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N-PROTONATED 2-PYRIDYLNICKEL(II) COMPLEXES. INSERTION OF ISOCYANIDES INTO THE NICKEL–2-PYRIDYL BOND

BRUNO CROCIANI*, FRANCESCA DI BIANCA, AMALIA GIOVENCO
Istituto di Chimica Generale, University of Palermo (Italy)

and ADRIANO BERTON
Centro Chimica Tecnologia Composti Metallorganici Elementi Transizione, C.N.R., Padova (Italy)

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Summary

The reaction of the binuclear complex [NiCl(μ-2-py)(PPh_3)]$_2$ (μ-2-py = μ-C_5H_4N-C^2,N) with the phosphines L (L = PPh_3, $PMePh_2$, PMe_2Ph or PEt_3) or dppe (= 1,2-bis(diphenylphosphino)ethane) in the presence of $HClO_4$ yields the *N*-protonated 2-pyridyl derivatives *trans*-[NiCl(2-pyH)(L)$_2$]ClO_4 or [NiCl(2-pyH)(dppe)] ClO_4 (2-pyH = C_5H_5N-C^2) with a square-planar coordination around the nickel(II) center. These products are largely associated through hydrogen bonding between the N–H group and the perchlorate anion, both in the solid and in chlorinated solvents. The configuration in solution has been studied by ^1H and ^{31}P NMR spectroscopy. In the complex *trans*-[NiCl(2-pyH)(PMe_2Ph)$_2$]ClO_4, the planar 2-pyH ligand is oriented perpendicularly to the coordination plane, with restricted rotation about the Ni–C^2 bond. The reaction of *trans*-[NiCl(2-pyH)($PMePh_2$)$_2$]ClO_4 with CNC_6H_4OMe-*p* and then with NEt_3 yields the unstable compound *trans*-[NiCl{C(2-py)=NC_6H_4OMe-*p*}($PMePh_2$)$_2$] through a fast migratory insertion of the isocyanide into the nickel–2-pyridyl bond. This product can be isolated and characterized only when the imino(2-pyridyl)methyl group is σ,σ'-N,N'-chelated to $ZnCl_2$.

Introduction

The terminal 2-pyridyl group C_5H_4N-C^2 (denoted throughout by 2-py) in complexes of the type *trans*-[MX(2-py)(L)$_2$] (M = Pd, Pt; X = Cl, Br; L = tertiary phosphine) [1,2] is readily *N*-protonated by strong mineral acids such as $HClO_4$. The reaction is very fast and occurs without cleavage of the metal–carbon bond. Similarly, the bridging 2-pyridyl group μ-C_5H_4N-C^2,N(μ-2-py) in the binuclear complexes [PdX(μ-2-py)(PPh_3)]$_2$ is also *N*-protonated by HX (X = Cl, Br), but at

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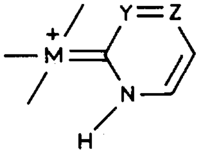
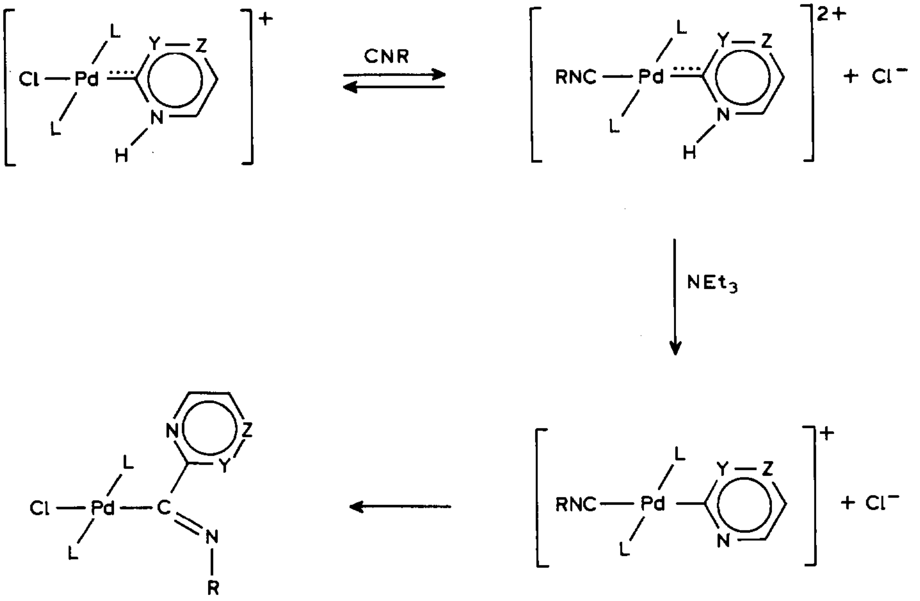
markedly lower rates [1]. Analogous protonations at the N^1 nitrogen atom have been reported for related C^2-bonded heterocycles in $[PdCl(\mu\text{-}C_4H_3N_2\text{-}C^2,N^1)(PPh_3)]_2$ and *trans*-$[PdCl(C_4H_3N_2\text{-}C^2)(L)_2]$ ($C_4H_3N_2$ = 2-pyrimidyl or 2-pyrazyl group; L = tertiary phosphine) [3]. The protonated derivatives are of interest for theoretical and synthetic reasons. Thus the multinuclear NMR spectra suggest that there is a significant contribution of the carbene-like resonance structure **A** to the electronic configuration of the ligands.



