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PHOSPHINE COMPLEXES OF POLYCHLOROPHENYLNICKEL(II)

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Summary

The reaction of the Grignard reagents obtained from the isomers of tetrachlorobenzene and 1,3,5-trichlorobenzene, with compounds of the formula $[NiCl_2L_2]$ leads to the new stable complexes: $[NiCl(2,3,4,5\text{-}C_6HCl_4)L_2]$, $[NiCl(2,3,4,6\text{-}C_6HCl_4)L_2]$, $[NiCl(2,3,5,6\text{-}C_6HCl_4)L_2]$, $[NiCl(2,3,6\text{-}C_6H_2Cl_3)L_2]$ and $[NiCl(2,4,6\text{-}C_6H_2Cl_3)L_2]$ ($L_2 = 2\ PPh_3$ or dpe). The nature of the products indicates that in some cases the initial formation of the expected Grignard reagent is followed by a metalation involving replacement of a hydrogen atom.

The spectra of the new complexes, and their reactions with silver salts, alkali metal salts and hydrogen chloride are discussed.

Introduction

Various explanations have been put forward to account for the unusual stability of the σ(M—C) bond in organometallic compounds of transition elements containing the C_6Cl_5 group; of these (a) the presence of bulky substituents *ortho* to the M—C bond [1], and (b) the high electronegativity of the C_6Cl_5 group [2] are the most plausible.

In continuation of our studies on these effects [3], we now describe new derivatives of nickel(II) obtained from the three isomers of tetrachlorobenzene and from 1,3,5-trichlorobenzene. The products are stabilized by the *ortho*-effects of two chlorine atoms [1]. From the isomer $1,2,3,4\text{-}C_6H_2Cl_4$, stable organometallic complexes with one chlorine atom in *ortho* position are also obtained.

Results and discussion

Preparation and properties

We began the study from $1,3,5\text{-}C_6H_3Cl_3$ assuming that the formation and

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further reaction of the Grignard reagent would lead to compounds with the hydrogen atoms *ortho* with respect to the σ(M—C) bond. However, we have observed that the action of the Grignard reagent solutions obtained from 1,3,5-$C_6H_3Cl_3$, Mg and I_2 as initiator, in THF, on $[NiCl_2L_2]$ (where L_2 = 2 PPh_3 or dpe) leads to the formation of $[NiCl(2,4,6\text{-}C_6H_2Cl_3)L_2]$ (eq. 1).

$$1,3,5\text{-}C_6H_3Cl_3 \xrightarrow[(2)\ [NiCl_2L_2]]{(1)\ Mg} [NiCl(2,4,6\text{-}C_6H_2Cl_3)L_2] \quad (1)$$

The nature of the products indicates that initial formation of the Grignard reagent is followed by a metalation involving replacement of hydrogen (eq. 2 and 3).

$$1,3,5\text{-}C_6H_3Cl_3 + Mg \rightarrow \underset{(I)}{3,5\text{-}C_6H_3Cl_2MgCl} \quad (2)$$

$$3,5\text{-}C_6H_3Cl_2MgCl + 1,3,5\text{-}C_6H_3Cl_3 \rightarrow 2,4,6\text{-}C_6H_2Cl_3MgCl + 1,3\text{-}C_6H_4Cl_2 \quad (3)$$

The formation of $[NiCl(2,4,6\text{-}C_6H_2Cl_3)L_2]$ would be favoured on adding a solution of the mixture of Grignard reagent to $[NiCl_2L_2]$, because of the two possible isomeric products it is the one stabilized by the *ortho* effect.

The reaction of $C_6H_5CH_2MgCl$ or n-BuLi with 1,3,5-$C_6H_3Cl_3$ followed by coupling with $[NiCl_2L_2]$ leads to $[NiCl(2,4,6\text{-}C_6H_2Cl_3)L_2]$ confirming that 1,3,5-$C_6H_3Cl_3$ does readily undergo metalation involving replacement of hydrogen.

