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PREPARATION OF (*ORTHO*-HALOGENO)-η^1-PYRIDYLNICKEL(II) COMPLEXES, PRECURSORS FOR THE GENERATION OF PYRIDYNE–NICKEL(0) COMPLEXES*

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Abstract—Monomeric η^1-(3-chloro)-2-pyridyl complexes of nickel(II), NiCl(3-ClC_5H_3N-2)L_2 [$L_2 = 2PEt_3$ (**1**), dcpe (**2**); dcpe = 1,2-bis(dicyclohexylphosphino)ethane, $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$], have been prepared by the reaction of 2,3-dichloropyridine with $Ni(COD)_2$ in the presence of PEt_3 or with $Ni(\eta^2\text{-}C_2H_4)$(dcpe), respectively. Reaction of 2,3-dichloropyridine with $NiCl_2(PPh_3)_2$ in the presence of zinc gave the dimeric (C,N)-bridged (3-chloro)-2-pyridyl complex $[NiCl(\mu\text{-}3\text{-}ClC_5H_3N\text{-}2)(PPh_3)]_2$ (**4**), which re-forms **1** on addition of PEt_3. A similar reaction between $NiBr_2(PPh_3)_2$ and 3,4-dibromopyridine gave a mixture of the isomers NiBr(3-BrC_5H_3N-4)$(PPh_3)_2$ (**5**) and NiBr(4-BrC_5H_3N-3)$(PPh_3)_2$ (**6**), from which the PPh_3 ligands could easily be replaced by dcpe to give NiBr(3-BrC_5H_3N-4)(dcpe) (**7**) and NiBr(4-BrC_5H_3N-3)(dcpe) (**8**). Alkali metal reduction of **2**, and of the mixture of **7** and **8**, gave unstable species that could not be isolated, which are thought to be nickel(0) complexes of 2,3- and 3,4-pyridyne, respectively, on the basis of their ^{31}P NMR spectra. The structure of **4** has been solved by heavy atom methods and refined by least squares methods.

Pyridynes (didehydropyridines) are short-lived intermediates that are heterocyclic analogues of benzyne.[1–4] They are believed to be generated when 3-bromopyridine derivatives are treated with strong bases, the 3,4-pyridyne being formed preferentially if the 4-position is not blocked.[5–7] The greater stability of 3,4-pyridyne relative to its 2,3-isomer has been confirmed by both extended Hückel[8] and higher level MO calculations.[9–11] Both isomers can be trapped *in situ* by Diels–Alder reactions,[6,12–14] or by 1,3-dipolar cycloadditions.[15] A band at 2085 cm^{-1} has been assigned to the C≡C stretching frequency of 3,4-pyridyne, which was assumed to be the sole product of irradiation of 3,4-pyridine dicarboxylic anhydride in nitrogen or argon matrices.[16] Under the same conditions, 2,3-pyridyne was not stable enough to be observed.[16,17]

Arynes can be stabilized in the form of mononuclear transition metal complexes.[18] For example, the reduction of *o*-halogenoaryl-nickel(II) complexes such as $NiX(2\text{-}XC_6H_4)L_2$ [X = Br, Cl; $L_2 = 2PEt_3$, dcpe]‡ with alkali metals gives monomeric, highly reactive benzyne-nickel(0) complexes $Ni(\eta^2\text{-}C_6H_4)L_2$.[19,20] We were therefore interested to see if this procedure could be extended to prepare 2,3- and 3,4-pyridyne-nickel(0) complexes, for which the required precursors are *o*-halogeno (2-3- and 4-pyridyl)nickel(II) complexes $NiX(XC_5H_3N)L_2$. The preparation of such compounds is reported in this paper, together with a preliminary investigation of their reduction with alkali metals.

* Dedicated to Prof. Edward W. Abel on the occasion of his retirement from the Chair of Inorganic Chemistry at the University of Exeter, with thanks for his unfailing support, hospitality and good advice over many years.

