

Pentachlorophenyl Nickel(II) Complexes With Aromatic Amines

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Addition of an excess of NaClO_4 to benzene solutions of $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ in the presence of an excess of pyridine, β -picoline, γ -picoline, or 3,5-lutidine, leads to $[\text{Ni}(\text{C}_6\text{Cl}_5)_3]\text{ClO}_4$. The formation of the new ionic organometallic compounds depends on its insolubility; thus, the reaction in acetone leads to $[\text{Ni}(\text{C}_6\text{Cl}_5)_2\text{py}_2(\text{PPh}_3)]\text{ClO}_4$, insoluble in that solvent.

The action of potassium salts (KX) or phosphines (PR_3) on the ionic compounds gives $[\text{NiX}(\text{C}_6\text{Cl}_5)_2\text{L}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{NO}_2, \text{C}_6\text{Cl}_5\text{O}$ and NCS), and $[\text{Ni}(\text{C}_6\text{Cl}_5)_2\text{py}(\text{PR}_3)_2]\text{ClO}_4$ [$\text{R} = \text{Ph}$ and Et] respectively. By partial or total replacement of amines by phosphines in $[\text{NiX}(\text{C}_6\text{Cl}_5)_2\text{py}_2]$, the complexes $[\text{NiCl}(\text{C}_6\text{Cl}_5)_2\text{py}(\text{PET}_3)]$ and $[\text{Ni}(\text{NO}_2)(\text{C}_6\text{Cl}_5)_2(\text{PPh}_3)_2]$ have been obtained. $[\text{Ni}(\text{NCS})(\text{C}_6\text{Cl}_5)_2\text{py}(\text{PPh}_3)]$ is prepared from $[\text{Ni}(\text{C}_6\text{Cl}_5)_2\text{py}_2(\text{PPh}_3)]\text{ClO}_4$ and excess KNCS .

Introduction

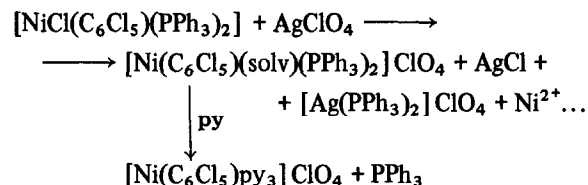
A number of organonickel compounds containing tertiary phosphines and bulky organic groups as C_6Cl_5 have been reported [1]. With monodentate amines as stabilizing ligands, only $[\text{Ni}(\text{C}_6\text{F}_5)_2\text{py}_2]$ obtained from $[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{dioxane})_2]$ [2], and $[\text{NiCl}(\text{C}_6\text{Cl}_5)_2\text{py}_2]$ formed on treating the dinuclear species $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)]_2$ with an excess of pyridine [3] have been described. In contrast, the number of ionic organonickel compounds of the type $[\text{Ni}(\text{C}_6\text{Cl}_5)_2\text{L}(\text{PR}_3)_2]\text{ClO}_4$ ($\text{L} = \text{amine}$), obtained from $[\text{NiCl}(\text{C}_6\text{Cl}_5)_2(\text{PR}_3)_2]$, AgClO_4 and the appropriate amine, is fairly large, PET_3 [1], dpe [4], PPhMe_2 [5].

The action of $\text{C}_6\text{Cl}_5\text{MgCl}$ on $[\text{NiCl}_2\text{Py}_2]$ does not lead to any organonickel compound, nor is substitution of pyridine with phosphines achieved [3]. We describe the action of alkali metal salts (KX) on $[\text{Ni}(\text{C}_6\text{Cl}_5)_3]\text{ClO}_4$ as a preparative method to obtain $[\text{NiX}(\text{C}_6\text{Cl}_5)_2\text{L}_2]$ ($\text{L} = \text{amine}$) complexes.

