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# NEUTRAL AND CATIONIC PENTAFLUOROPHENYLNICKEL(II) COMPLEXES

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## Summary

Metathetical reactions of $Br(C_6F_5)Ni(PPh_3)_2$ with metal salts MX (NaI, $NaNO_2$, $NaNO_3$, KCN, KSCN, $AgClO_4$) have given the corresponding $X(C_6F_5)Ni(PPh_3)_2$ complexes. The perchlorate group of the complex $(O_3ClO)Ni(C_6F_5)(PPh_3)_2$ is readily displaced. In this way cationic complexes $[(C_6F_5)Ni(PPh_3)_2L]ClO_4$ have been prepared with L = $PPh_3$, $PEt_3$, P-t-$Bu_3$, $AsPh_3$, $C_5H_5N$, $OPPh_3$, $SPPh_3$, $H_2O$, or $CH_3NO_2$.

## Introduction

We recently described [1] the isolation in high yield of pure halopentafluorophenylnickel(II) complexes by the oxidation with $XTl(C_6F_5)_2$ (X = Br, I) of nickel(I) complexes $XNiL_3$ and $XNi(CO)_2(PPh_3)_2$. We now report the results obtained in substitution reactions which give new neutral and cationic pentafluorophenylnickel(II) complexes.

## Results and discussion

### *(a) Preparative results*

Reaction 1 takes place when solutions of bromopentafluorophenylbis(triphenylphosphine)nickel(II) are treated with salts such as NaI, $NaNO_2$, $NaNO_3$, KSCN, KCN and $AgClO_4$ (see Table 1).

$$Br(C_6F_5)Ni(PPh_3)_2 + MX \rightarrow X(C_6F_5)Ni(PPh_3)_2 + MBr \qquad (1)$$

The reaction with an excess of solid KCN gives $(CN)_2Ni(PPh_3)_2$ as the sole product. If the CN/Ni ratio is 1/1, the expected neutral pentafluorophenyl complex is obtained, and it is clear that the excess of KCN causes cleavage of the $C_6F_5$—Ni bond.

The reaction with $AgClO_4$ must be carried out in benzene to avoid the formation of cationic derivatives, which would be formed in polar solvents.

Addition of ligands to benzene solutions of complex VI gives cationic com-

TABLE 1

ANALYSES FOR PENTAFLUOROPHENYLNICKEL(II) COMPLEXES

| No. | Complex | Analyses found (calcd.) (%) | | | |
|---|---|---|---|---|---|
| | | C | H | N or Hal. | Ni |
| I | $I(C_6F_5)Ni(PPh_3)_2$ | 57.91 | 3.63 | 14.18 | 6.63 |
| | | (57.50) | (3.42) | (14.47) | (6.69) |
| II | $NO_2(C_6F_5)Ni(PPh_3)_2$ | 63.19 | 4.35 | 1.69 | 7.25 |
| | | (63.37) | (3.79) | (1.76) | (7.38) |
| III | $NO_3(C_6F_5)Ni(PPh_3)_2$ | 61.98 | 3.93 | 1.71 | 7.02 |
| | | (62.12) | (3.69) | (1.72) | (7.23) |
| IV | $CN(C_6F_5)Ni(PPh_3)_2$ | 67.03 | 4.23 | 1.73 | 7.24 |
| | | (66.56) | (3.87) | (1.80) | (7.57) |
| V | $SCN(C_6F_5)Ni(PPh_3)_2$ | 64.02 | 4.26 | 1.68 | 7.12 |
| | | (63.92) | (3.71) | (1.73) | (7.27) |
| VI | $ClO_4(C_6F_5)Ni(PPh_3)_2$ | 59.65 | 3.87 | 4.72 | 7.04 |
| | | (59.36) | (3.55) | (4.17) | (6.91) |
| VII | $[(C_6F_5)Ni(PPh_3)_3]ClO_4$ | 64.97 | 4.27 | | 4.96 |
| | | (64.74) | (4.04) | | (5.28) |
| VIII | $[(C_6F_5)Ni(PPh_3)_2PEt_3]ClO_4$ | 59.68 | 4.39 | | 5.68 |
| | | (59.57) | (4.65) | | (6.07) |
| IX | $[(C_6F_5)Ni(PPh_3)_2P\text{-}t\text{-}Bu_3]ClO_4$ | 61.58 | 5.43 | | 5.66 |
| | | (61.87) | (5.44) | | (5.58) |
| X | $[(C_6F_5)Ni(PPh_3)_2AsPh_3]ClO_4$ | 62.34 | 4.06 | | 4.83 |
| | | (62.35) | (3.89) | | (5.08) |
| XI | $[(C_6F_5)Ni(PPh_3)_2py]ClO_4$ | 60.93 | 4.03 | 1.49 | 5.98 |
| | | (60.84) | (3.77) | (1.51) | (6.32) |
| XII | $[(C_6F_5)Ni(PPh_3)_2OPPh_3]ClO_4$ | 63.65 | 4.06 | | 4.65 |
| | | (63.85) | (3.99) | | (5.20) |
| XIII | $[(C_6F_5)Ni(PPh_3)_2SPPh_3]ClO_4$ | 62.85 | 3.88 | | 4.86 |
| | | (63.00) | (3.93) | | (5.13) |
| XIV | $[(C_6F_5)Ni(PPh_3)_2H_2O]ClO_4$ | 58.63 | 3.48 | | 6.28 |
| | | (58.19) | (3.69) | | (6.77) |
| XV | $[(C_6F_5)Ni(PPh_3)_2CH_3NO_2]ClO_4$ | 56.91 | 3.91 | 1.42 | 6.02 |
| | | (56.72) | (3.62) | (1.53) | (6.45) |