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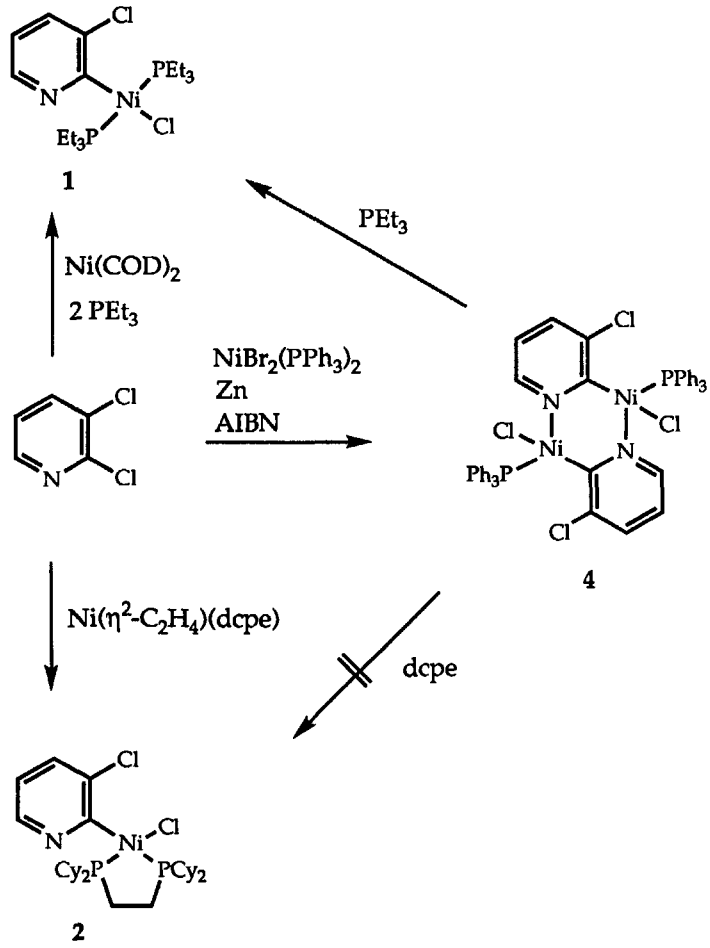
‡ Abbreviations: dcpe = 1,2-bis(dicyclohexylphosphino)ethane, $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$; COD = cycloocta-1,5-diene; AIBN = azabis(isobutyronitrile).

RESULTS AND DISCUSSION

Preparation of η^1-pyridylnickel(II) complexes

Reaction between $Ni(COD)_2$ and 2,3-dichloropyridine in the presence of two equivalents of PEt_3 gave the yellow 2-(3-chloropyridyl)nickel(II) complex $NiCl(3\text{-}ClC_5H_3N\text{-}2)(PEt_3)_2$ (**1**) in 65% yield (Scheme 1); this showed just a singlet at δ 12.5 in its $^{31}P\{^1H\}$ NMR spectrum, indicative of one species containing *trans*-PEt_3 ligands. The regioselectivity of the oxidative addition was confirmed by a two-dimensional nuclear Overhauser effect experiment (PSNOE). Both *meta* aromatic protons [H(4) and H(6)] at δ 6.80 and 8.34 in **1** were affected when the signal due to the methyl protons of PEt_3 at δ 1.06 was irradiated. The other isomer having the nickel atom at C(3) would be expected to show a response only from H(4). A similar reaction between 2,3-dichloropyridine and $Ni(\eta^2\text{-}C_2H_4)(dcpe)$ also gave the 2-(3-chloropyridyl) complex $NiCl(3\text{-}ClC_5H_3N\text{-}2)(dcpe)$ (**2**) as the main product, which showed an AB quartet (J_{PP} = 26 Hz) in its $^{31}P\{^1H\}$ NMR spectrum typical of *cis*-inequivalent phosphorus atoms. In this case, a small amount (< 10%) of the isomeric 3-(2-chloropyridyl)nickel(II) complex $NiCl(2\text{-}ClC_5H_3N\text{-}3)(dcpe)$ (**3**) was also formed; this was evident from the presence of a second AB quartet (J_{PP} = 32 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. The preferential formation of the 2-pyridylnickel(II) complex suggests that the pyridine nitrogen atom may coordinate to the nickel(0) in the first step, thus directing the oxidative addition to the C(2)—Cl bond.

When $NiCl_2(PPh_3)_2$ was treated with 2,3-dichloropyridine in the presence of zinc and AIBN, the reaction occurred as expected at the 2-position of the pyridine ring, but the product was the dimeric complex $[NiCl(\mu\text{-}3\text{-}ClC_5H_3N\text{-}2)(PPh_3)]_2$ (**4**) instead of $NiCl(3\text{-}ClC_5H_3N\text{-}2)(PPh_3)_2$ (Scheme 1). Evidently, one of the labile PPh_3 ligands of the latter is displaced by the pyridine nitrogen atom of a second molecule of the nickel complex. The compound shows only one signal at δ 20.7 in its ^{31}P NMR spectrum, and the presence of the bridging (C,N)-2-(3-chloropyridyl) group was confirmed by



Scheme 1.

