REACTIVITY OF DI-μ-CHLOROBIS[PENTACHLOROPHENYL-(TRIPHENYLPHOSPHINE)NICKEL(II)] WITH NEUTRAL BASES

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Summary

The action of pyridine, α-, β-, γ-picoline, 2,4-lutidine and PEt_3 on CCl_4 solutions of $[NiCl(C_6Cl_5)(PPh_3)]_2$ gives the new compounds $[NiCl(C_6Cl_5)L(PPh_3)]$. In the case of pyridine only, use of an excess of the base gives the compound $[NiCl(C_6Cl_5)(py)_2]$. The concomitant formation of $[NiCl(C_6Cl_5)(PPh_3)_2]$ in all the reactions, and the formation of $[NiCl(C_6Cl_5)(py)_2]$ suggest that replacement of PPh_3 by L occurs before cleavage of the dinuclear compound. The action of HCl on chloroform solutions of the new compounds indicates a greater stability for those containing only phosphines as ligands.

Introduction

Although extensive studies have been made of the dinuclear compounds of palladium and platinum, $[M_2X_2P_4]$ and their reactions with neutral bases L in which cleavage of the M—halogen bridges occurs with formation of mononuclear species $[MXLP_2]$, the analogous nickel compounds are little known. We describe below a study of the action of pyridine and its methyl derivatives on the dinuclear organometallic compound $[NiCl(C_6Cl_5)(PPh_3)]_2$. The reactions give the first known neutral organometallic compounds of nickel containing monodentate amines, the only analogous compounds previously reported being those containing bidentate amines, such as dipyridyl [1,2] *.

Results and discussion

The compounds $[NiCl(C_6Cl_5)L(PPh_3)]$ were made by adding a stoichiometric amount of the appropiate base L, (L = pyridine (py), α-pic, β-pic, γ-pic (pic = picoline), 2,4-lutidine (lut) and PEt_3) to a CCl_4 solution of $[NiCl(C_6Cl_5)-(PPh_3)]_2$. Addition of an excess of neutral base gives the same compounds, except for pyridine, from which the compound containing two py groups,

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* Added in proof: The preparation of $[Ni(C_6F_5)_2(py)_2]$ has recently been reported [12].

[NiCl(C_6Cl_5)(py)$_2$], is also obtained. In all cases [NiCl(C_6Cl_5)(PPh$_3$)$_2$] and nickel(II) salts are also formed.

The formation of [NiCl(C_5Cl_5)(PPh$_3$)$_2$] and salts of nickel(II), and the production of [NiCl(C_6Cl_5)(py)$_2$] when an excess of pyridine is used cannot be explained in terms of the accepted mechanism for the cleavage of dinuclear complexes, which involves attack of the entering ligand and/or solvent (Scheme 1, mechanism A), and which would lead only to compounds of the type [NiCl(C_6Cl_5)L(PPh$_3$)] [4]. Furthermore, [NiCl(C_6Cl_5)(py)$_2$] cannot result from the subsequent replacement of PPh$_3$ by py in [NiCl(C_6Cl_5)(py)(PPh$_3$)], as such a reaction does not occur in the case of mononuclear complexes under the conditions used. On the other hand, formation of [NiCl(C_6Cl_5)(PPh$_3$)$_2$] and salts of nickel(II) cannot be explained in terms of a solvent participation, because [NiCl(C_6Cl_5)(PPh$_3$)$_2$]$_2$ is fairly stable in CCl$_4$ (no decomposition is observed in 24 h). If the reaction is carried out in acetone, a solvent which itself causes decomposition of the dinuclear compound with formation of [NiCl(C_6Cl_5)(PPh$_3$)$_2$] and salts of nickel(II) better yields of the compounds [NiCl(C_6Cl_5)L(PPh$_3$)], and smaller amounts of [NiCl(C_6Cl_5)(PPh$_3$)$_2$] are observed and it seem that in this case mechanism A is favoured by participation of the solvent.

