

Bispentafluorophenyl Nickel(II) Complexes

A. ARCAS and P. ROYO

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Murcia, Spain

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Solutions apparently containing $Ni(C_6F_5)_2$ are obtained by reaction of anhydrous $NiBr_2$ with $(C_6F_5)_2MgBr$ in THF. The addition of different ligands to these solutions gives four-coordinate nickel(II) complexes of the type $(C_6F_5)_2NiL_2$ [$L = PEt_3, PBu_3, PPh_3, AsPh_3, SbPh_3, OPPh_3, OAsPh_3, p$ -Dioxane]. Structural data for these compounds are obtained by visible-UV and IR spectroscopy and magnetic susceptibility measurements.

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Introduction

Bispentafluorophenyl nickel(II) complexes $(C_6F_5)_2NiL_2$ [$L = PEt_3, PPh_3, 2,2'$ -bipyridine] have been isolated [1] by the Grignard reaction on the corresponding bis-halo nickel(II) complexes. Smith and Tamborski described [2] the preparation of THF solutions containing $Co(C_6F_5)_2$ which cannot be isolated in the solid state.

As a part of our studies on transition metal pentafluorophenyl complexes [3] we have discovered a new preparative method to obtain bispentafluorophenyl nickel(II) complexes using solutions of “Ni- $(C_6F_5)_2$ ” as precursor.

Experimental

Materials

$(C_6F_5)_2MgBr$ was prepared by the method given in ref. [4]. Anhydrous $NiBr_2$ was obtained from the hexahydrate by heating at 140 °C for 3h.

Methods

Magnetic susceptibility was determined by the Gouy method at room temperature. Visible-UV spectra were recorded on a Perkin-Elmer 124 spectrophotometer using different solvents and diffuse reflectance for solids. The IR spectra were recorded in the region 250–4000 cm^{-1} on a Perkin-Elmer 457 spectrophotometer using nujol and KBr pellets. Conductivities were measured with a Phillips PW 9501/01 conductimeter. Melting points were measured with a Reichter microscope provided with

heating plate. Gas chromatographic analyses were performed on a Hewlett-Packard Gas chromatograph Mod. 5710 A. Mass spectra were recorded on a Hewlett-Packard spectrometer Mod. 5980 A.

Microanalyses

The C, H, analyses were made with a Perkin-Elmer 240 microanalyzer. Nickel was determined gravimetrically as the dimethylglyoximate [5].

Preparation of the Complexes

Solution of $Ni(C_6F_5)_2$

A freshly prepared and filtered solution of $(C_6F_5)_2MgBr$ (from 13 ml of C_6F_5Br ; 103 mmol) in THF (150 ml) was added to a suspension of anhydrous $NiBr_2$ (10 g; 45.76 mmol) in THF (50 ml). After refluxing for 4 h a red solution containing an insoluble white solid was obtained. The addition of dioxane (70 ml) separated most of the magnesium salt as the dioxane complex. After standing in the cold for 12h, the solid was filtered off and a yellow solution was obtained. The filtrate contained unreacted $NiBr_2$ as the THF or dioxane complex, excess of $(C_6F_5)_2MgBr$ and some magnesium salt. This solution was unchanged during storage for several weeks under dry nitrogen and was used for the following experiments.

$(C_6F_5)_2NiL_2$ complexes

In separate experiments, (8.5 mmol) solutions in THF of triethylphosphine, tri-*n*-butylphosphine, triphenylphosphine, triphenylarsine, triphenylstibine, triphenylphosphine oxide and triphenylarsine oxide were added to 50 ml of the yellow solution of $(C_6F_5)_2Ni$. Different color changes were observed depending on the ligand. Solutions were then evaporated to dryness under vacuum and solid residues were extracted with chloroform. The addition of ethanol to the previously concentrated chloroform solutions gave the crystalline organocomplexes. Yields 70–80%.