plexes VII—XV according to eq. 2:

$$O_3ClONi(C_6F_5)(PPh_3)_2 + L \rightarrow [(C_6F_5)Ni(PPh_3)_2L]ClO_4 \qquad (2)$$

### *(b) Properties of complexes*

Complexes I—V are soluble in benzene, acetone and chloroform and insoluble in ethyl ether and hexane. They are stable in the air at room temperature and nonconductors in acetone or nitromethane. Complex VI is stable in a dry atmosphere, but it is immediately destroyed in the presence of moisture, and the IR spectra always show absorptions due to coordinated water. Nevertheless it is nonconducting in benzene, and the solution is stable enough to be used for preparative purposes.

All the cationic complexes behave as 1 : 1 electrolytes (see Table 2). Even solutions of VI in polar solvents such as acetone show conductivities corresponding to a 1 : 1 electrolyte because the solvent displaces the perchlorate anion which has a weaker donor ability, although the acetone complex is too unstable to be isolated in the solid.

All the cationic complexes VII—XV are stable as solids, and some of them melt without decomposition between 180 and 205°C.

### *(c) IR spectra*

Characteristic vibrations of triphenylphosphine [2] and the pentafluorophenyl group [3] are present in all the complexes. Absorptions due to nitro and nitrite groups would lie in regions containing intense bands assigned to internal vibrations of the ligands, and so it is impossible to distinguish clearly between the two types of coordination in complex II. Complex III shows an intense absorption at 1265 $cm^{-1}$ which must be assigned to the $\nu(NO_2)_{sym}$ frequency of a monocoordinated $NO_3$ $C_{2v}$ group [4]. The cyano complex IV shows an absorption of medium intensity at 2120 $cm^{-1}$ due to the $\nu(C\equiv N)$ stretching vibration. Similarly, complex V shows the $\nu(C\equiv N)$ frequency at 2100 $cm^{-1}$, which indicates the coordination through the sulphur atom, i.e. Ni—SCN [5]. The unavoidable presence of water in mulls handled in the air prevents a reliable assignment of the IR absorptions of complex VI.

All the cationic complexes show the characteristic broad absorption of the free $ClO_4$ anion at 1090 $cm^{-1}$ [6]. Furthermore, the spectra of these complexes exhibit new absorptions corresponding to the new ligand intoduced, some of these are displaced with respect to those in the free ligand. Thus, complex XII shows a band at 1180 $cm^{-1}$ which must be assigned to the stretching vibration $\nu(P—O)$ located at 1195 $cm^{-1}$ in the free ligand. This displacement results from the reduction in the P—O bond order upon coordination of the oxygen to the metal atom [7]. Similarly the absorption at 637 $cm^{-1}$ for the free triphenylphosphine sulphide is displaced to 620 $cm^{-1}$ in complex XIII. The effect is the same as that observed for the oxide [8]. However the displacement in both cases is lower than that for other nickel(II) complexes.