SCHEME 1
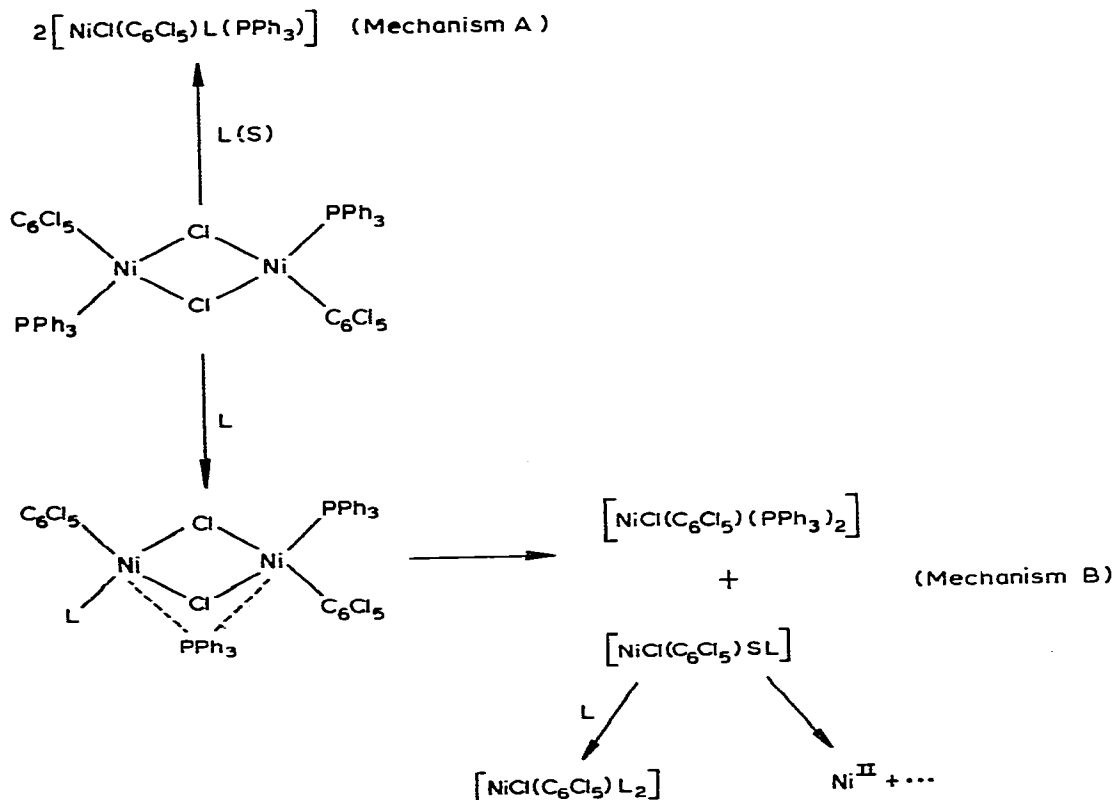
The formation of $[NiCl(C_6Cl_5)(PPh_3)_2]$ leads us to propose an initial replacement of triphenylphosphine by L in the dinuclear species, and an immediate cleavage by PPh_3 (mechanism B). The species formed, $[NiCl(C_6Cl_5)SL]$ (possibly by participation of the solvent) gives nickel(II) salts, and $[NiCl(C_6Cl_5)L_2]$ if the formation of the latter is favoured, as it is in the case of pyridine because of the low solubility of $[NiCl(C_6Cl_5)(py)_2]$ in CCl_4.

The two routes proposed must operate simultaneously, since as replacement of PPh_3 by PEt_3 does not take place in CCl_4, formation of $[NiCl(C_6Cl_5)(PEt_3)-(PPh_3)]$ and the other mixed compounds containing amines can only proceed via mechanism A. If the reaction of the dinuclear complex with an excess of triethylphosphine is carried out in chloroform, a solvent in which replacement of PPh_3 by PEt_3 occurs [5], only $[NiCl(C_6Cl_5)(PEt_3)_2]$ and nickel(II) salts are formed as products, since both $[NiCl(C_6Cl_5)(PEt_3)(PPh_3)]$ formed via mechanism A, and $[NiCl(C_6Cl_5)(PPh_3)_2]$ formed via mechanism B will undergo phosphine exchange.

Characterization

The new solids prepared are soluble in benzene, dichloromethane, chloroform and (except for $[NiCl(C_6Cl_5)(py)_2]$) carbon tetrachloride; but only slightly soluble in acetone and alcohol. They are air-stable as solids and in solution. Analytical data, melting temperatures and molecular weights are given in Table 1. Conductivity measurements in acetone (10^{-4} M) at $18°C$ indicate that they are non-electrolytes (2—4 ohm^{-1} cm^2 mol^{-1}). All of them are diamagnetic, thus indicating a square-planar geometry. The infrared spectra show the bands due to C_6Cl_5 [6], PPh_3 [7], PEt_3 [8], and coordinated amines [9]. Two bands assigned to the ν_{11} vibration of pyridine appear in the spectrum of solid $[NiCl(C_6Cl_5)(py)_2]$, at 770 and 760 cm^{-1}. This seems to agree with a *cis* configuration [9].

Features of the PMR data given in Table 2 are the strong downfield shifts of the methyls of α-pic and that of the *ortho* position in 2,4-lut. The shifts are due to the paramagnetic effect of the central ion, and indicate that the nitrogen-containing ligand rings are perpendicular to the plane of the complex [10]. Analogous shifts are also observed for the *ortho* protons in the coordinated amines; the *meta*- and *para*-protons are more difficult to assign since they appear very near or overlap with the aromatic protons of triphenylphosphine.

The *ortho*-protons of py in $[NiCl(C_6Cl_5)(py)_2]$ appear as a doublet centered at δ 9.1 ppm and J 5 Hz. The magnitude of the splitting is similar to that due to aromatic coupling observed for the free pyridine derivatives [11]. This indicates a *trans* configuration for the compound in solution in contrast with that deduced from IR evidence for the solid state. The product is too insoluble to give a satisfactory IR spectrum in the 700—800 cm^{-1} region.

