Supplementary Material (ESI) for Chemical Communications

# A key step in the formation of acrylic acid from $CO_2$ and ethylene: the transformation of a nickelalactone into a nickel-acrylate complex

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## Experimental Section

### Instrumentation and Materials

$^1H$ NMR and $^{13}C$ 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. J values are given in Hz. 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, toluene and diethyl ether were dried over potassium hydroxide and distilled over Na/ benzophenone. Dmf and pyridine were distilled over $CaH_2$.

Dppm, dppe, dppp, dppb, neocuproine, bromocyclopentane, 1-bromo-4-fluorobenzene, 5-bromo-1,2,3-trifluorobenzene and 1,2-bis(dichlorophosphino)-ethane were obtained from Aldrich. Succinic acid-$d_6$ was purchased from Cambridge Isotope Laboratories, Inc. $[(tmeda)Ni(C_2H_4COO)]$ and $[(py)_2Ni(C_2H_4COO)]$ were prepared according to literature procedures [1,2]. Their deuterium labelled analogues $[(tmeda)Ni(C_2D_4COO)]$ and $[(py)_2Ni(C_2D_4COO)]$ were prepared analogously.

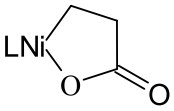
## Syntheses

### F$_{12}$-dppe:

A Grignard solution was prepared from 5-bromo-1,2,3-trifluorobenzene (6.5 g, 30.8 mmol) and magnesium turnings (1.0 g, 41.1 mmol) in ether (40 cm$^3$). The solution of *m*,*m*',*p*-trifluorophenylmagnesiumbromide was filtered and its concentration was obtained by titration of an aliquote with 0.1 n hydrochloric acid (yield: 84 %). To the stirred Grignard solution bis(dichlorphosphino)-ethane (1.15 g, 4.96 mmol) was added by a syringe. After the exothermic reaction finished the reaction mixture was refluxed for 1 h. The reaction mixture was hydrolysed by an aqueous solution of $NH_4Cl$. The organic layer was separated, dried with anhydrous $Na_2SO_4$ and the ether was removed. The product was washed with cold methanol and dried in a vacuum. F$_{12}$-dppe crystallised as colourless crystals (yield: 2.70 g, 88.6 %), mp. 184-186 °C (from diethylether). (Found: C, 50.8; H, 2.0. $C_{26}H_{12}F_{12}P_2$ requires C, 51.0; H: 2.0%); $\delta_H$(200 MHz; $CDCl_3$; 25 °C) 1.94 (4 H, t, $^2J_{P,H}$ 4.9, P-CH$_2$) and 6.9 (8 H, dddd, *o*-CH Ph); $\delta_{P\{H\}}$(81 MHz; $CDCl_3$; 25 °C) -6.9 (s); $\delta_{F\{H\}}$(188 MHz; $CDCl_3$; 25 °C) -157,3 (t, $^3J_{F,F}$ 20.1, *p*-CF Ph) and -132.3 (d, $^3J_{F,F}$ 20.1, *m*-CF Ph); *m/z* (EI) 456 (M$^+$), 379 (M$^+$ - F$_3$-Ph).

Cyp$_2$P(CH$_2$)$_2$Cyp$_2$ and F$_4$-dppe were prepared in a similar procedure given for F$_{12}$-dppe.

### Synthesis of the nickelalactones



**Complex 1** L = glyoxal-bis(mesityl)-1,2-diimine (Mes$_2$DAD)

Solid glyoxal-bis-mesitylimine (0.51 g, 1.73 mmol) was added to a stirred suspension of green (py)$_2$Ni(C$_2$H$_4$COO) (0.50 g, 1.73 mmol) in dmf (15 cm$^3$) at r.t.. After 30 min of stirring, the formed dark violet solid was collected by filtration, washed twice with thf and dried in a vacuum. The product is only slightly soluble in dmf and dmso. Suitable crystals for X-ray diffraction were obtained from a solution of dmf at 5 °C. Yield: 0.52 g (71 %). (Found: C, 64.6; H, 6.5; N, 6.6. $C_{23}H_{28}N_2NiO_2$ requires C, 65.3; H, 6.7; N, 6.60%.); $\nu_{max}$(nujol)/cm$^{-1}$ 1628vs (CO); $\delta_H$(200 MHz; dmf-d$_7$; 25 °C) 1.3-1.6 (4 H, br, Ni-CH$_2$ + CH$_2$COO), 2.33 (12 H, s, *o*-CH$_3$ mesityl), 2.42 (6 H, s, *p*-CH$_3$ mesityl), 6.96 (2 H, s, *m*-H mesityl), 7.05 (2 H, s, *m*-H' mesityl), 8.65 (1 H, br, -CH=N) and 8.73 (1 H, br, -CH'=N); *m/z* (FAB) 423 (31%, M+1$^+$), 350 (100, M$^+$ - CO$_2$ - C$_2$H$_4$), 293 (15), 277 (35); *m/z* (ESI, positive ion, MeOH) 445.1405 (100, M$^+$ + Na. $C_{23}H_{28}N_2NaNiO_2$ requires 445.1402).

**Complex 2** L = neocuproine (2,9-dimethyl-1,10-phenanthroline, dmp)

Solid 2,9-dimethyl-1,10-phenanthroline (0.39 g, 1.87 mmol) was added to a stirred suspension of green [(py)$_2$Ni(C$_2$H$_4$COO)] (0.54 g, 1.87 mmol) in dmf (8 cm$^3$). The colour of the solution immediately changed to red und a red precipitate was formed. The mixture was stirred for 30 min, after which the red precipitate was separated by filtration and dried in a vacuum.

Yield: 0.42 g (66%) dark red powder. (Found: C, 59.4; H, 4.95; N, 8.6. $C_{17}H_{16}N_2NiO_2$ requires C, 60.2; H, 4.8; N, 8.3%); $\nu_{max}$(nujol)/cm$^{-1}$ 1622vs (CO); $\delta_H$(200 MHz; dmf-d$_7$; 25 °C) 1.40 (2 H, t, *J* 7.3, Ni-CH$_2$), 1.78 (2 H, t, *J* 7.3, CH$_2$-COO), 3.00 (6 H, s, CH$_3$), 7.90 (2 H, d, *J* 8.3, CH dmp), 8.23 (2 H, s, CH dmp), 8.76 (2 H, d, J 8.3 CH dmp). Suitable crystals (**2***C$_2$H$_5$OH) for X-ray measurement were isolated from a saturated solution of **2** in dmf at -20 °C after addition of a small amount of ethanol.