(A)

(Y = Z = CH ;
Y = N , Z = CH ;
Y = CH , Z = N)

On the other hand, these compounds are useful in the synthesis of imino(2-pyridyl)methyl- and imino(2-pyrazyl)methylpalladium(II) complexes through migratory insertion of isocyanides into the Pd–C^2 bond of the corresponding deprotonated species [4,5]:



(R = Me, C_6H_4OMe-*p*)

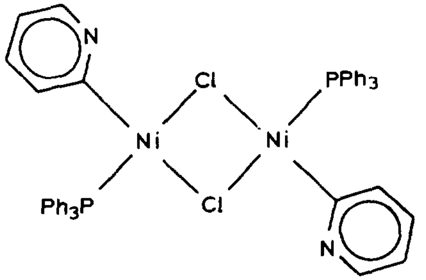
As an extension of our studies on carbon-metallated nitrogen ligands, we report here the preparation and characterization of *N*-protonated 2-pyridyl-nickel(II) derivatives, together with some preliminary results on the insertion of isocyanides into the nickel–2-pyridyl bond.

Results and discussion

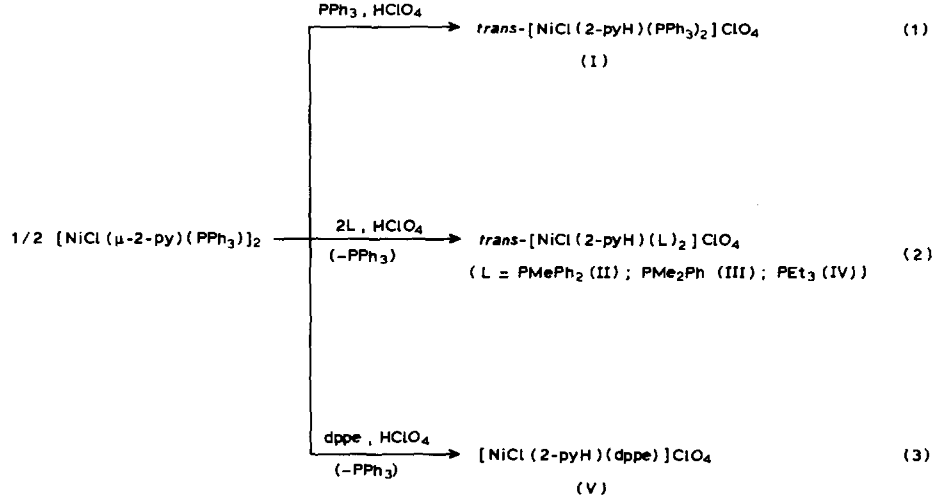
Protonation of [NiCl(μ-2-py)(PPh$_3$)]$_2$

The nickel(II) complexes containing the *N*-protonated 2-pyridyl ligand (2-pyH) are conveniently prepared by the reactions shown in Scheme 1.

The course of reaction 1 can be monitored by ^{31}P NMR spectroscopy. When a 2.5×10^{-2} *M* CDCl$_3$ solution of the dimer [NiCl(2-py)(PPh$_3$)]$_2$ is treated with methanolic HClO$_4$ (Ni/HClO$_4$ molar ratio 1/1.1) no protonation of the 2-pyridyl ligand is observed during 6 h at 30°C. Only upon addition of PPh$_3$ (Ni/PPh$_3$ 1/1) the reaction 1 proceeds slowly and goes nearly to completion in ca. 6 h, as shown by the progressive decrease with time of the singlets at 26.2 and −5.1 ppm, due to the starting dimer and to free PPh$_3$, respectively, and the concomitant increase of the singlet at 21.4 ppm due to the final product I. This behaviour cannot satisfactorily be interpreted in terms of the chloro-bridged structure **B**, originally proposed for the binuclear complex [6], since the terminal 2-pyridyl groups are expected to be protonated almost immediately by HClO$_4$ because of their enhanced basicity [1,7]:

