

*Journal of Organometallic Chemistry*, 94 (1975) 107-113  
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## ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS CONTAINING PHOSPHINE AND PERCHLOROARYL LIGANDS

### I. PREPARATION AND STUDIES OF COMPOUNDS OF THE TYPE [MX(C<sub>6</sub>Cl<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (M = Ni, Pd)

J.M. CORONAS and J. SALES

*Department of Inorganic Chemistry, Faculty of Chemistry, University of Barcelona (Spain)*  
(Received February 17th, 1975)

#### Summary

Several stable new compounds of transition metals with C<sub>6</sub>Cl<sub>5</sub> as ligand, of the type [MX(C<sub>6</sub>Cl<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (M = Pd and X = Cl, Br, I, NCS, NCO, N<sub>3</sub>; M = Ni and X = NCS, NCO, N<sub>3</sub>) are described. Their preparation in some cases required in situ reaction of [MX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], Mg and C<sub>6</sub>Cl<sub>6</sub>. The action of gaseous HCl and Cl<sub>2</sub> on the solutions of these compounds has been examined. The IR spectra of the cyanato and thiocyanato complexes indicates coordination through the nitrogen atom.

#### Introduction

The stability of organometallic compounds of transition metals increases with replacement of hydrogens in the organic groups by halogens. This increase of stability was attributed by Nyholm [1] to the greater electronegativity of the halogenated group. Although many organometallic compounds with perfluoro groups have been described, there are very few containing perchloro groups [2-5]. The preparation of new organometallic compounds with perchlorophenyl groups would enable us to compare their behaviour with that of analogous perfluoro derivatives. Since similar electronegativities have been attributed to pentachlorophenyl and pentafluorophenyl groups [6], the same degree of stability can be expected for compounds of the same type containing either one or the other ligand; even greater stability for the chloro compounds could be expected in view of the shorter bond length for Ni-C<sub>6</sub>Cl<sub>5</sub> relative to Ni-C<sub>6</sub>F<sub>5</sub>, found in the compound [Ni(C<sub>6</sub>F<sub>5</sub>)(C<sub>6</sub>Cl<sub>5</sub>)(PPh<sub>2</sub>Me)<sub>2</sub>] [7].

New compounds of the type [MX(C<sub>6</sub>Cl<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (M = Pd; X = Cl, Br, I, NCS, NCO, N<sub>3</sub>; M = Ni; X = NCS, NCO, N<sub>3</sub>) are described below.

TABLE 1  
ANALYTICAL DATA

Compound	Found (calcd.) (%)					Br or N	Ni or Pd	Decomposition temperature (°C)
	C	H	Cl					
$[\text{Ni}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]^a$	58.5 (58.07)	3.6 (3.48)	23.8 (24.50)	—	—	—	6.6 (6.76)	240-260
$[\text{NiBr}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]^a$	55.2 (55.24)	3.2 (3.31)	19.6 (19.42)	8.8 (8.75)	—	—	6.3 (6.48)	230-235
$[\text{Ni}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]^a$	52.9 (52.55)	3.5 (3.15)	18.7 (18.47)	—	—	—	6.0 (6.12)	200-210
$[\text{Ni}(\text{NCS})(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$	57.4 (57.95)	3.6 (3.40)	20.1 (19.90)	1.5 (1.57)	—	—	6.4 (6.59)	220-225
$[\text{Ni}(\text{NCO})(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$	59.7 (58.97)	3.7 (3.45)	20.0 (20.24)	1.5 (1.60)	—	—	6.6 (6.71)	230-235
$[\text{NiN}_3(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$	58.1 (57.64)	3.4 (3.45)	20.2 (20.24)	4.6 (4.81)	—	—	6.6 (6.71)	195-205
$[\text{PdCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$	54.8 (55.00)	3.4 (3.32)	23.0 (23.22)	—	—	—	11.3 (11.62)	280-290
$[\text{PdBr}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$	53.0 (52.47)	3.2 (3.15)	18.2 (18.44)	8.7 (8.32)	—	—	11.2 (11.80)	280-285
$[\text{PdI}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$	49.9 (50.10)	2.9 (3.01)	17.4 (17.00)	—	—	—	10.1 (10.33)	275-280
$[\text{Pd}(\text{NCS})(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$	54.4 (55.02)	3.3 (3.22)	18.8 (18.90)	1.6 (1.49)	—	—	11.2 (11.36)	195-200
$[\text{Pd}(\text{NCO})(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$	57.0 (55.95)	3.4 (3.28)	19.1 (19.22)	1.5 (1.52)	—	—	11.3 (11.54)	245-250
$[\text{PdN}_3(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$	54.3 (54.65)	3.3 (3.28)	19.0 (19.21)	4.4 (4.55)	—	—	11.3 (11.53)	235-240

<sup>a</sup> Compounds previously reported [5].

