

Low-Valent Nickel and Palladium Complexes with 1,1'-Bis(phosphanyl)-ferrocenes: Syntheses and Structures of Acrylic Acid and Ethylene Complexes

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Thermally stable acrylic acid complexes with low-valent nickel or palladium of the type $[(L)M(\eta^2\text{-CH}_2\text{=CH-COOH})]$ [**1a**: M = Ni, L = 1,1'-bis(diphenylphosphanyl)ferrocene (dppf), **1b**: M = Ni, L = 1,1'-bis(diisopropylphosphanyl)ferrocene (dippf), **1c**: M = Pd, L = dippf] were obtained by reaction of $[\text{Ni}(\text{cod})_2]$ or $[(L)\text{Pd}(\text{nb})]$ with acrylic acid in the presence of the phosphane ligands. X-ray diffraction analysis of **1a** and **1c**, respectively display that only the olefin part is coordinated. Hydrogen bonds between two carboxyl groups result in dimers in the solid state. The isomeric nickela-cyclic carboxylates of the type $[(L)\text{Ni}(\text{CH}_2\text{CH}_2\text{COO})]$ are stable com-

plexes in case of **2a** (L = dppf) and **2b** (L = dippf) whereas the unstable compound **2c** [L = 1,1'-bis(di-*tert*-butylphosphanyl)ferrocene (dtbpf)] undergoes fast reductive decoupling to form CO_2 and the ethylene complex $[(\text{dtbpf})\text{Ni}(\text{ethylene})]$ (**3c**). The related complex $[(\text{dippf})\text{Ni}(\text{ethylene})]$ (**3b**) was prepared from nickel(0) complexes by ligand exchange reaction. **3b** and **3c** were characterized by elemental analyses, NMR spectroscopy and X-ray structure analysis of single crystals.

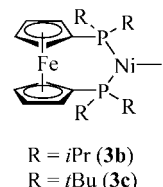
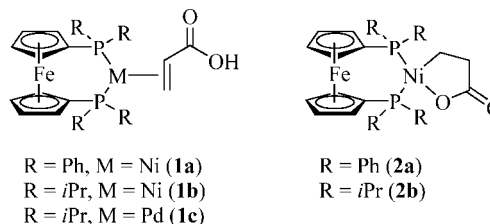
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Introduction

Recently we have described some model complexes of the hypothetical catalytic reactions between ethylene and CO_2 to form acrylic acid or its derivatives.^[1] In connection with these investigations we have also tried to synthesize the hitherto unknown nickel(0) complexes with η^2 -coordinated acrylic acid which are assumed to be model compounds of the final intermediate of the catalytic cycle. However, such complexes could not be obtained with N-donor ligands or phosphanes of the type $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$.

In this paper we report that some 1,1'-bis(phosphanyl)-ferrocenes (L) are able to form surprisingly stable complexes of the type $[(L)M(\eta^2\text{-acrylic acid})]$. Furthermore, we have isolated the isomeric form of $[(\text{dippf})\text{Ni}(\text{acrylic acid})]$, the metallacycle $[(\text{dippf})\text{Ni}(\text{CH}_2\text{CH}_2\text{COO})]$, and we also succeeded in obtaining ethylene nickel(0) complexes with bis(phosphanyl)ferrocene ligands which are also hitherto unknown. These three types of complexes may also be considered as model compounds for intermediates of the metal-mediated reaction between ethylene and CO_2 to form acrylic acid.

Generally, the low-valent nickel chemistry with 1,1'-bis-(phosphanyl)ferrocene ligands L is rather limited. To the best of our knowledge the only isolated nickel(0) compounds are some carbonyl complexes^[2,3] and $[(\text{dppf})\text{-Ni}(\text{cod})]$.^[4] The compound $[(\text{dppf})_2\text{Ni}]$ was only prepared in



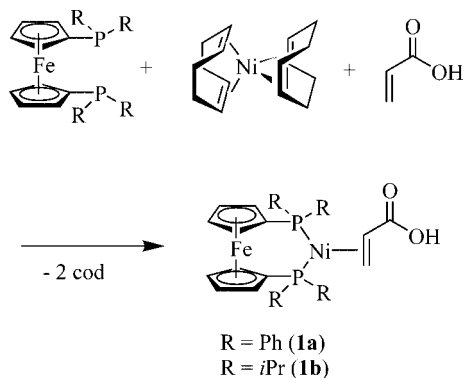
situ.^[5,6] This is somewhat surprising since low-valent nickel complexes with 1,1'-bis(phosphanyl)ferrocene ligands are known to be intermediates in numerous homogeneous catalytic reactions.^[7–13] In addition, they may serve as precursors for new catalysts and for the study, in a stoichiometric manner, of key steps in the catalytic reactions.

Results and Discussion

Nickel(0) and Palladium(0) Complexes with Acrylic Acid

The acrylic acid complexes **1a** and **1b** were obtained by reacting a mixture of $[\text{Ni}(\text{cod})_2]$, dppf or dippf and acrylic acid in a solution of THF at 0 °C according to Scheme 1.

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Scheme 1. Formation of nickel complexes with acrylic acid.

1a was isolated in good yields (71%) as red crystalline compound. NMR spectroscopic data showed that both phosphorus donor atoms coordinate to the nickel in a different chemical environment ($^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$): 26.7 and 32.6 ppm). In the ^1H NMR spectrum ($[\text{D}_8]\text{THF}$) the proton signals of the olefinic CH_2 group appeared at $\delta = 1.95$ and 2.25 ppm and the resonance of the olefinic CH group was found at $\delta = 2.98$ ppm. A broad signal for the COOH proton appeared at $\delta = 9.64$ ppm. Furthermore, six different signals of the cp groups integrating together to eight protons were observed, and the 20 protons of phenyl groups appeared between 7.28 and 7.80 ppm. The ^{13}C NMR spectrum also confirmed the olefin-like coordination of the acrylic acid with the two signals for the olefinic carbons at $\delta = 43.9$ and 49.8 ppm and the signal of the COOH group at $\delta = 175.9$ ppm.

Single crystals of **1a** were grown from a solution of THF and an X-ray diffraction analysis (Figure 1) showed the nickel atom, surrounded by two phosphorus atoms and the two carbon atoms C1 and C2 of the alkene group. Since the angle between the P1,P2,Ni plane and the C1,C2,Ni plane is only 6.24° , the coordination geometry around the metal centre can be considered as essentially planar. The COOH group is not coordinated. Complex **1a** forms a dimer in the solid state since two carboxylic groups are connected by the typical hydrogen bond pattern of carboxylic acids. As expected, the bond length between C1 and C2 of the olefin group [$1.417(4)$ Å] is slightly enlarged compared with the uncoordinated state of acrylic acid. Other relevant bond lengths and angles (see caption of Figure 1) are within the normal range and need therefore no further discussion.

The reaction between $[\text{Ni}(\text{cod})_2]$, dppf und acrylic acid in THF resulted in a mixture of the acrylic acid complex **1b** as main product and traces of a second compound, suspected to be the isomeric nickela-cyclic carboxylate $[(\text{dppf})\text{-Ni}(\text{CH}_2\text{CH}_2\text{COO})]$ (**2b**, see below) according to the signals in the ^{31}P NMR spectrum of the mother liquor.