**2** is insoluble in thf, diethylether and toluene and only sparely soluble in dmf and dmso. The compound slowly decomposes in solution (dmf), preventing further nmr measurement and finally resulting in the formation of (dmp)$_2$Ni (**10**) [3] besides other unidentified products.

**Complex 3**: L = Ph$_2$P(CH$_2$)$_2$PPh$_2$ (dppe)

Dppe (1.0 g, 2.52 mmol) was added to a stirred suspension of greenish yellow (tmeda)Ni(C$_2$H$_4$COO) (0.62 g, 2.50 mmol) in thf (30 cm$^3$). The starting materials dissolved while the colour changed to yellow. Finally fine crystals of (dppe)Ni(C$_2$H$_4$COO) occurred. The product was separated and recrystallised from a solution of methylene chloride. Yield: 1.20 g (92 %) orange crystals. (Found: C, 65.6; H, 5.4. $C_{29}H_{28}NiO_2P_2$ requires C, 65.8; H, 5.3%); $\delta_{P\{H\}}$ (81 MHz; dmf-d$_7$; 25 °C) 60.3 (s) and 36.3 (s). The NMR spectra of the product were identical with that compound described by Yamamoto [4].

**Complex 4** L = Cyp$_2$P(CH$_2$)$_2$Cyp$_2$

Cyp$_2$P(CH$_2$)$_2$Cyp$_2$ (0.93 g, 2.53 mmol) was added to a suspension of (tmeda)Ni(C$_2$H$_4$COO) (0.62 g, 2.50 mmol) in thf (30 cm$^3$). While the starting compounds dissolved, the colour of the solution changed from green to yellow. Finally (Cyp$_2$P(CH$_2$)$_2$Cyp$_2$)Ni(C$_2$H$_4$COO) precipitated from the solution. The product was separated and recrystallised from a solution of dmf. Yield: 0.67 g (54 %) yellow crystals. (Found: C, 60.2; H, 9.0. $C_{25}H_{44}NiO_2P_2$, requires C, 60.4; H, 8.8%.); $\nu_{max}$ (nujol)/cm$^{-1}$ 1615vs (CO); $\delta_H$ (200 MHz; dmf-d$_7$; 25 °C) 0.76 (2 H, ddt, *J* 9.8, Ni-CH$_2$), 1.10 (1 H, d, *J* 5.9) and 1.55 – 2.26 (43 H, br); $\delta_{C\{H\}}$(50 MHz; dmf-d$_7$; 25 °C) 11.1 (1 C, dd, $^2J_{P,C}$ 63.4 and 26.3, Ni-CH$_2$), 18.2 (1 C, dd, $J_{P,C}$ 24.0 and 10.6, CH$_2$-P), 23.5 (1 C, dd, $J_{P,C}$

26.2 and 21.0, $CH_2$-P), 25.1-26.0 (8 C, m, $CH_2$), 28.6-29.7 (8 C, m, $CH_2$-CH-P), 35.4 (2 C, d, $^1J_{P,C}$ 17.6, CH-P), 36.3 (2 C, dd, $^1J_{P,C}$ 28.7 $^3J_{P,C}$ 1.5, CH-P), 36.7 (1 C, dd, $^3J_{P,C}$ 3.8 and 1.5, $CH_2$-COO) and 188.8 (1 C, dd, $^3J_{P,C}$ 15.0 and 1.9, COO); $\delta_{P\{H\}}$(81 MHz; dmf-$d_7$; 25 °C) 59.6 (d, $^2J$ 5.2) and 67.4 (d, $^2J$ 5.2).

**Complex 5** L = ($p$-F-Ph)$_2$P($CH_2$)$_2$P($p$-F-Ph)$_2$ ($F_4$-dppe)

$F_4$-dppe (515 mg, 1.09 mmol) was added to a stirred suspension of (tmeda)Ni($C_2H_4COO$) (0.27 g, 1.09 mmol) in thf (30 $cm^3$). The starting materials dissolved while the colour changed form green to yellow. Finally fine crystals of ($F_4$-dppe)Ni($C_2H_4COO$) occurred. The product was separated and recrystallised from a solution of methylene chloride which contains a layer of ether. Yield: 0.52 g (79 %) yellow crystals. $\delta_H$ (200 MHz; $CDCl_3$; 25 °C) 0.81 (2 H, m, Ni-$CH_2$), 1.97 (2 H, m, $CH_2$-P), 2.12 (2 H, m, $CH_2$-P), 2.39 (2 H, m, $CH_2$-COO), 7.11 (4 H, m, $m$-CH), 7.15 (4 H, m, $m$-CH), 7.61 (4 H, m, $o$-CH) and 7.86 (4 H, m, $o$-CH); $\delta_{P\{H\}}$ (81 MHz; $CDCl_3$; 25 °C) 61.7 (s) and 36.2 (s); $\delta_{F\{H\}}$ (188 MHz; $CDCl_3$; 25 °C) -108.5 (s) and -107.4 (s).

**Complex 6** $L_2$ = ($p,m,m'$-$F_3$-Ph)$_2$P($CH_2$)$_2$P($p,m,m'$-$F_3$-Ph)$_2$ ($F_{12}$-dppe)

$F_{12}$-dppe (1.10 g, 1.74 mmol) was added to a stirred suspension of (tmeda)Ni($C_2H_4COO$) (0.43 g, 1.74 mmol) in thf (40 $cm^3$). The reaction mixture was warmed on a water bath until all insoluble material was dissolved. The warm solution was filtered clear. From the filtrate yellow crystals of ($F_{12}$-dppe)Ni($C_2H_4COO$) * thf were obtained which were separated and dried in a vacuum. Yield: 1.19 g (84%) yellow crystals. (Found: C, 48.4; H, 3.3. $C_{33}H_{24}F_{12}NiO_3P_2$ requires C, 48.5; H, 3.0%); $\delta_H$ (200 MHz; dmso-$d_6$; 25 °C) 0.74 (2 H, m, Ni-$CH_2$), 2.17 (2 H, m, $CH_2$-COO), 2.32-2.45 (2 H, m, $CH_2$-P), 2.61-2.72 (2 H, m, $CH_2$-P), 7.71 (4 H, m, $o$-CH) and 7.90 (4 H, m, $o$-CH); $\delta_{P\{H\}}$(81 MHz; dmso-$d_6$; 25 °C) 68.6 (s) and 42.0 (s).