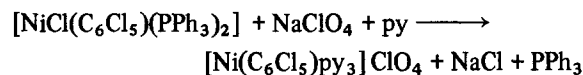
Results and Discussion

Addition of the stoichiometric amount of AgClO_4 to benzene solution of $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ gives a

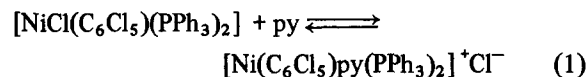
white precipitate of AgCl , $[\text{Ag}(\text{PPh}_3)_2]\text{ClO}_4$, and, on concentrating the solution, a fraction of the starting $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ is recovered. On heating, only $[\text{Ag}(\text{PPh}_3)_2]\text{ClO}_4$ and nickel salts are recovered. In no case $[\text{Ni}(\text{ClO}_4)(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ is isolated. After filtration of the white solid formed, addition of ligands like pyridine leads to $[\text{Ni}(\text{C}_6\text{Cl}_5)_2\text{py}_3]\text{ClO}_4$ with a 40% yield. The exchange triphenylphosphine/pyridine is supposed to take place *via* an ionic compound of the type $[\text{Ni}(\text{C}_6\text{Cl}_5)(\text{solv})(\text{PPh}_3)_2]\text{ClO}_4$, since the neutral organonickel compounds do not undergo replacement of phosphines by amines [3].



NaClO_4 has been used in similar reactions such as in the preparation of $[\text{PtArL}(\text{PET}_3)_2]\text{ClO}_4$ from *cis*- $[\text{PtClAr}(\text{PET}_3)_2]$, NaClO_4 and L [6]. Thus the reaction was examined for the present case; addition of excess pyridine and NaClO_4 to a benzene solution of $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ (1.4 g/100 ml) gives a yellow suspension, and after 6 h, $[\text{Ni}(\text{C}_6\text{Cl}_5)_2\text{py}_3]\text{ClO}_4$ (III) can be filtered with a 90% yield.

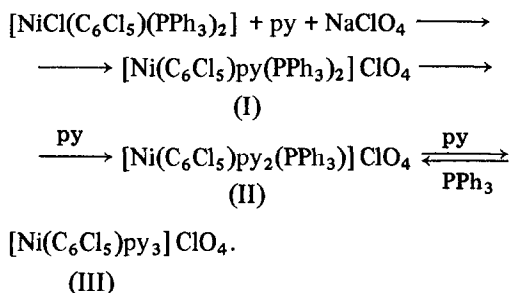


The starting neutral organometallic compound is recovered in the absence of pyridine, indicating that pyridine favours the departure of Cl and that the overall result depends on the formation of insoluble species, which are formed in the presence of bulky anions as ClO_4^- ,



In acetone the reaction gives $[\text{Ni}(\text{C}_6\text{Cl}_5)_2\text{py}_2(\text{PPh}_3)]\text{ClO}_4$ (II), insoluble in this solvent; if the benzene solutions of $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ are treated with

pyridine in a 1:2 molar ratio, (II) is also formed. With a 1:1 molar ratio, in benzene, the equilibrium (1) is not sufficiently shifted, and (I) does not precipitate; on increasing the concentration of py, (I) or (II) precipitates. In acetone (molar ratio 1:1) the equilibrium (1) is significantly shifted – an increase in the conductivity is observed on adding pyridine to the solution of $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ – but (I) does not precipitate probably because it is soluble in this solvent, similarly to $[\text{Ni}(\text{C}_6\text{Cl}_5)\text{py}(\text{PR}_3)_2]\text{ClO}_4$, $\text{PR}_3 = \text{PEt}_3$, 1/2 dpe [1, 4]. The process probably involves the following steps:



The product which separates depends on the relative concentration of py and PPh_3 , and on its solubility in the solvent used. Thus, if the benzene solutions of $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ are more concentrated (2 g/100 ml), on adding NaClO_4 and pyridine, (II) is obtained; in this case the excess of the free PPh_3 prevents the formation of (III). Analogously, addition of $\text{L} = \beta\text{-pic}$, $\gamma\text{-pic}$ or 3,5-lut and NaClO_4 to the benzene solutions of $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ leads to $[\text{Ni}(\text{C}_6\text{Cl}_5)\text{L}_3]\text{ClO}_4$, (the compound with 3,5-lut had already been reported [5]). On the other hand, when $\text{L} = \alpha\text{-pic}$, 2,4-lut or 2,4,6-colidine, $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ is recovered even when the mixture is refluxed for 24 h. This may be due to the presence of the C_6Cl_5 group with two bulky substituents in the *ortho* position, which prevents the entrance of amines having also *ortho* substituents.