The pure complex **1b** was isolated upon crystallisation from a solution of THF or DMF in good yields. ^1H NMR spectroscopy of **1b** revealed that the compound has a similar structure as found for **1a**: The proton signals of the coordinated $\text{CH}_2=\text{CH}-$ group at 2.57 and 2.88 are only slightly downfield shifted compared with those of **1a**, and

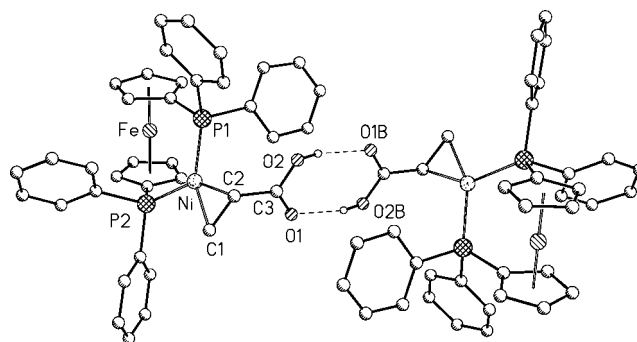
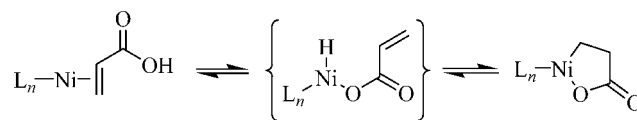


Figure 1. Molecular structure of **1a** (H atoms except the one at O2 are omitted for clarity, cocrystallized THF not shown). Selected bond lengths [Å] and angles $^\circ$: Ni–C1 1.945(2), Ni–C2 1.993(3), Ni–P1 2.1781(7), Ni–P2 2.1411(8), C1–C2 1.417(4), C2–C3 1.446(4), C3–O1 1.275(4), C3–O2 1.291(4), P1–Ni–P2 109.71(3), P1–Ni–C2 111.55(9), P2–Ni–C1 109.71(3), C1–Ni–C2 42.2(1), plane(P1,P2,Ni)–plane(Ni,C1,C2) 6.24° .

the resonance of the COOH proton appeared at $\delta = 10.35$ ppm. The ^{13}C resonances of **1b** for the olefin group were found at 32.7 ($=\text{CH}_2$) and 42.7 ($=\text{CH}$) ppm and the signal of the COOH group was observed at $\delta = 177.7$ ppm confirming the olefin-like coordination of the acrylic acid ligand as well. In addition, X-ray structure of single crystals (not depicted) showed that **1b** has essentially the same solid-state structure as **1a** with the η^2 coordination of the acrylic acid ligand and hydrogen bonds between two acrylic acid ligands resulting in a dimer.

Reaction between acrylic acid and nickel(0) complexes in the presence of Cy_3P was already investigated by Yamamoto et al.^[14] In this case, however, no stable nickel(0) complex of acrylic acid was formed, instead the interconversion into the isomeric nickela-cyclic carboxylate $[(\text{Cy}_3\text{P})\text{-Ni}(\text{CH}_2\text{CH}_2\text{COO})]_n$ was observed. This clearly demonstrates the strong influence of the supporting ligands on the following equilibrium (Scheme 2).



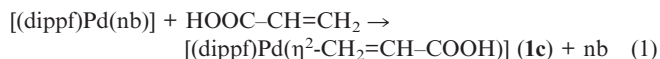
Scheme 2. Equilibrium between $\text{L}_n\text{Ni}(\text{CH}_2=\text{CH}-\text{COOH})$ and $[(\text{L}_n)\text{Ni}(\text{CH}_2\text{CH}_2\text{COO})]$.

1a is surprisingly thermally stable in THF as well in the solid state. Even heating the complex for 3 h in refluxing THF did not result in any reaction. This demonstrates that the isomerization into the nickela-cyclic carboxylate (see Scheme 2) is in this case an energetically unfavourable pathway.

So far, only the metal(0) acrylic acid complex $[(\text{acrylic acid})\text{Fe}(\text{CO})_4]$ was described.^[15] Furthermore, the dimeric Cu^{I} compound $[\text{ClCu}(\text{acrylic acid})]_2$ with η^2 coordinated acrylic acid has been prepared.^[16] In addition, Carmona has found that acrylate hydrido molybdenum(II) and tungsten(II) complexes were formed by reaction of ethylene and CO_2 at an electron-rich $\text{Mo}(0)$ or W^0 fragment.^[17] In contrast, acrylic ester complexes with Ni^0 or Pd^0 have been

found to be stable^[18,19] due to the lack of the reactive COOH group.

To demonstrate that the ability of 1,1'-bis(phosphanyl)-ferrocene ligands in stabilizing acrylic acid complexes is not restricted to nickel(0) we also prepared the related Pd⁰ complex [(dippf)Pd(acrylic acid)] **1c** by reacting of [(dippf)Pd(nb)] (nb = norbornene) with an excess of acrylic acid in THF [Equation (1)].



Isolation of the orange solid and recrystallisation from diethyl ether resulted in orange single crystals. To confirm the structure in the solid state, the X-ray crystal structure analysis of **1c** was carried out. Figure 2 reveals the molecule structure which shows that **1c** has the same arrangement of the ligands as the related nickel(0) acrylic acid complexes with the olefin part of acrylic acid being coordinated at Pd⁰ centre and with a C=C bond lengths of 1.419(3) Å. Also, the other bond lengths and angles lie within a typical range. The angle between the plane (P1,P2,Pd) and the (Pd, C1,C2) is only 2.27° which undoubtedly shows that the Pd⁰ centre is in a planar environment formed by the two P donor atoms and the carbons C1 and C2 of the olefinic part of the acrylic acid ligand. **1c** forms also a dimer in the solid state in which two carboxylic groups are connected by hydrogen bonds.

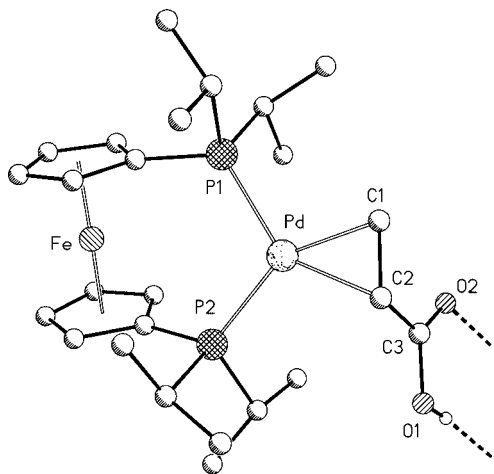
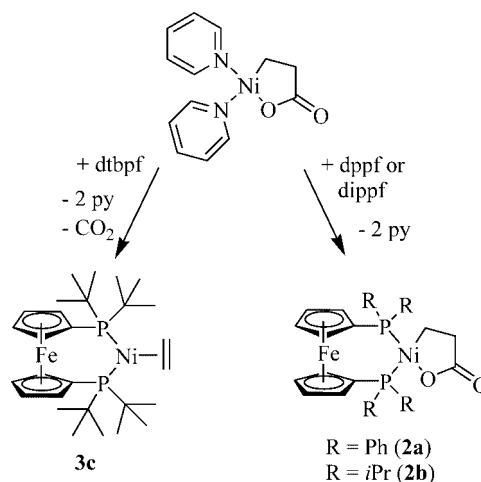


Figure 2. Molecular structure of **1c** (the formation of hydrogen bonds analogously to fig. 1 is indicated by the dotted lines indicating the points at which the dimer is formed; H atoms except the one at O1, and cocrystallized THF have been omitted clarity). Selected bond lengths [Å] and angles [°]: Pd–C1 2.100(2), Pd–C2 2.154(2), Pd–P1 2.3116(7), Pd–P2 2.3215(8), C1–C2 1.419(3), C2–C3 1.457(3), C3–O1 1.327(3), C3–O2 1.237(3), P1–Pd–P2 105.98(3), P1–Pd–C1 104.35(7), P2–Pd–C2 110.67(7), C1–Pd–C2 38.95(9), plane (P1,P2,Pd)-plane(Pd, C1,C2) 2.27.