**Complex 7** $L_2$ = $Ph_2P(CH_2)_3PPh_2$ (dppp)

Dppp (1.04 g, 2.53 mmol) was added to a suspension of (tmeda)Ni($C_2H_4COO$) (0.62 g, 2.50 mmol) in thf (30 $cm^3$). While the starting compounds dissolved, the colour of the solution changed from green to yellow. Finally (dppp)Ni($C_2H_4COO$) precipitated from the solution. Yield: 1.11 g (82 %) fine yellow crystals. (Found: C, 65.7; H, 5.9. $C_{30}H_{30}NiO_2P_2$ requires C, 66.3; H, 5.6%); $\nu_{max}$ (nujol)/$cm^{-1}$ 1626vs (CO); $\delta_{P\{H\}}$ (81 MHz; dmf-$d_7$; 25 °C) 31.1 (d, $J_{P,P}$ 30.9) and -0.9 (d, $J_{P,P}$ 30.9).

**Complex 8** $L_2 = Ph_2P(CH_2)_4PPh_2$

Dppb (1.08 g, 2.53 mmol) was added to a suspension of (tmeda)Ni($C_2H_4COO$) (0.62 g, 2.50 mmol) in THF (30 cm$^3$). While the starting compounds dissolved the colour of the solution changed from green to yellow. Finally (dppb)Ni($C_2H_4COO$) precipitated from the solution. Single crystals were obtained by diffusion of benzene in a saturated solution of the compound in dmf. Yield: 1.32 g (84 %) yellow crystals, which slowly lose DMF

(Found: C, 64.2; H, 4.2; N, 1.9. $C_{34}H_{39}NNiO_3P_2$ requires C, 64.8; H, 6.2; N 2.2%); $\delta_{P\{H\}}$ (81 MHz; dmf/$C_6D_6$; 25 °C) 38.1 (d, $J_{P,P}$ 12.9) and 13.6 (d, $J_{P,P}$ 12.9).

**Complex 9** $L_2 = (Ph_2P\text{-}CH_2)_3N$

Solid $(Ph_2P\text{-}CH_2)_3N$ (0.70 g, 1.14 mmol) was added to a stirred suspension of [$(py)_2$Ni($C_2H_4COO$)] (0.33 g, 1.14 mmol) in thf (10 cm$^3$). The resulting mixture was stirred for 90 min, after which a brown solution was obtained. This solution was evaporated under reduced pressure to leave a sticky brown oil. After addition of diethylether (20 cm$^3$) a yellow precipitate was formed, which was isolated by filtration und dried in a vacuum. Yield: 0.74 g (87%) yellow powder. (Found: C, 67.3; H, 5.4; N, 1.8. $C_{42}H_{40}NNiO_2P_3$ requires C, 67.9; H, 5.4; N, 1.9%); $\nu_{max}$ (nujol)/cm$^{-1}$ 1626vs (CO); $\delta_H$ (400 MHz; dmf-$d_7$; 25 °C) 0.57 (2 H, t, $J$ 6.8, Ni-$CH_2$), 2.05 (2 H, t, $J$ 7.0, $CH_2$-COO), 3.69 (6 H, s, P-$CH_2$-N) and 7.1-7.7 (30 H, m, CH Ph); $\delta_{C\{H\}}$ (100 MHz; dmf-$d_7$; 25 °C) 21.3 (1 C, q, $^2J_{P,C}$ 11.6, Ni-$CH_2$), 37.6 (1 C, s, $CH_2$-COO), 59.9 (3 C, br, P-$CH_2$-N), 129.1 (8 C, d, $J_{P,C}$ 8.4, *m*-CH Ph), 130.4 (4 C, s, *p*-CH Ph), 133.6 (4 C, detected by HMBC experiment, *i*-C Ph), 133.8 (8 C, d, $J_{P,C}$ 13.1, *o*-CH Ph) and 193.3 (1 C, s, COO); $\delta_{P\{H\}}$(81 MHz; dmf-$d_7$; -50 °C) -27.0 (s), 0.8 (d, $^2J_{P,P}$ 38.8, Ni-P) and 31.9 (d, $^2J_{P,P}$ 38.8, Ni-P$'$).

Suitable crystals for X-ray measurement were obtained by slow diffusion of ether in a saturated solution in dmf.

**Complex 11** $L_2 = Ph_2P(CH_2)_3PPh_2$ (dppp)

(dppp)Ni($C_2H_4COO$) (1.08 g, 2.0 mmol) was dissolved in dmf. The solution was heated to 60 °C while argon gas was slowly passing over the solution for 1 h. The argon stream finally was bubbling through a solution of $Ba(OH)_2$ in water. From the solution precipitated white $BaCO_3$. The yellow solution of dmf became orange. Crystals occurred overnight at room temperature. Yield: 0.56 g (63 %) orange crystals. (Found: C, 73.7; H, 6.4. $C_{54}H_{52}NiP_4$ requires C, 73.4); H, 5.9%); $\delta_{P\{H\}}$(81 MHz; dmf/$C_6D_6$; 25 °C) 12.1 (s).

**Complex 12** L = $Ph_2P(CH_2)_4PPh_2$ (dppb)

(dppb)Ni($C_2H_4COO$) * dmf (1.26 g, 2.0 mmol) was dissolved in dmf. The solution was heated to 60 °C. The yellow solution of dmf became red in a few minutes. Red crystals occurred at room temperature overnight. Yield: 0.56 g (73 %) red crystals. (Found: C, 73.7; H, 6.4. $C_{54}H_{52}NiP_4$ requires C, 73.4; H, 5.9%); $\delta_{P\{H\}}$(81 MHz; dmf/$C_6D_6$; 25 °C) 28.2 (s).