The presence of I in the Grignard solution is shown by the formation of 3,5-dichlorobenzoic acid by carbonation. The use of C_2H_5Br as initiator leads to identical results to those obtained with I_2. The possible participation of benzynes is ruled out by the fact that action of the Grignard reagents on $[NiBr_2L_2]$ leads to $[NiBr(2,4,6\text{-}C_6H_2Cl_3)L_2]$ rather than to the compound with one bromine atom in the benzene ring.

Similar results are obtained with tetra- and penta-chlorophenyl derivatives; thus the action of the Grignard reagent solutions obtained from 1,2,3,5- or 1,2,4,5-$C_6H_2Cl_4$, on $[NiCl_2L_2]$ leads to the formation of $[NiCl(2,3,4,6\text{-}C_6HCl_4)L_2]$ and $[NiCl(2,3,5,6\text{-}C_6HCl_4)L_2]$, respectively. The same compounds are obtained by using Grignard reagent solutions prepared from 1,2,3,5- or 1,2,4,5-$C_6H_2Cl_4$ and $C_6H_5CH_2MgCl$, with $[NiCl_2L_2]$. The processes occurring may be represented by the general equations 4, 5, and 6.

$$C_6H_{6-n}Cl_n \rightarrow C_6H_{6-n}Cl_{n-1}MgCl \quad (4)$$

$$C_6H_{6-n}Cl_{n-1}MgCl + C_6H_{6-n}Cl_n \rightarrow C_6H_{5-n}Cl_nMgCl + C_6H_{6-n-1}Cl_{n-1} \quad (5)$$

$$C_6H_{6-n}Cl_n + C_6H_5CH_2MgCl \rightarrow C_6H_{5-n}Cl_nMgCl + C_6H_5CH_3 \quad (6)$$

In contrast the Grignard solutions obtained from 1,2,3,4-$C_6H_2Cl_4$ and Mg, with I_2 or C_2H_5MgBr as initiator, on $[NiCl_2L_2]$ gives an organonickel compound with a trichlorinated ligand, i.e. $[NiCl(2,3,6\text{-}C_6H_2Cl_3)L_2]$. In this case the Grignard reagent formed according to eq. 4 leads directly to an organometallic compound stabilized by the presence of two chlorine atoms in *ortho* position, and reaction 5 will be less favoured than in the other two tetrachlorobenzenes because of the lower acidity of hydrogen atoms with only one neighbouring chlorine atom. However, when the solution of the Grignard reagent correspond-

TABLE 1

ANALYTICAL DATA FOR [$NiClRL_2$] COMPOUNDS

Compound	Found (calcd.) (%)				Decomposition temperature (°C)
	C	H	Cl	Ni	
[$NiCl(2,3,4,5\text{-}C_6HCl_4)(PPh_3)_2$]	60.6 (60.51)	3.9 (3.75)	21.5 (21.26)	6.9 (7.04)	187—190
[$NiCl(2,3,4,6\text{-}C_6HCl_4)(PPh_3)_2$]	60.6 (60.51)	3.7 (3.75)	21.2 (21.26)	7.1 (7.04)	231—233
[$NiCl(2,3,5,6\text{-}C_6HCl_4)(PPh_3)_2$]	60.8 (60.51)	3.8 (3.75)	21.2 (21.26)	6.9 (7.04)	231—233
[$NiCl(2,3,6\text{-}C_6H_2Cl_3)(PPh_3)_2$]	63.0 (63.12)	4.0 (4.03)	17.9 (17.74)	7.3 (7.35)	224—226
[$NiCl(2,4,6\text{-}C_6H_2Cl_3)(PPh_3)_2$]	62.8 (63.12)	4.0 (4.03)	17.8 (17.74)	7.3 (7.35)	226—229
[$NiCl(2,3,4,5\text{-}C_6HCl_4)(dpe)$]	54.2 (54.33)	3.5 (3.56)	25.2 (25.05)	8.3 (8.30)	180—183
[$NiCl(2,3,4,6\text{-}C_6HCl_4)(dpe)$]	54.6 (54.33)	3.8 (3.56)	25.0 (25.05)	8.2 (8.30)	209—212
[$NiCl(2,3,5,6\text{-}C_6HCl_4)(dpe)$]	54.4 (54.33)	3.7 (3.56)	24.9 (25.05)	8.2 (8.30)	230—232
[$NiCl(2,3,6\text{-}C_6H_2Cl_3)(dpe)$]	57.3 (57.11)	4.0 (3.90)	21.2 (21.07)	8.7 (8.72)	221—224
[$NiCl(2,4,6\text{-}C_6H_2Cl_3)(dpe)$]	57.0 (57.11)	4.1 (3.90)	21.2 (21.07)	8.8 (8.72)	237—240

