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A new set of nickelacyclic carboxylates (''nickelalactones'') containing pyridine as supporting ligand: synthesis, structures and application in C–C– and C–S– linkage reactions

Jens Langer, Reinald Fischer, Helmar Görls, Dirk Walther *

Institut für Anorganische und Analytische Chemie der Friedrich-Schiller-Universität Jena, August-Bebel-Strasse 2, 07743 Jena, Germany

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Abstract

Nickelacycles of the type $[(py)_2Ni(CH_2CH_2COO)]$ (**1a**), $[(py)_2Ni(C(Et)=C(Et)–COO)]$ (**2a**), and $[(py)Ni(CH_2\cdots C(CH_3)\cdots C(CH_3)–CH_2–COO)]$ (**3a**) were synthesized and structurally investigated by NMR, IR spectroscopy and in case of **1a** and **2a** by X-ray diffraction analysis. In **1a** and **2a** the Ni(II) ion has square-planar geometry, in contrast to the η^3allyl compound $[(bipy)Ni(CH_2\cdots C(CH_3)\cdots C(CH_3)–CH_2–COO)]$ (**3b**), in which nickel center adopts square-pyramidal geometry. **1a** reacts with di(2-pyridyl)dimethylsilane ($Me_2(2\text{-}py)_2Si$) under exchange of the pyridine ligands to give **1c**. **1a**–**3a** and their bipy derivatives react with di-*p*-tolyldisulfide to form β-thioesters upon workup. Furthermore, reaction of 2-bromopropiophenone with nickelacycles of the type **2** results in the formation of 3,4-diethyl-6-hydroxy-5-methyl-6-phenyl-5,6-dihydro-*2H*-pyrane-2-one in good yields (64–75%). These reactions offer attractive new preparative routes for functionalized organic compounds.

Keywords: Nickelacyclic compounds; N ligands; Disulfides; Bromopropiophenone; Organic synthesis

1. Introduction

Nickelacyclic carboxylates (''nickelalactones'') (Scheme 1) consisting of a Ni–C–C–COO- framework and N–N chelating ligands or phosphines as supporting ligands are well-known compounds which have been synthesized by different synthetic approaches [1–17]. Of special interest is the oxidative coupling between carbon dioxide, unsaturated substrates and Ni(0) complexes which may open new ways for using CO_2 as building block in organic synthesis.

Some of these nickelacycles are interesting starting products for the syntheses of saturated or unsaturated carboxylic acids or their derivatives, for example by alkylation with alkyl halides [4,5,18–21], insertion of unsaturated compounds (CO [10,14,16,20], CO_2 [16,20,22,23], RNC [24,25], alkenes [12,26], alkynes [18,27–32]) or transmetalation reaction with ZnR_2 [33–35]. Furthermore, nickelacyclic carboxylates are also found to be useful reagents for the construction of functionalized steroid side chains [36–38]. Additionally, complexes with an olefin or allyl group in the organic ring system are considered to act as intermediate in catalytic reactions of unsaturated substrates with CO_2 [18,27–32,34,39–41].

However, some limitations prevent a broader scope of the known organometallic compounds, such as the low selectivity of some formation reactions of the metallacycles and their low solubility in organic solvents often resulting in long reaction times with organic

* Corresponding author. Tel.: +49-3641-9-48110; fax: +49-3641-9-48102.
E-mail address: cdw@uni-jena.de (D. Walther).

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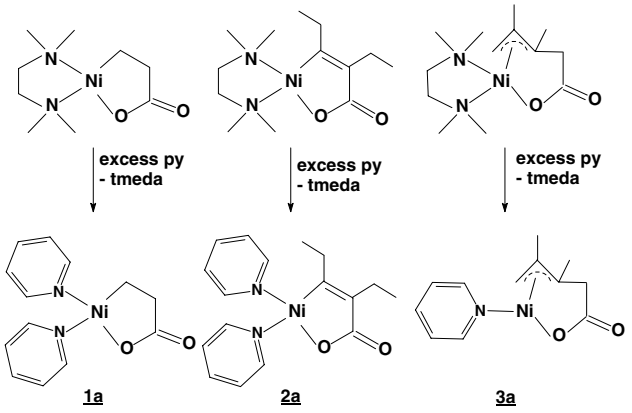


Scheme 1. Synthesis of the complexes **1a**–**3a**.

substrates. Furthermore, in many cases the supporting ligands do not efficiently control the reactions with the organic substrate.

In view of these facts, it would be highly desirable to have a set of soluble metal complexes of the above type, consisting of different metallacyclic units and simple neutral ligands which could be easily displaced by a great variety of other ligands. This would allow elucidating the influence of steric and electronic properties of these ligands on the reactivity of the metallacyclic unit. Consequently, these studies should result in developing new efficient synthons for the synthesis of organic fine chemicals and drugs.

In this initial paper we describe the hitherto unknown reactive pyridine complexes **1a**–**3a** containing three different types of metallacyclic moieties. These complexes can indeed serve as useful starting compounds for substitution reactions with other neutral ligands resulting in new metallacycles with very different reactivity. Additionally, **1a**–**3a** can themselves act as synthons for reactions with organic substrates. To proof this point, we have examined their reactions with di-*p*-tolyldisulfide and 2-bromopropiophenone resulting in new functionalized carboxylic acids or their derivatives. For comparison, analogous experiments were carried out with the known bipy stabilized derivatives **1b**–**3b** [1,7,28] to study the influence of different ligands on the organometallic reactivity. Interestingly, some of these reactions offer interesting alternative synthetic methods for preparing functionalized organic compounds.

2. Results and discussion

2.1. Synthesis and structures of the complexes *1–3*

Although for the complexes **1a**–**3a** different preparative methods may exist, the best way of synthesizing these complexes starts from the corresponding tmeda stabilized complexes according to Scheme 1.

Reaction of the tmeda complexes with an excess of pyridine followed by evaporating tmeda and pyridine under reduced pressure results in almost quantitative yields of the pyridine complexes. Both **1a** and **2a** were obtained as green single crystals upon recrystallization from pyridine.

The ^{1}H NMR spectrum of **1a** in [D_7]DMF displays two triplets for the CH_2 groups at $\delta = 0.69$ (Ni–CH_2) and 1.85 ppm (CH_2–COO) and four resonances of the pyridine ligand protons between 7.47 and 9.0 ppm. A similar simple pattern was observed in the ^{13}C NMR spectrum. As expected, six signals for the carbon atoms were observed. Furthermore, the IR spectrum shows the C=O stretching frequency at 1617 cm^{-1}.

The molecular structure determined by an X-ray diffraction analysis clearly shows the essentially planar geometry of Ni (Fig. 1). The bond lengths and bond angles are quite normal and are comparable with those of similar complexes [12,42,43].

Analogously to **1a**, complex **2a** forms well-shaped green single crystals from pyridine. Its solid-state structure has been also fully characterized by X-ray diffraction. Fig. 2 shows the structure of **2a** with the atom-numbering scheme and selected bond distances and angles.

