Journal of Organometallic Chemistry, 121 (1976) 265—269
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ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS CONTAINING PHOSPHINE AND PERCHLOROARYL LIGANDS

IV *. NEUTRAL AND CATIONIC 1,2-BIS(DIPHENYLPHOSPHINOETHANE)-PENTACHLOROPHENYLNICKEL COMPLEXES

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(Received May 12th, 1976)

Summary

New stable complexes [NiX(C_6Cl_5)(dpe)] (X = NO_3, CH_3COO, C_6Cl_5O; dpe = 1,2-bis(diphenylphosphino)ethane) and [NiL(C_6Cl_5)(dpe)]ClO_4 (L = pyridine, imidazole, 3,5-dimethylpyrazole, α-, β- and γ-picoline) have been prepared from [Ni(ClO_4)(C_6Cl_5)(dpe)]. Their IR and PMR spectra are described and discussed The compound [NiCl(C_6Cl_5)(bipy)] has been prepared from C_6Cl_5MgCl and [$NiCl_2$(bipy)]. New complexes of silver(I) of the type [Ag(dpe)]X (X = NO_3, CH_3COO, and ClO_4) have been obtained from the action of an excess of AgX on [NiCl(C_6Cl_5)(dpe)].

Introduction

Organometallic compounds of transition metals containing perchlorate groups are useful synthetic intermediates because of the poor coordinating ability of the ClO_4 group, which can be readily replaced by other anionic or neutral ligands. In the latter case cationic complexes are formed in which the ClO_4 group functions as the anion [2].

From [Ni(ClO_4)(C_6Cl_5)(dpe)] the preparations of the new nickel cationic complexes [NiL(C_6Cl_5)(dpe)]ClO_4 (L = imidazole (Im), 3,5-dimethylpyrazole (3,5-$(CH_3)_2$pyr), pyridine (Py), α-, β- and γ-picoline (pic) and of neutral complexes with formula [NiX(C_6Cl_5)(dpe)] (X = NO_3, CH_3COO, and C_6Cl_5O) are described in this paper.

The three neutral complexes could not be made by the addition of the ap-

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* For part III see ref. 1.

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propriate alkali metal salt to acetone solutions of [$NiCl(C_6Cl_5)(dpe)$] [3] or by the action of silver salts of the appropriate anion. In the latter case this is because of decomposition of the organonickel compounds and formation of silver(I) complexes of the formula [Ag(dpe)]X.

Results and discussion

Preparation and properties

A solution of [$Ni(ClO_4)(C_6Cl_5)(dpe)$] was prepared by adding the stoichiometric quantity of $AgClO_4$ to an acetone solution of [$NiCl(C_6Cl_5)(dpe)$] and filtering off the AgCl, but it could not be isolated as a solid; concentration of the solution in vacuo gave the compound [$Ni(dpe)_2$](ClO_4)$_2$ described by Hudson et al. [4]. However from the acetone solutions of [$Ni(ClO_4)(C_6Cl_5)(dpe)$] it was possible to isolate the cationic complexes [$NiL(C_6Cl_5)(dpe)$]ClO_4 (L = imidazole, 3,5-dimethylpyrazole, pyridine, and α-, β-, or γ-picoline).

$$[Ni(ClO_4)(C_6Cl_5)(dpe)] + L \rightarrow [NiL(C_6Cl_5)(dpe)]ClO_4$$

The addition of alkali metal salts of the anions NO_3^-, CH_3COO^-, and $C_6Cl_5O^-$ to acetone solutions of [$Ni(ClO_4)(C_6Cl_5)(dpe)$] leads to the formation of the new compounds [$NiX(C_6Cl_5)(dpe)$] (X = NO_3, CH_3COO, and C_6Cl_5O).

Only the stoichiometric amount of $AgClO_4$ is used in the preparation of the solution of [$Ni(ClO_4)(C_6Cl_5)(dpe)$], since an excess of the salt causes the breakdown of [$NiCl(C_6Cl_5)(dpe)$] with formation of [Ag(dpe)]ClO_4. The same type of reaction occurs on adding an excess of $AgNO_3$ or $AgCH_3OO$ to acetone solutions of [$NiCl(C_6Cl_5)(dpe)$]; the products in this case are [Ag(dpe)]NO_3 and [Ag(dpe)]CH_3COO.