ing to 1,2,3,4-$C_6H_2Cl_4$ is prepared according to eq. 6 then [$NiCl(2,3,4,5\text{-}C_6HCl_4)L_2$] is obtained.

The σ(M—C) bond in the last compound has only one chlorine atom in *ortho* position, and this leads to lower thermal stability and a higher reactivity (see below).

The reaction with pentachlorobenzene can also be interpreted similarly; mixtures of [$NiCl(2,3,5,6\text{-}C_6HCl_4)L_2$] and [$NiCl(C_6Cl_5)L_2$] are obtained. The solution obtained from $C_6H_5CH_2MgCl$ and pentachlorobenzene gives only [$NiCl(C_6Cl_5)L_2$] eq. 6.

The elemental analyses for all new compounds are given in Table 1 along with the decomposition temperatures. The compounds are air-stable, soluble in benzene, chloroform and acetone, and slightly soluble in ethanol, ether and hexane. Molar conductivities in acetone correspond to non-electrolytic compounds. The compounds are diamagnetic, and thus square-planar.

Chemical reactivity

The results of the action of gaseous HCl and Cl_2 on chloroform solutions of the new compounds are indicated in Table 3. The results for the HCl reaction show that the ease of cleavage of the σ(M—C) bond depends on the number of chlorine atoms present in the polychlorophenyl ring upon whether one or two chlorine atoms are present *ortho* to the carbon atom attached to metal. The *trans* effect of the phosphine group is also apparent in the compounds containing dpe.

Thus: (a) The higher lability of the complexes of the types [$NiCl(2,4,6\text{-}C_6H_2$-

TABLE 2

ANALYTICAL DATA FOR $[NiX(2,4,6\text{-}C_6H_2Cl_3)L_2]$ AND $[Ni\text{-}\gamma\text{-}pic(2,4,6\text{-}C_6H_2Cl_3)L_2]ClO_4$ COMPOUNDS