Nickela-Cyclic Carboxylates of the Type [(L)NiCH₂CH₂COO] (L = dppf, dippf)

In order to proof whether the isomers of **1**, the nickela-cyclic carboxylates of the type [(L)Ni(CH₂CH₂COO)] (L:

dppf, dippf, dtbpf) (**2**) are stable compounds, we reacted [(py)₂Ni(CH₂CH₂COO)] with these ligands in DMF at room temperature. This pyridine complex is a labile ligand complex which serves as precursor for many other reactions.^[20–22] Scheme 3 displays that, depending on the bis-(phosphanyl)ferrocene ligands, different products were formed.



Scheme 3. Reactions of bis(phosphanyl)ferrocene ligands with a nickela-lactone.

In contrast to the formation of the thermally unstable complex **2a** from dppf and [(py)₂Ni(CH₂CH₂COO)], the reaction with dippf resulted in the formation of the thermally stable nickela-cyclic carboxylate **2b** which was isolated as orange crystals in high yields (85%). **2b** was fully characterized by elemental analyses, IR, and NMR spectroscopy, and by X-ray analysis of single crystals. In the ¹H NMR spectrum of **2b** in [D₈]THF the Ni–CH₂ protons were observed at δ = 0.96 ppm and those of the CH₂COO unit resonated at δ = 1.96 ppm; each of these signals correspond to two protons. The signals of the CH₃ groups appeared at 1.23–1.54 ppm, the signals of the CH groups were found at 2.20–2.47 ppm and the cp protons were observed as singlets at δ = 4.40 and 4.44 ppm. In addition, the ¹³C NMR spectrum showed the expected simple pattern of signals for the Ni–CH₂ group at 12.4 and for the CH₂–COO- fragment at δ = 37.2 ppm, besides the resonances for the ligand carbons, and in the ³¹P{¹H} NMR spectrum in [D₇]DMF the ³¹P signals appeared at δ = 36.4 and 44.7 ppm. In the IR spectrum the ν(C=O) band was found at 1634 cm^{–1}.

Single crystals were grown from DMF at –20 °C and the crystal structure of **2b** has been solved by X-ray diffraction analysis. Its molecule structure is displayed in Figure 3 and shows it to be very similar to the starting complex [(py)₂Ni(CH₂CH₂COO)]^[22] and other closely related nickela-cyclic carboxylates.^[1,21] However, due to the disorder of the nickela-cyclopentanone unit a closer comparison with other nickela-cyclic carboxylates is not possible.

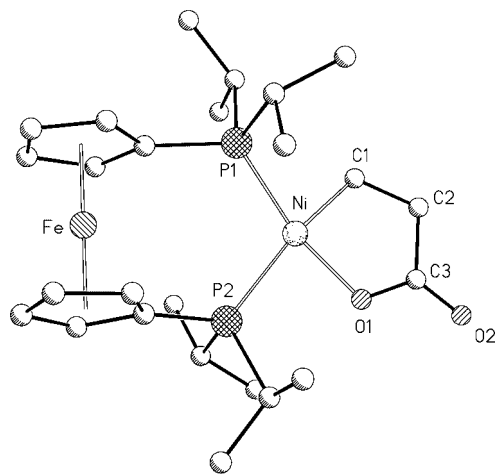


Figure 3. Molecular structure of **2b** (H atoms have been omitted for clarity).

2a is extremely sparingly soluble in organic solvents preventing complete characterization by NMR spectroscopy. The compound shows the typical $\nu(\text{C}=\text{O})$ band for a nickel-cyclic carboxylate at 1642 cm^{-1} in nujol suspension. Furthermore, ^{31}P NMR measurements in $[\text{D}_7]\text{DMF}$ at 25°C gave two signals for the coordinated P atoms in a different chemical environment at $\delta = 19.4$ and 39.0 ppm. In addition, in the ^1H NMR spectrum the two resonances of the coordinated $\text{CH}_2\text{CH}_2\text{COO}$ fragment were observed at $\delta = 0.64$ ppm (as a multiplet of the Ni- CH_2 group) and at $\delta = 1.93$ ppm. The latter appears as a triplet and is assigned to the CH_2COO protons. Comparison of these data with those of the nickel-cyclic carboxylate **2b** suggest that **2a** is also the expected nickel-cyclic carboxylate according to Scheme 3.

2a is a thermally unstable compound. Even at 40°C in DMF the complex decomposes into a mixture of compounds. One product isolated from the reaction mixture was the nickel(0) complex $[(\text{dppf})_2\text{Ni}]$ (**4**). This compound was already generated in situ either by reaction of NiBr_2 , dppf and Zn or by reduction of $[\text{Ni}(\text{acac})_2]$ using DIBAL-H in the presence of dppf ,^[5,6] however to the best of our knowledge it has not been isolated so far. Complex **4** was characterized by elemental analyses, ^1H and ^{13}C NMR spectroscopy and by a single crystal structure analysis. Figure 4 shows its molecule structure and contains the most relevant bond lengths and angles in the caption.

The nickel centre is in the tetrahedral environment of four P donor atoms with typical Ni–P bond lengths. In the dppf ligand A the two cp ligands have a synclinal staggered conformation with a torsion angle τ of 43.9° . This conformation is the most common one found for dppf in its metal complexes (characteristic values: $18^\circ < \tau < 54^\circ$).^[23] In the other ligand B, however, the torsion angle is only 15.0° and the cp ligands have a synperiplanar eclipsed conformation (characteristic region: $0^\circ < \tau < 18^\circ$).^[23] This different arrangement results in different bite angles (106.3° for P1A–Ni–P2A and 101.6° for P1B–Ni–P2B).

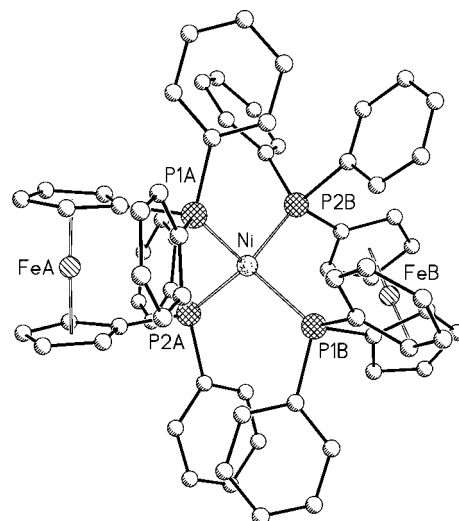


Figure 4. Molecular structure of **4** (H atoms have been omitted for clarity). Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Ni–P1A 2.269(2), Ni–P2A 2.238(2), Ni–P1B 2.243(2), Ni–P2B 2.237(2), P1A–Ni–P1B $120.93(4)$, P1A–Ni–P2A $106.28(5)$, P1A–Ni–P2B $115.62(4)$, P1B–Ni–P2A $106.47(5)$, P1B–Ni–P2B $101.64(4)$, P2A–Ni–P2B $115.62(4)$.

Complexes of the Type $[(\text{L})\text{Ni}(\text{ethylene})]$ [L: dtbpf, (dippf)]

The steric bulky ligand dtbpf yielded in the reaction with $[(\text{py})_2\text{Ni}(\text{CH}_2\text{CH}_2\text{COO})]$ under similar conditions a different product compared to the dippf complex. In this case reductive decoupling of the $\text{NiCH}_2\text{CH}_2\text{COO}$ -unit was observed resulting in the formation of the nickel(0) ethylene complex $[(\text{dtbpf})\text{Ni}(\text{ethylene})]$ **3c** and CO_2 (Scheme 1). This demonstrates how sensitive the reactivity can be influenced by the steric demand of the ligands. **3c** was characterized by NMR spectroscopy in $[\text{D}_7]\text{DMF}$ and by an X-ray analysis of single crystals grown from DMF. When the nickelacycle **2b** was heated at 80°C , reductive decoupling was observed as well, resulting in the formation of $[(\text{dippf})\text{Ni}(\text{ethylene})]$ (**3b**) in good yields.

