHz, [*D*₇]DMF, 25 °C): δ = 0.15 (t, ³J_{H-H} = 7.2 Hz, 2H, Ni-CH₂), 1.58 (t, ³J_{H-H} = 7.2 Hz, 2H, CH₂-COO), 2.24 (s, 12H, *o*-CH₃ Mes), 2.40 (s, 6H, *p*-CH₃ Mes), 7.14 (m, 2H, *m*-CH py); 7.18 (s, 4H, *m*-CH Mes), 7.48 (s, 2H, CH); 7.71 (m, 1H, *p*-CH py), 8.04 (m, 2H, *o*-CH py). ¹³C{¹H} NMR (100 MHz, [*D*₇]DMF, 25 °C): δ = 1.4 (Ni-CH₂), 18.9 (*o*-CH₃ Mes), 20.9 (*p*-CH₃ Mes), 39.1 (CH₂COO), 124.5 (*m*-CH py or =CH-N), 124.8 (=CH-N or *m*-CH py), 129.6 (*m*-CH Mes), 136.7 (*i*-C-N Mes), 136.6 (*p*-CH py), 137.2 (C Mes), 139.1 (C Mes), 150.6 (*o*-CH py), 179.3 (NCN), 185.7 (COO).

Single crystals suitable for the X-ray diffraction were obtained from the reaction solution by slow crystallization at room temperature.

4.3. [(*im*^{mes})Ni(CH₂CH₂COO)]₂ (**2**)

100 mg (0.19 mmol) of **1** were dissolved in 3 ml DMF and stirred for 15 min. Then the solvent was evaporated in a vacuum at 20 °C. The remaining brown oil was treated with 5 ml diethyl ether and stirred. After formation of a yellow solid the suspension was stirred for 10 min followed by filtration. The yellow product was dried i.v. yield: ca. 50 mg (59%). C₂₄H₂₈N₂O₂Ni (435.19): Calc.: C 66.24, H 6.49, N 6.44; Found: C 65.82, H 6.36, N 6.29%; IR (nujol, cm⁻¹) ν_{CO} 1673 (s). ¹H NMR (200 MHz, [*D*₇]DMF, 25 °C): δ = 0.00 (t, ³J_{H-H} = 7.2 Hz, 2H, Ni-CH₂), 1.46 (t, ³J_{H-H} = 7.2 Hz, 4H, CH₂-COO), 2.24 (s, 12H, *o*-CH₃ Mes), 2.42 (s, 6H, *p*-CH₃ Mes), 7.18 (s, 4H, *m*-CH Mes), 7.47 (s, 2H, CH). ¹³C{¹H}NMR (100 MHz, [*D*₇]DMF, 25 °C): δ = -4.3 (Ni-CH₂), 18.4 (*o*-CH₃ Mes), 21.0 (*p*-CH₃ Mes), 39.3 (CH₂COO), 124.3 (2 × =CH-N), 129.6 (*m*-CH Mes), 136.2 (*i*-C-N Mes), 137.4 (C Mes), 138.9 (C Mes), 180.1 (Ni-C NHC), 184.4 (COO).

Single crystals suitable for the X-ray diffraction were obtained from the mother liquid by slow crystallization at -20 °C.

4.4. [(*im*^{*t-but*})Ni(C(Et)=C(Et)-COO)]₂ (**3**)

1,3-Di-*t*-butylimidazol-2-ylidene (*im*^{*tBu*}) 0.13 g (0.72 mmol) was added to a stirred suspension of 0.25 g (0.73 mmol) [(py)₂Ni(C(Et)=C(Et)-COO)] in 5 ml DMF. After stirring the resulting red solution for 1 h at r.t., the solvent was slowly distilled off at reduced pressure. The sticky brown residue was treated with ether (10 ml) with rapid stirring. The formed yellow solid was collected by filtration and dried in a vacuum. Yield: 0.18 g (67%). C₁₈H₃₀N₂O₂Ni,

(365.14): Calc.: C 59.21, H 8.28, N 7.67; Found: C 58.60, H 8.14, N 7.62%.