Compound	Found (calcd.) (%)					Decomposition temperature (°C)
	C	H	Halogen	N	Ni	
$[NiBr(2,4,6\text{-}C_6H_2Cl_3)(PPh_3)_2]$	59,8 (59,79)	3,8 (3,82)	17,0 (16,81)		6,9 (6,96)	209–211
$[NiI(2,4,6\text{-}C_6H_2Cl_3)(PPh_3)_2]$	57,3 (56,64)	3,8 (3,62)	16,0 (15,92)		6,4 (6,59)	200–201
$[NiNCS(2,4,6\text{-}C_6H_2Cl_3)(PPh_3)_2]$	62,6 (62,84)	4,2 (3,92)	12,8 (12,94)	1,7 (1,70)	7,1 (7,14)	182–185
$[NiNCO(2,4,6\text{-}C_6H_2Cl_3)(PPh_3)_2]$	64,3 (64,10)	4,0 (4,00)	13,2 (13,20)	1,7 (1,74)	7,2 (7,28)	228–230
$[NiN_3(2,4,6\text{-}C_6H_2Cl_3)(PPh_3)_2]$	62,5 (62,61)	4,0 (4,00)	13,3 (13,20)	5,2 (5,21)	7,2 (7,28)	180–184
$[NiBr(2,4,6\text{-}C_6H_2Cl_3)(dpe)]$	54,3 (53,57)	3,7 (3,65)	19,7 (19,76)		8,1 (8,18)	231–234
$[NiI(2,4,6\text{-}C_6H_2Cl_3)(dpe)]$	50,6 (50,28)	3,4 (3,43)	18,9 (18,55)		7,6 (7,68)	227–230
$[NiNCS(2,4,6\text{-}C_6H_2Cl_3)(dpe)]$	57,2 (56,98)	3,7 (3,77)	15,1 (15,29)	2,2 (2,01)	8,3 (8,44)	202–204
$[NiNCO(2,4,6\text{-}C_6H_2Cl_3)(dpe)]$	58,4 (58,33)	3,8 (3,83)	15,5 (15,65)	2,0 (2,06)	8,5 (8,64)	207–210
$[NiN_3(2,4,6\text{-}C_6H_2Cl_3)(dpe)]$	56,4 (56,56)	3,9 (3,86)	15,8 (15,65)	6,0 (6,18)	8,5 (8,64)	200–202
$[NiNO_2(2,4,6\text{-}C_6H_2Cl_3)(dpe)]$	56,4 (56,23)	3,8 (3,83)	15,5 (15,56)	1,8 (2,05)	8,4 (8,59)	197–200
$[Ni\text{-}\gamma\text{-}pic(2,4,6\text{-}C_6H_2Cl_3)(dpe)]ClO_4$	53,5 (54,98)	4,2 (4,01)	17,0 (17,08)	1,8 (1,69)	7,0 (7,07)	147–150

$Cl_3)L_2]$ and $[NiCl(2,3,6\text{-}C_6H_2Cl_3)L_2]$ containing dpe, as compared with those containing PPh_3, may be attributed to the strong *trans* effect exerted by the phosphine ligands.

(b) The complexes $[NiCl(2,4,6\text{-}C_6H_2Cl_3)(dpe)]$ and $[NiCl(2,3,6\text{-}C_6H_2Cl_3)(dpe)]$ are less stable than those with the analogous tetra- and penta-chlorinated ligands [4]. This can be associated with the lower electronegativity of the trichlorophenyl ligand.

(c) The lower stability of $[NiCl(2,3,4,5\text{-}C_6HCl_4)L_2]$ compared to the other tetrachlorinated compounds may be attributed to the presence of only one chlorine atom *ortho* to the $\sigma(M—C)$ bond.

The behaviour of the new complexes in substitution reactions is similar to that of the analogous compounds containing the C_6Cl_5 group [4]. Thus, refluxing acetone solutions of $[NiCl(2,4,6\text{-}C_6H_2Cl_3)L_2]$ with an excess of the appropriate alkali metal salts gives $[NiX(2,4,6\text{-}C_6H_2Cl_3)L_2]$ (X = Br, I, NCS, NCO and N_3 when $L_2 = 2\ PPh_3$; and X = Br, I, NCS, NCO, N_3 and NO_2 when L_2 = dpe). Silver salts ($AgNO_3$ and $AgNO_2$) react with $[NiCl(2,4,6\text{-}C_6H_2Cl_3)(PPh_3)_2]$ to give decomposition products, as for the analogous pentachlorophenyl derivates [5]. The reaction with $AgClO_4$ is similar to that of $[NiCl(C_6Cl_5)(dpe)]$ [5], i.e. a solution of $[Ni(ClO_4)(2,4,6\text{-}C_6H_2Cl_3)(dpe)]$ is obtained from which the cationic complex $[Ni(\gamma\text{-pic})(2,4,6\text{-}C_6H_2Cl_3)(dpe)]ClO_4$ can be isolated. Analytical data for these compounds are given in Table 2. The molar conductivity for $[Ni(\gamma\text{-pic})(2,4,6\text{-}C_6H_2Cl_3)(dpe)]ClO_4$ is 153 $ohm^{-1}\ cm^2\ mol^{-1}$, typical of a 1:1 electrolyte.