The ^{1}H and ^{13}C NMR spectra of **2a** in [D_6]DMSO confirm, that the solid-state structure is also maintained in solution. Two triplets for the CH_3 protons, two quartets for the CH_2 protons of the different ethyl groups and four signals for the pyridine protons were found – in agreement with the structure according Fig. 2. In

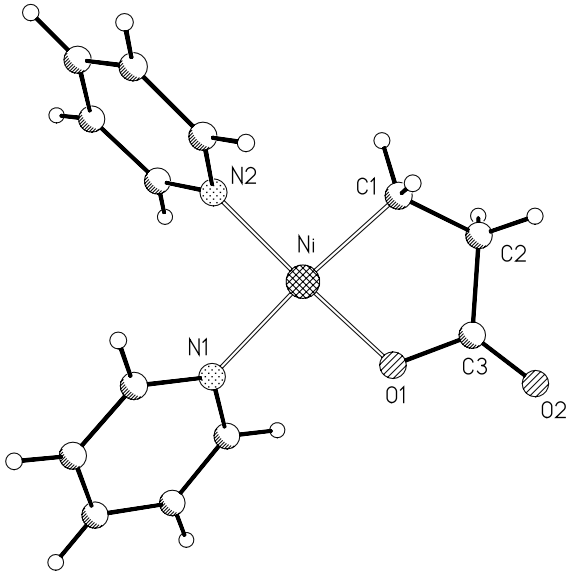


Fig. 1. Molecular structure of complex **1a**. Selected bond distances (Å) and bond angles (°): Ni–O1 1.8655(13), Ni–C1 1.917(2), Ni–N1 1.9884(17), Ni–N2 1.8814(15), O1–C3 1.292(2), O2–C3 1.237(2), C1–C2 1.521(3), C2–C3 1.511(3), N1–Ni–N2 92.07(*l*), N1–Ni–O1 89.96(6), N2–Ni–C1 92.06(8), C1–Ni–O1 85.97(8).

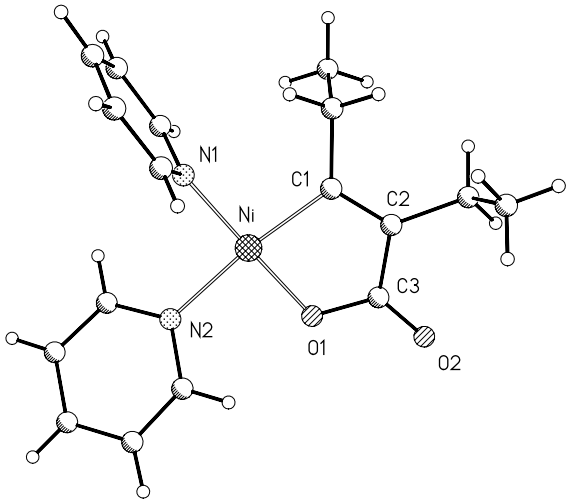


Fig. 2. Molecular structure of complex **2a**. Selected bond distances (Å) and bond angles (°): Ni–O1 1.864(3), Ni–C1 1.909(4), Ni–N1 1.895(4), Ni–N2 1.997(4), O1–C3 1,315(5), O2–C3 1.239(5), C1–C2 1.344(6), C2–C3 1,468(6), N1–Ni–N2 92.08(15), N2–Ni–O1 89.30(14), N1–Ni–C1 93.51(17), C1–Ni–O1 85.01(16).

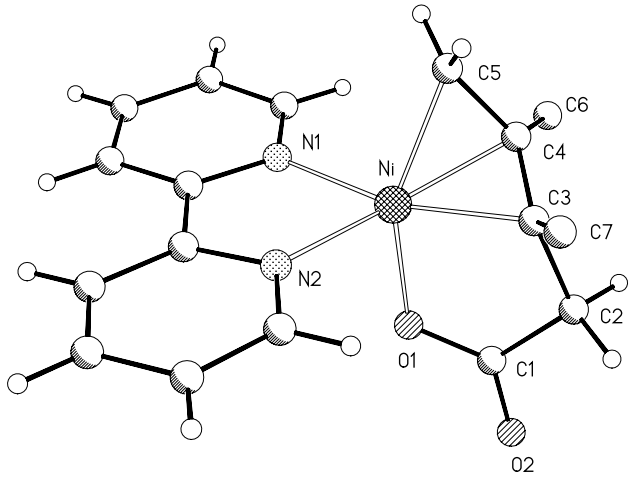


Fig. 3. Molecular structure of complex **3b*DMF**. (DMF and H-atoms bond to C6 and C7 are omitted for clairity). Selected bond distances (Å) and bond angles (°): Ni–O1 1.971(4), Ni–C5 2.003(7), Ni–C4 1.915(6), Ni–C3 1.955 (6), Ni–N1 1.999(4), Ni–N2 2.097(4), O1–C1 1.269(6), O2–C1 1.234(7), C1–C2 1.536(9), C2–C3 1.582(10), C3–C4 1.383(9), C4–C5 1.458(10), N1–Ni–N2 79.54(18), N1–Ni–O1 98.13(17), N2–Ni–O1 92.95(17), N1–Ni–C5 96.1(3), N1–Ni–C3 161.9(2), N2–Ni–C5 116.7(3), N2–Ni–C3 117.5(2), C3–Ni–O1 87.3(2), C5–Ni–O1 149.0(2).

the ^{13}C NMR spectrum, besides the resonances for the pyridine carbon atoms, the expected seven signals for the carbons of the metallacyclic ring appeared, assigned to two signals of the CH_3 groups, two resonances of the CH_2 groups, two resonances of the C=C carbons and one signal belonging to the carboxylate carbon.

Complex **3a** forms yellow crystals which were obtained in excellent yield (86%). It contains only one pyridine ligand, as shown by elemental analysis and NMR measurement, and its NMR spectra in [D_8]THF at ambient temperature give evidence for the η^3-arrangement of the allyl group. Besides the proton signals for the CH_2COO group at $\delta = 2.17$ and 2.97 ppm, one terminal proton of the allyl group appears at 2.00 ppm. The other terminal proton resonates at 2.39 ppm; however, this signal overlaps with the signal of a methyl group giving rise to a multiplet of the relative intensity of four. Furthermore, the singlet for the second methyl group was observed at 1.08 ppm. In addition, the three signals for the protons of the coordinated pyridine ligand complete the ^1H NMR spectrum. These data clearly demonstrate the presence of only one isomer in solution. The very simple ^{13}C NMR spectrum supports this finding: Only 10 ^{13}C signals were observed, additionally indicating that there is no detectable equilibrium between η^3- and η^1-coordination of the allyl group in [D_8]THF solution.

Several attempts to obtain single crystals failed so far. However, the related, diamagnetic bipy complex **3b** could be obtained in single crystals.