**Complex 13 $[(\eta^1\text{-dppm})Ni)_2(\mu\text{-}C_2H_3COO)(\mu\text{-}PPh_2)(\mu\text{-dppm})] \cdot 1.5\ PhCH_3$**

Dppm (2.02 g, 5.26 mmol) was added to a stirred suspension of (tmeda)Ni($C_2H_4COO$) (0.65 g, 2.63 mmol) in dmf (30 $cm^3$). The starting materials dissolved while the colour of the solution changed form green to yellow. The reaction mixture was heated to 60 °C. The reaction mixture became dark brown and all volatile material was removed in vacuum. The residue was recrystallised from a solution of toluene. Yield: 2.19 g (65 %) dark green diamagnetic crystals. (Found: C, 72.2; H, 5.8. $C_{100.5}H_{91}Ni_2O_2P_7$ requires C, 72.5; H, 5.5%); $\delta_{P\{H\}}$(81 MHz; $C_6D_6$; 25 °C) -23.5 (s, $CH_2$-$PPh_2$), 0.8 (d, $J_{P,P}$ 111.2, Ni-$PPh_2$-$CH_2$), 14.3 (dt, $J_{P,P}$ 30.0, μ-dppm) and 96.3 (tt, $J_{P,P}$ 111.2 and 30.0, μ-$PPh_2$).

The $^{31}P\{^1H\}$NMR spectrum of the mother liquor showed the singlet of the $CH_3$ protons of $Ph_2PCH_3$ at $\delta_{P\{H\}}$-25.4 (s) as well.

$^1H$ NMR in $C_6D_6$ $\delta_H$ (400 MHz, 25°C by HSQC-DEPT and HSQC-TOCSY experiments) for coordinated acrylat: 5.88 ($CH_2$=), 6.84 ($CH_2$=), 7.18 (CH=, overlapping with phenyl).

Although no complete signal set of **13** in the $^{13}C$ NMR spectrum were obtained (some *i*-C signals were not found), the signals of the acrylate ligand were located by HSQC-DEPT and HSQC-TOCSY experiments. $\delta_C$ (100 MHz; $C_6D_6$; 25 °C) 123.8 ($CH_2$=), 136.8 (CH=) and 179.3 (pt, *J* 4.5, COO).

**Reaction of [(tmeda)Ni($C_2D_4COO$)] with dppm in the presence of ethylene**

Dppm (1.78 g, 4.73 mmol) was added to stirred suspension of [(tmeda)Ni($C_2D_4COO$)] (0.58 g, 2.31 mmol) in dmf (30 $cm^3$). The starting materials dissolved while the colour of the solution changed from green to yellow. Finally ethylene (100 $cm^3$, 4.46 mmol) was added by a syringe. The reaction mixture was heated to 80 °C for 15 min in a closed Schlenk tube and the colour turned to dark brown. Then the temperature was increased to 110 °C and all volatile material was removed in a vacuum.

A sample of the greenish brown residue was analysed by $^1H$ NMR and $^{31}P\{^1H\}$ NMR spectroscopy (toluene-$d_8$). In the $^{31}P\{^1H\}$ NMR spectrum all typical signal of complex **13-$d_3$** were found. In the $^1H$ NMR spectrum no signals for acrylate ($CH_2$=CH-COO) were detected.

In comparison with a control experiment without ethylene neither changes in reaction rates nor in the product distribution were observed.

### Complex 14 [(η$^1$-dppm)$_2$(η$^2$-dppm)Ni]

The reaction between (py)$_2$Ni($C_2H_4COO$) and dppm (molar ratio 1:1) in dmf results in the formation of a yellow solid, if dmf is completely removed under reduced pressure und ether is added. This crude product mixture contains several species, among them dppm-stabilized nickelalactones. Recrystallisation of this mixture from thf/ether und storage of the resulting orange solution at -20 °C for 2 weeks give few red crystals of dppm$_3$Ni besides other unidentified products.

**14** is also formed by addition of one equivalent of dppm to a solution of (dppm)$_2$Ni in thf, which results in an equilibrium between the starting compound + dppm and (dppm)$_3$Ni (molar ratio at -50 °C: 1:3) as judged by nmr measurement.

$\delta_P$ (81 MHz; thf-d$_8$; -50 °C) -23.3 (br, Ph$_2$P dppm$_3$Ni), -20.8 (s, dppm), 4.1 (br, Ni-P, chelating, dppm$_3$Ni), 8.0 (s, Ni-P dppm$_2$Ni) and 26.3 (br, Ni-P monodentate, dppm$_3$Ni).

### Complex 15 (dppm)$_2$Ni [5]

Dppm (1.03 g, 2.68 mmol) was added to a stirred suspension of Ni(cod)$_2$ (0.37 g, 1.34 mmol) in thf (15 cm$^3$), followed by the addition of succinic anhydride (90 mg, 0.9 mmol). The resulting orange red solution was stirred for 30 min at 0 °C, after which the formed orange yellow precipitate was isolated by filtration and dried under reduced pressure. Yield: 0.75 g (62%) orange yellow crystals of (dppm)$_2$Ni * thf.

$\delta_H$ (200 MHz; thf-d$_8$; 25 °C) 3.85 (4 H, t, $^1J_{P,H}$ 6.0, CH$_2$) and 7.0-7.5 (40 H, m, CH Ph); $\delta_{P\{H\}}$(81 MHz; thf-d$_8$; 25 °C) 6.3 (s).