These silver(I) complexes, not previously reported are more easily prepared by mixing equimolar amounts of the appropriate salts and diphosphine (dpe) in warm ethanol. The perchlorate and nitrate salts show molar conductivities in nitrobenzene of 22.0 and 20.2 ohm^{-1} cm^2 mol^{-1}, respectively. The low solubility of the acetate in the ordinary organic solvents precludes the determination of its Λ. The IR spectra of these substances show bands due to the acetate anion at 1555s, 1405s, 920m, 650m and 610m cm^{-1}; those of perchlorate at 1030—1170vs (br), 920m and 620s cm^{-1}; and those of nitrate at 1380vs and 820w cm^{-}

No nickel compound containing two C_6Cl_5 groups has been obtained despite numerous attempts [5]. Addition of ether solutions of C_6Cl_5Li or THF solutions of C_6Cl_5MgCl to acetone solutions of [$Ni(ClO_4)(C_6Cl_5)(dpe)$] gave only [$NiCl(C_6Cl_5)(dpe)$]. Similarly, the action of THF solutions of C_6Cl_5MgCl on [$NiCl_2(bipy)$] does not give the disubstituted derivative, but instead, [$NiCl(C_6Cl_5)(bipy)$]. These results are in agreement with the *ortho* effect exhibited by the compounds containing the C_6Cl_5 group [6]. The existence of [$Pd(C_6Cl_5)_2(bipy)$] is attributed by Rausch et al. [7] to the larger covalent radius of Pd compared with that of Ni.

All the new organometallic compounds prepared are air-stable as solids and in solution. They are readily soluble in chloroform, carbon tetrachloride and benzene, and scarcely soluble in ethanol, ether, and hexane. Analyses and decomposition temperatures are given in Table 1.

Values of the molar conductivity in acetone at 25° C correspond to non-elec-

TABLE 1

ANALYTICAL DATA

Compound	Found (calcd.) (%)					Decomposition temperatures (°C)
	C	H	Cl	N	Ni	
$[NiPy(C_6Cl_5)(dpe)]ClO_4$[a]	50.2	3.3	24.0	1.7	6.5	232—235
	(50.23)	(3.30)	(24.04)	(1.58)	(6.6)	
$[NiIm(C_6Cl_5)(dpe)]ClO_4$	48.1	3.3	24.3	3.2	6.7	234—236
	(48.11)	(3.23)	(24.34)	(3.21)	(6.7)	
$[Ni[3,5\text{-}(CH_3)_2pyr](C_6Cl_5)(dpe)]ClO_4$	49.3	3.61	23.6	3.4	6.4	231—234
	(49.27)	(3.57)	(23.59)	(3.11)	(6.51)	
$[Ni(\alpha\text{-}pic)(C_6Cl_5)(dpe)]ClO_4$	50.4	3.4	23.5	1.4	6.5	170—175
	(50.77)	(3.47)	(23.66)	(1.55)	(6.52)	
$[Ni(\beta\text{-}pic)(C_6Cl_5)(dpe)]ClO_4$	51.6	3.7	23.3	1.3	6.4	217—218
	(50.77)	(3.47)	(23.66)	(1.55)	(6.52)	
$[Ni(\gamma\text{-}pic)(C_6Cl_5)(dpe)]ClO_4$	50.8	3.4	23.2	1.8	6.4	223—225
	(50.77)	(3.47)	(23.66)	(1.55)	(6.52)	
$[Ni(NO_3)(C_6Cl_5)(dpe)]$	50.1	3.2	23.0	1.6	7.6	224—227
	(50.03)	(3.15)	(23.08)	(1.82)	(7.64)	
$[Ni(CH_3COO)(C_6Cl_5)(dpe)]$	51.1	3.3	23.3	—	7.6	229—232
	(53.36)	(3.55)	(23.16)		(7.64)	
$[Ni(C_6Cl_5O)(C_6Cl_5)(dpe)]$	47.0	2.5	36.7	—	6.1	188—192
	(46.47)	(2.49)	(36.49)		(6.04)	
$[NiCl(C_6Cl_5)(bipy)]$	38.2	1.6	42.5	5.4	11.7	178—180
	(38.45)	(1.61)	(42.56)	(5.60)	(11.74)	

[a] Py = pyridine, Im = imidazole, pyr = pyrazole, pic = picoline.

trolytes for the neutral compounds ($\Lambda \simeq 5$ ohm^{-1} cm^2 mol^{-1}), and to AB-type electrolytes for the cationic complexes ($\Lambda \simeq 150$ ohm^{-1} cm^2 mol^{-1}). Magnetic measurements show diamagnetic behaviour, indicating square-planar geometry.