An X-ray diffraction study of this compound (Fig. 3) showed its molecular structure with the η^3-allyl coordination and a square-pyramidal coordination sphere of the nickel center, since bipy acts as chelating ligand. The atoms N1, O, C1 and C3 are in an essentially planar arrangement and N2 assumes the apical position. In the known complex [(tmeda)Ni($CH_2\cdots C(CH_3)\cdots C(CH_3)$–$CH_2COO$)] the chelating ligand tmeda strongly coordinates only with one nitrogen atom, the second is only weakly associated (Ni–N(2) 2,314(7) Å) [9]. So the molecular structure of **3b** in the solid-state is the first example of a nickelacyclic carboxylate with square-pyramidal coordination sphere.

The pyridine ligands in **1a** can easily be substituted by a number of other ligands. For example, reaction with di(2-pyridyl)dimethylsilane ($Me_2(2\text{-py})_2Si$) results in the formation of the corresponding di(2-pyridyl)dimethylsilane complex **1c** which was isolated in good yields (70%). In contrast, the corresponding tmeda complex, which is so far the most suitable starting compound for exchange reactions of the neutral ligand, is unreactive toward di(2-pyridyl)dimethylsilane. This comparison underlines the importance of the pyridine complexes as starting products for the formation of new nickelacyclic carboxylates with variable reactivity of the organometallic framework.

Suitable crystals for the X-ray diffraction analysis of **1c** were grown from a solution in DMF. Under these conditions the racemic mixture of both enantiomeric forms (planar chirality) crystallized. Fig. 4 shows the solid-state structure of one enantiomer of **1c** and displays selected bond lengths and angles in the caption. The ^1H NMR spectrum of **1c** in [D_7]DMF displays two signals for the Ni–CH_2-group

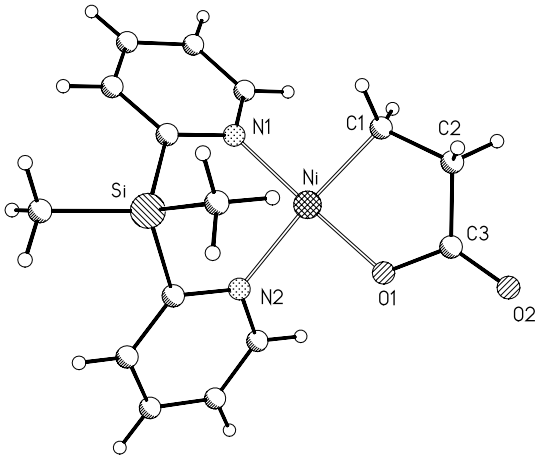


Fig. 4. Molecular structure of complex **1c**. (only one enantiomer shown) Selected bond distances (Å) and bond angles (°): Ni–O1 1.856(2), Ni–C1 1.922(3), Ni–N1 1.891(3), Ni–N2 1.986(3), O1–C3 1.310(4), O2–C3 1.226(4), C1–C2 1,512(5), C2–C3 1,503(5), N1–Ni–N2 93.28(11), N2–Ni–O1 88.19(10), N1–Ni–C1 91.62(13), C1–Ni–O1 86.91(13).

at 0.72 and 0.82 ppm with the relative intensity 1:1. This clearly shows the diasteriotopic character of the CH_2 groups in the CH_2CH_2COO fragment. In other words, the conversion of one enantiomeric form into the other in solution is slow, compared with the NMR time scale.

*2.2. Reactions of the complexes **1a–3a** and their bipy derivatives **1b–3b***

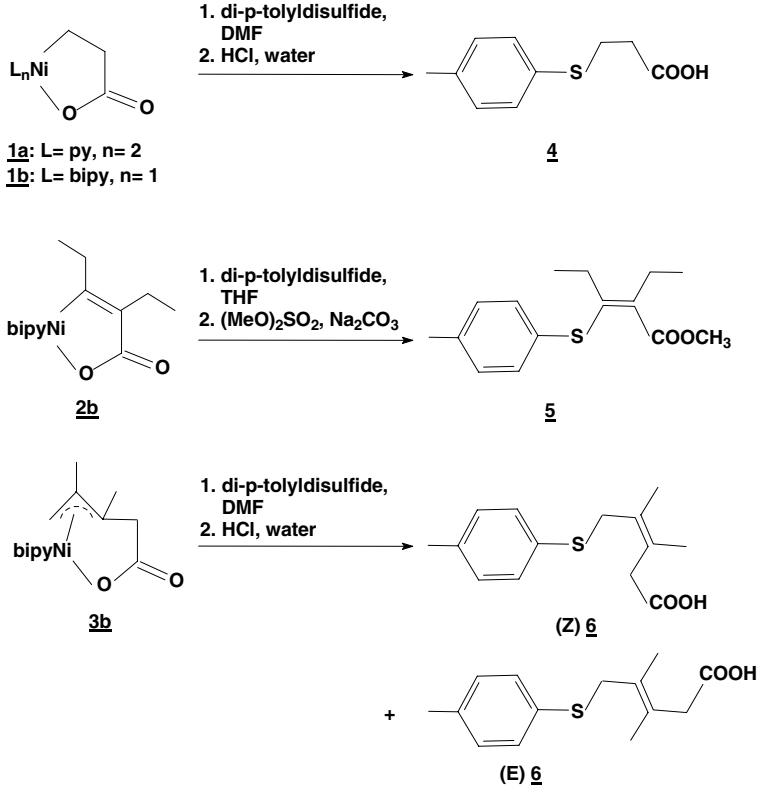
2.2.1. Reactions with di-p-tolyldisulfide

Reaction with di-*p*-tolyldisulfide with the pyridine and bipyridine complexes resulted in the formation of β-thiocarboxylic acids which were identified in some cases as methyl esters according to Scheme 2.

Whereas with complex **1a** 3-(*p*-tolylmercapto)-propionic acid (**4**) [44] could be detected only in low yield (22%), the bipy derivative **1b** afforded high yield (70%). This clearly demonstrates the influence of the neutral ligand on the reaction. In this case bipy tunes the reaction more efficiently than the pyridine ligands. Although the preparative value of this reaction starting from **1a** or **1b** is relatively low, by using substituted derivatives the organometallic route may be an interesting alternative to established methods and should open up an easy entry to substituted thiachroman-4-ones [44].

Of particular interest is the reaction of the organic sulfide with the bipy containing unsaturated metallacycle **2b**. In this reaction the unsaturated β-thioester (*Z*)-2-ethyl-3-(*p*-tolylmercapto)-pent-2-enoic acid methyl ester (**5**) bearing two alkyl substituents in a (*Z*)-arrangement was isolated in moderate yields (53%) upon workup with dimethyl sulfate.

To the best of our knowledge this compound has never been described before. Generally, this reaction



Scheme 2. Formation of ß-thio-carboxylic acids from complexes of the type **1**–**3**.

opens a simple and attractive general route for the preparation of unsaturated β-thioesters starting from CO_2, an alkyne and an organic disulfide in the presence of Ni(0) complexes. In contrast to a known method for synthesizing a similar β-thioester (predominantly the (*E*)-isomer) starting from an allenic ester [45], the organometallic way results in the formation of the (*Z*)-isomer using only commercial available starting products. Another advantage of the organometallic route is the possibility to vary the alkyl substituents in a wide range, whereas the known procedure needs a defined substitution pattern.