The spectrum of complex XIV shows a broad band at 3200—3400 $cm^{-1}$ which reveals the presence of coordinated water. Finally, complex XV shows an absorption at 1515 $cm^{-1}$ which must be assigned to the stretching $\nu(NO_2)_{asym}$ produced by coordination of the ligand through oxygen to the metal.

TABLE 2

CONDUCTIVITIES OF CATIONIC PENTAFLUOROPHENYLNICKEL(II) COMPLEXES IN ACETONE

| No. | Complex | Concentration ($10^{-4}$ mol $l^{-1}$) | Conductivity ($ohm^{-1}$ $cm^2$ $mol^{-1}$) |
|---|---|---|---|
| VI | $ClO_4(C_6F_5)Ni(PPh_3)_2$ | 6.18 | 74.7 |
| (in benzene) | | 6.35 | 5.46 |
| VII | $[(C_6F_5)Ni(PPh_3)_3]ClO_4$ | 6.70 | 70.2 |
| VIII | $[(C_6F_5)Ni(PPh_3)_2PEt_3]ClO_4$ | 5.70 | 65.1 |
| IX | $[(C_6F_5)Ni(PPh_3)_2P\text{-t-}Bu_3]ClO_4$ | 6.33 | 68.4 |
| X | $[(C_6F_5)Ni(PPh_3)_2AsPh_3]ClO_4$ | 4.03 | 76.1 |
| XI | $[(C_6F_5)Ni(PPh_3)_2py]ClO_4$ | 4.00 | 65.5 |
| XII | $[(C_6F_5)Ni(PPh_3)_2OPPh_3]ClO_4$ | 5.27 | 69.2 |
| XIII | $[(C_6F_5)Ni(PPh_3)_2SPPh_3]ClO_4$ | 3.28 | 71.4 |
| XIV | $[(C_6F_5)Ni(PPh_3)_2H_2O]ClO_4$ | 4.69 | 87.7 |
| XV | $[(C_6F_5)Ni(PPh_3)_2CH_3NO_2]ClO_4$ | 8.00 | 63.2 |

TABLE 3

VISIBLE AND IR SPECTRAL DATA FOR PENTAFLUOROPHENYLNICKEL(II) COMPLEXES (in benzene and KBr pellets respectively)

| No. | Complex | $\nu$ ($10^3$ cm$^{-1}$) [log $\epsilon_{max}$] $^1A_{1g} \rightarrow {}^1A_{2g}$ | IR frequencies $\nu$ (cm$^{-1}$) |
|---|---|---|---|
| I | $I(C_6F_5)Ni(PPh_3)_2$ | 23.2[2.85] | |
| II | $NO_2(C_6F_5)Ni(PPh_3)_2$ | 25.1[1.89] | |
| III | $NO_3(C_6F_5)Ni(PPh_3)_2$ | 25.6[1.39] | 1265 $\nu(NO_2)_{sym}$ |
| IV | $CN(C_6F_5)Ni(PPh_3)_2$ | 26.7[2.51] | 2120 $\nu(C{\equiv}N)$ |
| V | $SCN(C_6F_5)Ni(PPh_3)_2$ | 23.8[2.97] | 2100 $\nu(C{\equiv}N)$ |
| VI | $ClO_4(C_6F_5)Ni(PPh_3)_2$ | 23.6[2.32] | |
| VII | $[(C_6F_5)Ni(PPh_3)_3]ClO_4$ | 23.2[2.45] | |
| VIII | $[(C_6F_5)Ni(PPh_3)_2PEt_3]ClO_4$ | 23.4[2.17] | |
| IX | $[(C_6F_5)Ni(PPh_3)_2P\text{-}t\text{-}Bu_3]ClO_4$ | 23.3[2.04] | |
| X | $[(C_6F_5)Ni(PPh_3)_2AsPh_3]ClO_4$ | 23.2[2.46] | |
| XI | $[(C_6F_5)Ni(PPh_3)_2py]ClO_4$ | 23.8[1.81] | |
| XII | $[(C_6F_5)Ni(PPh_3)_2OPPh_3]ClO_4$ | 24.0[2.19] | 1180 $\nu$(P—O) |
| XIII | $[(C_6F_5)Ni(PPh_3)_2SPPh_3]ClO_4$ | 23.8[2.03] | 620 $\nu$(P—S) |
| XIV | $[(C_6F_5)Ni(PPh_3)_2H_2O]ClO_4$ | 24.1[1.75] | |
| XV | $[(C_6F_5)Ni(PPh_3)_2CH_3NO_2]ClO_4$ | 23.2[2.62] | 1515 $\nu(NO_2)_{asym}$ |