In a separate experiment 75 ml of the yellow $(C_6F_5)_2Ni$ solution were evaporated under vacuum at room temperature or by very mild heating to give

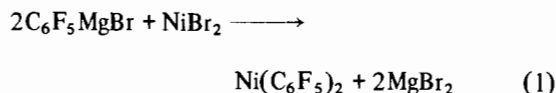
TABLE I. Analyses for Bis-pentafluorophenyl Nickel(II) Complexes.

No	Complex	Analyses found (calcd.) (%)		
		C	H	Ni
I	(C ₆ F ₅) ₂ Ni(Dioxane) ₂	42.2 (42.2)	3.2 (2.8)	11.0 (10.3)
II	(C ₆ F ₅) ₂ Ni(PEt ₃) ₂	46.6 (45.8)	4.9 (4.8)	9.2 (9.3)
III	(C ₆ F ₅) ₂ Ni(Pn-Bu ₃) ₂	54.0 (54.2)	7.3 (6.8)	7.4 (7.4)
IV	(C ₆ F ₅) ₂ Ni(PPh ₃) ₂	63.4 (62.8)	3.3 (3.3)	6.8 (6.4)
V	(C ₆ F ₅) ₂ Ni(AsPh ₃) ₂	56.1 (57.3)	3.1 (3.0)	5.8 (5.8)
VI	(C ₆ F ₅) ₂ Ni(SbPh ₃) ₂	51.7 (52.5)	3.1 (2.7)	5.5 (5.3)
VII	(C ₆ F ₅) ₂ Ni(OPPh ₃) ₂	60.4 (60.7)	3.5 (3.2)	6.3 (6.2)
VIII	(C ₆ F ₅) ₂ Ni(OAsPh ₃) ₂	55.6 (55.6)	2.5 (2.2)	5.6 (5.7)

(C₆F₅)₂Ni(Dioxane)₂ as an orange crystalline solid which was filtered and dried under vacuum. Yield 80%.

Results and Discussion

Red THF solutions of the presumed bis-organo-nickel(II)



are obtained according to equation (1). The reaction is not complete even when an excess of the Grignard reagent is used and when extending the treatment under reflux for several hours. It is convenient to use a molar ratio Mg/Ni of 2/1 as the excess of the Grignard reagent is unfavourable for the subsequent preparative use of the solution.

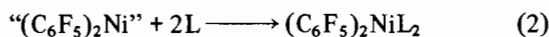
Although most of the magnesium salt can be eliminated by addition of dioxane in the form of the scarcely soluble magnesium complex, the resulting solution containing mainly Ni(C₆F₅)₂ also contains small amounts of nickel and magnesium dibromides and the excess of the Grignard reagent. All these derivatives are undoubtedly present as their solvates with THF or dioxane. Impurities do not disturb the isolation of complexes described in this paper.

It is noteworthy that addition of dioxane changes the red color of the initial THF solution to give a yellow color. This change suggests that dioxane replaces THF in the coordination sphere of nickel.

The yellow solution is indefinitely stable at room temperature under dry nitrogen. In the presence of acid it hydrolyses to produce pentafluorobenzene. By passage of air through the solution a green solid containing NiO is precipitated. Gas chromatographic analysis and mass spectrum of the resulting light yellow solution show the presence of decafluorobiphenyl, tetradecafluorotriphenyl and small amounts of perfluoropolyphenylenes.

Partial evaporation of the solution gives complex I as an orange crystalline solid (see Table I). Complex I is stable in the solid under dry nitrogen but decomposes rapidly in the presence of air. Solutions of complex I in donor solvents are stable at room temperature in the absence of air, but instantaneous decomposition takes place in non-donor solvents, such as chloroform and benzene.