When **3b** was used in this C–S-linkage reaction, two isomers of 3,4-dimethyl-5-(*p*-tolylmercapto)-pent-3-enoic acid (**6**) were formed besides some minor byproducts. **6** was characterized by GC–MS, GC–IR and NMR experiments. In ^{1}H NMR (NOESY) experiments a coupling through space between the two methyl groups of the main product was observed, assigned to be the (*Z*)-isomer. Generally, this synthesis is an interesting preparative route to new thioether substituted pent-3-enoic acids [46,47], since an overall yield of 60% was found. Mechanistical investigations of the reaction of organic disulfides with nickelacyclic carboxylates are subject of ongoing studies.

2.2.2. Reaction with 2-bromopropiophenone

The reaction of **1a** or **1b** with 2-bromopropiophenone followed by hydrolysis results in the formation of 4-benzoyl valeric acid (**7**) [48] in relatively low yields. In other words, both complexes are not useful for the selective synthesis of such types of carboxylic acids. Similarly, the corresponding reaction with **3b** yielded various carboxylic acid. Among these, the desired unsaturated carboxylic acid is only present as minor product, according to ^{1}H NMR- and MS analysis.

In contrast, the unsaturated complexes **2a** and **2b** reacts with 2-bromopropiophenone in good yields to 3,4-diethyl-6-hydroxy-5-methyl-6-phenyl-5,6-dihydro-*2H*-pyrane-2-one (**8**), which was never synthesized before (Scheme 3). The product was isolated in yields up to 75%, if the reaction with **2a** was carried out in THF.

A very simple one-pot reaction to **8**, starting directly from CO_2, 3-hexyne and in situ generated (bipy)Ni(cod) without isolating the nickelacyclic carboxylate, is also possible (yield: 60%) and increases the preparative value of this synthesis.

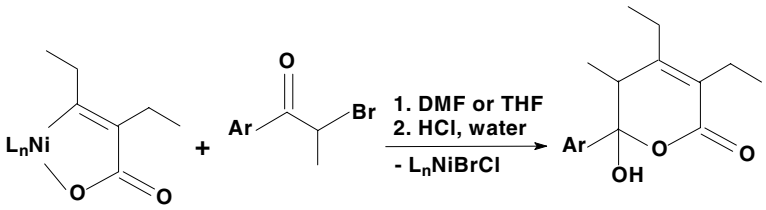
Single crystals of **8**, suitable for an X-ray diffraction study were grown from a solution of heptane/THF. Fig. 5 shows the molecular structure of the crystallizing pair of diastereomers and contains relevant bond lengths and bond angles in the figure caption.

As can be seen from the figure the two ethyl groups on the olefinic bond assume *Z*-positions and two molecules are linked via hydrogen bonds between the OH groups and the carbonyl group of the neighboring molecule.

The ^{1}H NMR spectrum in $CDCl_3$ at ambient temperature clearly demonstrates, that two pairs of diastereoisomers (in a ratio of about 5:1) are present in solution. The equilibrium between both forms may proceed via a ring-opening reaction [49,50], however; this intermediate could not be detected in the solution.

Generally, the organometallic reaction from three simple organic compounds (alkynes, CO_2 and a 2-halogenoketone or -aldehyde) may open an easy access to functionalized 6-hydroxy-5,6-dihydro-*2H*-pyrane-2-ones and, after dehydratization, to substituted pyran-2-ones. Substituted 5,6-dihydro-*2H*-pyran-2-ones should also be accessible through reduction with $NaBH_4$ [51] These compounds are of interest because they are part of natural products and drugs such as withaferin A and kaiwan [52]. Furthermore, some 5,6-dihydro-*2H*-pyrane-2-one derivatives show antitumoral or antibiotic abilities or inhibit HIV-protease [52].

Established methods to substituted 6-hydroxy-5,6-dihydro-*2H*-pyrane-2-ones, such as the reaction of substituted cyclohexenones with superoxide radicals, generated by KO_2/18-crown-6, [51,53] are often limited to a special substitution pattern. In contrast, the organometallic reaction described here, should allow preparing a much larger group of substituted pyranones in a very simple reaction by using different alkynes and 2-bromoketones.



2a: L= py, n=2
2b: L= bipy, n=1

8

Scheme 3. Reaction of complexes of the type 2 with 2-bromopropiophenone.

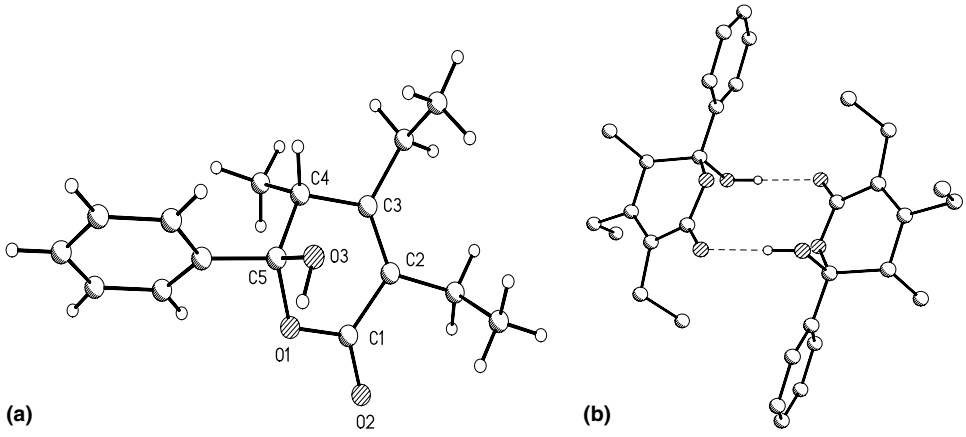


Fig. 5. (a) Molecular structure of compound **8** (only one diastereomer shown) (left); (b) dimeric unit (H–atoms except the one bond to O3 are omitted for clairity) (right). Selected bond distances (Å) and bond angles (°): O1–C1 1.3500(17), O1–C5 1.4648(16), O2–C1 1.2208(17), O3–C5 1.3938(16), C1–C2 1.474(2), C2–C3 1.341(2), C3–C4 1.509(2), C4–C5 1.527(2), O1–C1–O2 117.23(13), O1–C1–C2 119.99(12), O1–C5–O3 108.90(10), O1–C5–C4 109.10(11), O2–C1–C2 122.72(13), O3–C5–C4 107.15(12), C1–C2–C3 119.21(13), C2–C3–C4 120.22(14), C3–C4–C5 110.12(12).