IR spectra

The IR spectra of the new compounds show the bands due to the dpe ligand [8] and coordinated pentachlorophenyl [9]. Further bands are observed in the IR spectra of the neutral $[NiX(C_6Cl_5)(dpe)]$ complexes at 1480s, 1290s, 1010w and 800w cm^{-1} for X = NO_3; at 1370m and 1720m cm^{-1} for X = CH_3COO; at 1530s, 1400vs, 1360m, 995m and 770s cm^{-1} for X = C_6Cl_5O. The bands due to the ClO_4^- ion are observed in the cationic complexes at 1090vs(br) (ν_3), 620m (ν_4) and 930w (ν_1) cm^{-1}. The bands due to the ligand L are listed in Table 2.

PMR spectra

PMR spectra of the cationic complexes exhibit the signals indicated in Table 2. The triplet which in dpe is centered at τ 7.9 ppm [10], disappears because of the loss of free rotation upon coordination; the four aliphatic protons and the two phosphorus atoms form an AA'BB'XY system and, accordingly, only a slight shift of the base line is observed in the region between τ 6.5 and 8.5 ppm.

The spectrum of $[Ni[3,5\text{-}(CH_3)_2pyr](C_6Cl_5)(dpe)]ClO_4$ shows two singlets at τ 7.78 and 8.32 ppm. The latter exhibits a strong diamagnetic shift with respect to the only signal in the spectrum of free 3,5-dimethylpyrazole (τ 7.79 ppm).

TABLE 2

INFRARED FREQUENCIES (cm^{-1}) OF THE LIGAND L AND PMR SPECTRA OF [$NiL(C_6Cl_5)(dpe)$]ClO_4 (in $CDCl_3$)

	IR	PRM (τ(ppm))
[$NiPy(C_6Cl_5)(dpe)$]ClO_4 [a]	1600s, 1440s, 1210s	1.30 $(2H)_\alpha$, 2.28 $(H)_\gamma$ 2.49, 2.74 (C_6H_5) [b]
[$NiIm(C_6Cl_5)(dpe)$]ClO_4	1545w, 1500w, 845w	2.35, 2.50 (C_6H_5), 2.80 (H_4) 3.08 (H_5) [c]
[$Ni[3,5\text{-}(CH_3)_2pyr](C_6Cl_5)(dpe)$]$ClO_4$ [d]	1580m, 1345w, 800w	2.46, 2.56 (C_6H_5), 4.32 (H), 7.78 (CH_3) 8.32 (CH_3) [e]
[$Ni(\alpha\text{-pic})(C_6Cl_5)(dpe)$]$ClO_4$	1605s, 1570m, 805w, 495w	2.45, 2.65 (C_6H_5), 7.26 (CH_3) [f]
[$Ni(\beta\text{-pic})(C_6Cl_5)(dpe)$]$ClO_4$	1605m, 1020w, 810m	2.45, 2.56 (C_6H_5), 7.94 (CH_3) [f]
[$Ni(\gamma\text{-pic})(C_6Cl_5)(dpe)$]$ClO_4$	1615s, 1500m, 1205m, 820s, 500w	2.45, 2.70 (C_6H_5), 7.70 (CH_3) [f]

[a] See footnote [a] Table 1. [b] $\tau(2H)_\beta$ overlapped with C_6H_5 resonance. [c] $\tau(H_2)$ overlapped with C_6H_5 resonance. [d] In DMSO. [e] See text. [f] τ(4H) overlapped with C_6H_5 resonance.

Upon coordination of the latter restriction of rotation due to steric hindrance raises the possibility of the existence of two isomers; the methyl group lies oposite to a phenyl group of the phosphine in one isomer but not in the other. Since the signal appearing at τ 8.32 ppm corresponds to a methyl group exhibiting significant diamagnetic behaviour the isomer obtained appears to be of the first type.

Experimental

The solution of C_6Cl_5MgCl was prepared under oxygen-free nitrogen. [$NiCl(C_6Cl_5)(dpe)$] and [$NiCl_2(bipy)$] were prepared by published methods [3,11].

Preparation of the acetone solution of [$Ni(ClO_4)(C_6Cl_5)(dpe)$]

Silver perchlorate (0.20 g) was added to [$NiCl(C_6Cl_5)(dpe)$] (0.74 g) in acetone (100 ml) at room temperature and the AgCl formed was filtered off.