X-ray analysis (see below). Similar dimeric (μ-C,N-2-pyridyl)nickel(II) complexes have been made previously by oxidative addition of 2-halogenopyridines to $Ni(PPh_3)_4$, although they were first formulated as μ-chloro-bridged dimers.[21] The correct structure was proposed on the basis of studies of the protonation of the complexes,[22] but to the best of our knowledge no crystallographic evidence has been reported. Analogous palladium[23,24] and platinum[23,25] complexes have been made, although more vigorous conditions are required than for nickel, and the X-ray structure of $[PdBr(C_5H_4N\text{-}2)(PPh_3)]_2$ has been reported.[26,27]

In **4** the geometry around each nickel atom is square planar; the maximum deviations are those of carbon atoms C(1) and C(6) of the pyridyl group (0.28 and 0.13 Å, respectively). The chlorine atoms are *trans* to the carbon atoms of the pyridyl group and the phosphine ligands are *trans* to the nitrogen atoms, as shown in Fig. 1. Some selected bond distances and bond angles are summarized in Table 1. The nickel atoms lie almost in the planes formed by the two pyridyl rings (maximum deviation 0.217 Å). The Ni—Ni separation [3.076(2) Å] implies no bonding interaction between the two metal atoms. As expected, the nickel–ligand distances are less than the corresponding distances for the palladium analogue $[PdBr(C_5H_4N\text{-}2)(PPh_3)]_2$:[26,27] r(Ni—P) is 2.20 Å (Pd—P 2.27 Å), r(Ni—C) is 1.87 Å (Pd—C 1.99 Å) and r(Ni—N) is 1.92–1.93 Å (Pd—N 2.09 Å). The C—C and C—N distances in the pyridine rings (1.37–1.39 and 1.34–1.36 Å, respectively) are unexceptional.

In contrast with the behaviour of the μ-C,N-pyridyl-dipalladium and -diplatinum complexes, the pyridine nitrogen atom of **4** was not displaced by an excess of PPh_3, but addition of two equivalents of PEt_3 to **4** readily gave **1**. This type of reaction also occurs when tertiary phosphines more basic than PPh_3 (e.g. PEt_3, PMe_2Ph or dppe) are added to the μ-C,N-pyridyldipalladium(II) complexes to give monomeric species such as $PdX(2\text{-}C_5H_4N)L_2$ (X = Br, Cl).[28,29] However, addition of dcpe to **4** formed an unidentifiable mixture of compounds. Complex **4** also reacted with water at 0°C to give a poorly soluble complex with a $^{31}P\{^1H\}$ NMR signal at δ 22.3, which could not be purified or crystallized. It readily re-formed **4** on addition of aqueous HCl, and may be a hydroxide $[Ni(OH)(3\text{-}ClC_5H_3N\text{-}2)(PPh_3)]_2$ or a polymeric oxo-species $[Ni(O)(3\text{-}ClC_5H_3N\text{-}2)(PPh_3)]_n$.

In the reaction of 3,4-dibromopyridine with $NiBr_2(PPh_3)_2$ in the presence of zinc, PPh_3 was not eliminated, but the resulting pyridyl complexes were not formed regioselectively. A 2.4:1 mixture of the 4-(3-bromopyridyl) complex $NiBr(3\text{-}BrC_5H_3N\text{-}4)(PPh_3)_2$ (**5**) and the 3-(4-bromopyridyl) complex $NiBr(4\text{-}BrC_5H_3N\text{-}3)(PPh_3)_2$ (**6**) was obtained (Scheme 2); these species were identified by singlets in the $^{31}P\{^1H\}$ NMR spectrum at δ 23.3 and 23.5, respectively, and we did not attempt to separate them. Oxidative addition of the likely intermediate