3. Conclusions

The new pyridine complexes **1a**–**3a** are easily accessible and can be used as valuable starting products for the synthesis of many other nickelacycles with different neutral ligands opening the possibility to tune the reactivity of the organometallic moiety towards organic substrates. Initial investigations have shown that some of the nickelacyclic lactones are useful building blocks for synthesizing organic fine chemicals. Especially unsaturated β-thioesters and 3,4-diethyl-6-hydroxy-5-methyl-6-phenyl-5,6-dihydro-*2H*-pyrane-2-one can be prepared by simple routes in good yields. Scope and limitation of these and similar reactions are subject of ongoing studies.

4. Experimental

4.1. General procedures

^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker AC 200 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, tetrahydrofurane and diethyl ether were dried over potassium hydroxide and distilled over Na/benzophenone.

Pyridine and DMF were distilled over CaH_2. Di-*p*-tolyldisulfide, 3-hexyne and 2,3-dimethylbutadiene was purchased from Aldrich and used without further purification. 2-bromopropiophenone [54] and di(2-pyridyl)dimethylsilane [55] were prepared according to known procedures. The nickelacycles [(L)Ni(C_2H_4-COO)], [(L)Ni(C(C_2H_5)═C(C_2H_5)COO)], [(L)Ni (CH_2┈C(CH_3)┈C(CH_3)–CH_2COO)] (L: tmeda, bipy) and Ni(cod)$_2$ were prepared by using literature procedures [1,4,7,28,31,56].

4.2. Synthesis of [$py_2Ni(C_2H_4COO)$] (*1a*)

To [(tmeda)Ni(C_2H_4COO)] (0.32 g, 1.3 mmol) pyridine (10 ml) was added, the resulting suspension was stirred for 20 min and the solvent was removed in vacuum (2×). The resulting residue was the desired product as green solid in quantitative yield (0.38 g, 1.3 mmol). $C_{13}H_{14}N_2NiO_2$ (288.96) Calc.: C 54.04, H 4.88, N 9.69; Found C 54.20, H 4.93, N 9.65. IR (nujol, cm^{-1}): *v*(C═O) 1617 (s). ^{1}H NMR (200 MHz, [D$_7$]DMF, 25 °C): $\delta = 0.69$ (t, $^3J_{H,H} = 7.5$ Hz, 2H, Ni–CH_2), 1.85 (t, $^3J_{H,H} = 7.5$ Hz, 2H, CH_2–COO), 7.43 (t, 4H, *m*-CH py), 7.89 (t, 2H, *p*-CH py), 8.42 (br, 2H, *o*-CH py), 9.0 (d, 2H, *o*-CH py) ppm. ^{13}C{^{1}H}NMR (50 MHz, [D$_7$]DMF, 25 °C): $\delta = 3.6$ (br, Ni–CH_2), 38.1 (CH_2–COO), 125.8 (4×*m*-CH, py), 137.9 (2×*p*-CH, py), 152.7 (4×*o*-CH, py), 186.8 (COO) ppm.

Single crystals suitable for the X-ray diffraction were obtained from a solution of pyridine.

4.3. Synthesis of [(Me_2(2-py)$_2$Si)Ni(C_2H_4COO)] (*1c*)

A solution of Me_2(2-py)$_2$Si (0.44 g, 2.08 mmol) in THF (10 ml) was added to green [py_2Ni(C_2H_4COO)] (**1a**) (0.6 g, 2.08 mmol) at r.t. The resulting suspension was stirred for 2 h and turned slowly to yellow. The yellow solid was removed by filtration, washed with ether and dried in vacuum. This THF-containing product was dissolved in DMF and evaporated to dryness under

reduced pressure to yield solvent free product. Yield: 0.50 g (70%). $C_{15}H_{18}N_2NiO_2Si$ (345.1) Calc.: C 52.21, H 5.26, N 8.12; Found C 52.10, H 5.22, N 8.41%.

IR (nujol, cm^{-1}): ν(C═O) 1617 (s),^{1}H NMR (400 MHZ, [D_7]DMF, 25 °C): $\delta = 0.72$ (m, 1H, Ni–C*H* H′), 0.82 (m, 1H, Ni–CH*H*′), 1.00 (s, 3H, Si–CH_3), 1.82 (m, 1H, C*H* H′–COO), 1.86 (s, 3H, Si–CH_3), 2.02 (m, 1H, CH*H*′–COO), 7.38 (m, 1H, CH py), 7.45 (m, 1H, CH py), 7.70 (d, 1H, CH py), 7.82–7.92 (m, 3H, CH py), 8.94 (d, 1H, CH py), 9.03 (d, 1H, CH py) ppm. ^{13}CNMR (100 MHz, [D_7]DMF, 25 °C): $\delta = -5.9$ (Si–CH_3),−0.8 (Si–CH_3), 7.9 (Ni–CH_2), 38.4 (*CH_2*–COO), 124.6 (CH py), 125.4 (CH py), 130.8 (CH py), 131.2 (CH py), 135.7 (CH py), 136.4 (CH py), 152.4 (CH py), 153.8 (CH py), 164.9 (Si–C py), 186.6 (COO) ppm (1 signal (Si–C py) overlaps with the signal of the C═O group from DMF).

Single crystals suitable for the X-ray diffraction were obtained from a solution of DMF.

4.4. Synthesis of [$py_2NiC(C_2H_5)$═$C(C_2H_5)$–COO] (**2a**)

Orange [(tmeda)NiC(C_2H_5)═C(C_2H_5)–COO] (0.30 g, 1.0 mmol) was suspended in pyridine (10 ml) and stirred for 20 min. The suspension turned from initial orange to green. The solvent was removed under reduced pressure and the solid formed was dried in vacuum. **2** was obtained as a green solid in quantitative yield (0.34 g, 1.0 mmol). $C_{17}H_{20}N_2NiO_2$ (343.05) Calc.: C 59.52, H 5.88, N 8.17; Found: C 59.15, H 5.95, N 8.51; IR (nujol, cm^{-1}): ν(C═O) 1619 (s). ^{1}H NMR (200 MHz, [D_6]DMSO, 25 °C): $\delta = 0.46$ (t, $^3J_{H,H} = 7.0$ Hz, 3H, Ni–C–CH_2–*CH_3*), 0.76 (t, $^3J_{H,H} = 7.3$ Hz, 3H, CH_3), 0.92 (q, $^3J_{H,H} = 7.0$ Hz, 2H, Ni–C–CH_2–), 1.80 (q, $^3J_{H,H} = 7.3$ Hz, 2H, CH_2), 7.37 (pseudo-*t*, 4H, *m*-CH py), 7.80 (br, 2H, *p*-CH py), 8.55 (br, 2H, *o*-CH py), 9.08 (br, 2H, *o*-CH py) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D_6]DMSO, 25 °C): $\delta = 14.1$ (CH_3), 14.8 (CH_3), 20.5 (CH_2), 24.6 (CH_2), 124.8 (4×*m*-CH py), 137.8 (2×*p*-CH py), 139.0 (═C–COO), 152.2 (4×*o*-CH py), 159.0 (Ni–C═), 178.9 (COO) ppm.

Single crystals suitable for the X-ray diffraction were obtained from a solution of pyridine.