PMR

The features of the PMR spectra of the new compounds, in $CDCl_3$, are indicated in Table 4. The signal due to the two protons of trichlorobenzene in the compound $[NiCl(2,4,6\text{-}C_6H_2Cl_3)(dpe)]$ exhibit a splitting attributable to the dif-

TABLE 3

ACTION OF GASEOUS CHLORINE [a] AND OF GASEOUS HYDROGEN CHLORIDE

Substrate	Identified products
Chlorine	
$[NiCl(2,4,6\text{-}C_6H_2Cl_3)L_2]$	$1,2,3,5\text{-}C_6H_2Cl_4$
$[NiCl(2,3,6\text{-}C_6H_2Cl_3)L_2]$	$1,2,3,4\text{-}C_6H_2Cl_4$
$[NiCl(2,3,4,5\text{-}C_6HCl_4)L_2]$	C_6HCl_5
$[NiCl(2,3,4,6\text{-}C_6HCl_4)L_2]$	C_6HCl_5
$[NiCl(2,3,5,6\text{-}C_6HCl_4)L_2]$	C_6HCl_5
Hydrogen chloride	
$[NiCl(2,4,6\text{-}C_6H_2Cl_3)(PPh_3)_2]$	$[NiCl(2,4,6\text{-}C_6H_2Cl_3)(PPh_3)]$
$[NiCl(2,4,6\text{-}C_6H_2Cl_3)(dpe)]$	$[NiCl_2(dpe)]$ and $1,3,5\text{-}C_6H_3Cl_3$
$[NiCl(2,3,6\text{-}C_6H_2Cl_3)(PPh_3)_2]$	$[NiCl(2,3,6\text{-}C_6H_2Cl_3)(PPh_3)_2]$
$[NiCl(2,3,6\text{-}C_6H_2Cl_3)(dpe)]$	$[NiCl_2(dpe)]$ and $1,2,4\text{-}C_6H_3Cl_3$
$[NiCl(2,3,4,5\text{-}C_6HCl_4)(PPh_3)_2]$	$1,2,3,4\text{-}C_6H_2Cl_4$, PPh_3 and Ni^{2+}
$[NiCl(2,3,4,5\text{-}C_6HCl_4)(dpe)]$	$[NiCl_2(dpe)]$ and $1,2,3,4\text{-}C_6H_2Cl_4$
$[NiCl(2,3,4,6\text{-}C_6HCl_4)L_2]$	$[NiCl(2,3,4,6\text{-}C_6HCl_4)L_2]$
$[NiCl(2,3,5,6\text{-}C_6HCl_4)L_2]$	$[NiCl(2,3,5,6\text{-}C_6HCl_4)L_2]$

[a] In all cases causes decomposition, with formation of phosphine and nickel(II) salts.

TABLE 4

INFRARED FREQUENCIES ASSIGNED TO COORDINATED POLYCHLOROPHENYL AND PMR SIGNALS OF THE POLYCHLOROPHENYL PROTONS AND OF THE PHOSPHINE PROTONS