Passage of hydrogen chloride through the chloroform solutions of the new compounds causes decomposition, except for $[NiCl(C_6Cl_5)(PEt_3)(PPh_3)]$ which is recovered unchanged after 6 h. This is consistent with the greater stability of the pentachlorophenylnickel compounds containing phosphines compared with those containing nitrogen bases [2].

TABLE 1

ANALYTICAL AND PHYSICAL DATA OF THE COMPOUNDS OBTAINED

Compound	Analysis (Found (calcd.) (%))				Decomposition temperature (°C)	Molecular weight (g/mol)
	C	H	N	Cl		
[NiCl(C$_6$Cl$_5$)(Py)$_2$]	38.2 (38.30)	1.9 (1.97)	5.4 (5.58)	41.5 (42.40)	210–212	505 (501.6)
[NiCl(C$_6$Cl$_5$)(py)(PPh$_3$)]	51.4 (50.92)	2.8 (2.94)	2.0 (2.04)	30.2 (31.05)	217–220	680 (684.8)
[NiCl(C$_6$Cl$_5$)(α-pic)(PPh$_3$)]	49.6 (51.48)	3.3 (3.10)	2.2 (2.10)	29.3 (30.51)	178–181	670 (698.9)
[NiCl(C$_6$Cl$_5$)(β-pic)(PPh$_3$)]	49.5 (51.48)	3.3 (3.10)	2.2 (2.10)	30.1 (30.51)	208–210	687 (698.9)
[NiCl(C$_6$Cl$_5$)(γ-pic)(PPh$_3$)]	49.7 (51.84)	3.3 (3.10)	1.8 (2.10)	30.2 (30.51)	212–214	690 (698.9)
[NiCl(C$_6$Cl$_5$)(2,4-lut)(PPh$_3$)]	52.1 (53.18)	3.4 (3.36)	1.8 (1.96)	28.8 (29.03)	175–177	700 (712.9)
[NiCl(C$_6$Cl$_5$)(PEt$_3$)(PPh$_3$)]	48.2 (49.78)	4.1 (4.14)		28.9 (29.42)	165–168	748 (723.6)

TABLE 2

PMR SPECTRA (δ, ppm)

Compounds	Nitrogen-containing ligand			
	Methyl	H-*ortho*	H-*meta*	H-*para*
[NiCl(C_6Cl_5)(py)$_2$]		9.05—9.15	7.15	7.5
[NiCl(C_6Cl_5)(py)(PPh$_3$)]		9.15		
[NiCl(C_6Cl_5)(α-pic)(PPh$_3$)]	3.75	9.3		
[NiCl(C_6Cl_5)(β-pic)(PPh$_3$)]	2.25	9.2		
[NiCl(C_6Cl_5)(γ-pic)(PPh$_3$)]	2.25	9.1—9.2		
[NiCl(C_6Cl_5)(2,4-lut)(PPh$_3$)]	3.55 o- 2.25 p-			
	Free ligand			
pyridine		8.5	7.06	7.46
α-picoline	2.55	8.5	7.1	7.45
β-picoline	2.32	8.42	7.15	7.4
γ-picoline	2.37	8.33	6.9	
2,4-lutidine	2.48 o- 2.22 p-	8.45	6.93	

Experimental

[NiCl(C_6Cl_5)(PPh$_3$)$_2$] and [NiCl(C_6Cl_5)(PPh$_3$)]$_2$ were prepared according to published methods [3]. Infrared spectra were recorded on a Beckman IR-20A spectrophotometer. PMR spectra were obtained on a Perkin—Elmer R12 spectrometer in CDCl$_3$ solutions, TMS was used as reference. Molecular weights were determined with benzene solutions at 60°C on a Knauer osmometer. Elemental analyses were carried out at the "Instituto de Química Organica de Catalunya".

Preparation of [NiCl(C_6Cl_5)(py)$_2$]

A large excess of pyridine (3 ml) was added to a solution of [NiCl(C_6Cl_5)-(PPh$_3$)]$_2$ (0.5 g, 0.4 mmol) in CCl$_4$ (25 ml). The initially red solution rapidly became orange. It was cooled to —10°C and the [NiCl(C_6Cl_5)(py)$_2$] which precipitated was filtered off. On concentration of the resulting solution [NiCl(C_6Cl_5)(py)(PPh$_3$)] and [NiCl(C_6Cl_5)(PPh$_3$)$_2$] separated out.

Preparation of [NiCl(C_6Cl_5)L(PPh$_3$)] L = py, α-pic, β-pic, γ-pic, 2,4-lut and PEt$_3$

The stoichiometric amount of L (0.8 mmol) was added to a solution of [NiCl(C_6Cl_5)(PPh$_3$)]$_2$ (0.5 g, 0.4 mmol) in CCl$_4$ (25 ml). The initially red solution immediately changed to yellow. After concentrating, [NiCl(C_6Cl_5)L-(PPh$_3$)] was precipitated with alcohol (or acetone when L = PEt$_3$). The products were recrystallized from dichloromethane/ethanol. Yields were about 40%.

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