4.5. Synthesis of [$pyNi(CH_2$···$C(CH_3)$···$C(CH_3)$–CH_2–COO)] (**3a**)

[(tmeda)Ni(CH_2···$C(CH_3)$···$C(CH_3)$–CH_2COO)] (0.99 g, 3.29 mmol) was dissolved in 10 ml pyridine, stirred for 20 min and evaporated to dryness (2×). To the resulting orange oil diethyl ether (20 ml) was added. After 30 min of stirring, **3** was isolated as yellow solid by filtration. Yield: 0.75 g (86%). $C_{12}H_{15}NNiO_2$(263.94) Calc.: C 54.61, H 5.73, N 5.31; Found: C 54.64, H 5.55, N 5.56. IR (nujol, cm^{-1}): ν(C═O) 1636 (s). ^{1}H NMR (200 MHz, [D_8]THF, 25 °C): $\delta = 1.08$ (s, 3H, CH_3), 2.00 (br, 1H, *H* H′C···), 2.17 (d, $^2J_{H,H} = 16.1$ Hz, 1H,–C*H* H′–COO), 2.39 (s, 4H, CH_3 + H*H*′ C···), 2.97 (d, $^2J_{H,H} = 15.4$ Hz, 1H,–CH*H*′–COO), 7.39 (br, 2H, *m*-CH py), 7.86 (br, 1H, *p*-CH py), 8.56 (br, 2H, *o*-CH py) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D_6]DMSO, 25 °C): $\delta = 19.7$ (CH_3), 21.4 (CH_3), 43.6 (*CH_2*–COO), 45.8 (CH_2 allyl), 73.8 (C allyl), 116.4 (C allyl), 124.8 (*m*-CH py), 138.2 (*p*-CH py), 151.1 (*o*-CH py), 181.0 (COO) ppm.

4.6. Coupling reactions with organic substrates

4.6.1. Standard work up

The reaction mixture was evaporated to dryness in vacuum. The residue was stirred for 1 h with diluted, aqueous HCl solution (20 ml) and extracted with chloroform (2×20 ml). The organic phases were extracted with saturated, aqueous sodium carbonate solution (2 ×20 ml). Then the combined aqueous phases were acidified (HCl) and extracted with chloroform (3×20 ml). These organic layers were dried with anhydrous sodium sulfate and the solvent was removed in vacuum to give the crude product.

4.7. Synthesis of 3-(p-tolylmercapto)-propionic acid (**4**) [44]

4.7.1. (a) From [$py_2Ni(C_2H_4COO]$) (**1a**)

Di-*p*-tolyldisulfide (0.64 g, 2.60 mmol) was added to a stirred solution of green [$py_2Ni(C_2H_4COO)$] (0.75 g, 2.60 mmol) in DMF (30 ml) and a slow color change to brown was observed. Stirring was continued over night, followed by standard work up. Yield: 110 mg (22%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.25$ (s, 3H, CH_3), 2.57 (t, $^3J_{H,H} = 7.4$ Hz, 2H, CH_2), 3.05 (t, $^3J_{H,H} = 7.4$ Hz, 2H, CH_2), 7.04 (AA′BB′, 2H, CH tolyl), 7.22 (AA′BB′, 2H, CH tolyl), 8.65 (br, 1H, COOH) ppm. MS (DEI): *m/z* (%) = 196 [M^+] (100), 179 [M^+–OH] (12), 137 [M^+–CH_2–COOH] (58), 123 [*p*-tolyl-S^+] (19), 91 [*p*-tolyl$^+$] (40).

4.7.2. (b) From [(bipy)Ni(C_2H_4COO)] (**1b**)

[(bipy)Ni(C_2H_4COO)] (0.94 g, 3.28 mmol) and di-*p*-tolyldisulfide (0.81 g, 3.29 mmol) in DMF (40 ml) were reacted as described in Section 4.7.1. Reaction was completed after 30 h. Yield: 450 mg (70%).

4.7.3. (Z)-2-ethyl-3-(p-tolylmercapto)-pent-2-enoic acid methylester (**5**)

To a suspension of orange [(bipy)Ni(C (C_2H_5)═C(C_2H_5)–COO)] (0.96 g, 2.81 mmol) in THF (40 ml) di-*p*-tolyldisulfide (0.70 g, 2.84 mmol) was added. The mixture was stirred for 36 h, after which dimethyl sulfate (1.07 g, 8.48 mmol) was added. Upon stirring for 24 h the excess of dimethyl sulfate was hydrolyzed by

addition of an aqueous solution of sodium carbonate (20 ml) and rapid stirring of the resulting mixture for 2 h. Then THF was removed in vacuum and the aqueous phase was extracted with heptane (3×20 ml). The collected organic layers were concentrated and the **5** was separated by column chromatography on silica gel (heptane/ethyl acetate 10:1) as nearly colorless oil. Yield: 400 mg (53%). IR (nujol, cm^{-1}): ν(C═O) 1731 (s). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.95$ (t, $^3J_{H,H} = 7.4$ Hz, 3H, CH_3), 1.05 (t, $^3J_{H,H} = 7.4$ Hz, 3H, CH_3), 2.16 (q, $^3J_{H,H} = 7.4$ Hz, 2H, CH_2), 2.31 (s, 3H, CH_3 *p*-tolyl), 2.38 (q, $^3J_{H,H} = 7.4$ Hz, 2H, CH_2), 3.75 (s, 3H, $COOCH_3$), 7.09 (AA′BB′, 2H, CH tolyl), 7.30 (AA′BB′, 2H, CH tolyl) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 13.6$ (CH_3), 13.7 (CH_3), 21.1 (CH_3 tolyl), 23.8 (CH_2), 24.8 (CH_2), 51.5 (CH_3–O), 129.6 (2×CH tolyl), 130.0 (*i*-C–S tolyl), 132.9 (═C<), 133.2 (2×CH tolyl), 137.9 (*i*-*C*–CH_3 tolyl), 145.3 (>C═), 169.2 (COO) ppm. MS (DEI): *m/z* (%) = 265 [$M^+ + 1$] (21), 264 [M^+] (100), 233 [M^+–OCH_3] (51), 141 [M^+–S-tolyl] (12), 109 (12).