As expected for a symmetrical structure in solution, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3c** in $[\text{D}_7]\text{DMF}$ at room temperature showed only one signal at $\delta = 65.6$ ppm. In the ^1H NMR spectrum the ethylene protons appeared at $\delta = 1.86$ ppm. The methyl protons of the *tert*-butyl group resonated at $\delta = 1.35$ ppm and the singlets at $\delta = 4.06$ and 4.21 ppm (each integrating to four protons) were assigned to the cp ring protons. Single crystals of **3c** were grown from DMF suitable for X-ray structure determination, and its molecule structure is shown in Figure 5.

The nickel(0) centre is in the distorted tetrahedral environment of the two P donor groups and the carbons of the ethylene ligand with typical bond lengths for the Ni–P and Ni–C bonds. As expected, the double bond of the coordinated ethylene ligand [$\text{C}(1)–\text{C}(2)$ $1.399(4)\text{ \AA}$] is significantly elongated compared to free ethylene.

It is noteworthy, that the hitherto unknown ethylene complexes with 1,1'-bis(phosphanyl)ferrocene ligands can also be formed by other methods. For example, the ethylene

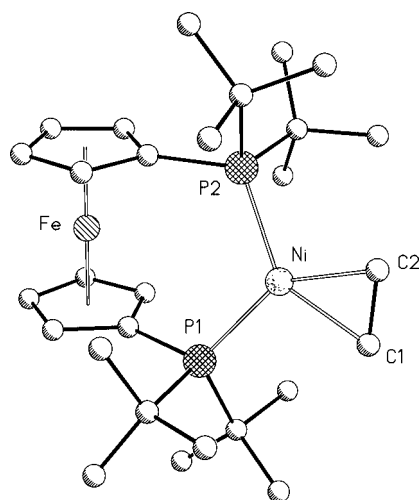


Figure 5. Molecular structure of **3c** (H atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Ni–C1 1.980(3), Ni–C2 1.984(3), Ni–P1 2.1893(6), Ni–P2 2.1908(6), C1–C2 1.399(4), P1–Ni–P2 111.95(3), P1–Ni–C1 103.96(9), P2–Ni–C2 104.03(9), C1–Ni–C2 41.3(2), plane (P1,P2,Ni)–plane(Ni,C1,C2) 15.71.

complex **3b** was additionally prepared by ligand displacement from (cyclododeca-1,5,9-triene)nickel(0) [Equation (2)].



NMR spectroscopic data are very similar to those of the dtbpf complex **3c**, and the crystal structure of single crystals of **3b** (not depicted) is also comparable with that of the closely related complex **3c** and need therefore no further discussion.

Conclusions

Complexes of the type $[(\text{L})\text{M}(\eta^2\text{-CH}_2=\text{CH-COOH})]$ (**1a–1c**) are the first Ni- and Pd⁰ complexes with acrylic acid as olefin-like ligand. Due to the rigidity and the bulkiness of the ferrocenyl-bisphosphane ligands these complexes are surprisingly stable and do not thermally interconvert into the isomeric nickela-lactones of the type $[(\text{L})\text{Ni}(\text{CH}_2\text{CH}_2\text{-COO})]$ (**2**) which could be independently prepared by ligand exchange from $[(\text{py})_2\text{Ni}(\text{CH}_2\text{CH}_2\text{COO})]$ as thermally stable compounds. The nickela-lactones **2b** and **2c** react at heating under reductive decoupling to yield the new ethylene complexes of the type **3**, however, the isomerization of the complexes of the type **2** to form the acrylic acid complexes **1** was not observed.

Experimental Section

General: Infrared spectra were recorded using a Perkin–Elmer 2000 FT-IR; ¹H-NMR spectra were recorded on a Bruker 400 MHz/200 MHz spectrophotometer. The mass spectra were recorded using a SSQ 170, Finnigan Mat. Electro spray mass spectra were recorded on a Finnigan MAT, MAT 95 XL. Values for *m/z* are for the most intense peak of isotope envelope.

All manipulations were carried out by using modified Schlenk techniques under an atmosphere of argon. Prior to use, THF, benzene and diethyl ether were dried with potassium hydroxide and distilled from sodium/benzophenone. DMF was dried with CaH₂.

dppf, dippf, and dtbpf were prepared in analogy to known procedures by reaction of *n*BuLi/tmeda with ferrocene, followed by addition of the chlorodiphenylphosphane, chlorodiisopropylphosphane or chlorodi-*tert*-butylphosphane.^[24–27] $[\text{Ni}(\text{cod})_2]$,^[28] $[(\text{py})_2\text{-Ni}(\text{C}_2\text{H}_4\text{COO})]$ ^[22] and $[\text{Pd}(\eta^2\text{-C}_7\text{H}_{10})_3]$ ^[29] were prepared according to literature procedures.

[(dppf)Ni(η²-CH₂=CH-COOH)] (1a**):** A solution of dppf (2.67 g, 4.82 mmol) in THF (30 mL) was added to solid $[\text{Ni}(\text{cod})_2]$ (1.32 g, 4.80 mmol). The suspension was stirred until all solids had dissolved. Afterwards the stirred solution was cooled to 0 °C and acrylic acid (0.37 g, 5.13 mmol) was added, resulting in formation of a yellow precipitate. This solid was isolated by filtration and dried in a vacuum. Yield: 2.83 g (71%). Suitable crystals of (**1a**)·2THF for X-ray measurement were obtained by slowly cooling a saturated solution in THF from room temperature to 5 °C. In a similar manner, crystals of $[(\text{dppf})\text{Ni}(\eta^2\text{-CH}_2=\text{CH-COOH})]\cdot 1.5\text{DMF}$ were obtained from a solution of DMF. Those crystals were used for elemental analysis. C_{41.5}H_{42.5}FeN_{1.5}NiO_{3.5}P₂ (794.8) calcd. C 62.71, H 5.39, N 2.64; found C 62.11, H 5.54, N 2.53. ¹H NMR ([D₈]THF, 25 °C): δ = 1.95 (m, 1 H, CH₂=), 2.25 (m, 1 H, CH₂=), 2.98 (m, 1 H, CH=), 3.89 (s, 1 H, CH cp), 4.07 (s, 1 H, CH cp), 4.22 (s, 2 H, CH cp), 4.26 (s, 1 H, CH cp), 4.29 (s, 1 H, CH cp), 4.35 (s, 2 H, CH cp), 7.28–7.80 (m, 20 H, CH ph), 9.64 (br., 1 H, COOH). ¹³C{¹H} NMR ([D₈]THF, 25 °C): 43.9 (d, *J*_{PC} = 19.6 Hz, CH₂=), 49.8 (d, *J*_{PC} = 11.6 Hz, CH=), 71.1 (dd, *J*_{PC} = 7.3 Hz, *J*_{PC} = 4.1 Hz, CH cp), 72.9 (d, *J*_{PC} = 6.4 Hz, CH cp), 74.4 (dd, *J*_{PC} = 20.0 Hz, *J*_{PC} = 6.0 Hz, CH cp), 75.3 (dd, *J*_{PC} = 17.5 Hz, *J*_{PC} = 13.8 Hz, CH cp), 81.9 (dd, *J*_{PC} = 40.4 Hz, *J*_{PC} = 5.1 Hz, C cp), 82.2 (dd, *J*_{PC} = 40.4 Hz, *J*_{PC} = 5.1 Hz, C cp), 128.4 (dd, *J*_{PC} = 7.5 Hz, *J*_{PC} = 2.9 Hz, CH), 128.7 (d, *J*_{PC} = 9.3 Hz, CH), 129.3 (d, *J*_{PC} = 8.3 Hz, CH), 130.2 (d, *J*_{PC} = 20.1 Hz, CH), 134.0 (dd, *J*_{PC} = 12.2 Hz, *J*_{PC} = 5.9 Hz, CH), 135.5 (dd, *J*_{PC} = 49.6 Hz, *J*_{PC} = 15.2 Hz, CH), 137.2 (d, *J*_{PC} = 37.8 Hz, C), 137.2 (d, *J*_{PC} = 37.8 Hz, C), 175.9 (COOH). ³¹P{¹H} NMR ([D₈]THF, 25 °C): δ = 26.7 (d, *J*_{PP} = 21.9 Hz), 32.6 (d, *J*_{PP} = 21.9 Hz).