### (d) Visible-UV spectra

In agreement with results obtained for other square-planar nickel(II) complexes [9], all the pentafluorophenyl derivatives here described exhibit only an absorption which can be assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition along with intense absorptions between 29000 and 40000 cm$^{-1}$ (log $\epsilon_{max}$ 3.5—4.1) due to charge transfers. The spectral data are given in Table 3.

The higher frequencies of the *d—d* transition for complexes II—IV are associated with anions having a delocalized $\pi$ system, such as CN, $NO_2$ and $NO_3$. All the other complexes have the *d—d* transition roughly at the same frequency, between 23200 and 24000 cm$^{-1}$, independent of the nature of the donor atom. This implies the small extension of the $\pi$ bond interaction which is as significant with ligands of $\pi$ donor atoms such as oxygen as with $\pi$ acceptor ligands such as phosphine and arsine. It would be pointless to attempt to define a sequence of the ligands according with their capacity to cause *d* orbital splittings because the observed differences are too small. It can be concluded, however, that cyanide behaves as a high field ligand and anions with delocalized $\pi$ systems produce higher fields than other types of ligand.

## Experimental

The IR spectra were recorded on a Perkin—Elmer 457 spectrophotometer using KBr pellets. Visible UV spectra were recorded on a Perkin—Elmer 124 spectrophotometer using benzene as solvent. The C, H analyses were made with a Perkin—Elmer 240 microanalyzer. Magnetic susceptibilities were measured at room temperature by the Gouy method.

Bromopentafluorophenylbis(triphenylphosphine)nickel(II) was prepared by oxidation or $BrNi(PPh_3)_3$ with $BrTl(C_6F_5)_2$ [1].

*$I(C_6F_5)Ni(PPh_3)_2$ (I).* An excess of NaI (0.105 g; 0.70 mmol) is added to a

solution of $Br(C_6F_5)Ni(PPh_3)_2$ (0.39 g; 0.50 mmol) in acetone and the mixture stirred for 3 h at room temperature. The solution is evaporated to dryness and the solid residue repeatedly washed with water. Recrystallization from acetone/ethanol gives yellow crystals of I, m.p. 270°C (dec.).

*$NO_2(C_6F_5)Ni(PPh_3)_2$ (II).* $NaNO_2$ (0.11 g; 1.50 mmol) is added to a solution of $Br(C_6F_5)Ni(PPh_3)_2$ (0.83 g; 1.0 mmol) in acetone with two or three drops of water. The subsequent procedure is as for I. II forms yellow crystals, m.p. 220°C (dec.).

*$NO_3(C_6F_5)Ni(PPh_3)_2$ (III).* $NaNO_3$ (0.08 g; 0.90 mmol) is added to a solution of $Br(C_6F_5)Ni(PPh_3)_2$ (0.75 g; 0.90 mmol) in acetone with two drops of water. The mixture is stirred for 3 h at room temperature and evaporated to dryness. The solid residue is extracted with chloroform. Addition of hexane to the concentrated chloroform solution gives III as yellow crystals, m.p. 170°C.