The addition of different ligands to the solution of "(C₆F₅)₂Ni" in THF-dioxane gives complexes II-VIII



The process in fact is a substitution reaction because the organonickel(II) is present in solution as the solvate with THF or more probably with dioxane according with the change in color observed on addition of dioxane. NiBr₂ also present in the solution will actually react with the ligand to give the corresponding halocomplex. This reaction is observed in most cases by the color appearing in the solution by addition of ligands. All the organocomplexes here described have different solubilities, so that formation of the halocomplexes does not disturb the isolation of the desired derivatives, which can be crystallized as pure solids. All the complexes are soluble in THF, dioxane, chloroform, carbon tetrachloride, benzene and acetone and insoluble in hexane, methanol and ethanol.

Most of the complexes are stable in solution for several weeks, and indefinitely in the solid except complex VII, which slowly turns green and more quickly in solution in the presence of air. Complexes V-VIII decompose slowly in solution.

All the bis-pentafluorophenyl nickel(II) complexes here described are non-conductors in acetone.

Characteristic vibrations of the pentafluorophenyl groups [6] are present in all the complexes, as well as those vibrations due to the corresponding ligands.

All the complexes are diamagnetic in the solid at room temperature, so that they are square planar species. In agreement with results obtained for square nickel(II) complexes [7], all the bis-pentafluorophenyl derivatives exhibit only an absorption which can be assigned to a d-d transition, along with an intense absorption above 31.000 cm⁻¹ (log ε_{max} ≅ 4) due to charge transfers. The spectral data are given in Table II. The absorption observed in the range 21.000-26.300 cm⁻¹ must be assigned to the ¹A_{1g} →

TABLE II. Visible Data for Bis-pentafluorophenyl Nickel(II) Complexes.

No	Complex	$\nu(10^3 \text{ cm}^{-1})(\log \epsilon_{\text{max}})$		
		Benzene	THF	Solid
I	(C ₆ F ₅) ₂ Ni(Dioxane) ₂	–	21.64(2.70)	21.64
II	(C ₆ F ₅) ₂ Ni(PEt ₃) ₂	26.3 (2.54) 29.41sh	26.3 (2.54) 29.41sh	26.30
III	(C ₆ F ₅) ₂ Ni(Pn-Bu ₃) ₂	26.18(2.58) 29.85sh	26.18(2.58) 29.85sh	26.18
IV	(C ₆ F ₅) ₂ Ni(PPh ₃) ₂	24.75(2.78)	24.75(2.78)	24.75
V	(C ₆ F ₅) ₂ Ni(AsPh ₃) ₂	23.53(2.60)	21.74(2.57)	23.53
VI	(C ₆ F ₅) ₂ Ni(SbPh ₃) ₂	22.73(2.60)	21.74(2.48)	22.73
VII	(C ₆ F ₅) ₂ Ni(OPPh ₃) ₂	21.14(2.50)	21.74(2.48)	21.14
VIII	(C ₆ F ₅) ₂ Ni(OAsPh ₃) ₂	21.05(2.95)	21.05(2.95)	21.05

¹A_{2g} transition between d_{xy} and d_{x²-y²} in-plane orbitals. In fact for complexes I–IV and VIII this absorption is not displaced on using different solvents (see Table II), such as THF and benzene and also remains unmodified in the solid. On the other hand, this is the transition of lowest energy and we do not observe any other absorption in the region of lower frequency. The absorption observed for complexes V–VII in THF is always located at 21.700 cm⁻¹ which is also the same value observed for complex I containing a ligand similar to THF. It must be therefore concluded that ligands are substituted by the solvent in all these complexes. In fact, they contain the larger donor atom which gives generally less stable organo-complexes.

The frequency of the d–d transition increases in the order OPPh₃ ≅ OAsPh₃ < Dioxane < SbPh₃ < AsPh₃ < PPh₃ < Pn-Bu₃ ≅ PEt₃. Comparing the frequency of this absorption found for complexes X(C₆F₅)Ni(PPh₃)₂ with that of complex IV containing the same ligand, one can conclude that the C₆F₅

group causes a rather high orbital splitting similar to that produced by anions also having a delocalized π system such as NO₂.

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