[(dippf)Ni(η²-CH₂=CH-COOH)] (1b**):** A solution of dippf (2.21 g, 5.28 mmol) in THF (30 mL) was added to $[\text{Ni}(\text{cod})_2]$ (1.45 g, 5.27 mmol). The mixture was stirred until all solids had dissolved and then cooled to 0 °C. At this temperature acrylic acid (0.38 g, 5.27 mmol) was added drop wise. The resulting reaction mixture was stored at 5 °C overnight. Afterwards the solvent was removed by distillation under reduced pressure and ether was added to the remaining residue, resulting in the formation of a yellow precipitate. This solid was isolated by filtration and dried in a vacuum. Suitable crystals for X-ray measurement were obtained by layering a saturated solution of **1b** in DMF with ether. Yield: 1.76 g (60.6%). C₂₅H₄₀FeNiO₂P₂ (549.0) calcd. C 54.68, H 7.34; found C 54.36, H 7.53. ¹H NMR ([D₈]THF): δ = 0.65 (dd, *J* = 10.3 Hz, *J* = 3.6 Hz, 3 H, CH₃), 0.74 (m, 3 H, CH₃), 0.65 (dd, *J* = 10.3 Hz, *J* = 3.6 Hz, 3 H, CH₃), 1.03 (dd, *J* = 15.6 Hz, *J* = 7.1 Hz, 3 H, CH₃), 1.15 (dd, *J* = 13.7 Hz, *J* = 6.9 Hz, 3 H, CH₃), 1.27–1.56 (m, 12 H, CH₃), 1.85 [m, 2 H, CH(CH₃)₂], 1.97 [m, 2 H, CH(CH₃)₂], 2.57 (br., 1 H, =CH₂), 2.88 (br., 1 H, CH=), 3.94 (s, 2 H, CH cp), 3.99 (s, 1 H, CH cp), 4.01 (s, 1 H, CH cp), 4.03 (s, 2 H, CH cp), 4.16 (s, 1 H, CH cp), 4.29 (s, 1 H, CH cp), 10.35 (br., 1 H, COOH). ¹³C{¹H} NMR ([D₈]THF): δ = 17.7 (CH₃), 17.8 (CH₃), 19.2 (CH₃), 19.4 (CH₃), 20.5 (d, *J*_{PC} = 7.3 Hz, CH₃), 21.2 (CH₃), 22.5 (d, *J*_{PC} = 9.2 Hz, CH₃), 22.6 (d, *J*_{PC} = 8.7 Hz, CH₃), 26.3 (d, *J*_{PC} =

38.6 Hz, $2 \times \text{CH-P}$), 26.7 (d, $^1J_{\text{PC}} = 23.5$ Hz, $2 \times \text{CH-P}$), 32.7 (br., $=\text{CH}_2$), 42.7 (br., $=\text{CH}$), 69.3 (CH, cp), 69.4 (CH, cp), 71.0 ($2 \times \text{CH}$, cp), 72.4 (CH, cp), 72.7 (CH, cp), 73.8 (d, $J_{\text{PC}} = 4.0$ Hz, CH, cp), 73.9 (d, $J_{\text{PC}} = 4.7$ Hz, CH, cp), 83.8 (dd, $^1J_{\text{PC}} = 23.7$ Hz, $^3J_{\text{PC}} = 5.1$ Hz, C-P, cp), 84.7 (d, $^1J_{\text{PC}} = 25.4$ Hz, C-P, cp), 177.7 (br., COOH). $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$, 25 °C): $\delta = 46.9$ (d, $^2J_{\text{PP}} = 15.3$ Hz), 39.3 (d, $^2J_{\text{PP}} = 15.3$ Hz).

[(dippf)Pd(nb)]: A solution of dippf (0.36 g, 0.86 mmol) in THF (20 mL) was cooled to -30 °C and added to solid $[(\text{nb})_3\text{Pd}]$ (0.30 g, 0.77 mmol) at this temperature. The stirred solution was allowed to slowly warm to room temperature. Afterwards half of the solvent was distilled off under reduced pressure. The remaining orange coloured solution was stored at -20 °C for several days, resulting in the formation of orange red crystals. These crystals were separated by filtration and dried in a vacuum. From the mother liquor a second crop of product was obtained by further reduction of the volume and layering with diethyl ether. Yield: 120 mg (25%). $\text{C}_{29}\text{H}_{46}\text{P}_2\text{FePd}$ (618.9) calcd. C 56.28, H 7.49; found C 56.12, H 7.52. ^1H NMR ($[\text{D}_8]\text{THF}$, 25 °C): $\delta = 0.58$ (d, $^2J_{\text{H,H}} = 7.6$ Hz, 1 H, CHH' bridge), 1.05–1.30 (m, 15 H, $4 \times \text{CH}_3$, $2 \times \text{CHH}'$, CHH' bridge), 1.52 (m, 2 H, $2 \times \text{CHH}'$), 2.19 (m, $^2J_{\text{H,P}} = 6.0$ Hz, 4 H, CH *iPr*), 2.88 (s, 2 H, CH), 2.99 (d, $^2J_{\text{H,P}} = 6.0$ Hz, 2 H, CH), 4.23 (s, 2 H, CH cp), 4.28 (s, 6 H, CH cp). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$): $\delta = 20.0$ (t, $^2J_{\text{C,P}} = 5.0$ Hz, $4 \times \text{CH}_3$ *iPr*), 20.4 (br., $4 \times \text{CH}_3$ *iPr*), 26.9 (t, $^1J_{\text{C,P}} = 6.3$ Hz, $2 \times \text{CH}$ *iPr*), 27.0 (t, $^1J_{\text{C,P}} = 7.6$ Hz, $2 \times \text{CH}$ *iPr*), 29.9 (t, $^4J_{\text{CP}} = 5.0$ Hz, $2 \times \text{CHH}'$), 43.4 (s, CHH'), 45.6 (s, $2 \times \text{CH}$), 64.2 (pseudo-dt, $2 \times = \text{CH-}$), 69.8 (s, $4 \times \text{CH}$ cp), 73.7 (t, $^2J_{\text{C,P}} = 3.8$ Hz, $4 \times \text{CH}$ cp), 85.3 (t, $^1J_{\text{C,P}} = 9.5$ Hz, $2 \times \text{C}$ cp). $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, $[\text{D}_8]\text{THF}$, 25 °C): $\delta = 36.4$ (s).