## Results and discussion

### Preparation and properties

Compounds of formula  $[\text{NiX}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  with  $\text{X} = \text{Cl}, \text{Br},$  and  $\text{I}$ , have been described by MacKinnon and West [5], but we have made these compounds by different procedures. Furthermore, better yields have been obtained (1) by reducing the heating and reaction time during the formation of pentachlorophenylmagnesium chloride, and (2) by using  $\text{C}_2\text{H}_5\text{Br}$  as initiator rather than  $\text{ClCH}_2\text{C}_6\text{H}_5$ .  $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  has been made by treating  $[\text{NiCl}_2(\text{PPh}_3)_2]$  with solutions of  $\text{LiC}_6\text{Cl}_5$  in ether.  $[\text{NiBr}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  has been prepared by treating  $[\text{NiBr}_2(\text{PPh}_3)_2]$  with a solution of pentachlorophenylmagnesium chloride or bromide, in contrast with the results obtained by MacKinnon and West. Furthermore, the three compounds  $[\text{NiX}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) were also prepared directly by treating the corresponding dihalogenated derivative,  $[\text{NiX}_2(\text{PPh}_3)_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), with magnesium and hexachlorobenzene.

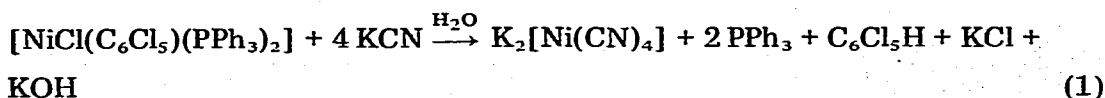
Other compounds of formula  $[\text{NiX}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  ( $\text{X} = \text{Br}, \text{I}, \text{NCS}, \text{NCO}, \text{N}_3$ ) are obtained by treating  $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  in an acetone-benzene mixture, with an excess of the appropriate alkaline salt. Those containing the ligands  $\text{NCS}, \text{NCO}$  and  $\text{N}_3$  have not been previously described.

$[\text{PdCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ , the first palladium compound containing pentachlorophenyl and triphenylphosphine ligands, could be obtained only by the *in situ* method outlined above. Five novel compounds of palladium,  $[\text{PdX}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  ( $\text{X} = \text{Br}, \text{I}, \text{NCS}, \text{NCO}, \text{N}_3$ ) were prepared by heating solutions of  $[\text{PdCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  in acetone-benzene mixtures under reflux with an excess of the corresponding alkaline salt.

All the compounds prepared are stable in the solid state and in solution. Analytical results and decomposition temperatures are given in Table 1. They are soluble in benzene, toluene, carbon tetrachloride and acetone; slightly soluble in alcohol and hexane, and insoluble in water. All of them are diamagnetic and their solutions in anhydrous acetone show very low conductivities ( $2\text{--}10 \text{ ohm}^{-1} \text{ cm}^{-1} \text{ mol}^{-1}$ ). The new compounds are assigned a *trans* configuration by analogy with other reported compounds of the same type, and on the basis of some features in their IR spectra (see below).

Attempts to obtain compounds with two pentachlorophenyl groups,  $[\text{M}(\text{C}_6\text{Cl}_5)_2(\text{PPh}_3)_2]$  by using a large excess of  $\text{C}_6\text{Cl}_5\text{MgCl}$  led only to products with one  $\text{C}_6\text{Cl}_5$  group, in agreement with results of other authors in similar cases [4,5].

Attempts to replace the  $\text{Cl}$  ligand by  $\text{CN}, \text{NO}_2, \text{NO}_3$  and  $\text{CH}_3\text{CO}_2$  were also unsuccessful.  $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  was recovered unchanged after its solution was heated with excess of  $\text{KCN}$ . If several drops of water are added to the solvent to increase the concentration of cyanide, decomposition occurs. This decomposition is represented by eqn. 1, as confirmed by identification of the decomposition products.



The action of  $\text{AgNO}_3, \text{AgNO}_2$  or  $\text{AgCH}_3\text{CO}_2$  on solutions of  $[\text{MCl}(\text{C}_6\text{Cl}_5)-$

(PPh<sub>3</sub>)<sub>2</sub>] led to decomposition, possibly with formation of silver complexes containing triphenylphosphine ligands.