Compound	IR (cm^{-1})	PMR (τ(ppm))	
		polychlorophenyl	phosphine
[$NiCl(2,3,4,5\text{-}C_6HCl_4)(PPh_3)_2$]	1520w, 1505m, 1380s, 1310s, 1230m, 1180m, 1170m, 1050m, 850m, 790s, 630s, 580w,	3.35	2.25 (H *ortho*) 2.62 (H *meta* and *para*)
[$NiCl(2,3,4,6\text{-}C_6HCl_4)(PPh_3)_2$]	1530w, 1510w, 1400m, 1380s, 1320w, 1300s, 1240w, 1230w, 1040m, 790s, 630s	3.64	2.25 (H *ortho*) 2.62 (H *meta* and *para*)
[$NiCl(2,3,5,6\text{-}C_6HCl_4)(PPh_3)_2$]	1540m, 1520s, 1400w, 1370s, 1350s, 1300m, 1150s, 1120w, 1040m, 850m, 640s	3.75	2.25 (H *ortho*) 2.62 (H *meta* and *para*)
[$NiCl(2,3,6\text{-}C_6H_2Cl_3)(PPh_3)_2$]	1540w, 1530w, 1400s, 1380w, 1330m, 1310w, 1250w, 1150m, 1020m, 800m, 740s, 580w, 550w	3.8 (H *meta*) 3.9 (H *para*)	2.25 (H *ortho*) 2.62 (H *meta* and *para*)
[$NiCl(2,4,6\text{-}C_6H_2Cl_3)(PPh_3)_2$]	1550w, 1520s, 1375s, 1350s, 1250m, 1160s, 1120m, 1020w, 860w, 850s, 800s, 775s, 425w, 410w	3.85	2.25 (H *ortho*) 2.62 (H *meta* and *para*)
[$NiCl(2,3,4,5\text{-}C_6HCl_4)(dpe)$]	1520w, 1505m, 1380s, 1300s, 1230m, 1180m, 1170m, 1050m, 850m, 780s, 630s, 580w	*b*	2.5—3 (H aromatic) 7.85 (H aliphatic)
[$NiCl(2,3,4,6\text{-}C_6HCl_4)(dpe)$]	1530w, 1510w, 1380s, 1310w, 1290s, 1240w, 1230w, 1040m, 860m, 780s, 620s	3.18—3.20 [a]	2.5—3 (H aromatic) 7.85 (H aliphatic)
[$NiCl(2,3,5,6\text{-}C_6HCl_4)(dpe)$]	1540m, 1520s, 1370s, 1350s, 1300m, 1295w, 1150s, 1120w, 1040m, 850m, 640s	3.19	2.5—3 (H aromatic) 7.85 (H aliphatic)
[$NiCl(2,3,6\text{-}C_6H_2Cl_3)(dpe)$]	1540w, 1530w, 1400s, 1380w, 1330m, 1310w, 1250w, 1150m, 1020m, 790s, 580w, 550w	3.40 (H *meta* and *para*)	2.5—3 (H aromatic) 7.85 (H aliphatic)
[$NiCl(2,4,6\text{-}C_6H_2Cl_3)(dpe)$]	1550w, 1520s, 1375s, 1350s, 1250m, 1160s, 1120m, 1025w, 860w, 850s, 800s, 775s, 425w, 410w	3.35—3.37 [a]	2.5—3 (H aromatic) 7.85 (H aliphatic)

[a] See text. [b] Overlapped with aromatic protons of the dpe.

fering influence of one of the dpe phenyl groups on the hydrogen atoms. The breadth of the signal at τ 3.18—3.20 ppm corresponding to the proton of the organic ligand in the compound [NiCl(2,3,4,6-C_6HCl_4)(dpe)] may indicate the presence of two isomers, which would arise from the different positions which the *meta* hydrogen atom may attain above or below the plane of the molecule. Similar splitting could be expected for [NiCl(2,3,4,5-C_6HCl_4)(dpe)], but cannot be observed because of overlapping with the signal corresponding to dpe aromatic protons. The expected splitting for the *meta* proton in [NiCl(2,3,6-$C_6H_2Cl_3$)(dpe)] appears only as a broadening of the signal due to the presence of the signal of *para* protons in the same zone. All attempts to separate these possible isomers by chromatographic techniques were unsuccessful.

The chemical shifts for the protons in the complexes with polychlorophenyl ligands vary as expected with the increase in the number of chlorine atoms in the ring. A shift towards lower field for the ligand protons on going from triphenylphosphine to dpe is evident from the data for a fixed ligand with varying phosphines. This can be accounted for by the differing influence exerted by the phenyl groups of the phosphines on these protons; the number of phenyl groups which can influence the protons of coordinated polychlorophenyl will be greater for the complex with triphenylphosphine than for those containing dpe due to the *trans* and *cis* configurations, respectively.