[(dippf)Pd($\eta^2\text{-CH}_2=\text{CH-COOH}$)] (1c): Acrylic acid (0.03 mL, 0.44 mmol) was added to a solution of $[(\text{dippf})\text{Pd}(\text{nb})]$ (40 mg, 0.065 mmol) in THF (1 mL) at 0 °C with rapid stirring. The resulting mixture was warmed to room temperature and stirred for additional 30 min. Afterwards the solvent was completely removed by distillation under reduced pressure. The remaining orange red sticky oil was treated with diethyl ether (2 mL) and stirred for 20 min. The resulting suspension was filtered and the clear yellow solution was stored at -20 °C. The isolated solid was redissolved in a few drops of THF and that solution was kept at 5 °C for several days. From both solutions, suitable crystals for X-ray measurement were obtained; $[(\text{dippf})\text{Pd}(\eta^2\text{-CH}_2=\text{CH-COOH})]$ from ether, $[(\text{dippf})\text{Pd}(\eta^2\text{-CH}_2=\text{CH-COOH})]\cdot\text{THF}$ from THF. The yield was not determined.

[(dppf)Ni($\text{C}_2\text{H}_4\text{-COO}$)] (2a): Yellow dppf (0.77 g, 1.39 mmol) was added to a suspension of green $[(\text{py})_2\text{Ni}(\text{C}_2\text{H}_4\text{COO})]$ (0.40 g, 1.38 mmol) in DMF (8 mL) at 0 °C. The solution was allowed to slowly warm to room temperature, while the starting materials dissolved and a yellow precipitate was formed. To remove liberated pyridine, 2 mL of DMF was distilled off under reduced pressure at room temperature. Afterwards the yellow solid was isolated by filtration, washed with diethyl ether and dried in a vacuum. Yield: 0.91 g (96%) yellow powder. ^1H NMR ($[\text{D}_7]\text{DMF}$, 25 °C): $\delta = 0.64$ (m, 2 H, Ni- CH_2), 1.93 (t, $J = 6.9$ Hz, 2 H, $\text{CH}_2\text{-COO}$), 4.45 (s, 4 H, CH cp), 7.45–8.00 (m, 20 H Phenyl). $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_7]\text{DMF}$, 25 °C): $\delta = 19.4$ (br), 39.0 (br). IR (nujol): $\tilde{\nu} = (\text{C=O})$ 1642 cm^{-1} .

[(dippf)Ni($\text{C}_2\text{H}_4\text{-COO}$)] (2b): A solution of dippf (0.83 g, 1.98 mmol) in DMF (4 mL) was added to a suspension of green $[(\text{py})_2\text{Ni}(\text{C}_2\text{H}_4\text{COO})]$ (0.49 g, 1.70 mmol) in DMF (4 mL) at room temperature. The resulting solution was stirred for 1 h. Meanwhile an orange yellow precipitate was formed. The solid was afterwards collected by filtration and dried in a vacuum. Suitable crystals for X-ray measurement were obtained from a saturated solution of the

complex in DMF at room temp. und subsequent cooling to -20 °C. Yield: 0.8 g (85%). $\text{C}_{25}\text{H}_{40}\text{P}_2\text{O}_2\text{FeNi}$ (549.08) calcd. C 54.69, H 7.34; found. C 54.21, H 7.39. ^1H NMR ($[\text{D}_8]\text{THF}$, 25 °C): $\delta = 0.96$ (tdd, $^3J_{\text{H,H}} = 6.9$ Hz, $^3J_{\text{P,H}} = 4.0$ Hz, $^3J_{\text{P,H}} = 8.7$ Hz, 2 H, Ni- CH_2), 1.23–1.54 (m, 24 H, CH_3), 1.96 (tdd, $^3J_{\text{H,H}} = 7.0$ Hz, $^4J_{\text{P,H}} = 5.1$ Hz, $^4J_{\text{P,H}} = 7.2$ Hz, 2 H, $\text{CH}_2\text{-COO}$), 2.20–2.47 (m, 4 H, CH), 4.40 (m, 4 H, CH cp), 4.44 (m, 4 H, CH cp). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$, 25 °C): $\delta = 12.4$ (dd, $J = 31.6$ Hz, $J = 59.9$ Hz, Ni- CH_2), 19.8 (d, $J = 11.5$ Hz, CH_3), 20.6 (d, $J = 5.7$ Hz, CH_3), 37.2 (dd, $J = 2.7$ Hz, $J = 4.6$ Hz, $\text{CH}_2\text{-COO}$), 71.1 (d, $J = 4.5$ Hz, CH cp), 71.9 (d, $J = 3.9$ Hz, CH' cp), 73.3 (d, $J = 6.3$ Hz, CH cp), 73.5 (d, $J = 6.2$ Hz, CH' cp), 82.2 (d, $J = 10.7$ Hz, C cp), 82.8 (d, $J = 10.7$ Hz, C' cp), 185.5 (m, COO). The signals for CH groups of the isopropyl substituents overlap with the signals of the used solvent and were therefore not detected. $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_7]\text{DMF}$, 25 °C): $\delta = 36.5$ (d, $J_{\text{P,P}} = 14.4$ Hz), 44.7 (d, $J_{\text{P,P}} = 14.4$ Hz). IR (nujol): $\tilde{\nu} = (\text{C=O})$ 1634 cm^{-1} (s).

[(dippf)Ni($\eta^2\text{-C}_2\text{H}_4$)] (3b): a) A suspension of $[(\text{dippf})\text{Ni}(\text{C}_2\text{H}_4\text{-COO})]$ (2b) (200 mg, 0.36 mmol) in DMF (5 mL) was heated to 80 °C. The resulting clear solution was stirred at this temperature for additional 3 h. Upon slow cooling to room temperature orange coloured crystals were formed overnight. These crystals were collected by filtration and dried in a vacuum. A second crop of product was obtained by storing the mother liquor at 0 °C for 3 d. Yield: 130 mg (70%). $\text{C}_{24}\text{H}_{40}\text{FeNiP}_2$ (505.06) calcd. C 57.07, H 7.98; found 57.17, H 8.16. ^1H NMR (C_6D_6 , 25 °C): $\delta = 1.13$ (sext, $J = 6.8$ Hz, 24 H, CH_3), 2.05 (m, 4 H, CH *iPr*), 2.19 (br., 4 H, C_2H_4), 4.06 (br., 4 H, CH cp), 4.21 (br., 4 H, CH cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C): $\delta = 19.9$ (t, $^2J_{\text{PC}} = 3.2$ Hz, CH_3), 20.1 (t, $^2J_{\text{PC}} = 3.2$ Hz, CH_3), 26.0 (t, $^1J_{\text{PC}} = 10.6$ Hz, CH *iPr*), 34.7 (t, $^2J_{\text{PC}} = 7.3$ Hz, CH_2), 69.3 (br., CH, cp), 72.7 (t, $^2J_{\text{PC}} = 2.9$ Hz, CH cp), 86.4 (t, $^1J_{\text{PC}} = 12.6$ Hz, C cp). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C): $\delta = 42.4$ (s).