Single crystals suitable for the X-ray diffraction were obtained by dissolution of the product in DMF at 20 °C and crystallization at 5 °C.

4.5. $[(im^{mes})Ni(C(Et)=C(Et)-COO)]_2$ (**4**)

1,3-Di-mesity-butylimidazol-2-ylidene (im^{mes}) (0.18 g, 0.59 mmol) was added to a stirred suspension of 0.25 g (0.73 mmol) $[(py)_2Ni(C(Et)=C(Et)-COO)]$ in 10 ml THF. After stirring the suspension for 30 min at r.t. from the red solution a yellow solid precipitated.

A part of this compound was suspended in DMF (4 ml) and treated with some portions of pyridine under stirring (each portion 0.5 ml within 20 min reaction time). After nearly complete dissolution of the compound and filtration the solvent was slowly removed at reduced pressure. The remaining brown residue was treated with diethyl ether (5 mL) and the formed yellow solid was collected by filtration and dried in a vacuum.

$C_{28}H_{34}N_2O_2Ni$, (489.28): Calc.: C 68.73, H 7.00, N 5.73; Found: C 68.45, H 7.15, N 5.63%. IR (nujol, cm^{-1}) $\nu_{(CO)}$ 1638 (s). 1H NMR (400 MHz, $[D_7]DMF$, 25 °C): $\delta = 0.35$ (t, $^3J_{H-H} = 7.2$ Hz, 3H, CH_3), 0.73 (3H, t, $^3J_{H-H} = 7.2$ Hz, CH_3), 1.19 (q, $^3J_{H-H} = 7.2$ Hz, 2H, CH_2), 1.71 (q, $^1J_{H-H} = 7.2$ Hz, 2H, CH_2), 2.31 (s, 6H, (*o*- CH_3 Mes)), 2.38 (6H, s, *o*- CH_3 Mes), 2.40 (6H, s, *p*- CH_3 Mes), 7.16 (s, 2H, *p*-CH Mes), 7.19 (s, 2H, *p*-CH Mes), 7.59 (s, 2H, =CH–N). $^{13}C\{^1H\}$ NMR (100 MHz, $[D_7]DMF$, 25 °C): $\delta = 14.6$ (CH_3), 14.7 (CH_3), 19.4 (*o*- CH_3 Mes), 19.5 (*o*- CH_3 Mes), 20.9 (*p*- CH_3), 21.8 (CH_2), 31.3 (CH_2), 125.0 (=CH–N), 129.9 (*m*-CH Mes), 130.2 (*m*-CH Mes), 135.6 (*o*-C Mes), 136.6 (*o*-C Mes), 137.1 (N–C Mes), 138.8 (*p*-C Mes), 141.5 (C=), 158.6 (=C), 178.5 (COO), 179.8 (N–C–N).

4.6. $[(im^{mes})Ni(CH_2C(CH_3)C(CH_3)-CH_2-COO)]$ (**5**)

0.29 g (0.95 mmol) 1,3-di-mesity-butylimidazol-2-ylidene im^{mes} (0.28 g, 0.95 mmol) was added to a stirred solution of $[(tmeda)Ni(CH_2-C(Me)-C(Me)-CH_2-COO)]$ (0.29 g, 0.93 mmol) in DMF (10 ml). After stirring the resulting orange solution for 30 min at r.t., the solvent was slowly distilled off at reduced pressure. The sticky brown residue was treated with ether (15 ml) with rapid stirring. The resulting solution was filtered. After 24 h standing at –20 °C the formed orange solid was collected by filtration and dried in a vacuum for 5 h at r.t. The product still contained diethyl ether which could not be completely removed in a vacuum. Yield: 0.30 g (63%) of **(5)** diethyl ether_{0.35}. IR (nujol, cm^{-1}) $\nu_{(CO)}$ 1639. 1H NMR (200 MHz, $[D_8]THF$, 25 °C): $\delta = 0.43$ (s, 3H, CH_3); 1.04 (d, $^2J_{H-H} = 2.4$ Hz, 1H, CHH'), 1.12 (t, $^3J_{H-H} = 7.0$ Hz, CH_3 of Et_2O), 1.47 (s, 3H, CH_3), 1.72 (d, $^2J_{H-H} = 2.4$ Hz, 1H, CH'), 1.88 (d, $^2J_{H-H} = 15.8$ Hz, 1H, CHH' -COO), 2.08 (s, 6H, *o*- CH_3 Mes), 2.17 (s, 6H, *o*- CH_3 Mes), 2.34