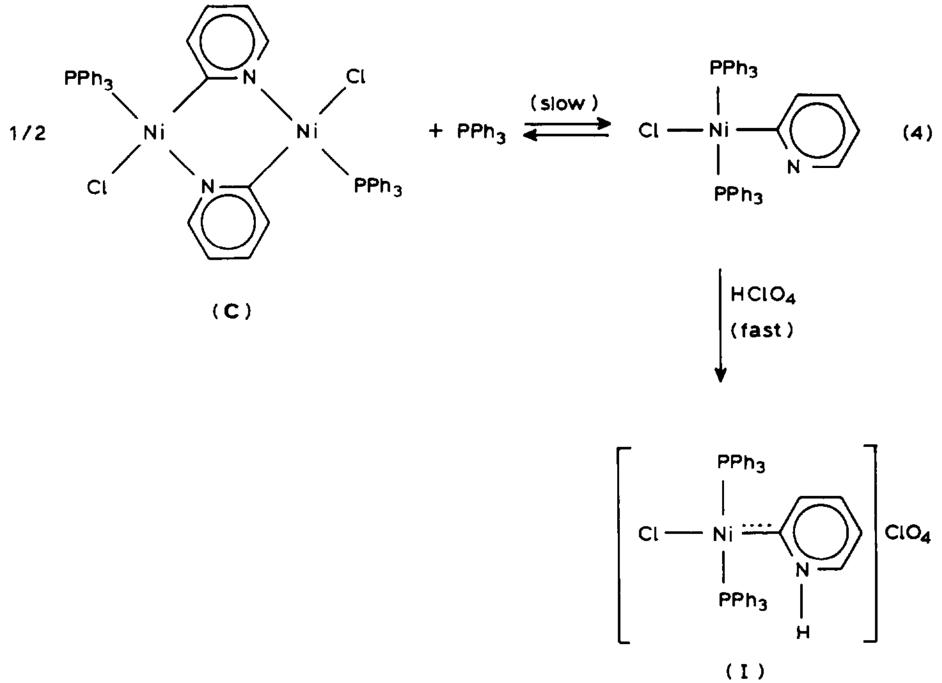


(B)



SCHEME 1. 2-pyH = C$_5$H$_5$N-*C*^{2}; dppe = 1,2-bis(diphenylphosphino)ethane.

The results are better interpreted in terms of structure C with a C^2,N-bridging 2-pyridyl ligand, analogous to that in $[PdBr(\mu\text{-}2\text{-}py)(PPh_3)]_2$ [8], according to the following step-wise mechanism:



Reactions 2 and 3 with the more basic phosphines L and the chelating 1,2-bis(diphenylphosphino)ethane proceed much faster, and involve also displacement of the coordinate PPh_3 ligand (as an example, reaction 3 with dppe is complete in less than 2 h under conditions comparable to those for reaction 1).

The products I and V crystallize with 1/2 of a CH_2Cl_2 and 2/3 of a $CHCl_3$ molecule, respectively, as shown by elemental analysis and by GLC analyses of their solutions in 1,2-dichloroethane.

All the protonated compounds are stable for months as solids if kept in a dry atmosphere. They are also moderately stable in anhydrous chlorinated solvents, whereas a slow decomposition takes place in MeOH or $MeNO_2$, as suggested by the slow increase in electrical conductivity with time. In the latter solvents, the molar conductivities (measured immediately after dissolution) are in the expected range for uni-univalent electrolytes [9]. For 10^{-3} M 1,2-dichloroethane solutions, however, the molar conductivity values are much lower than those reported for uni-univalent electrolytes [9], indicating an extensive cation–anion association. From the splitting of the ν(N–H), ν(Cl–O) and δ(Cl–O) vibrations into two or three bands in the IR spectra (see Table 1), it appears that the cationic complexes I–V are largely associated through hydrogen bonding between the N–H group and the perchlorate anion both in the solid and in CH_2Cl_2 solution.

For the *cis* dppe derivative V, a ν(Ni–Cl) band is observed at 343 cm^{-1}, in a good agreement with the reported ν(Ni–Cl) values for the neutral *cis* planar complexes [$NiCl_2$(dppe)] (330 and 320 cm^{-1}), and [NiCl(C_6Cl_5)(dppe)] (340 cm^{-1}) [10,11]. The ν(Ni–Cl) bands for the *trans* complexes I–IV are difficult to detect because of the low intensity of the few absorptions in the range 400–300 cm^{-1}, where such bands are likely to occur (cf., the ν(Ni–Cl) values in the range 373–327 cm^{-1} for *trans*-[NiCl(Ar)$(L)_2$] (Ar = phenyl or substituted aryl group; L = tertiary phosphine) [12]. Thus only a tentative assignment is given in Table 1.

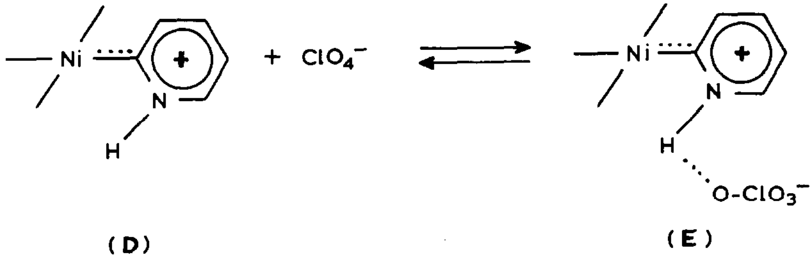
As shown by the NMR data (see further), all the examined nickel(II) derivatives are diamagnetic square-planar compounds, with a *trans* configuration for [NiCl(2-pyH)$(L)_2$]ClO_4 and *cis* for [NiCl(2-pyH)(dppe)]ClO_4.