[(dtbpf)Ni($\eta^2\text{-C}_2\text{H}_4$)] (3c): A solution of dtbpf (0.50 g, 1.05 mmol) in DMF (3 mL) was added to a suspension of green $[(\text{py})_2\text{Ni}(\text{C}_2\text{H}_4\text{-COO})]$ (0.29 g, 1.00 mmol) in DMF (3 mL) at room temperature. The resulting orange brown solution was stirred for 2 h and afterwards 3 mL of DMF were distilled off under reduced pressure at room temperature. The resulting orange coloured precipitate was collected by filtration and dried in a vacuum. Suitable crystals for X-ray measurement were obtained from a saturated solution of the complex in DMF at room temp. und subsequent cooling. Yield: 0.3 g (50%). $\text{C}_{28}\text{H}_{48}\text{P}_2\text{FeNi}$ (561.18). ^1H NMR ($[\text{D}_7]\text{DMF}$, 25 °C): $\delta = 1.35$ (d, $^3J_{\text{H,P}} = 11.5$ Hz, 36 H, CH_3 *tBu*), 1.80 (s, 4 H, CH_2), 4.40 (m, 4 H, CH cp), 4.45 (br., 4 H, CH cp). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$, 25 °C): $\delta = 32.0$ (s, CH_3 *tBu*), 36.6 (t, $^2J_{\text{C,P}} = 7.0$ Hz, C_2H_4), 37.3 (t, $^1J_{\text{C,P}} = 6.2$ Hz, C *tBu*), 69.6 (s, CH cp), 75.4 (s, CH cp), 87.0 (t, $^1J_{\text{C,P}} = 8.4$ Hz, C cp). $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_7]\text{DMF}$, 25 °C): $\delta = 65.6$ (s).

[(dppf) $_2$ Ni] (4):^[5,6] A suspension of 2a in THF was heated to 40 °C and DMF was added with rapid stirring until nearly all solids have dissolved. The resulting solution was filtered through celite and stored for 2 weeks at 5 °C. During this period, some precipitate was formed and afterwards removed by decantation. The remaining solution was concentrated in vacuo until all THF was removed. The residual orange brown coloured solution in DMF was stored for several weeks at -20 °C, after which orange red crystals had occurred. These crystals were collected by filtration and dried in a vacuum. The yield was not determined. $\text{C}_{68}\text{H}_{60}\text{P}_4\text{Fe}_2\text{Ni}$ (1171.51) calcd. C 69.72, H 5.16; found C 69.82, H 5.09. ^1H NMR ($[\text{D}_8]\text{THF}$, 25 °C): $\delta = 3.97$ (s, 8 H, CH cp), 4.10 (s, 8 H, CH cp), 6.84 (pt, $J = 7.4$ Hz, 16 H, *o*-CH ph), 7.01 (pt, $J = 7.2$ Hz, 8 H, *p*-CH ph),

7.45–7.55 (m, 16 H, *m*-CH ph). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$, 25 °C): δ = 70.5 (s, $8 \times \text{CH}$ cp), 75.2 (s, $8 \times \text{CH}$ cp), 87.5 (m, $4 \times \text{C}$ cp), 127.4 (s, $16 \times m\text{-CH}$ ph), 128.1 (s, $8 \times p\text{-CH}$ ph), 135.1 (pt, $J_{\text{C,P}}$ = 7.5 Hz, $16 \times o\text{-CH}$ ph), 142.0 (m, $8 \times \text{C}$ ph).

X-ray Crystallographic Studies: The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer by using graphite-monochromated Mo- K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.^[30,31] The structures were solved by direct methods (SHELXS^[32]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97^[33]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.^[4] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 1a-1.5DMF:^[34] $\text{C}_{37}\text{H}_{32}\text{FeNiO}_2\text{P}_2 \cdot 1.5\text{C}_3\text{H}_7\text{ON}$, M_r = 795.78 g mol⁻¹, orange prism, size $0.12 \times 0.12 \times 0.10$ mm³, monoclinic, space group $P2_1/n$, a = 14.5426(3), b = 13.9250(6), c = 19.0968(7) Å, β = 108.237(2)°, V = 3673.0(2) Å³, T = -90 °C, Z = 4, $\rho_{\text{calcd.}}$ = 1.439 g cm⁻³, μ (Mo- K_α) = 10.38 cm⁻¹, $F(000)$ = 1660, 12426 reflections in $h(-18/18)$, $k(-18/16)$, $l(-24/24)$, measured in the range $1.55^\circ \leq \theta \leq 27.60^\circ$, completeness Θ_{max} = 93%, 7921 independent reflections, R_{int} = 0.0553, 4887 reflections with $F_o > 4\sigma(F_o)$, 441 parameters, 0 restraints, $R_{1\text{obs}}$ = 0.0743, $wR_{2\text{obs}}$ = 0.2116, $R_{1\text{all}}$ = 0.1110, $wR_{2\text{all}}$ = 0.2206, GOOF = 1.058, largest difference peak and hole: 0.815/–0.499 e Å⁻³.

Crystal Data for 1a-2THF:^[34] $\text{C}_{37}\text{H}_{32}\text{FeNiO}_2\text{P}_2 \cdot 2\text{C}_4\text{H}_8\text{O}$, M_r = 829.33 g mol⁻¹, orange prism, size $0.18 \times 0.12 \times 0.08$ mm³, triclinic, space group $P\bar{1}$, a = 11.1233(7), b = 12.7648(6), c = 14.696(1) Å, α = 87.660(4), β = 79.684(3), γ = 77.065(3)°, V = 2000.8(2) Å³, T = -90 °C, Z = 2, $\rho_{\text{calcd.}}$ = 1.377 g cm⁻³, μ (Mo- K_α) = 9.55 cm⁻¹, $F(000)$ = 868, 13225 reflections in $h(-14/14)$, $k(-16/16)$, $l(-19/18)$, measured in the range $1.64^\circ \leq \theta \leq 27.49^\circ$, completeness Θ_{max} = 95.6%, 8782 independent reflections, R_{int} = 0.0588, 5591 reflections with $F_o > 4\sigma(F_o)$, 484 parameters, 0 restraints, $R_{1\text{obs}}$ = 0.0447, $wR_{2\text{obs}}$ = 0.0980, $R_{1\text{all}}$ = 0.0746, $wR_{2\text{all}}$ = 0.1036, GOOF = 0.901, largest difference peak and hole: 0.719/–0.765 e Å⁻³.

Crystal Data for 1b:^[34] $\text{C}_{25}\text{H}_{40}\text{FeNiO}_2\text{P}_2$, M_r = 549.07 g mol⁻¹, orange prism, size $0.12 \times 0.12 \times 0.10$ mm³, triclinic, space group $P\bar{1}$, a = 10.2600(4), b = 10.8590(4), c = 12.7729(3) Å, α = 84.885(2), β = 73.799(2), γ = 68.3570(10)°, V = 1270.07(7) Å³, T = -90 °C, Z = 2, $\rho_{\text{calcd.}}$ = 1.436 g cm⁻³, μ (Mo- K_α) = 14.58 cm⁻¹, $F(000)$ = 580, 8596 reflections in $h(-12/13)$, $k(-14/12)$, $l(-16/14)$, measured in the range $2.40^\circ \leq \theta \leq 27.48^\circ$, completeness Θ_{max} = 96.6%, 5633 independent reflections, R_{int} = 0.0549, 4352 reflections with $F_o > 4\sigma(F_o)$, 304 parameters, 0 restraints, $R_{1\text{obs}}$ = 0.0341, $wR_{2\text{obs}}$ = 0.0920, $R_{1\text{all}}$ = 0.0458, $wR_{2\text{all}}$ = 0.0949, GOOF = 1.002, largest difference peak and hole: 0.553/–0.532 e Å⁻³.