4.7.4. Dimethyl-5-(p-tolylmercapto)-pent-3-enoic acid (6)

A solution of [(bipy)Ni(CH_2┈$C(CH_3)$┈$C(CH_3)$–CH_2COO)] **3b** (0.46 g, 1.35 mmol) and di-*p*-tolyldisulfide (0.34 g, 1.38 mmol) in DMF (30 ml) was stirred at ambient temperature over night. Usual work up yielded sticky oil (260 mg). GC/IR, GC/MS analysis (after esterification with diazomethane) and ^{1}HNMR (NOESY) of the crude product showed the presence of (*Z*)-**6** and (*E*)-**6** beside further minor products. (*Z*)-**6**: yield (155 mg, 46%). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.73$ (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 2.30 (s, 3H, CH_3 tolyl), 2.89 (s, 2H, CH_2), 3.51 (s, 2H, CH_2), 7.06 (AA′BB′, 2H, CH tolyl), 7.25 (AA′BB′, 2H, CH tolyl), 8.50–9.50 (br, 1H, COOH) ppm. IR (as methyl ester) (pure, gas phase, cm^{-1}): 3025, 2959, 2932, ν(C═O) 1756 (s), 1492, 1437, 1251, 1162 (s), 1018, 807. MS (DEI, as methyl ester): *m/z* (%) = 264 [M^+] (62), 233 [M^+–OCH_3] (4), 141 [M^+–S-tolyl] (100), 109 (4), 99 (6). (*E*)-**6**: yield (45 mg, 13%). IR (as methyl ester) (pure, gas phase, cm^{-1}): 3024, 2960, 2932, ν(C═O) 1756 (s), 1492, 1438, 1246, 1197, 1151 (s),1018, 805. MS (DEI, as methyl ester): *m/z* (%) = 264 [M^+] (51), 233 [M^+–OCH_3] (4), 205 [M^+–$COOCH_3$] (7), 141 [M^+–S-tolyl] (100), 123 [tolyl-S^+] (23), 109 (14), 99 (10).

4.8. Benzoylvaleric acid (7) [47]

4.8.1. (a) From [py$_2$Ni(C_2H_4COO)] (1)

To a solution of **1** (0.98 g, 3.4mmol) in DMF (40 ml) 2-bromopropiophenone (0.52 ml, 3.4 mmol) was added at r.t. The resulting solution was stirred overnight and than the reaction mixture was worked up according to the above standard procedure. The crude product contained **7** together with DMF. Yield: 100 mg (14%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.17$ (d, $^3J_{H,H} = 6.9$ Hz, 3H, CH_3), 1.73 (m, 1H, C*H* H′), 2.13 (m, 1H, CH*H*′), 2.35 (m, 2H, CHH′–COO), 3.56 (m, 1H, C*H*–CH_3), 7.42 (m, 2H, *m*-CH Ph), 7.51 (m, 1H, *p*-CH Ph), 7.93 (m, 2H, *o*-CH Ph) 8.2-9.5 (br, 1H, COOH) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 17.3$ (CH_3), 28.1 (CH_2), 31.6 (CH_2–COO), 43.6 (CH), 128.4 (2×*o*-CH Ph), 128.7 (2×*m*-CH Ph), 133.0 (*p*-CH Ph), 136.3 (*i*-C Ph), 177.1 (COO), 203.7 (C═O) ppm. MS (DEI): *m/z* (%) = 207 [$M^+ + 1$] (18), 206 [M^+] (34), 189 [M^+–OH] (100), 105 [Ph–CO^+] (100).

4.8.2. (b) From [(bipy)Ni(C_2H_4COO)]

Starting from (2.79 mmol) [(bipy)Ni(C_2H_4COO)] (0.80 g, 2.79 mmol) and 2-bromopropiophenone (0.42 ml, 2.76 mmol) in DMF (40 ml) reaction was carried out analogously to (a). Yield: 40 mg (7%) of **7**.

4.9. Synthesis of 3,4-diethyl-6-hydroxy-5-methyl-6-phenyl-5,6-dihydro-2H-pyran-2-one (8)

4.9.1. (a) In DMF

[(bipy)Ni($C(C_2H_5)$═$C(C_2H_5)$–COO)] (0.64 g, 1.88 mmol) was dissolved in DMF (30 ml) and 2-brompropiophenone (0.42 g, 1.97 mmol) was added. The solution was stirred at ambient temperature overnight and turned from initial red to green. Following standard procedure, 5,6-dihydro-*2H*-pyran-2-one **5** was obtained as a white solid. Yield: 230 mg (47%). $C_{16}H_{20}O_3$ (260.33) Calc.: C 73.82, H 7.74; Found: C 73.88, H 7.76. IR (KBr, cm^{-1}): ν(OH) 3290 (br, s), ν(C═O) 1686(s). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): major pair of diastereomers (ratio 5:1): $\delta = 0.74$ (d, $^3J_{H,H} = 7.2$ Hz, 3H, CH_3), 1.08 (t, $^3J_{H,H} = 7.5$ Hz, 3H, CH_3), 1.21 (t, $^3J_{H,H} = 7.6$ Hz, 3H, CH_3), 2.09 (m, 1H, C*H* H′), 2.40 (m, 2H, CHH′), 2.54 (m, 1H, CH*H*′), 2.66 (q, $^3J_{H,H} = 7.2$ Hz, 1H, CH), 3.50 (br, 1H, OH), 7.32–7.45 (m, 3H, *m*-CH + *p*-CH Ph), 7.58–7.63 (m, 2H, *o*-CH Ph) ppm, minor pair of diastereomers: $\delta = 0.73$ (t, $^3J_{H,H} = 7.7$ Hz, 3H, CH_3), 0.92 (t, $^3J_{H,H} = 7.4$ Hz, 3H, CH_3), 1.29 (d, $^3J_{H,H} = 7.0$ Hz, 3H, CH_3), 1,.9 (m, 1H, C*H* H′), 2.19–2.40 (m, 3H, C*HH*′ + CH*H*′), 2.90 (q, $^3J_{H,H} = 6.9$ Hz, 1H, CH), 3.67 (br, 1H, OH), 7.32–7.45 (m, 3H, *m*-CH + *p*-CH Ph), 7.58–7.63 (m, 2H, *o*-CH Ph) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): major pair of diastereomers: $\delta = 12.3$ (CH_3), 13.9 (CH_3), 16.5 (CH_3), 19.9 (CH_2), 25.1 (CH_2), 42.5 (CH), 102.8 (C–OH), 125.6 (2×*m*-CH Ph), 125.7 (>C═), 128.4 (2×*o*-CH Ph), 128.8 (*p*-CH Ph), 140.7 (*i*-C Ph), 157.7 (═C<), 164.7 (COO) ppm. MS (DEI): *m/z* (%)] = 261 [$M^+ + 1$] (21), 243 [M^+–OH] (86), 138 [M^+–OH–Ph–CO] (100), 105 [Ph–CO^+] (36).

Single crystals suitable for the X-ray diffraction were obtained from a heptane/THF mixture.

4.9.2. (b) In THF

Reaction was carried out as described above using [(bipy)Ni(C(C_2H_5)=C(C_2H_5)–COO)] (1.05 g, 3.08 mmol) and 2-bromopropiophenone (0.66 g, 3.09 mmol) in THF (40 ml). Yield: 510 mg (64%) of **8**.

*4.9.3. (c) From [py$_2$ Ni(C(C$_2$H$_5$)=C(C$_2$H$_5$)–COO)] (**2a**)*

Instead of the bipy-complex, **2** (0.47 g, 1.37 mmol) was treated with 2-bromopropiophenone (0.21 ml, 1.37 mmol) in THF (20 ml). Yield: 270 mg (75%) of **8**.