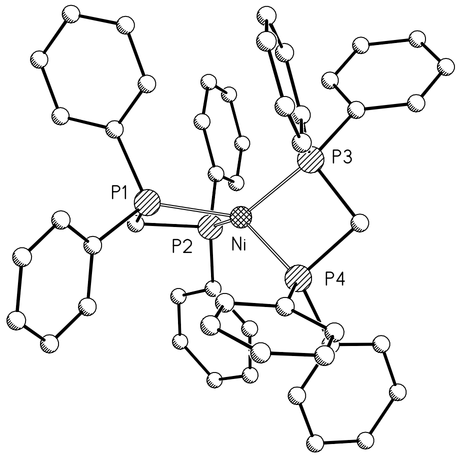


**Figure 1** Molecular structure of complex **15** (H-atoms are omitted for clairity). Selected bond distances (Å) and bond angles (deg) : Ni-P1 2.1904(7), Ni-P2 2.1771(6), Ni-P3 2.1889(7), Ni-P4 2.1706(7), P1-Ni-P2 77.70(2), P1-Ni-P3 125.19(2), P1-Ni-P4 128.54(3), P2-Ni-P3 130.17(3), P2-Ni-P4 126.65(3), P3-Ni-P4 76.77(2).

### Complex 16 [(py)(dppm)Ni($CH_2CH_2COO$)]*dmf and [(py)(dppmO)Ni($CH_2CH_2COO$)] (17)

Dppm (0.29 g, 0.75 mmol) was added to a stirred suspension of green $(py)_2Ni(C_2H_4COO)$ (0.44 g, 1.52 mmol) in dmf (7 $cm^3$). After a few minutes a clear, orange solution was obtained. Uncoordinated pyridine and 1 $cm^3$ dmf were removed by distillation (r.t.) under reduced pressure. The residual solution was kept at -20 °C for 3 days, after which the formed yellow crystals (90 mg, 9%) were collected by filtration and dried in a vacuum.

$\nu_{max}$ (nujol)/$cm^{-1}$ 1621vs (CO) and 1666s (CO dmf); $\delta_H$ (200 MHz; dmf-$d_7$; 25 °C) 0.22 (2 H, br, Ni-$CH_2$), 1.69 (2 H, br, $CH_2COO$); 3.32 (2 H, t, ${}^2J_{P,H}$ 4.8, P-$CH_2$-P), 7.25-8.0 (13 H, m, CH Ph + *p*-CH py+ *m*-CH py) and 8.65 (2 H, br, *o*-CH py); $\delta_{P\{H\}}$(81 MHz; dmf-$d_7$; -50 °C) -24.6 (d, ${}^2J_{P,P}$ 54.9), -24.0 (d, ${}^2J_{P,P}$ 110), -21.3 (s, dppm); 26.6 (d, ${}^2J_{P,P}$ 9.6), 29.1 (d, ${}^2J_{P,P}$ 110), 29.4 (d, ${}^2J_{P,P}$ 9.6) and 31.0 (d, ${}^2\mathrm{J}_{P,P}$ 54.9).

Suitable crystals (30 mg, 3%) for X-ray measurement were obtained from the mother liquor at -20 °C after several days. These crystals contain [(py)(dppmO)Ni($CH_2CH_2COO$)] (≈25%) as impurity. Attempts to purify the substance by recystallisation from thf yield only crystals of [(py)(dppmO)Ni($CH_2CH_2COO$)]*thf.

### Crystal Structure Determination

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-$K_\alpha$ radiation. For compound **16** measurments were carried out at beamline ID11 at the European Synchrotron Radiation Facility (ESRF). Data were collected using a Bruker "Smart" CCD-camera system at fixed 2θ, while the sample was rotated over 0.1° intervals during 2 s exposures, using monochromated radiation from $\lambda = 0.46409$ Å. Data were corrected for Lorentz and polarization effects, but not for absorption effects [6-8].

The structures were solved by direct methods (SHELXS [9]) and refined by full-matrix least squares techniques against $Fo^2$ (SHELXL-97 [10]). All hydrogen atoms of compounds **3** and **11** and the hydrogen atom of the hydroxyl-group of the ethanol molecule of **2** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically [10]. The compound **11** and **12** have imposed twofold symmetry. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

*Crystal Data for* **1**[11]: $C_{23}H_{28}N_2NiO_2$, Mr = 423.18 $gmol^{-1}$, black prism, size 0.08 x 0.06 x 0.04 $mm^3$, orthorhombic, space group Pbca, a = 13.3813(3), b = 15.6376(3), c = 20.5571(5) Å, V = 4301.60(16) $Å^3$ , T= -90 °C, Z = 8, $\rho_{calcd.}$ = 1.307 $gcm^{-3}$, $\mu$ (Mo-$K_\alpha$) = 9.22 $cm^{-1}$, F(000) = 1792, 8988 reflections in h(-17/17), k(-19/19), l(-26/26), measured in the range 2.79° ≤ Θ ≤ 27.48°, completeness $\Theta_{max}$ = 99.1 %, 4887 independent reflections, $R_{int}$ = 0.033, 3432 reflections with $F_o > 4\sigma(F_o)$, 253 parameters, 0 restraints, $R1_{obs}$ = 0.038, $wR^2_{obs}$ = 0.082, $R1_{all}$ = 0.067, $wR^2_{all}$ = 0.092, GOOF = 1.011, largest difference peak and hole: 0.319 / -0.330 e $Å^{-3}$.

*Crystal Data for* **2**[11]: $C_{17}H_{16}N_2NiO_2 * C_2H_5OH$, Mr = 385.10 $gmol^{-1}$, orange prism, size 0.10 x 0.08 x 0.06 $mm^3$, monoclinic, space group P21/n, a = 8.6500(3), b = 14.8065(6), c = 13.6843(6) Å, β = 96.718(2) °, V = 1740.60(12) $Å^3$ , T= -90 °C, Z = 4, $\rho_{calcd.}$ = 1.470 $gcm^{-3}$, $\mu$ (Mo-$K_\alpha$) = 11.35 $cm^{-1}$, F(000) = 808, 6956 reflections in h(-11/11), k(-17/19), l(-17/17), measured in the range 4.04° ≤ Θ ≤ 27.53°, completeness $\Theta_{max}$ = 99.3 %, 3972 independent reflections, $R_{int}$ = 0.075, 2775 reflections with $F_o > 4\sigma(F_o)$, 230 parameters, 0 restraints, $R1_{obs}$ = 0.063, $wR^2_{obs}$ = 0.153, $R1_{all}$ = 0.096, $wR^2_{all}$ = 0.1722, GOOF = 1.084, largest difference peak and hole: 1.058 / -0.888 e $Å^{-3}$.