Formation of $[\text{NiX}(\text{C}_6\text{Cl}_5)\text{L}_2]$

The action of potassium salts on the acetone solutions of $[\text{Ni}(\text{C}_6\text{Cl}_5)\text{L}_3]\text{ClO}_4$, leads to the neutral compounds $[\text{NiX}(\text{C}_6\text{Cl}_5)\text{L}_2]$. The reaction is fast for $\text{L} = \text{py}$, but slow for the other amines, and CCl_4 must be added to increase the refluxing temperature, in agreement with the greater basicity of these amines. The reaction applies to anions with different size and electronic characteristics such as, Cl, Br, NCS, NO_2 , $\text{C}_6\text{Cl}_5\text{O}$. The compounds prepared are listed in Table I.

Reactivity

The action of phosphines on the solution of neutral and ionic compounds containing pyridine has been examined, in order to compare the relative stability of the Ni–N and Ni–P bonds.

Addition of phosphines to $[\text{Ni}(\text{C}_6\text{Cl}_5)\text{py}_3]\text{ClO}_4$

The action of an excess of PPh_3 on the acetone solution of (III) leads to substitution of only one pyridine group, and compound (II) is obtained; with the more basic and less bulky PEt_3 , and on using a 1:1 molar ratio or an excess, $[\text{Ni}(\text{C}_6\text{Cl}_5)\text{py}_2(\text{PEt}_3)]\text{ClO}_4$ or $[\text{Ni}(\text{C}_6\text{Cl}_5)\text{py}(\text{PEt}_3)_2]\text{ClO}_4$ are formed respectively.

Addition of phosphines to the neutral compounds $[\text{NiX}(\text{C}_6\text{Cl}_5)\text{py}_2]$

The action of the stoichiometric amount of phosphines (PEt_3 or PPh_3) on the dichloromethane solutions of $[\text{NiX}(\text{C}_6\text{Cl}_5)\text{py}_2]$ leads to compounds with one amine and one phosphine, $[\text{NiX}(\text{C}_6\text{Cl}_5)\text{py}(\text{PR}_3)]$. An excess of both phosphines gives $[\text{NiX}(\text{C}_6\text{Cl}_5)(\text{PR}_3)_2]$; this substitution leads to $[\text{Ni}(\text{NO}_2)(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$, a product which cannot be prepared by metathesis of $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ with KNO_2 or AgNO_2 [7]. $[\text{NiX}(\text{C}_6\text{Cl}_5)\text{py}(\text{PPh}_3)]$ ($\text{X} = \text{Cl}$, NCS) may also been obtained from $[\text{Ni}(\text{C}_6\text{Cl}_5)\text{py}(\text{PPh}_3)_2]\text{ClO}_4$ and the appropriate potassium salt.

Action of hydrogen chloride

Passage of hydrogen chloride through the chloroform solutions of these compounds causes decomposition with formation of $\text{C}_6\text{Cl}_5\text{H}$ and nickel salts, except for $[\text{Ni}(\text{NO}_2)(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$, in accordance with the greater stability of pentachlorophenylnickel complexes containing phosphines as stabilizing ligands [3].

Characterization

The new compounds are yellow or red, air-stable solids; the neutral species $[\text{NiX}(\text{C}_6\text{Cl}_5)\text{L}_2]$, decompose slowly in solution. Analytical data and decomposition temperatures are given in Table I. The neutral species are soluble in chloroform, dichloromethane, sparingly soluble in benzene, acetone, carbon tetrachloride, and insoluble in alkanes and alcohols. The ionic compounds are generally less soluble, usually only in dichloromethane and acetone; as a rule solubility increases in the order, $\text{py} > \beta\text{-pic} \sim \gamma\text{-pic} > 3,5\text{-lut}$. Molar conductivities in acetone, at 18 °C and concentration 10^{-4} M are $2\text{--}3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for the neutral compounds and $140\text{--}150 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for the ionic compounds. All of them are diamagnetic and therefore square-planar. The infrared spectra show bands due to C_6Cl_5 [8], PPh_3 [9], PEt_3 [10], and coordinated amines [11]. Bands due to the ClO_4 anion (T_d) are observed in the ionic compounds at $1100 (\nu_3)$ and $620 (\nu_4) \text{ cm}^{-1}$. *Cis-trans* configuration assignment was precluded due to the low solubility in the non polar solvents used to determine dipolar moments; nor has it been possible to do it by PMR spectroscopy (60 MHz), since even

TABLE I. Analytical Data [Found (Calcd.)%] and Melting Point (°C).