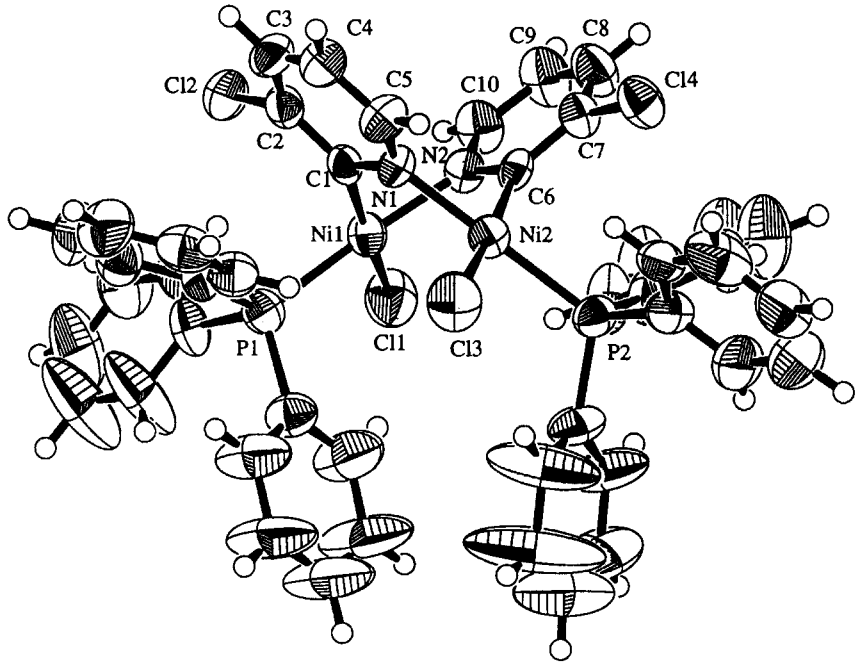
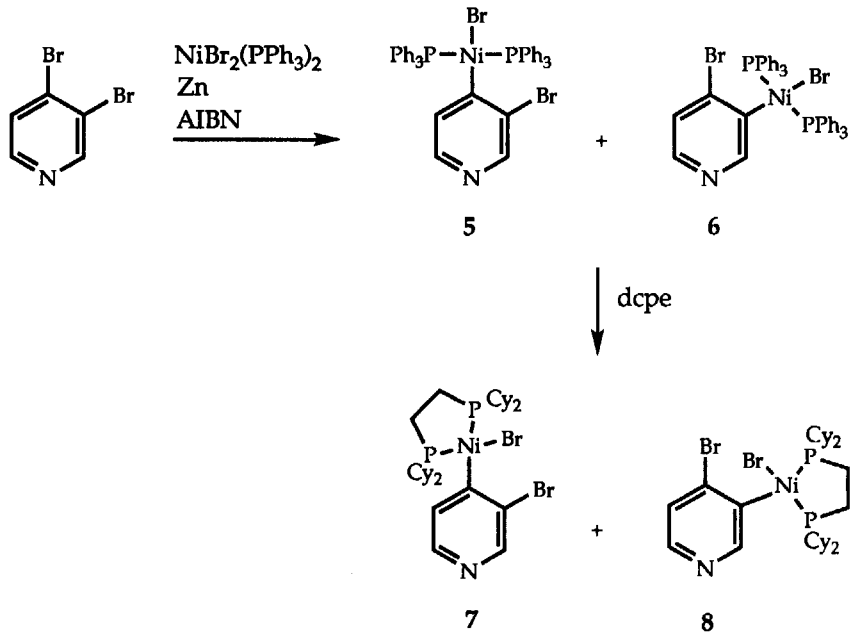


Fig. 1. ORTEP diagram for **4** with atom labelling (except for the phenyl groups of the PPh_3 ligands) and with 50% probability ellipsoids.

Table 1. Selected bond distances (Å) and bond angles (°) for the dimer [NiCl(μ-3-ClC$_5$H$_3$N-2)(PPh$_3$)]$_2$ (**4**)

Ni(1)—Ni(2)	3.076(2)	Ni(1)—Cl(1)	2.215(3)
Ni(1)—P(1)	2.197(3)	Ni(1)—N(2)	1.931(7)
Ni(1)—C(1)	1.866(10)	Ni(2)—Cl(3)	2.211(3)
Ni(2)—P(2)	2.206(3)	Ni(2)—N(1)	1.919(7)
Ni(2)—C(6)	1.867(9)		

Cl(1)—Ni(1)—P(1)	93.1(1)	Cl(1)—Ni(1)—N(2)	91.5(2)
Cl(1)—Ni(1)—C(1)	170.1(3)	P(1)—Ni(1)—N(2)	172.2(2)
P(1)—Ni(1)—C(1)	92.0(3)	N(2)—Ni(1)—C(1)	84.4(3)
Cl(3)—Ni(2)—P(2)	92.8(1)	Cl(3)—Ni(2)—N(1)	91.1(2)
Cl(3)—Ni(2)—C(6)	173.1(3)	P(2)—Ni(2)—N(1)	175.4(2)
P(2)—Ni(2)—C(6)	92.1(3)	N(1)—Ni(2)—C(6)	84.1(3)

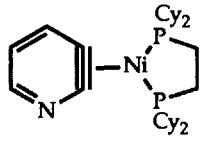


Scheme 2.

Ni(PPh$_3$)$_2$ probably occurs preferentially at C(4), because, as calculations show,[8] this position is likely to accommodate the radical formed after electron transfer from nickel(0) to the C—Br bond more easily than C(3); the same calculations also showed that this position is preferred for nucleophilic additions.[8] Addition of dcpe to the mixture of isomers formed almost quantitatively a mixture of NiBr(3-BrC$_5$H$_3$N-4)(dcpe) (**7**) and NiBr(4-BrC$_5$H$_3$N-3)(dcpe) (**8**) in a ratio of 2.1:1 (as calculated from the ^{31}P{^{1}H} NMR spectrum). The ^{31}P NMR chemical shifts of phosphorus *trans* to bromine are the same for both compounds (δ_P 68.6), whereas the phosphorus *trans* to the Ni—C bond of **7** (δ_P 71.9) is more shielded than that of **8** (δ_P 73.5), possibly as a consequence of a resonance interaction with the pyridine nitrogen atom.