*Crystal Data for* **3**[11]: $C_{29}H_{28}NiO_2P_2$, Mr = 529.16 $gmol^{-1}$, yellow-orange prism, size 0.32 x 0.22 x 0.12 $mm^3$, monoclinic, space group $P2_1$, a = 9.5487(3), b = 14.9037(8), c = 9.8115(5) Å, β = 115.807(3) °, V = 1257.0(1) $Å^3$ , T= -90 °C, Z = 2, $\rho_{calcd.}$ = 1.398 $gcm^{-3}$, $\mu$ (Mo-$K_\alpha$) = 9.24 $cm^{-1}$, F(000) = 552, 5291 reflections in h(-12/12), k(-17/19), l(-12/12), measured in the range 3.62° ≤ Θ ≤ 27.52°, completeness $\Theta_{max}$ = 98.4 %, 5291 independent reflections, 4871 reflections with $F_o > 4\sigma(F_o)$, 418 parameters, 1 restraints, $R1_{obs}$ = 0.038, $wR^2_{obs}$ = 0.076, $R1_{all}$ = 0.045,

$wR^2_{all}$ = 0.079, GOOF = 1.037, Flack-parameter -0.007(11), largest difference peak and hole: 0.453 / -0.392 e Å$^{-3}$.

*Crystal Data for* **4**[11]: $C_{25}H_{44}NiO_2P_2$, Mr = 497.25 gmol$^{-1}$, yellow prism, size 0.20 x 0.18 x 0.12 mm$^3$, monoclinic, space group C2/c, a = 24.4910(8), b = 14.8852(6), c = 17.1908(4) Å, β = 125.904(2) °, V = 5076.2(3) Å$^3$ , T= -90 °C, Z = 8, $\rho_{calcd.}$ = 1.301 gcm$^{-3}$, μ (Mo-$K_\alpha$) = 9.09 cm$^{-1}$, F(000) = 2144, 9876 reflections in h(-31/31), k(-19/17), l(-22/22), measured in the range 2.82° ≤ Θ ≤ 27.46°, completeness $\Theta_{max}$ = 99.4 %, 5794 independent reflections, $R_{int}$ = 0.033, 4799 reflections with $F_o > 4\sigma(F_o)$, 271 parameters, 4 restraints, $R1_{obs}$ = 0.051, $wR^2_{obs}$ = 0.105, $R1_{all}$ = 0.068, $wR^2_{all}$ = 0.111, GOOF = 1.055, largest difference peak and hole: 0.779 / -0.640 e Å$^{-3}$.

*Crystal Data for* **5**[11]: $C_{29}H_{24}F_4NiO_2P_2$ * ½ $C_4H_{10}O$ * $CH_3OH$, Mr = 670.23 gmol$^{-1}$, yellow-orange prism, size 0.06 x 0.06 x 0.04 mm$^3$, orthorhombic, space group Pccn, a = 27.6383(5), b = 10.5990(2), c = 22.8711(4) Å, V = 6699.8(2) Å$^3$ , T= -90 °C, Z = 8, $\rho_{calcd.}$ = 1.329 gcm$^{-3}$, μ (Mo-$K_\alpha$) = 7.28 cm$^{-1}$, F(000) = 2776, 14297 reflections in h(-35/35), k(-13/13), l(-29/29), measured in the range 1.93° ≤ Θ ≤ 27.47°, completeness $\Theta_{max}$ = 99.4 %, 7633 independent reflections, $R_{int}$ = 0.055, 4924 reflections with $F_o > 4\sigma(F_o)$, 380 parameters, 0 restraints, $R1_{obs}$ = 0.071, $wR^2_{obs}$ = 0.187, $R1_{all}$ = 0.117, $wR^2_{all}$ = 0.209, GOOF = 1.075, largest difference peak and hole: 0.965 / -0.455 e Å$^{-3}$.

*Crystal Data for* **6**[11]: $C_{29}H_{16}F_{12}NiO_2P_2$ * $C_4H_8O$, Mr = 817.17 gmol$^{-1}$, yellow-orange prism, size 0.03 x 0.03 x 0.02 mm$^3$, monoclinic, space group $P2_1/n$, a = 13.1415(5), b = 15.6809(7), c = 16.0563(7) Å, β = 99.673(3) °, V = 3261.7(2) Å$^3$ , T= -90 °C, Z = 4, $\rho_{calcd.}$ = 1.664 gcm$^{-3}$, μ (Mo-$K_\alpha$) = 7.97 cm$^{-1}$, F(000) = 1648, 20802 reflections in h(-16/16), k(-19/20), l(-19/20), measured in the range 2.19° ≤ Θ ≤ 27.46°, completeness $\Theta_{max}$ = 98.3 %, 7333 independent reflections, $R_{int}$ = 0.096, 5158 reflections with $F_o > 4\sigma(F_o)$, 460 parameters, 0 restraints, $R1_{obs}$ = 0.076, $wR^2_{obs}$ = 0.202, $R1_{all}$ = 0.109, $wR^2_{all}$ = 0.2284, GOOF = 1.103, largest difference peak and hole: 1.533 / -0.844 e Å$^{-3}$.

*Crystal Data for* **8**[11]: $C_{31}H_{32}NiO_2P_2$ * $C_3H_7NO$, Mr = 630.31 gmol$^{-1}$, green-yellow prism, size 0.09 x 0.08 x 0.07 mm$^3$, triclinic, space group P-1, a = 10.0133(9), b = 10.9437(9), c = 16.2880(1) Å, α = 82.934(6), β = 72.900(7), γ = 66.730(8) °, V = 1567.1(2) Å$^3$ , T= -90 °C, Z = 2, $\rho_{calcd.}$ = 1.336 gcm$^{-3}$, μ (Mo-$K_\alpha$) = 7.56 cm$^{-1}$, F(000) = 664, 9865 reflections in h(-12/12), k(-14/11), l(-17/21), measured in the range 2.30° ≤ Θ ≤ 27.46°, completeness $\Theta_{max}$ = 90.6 %, 6467 independent reflections, $R_{int}$ = 0.0456, 4289 reflections with $F_o > 4\sigma(F_o)$, 370 parameters, 0 restraints, $R1_{obs}$ = 0.053, $wR^2_{obs}$ = 0.113, $R1_{all}$ = 0.099, $wR^2_{all}$ = 0.131, GOOF = 1.019, largest difference peak and hole: 0.690 / -0.659 e Å$^{-3}$.

