Journal of Organometallic Chemistry, 97 (1975) 473—477

ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS CONTAINING PHOSPHINE AND PERCHLOROARYL LIGANDS

II*. PREPARATION AND STUDIES OF COMPOUNDS OF THE TYPE [NiX(C_6Cl_5)(dpe)]

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(Received April 22nd, 1975)

Summary

The preparation and characterization of a number of stable compounds with σ-type bonds and general formula [NiX(C_6Cl_5)(dpe)] (X = Cl, Br, I, NCS, NCO, N_3, CN and NO_2; dpe = 1,2-bis(diphenylphosphino)ethane) is described. The IR spectra of the cyanato, thyocianato, and nitro complexes indicate coordination through the nitrogen. The action of gaseous HCl and Cl_2 on solutions of the compounds is described.

Introduction

Following our studies on organometallic compounds of transition elements with perchloro groups [1], we now report the preparation and studies of a new series of compounds with formula [NiX(C_6Cl_5)(dpe)] (X = Cl, Br, I, NCS, NCO, N_3, CN, and NO_2).

Replacement of chlorine by a further pentachlorophenyl in *cis*-[NiCl(C_6Cl_5)-(dpe)] was not achieved despite the strong *trans* effect of the phosphine ligands. This can be attributed to the steric effects of the two *ortho*-chlorine atoms of the C_6Cl_5 group, which hinders the approach of the reagent [2].

Results and discussion

Preparation and properties

The compound [NiCl(C_6Cl_5)(dpe)] was prepared by mixing a solution of C_6Cl_5MgCl in THF with solid [$NiCl_2$(dpe)] at room temperature. The com-

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TABLE 1

ANALYTICAL DATA

Compound	Found (calcd.) (%)					Decomposition temperatures (°C)
	C	H	Cl or total halogen	N	Ni	
[$NiCl(C_6Cl_5)(dpe)$]	50.9	3.2	28.3	—	7.8	254-256
	(51.82)	(3.23)	(28.67)		(7.91)	
[$NiBr(C_6Cl_5)(dpe)$]	48.3	3.1	33.0	—	7.6	252-255
	(48.21)	(3.08)	(32.71)		(7.47)	
[$NiI(C_6Cl_5)(dpe)$]	46.1	2.9	36.6	—	7.1	252-255
	(46.13)	(2.90)	(36.51)		(7.05)	
[$Ni(NCS)(C_6Cl_5)(dpe)$]	52.6	3.2	23.0	2.0	7.6	214-215
	(51.86)	(3.16)	(23.20)	(1.83)	(7.68)	
[$Ni(NCO)(C_6Cl_5)(dpe)$]	54.0	3.3	23.5	1.5	7.8	235-238
	(52.96)	(3.21)	(23.68)	(1.87)	(7.85)	
[$NiN_3(C_6Cl_5)(dpe)$]	51.7	3.2	23.5	5.6	7.8	228-230
	(51.37)	(3.23)	(23.70)	(5.62)	(7.85)	
[$Ni(CN)(C_6Cl_5)(dpe)$]	54.3	3.4	24.1	2.0	7.9	228-230
	(54.10)	(3.30)	(24.20)	(1.91)	(8.02)	
[$Ni(NO_2)(C_6Cl_5)(dpe)$]	51.0	3.2	23.5	1.6	7.7	242-243
	(51.09)	(3.21)	(23.56)	(1.86)	(7.80)	

pounds of formula [$NiX(C_6Cl_5)(dpe)$] (X = Br, I, NCO, NCS, N_3 and NO_2) were obtained by heating an acetone solution of [$NiCl(C_6Cl_5)(dpe)$] with an excess of the appropriate alkali metal salt. [$NiCN(C_6Cl_5)(dpe)$] was prepared by use of AgCN rather than KCN.

All the compounds are stable as solids and in solution. They are readily soluble in benzene and chloroform, but sparingly soluble in ethanol, ether and hexane. Analyses and decomposition temperatures are given in Table 1. The low values of the molar conductivity in anhydrous acetone (2-10 ohm^{-1} cm^2 mol^{-1}) indicate the non-electrolytic character of the complexes.

All the compounds show diamagnetic behaviour, indicating a square-planar geometry.

Attempts to prepare [$Ni(NO_3)(C_6Cl_5)(dpe)$] and [$Ni(CH_3COO)(C_6Cl_5)$-(dpe)] were unsuccessful. Treatment of a solution of [$NiCl(C_6Cl_5)(dpe)$] in acetone with an excess of KNO_3 and KCH_3COO did not bring about replacement of chloride; and the reaction with the silver salts of these anions gave Ag^I complexes of formula [Ag(dpe)]X [3].

Attempts to obtain [$Ni(C_6Cl_5)_2(dpe)$] by the action of C_6Cl_5Li and C_6Cl_5-MgCl on [$NiCl(C_6Cl_5)(dpe)$] were also unsuccessful, the starting materials being recovered in both cases. This is in agreement with the results reported for the attempted preparation of analogous Ni^{II} compounds containing two pentachlorophenyl groups and different phosphines [1,4].