(s, 6H, *p*- CH_3 Mes) 2.52 (d, $^2J_{H-H} = 15.8$ Hz, 1H, CHH' -COO), 3.39 (q, $^3J_{H-H} = 7.0$ Hz, CH_2 of Et_2O), 7.02 (s, 2H, *m*-H Mes), 7.06 (s, 2H, *m*-H Mes), 7.34 (s, 2H, =CH–N).

$^{13}C\{^1H\}$ NMR (100 MHz, $[D_8]THF$, 25 °C): $\delta = 5.6$ (CH_3 Et_2O), 17.9 (*o*- CH_3 Mes), 18.1 (*o*- CH_3 Mes), 19.2 (CH_3), 20.5 (CH_3); 21.0 (*p*- CH_3 Mes), 39.5 (– CH_2), 43.0 (CH_2 -COO), 66.2 (CH_2 Et_2O), 83.6 (–C(Me)–), 112.9 (–C(Me)–), 123.9 (=CH–N), 129.5 (4× *m*-CH Mes), 136.8 (C Mes), 137.5 (*i*-C Mes), 139.2 (C Mes), 183.7 (COO), 189.5 (C–Ni NHC).

4.6.1. $[(im^{mes})Ni(C_{13}H_{20}O_2)]_2$ (**6**)

$[(im^{mes})_2Ni]$ (0.45 g, 0.67 mmol) was dissolved in toluene (50 mL) at room temperature and 2,3-dimethylbuta-(1,3)diene (1.10 g, 13.40 mmol) was added. After cooling to 0 °C gaseous CO_2 was added to form a saturated solution. This solution was stirred at r.t. for 72 h, afterwards the formed white solid (im^{mes} -COO) was filtered off. From the clear orange solution most of the solvent was evaporated and the remaining yellow-brown solution (ca. 5 ml) was kept at –5 °C. Under these conditions **6** crystallized as yellow single crystals containing different amounts of toluene. Therefore, neither yield nor elemental analyses are given.

1H NMR (400 MHz, $[D_8]THF$, 25 °C): $\delta = 0.36$ (dt, $^3J_{H-H} = 5.6$ Hz; $^2J_{H-H} = 12.4$ Hz, 1H, CHH'), 0.74 (s, 4H, CH_3 + $H'HC$), 0.81 (s, 3H, CH_3); 1.16 (d, $^2J_{H-H} = 1.6$ Hz, 1H, $H'HC$); 1.24 (t, (br), $^2J_{H-H} = 12.4$ Hz, 1H, CHH'), 1.46 (m, 4H, CH_3 + CHH'), 1.58 (s, 3H, CH_3), 1.94 (t, (br), $^2J_{H-H} = 12.0$ Hz, 1H, CHH'), 2.0–2.1 (br), 12H, (*o*- CH_3 Mes), 2.31 (s, 3H, CH_3 toluene), 2.34 (6H, (br) *p*- CH_3), 4.41 (m, 1H, $H'HC$), 4.52 (pd, $^2J_{H-H} = 2.0$ Hz, 1H, $H'HC$), 6.90–7.23 (m, 11H, CH Toluol + =CH–N + *p*-CH Mes). $^{13}C\{^1H\}$ NMR (100 MHz, $[D_8]THF$, 25 °C): $\delta = 17.0$ – 19.0 (br, *o*- CH_3 Mes), 19.9 (CH_3), 20.8 (–21.5 (br, *p*- CH_3 Mes), 21.2 (CH_3), 21.3 (CH_3 + CH_3 Toluol), 22.6 (CH_3), 32.3 (CH_2), 32.8 (H_2C), 35.5 (CH_2), 52.7 (C), 100.0 (–C–), 108.2 (H_2C), 111.7 (–C–), 124.2 (br, =CH–N), 125.9 (*p*-CH toluene), 128.8 (*o*-CH toluene), 129.5 (*m*-CH Toluol), 128.0–131.0 (br), (*m*-CH Mes), 134.0–136.0 (br), (*o*-C Mes), 137.6 (br), N(–C Mes), 138.3 (*i*-C toluene); 138.5–139.5 (br, *p*-C Mes), 152.4 (>C=), 176.9 (COO), 189.1 (NCN NHC).