### Infrared spectra

All the bands reported [8] for coordinated triphenylphosphine appear in the infrared spectra of the compounds prepared. The bands due to coordinated pentachlorophenyl, assigned in a previous paper [9] at 1225-1230 cm<sup>-1</sup> ( $\nu_1$ ), 1312-1318 and 1322-1328 (both  $\nu_{13}$ ), 1280-1290 cm<sup>-1</sup> ( $\nu_6$ ) and 665-670 cm<sup>-1</sup> (one of the components of the  $\nu_{12}$  vibration), are also observed. The other component of this latter mode is not observed because it overlaps with the "v" vibration of triphenylphosphine which absorbs at 692 cm<sup>-1</sup>. Several weak bands appearing in the low energy zone (400-250 cm<sup>-1</sup>) are assigned to the M—X stretching vibration (Table 2). Another weak band observed in the 590-575 cm<sup>-1</sup> zone is assigned to the M—C vibration [9]. No band attributable to the M—P vibration is observed, suggesting that this vibration occurs below 250 cm<sup>-1</sup>.

Occasionally the bands appearing at 400-450 cm<sup>-1</sup> in the spectra of analogous compounds have been assigned to M—P vibrations and have been used to determine *cis* or *trans* configurations [10]. However, this assignment has been very controversial since the bands may be equally assigned to triphenylphosphine vibrations (these bands are also observed in free triphenylphosphine) [11].

Recently [12] M—P vibrations have been assigned to bands appearing at 160-200 cm<sup>-1</sup> in compounds of the type [PtX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (*cis* or *trans*), furthermore the intensity of the band at 550 ± 5 cm<sup>-1</sup> has been found to be related to the geometry of the compound. The band is strong for *cis*-isomers but weak for the *trans* compounds. The fact that no band is clearly observed in the spectra of the compounds studied, leads us to propose a *trans* configuration for all of them.

Again, Bland and Kemmit [13], when studying compounds of the type [PtXR(PPh<sub>3</sub>)<sub>2</sub>], found a relation between the relative intensities of triphenylphosphine bands at 1586 and 1575 cm<sup>-1</sup>, and the geometry of the compound; in the *cis* isomer the first band is more intense whereas in the *trans* isomer the band appearing at 1575 cm<sup>-1</sup> is more intense. In our compounds the more

TABLE 2

METAL—HALOGEN AND METAL—CARBON INFRARED FREQUENCIES (cm<sup>-1</sup>)

Compounds	$\nu(\text{M—X})$	$\nu(\text{M—C})$
[NiCl(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	360-340	587
[NiBr(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	305	583
[NiI(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]		581
[Ni(NCS)(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	360	585
[Ni(NCO)(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	400	588
[NiN <sub>3</sub> (C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	400	587
[PdCl(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	305	583
[PdBr(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	250	580
[PdI(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]		579
[Pd(NCS)(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	298	582
[Pd(NCO)(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	350	582
[PdN <sub>3</sub> (C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	360	580

TABLE 3

INFRARED FREQUENCIES ( $\text{cm}^{-1}$ ) ARISING FROM PSEUDOHALIDE GROUPS

Compounds	$\nu_1(\nu_2)$	$\nu_2(\delta)$	$\nu_3(\nu_{as})$
[Ni(NCS)(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	850	a	2075
[Pd(NCS)(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	830	a	2050
[Ni(NCO)(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	1345	605	2220
[Pd(NCO)(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	b	598	2215
[NiN <sub>3</sub> (C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	1345	570	2055
[PdN <sub>3</sub> (C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	1340		2040

<sup>a</sup> Overlapped with PPh<sub>3</sub> bands. <sup>b</sup> Overlapped with C<sub>6</sub>Cl<sub>5</sub> bands.

intense band occurs at  $1575 \text{ cm}^{-1}$ , thus agreeing with the proposed *trans* configuration.

When the complexes contain thiocyanate, cyanate or azide, the bands due to these anions also appear in the spectra (Table 3). The position of these bands indicates coordination of thiocyanate and cyanate through the nitrogen in all cases [14].

#### Chemical reactivity

In order to examine the stability of the M—C bond in these compounds and study the possibility of formation of hexacoordinated compounds of M<sup>IV</sup>, the action of gaseous HCl and Cl<sub>2</sub> on the solutions of these compounds was studied.