^{1}*H and* ^{31}*P NMR spectra*

The ^{1}H and ^{31}P NMR spectra are listed in Table 2. The 2-pyridyl protons give rise to second-order ABCD spectra, similar to those of *trans*-[MX(2-pyH)$(L)_2$]ClO_4 and [MX(2-pyH)(dppe)]ClO_4 (M = Pd, Pt) [1], with a characteristic resonance pattern for each proton as shown in Fig. 1 for the PEt_3 derivative IV.

For this compound, the $\delta(H^6)$ signal at 8.60 ppm appears as a triplet because the main coupling constants $^3J(H^1\text{–}H^6)$ and $^3J(H^5\text{–}H^6)$ are of comparable magnitude.

The N–H resonances ($\delta(H^1)$) appear as broad unresolved multiplets in the range 10.2–9.5 ppm at 30°C. On cooling the CD_2Cl_2 solutions to −20°C, these signals undergo large downfield shifts of 2–3 ppm, with the exception of the $PMePh_2$ complex II, for which a shift of only 0.2 ppm is observed. In line with conductivity measurements and IR data in chlorinated solvents, this behaviour can be interpreted in terms of a fast association equilibrium 5, which is shifted markedly towards the hydrogen-bonded species E at lower temperatures:



(5)

For the dppe complex V, the ^{31}P resonances appear as an AB system, which is consistent with a *cis* square-planar geometry, with the phosphorous donor atoms of the chelating diphosphine *trans* to different ligands, such as the chloride and the 2-pyH group. The ^{31}P NMR spectra of the cationic complexes I–IV, [NiCl(2-pyH)$(L)_2$]$^+$, are characterized by singlet ^{31}P resonances, which are indicative of mutually *trans* L ligands. Furthermore, the ^{1}H NMR spectra of II and III exhibit 1/2/1 triplet patterns for δ(P-Me), typical of virtually coupled phosphines in a *trans* L–Ni–L geometry (L = $PMePh_2$, PMe_2Ph). The equivalence of the two ^{31}P phosphine nuclei and the appearance of two separate P-Me triplets (1/1 integration ratio) for the PMe_2Ph complex III suggest a molecular structure in which the asymmetric 2-pyH ligand lies in a plane perpendicular to the coordination plane, with hindered rotation around the nickel–carbon bond. This may be the result of steric or electronic factors (or from an interplay of the two). If steric factors are of

TABLE 1

ANALYTICAL AND PHYSICAL DATA. CHARACTERISTIC IR BANDS

Compound	Analyses (Found (calc) (%))				Molar conductivity [a] (ohm^{-1} cm^2 mol^{-1})
	C	H	N	Cl	
trans-[NiCl(2-pyH)(PPh$_3$)$_2$]ClO$_4$·1/2CH$_2$Cl$_2$	59.1	4.2	1.6	12.4	94.5 [c]
(I)	(59.35)	(4.32)	(1.67)	(12.66)	
trans-[NiCl(2-pyH)(PMePh$_2$)$_2$]ClO$_4$	55.1	4.6	2.1	10.7	87.5 [c]
(II)	(55.31)	(4.64)	(2.08)	(10.53)	8.7 [e]
					109.5 [f]
trans-[NiCl(2-pyH)(PMe$_2$Ph)$_2$]ClO$_4$	46.1	4.9	2.5	13.1	97.1 [c]
(III)	(45.94)	(4.96)	(2.55)	(12.91)	
trans-[NiCl(2-pyH)(PEt$_3$)$_2$]ClO$_4$	39.8	7.0	2.6	14.1	104.8 [c]
(IV)	(40.11)	(6.93)	(2.75)	(13.93)	5.8 [e]
					102.5 [f]
[NiCl(2-pyH)(dppe)]ClO$_4$·2/3CHCl$_3$	50.5	4.0	1.9	18.6	71.4 [c]
(V)	(50.66)	(3.98)	(1.87)	(18.89)	
trans-[NiCl{C(2-$\overline{\mathrm{py)=NC_6H_4OMe\text{-}}p\mathrm{(Zn}}Cl_2$)}-					
(PMePh$_2$)$_2$]	55.3	4.5	3.3	12.7	
(VI)	(55.62)	(4.43)	(3.33)	(12.63)	

[a] For 10^{-3} *M* solutions at 20°C. [b] Tentative assignment. [c] In MeNO$_2$. [d] In CH$_2$Cl$_2$. [e] In 1,2-dichloroethane. [f] In MeOH. [g] Not observed, probably masked by the intense ν(Zn–Cl) bands at 335 and 312 cm^{-1}.