Infrared spectra

The IR spectra of the compounds show bands due to coordinated triphenylphosphine and dpe [6,7]. The IR bands due to polychlorophenyl ligands, which appear at similar frequencies to those observed for polychlorophenyl analogs [8], are listed in Table 4. The bands corresponding to the Ni—Cl bonds appear in the 350—360 zone for the compounds containing PPh_3 and at 300—330 cm^{-1} for those containing dpe. Data corresponding to compounds [NiX(2,4,6-$C_6H_2Cl_3$)L_2] are given in Table 5. Furthermore the bands due to NO_2 groups are observed in the spectrum of [$NiNO_2$(2,4,6-$C_6H_2Cl_3$)(dpe)] at 1365, 1320, 810, 540 and 340 cm^{-1} and are assigned to $\nu_{as}(NO_2)$, $\nu_s(NO_2)$, $\delta(ONO)$, $\rho_w(NO_2)$ and $\nu(Ni-N)$, respectively. The position of these bands indicates coordination of thiocyanate, cyanate and nitrite through the nitrogen atom in all cases [9].

The infrared spectrum of [Ni-γ-pic(2,4,6-$C_6H_2Cl_3$)(dpe)]ClO_4 shows bands due to the ionic perchlorate group at 1100(ν_3) and 620(ν_4) cm^{-1} and to γ-picoline at 1620, 1500, 1210, 815 and 505 cm^{-1} [10]

TABLE 5

INFRARED FREQUENCIES (cm^{-1}) OF PSEUDOHALIDE GROUPS

	ν_s	δ	ν_{as}	ν(Ni—X)
[NiNCS(2,4,6-$C_6H_2Cl_3$)(PPh_3)$_2$]	850m	[a]	2080vs	350w
[NiNCO(2,4,6-$C_6H_2Cl_3$)(PPh_3)$_2$]	1340m	590m	2220vs	385m
[NiN_3(2,4,6-$C_6H_2Cl_3$)(PPh_3)$_2$]	1340m	575w	2060vs	390m
[NiNCS(2,4,6-$C_6H_2Cl_3$)(dpe)]	830m	[b]	2060vs	330w
[NiNCO(2,4,6-$C_6H_2Cl_3$)(dpe)]	1330m	585w	2205vs	395w
[NiN_3(2,4,6-$C_6H_2Cl_3$)(dpe)]	1330m	590(sh)	2020vs	405m

[a] Overlapped with PPh_3 bands. [b] Overlapped with dpe bands.

Experimental

Preparative methods

Preparation of the reagents and subsequent reactions were carried out under dry oxygen-free nitrogen. $[NiCl_2(PPh_3)_2]$, $[NiCl_2(dpe)]$, and the ligand dpe were prepared by literature procedures [11—13].

Preparation of $[NiClRL_2]$ ($R = 2,3,4,5\text{-}C_6HCl_4$, $2,3,4,6\text{-}C_6HCl_4$, $2,3,5,6\text{-}C_6HCl_4$, $2,3,6\text{-}C_6H_2Cl_3$ or $2,4,6\text{-}C_6H_2Cl_3$ and $L_2 = 2\ PPh_3$ or dpe)

(a) From polychlorobenzene and Mg. The Grignard reagent prepared from Mg (0.60 g, 25 mmol), polychlorobenzene (20 mmol), THF (10 ml) and I_2 or C_2H_5MgBr (as initiator) was added to 1.5 g of $[NiCl_2(PPh_3)_2]$ or $[NiCl_2(dpe)]$ at room temperature. The yellow solid which formed was filtered off, washed with water, recrystallized from methanol/chloroform (1/2), and dried in vacuo. The yield was about 70%.