4.7. Crystal structure determination

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 [27,28]. The structures were solved by direct methods (SHELXS [29]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [30]). Since the quality of the data of compound **1** is too bad, we will only publishing the conformation of the molecule and the crystallographic

data. We will not deposit the data in the Cambridge Crystallographic Data Centre. The hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [30]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal data for 1: $C_{29}H_{33}N_3NiO_2$, Mr = 514.29 g mol⁻¹, yellow prism, size 0.08 × 0.02 × 0.02 mm³, monoclinic, space group $P2_1/c$, $a = 9.0029(6)$, $b = 13.6989(9)$, $c = 20.9618(12)$ Å, $\beta = 98.546(5)^\circ$, $V = 2556.5(3)$ Å³, $T = -90^\circ\text{C}$, $Z = 4$, $\rho_{\text{calcd}} = 1.336$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 7.9$ cm⁻¹, $F(000) = 1088$, 14467 reflections in $h(-11/11)$, $k(-17/14)$, $l(-26/26)$, measured in the range $2.78^\circ \leq \theta \leq 27.50^\circ$, completeness $\Theta_{\text{max}} = 97.2\%$, 5720 independent reflections, $R_{\text{int}} = 0.081$, 3604 reflections with $F_o > 4\sigma(F_o)$, 316 parameters, 0 restraints.

Crystal data for 2 [31]: $C_{48}H_{56}N_4Ni_2O_4$, Mr = 870.39 g mol⁻¹, yellow prism, size 0.10 × 0.10 × 0.08 mm³, triclinic, space group $P\bar{1}$, $a = 9.0114(6)$, $b = 10.5817(9)$, $c = 12.0656(8)$ Å, $\alpha = 112.485(3)$, $\beta = 94.216(4)$, $\gamma = 93.767(4)^\circ$, $V = 1054.68(13)$ Å³, $T = -90^\circ\text{C}$, $Z = 1$, $\rho_{\text{calcd}} = 1.370$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 9.42$ cm⁻¹, $F(000) = 460$, 7616 reflections in $h(-11/11)$, $k(-13/12)$, $l(-15/15)$, measured in the range $2.09^\circ \leq \theta \leq 27.48^\circ$, completeness $\Theta_{\text{max}} = 99.3\%$, 4805 independent reflections, $R_{\text{int}} = 0.037$, 3622 reflections with $F_o > 4\sigma(F_o)$, 267 parameters, 0 restraints, $R_{\text{obs}} = 0.048$, $wR_{\text{obs}}^2 = 0.107$, $R_{\text{all}} = 0.077$, $wR_{\text{all}}^2 = 0.124$, GOOF = 0.954, largest difference peak and hole: 0.478/−0.524 e Å⁻³.