Compound	Analysis				
	C	H	Total halogen	N	M.P. °C
[Ni(C ₆ Cl ₅)py ₃]ClO ₄	38.9 (39.13)	2.3 (2.34)	33.1 (32.99)	6.4 (6.52)	250
[Ni(C ₆ Cl ₅)(β-pic) ₃]ClO ₄	42.0 (41.97)	3.0 (3.08)	30.8 (30.97)	5.8 (6.12)	230–5
[Ni(C ₆ Cl ₅)(γ-pic) ₃]ClO ₄	43.0 (41.97)	3.3 (3.08)	30.6 (30.97)	6.2 (6.12)	145–50
[Ni(C ₆ Cl ₅)py ₂ (PPh ₃)]ClO ₄	50.5 (49.32)	3.2 (3.04)	25.4 (25.69)	3.1 (3.38)	196 (d)
[Ni(C ₆ Cl ₅)py ₂ (PEt ₃)]ClO ₄	38.7 (38.64)	3.6 (3.68)	30.9 (31.06)	4.1 (4.09)	203–6
[NiCl(C ₆ Cl ₅)(β-pic) ₂]	40.8 (40.81)	2.5 (2.66)	39.9 (40.15)	5.2 (5.29)	225–30
[NiCl(C ₆ Cl ₅)(γ-pic) ₂]	39.8 (40.81)	2.6 (2.66)	40.1 (40.15)	5.0 (5.29)	250–1
[NiBr(C ₆ Cl ₅)py ₂]	35.1 (35.18)	1.8 (1.84)	46.7 (47.08)	4.9 (5.12)	250 (d)
[Ni(NCS)(C ₆ Cl ₅)py ₂]	38.7 (38.94)	1.9 (1.92)	33.5 (33.80)	8.01 (8.00)	185 (d)
[Ni(C ₆ Cl ₅ O)(C ₆ Cl ₅)py ₂]	36.0 (36.10)	1.3 (1.37)	47.4 (48.38)	3.8 (3.83)	247–9 (d)
[Ni(NO ₂)(C ₆ Cl ₅)py ₂]	38.2 (37.51)	2.0 (1.96)	34.2 (34.6)	8.2 (8.20)	200–5 (d)
[Ni(NCS)(C ₆ Cl ₅)(β-pic) ₂]	41.2 (41.31)	2.6 (2.55)	31.9 (32.09)	7.6 (7.60)	179–81 (d)
[Ni(C ₆ Cl ₅ O)(C ₆ Cl ₅)(β-pic) ₂]	37.8 (37.94)	1.7 (1.59)	46.6 (46.69)	3.6 (3.68)	216–19 (d)
[Ni(NCS)(C ₆ Cl ₅)(γ-pic) ₂]	41.2 (41.31)	2.6 (2.55)	32.3 (32.09)	7.6 (7.60)	220 (d)
[Ni(C ₆ Cl ₅ O)(C ₆ Cl ₅)(γ-pic) ₂]	37.7 (37.94)	1.7 (1.59)	46.7 (46.69)	3.6 (3.68)	235–6 (d)
[Ni(NCS)(C ₆ Cl ₅)(3,5-lut) ₂]	44.0 (43.46)	3.2 (3.12)	30.2 (30.54)	7.2 (7.24)	197–99 (d)
[Ni(C ₆ Cl ₅ O)(C ₆ Cl ₅)(3,5-lut) ₂]	39.6 (39.65)	2.1 (2.30)	45.0 (45.02)	3.5 (3.55)	249–51 (d)
NiCl(C ₆ Cl ₅)py(PEt ₃)	37.0 (37.76)	3.7 (3.72)	38.8 (39.33)	2.5 (2.59)	167–8
[Ni(NCS)(C ₆ Cl ₅)py(PPh ₃)]	49.8 (50.93)	2.7 (2.85)	25.0 (25.02)	3.5 (3.96)	227–30 (d)
[Ni(NO ₂)(C ₆ Cl ₅)(PPh ₃) ₂]	57.3 (57.41)	3.3 (3.44)	20.0 (20.17)	1.3 (1.59)	124–28 (d)

with $[\text{Ni}(\text{C}_6\text{Cl}_5)_3]\text{ClO}_4$ only one signal is observed for the methyl protons of the picolines.