Crystal Data for 1c-THF:^[34] $\text{C}_{25}\text{H}_{40}\text{FeO}_2\text{P}_2\text{Pd} \cdot \text{C}_4\text{H}_8\text{O}$, M_r = 668.86 g mol⁻¹, yellow prism, size $0.05 \times 0.05 \times 0.05$ mm³, monoclinic, space group $P2_1/n$, a = 10.242(2), b = 15.994(3), c = 18.487(4) Å, β = 96.18(3)°, V = 3010.8(10) Å³, T = -90 °C, Z = 4, $\rho_{\text{calcd.}}$ = 1.476 g cm⁻³, μ (Mo- K_α) = 12.13 cm⁻¹, $F(000)$ = 1392, 20354 reflections in $h(-10/13)$, $k(-20/20)$, $l(-23/23)$, measured in the range $1.69^\circ \leq \theta \leq 27.47^\circ$, completeness Θ_{max} = 99.6%, 6871 independent reflections, R_{int} = 0.0232, 6267 reflections with $F_o > 4\sigma(F_o)$, 349 parameters, 0 restraints, $R_{1\text{obs}}$ = 0.0291, $wR_{2\text{obs}}$ = 0.0789, $R_{1\text{all}}$ = 0.0327, $wR_{2\text{all}}$ = 0.0820, GOOF = 0.983, largest difference peak and hole: 1.891/–0.850 e Å⁻³.

Crystal Data for 1c:^[34] $\text{C}_{25}\text{H}_{40}\text{FeO}_2\text{P}_2\text{Pd}$, M_r = 596.76 g mol⁻¹, yellow prism, size $0.06 \times 0.04 \times 0.04$ mm³, monoclinic, space group $C2/c$, a = 19.7868(7), b = 10.0423(4), c = 27.6093(9) Å, β =

106.060(2)°, V = 5272.0(3) Å³, T = -90 °C, Z = 8, $\rho_{\text{calcd.}}$ = 1.504 g cm⁻³, μ (Mo- K_α) = 13.73 cm⁻¹, $F(000)$ = 2464, 15456 reflections in $h(-24/25)$, $k(-13/9)$, $l(-35/34)$, measured in the range $2.14^\circ \leq \theta \leq 27.50^\circ$, completeness Θ_{max} = 97.4%, 5901 independent reflections, R_{int} = 0.1058, 4654 reflections with $F_o > 4\sigma(F_o)$, 300 parameters, 0 restraints, $R_{1\text{obs}}$ = 0.0537, $wR_{2\text{obs}}$ = 0.1336, $R_{1\text{all}}$ = 0.0736, $wR_{2\text{all}}$ = 0.1471, GOOF = 1.028, largest difference peak and hole: 0.847/–0.871 e Å⁻³.

Crystal Data for 2b:^[34] $\text{C}_{25}\text{H}_{40}\text{FeNiO}_2\text{P}_2$, M_r = 549.07 g mol⁻¹, yellow-green prism, size $0.10 \times 0.10 \times 0.02$ mm³, monoclinic, space group $P2_1/c$, a = 17.3484(9), b = 8.7957(6), c = 16.7547(8) Å, β = 96.382(4)°, V = 2540.8(2) Å³, T = -90 °C, Z = 4, $\rho_{\text{calcd.}}$ = 1.435 g cm⁻³, μ (Mo- K_α) = 14.57 cm⁻¹, $F(000)$ = 1160, 9791 reflections in $h(-22/22)$, $k(-10/11)$, $l(-21/21)$, measured in the range $2.36^\circ \leq \theta \leq 27.45^\circ$, completeness Θ_{max} = 99.4%, 5774 independent reflections, R_{int} = 0.0555, 3696 reflections with $F_o > 4\sigma(F_o)$, 288 parameters, 0 restraints, $R_{1\text{obs}}$ = 0.0740, $wR_{2\text{obs}}$ = 0.1567, $R_{1\text{all}}$ = 0.1260, $wR_{2\text{all}}$ = 0.1807, GOOF = 1.066, largest difference peak and hole: 1.321/–0.610 e Å⁻³.

Crystal Data for 3b:^[34] $\text{C}_{24}\text{H}_{40}\text{FeNiP}_2$, M_r = 505.06 g mol⁻¹, orange prism, size $0.10 \times 0.09 \times 0.08$ mm³, triclinic, space group $P\bar{1}$, a = 8.7665(2), b = 9.0021(2), c = 17.1663(3) Å, α = 87.0310(10), β = 82.8390(10), γ = 65.4730(10)°, V = 1222.86(4) Å³, T = -90 °C, Z = 2, $\rho_{\text{calcd.}}$ = 1.372 g cm⁻³, μ (Mo- K_α) = 15.02 cm⁻¹, $F(000)$ = 536, 9447 reflections in $h(-10/11)$, $k(-11/11)$, $l(-22/22)$, measured in the range $2.74^\circ \leq \theta \leq 27.43^\circ$, completeness Θ_{max} = 99.5%, 5557 independent reflections, R_{int} = 0.0345, 4870 reflections with $F_o > 4\sigma(F_o)$, 277 parameters, 0 restraints, $R_{1\text{obs}}$ = 0.0343, $wR_{2\text{obs}}$ = 0.0894, $R_{1\text{all}}$ = 0.0416, $wR_{2\text{all}}$ = 0.0950, GOOF = 1.016, largest difference peak and hole: 0.374/–0.557 e Å⁻³.

Crystal Data for 3c:^[34] $\text{C}_{28}\text{H}_{48}\text{FeNiP}_2$, M_r = 561.16 g mol⁻¹, orange prism, size $0.10 \times 0.08 \times 0.07$ mm³, orthorhombic, space group $Pbca$, a = 16.0359(2), b = 11.61920(10), c = 29.9821(4) Å, V = 5586.39(11) Å³, T = -90 °C, Z = 8, $\rho_{\text{calcd.}}$ = 1.334 g cm⁻³, μ (Mo- K_α) = 13.22 cm⁻¹, $F(000)$ = 2400, 11956 reflections in $h(-20/20)$, $k(-15/15)$, $l(-38/38)$, measured in the range $2.88^\circ \leq \theta \leq 27.48^\circ$, completeness Θ_{max} = 99.4%, 6363 independent reflections, R_{int} = 0.0422, 4695 reflections with $F_o > 4\sigma(F_o)$, 317 parameters, 0 restraints, $R_{1\text{obs}}$ = 0.0368, $wR_{2\text{obs}}$ = 0.0784, $R_{1\text{all}}$ = 0.0630, $wR_{2\text{all}}$ = 0.0863, GOOF = 0.985, largest difference peak and hole: 0.376/–0.447 e Å⁻³.

Crystal Data for 4:^[34] $\text{C}_{68}\text{H}_{56}\text{Fe}_2\text{NiP}_4$, M_r = 1167.42 g mol⁻¹, orange prism, size $0.03 \times 0.03 \times 0.02$ mm³, triclinic, space group $P\bar{1}$, a = 12.9787(5), b = 13.8150(6), c = 15.2711(7) Å, α = 86.939(2), β = 89.940(2), γ = 87.033(2)°, V = 2730.5(2) Å³, T = -90 °C, Z = 2, $\rho_{\text{calcd.}}$ = 1.420 g cm⁻³, μ (Mo- K_α) = 10.26 cm⁻¹, $F(000)$ = 1208, 18086 reflections in $h(-16/15)$, $k(-16/17)$, $l(-19/19)$, measured in the range $2.10^\circ \leq \theta \leq 27.50^\circ$, completeness Θ_{max} = 95.8%, 11986 independent reflections, R_{int} = 0.0487, 7647 reflections with $F_o > 4\sigma(F_o)$, 676 parameters, 0 restraints, $R_{1\text{obs}}$ = 0.0629, $wR_{2\text{obs}}$ = 0.1086, $R_{1\text{all}}$ = 0.1191, $wR_{2\text{all}}$ = 0.1295, GOOF = 1.045, largest difference peak and hole: 0.444/–0.472 e Å⁻³.

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