Generation of pyridyne–nickel(0) complexes

Attempts to reduce **1** with alkali metals led only to decomposition, but the solution obtained by treatment of **2** with 1% Na–Hg amalgam for 1.5 h at room temperature showed an AB quartet at δ 72.6 and 79.1 ($J = 24$ Hz) in the ^{31}P NMR spectrum, which is clearly due to a species containing *cis*-inequivalent phosphorus atoms. The chemical shifts are in the range expected for an aryne-nickel(0) complex containing dcpe, e.g. δ 77.6 for Ni(η^2-C_6H_4)(dcpe),[19] and we therefore tentatively assign the new signal to the 2,3-pyridyne complex Ni(2,3η-C_5H_3N)(dcpe) (**9**). However, this complex appeared to be highly sensitive and attempts to bring the reaction to completion led only to decomposition. Treatment of the mixture of **7** and **8** with lithium caused **8** to disappear more rapidly than **7**, probably because the C—Br bond *para* to the pyridine nitrogen atom accepts electrons more readily. The reaction led, after 2.5 h between -40 and -25°C, to the appearance in the ^{31}P NMR spectrum of an AB quartet at δ 78.1 and 78.6 ($J = 23$ Hz), which we assign tentatively to the 3,4-pyridyne–nickel(0) complex Ni(3,4-η-C_5H_3N)(dcpe) (**10**); the yield is estimated to be >80% from the $^{31}P\{^1H\}$ NMR spectrum. This compound seems to be more long-lived than its 2,3-isomer, in agreement with predicted trends for the free arynes,[8–11] but attempts to isolate it have so far failed. As benzyne–nickel(0) complexes are known to undergo double insertion with acetylenes to form naphthalenic derivatives,[20] we reduced the mixture of **7** and **8** with lithium in the presence of 3-hexyne in an attempt to form 5,6,7,8-tetraethylisoquinoline. Although **10** was formed, the insertion product was not detected and the only identifiable species formed finally was Ni(η-C_2Et_2)(dcpe) (δ_P 70.9), arising from displacement of the pyridyne by the acetylene. This compound was synthesized independently by reaction of Ni(η-C_2H_4)(dcpe) with 3-hexyne.



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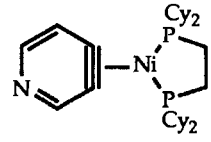

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CONCLUSIONS

(1) The oxidative addition of 2,3-dichloropyridine to zero-valent nickel fragments NiL_2 ($L_2 = 2PEt_3$, $2PPh_3$, dcpe) gives 2-pyridylnickel(II) complexes with high regioselectivity and is probably governed by prior coordination of the pyridine nitrogen atom. The more labile phosphine PPh_3 can be displaced from the coordination sphere to form a dimeric C,N-bridged 2-pyridyl complex (**4**), which is similar to known complexes of nickel(II), palladium(II) and platinum(II) derived from 2-halogenopyridine derivates.

(2) The corresponding oxidative additions of 3,4-dibromopyridine show a slight preference for the formation of 4-pyridylnickel(II) complexes, probably resulting from the electronic influence of the nitrogen atom.

(3) Alkali metal reduction of the *o*-halogenopyridylnickel(II) halide complexes generates new species which, on the basis of their ^{31}P NMR spectra, are believed to be nickel(0) complexes Ni(η^2-C_5H_3N)(dcpe) containing 2,3- or 3,4-pyridyne.

EXPERIMENTAL

General procedures

All experiments were performed under an inert atmosphere with use of standard Schlenk techniques, and all solvents were dried and degassed prior to use. All reactions involving pyridyne complexes were carried out under argon. NMR spectra were recorded on a Varian XL-200E (^1H at 200 MHz, ^{13}C at 50.3 MHz, ^{19}F at 188.1 MHz and ^{31}P at 80.96 MHz), a Varian Gemini-300 BB (^1H at 300 MHz, ^{13}C at 75.4 MHz and ^{31}P at 121.4 MHz) or a Varian VXR-300 instrument (^1H at 300 MHz and ^{13}C at 75.4 MHz). The chemical shifts (δ) for ^1H and ^{13}C are given in ppm relative to residual signals of the solvent and to external 85% H_3PO_4 for ^{31}P. The spectra of all nuclei (except ^1H) were ^1H decoupled. The coupling constants (J) are given in Hz. IR spectra were measured in solution (KBr cells) on a Perkin–Elmer 683 instrument. Mass spectra of the complexes were obtained on a VG ZAB2-SEQ spectrometer by the Fast-Atom Bombardment (FAB) technique. Solutions of the samples were prepared in CH_2Cl_2 and added to a matrix of 3-

nitrobenzylalcohol. Microanalyses were done in-house. We have experienced difficulty in obtaining acceptable microanalyses for some compounds, but the spectroscopic data and the X-ray structure for compound **4** leave no doubt about the formulations.