Crystal data for 3 [31]: $C_{36}H_{60}N_4Ni_2O_4$, Mr = 730.30 g mol⁻¹, yellow prism, size 0.03 × 0.03 × 0.03 mm³, monoclinic, space group $P2_1/n$, $a = 9.6680(7)$, $b = 9.8508(5)$, $c = 20.2516(13)$ Å, $\beta = 99.391(3)^\circ$, $V = 1902.9(2)$ Å³, $T = -90^\circ\text{C}$, $Z = 2$, $\rho_{\text{calcd}} = 1.275$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 10.3$ cm⁻¹, $F(000) = 784$, 13035 reflections in $h(-12/11)$, $k(-12/12)$, $l(-26/21)$, measured in the range $2.04^\circ \leq \theta \leq 27.51^\circ$, completeness $\Theta_{\text{max}} = 99.3\%$, 4346 independent reflections, $R_{\text{int}} = 0.095$, 2739 reflections with $F_o > 4\sigma(F_o)$, 208 parameters, 0 restraints, $R_{\text{obs}} = 0.059$, $wR_{\text{obs}}^2 = 0.118$, $R_{\text{all}} = 0.113$, $wR_{\text{all}}^2 = 0.139$, GOOF = 1.031, largest difference peak and hole: 0.505/−0.699 e Å⁻³.

Crystal data for 5 [31]: $C_{28}H_{34}N_2NiO_2 \cdot \frac{1}{2}C_4H_{10}O$, Mr = 526.34 g mol⁻¹, yellow prism, size 0.06 × 0.06 × 0.05 mm³, monoclinic, space group $P2_1/n$, $a = 8.8639(3)$, $b = 21.2441(5)$, $c = 15.1341(6)$ Å, $\beta = 92.404(2)^\circ$, $V = 2847.33(16)$ Å³, $T = -90^\circ\text{C}$, $Z = 4$, $\rho_{\text{calcd}} = 1.228$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 7.11$ cm⁻¹, $F(000) = 1124$, 20091 reflections in $h(-10/11)$, $k(-25/27)$, $l(-17/19)$, measured in the range $1.65^\circ \leq \theta \leq 27.48^\circ$, completeness $\Theta_{\text{max}} = 99.8\%$, 6529 independent reflections, $R_{\text{int}} = 0.044$, 4657 reflections with $F_o > 4\sigma(F_o)$, 302 parameters, 0 restraints, $R_{\text{obs}} = 0.060$, $wR_{\text{obs}}^2 = 0.157$, $R_{\text{all}} = 0.090$, $wR_{\text{all}}^2 = 0.176$, GOOF = 0.961, largest difference peak and hole: 0.913/−0.639 e Å⁻³.

Crystal data for 6 [31]: $C_{68}H_{88}N_4Ni_2O_4$, Mr = 1142.84 g mol⁻¹, yellow prism, size 0.12 × 0.12 × 0.09 mm³, monoclinic, space group $P2_1/n$, $a = 13.2409(6)$, $b = 16.7128(9)$, $c = 14.1738(5)$ Å, $\beta = 91.288(3)^\circ$, $V =$

$3135.8(2)$ Å³, $T = -90^\circ\text{C}$, $Z = 2$, $\rho_{\text{calcd}} = 1.210$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 6.5$ cm⁻¹, $F(000) = 1224$, 20758 reflections in $h(-17/17)$, $k(-20/21)$, $l(-18/17)$, measured in the range $2.13^\circ \leq \theta \leq 27.49^\circ$, completeness $\Theta_{\text{max}} = 99.2\%$, 7144 independent reflections, $R_{\text{int}} = 0.052$, 4856 reflections with $F_o > 4\sigma(F_o)$, 359 parameters, 0 restraints, $R_{\text{obs}} = 0.057$, $wR_{\text{obs}}^2 = 0.138$, $R_{\text{all}} = 0.095$, $wR_{\text{all}}^2 = 0.161$, GOOF = 0.973, largest difference peak and hole: 0.568/−0.360 e Å⁻³.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.016.

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