importance in the hydrogen-bonded species **E**, they are less relevant in the unassociated cations **D**, since the steric requirements of the 2-pyH group are comparable with those of the cyclic α-alkoxyvinyl or alkyl(alkoxy)carbene ligands, which were found to be freely rotating around the Ni–C bond at ambient temperature in the complexes *trans*-[NiR{$\overline{\mathrm{C{=}CH(CH_2)_nO}}$}(PMe$_2$Ph)$_2$] and *trans*-[NiR-{$\overline{\mathrm{CCH_2(CH_2)_nO}}$}(PMe$_2$Ph)$_2$]ClO$_4$ (R = C$_6$H$_2$Me$_3$-2,4,6 and C$_6$Cl$_5$; n = 2,3) [13]. Thus, the restricted rotation of the 2-pyH ligand is probably due to electronic factors, such as an increased double bond character in the Ni–C^2 bond, resulting

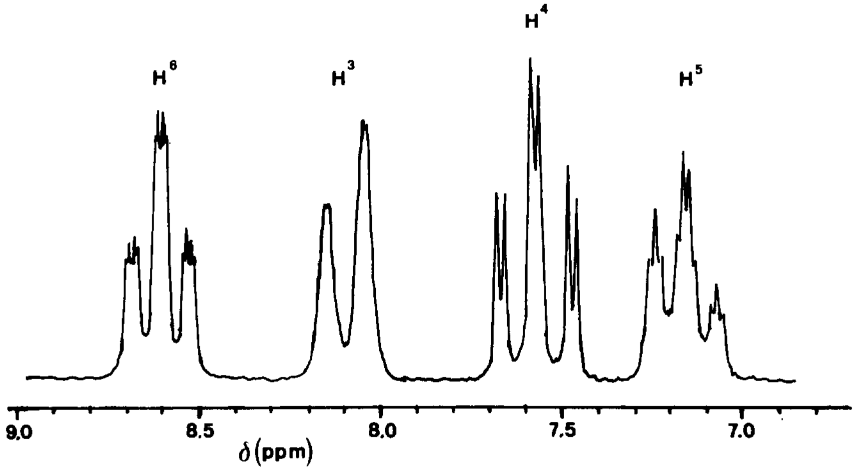


Fig. 1. ^{1}H NMR spectrum of *trans*-[NiCl(2-pyH)(PEt$_3$)$_2$]ClO$_4$ (IV) in the pyridyl proton range.

IR (cm^{-1})			
ν(N–H)	ν(Cl–O)	δ(Cl–O)	ν(Ni–Cl) [b]
3225mw; 3200sh; 3140mw	1115s; 1096vs; 1054s	627sh; 622s; 614s	381mw
[3225m; 3190sh; 3140mw] [d]	[1110vs; 1055s] [d]	[626s; 618s] [d]	
3240m,br; 3190sh; 3140mw	1104vs; 1080sh; 1060sh	625s; 621s; 615sh	379mw or
[3230m; 3190sh; 3130m] [d]	[1110vs; 1080sh; 1060s] [d]	[627s; 617s] [d]	351m
3230m,br; 3190sh; 3140m	1105vs,br; 1060s	626s; 620sh; 615sh	378mw or
[3225m,br; 3190sh; 3135m] [d]			365mw
3210m,br; 3180m; 3130m	1125sh; 1100s,br; 1060s	624s; 615sh	378mw
[3220m,br; 3185m; 3140m] [d]			
3240m,br; 3190w; 3140m	1100vs,br; 1065sh	624s; 615sh	343m
[3235m,br; 3190w; 3150m] [d]			
			n.o. [g]

from an increased $d_\pi \rightarrow p_\pi$ back-donation from the nickel center to 2-pyH, as in the case of the corresponding compounds *trans*-[MX(2-pyH)(PMe_2Ph)$_2$]ClO_4 (M = Pd, Pt) [1].

Insertion of p-methoxyphenylisocyanide into the nickel–2-pyridyl bond

When a CH_2Cl_2 solution of the $PMePh_2$ derivative II is treated with an equimolar amount of CNC_6H_4OMe-*p* at room temperature, an immediate and quantitative coordination of the isocyanide takes place, as indicated by the strong ν(C≡N) band for the ligand at 2170 cm^{-1} in the IR spectrum. The subsequent deprotonation of the 2-pyH group with NEt_3 brings about a very fast disappearance of the ν(C≡N) absorption and a marked change of the IR spectrum in the range 1650–1500 cm^{-1}. These spectral changes parallel those observed in the corresponding reactions of *trans*-[PdCl(2-pyH)(PPh_3)$_2$]$^+$ under comparable conditions [4], and can be accounted for in terms of an analogous reaction sequence (Scheme 2), in which the deprotonation step (ii) is followed by a very fast migratory insertion of the coordinate isocyanide into the Ni–2-py bond (step (iii)) to yield the imino(2-pyridyl)methyl complex F.

In contrast to the corresponding palladium(II) derivatives, the product F cannot be isolated because of extensive decomposition during the work-up of the reaction mixture. However, it is possible to isolate (and hence characterize) its $ZnCl_2$ adduct VI by addition of a methanolic solution of zinc chloride to the system before the deprotonation step (ii).