Starting materials

1,2-Dichloropyridine was obtained commercially and used as received. 3,4-Dibromopyridine was prepared from 3-bromopyridine as follows. Reaction with *m*-chloroperoxybenzoic acid gave 3-bromopyridine-*N*-oxide, which was treated with fuming HNO_3 to form 3-bromo-4-nitropyridine-*N*-oxide.[30] Bromination with CH_3COBr gave 3,4-dibromopyridine-*N*-oxide, which was reduced to 3,4-dibromopyridine with iron.[31] The complexes $NiX_2(PPh_3)_2$ (X = Cl, Br) were prepared from NiX_2 and PPh_3.[32]

Preparation of $NiCl(3\text{-}ClC_5H_3N\text{-}2)(PEt_3)_2$ (**1**)

To a vigorously stirred suspension of $Ni(COD)_2$ (0.50 g, 1.8 mmol) and hexane (15 cm^3) under argon was added dropwise PEt_3 (0.55 cm^3, 3.75 mmol) at room temperature. After 5 min, 2,3-dichloropyridine (0.31 g, 2.1 mmol) was added to the red solution at 0°C and the mixture was stirred at 0°C for 20 min and at room temperature for 3 h. The solution was filtered through Celite and the solution was evaporated to yield 0.52 g (65%) of **1** as a yellow solid. IR (CH_2Cl_2): 3040 (w), 2965 (s), 2935 (m), 2910 (m), 2890 (m), 1555 (m), 1535 (w), 1455 (m), 1415 (m), 1365 (vs), 1105 (m), 1035 (s), 1010 (m), 785 (m) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 1.02–1.15 ([A_3B_2X] m, 18H, $J = 7.7$, CH_3), 1.32–1.42 ([A_3B_2X] m, 12H, CH_2), 6.12–6.16 [m, 1H, H(5)], 6.80 [dd, 1H, $^3J = 7.8$, $^4J = 1.4$, H(4)], 8.34 [dd, 1H, $^3J = 4.5$, $^4J = 1.4$ H(6)]. A two-dimensional Nuclear Overhauser Effect (PSNOE) experiment yielded a response from both the aromatic protons at C(4, 6) on irradiation of the signal attributed to the methyl protons of PEt_3 (δ 1.06). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6): δ 8.15 (CH_3), 13.95 (t, $J_{CP} = 12.5$, CH_2), 116.19 (t, $J_{CP} = 2.5$, CH), 130.29 (t, $J_{CP} = 2.5$, CH), 140.42 [t, $J_{CP} = 4.7$, C(3)], 145.80 (t, $J_{CP} = 2.6$, CH), 186.45 [t, $J_{CP} = 35.0$, C(2)]. $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 12.5 (s). FAB-MS (3-nitrobenzyl alcohol, $C_{17}H_{33}Cl_2NNiP_2$): 444 (9, M+3), 442 (11, M+1), 408 (74), 406 (100). Found for $C_{17}H_{33}Cl_2NNiP_2$: C, 45.4; H, 7.6; N, 3.1. Calc.: C, 46.1; H, 7.5; N, 3.2%.

Preparation of $NiCl(3\text{-}ClC_5H_3N\text{-}2)(dcpe)$ (**2**)

A solution of $Ni(\eta^2\text{-}C_2H_4)(dcpe)$ (0.452 g, 1 mmol) in THF (15 cm^3) at −65°C was treated with a solution of 2,3-dichloropyridine (0.16 g, 1.1 mmol) in THF (5 cm^3). The mixture was stirred for 2 h at room temperature, and the solvent was removed by evaporation. The complex was extracted with CH_2Cl_2, the extract was filtered through Celite and the solvent was removed *in vacuo*. The residue was crystallized from ether (10 cm^3)–hexane (20 cm^3) to give a yellow solid (234 mg, 37%) containing **2** together with *ca* 10% of $NiCl(2\text{-}ClC_5H_3N\text{-}3)(dcpe)$ (**3**). Compound **2**: ^1H NMR (200 MHz, CD_2Cl_2): δ 1.10–2.00 (m, 40H, CH_2 of C_6H_{11}), 2.00–2.65 (m, 8H, CH_2 and CH of C_6H_{11}), 6.60 [dd, 1H, $J = 7.8, 4.6$, H(5)], 7.08 [ddd, 1H, $J = 7.8, 2.4, 1.2$, H(4)], 8.38 [dd, 1H, $J = 4.6, 1.2$, H(6)]. ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 18.00–37.00 (m, CH_2 and C_6H_{11}), 117.40, 131.55 (CH), 142.19 [d, $J_{CP} = 5.5$, C(3)], 145.74 [d, $J_{CP} = 8.8$, C(6)—H]; resonance due to C(2) was not located. $^{31}P\{^1H\}$ NMR (80.96 MHz, CD_2Cl_2): δ 64.6, 67.4 (AB q, $J_{PP} = 26$). FAB-MS (3-nitrobenzyl alcohol, $C_{31}H_{51}Cl_2NNiP_2$): 630 (5, M+3), 628 (5, M+1), 531 (71), 529 (100). Found for $C_{31}H_{51}Cl_2NNiP_2$: C, 59.0; H, 8.5; N, 1.9. Calc.: C, 59.2; H, 8.2; N, 2.2%. Compound **3**: ^1H NMR (200 MHz, CD_2Cl_2): δ 1.10–2.65 (m, 48H, CH and CH_2 of C_6H_{11}), 6.85 [dd, 1H, $J = 7.8, 4.6$, H(5)], 7.46–7.55 [m, 1H, H(4)], 7.78–7.83 [m, 1H, H(6)]. $^{31}P\{^1H\}$ NMR (80.96 MHz, CD_2Cl_2): δ 67.9, 68.7 (AB q, $J = 32$).