Infrared spectra

The infrared spectra of the compounds show the bands due to 1,2-bis(diphenylphosphino)ethane observed for [$NiCl_2(dpe)$]. The bands due to coordinated pentachlorophenyl [5] are also observed, at 1230-1235 cm^{-1} (ν_I), 1315-

TABLE 2

INFRARED FREQUENCIES (cm^{-1}) ARISING FROM PSEUDOHALIDE GROUPS AND METAL—HALOGEN VIBRATIONS

	ν_s (cm^{-1})	δ (cm^{-1})	ν_{as} (cm^{-1})	ν(Ni—X) (cm^{-1})
[NiCl(C_6Cl_5)(dpe)]	—	—	—	340 w
[Ni(NCS)(C_6Cl_5)(dpe)]	840 m	[a]	2.090 vs	320 w
[Ni(NCO)(C_6Cl_5)(dpe)] [c]	1.340 m	610 (sh)	2.220 vs	400 w
[NiN_3(C_6Cl_5)(dpe)]	[b]	1.580	2.040 vs	410 m
[Ni(CN)(C_6Cl_5)(dpe)]	—	—	2.110 vs	455 w

[a] Overlapped with bands of dpe. [b] Overlapped with bands of C_6Cl_5. [c] A band, assigned to the combination band, $\nu_{as} + \nu_s$ is also found at 3.550 cm^{-1} in this compound.

1320 cm^{-1} and 1325-1330 cm^{-1} (the two components of the ν_{13} vibration), 1280-1290 cm^{-1} (ν_6) and 665-670 cm^{-1} (one of the two components of the ν_{12} vibration). The other component of the latter mode is not observed because of the overlapping with a band of the diphosphine absorbing at 690 cm^{-1}. A low intensity band, attributable to the nickel—carbon bond vibration, occurs at 580–585 cm^{-1} [5].

Given the complexity of the spectrum in the lower energy region studied, associated with internal vibrations of the ligand dpe, the assignment of observed bands to Ni—P and Ni—X vibrations is difficult [6]. However, new bands attributable to Ni—X vibrations appear in the spectrum when X = Cl, NCS, NCO, N_3, and CN (Table 2). Furthermore, the bands due to the internal vibrations of the coordinated anions are also observed for the compounds with X = NCO, NCS and N_3 (Table 2). The bands due to the NO_2 group also occur in the spectrum of [$NiNO_2$(C_6Cl_5)(dpe)] at 1370, 1320, 810, 545 and 350 cm^{-1}. These vibrations are assigned to $\nu_{as}(NO_2)$, $\nu_s(NO_2)$, δ(ONO), $\rho_w(NO_2)$ and ν(Ni— N), respectively. The positions of these bands indicate coordination of thiocyanate, cyanate and nitrite through the nitrogen atom in all cases [7].

Action of chlorine and hydrogen chloride

With the object of studying the stability of the nickel—carbon bond and exploring the possibility of formation of nickel compounds of higher oxidation and coordination numbers, the action of gaseous HCl and Cl_2 on the solutions of the new compounds was examined. The passage of gaseous hydrogen chloride through chloroform solutions of the compounds [NiX(C_6Cl_5)(dpe)] in no case led to replacement of the pentachlorophenyl group by chloride. This is in agreement with the inertness of the metal—carbon bond observed in other compounds containing the pentachlorophenyl group [1]. The anionic ligand X was replaced by Cl in the compounds with X = NCO, NCS, N_3, NO_2 and CN; but no replacement was observed for [NiBr(C_6Cl_5)(dpe)] and [NiI(C_6Cl_5)(dpe)].

These results are in agreement with those found for the compounds *trans*-[NiX(C_6Cl_5)(PPh_3)$_2$] [1] with the exception of the compound with X = NCS. The different behaviour in this case may be attributed to a greater *trans* effect by the phosphine groups compared with pentachlorophenyl.

Passage of chlorine through a carbon tetrachloride solution of [NiCl(C_6Cl_5)-

(dpe)] caused decomposition of the compound in a few seconds, On the basis of the identified products the process may be represented as follows:

$[NiCl(C_6Cl_5)(dpe)] + Cl_2 \rightarrow C_6Cl_6 + dpe + NiCl_2$

The action of the stoichiometric quantity of chlorine dissolved in CCl_4 gave the same result but the decomposition was slower.

Experimental

The solvents used were dried over molecular sieves. The preparation of C_6Cl_5MgCl was carried out under dry oxygen-free nitrogen. The ligand dpe and $[NiCl_2(dpe)]$ were prepared by literature procedures [8,9].

Preparation of $[NiCl(C_6Cl_5)(dpe)]$

A solution of C_6Cl_5MgCl was prepared from Mg (0.36 g) C_6Cl_6 (4.2 g) and THF (15 ml) (C_2H_5MgBr being used as initiator), was added at room temperature to 2.7 g of $[NiCl_2(dpe)]$. The yellow solid was filtered off, washed with water, recrystallized from an ethanol/chloroform mixture (1/3) and dried in vacuo. The yield was about 75%.

Preparation of $[NiX(C_6Cl_5)(dpe)]$ ($X = Br$, I, NCS, NCO, N_3 and NO_2)

The compounds were prepared in good yields (80-90%) by refluxing for 2-6 h a solution of $[NiCl(C_6Cl_5)(dpe)]$ 1.0 g in 100 ml of acetone with an excess of the appropriate alkali metal salt (LiBr, KI, KNCO, KNCS, NaN_3 and KNO_2). After filtering off of the alkali 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 $[Ni(CN)(C_6Cl_5)(dpe)]$

Silver cyanide (0.13 g) was added to $[NiCl(C_6Cl_5)(dpe)]$ (0.52 g) in acetone (50 ml) at room temperature. After 15 minutes, the AgCl formed was filtered off and the product was separated and recrystallized as above. The yield was about 60%.

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 [10]. 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 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 were accurate to ± 2 cm^{-1}.

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