(a). *Action of HCl*. The products resulting from treatment of the solutions of [MX(C<sub>6</sub>Cl<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>] in chloroform with gaseous HCl at room temperature for 6 h are shown in Table 4. A high stability of the M—C<sub>6</sub>Cl<sub>5</sub> bond is indicated by the results since in no case does replacement of the C<sub>6</sub>Cl<sub>5</sub> group occur. This stability can be related to that found for analogous compounds with aryl groups having *ortho* substituents, which reduce the possibility of attack on the metal [2]. An enhanced tendency for replacement of the group *trans* to C<sub>6</sub>Cl<sub>5</sub> is also observed for the palladium complexes. This behaviour in the case of the complexes containing thiocyanate may be explained in terms of a central atom—

TABLE 4

ACTION OF GASEOUS HYDROGEN CHLORIDE

Starting	Product
[NiBr(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	[NiBr(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]
[NiI(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	[NiI(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]
[Ni(NCS)(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	[Ni(NCS)(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]
[Ni(NCO)(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	[NiCl(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]
[NiN <sub>3</sub> (C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	[NiCl(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]
[PdBr(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	[PdCl(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ] + [PdBr(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]
[PdI(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	[PdI(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ] + [PdCl(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>a</sup>
[Pd(NCS)(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	[PdCl(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]
[Pd(NCO)(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	[PdCl(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]
[PdN <sub>3</sub> (C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]	[PdCl(C <sub>6</sub> Cl <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]

<sup>a</sup> A small amount of [PdCl(C<sub>6</sub>Cl<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>] was detected.

thiocyanate bond through the nitrogen of the latter, rather than through sulphur as normally occurs in palladium compounds. Coordination through nitrogen in  $[\text{Pd}(\text{NCS})(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  is probably due to the presence of phosphine [15].

(b). *Action of chlorine.* The action of chlorine on the solutions of  $[\text{MCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  in carbon tetrachloride at room temperature was studied. Prolonged action of chlorine in both cases causes decomposition, with formation of  $\text{C}_6\text{Cl}_6$ , triphenylphosphine, and the corresponding metal halide. However the palladium compound shows practically no sign of decomposition after passage of chlorine through its solution for 3 h (only a small amount of decomposition products is detected), whereas the nickel compound is completely decomposed in the same period.

(c). *Action of heat under vacuum.* Upon heating of the new compounds under reduced pressure ( $10^{-2}$ - $10^{-3}$  Torr), triphenylphosphine is evolved, and compounds with formula  $[\text{M}_2\text{X}_2(\text{C}_6\text{Cl}_5)_2(\text{PPh}_3)_2]$  are obtained, in agreement with the results of MacKinnon and West for the analogous nickel compounds with  $\text{X} = \text{Cl}, \text{Br}$ . The study of these compounds containing two metallic atoms will be the subject of another publication.

## Experimental

### Preparative methods

Preparation of the Grignard reagents and subsequent reactions were carried out in dry oxygen-free nitrogen. The solvents used were dried over molecular sieves (4 Å) or over sodium metal. Published methods [16,17] were used for the preparation of the starting materials  $[\text{NiX}_2(\text{PPh}_3)_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and  $[\text{PdCl}_2(\text{PPh}_3)_2]$ .

#### (a). *In situ method*

*Preparation of  $[\text{NiX}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ .* A solution of 5 mmol of  $[\text{NiX}_2(\text{PPh}_3)_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), 0.24 g of magnesium (10 mmol), 2.8 g of  $\text{C}_6\text{Cl}_6$  (10 mmol), and 0.3 ml of benzyl chloride, in 20 ml of THF-benzene (1/1) was heated under reflux for several hours. The filtered solution was concentrated under reduced pressure, and the solid remaining washed with water to remove any magnesium chloride. Excess of  $\text{C}_6\text{Cl}_6$  was removed by vacuum sublimation ( $120^\circ\text{C}$ ,  $10^{-2}$  Torr). The product was recrystallized from acetone. Yield was about 40%.

*Preparation of  $[\text{PdCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ .* This compound was prepared by a method similar to that above, but using a larger excess of magnesium and hexachlorobenzene relative to  $[\text{PdCl}_2(\text{PPh}_3)_2]$  (molar ratio 4/4/1). The yield was about 40%.

#### (b). *With the previous preparation of the Grignard reagent solution*

Several ml of a solution of  $\text{C}_2\text{H}_5\text{MgBr}$  in THF (obtained previously from magnesium and  $\text{C}_2\text{H}_5\text{Br}$ ) were added to a warm suspension of magnesium (0.24 g) and  $\text{C}_6\text{Cl}_6$  (2.8 g) in 10 ml of THF. The heating was discontinued when all the solution had been added, but the stirring was maintained until the solution of  $\text{C}_6\text{Cl}_5\text{MgCl}$  reached room temperature. 2.4 g of  $[\text{NiCl}_2(\text{PPh}_3)_2]$  were

then added. After several minutes yellow  $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  began to crystallize. The product was filtered, purified and recrystallized as above.