Preparation of $[NiCl(\mu\text{-}3\text{-}ClC_5H_3N\text{-}2)(PPh_3)]_2$ (**4**)

A suspension of zinc dust (1.1 g, 15.9 mmol) in THF (20 cm^3) was activated by ultrasound for 30 min at room temperature, and 2,3-dichloropyridine (2 g, 13.5 mmol), $NiCl_2(PPh_3)_2$ (7.54 g, 11.5 mmol), AIBN (130 mg) and THF (15 cm^3) were added successively. The green mixture was stirred for 1 h at room temperature to give a brown solution. The solvent was removed by evaporation and the complex was extracted with CH_2Cl_2. The solution was then filtered through Celite and evaporated to dryness. The poorly soluble yellow-brown solid was stirred with ether and filtered off to yield **4** quantitatively. Crystals suitable for X-ray analysis were obtained from CH_2Cl_2. ^1H NMR (200 MHz, CD_2Cl_2): δ 6.44–6.56 [m, 1H, H(5)], 6.79 [d, 1H, $^3J = 8$, H(4)], 7.10–7.90 [m, 31H, PPh_3+H(6)]. $^{31}P\{^1H\}$ NMR (80.96 MHz, C_6D_6): δ 20.7 (s).

Found for $C_{46}H_{36}Cl_4N_2Ni_2P_2$: C, 57.0; H, 4.4. Calc. C, 58.9; H, 3.9%.

Preparation of NiBr(3-BrC_5H_3N-4)$(PPh_3)_2$ (**5**) *and* NiBr(4-BrC_5H_3N-3)$(PPh_3)_2$ (**6**)

Following the procedure described above, $NiBr_2(PPh_3)_2$ (6.8 g, 9.1 mmol) was treated for 2 h at room temperature with 3,4-dibromopyridine (2.8 g, 11.8 mmol) in THF (60 cm^3) in the presence of zinc (1.33 g, 20 mmol) and AIBN (180 mg). The solution was filtered through a silica gel column and the solvent was removed by evaporation . The solid was crystallized at −78°C from CH_2Cl_2 (30 cm^3)–ethanol (40 cm^3) to give 8.53 g (88%) of a 2.4:1 mixture of **5** and **6**. Compound **5**: ^1H NMR (200 MHz, CD_2Cl_2): δ 7.20–7.90 (m, 33H, PPh_3+H^{arom}). $^{31}P\{^1H\}$ NMR (80.96 MHz, CD_2Cl_2): δ 23.3 (s) (**5**), 23.5 (s) (**6**).

Preparation of NiBr(3-BrC_5H_3N-4)(dcpe) (**7**) *and* NiBr(4-BrC_5H_3N-3)(dcpe) (**8**)

A suspension of **5** and **6** (8.53 g, 10.4 mmol) in THF (160 cm^3) was treated with dcpe (4.53 g, 10.7 mmol) for 3 h at room temperature. The solvent was removed by evaporation and the solid residue was dissolved in CH_2Cl_2 (15 cm^3). Addition of hot ethanol (30 cm^3) yielded 7.0 g (93%) of a 2.1:1 mixture of **7** and **8**. Complex **7** could be separated from **8** on a silica gel column (CH_2Cl_2), but with considerable loss owing to decomposition. Compound **7**: IR (CH_2Cl_2): 3035 (w), 2930 (s), 2850 (m), 1570 (m), 1445 (m) cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2): δ 1.10–2.15 (m, 40H, CH_2 of C_6H_{11}), 2.15–2.50 (m, 8H, CH_2 and CH of C_6H_{11}), 7.30–7.40 [m, 1H, H(5)], 7.49 [m, 1H, H(6)], 7.97 [d, 1H, $J = 5$, H(2)]. $^{31}P\{^1H\}$ NMR (80.96 MHz, CD_2Cl_2): δ 68.6, 71.9 (AB q, $J_{PP} = 33$). FAB-MS (3-nitrobenzyl alcohol, $C_{31}H_{51}Br_2NNiP_2$): 720 (35, M+3), 718 (46, M+1), 638 (32), 455 (100). Compound **8**: ^1H NMR (200 MHz, CD_2Cl_2): δ 1.10–2.10 (m, 48H, CH_2 of C_6H_{11}), 2.10–2.50 (m, 8H, CH_2 and CH of C_6H_{11}), 7.30–7.40 [m, 2H, H(5,6)], 8.07 [s, 1H, H(2)]. $^{31}P\{^1H\}$ NMR (80.96 MHz, CD_2Cl_2): δ 68.6, 73.5 (AB q, $J_{PP} = 33$).