*Crystal Data for* **9**[11]: $C_{42}H_{40}NNiO_2P_3$, Mr = 742.37 gmol$^{-1}$, yellow prism, size 0.03 x 0.03 x 0.03 mm$^3$, orthorhombic, space group Pbca, a = 19.0310(5), b = 16.9081(4), c = 23.1607(7) Å, V = 7452.6(3) Å$^3$ , T= -90 °C, Z = 8, $\rho_{calcd.}$ = 1.323 gcm$^{-3}$, μ (Mo-$K_\alpha$) = 6.86 cm$^{-1}$, F(000) = 3104, 45196 reflections in h(-24/23), k(-21/21), l(-29/28), measured in the range 1.84° ≤ Θ ≤ 27.50°, completeness $\Theta_{max}$ = 98.9 %, 8459 independent reflections, $R_{int}$ = 0.143, 5010 reflections with $F_o > 4\sigma(F_o)$, 442 parameters, 0 restraints, $R1_{obs}$ = 0.062, $wR^2_{obs}$ = 0.126, $R1_{all}$ = 0.127, $wR^2_{all}$ = 0.156, GOOF = 1.037, largest difference peak and hole: 0.458 / -0.424 e Å$^{-3}$.

*Crystal Data for* **10**[11]: $C_{28}H_{24}N_4Ni$, Mr = 475.20 gmol$^{-1}$, black prism, size 0.10 x 0.09 x 0.08 mm$^3$, monoclinic, space group C2/c, a = 22.7003(4), b = 22.7328(4), c = 18.2480(4) Å, β = 107.915(1)°, V = 8960.1(3) Å$^3$ , T= -90 °C, Z = 16, $\rho_{calcd.}$ = 1.409 gcm$^{-3}$, μ (Mo-$K_\alpha$) = 8.9 cm$^{-1}$, F(000) = 3968, 21970 reflections in h(-29/29), k(-28/29), l(-22/23), measured in the range 1.30° ≤ Θ ≤ 27.46°, completeness $\Theta_{max}$ = 94.4 %, 9693 independent reflections, $R_{int}$ = 0.077, 7905 reflections with $F_o > 4\sigma(F_o)$, 604 parameters, 0 restraints, $R1_{obs}$ = 0.089, $wR^2_{obs}$ = 0.233, $R1_{all}$ = 0.111, $wR^2_{all}$ = 0.252, GOOF = 1.162, largest difference peak and hole: 1.751 / -1.132 e Å$^{-3}$.

*Crystal Data for* **11**[11]: $C_{54}H_{52}NiP_4$, Mr = 883.55 gmol$^{-1}$, orange prism, size 0.22 x 0.22 x 0.20 mm$^3$, monoclinic, space group C2/c, a = 18.1812(6), b = 13.2156(5), c = 19.9132(4) Å, β = 109.690(2) °, V = 4504.9(2) Å$^3$ , T= -90 °C, Z = 4, $\rho_{calcd.}$ = 1.303 gcm$^{-3}$, μ (Mo-$K_\alpha$) = 6.09 cm$^{-1}$, F(000) = 1856, 8793 reflections in h(-23/23), k(-17/15), l(-24/24), measured in the range 3.20° ≤ Θ ≤ 27.47°, completeness $\Theta_{max}$ = 98.5 %, 5093 independent reflections, $R_{int}$ = 0.034, 4239 reflections with $F_o > 4\sigma(F_o)$, 371 parameters, 0 restraints, $R1_{obs}$ = 0.041, $wR^2_{obs}$ = 0.079, $R1_{all}$ = 0.058, $wR^2_{all}$ = 0.084, GOOF = 1.033, largest difference peak and hole: 0.309 / -0.331 e Å$^{-3}$.

*Crystal Data for* **12**[11]: $C_{56}H_{56}NiP_4$, Mr = 911.60 gmol$^{-1}$, red prism, size 0.10 x 0.10 x 0.08 mm$^3$, monoclinic, space group C2/c, a = 20.9448(4), b = 11.8350(3), c = 20.0660(4)Å, β = 110.142(2) °, V = 4669.8(2) Å$^3$ , T= -90 °C, Z = 4, $\rho_{calcd.}$ = 1.297 gcm$^{-3}$, μ (Mo-$K_\alpha$) = 5.9 cm$^{-1}$, F(000) = 1920, 9633 reflections in h(-27/27), k(-15/14), l(-26/25), measured in the range 2.44° ≤ Θ ≤ 27.46°, completeness $\Theta_{max}$ = 99.8 %, 5338 independent reflections, $R_{int}$ = 0.0281, 4257 reflections with $F_o > 4\sigma(F_o)$, 276 parameters, 0 restraints, $R1_{obs}$ = 0.0329, $wR^2_{obs}$ = 0.0782, $R1_{all}$ = 0.0489, $wR^2_{all}$ = 0.0857 , GOOF = 1.004, largest difference peak and hole: 0.288 / -0.296 e Å$^{-3}$.

*Crystal Data for* **13**[11]: $C_{90}H_{79}Ni_2O_2P_7$ * 2 $C_7H_8$, Mr = 1711.01 gmol$^{-1}$, green prism, size 0.12 x 0.10 x 0.08 mm$^3$, triclinic, space group P-1, a = 13.8923(5), b = 16.8347(9), c = 24.148(1) Å, $\alpha$ = 103.947(3), $\beta$ = 95.888(3), $\gamma$ = 113.132(3) °, V = 4915.7(4) Å$^3$ , T= -90 °C, Z = 2, $\rho_{calcd.}$ = 1.157 gcm$^{-3}$, $\mu$ (Mo-K$_\alpha$) = 5.42 cm$^{-1}$, F(000) = 1794, 32946 reflections in h(-18/14), k(-21/20), l(-31/31), measured in the range 1.86° $\leq \Theta \leq$ 27.49°, completeness $\Theta_{max}$ = 96.5 %, 21771 independent reflections, $R_{int}$ = 0.104, 9128 reflections with $F_o > 4\sigma(F_o)$, 942 parameters, 0 restraints, $R1_{obs}$ = 0.085, $wR^2_{obs}$ = 0.221, $R1_{all}$ = 0.196, $wR^2_{all}$ = 0.264, GOOF = 0.937, largest difference peak and hole: 1.281 / -0.542 e Å$^{-3}$.