The binuclear complex VI is a monomer in 1,2-dichloroethane. The IR spectrum shows the typical bands of the PMe_2Ph, 2-py, and C_6H_4OMe-*p* groups and those of the $ZnCl_2$ unit in a pseudo-tetrahedral coordination (ν(Zn–Cl) at 335 and 312

TABLE 2

^{1}H AND ^{31}P NMR DATA[a]

Compound	2-Pyridyl ring protons [b]					Phosphine protons			$\delta(^{31}P)$
	H^1	H^3	H^4	H^5	H^6	P-C_6H_5	P-CH_3	P-CH_2- or P-CH_2-CH_3	
I	10.2br (12.2br) [d]	mk [c]	6.89m	6.44m	mk [c]	8.0–7.1m			21.2s
II	10.1br (10.3br) [d]	mk [c]	6.92m	6.44m	mk [c]	8.0–7.1m	2.08t J(P–H) 8.5 [e]		10.3s
III	9.8vbr (12.7br) [d]	mk [c]	7.13m	6.68m	mk [c]	8.1–7.2m	1.69t J(P–H) 8.6 [e] 1.47t J(P–H) 8.4 [e]		−2.9s
IV	9.5vbr (13.1br) [d]	8.10m	7.57m	7.15m	8.60m $^3J(H^1-H^6) \approx 6$ $^3J(H^5-H^6) \approx 6$			1.8–0.8m [f]	15.9s
V	9.8br (12.7br) [d]	mk [c]	mk [c]	6.90m	mk [c]	8.2–7.1m		3.0–1.75m	61.3d; 47.0d $^2J(P-P)$ 49.7
VI [g]		9.12m	mk [c]	mk [c]	8.34m	7.8–7.2m	1.45t J(P–H) 8.1 [e]		2.7s

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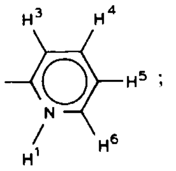
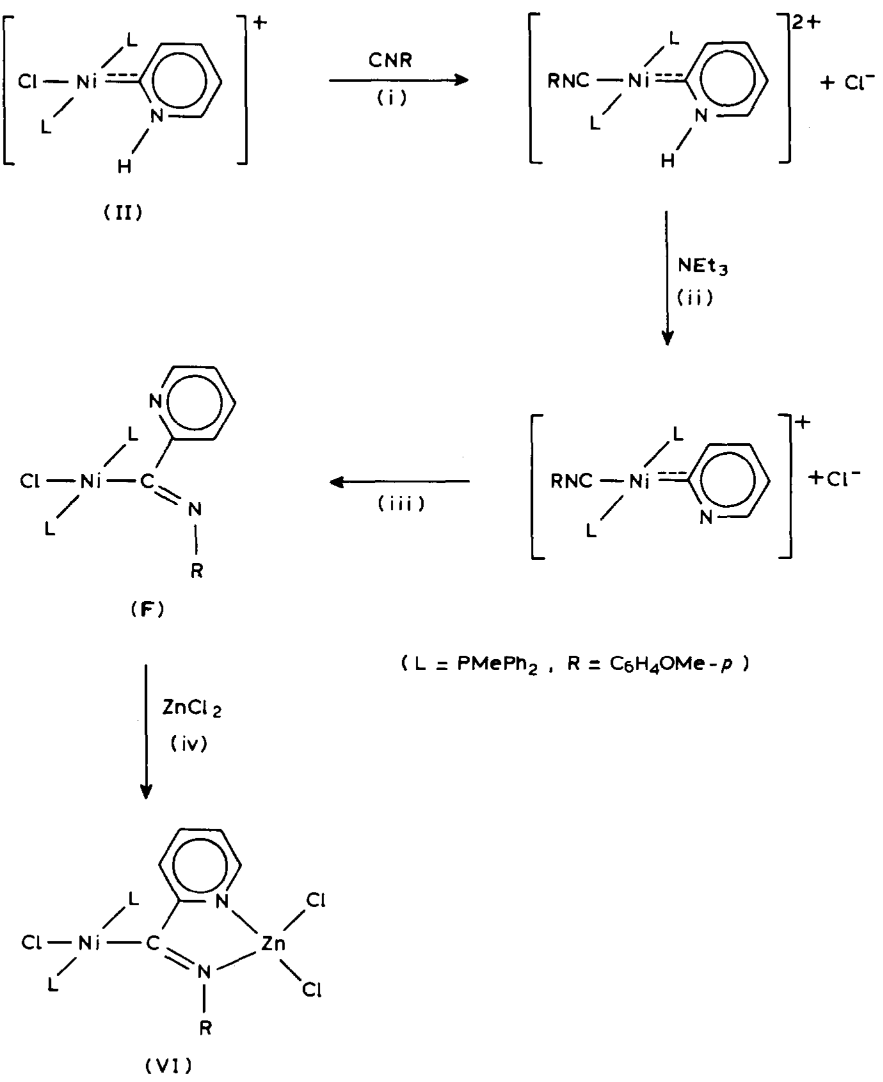
[a] In CD_2Cl_2 solution at 30°C; ^{1}H chemical shifts (δ) in ppm from TMS; ^{31}P chemical shifts (δ) from external 85% H_3PO_4 (downfield shifts taken as positive); coupling constants in Hz; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, vbr = very broad; satisfactory integration values have been obtained. [b] Pyridyl labelling:



the chemical shifts of these protons refer to the center of the corresponding multiplets. [c] Masked by the intense phenyl proton resonances. [d] At −20°C. [e] $J(P-H) = |^2J(P-H) + ^4J(P'-H)|$. [f] Overlapping multiplets. [g] The C_6H_4OMe-p group in this compound is characterized by a symmetric AA′BB′ system for the phenyl protons (see Fig. 2), and by a singlet at 3.89 ppm for the methyl protons.



SCHEME 2

cm^{-1}) [4,5]. The *trans* square-planar configuration around the nickel center of the starting compound II is retained in the final product VI (which gives a singlet at 2.7 ppm in the ^{31}P and a 1/2/1 triplet at 1.45 ppm in the ^{1}H NMR spectrum (see Table 2)).

The ^{1}H NMR spectrum of VI in the aromatic proton region is shown in Fig. 2.

As can be seen, the 2-pyridyl H^{3} and the C_6H_4OMe-*p* *ortho* protons resonate at markedly low fields (9.12 and 9.40 ppm, respectively), as in the case of the $ZnCl_2$ adduct of *trans*-[PdCl{C(2-py)=NC_6H_4OMe-*p*}($(PEt_3)_2$)] [5]. In both compounds, the imino(2-pyridyl)methyl moiety is forced to assume an *E-cis* conformation by the σ,σ'-*N,N'*-chelation, and this brings the 2-pyridyl H^{3} and the C_6H_4OMe-*p* *ortho* protons rather close to nickel or palladium, above and below the coordination

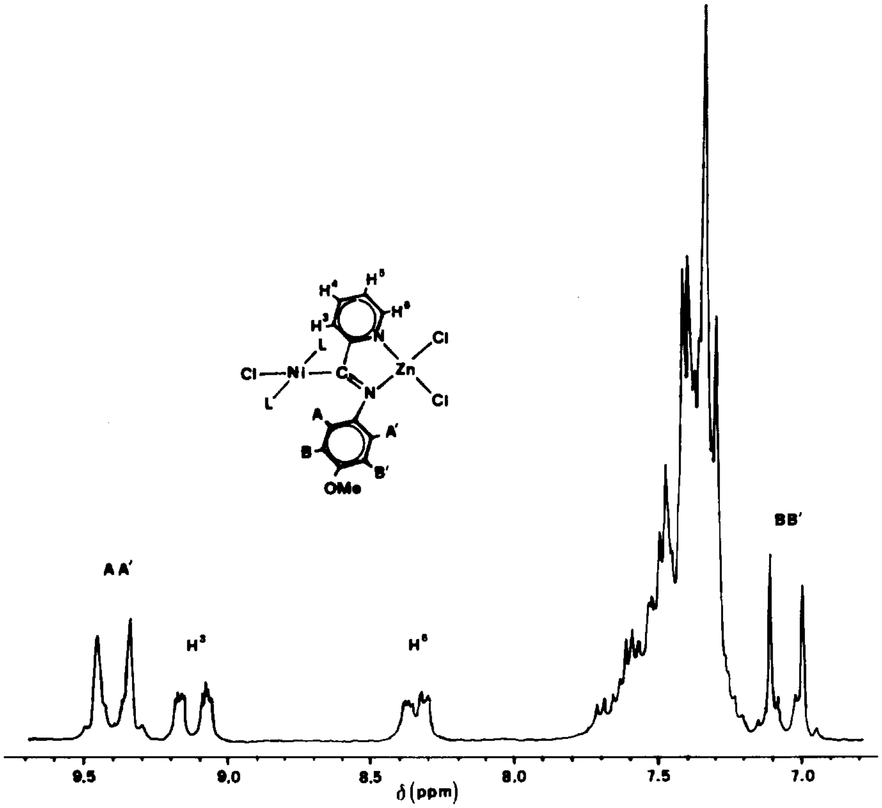


Fig. 2. ^1H NMR spectrum of *trans*-$[NiCl\{C(2\text{-}\overline{py)=NC_6H_4OMe\text{-}p(Zn}Cl_2)\}(PMePh_2)_2]$ (VI) in the aromatic proton region.

plane, with a consequent large deshielding effect on these protons due to the magnetic anisotropy of the d^8 metal centers.