Experimental

$[\text{Ni}(\text{C}_6\text{Cl}_5)_3]\text{ClO}_4$, $L = \text{py}$, $\beta\text{-pic}$, $\gamma\text{-pic}$, $3,5\text{-lut}$

An excess of NaClO_4 (1 g) and 2 ml of L were added to $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ (2.59 g), prepared from $[\text{NiCl}_2(\text{PPh}_3)_2]$ and $\text{C}_6\text{Cl}_5\text{MgCl}$ [7], in benzene (175 ml). The mixture was stirred at room temperature for 6 h (12 h for $L = 3,5\text{-lut}$). The precipitate was filtered, washed with benzene and water and recrystallized from acetone-dichloromethane. Yield about 90%.

$[\text{NiX}(\text{C}_6\text{Cl}_5)_2]\text{ClO}_4$, $L = \text{py}$; $X = \text{Cl}$, Br , NCS , $\text{C}_6\text{Cl}_5\text{O}$, NO_2 . $L = \beta\text{-pic}$, $\gamma\text{-pic}$; $X = \text{Cl}$, NCS , $\text{C}_6\text{Cl}_5\text{O}$. $L = 3,5\text{-lut}$; $X = \text{NCS}$, $\text{C}_6\text{Cl}_5\text{O}$

The procedure is general for all of them, only differing in some cases in the solvent used and in the appropriate conditions for the precipitation. As a typical case, $[\text{NiBr}(\text{C}_6\text{Cl}_5)_2]\text{ClO}_4$ was obtained by adding an excess of KBr (0.5 g) to $[\text{Ni}(\text{C}_5\text{Cl}_5)_3]\text{ClO}_4$ (0.5 mmol) in acetone (40 ml). The yellow solution was stirred for 6 h, the red precipitate filtered, washed with water and recrystallized from dichloromethane-methanol. Yield about 80%.

A mixture of acetone and carbon tetrachloride must be used in the preparation of the compounds with $L = \beta\text{-pic}$, $\gamma\text{-pic}$ or $3,5\text{-lut}$; precipitation is assisted by concentration and cooling.

$[\text{Ni}(\text{C}_6\text{Cl}_5)_2\text{py}_2(\text{PR}_3)]\text{ClO}_4$

An excess of PPh_3 , or the stoichiometric amount of PEt_3 was added under nitrogen to a solution of $[\text{Ni}(\text{C}_6\text{Cl}_5)_3]\text{ClO}_4$ (0.64 g, 1 mmol) in acetone (60 ml). After stirring at room temperature for 2 h, concentrating and adding ethanol, the solution was cooled. The precipitate was filtered, washed with ethanol and recrystallized from dichloromethane. Yield about 70%.

$[\text{NiCl}(\text{C}_6\text{Cl}_5)_2\text{py}(\text{PEt}_3)]$

PEt_3 (0.5 mmol) was added, under nitrogen, to a solution of $[\text{NiCl}(\text{C}_6\text{Cl}_5)_3]$ (0.5 mmol) in dichloromethane (30 ml). The solution was stirred at room temperature for 1 h, treated with a small amount of methanol and concentrated. The precipi-

tate was filtered, washed with ethanol and recrystallized from dichloromethane-methanol. Yield about 70%.

$[\text{Ni}(\text{NCS})(\text{C}_6\text{Cl}_5)_2\text{py}(\text{PPh}_3)]$

A small excess of KNCS (0.6 g) was added to a solution of $[\text{Ni}(\text{C}_6\text{Cl}_5)_2\text{py}_2(\text{PPh}_3)]\text{ClO}_4$ (0.41 g) in 80 ml of dichloromethane, and the mixture stirred at room temperature for 6 h. The filtered solution was treated with methanol and concentrated. The dark yellow precipitate was filtered, washed with water and methanol, and recrystallized from dichloromethane-methanol. Yield about 60%.

$[\text{Ni}(\text{NO}_2)(\text{C}_6\text{Cl}_5)_2(\text{PPh}_3)_2]$

An excess of PPh_3 (1.7 g) was added to $[\text{Ni}(\text{NO}_2)(\text{C}_6\text{Cl}_5)_2\text{py}_2]$ (0.5 mmol) in dichloromethane (40 ml). The resulting solution was stirred at room temperature for 6 h, concentrated, treated with several ml of ethanol and cooled. The yellow precipitate was filtered and recrystallized from chloroform. Yield about 60%.

Analyses

C, H, and N determinations were carried out at the Institute of Bio-Organic Chemistry of Catalunya. Halogens were determined by Schöninger's method. Infrared spectra were recorded on a Beckman IR-20 A spectrophotometer. Samples were prepared as KBr disks or Nujol mulls.

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