Preparation of [$NiX(C_6Cl_5)(dpe)$] (X = NO_3, CH_3COO and C_6Cl_5O)

The compounds were prepared by adding a slight excess of the alkali metal salt (KNO_3, KCH_3COO or NaC_6Cl_5O) to the solution of [$Ni(ClO_4)(C_6Cl_5)(dpe)$]. The mixture was kept at room temperature for two hours and the $KClO_4$ formed was filtered off. The solution was concentrated in vacuo and the solid which formed was filtered off, recrystallized from chloroform/ethanol (3/1), and dried under vacuum. The yield was about 60%.

Preparation of [$NiL(C_6Cl_5)(dpe)$]ClO_4 (L = pyridine, imidazole, 3,5-dimethylpyrazole, α-, β- and γ-picoline)

The compounds were obtained in good yields (75%) by refluxing 100 ml of an acetone solution of [$Ni(ClO_4)(C_6Cl_5)(dpe)$] with a slight excess of the appropriate organic base for an hour. The solution was concentrated under reduced pressure and the solid obtained was recrystallized from chloroform/ethanol (3 : 1) and dried in vacuo.

Preparation of [NiCl(C_6Cl_5)(bipy)]

A solution of C_6Cl_5MgCl, prepared from Mg (0.36 g), C_6Cl_6 (4.2 g), THF (15 ml) (with C_2H_5MgBr as initiator) was added to 2.84 g of [$NiCl_2$(bipy)]. The yellow solid was filtered off, washed with water, recrystallized from chloroform/ethanol (3 : 1) and dried in vacuo. The yield was about 70%.

Preparation of [Ag(dpe)]X (X = NO_3, CH_3COO and ClO_4)

The compounds were prepared by adding a solution of dpe (1 mmol) in hot ethanol to a solution of the appropriate silver salt (1 mmol) in 20 ml of ethanol/water (1 : 1). The mixture was stirred for 15 min and then cooled. The solid was washed with water and ethanol, and dried in vacuo. The yields were about 90%.

Anal. Found: C, 50.7; H, 4.0; Ag, 18.1; m.p. 234—235°C (decomp.). $C_{26}H_{24}AgClO_4P_2$ calcd.: C, 51.55; H, 3.99; Ag, 17.80%.

Anal. Found: C, 55.0; H, 4.2; N, 2.7; Ag, 19.4; m.p. 272—275°C (decomp.). $C_{26}H_{24}AgNO_3P_2$ calcd.: C, 54.95; H, 4.25; N, 2.46; Ag, 18.99%.

Anal. Found: C, 58.7; H, 4.8; Ag, 19.3; m.p. 262—263°C (decomp.). $C_{28}H_{27}AgO_2P_2$ calcd.: C, 59.49; H, 4.81; Ag, 19.08%.

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 Schöinger's method. Nickel was determined gravimetrically and silver volumetrically after destruction of the complexes with a boiling nitric acid/sulfuric acid mixture.

Spectra

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

References

1 J.M. Coronas, G. Muller and J. Sales, Syn. Inorg. Metal-org. Chem., 6 (1976) 217.
2 F. Bonati and G. Minguetti, J. Organometal. Chem., 22 (1970) 1956; R. Usón, P. Royo, and J. Fornies, Syn. Inorg. Metal-org. Chem., 3 (1973) 237.
3 J.M. Coronas, O. Rossell and J. Sales, J. Organometal. Chem., 97 (1975) 473.
4 M.J. Hudson, R.S. Nyholm and M.H.B. Stiddard, J. Chem. Soc. A, (1968) 40.
5 M.D. Rausch, F.E. Tibbets and H.B. Gordon, J. Organometal. Chem., 5 (1966) 493; M.D. Rausch and F.E. Tibbetts, Inorg. Chem., 9 (1970) 512; J.M. Coronas and J. Sales, J. Organometal. Chem., 94 (1975) 107.
6 J. Chatt and B.L. Shaw, J. Chem. Soc., (1960) 1718.
7 M.D. Rausch and F.E. Tibbetts, J. Organometal. Chem., 21 (1970) 487.
8 M. Bacci, Spectrochim. Acta A, 28 (1972) 2286.
9 J. Casabó, J.M. Coronas and J. Sales, Inorg. Chim. Acta, 11 (1974) 5.
10 H.G. Horn and K. Sommer, Spectrochim. Acta A, 27 (1971) 1049.
11 M. Uchino, K. Asagi, A. Yamamoto and G. Ikeda, J. Organometal. Chem., 84 (1975) 93.