(b) From polychlorobenzene and $C_6H_5CH_2MgCl$. Several ml of a THF solution of $C_6H_5CH_2MgCl$, obtained from Mg (0.50 g) and $C_6H_5CH_2Cl$ (2.3 ml), was added to solid polychlorobenzene (16 mmol) and the mixture was refluxed for 30 min. The resulting solution was added to 1.5 g of $[NiCl_2(PPh_3)_2]$ or $[NiCl_2(dpe)]$. The yellow solid was filtered off and recrystallized as above. The yield was about 65%.

Preparation of $[NiX(2,4,6\text{-}C_6H_2Cl_3)L_2]$ ($X = Br$, I, NCS, NCO and N_3 for $L_2 = 2\ PPh_3$ and $X = Br$, I, NCS, NCO, N_3 and NO_2 for $L_2 =$ dpe)

The compounds were prepared in good yields (80—90%) by refluxing a solution of $[NiCl(2,4,6\text{-}C_6H_2Cl_3)L_2]$ (1 g) in 100 ml of acetone for 2—6 h with an excess of the appropriate alkali metal salt (LiBr, KI, KNCO, KNCS, NaN_3 and KNO_2). After filtering off the precipitated salts, the solution was concentrated under reduced pressure and the compounds which separated were recrystallized from chloroform/ethanol (3/1) and dried in vacuo.

Preparation of $[Ni\text{-}\gamma\text{-picoline}(2,4,6\text{-}C_6H_2Cl_3)(dpe)]ClO_4$

Silver perchlorate (0.21 g, 1 mmol) was added to $[NiCl(2,4,6\text{-}C_6H_2Cl_3)(dpe)]$ (0.67 g, 1 mmol) in 50 ml of acetone at room temperature. After 2 min, AgCl was filtered off and 0.1 ml of γ-picoline was added. The mixture was stirred for 15 min and evaporated to dryness. The residue was recrystallized from ethanol/chloroform (1/3). The yield was about 40%.

Analyses

C, H and N determinations were carried out at the Instituto de Química Orgánica de Barcelona (C.S.I.C.). Halogens were determined by Schöniger's method [14]. Nickel was determined gravimetrically after destruction of the complexes with a boiling mixture of nitric and sulphuric acids.

Spectra

Infrared spectra were recorded on a Beckman IR 20A spectrophotometer. Samples were prepared using the pressed KBr disk technique and as Nujol mulls between CsI plates. PMR spectra were recorded on a Perkin—Elmer R-12A at 60 MHz. TMS was used as internal standard.

References

1 J. Chatt and B.L. Shaw, J. Chem. Soc., (1960) 1718.
2 R.S. Nyholm, Quart. Rev., 24 (1970) 1.
3 J.M. Coronas, G. Muller and J. Sales, Synth. Inorg. Metalorg. Chem., 6 (1976) 217.
4 J.M. Coronas, O. Rossell and J. Sales, J. Organometal. Chem., 97 (1975) 473.
5 J.M. Coronas, O. Rossell and J. Sales, J. Organometal. Chem., 121 (1976) 265.
6 G.B. Deacon and J.A.S. Green, Spectrochim. Acta, A, 24 (1968) 845.
7 (a) C. Udovich, J. Takemoto and K. Nakamoto, Coord. Chem. Rev., 1 (1971) 89; (b) O. Rossell, Thesis, Barcelona, 1976.
8 (a) J. Scherer and J.C. Evans, Spectrochim. Acta, A, 19 (1963) 1739; (b) R.J. Bertino, G.B. Deacon and F.B. Taylor, Aust. J. Chem., 25 (1975) 1645.
9 K. Nakamoto, Infrared spectra of inorganic and coordination compounds, Interscience, New York, 1970, p. 187.
10 M. Pfeffer, P. Braunstein and J. Dehand, Spectrochim. Acta, A, 30 (1974) 331.
11 J. Chatt and F.A. Hart, J. Chem. Soc., (1960) 1385.
12 L.M. Venanzi, J. Chem. Soc., (1958) 719.
13 G. Booth and J. Chatt, J. Chem. Soc., (1965) 3238.
14 W. Schöniger, Microchim. Acta, (1956) 859.