*$CN(C_6F_5)Ni(PPh_3)_2$ (IV).* KCN (0.052 g; 0.80 mmol) is added to a solution of $Br(C_6F_5)Ni(PPh_3)_2$ (0.66 g; 0.80 mmol) in acetone and the subsequent procedure is as for I. Recrystallization from acetone/ethanol gives yellow crystals of IV, m.p. 230°C (dec.).

With a CN/Ni = 2 molar ratio, yellow crystals of $(CN)_2Ni(PPh_3)_2$ are obtained.

*$SCN(C_6F_5)Ni(PPh_3)_2$ (V).* An excess of KSN (0.078 g; 0.80 mmol) is added to a solution of $Br(C_6F_5)Ni(PPh_3)_2$ (0.50 g; 0.60 mmol) in acetone. After stirring for 3 h at room temperature the precipitate is filtered off. Addition of methanol to the concentrated acetone solution gives yellow crystals of V, m.p. 257°C with decomposition.

*$ClO_4(C_6F_5)Ni(PPh_3)_2$ (VI).* $AgClO_4$ (0.38 g; 1.94 mmol) is added to a solution of $Br(C_6F_5)Ni(PPh_3)_2$ (1.61 g; 1.94 mmol) in benzene (100 ml). The mixture is stirred for 4 h and the insoluble silver bromide is filtered off. Evaporation of the solvent gives a few crystals of VI, which must be handled under dry nitrogen for analytical determinations.

The filtered benzene solution of VI without any further purification was used for preparative purposes in reactions described below.

*$[(C_6F_5)Ni(PPh_3)_3]ClO_4$ (VII).* Triphenylphosphine (0.26 g; 1.0 mmol) is added to a benzene solution of VI (1.0 mmol). The mixture is stirred for 2 h at room temperature. Partial evaporation of the solvent gives VII as a yellow crystalline solid, which is recrystallized from chloroform/ethanol, m.p. 195°C.

*$[(C_6F_5)Ni(PPh_3)_2PEt_3]ClO_4$ (VIII).* Similarly, triethylphosphine gives VIII, m.p. 180°C.

*$[(C_6F_5)Ni(PPh_3)_2P\text{-}t\text{-}Bu_3]ClO_4$ (IX).* Tributylphosphine gives IX, which is recrystallized from chloroform/hexane as yellow crystals, m.p. 205°C.

*$[(C_6F_5)Ni(PPh_3)_2AsPh_3]ClO_4$ (X).* A procedure similar to that for IX gives X m.p. 203°C (dec.).

*$[(C_6F_5)Ni(PPh_3)_2py]ClO_4$ (XI).* An excess of pyridine (0.30 ml; 3.60 mmol) is added to a benzene solution of complex VI (0.33 g; 0.40 mmol). After stirring for 0.5 h the solution is evaporated to dryness. The residue is recrystallized from chloroform/ethanol to give greenish yellow crystals of XI, m.p. 200°C (dec.).

*$[(C_6F_5)Ni(PPh_3)_2OPPh_3]ClO_4$ (XII).* A solution in benzene (50 ml) of triphenylphosphine oxide (0.42 g; 1.50 mmol) and VI (1.25 g; 1.50 mmol) is stirred for 2 h at room temperature. XII separates as a yellow microcrystalline

precipitate. Recrystallization from chloroform/ethanol gives a solid of m.p. 180°C.

*$[(C_6F_5)Ni(PPh_3)_2SPPh_3]ClO_4$ (XIII).* By the same procedure as used for XII, triphenylphosphine sulphide gives XIII, m.p. 197°C.

*$[(C_6F_5)Ni(PPh_3)_2H_2O]ClO_4$ (XIV).* A suspension in water (30 ml) of a benzene solution of complex VI is stirred for a day at room temperature to give complex XIV as a microcrystalline solid. Recrystallization from chloroform/ethanol gives XIV of m.p. 193°C (dec.).

*$[(C_6F_5)Ni(PPh_3)_2CH_3NO_2]ClO_4$ (XV).* An excess of nitromethane (0.10 ml; 2.30 mmol) is added to a benzene solution of VI (1.93 g; 2.26 mmol). After 12 h at room temperature the yellow crystals of XV are separated, m.p. 207°C (dec.).

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