Attempted preparation of Ni(2,3-η-C_5H_3N)(dcpe) (**9**)

To a 1% sodium amalgam prepared from sodium (26 mg, 1 mmol) in mercury (0.2 cm^3) was added successively ether (10 cm^3) and **2** (0.094 g, 0.15 mmol). The mixture was stirred vigorously at room temperature for 1.5 h while being monitored by ^{31}P NMR spectroscopy. A signal attributed to the 2,3-pyridyne complex **9** was observed, together with signals of the starting material and decomposition products. $^{31}P\{^1H\}$ NMR (80.96 MHz, CD_2Cl_2): δ 72.6, 79.1 (AB q, $J = 24$).

Attempted preparation of Ni(3,4-η-C_5H_3N)(dcpe) (**10**) *and trapping with* 3-*hexyne*

Glass beads (10 cm^3 volume) and lithium dispersion (30%, 210 mg) were placed in a flask under argon. The lithium was washed with hexane, dried *in vacuo* and THF (30 cm^3) was added. 3-Hexyne (0.7 cm^3, 6 mmol) was added, the mixture was cooled to −78°C, and a mixture of **7** and **8** (0.88 g, 1.2 mmol) was added. The mixture was stirred between −40 and −25°C for 2.5 h while being monitored by ^{31}P NMR spectroscopy. The spectrum showed a signal attributed to **10** (>80% yield) together with Ni(η-C_2Et_2)(dcpe) (δ 70.9). The mixture was stirred for 12 h while being allowed to warm up to room temperature. The ^{31}P NMR spectrum showed that **10** had disappeared and that Ni(η-C_2Et_2)(dcpe) remained, but after work-up, no 5,6,7,8-tetraethylisoquinoline could be isolated. $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 78.1, 78.6 (AB q, $J = 23$).

X-ray crystallography of [NiCl(μ-3-ClC_5H_3N-2)$(PPh_3)]_2$ (**4**)

Crystal data, details of data collection, data processing, structure analysis and structure refinement are given in Table 2. The structure of **4** was solved by Patterson methods (PATTY)[33] and was expanded using Fourier techniques (DIRDIF92).[33] All non-hydrogen atoms were refined anisotropically by full matrix least squares. Hydrogen atoms were included at calculated positions (C—H 0.95 Å) and held fixed. All calculations were performed using the teXsan Structure Analysis Software of the Molecular Structure Corporation.[34]

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Table 2. Crystal and structure refinement data for $[NiCl(\mu\text{-}3\text{-}ClC_5H_3N\text{-}2)(PPh_3)]_2$ (**4**)

Crystal data	
Chemical formula	$C_{46}H_{36}Cl_4N_2Ni_2P_2$
Formula weight	937.96
Crystal system	monoclinic
Unit cell dimensions	
a (Å)	16.944(5)
b (Å)	12.821(6)
c (Å)	21.055(4)
α (°)	
β (°)	107.34(2)
γ (°)	
V (Å^3)	4366(2)
Space group	$P2_1/c$ (no. 14)
D_c (g cm^{-3})	1.427
Z	4
$F(000)$	1920
Colour, habit	yellow/orange, needle
Crystal dimensions	$0.08 \times 0.06 \times 0.20$
μ (cm^{-1})	42.82 (Cu-K_α)
Data collection and processing	
Diffractometer	Rigaku AFC6R
X-radiation	Cu-K_α (graphite monochromated)
Scan mode	ω–2θ
ω-scan width	$1.10+0.30 \tan\theta$
2θ limits (°)	120.1
Data collected (h,k,l)	(−18,0,0) to (18,14,21)
No. of reflections	
Total	6892
Unique (R_{int}/%)	6682 (3.8)
Observed	2473 [$I > 3\sigma(I)$]
Absorption correction (trans. factors)	azimuthal scans (0.77–1.00)
Structure analysis and refinement[a]	
Structure solution	Patterson methods (PATTY,[33] DIRDIF92[33])
Refinement	full-matrix least-squares
No. of parameters	505
Weighting scheme	$w = \dfrac{4F_0^2}{[\sigma^2(F_0^2)+(0.008F_0^2)^2]}$
R (observed data) (%)	4.5
R_w (observed data)(%)	3.8

[a] All calculations were performed by use of teXsan[34] with neutral atom scattering factors from Cromer and Waber,[35] Δf and $\Delta f'$ values from ref. 36 and mass attenuation coefficients from ref. 37. Anomalous dispersion effects were included in F_{calc}.[38]

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