*Crystal Data for* **14**[11]: $C_{75}H_{66}NiP_6$, Mr = 1211.81 gmol$^{-1}$, red prism, size 0.04 x 0.04 x 0.04 mm$^3$, triclinic, space group P-1, a = 11.0266(1), b = 11.1318(2), c = 27.3260(3) Å, $\alpha$ = 92.840(1), $\beta$ = 98.429(1), $\gamma$ = 106.845(1) °, V = 3160.52(7) Å$^3$ , T= -90 °C, Z = 2, $\rho_{calcd.}$ = 1.273 gcm$^{-3}$, $\mu$ (Mo-K$_\alpha$) = 5.02 cm$^{-1}$, F(000) = 1268, 23848 reflections in h(-13/14), k(-13/14), l(-35/33), measured in the range 1.99° $\leq \Theta \leq$ 27.46°, completeness $\Theta_{max}$ = 98.3 %, 14212 independent reflections, $R_{int}$ = 0.027, 11438 reflections with $F_o > 4\sigma(F_o)$, 739 parameters, 0 restraints, $R1_{obs}$ = 0.045, $wR^2_{obs}$ = 0.109, $R1_{all}$ = 0.061, $wR^2_{all}$ = 0.118, GOOF = 1.038, largest difference peak and hole: 0.787 / -0.409 e Å$^{-3}$.

*Crystal Data for* **15**[11]: $C_{50}H_{44}NiP_4$ * ½ $C_4H_8O$, Mr = 863.49 gmol$^{-1}$, orange prism, size 0.03 x 0.03 x 0.02 mm$^3$, monoclinic, space group P2$_1$/n, a = 11.8283(3), b = 22.0688(4), c = 16.7883(4) Å, $\beta$ = 93.564(1) °, V = 4373.88(17) Å$^3$ , T= -90 °C, Z = 4, $\rho_{calcd.}$ = 1.311 gcm$^{-3}$, $\mu$ (Mo-K$_\alpha$) = 6.27 cm$^{-1}$, F(000) = 1808, 30846 reflections in h(-13/15), k(-28/28), l(-21/21), measured in the range 1.96° $\leq \Theta \leq$ 27.49°, completeness $\Theta_{max}$ = 99.8 %, 10025 independent reflections, $R_{int}$ = 0.056, 7297 reflections with $F_o > 4\sigma(F_o)$, 523 parameters, 0 restraints, $R1_{obs}$ = 0.042, $wR^2_{obs}$ = 0.089, $R1_{all}$ = 0.071, $wR^2_{all}$ = 0.099, GOOF = 0.881, largest difference peak and hole: 0.543 / -0.384 e Å$^{-3}$.

*Crystal Data for* **16**[11]**:** $C_{33}H_{31}NNiO_{2.25}P_2$ * $C_3H_7NO$, Mr = 671.33 gmol$^{-1}$, yellow prism, size 0.02 x 0.02 x 0.02 mm$^3$, monoclinic, space group P2$_1$/n, a = 21.3152(9), b = 8.0904(5), c = 21.7217(13) Å, $\beta$ = 118.410(2) °, V = 3294.7(3) Å$^3$ , T= -153 °C, Z = 4, $\rho_{calcd.}$ = 1.353 gcm$^{-3}$, $\mu$ ($\lambda$ = 0.46409 Å) = 3.84 cm$^{-1}$, F(000) = 1408, 24947 reflections in h(-26/27), k(-10/10), l(-28/28), measured in the range 1.79° $\leq \Theta \leq$ 17.54°, completeness $\Theta_{max}$ = 97.5 %, 7377 independent reflections, $R_{int}$ = 0.051, 6054 reflections with $F_o > 4\sigma(F_o)$, 402 parameters, 0 restraints, $R1_{obs}$ = 0.050, $wR^2_{obs}$ = 0.127, $R1_{all}$ = 0.062, $wR^2_{all}$ = 0.133, GOOF = 1.080, largest difference peak and hole: 0.745 / -0.636 e Å$^{-3}$.

*Crystal Data for* **17**[11]: $C_{33}H_{31}NNiO_3P_2 * C_4H_8O$, Mr = 682.34 gmol$^{-1}$, yellow prism, size 0.03 x 0.03 x 0.02 mm$^3$, monoclinic, space group $P2_1/c$, a = 18.3457(7), b = 8.2770(4), c = 22.1729(9) Å, β = 93.078(2) °, V = 3362.0(2) Å$^3$ , T= -90 °C, Z = 4, $\rho_{calcd.}$ = 1.348 gcm$^{-3}$, μ (Mo-$K_\alpha$) = 7.13 cm$^{-1}$, F(000) = 1432, 21829 reflections in h(-23/23), k(-10/9), l(-27/28), measured in the range 4.29° ≤ Θ ≤ 27.54°, completeness $\Theta_{max}$ = 98.6 %, 7646 independent reflections, $R_{int}$ = 0.137, 3956 reflections with $F_o > 4\sigma(F_o)$, 406 parameters, 0 restraints, $R1_{obs}$ = 0.078, $wR^2_{obs}$ = 0.172, $R1_{all}$ = 0.167, $wR^2_{all}$ = 0.218, GOOF = 1.058, largest difference peak and hole: 0.705 / -0.460 e Å$^{-3}$.

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[11] CCDC-600545 (**1**), CCDC-600546 (**2**), CCDC-600547 (**3**), CCDC-600548 (**4**), CCDC-600549 (**5**), CCDC-600550 (**6**), CCDC-600551 (**8**), CCDC-600552 (**9**), CCDC-600553 (**10**), CCDC-600554 (**11**), CCDC-600555 (**12**), CCDC-600556 (**13**), CCDC-600557 (1**4**), CCDC-600558 (**15**), CCDC-600559 (**16**) and CCDC-600812 (**17**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).