Experimental

The complex $[NiCl(\mu\text{-}2\text{-}py)(PPh_3)]_2$ [6] and the isocyanide $CNC_6H_4OMe\text{-}p$ [14] were prepared by published methods. All other chemicals were reagent grade and used without further purification. Infrared spectra were recorded with a Perkin–Elmer 983 instrument, using Nujol mulls and CsI plates in the range 4000–200 cm^{-1}, and KBr liquid cells of 0.5 mm path length for spectra in solution. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian FT 80A spectrometer. Molecular weights were determined with a Knauer osmometer at 37 °C. The conductivity measurements were carried out with a CDM 83 conductivity meter.

The reactions and purification of the products were carried out at room temperature, unless otherwise stated, in dried solvents, under N_2. The solvents were evaporated to small volume or to dryness at reduced pressure. "Methanolic $HClO_4$" refers to a solution made up by diluting 6 ml of 60–62% aqueous perchloric acid to 250 ml with MeOH : titration showed it to be 0.25 *M* in acid.

Preparation of trans-$[NiCl(2\text{-}pyH)(PPh_3)_2]ClO_4 \cdot 1/2CH_2Cl_2$ *(I)*

The binuclear complex $[NiCl(\mu\text{-}2\text{-}py)(PPh_3)]_2$ (0.87 g, 1 mmol), dissolved in CH_2Cl_2 (50 ml), was treated with PPh_3 (0.53 g, 2 mmol) and subsequently with 8.8 ml of methanolic $HClO_4$ 0.25 *M*. The dark-red solution was set aside overnight. Concentration to small volume and addition of Et_2O gave the crude product as a yellow-brown precipitate. The solid was redissolved in CH_2Cl_2, and the solution treated with charcoal then filtered. The filtrate was evaporated to small volume and diluted with Et_2O to yield the yellow microcrystalline compound I (1.06 g, 66.5% yield, based on the theoretical amount).

Preparation of trans-$[NiCl(2\text{-}pyH)(L)_2]ClO_4$ *(L =* $PMePh_2$ *(II);* PMe_2Ph *(III);* PEt_3 *(IV))*

A solution of $[NiCl(\mu\text{-}2\text{-}py)(PPh_3)]_2$ (0.87 g, 1 mmol) in 50 ml of CH_2Cl_2 was treated with the phosphine L (4 mmol) and with methanolic $HClO_4$ (8.8 ml). After 2 h stirring the solution was evaporated to dryness to leave a yellowish oily residue, which crystallized upon addition of Et_2O with stirring. The solid was redissolved in a CH_2Cl_2/MeOH mixture (1/1 v/v) and the solution treated with charcoal then filtered, concentrated to ca. 5 ml, and diluted with Et_2O (ca. 20 ml) to precipitate the yellow microcrystalline products II–IV (Yield: 55.7% II; 71.0% III; 90.4% IV).

Preparation of $[NiCl(2\text{-}pyH)(dppe)]ClO_4 \cdot 2/3CHCl_3$ *(V)*

A solution of $[NiCl(\mu\text{-}2\text{-}py)(PPh_3)]_2$ (0.87 g, 1 mmol) in 50 ml of CH_2Cl_2 was treated with dppe (0.80 g, 2 mmol) then with methanolic $HClO_4$ (8.8 ml). After 2 h stirring the solution was concentrated to small volume and the yellow product was precipitated by adding Et_2O. It was dissolved in $CHCl_3$, and the solution treated with charcoal then filtered; addition of ether then reprecipitated the solid (Yield 0.51 g, 34.0%).

Preparation of trans-$[NiCl\{C(2\text{-}\overline{py)=NC_6H_4OMe\text{-}p(Zn}Cl_2)\}(PMePh_2)_2]$ *(VI)*

A solution of *trans*-$[NiCl(2\text{-}pyH)(PMePh_2)_2]ClO_4$ (0.67 g, 1 mmol) in 30 ml of CH_2Cl_2 was treated with $CNC_6H_4OMe\text{-}p$ (10 ml of a 0.1 *M* CH_2Cl_2 solution) and then with anhydrous $ZnCl_2$ (0.15 g in 5 ml of MeOH). Deprotonation of the cationic intermediate $[Ni(2\text{-}pyH)(CNC_6H_4OMe\text{-}p)(PMePh_2)_2]^{2+}$ with NEt_3 (10 ml of a 0.1 *M* CH_2Cl_2 solution) gave the labile insertion product $[NiCl\{C(2\text{-}py)=NC_6H_4OMe\text{-}p\}(PMePh_2)_2]$ (see Scheme 2), some of which could be trapped as the more stable $ZnCl_2$ adduct VI. Some 10 min after the addition of NEt_3, the red-brown solution was taken to dryness and the brown residue was washed with H_2O (ca. 50 ml), filtered off, and dried in vacuo. The crude solid was redissolved in CH_2Cl_2, and the solution treated with charcoal then filtered. The clear solution was concentrated to small volume and diluted with Et_2O to precipitate the yellow-brown product VI (0.35 g, 41.5%). This compound proved to be a monomer in 1,2-dichloroethane: molecular weight, found 815, calc 842.1.

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