$[\text{NiBr}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  was prepared using the latter method but starting from  $[\text{NiBr}_2(\text{PPh}_3)_2]$ . The yield in both cases was about 85%.

(c). *From  $\text{LiC}_6\text{Cl}_5$*

4.90 g (7.5 mmol) of  $[\text{NiCl}_2(\text{PPh}_3)_2]$  were slowly added to 300 ml of a solution of  $\text{LiC}_6\text{Cl}_5$  (obtained at  $0^\circ\text{C}$  from 15 mmol of  $\text{C}_6\text{Cl}_6$  and 15 mmol of *n*-butyllithium [18]) in ether. After stirring at room temperature for an hour, the  $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  formed was filtered and recrystallized as described above. The yield was about 50%.

*Replacement reactions*

The other compounds with formula  $[\text{MX}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  ( $\text{M} = \text{Ni}, \text{Pd}$ ;  $\text{X} = \text{Br}, \text{I}, \text{NCS}, \text{NCO}, \text{N}_3$ ) were prepared in good yield (90%) by refluxing solutions of 5 mmol of  $[\text{MCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$  in 100 ml of a benzene-acetone mixture, with an excess of the corresponding alkaline salt  $\text{LiBr}, \text{KI}, \text{KNCS}, \text{KNCO}, \text{NaN}_3$ . (The volume of benzene used was that needed to dissolve the starting complex.) The alkaline chloride formed was filtered off, the solution was concentrated, and the crystalline compound was filtered off, recrystallized from acetone, and dried in vacuo.

*Analyses*

C, H, N and halogen determinations were performed at the "Instituto de Química Orgánica de Barcelona (C.S.I.C)". Ni and Pd were determined gravimetrically with dimethylglyoxime after destruction of the complexes with boiling nitric and sulphuric acids.

*Spectra*

Infrared spectra were recorded on a Beckman IR-20A spectrophotometer purged with dry air. Samples were prepared using the pressed KBr disk technique and as Nujol mulls between CsI plates. The spectrophotometer was calibrated with a polystyrene film. Frequencies are accurate to  $\pm 2 \text{ cm}^{-1}$ .

*References*

- 1 R.S. Nyholm, *Quart. Rev.*, 24 (1970) 1.
- 2 J. Chatt and B.L. Shaw, *J. Chem. Soc.*, (1960) 1718.
- 3 J. Chatt and B.L. Shaw, *J. Chem. Soc.*, (1961) 285.
- 4 M.D. Rausch and F.E. Tibbetts, *J. Organometal. Chem.*, 21 (1970) 487; *Inorg. Chem.*, 9 (1970) 512.
- 5 K. MacKinnon and B.O. West, *Aust. J. Chem.*, 21 (1968) 2801.
- 6 W.A. Sheppard, *J. Amer. Chem. Soc.*, 92 (1970) 5419.
- 7 M.R. Churchill and M.V. Veidis, *Chem. Commun.*, (1970) 1099.
- 8 G.B. Deacon and J.H.S. Green, *Spectrochim. Acta, Part A*, 24 (1968) 845.
- 9 J. Casabó, J.M. Coronas and J. Sales, *Inorg. Chim. Acta*, 11 (1974) 5.
- 10 H.C. Clark, K.R. Dixon and W.J. Jacobs, *J. Amer. Chem. Soc.*, 90 (1968) 2259.
- 11 D.M. Adams and P.J. Chandler, *J. Chem. Soc. A*, (1969) 588.
- 12 S.H. Mastin, *Inorg. Chem.*, 13 (1974) 1003.
- 13 W.J. Bland and R.D.W. Kemmitt, *J. Chem. Soc. A*, (1969) 2062.
- 14 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Interscience, New York, 1970, p. 187.
- 15 A. Turco and C. Pecile, *Nature (London)*, 191 (1961) 66.
- 16 L.M. Venanzi, *J. Chem. Soc.*, (1958) 719.
- 17 H. Itatani and J.C. Bailar Jr., *J. Amer. Oil Chem. Soc.*, 44 (1967) 147.
- 18 M.D. Rausch, F.E. Tibbetts and H.B. Gordon, *J. Organometal. Chem.*, 5 (1966) 493.