4.9.4. (d) One-pot reaction

To a solution of $Ni(cod)_2$ (0.97 g, 3.5 mmol) and bipy (0.54 g, 3.5 mmol) in THF (20 ml), 3-hexyne (0.8 ml, 7.0 mmol) was added. The solution was saturated with CO_2 at −20 °C and stirred for 24 h at r.t. Then 2-bromopropiophenone (0.53 ml, 3.5 mmol) was added and stirring was continued for additional 16 h. The isolation of the product was performed as described above. Yield: 550 mg (60%) of **8**.

5. Crystal structure determination

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects [57,58].

The structures were solved by direct methods (SHELXS [1]) and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97 [59]). For the compound **1a** and **8** the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. For the other compounds the hydrogen atoms were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically [60]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

*Crystal data for **1a**:* $C_{13}H_{14}N_2NiO_2$, M_r = 288.97 g mol^{-1}, yellow prism, size 0.12×0.10×0.08 mm^3, monoclinic, space group $P2_1/n$, a = 8.3785(3), b = 19.4013(8), c = 8.6247(3) Å, β = 114.505(2)°, V = 1275.69(8) Å^3, T = −90 °C, Z = 4, ρ_{calc} = 1.505 g cm^{-3}, μ(Mo Kα) = 15.15 cm^{-1}, $F(000)$ = 600, 4849 reflections in h(−10/10), k(−25/22), l(−10/11), measured in the range 2.85° ≤ Θ ≤ 27.47°, completeness Θ_{max} = 99.1%, 2894 independent reflections, R_{int} = 0.028, 2248 reflections with $F_o > 4\sigma(F_o)$, 219 parameters, 0 restraints, $R_{1\,obs}$ = 0.033, $wR_{2\,obs}$ = 0.0806, $R_{1\,all}$ = 0.042, $wR_{2\,all}$ = 0.082, Goodness-of-fit = 0.979, largest difference peak and hole: 0.536/−0.454 e Å^{-3}.

*Crystal data for **1c**:* $C_{15}H_{18}N_2NiO_2Si$, M_r = 345.11 g mol^{-1}, green prism, size 0.10×0.08×0.03 mm^3, triclinic, space group $P\bar{1}$, a = 8.3983(6), b = 9.8490(7), c = 10.2195(6) Å, α = 102.391(4), β = 101.163(4), γ = 103.154(4)°, V = 777.39(9) Å^3, T = −90 °C, Z = 2, ρ_{calc} = 1.474 g cm^{-3}, μ(Mo Kα) = 13.3 cm^{-1}, $F(000)$ = 360, 5458 reflections in h(−10/10), k(−11/12), l(−13/12), measured in the range 4.20° ≤ Θ ≤ 27.47°, completeness Θ_{max} = 98%, 3490 independent reflections, R_{int} = 0.046, 2854 reflections with $F_o > 4\sigma(F_o)$, 190 parameters, 0 restraints, $R_{1\,obs}$ = 0.051, $wR_{2\,obs}$ = 0.123, $R_{1\,all}$ = 0.066, $wR_{2\,all}$ = 0.135, Goodness-of-fit = 1.049, largest difference peak and hole: 0.663/−0.861 e Å^{-3}.

*Crystal data for **2a**:* $C_{17}H_{20}N_2NiO_2$, M_r = 343.06 g mol^{-1}, yellow prism, size 0.04×0.04×0.03 mm^3, triclinic, space group $P\bar{1}$, a = 8.9580(7), b = 9.6555(8), c = 10.2078(9) Å, α = 93.242(5), β = 97.040(5), γ = 114.918(7)°, V = 788.92(11) Å^3, T = −90 °C, Z = 2, ρ_{calc} = 1.444 g cm^{-3}, μ(Mo Kα) = 12.38 cm^{-1}, $F(000)$ = 360, 4853 reflections in h(−11/11), k(−12/9), l(−10/13), measured in the range 2.54° ≤ Θ ≤ 27.51°, completeness Θ_{max} = 92.5%, 3358 independent reflections, R_{int} = 0.043, 2433 reflections with $F_o > 4\sigma(F_o)$, 199 parameters, 0 restraints, $R_{1\,obs}$ = 0.061, $wR_{2\,obs}$ = 0.135, $R_{1\,all}$ = 0.093, $wR_{2\,all}$ = 0.153, Goodness-of-fit = 1.022, largest difference peak and hole: 0.668/−0.806 e Å^{-3}.

*Crystal data for **3b**:* $C_{17}H_{18}N_2NiO_2{}^*C_3H_7NO$, M_r = 414.14 g mol^{-1}, brown prism, size 0.03×0.02×0.01 mm^3, orthorhombic, space group $Pbca$, a = 11.0372(3), b = 12.9813(5), c = 27.0149(9) Å, V = 3870.6(2) Å^3, T = −90 °C, Z = 8, ρ_{calc} = 1.421 g cm^{-3}, μ(Mo Ka) = 10.28 cm^{-1}, $F(000)$ = 1744, 11889 reflections in h(−14/14), k(−16/11), l(−34/33), measured in the range 4.61° ≤ Θ ≤ 27.45°, completeness Θ_{max} = 97.3%, 4310 independent reflections, R_{int} = 0.082, 2699 reflections with $F_o > 4\sigma(F_o)$, 244 parameters, 0 restraints, $R_{1\,obs}$ = 0.074, $wR_{2\,obs}$ = 0.178, $R_{1\,all}$ = 0.132, $wR_{2\,all}$ = 0.209, Goodness-of-fit = 1.075, largest difference peak and hole: 0.895/−0.557 e Å^{-3}.

*Crystal data for **8**:* $C_{16}H_{20}O_3$, M_r = 260.32 g mol^{-1}, colorless prism, size 0.04×0.04×0.03 mm^3, monoclinic, space group $P2_1/n$, a = 11.7228(4), b = 10.5521(3), c = 11.7563(5) Å, β = 101.220(1)°, V = 1426.46(9) Å^3, T = −90 °C, Z = 4, ρ_{calc} = 1.212 g cm^{-3}, μ(Mo Kα) = .82 cm^{-1}, $F(000)$ = 560, 5449 reflections in h(−14/15), k(−12/13), l(−15/15), measured in the range 2.24° ≤ Θ ≤ 27.48°, completeness Θ_{max} = 99.3%, 3257 independent reflections, R_{int} = 0.027, 2318 reflections with $F_o > 4\sigma(F_o)$, 252 parameters, 0 restraints, $R_{1\,obs}$ = 0.046, $wR_{2\,obs}$ = 0.106, $R_{1\,all}$ = 0.075, $wR_{2\,all}$ = = 0.122, Goodness-of-fit = 0.996, largest difference peak and hole: 0.185/−0.234 e Å^{-3}.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 229215 (**1a**), 229216 (**1c**),

229217(**2a**), 229218 (**3b**), and 22919 (**8**). Copies of this information may be obtained free of charge from The Director, CCDC, 12, Cambridge CB2 IEZ, UK (fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www://www.ccdc.cam.ac.uk).

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