

New Bis(pentafluorophenyl) Nickel(II) Complexes

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By a similar method to that described in a previous paper [1] we have isolated new neutral tetracoordinate bis-pentafluorophenyl nickel(II) complexes using $(C_6F_5)_2Ni(p\text{-dioxane})_2$ as precursor. The new complexes $(C_6F_5)_2NiL_2$ ($L = PPh_2Cl, Ph_2P(CH_2)_2PPh_2, NH_3, py, en, 2,2'$ -bipyridine, 1,10-phenanthroline) have been studied by visible-UV and IR spectroscopy.

Introduction

We described [1] the preparation of solutions containing " $(C_6F_5)_2Ni$ " following the method of Smith and Tamborski [2] for similar cobalt derivatives. However the presence of nickel dibromide and the reactivity of the C_6F_5-Ni bond prevented the isolation of complexes with different types of ligands. We observed that oxygen donor ligands give labile complexes in which the ligand is easily substituted. The complex $(C_6F_5)_2Ni(p\text{-dioxane})_2$ is especially important to this aim because it can be easily obtained as a pure crystalline compound and releases the ligand so easily that it may be considered as a

precursor reagent for the isolation of complexes with almost any kind of ligand.

By substitution of the ligand in this complex we have isolated a new series of compounds which could not be conveniently prepared from the initial " $(C_6F_5)_2Ni$ " solution.

Experimental

Materials

$(C_6F_5)_2Ni(p\text{-dioxane})_2$ was prepared by the method previously described [1]. Ligands were commercial products.

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 $250-4000\text{ cm}^{-1}$ on a Perkin-Elmer 457 spectrophotometer using nujol and KBr pellets. Conductivities were measured with a Phillips PW

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

No.	Complex	Analyses, found (calc) (%)			
		C	H	N or Hal	Ni
I	$(C_6F_5)_2Ni(PPh_2Cl)_2$	50.70 (51.80)	2.60 (2.40)	8.58 (8.50)	7.11 (7.04)
II	$(C_6F_5)_2Ni(dpe)$	57.78 (57.70)	3.18 (3.06)	—	7.25 (7.42)
III	$(C_6F_5)_2Ni(NH_3)_2$	33.56 (33.76)	1.75 (1.42)	6.05 (6.56)	13.60 (13.75)
IV	$(C_6F_5)_2Ni(py)_2$	48.19 (47.95)	1.66 (1.83)	5.23 (5.09)	10.33 (10.65)
V	$(C_6F_5)_2Ni(en)$	36.12 (37.12)	2.11 (1.78)	6.05 (6.18)	13.03 (12.96)
VI	$(C_6F_5)_2Ni(bipy)$	49.01 (48.13)	1.44 (1.47)	5.65 (5.10)	10.09 (10.69)
VII	$(C_6F_5)_2Ni(phen)$	50.20 (50.30)	1.62 (1.41)	5.01 (4.89)	10.34 (10.24)

9501/01 conductimeter. Melting points were measured with a Reichter microscope with heating plate.

Microanalyses

The C,H,N analyses were made with a Perkin-Elmer 240 microanalyser. Nickel was determined gravimetrically as the dimethylglyoximate [3] (Table I).

Preparation of Complexes

A solution of a known amount of the dioxane complex in THF was treated with a THF solution of the ligand in a molar ratio Ni/L 1/2 for monodentate ligands or 1/1 for bidentate ligands. The reaction was almost instantaneous for most of the ligands so that, after stirring for a few minutes, the solution was evaporated to dryness and the residue crystallized. The reaction with NH₃ was carried out by passing of dry NH₃ gas through a THF solution of the dioxane complex. Passing of NH₃ must be cut off in a few seconds, as soon as the solution becomes yellow, because the presence of an excess produces the decomposition of the previously formed organocomplex. Complex I was recrystallized from acetone. Yield 95%. Complex II was recrystallized from benzene. Yield 60%. Complex III was recrystallized from methanol-benzene. Yield 60%. Complex IV was recrystallized from THF-methanol. Yield 60%. Complex V was recrystallized from methanol by addition of a few drops of hexane. Yield 55%. Complexes VI-VII were recrystallized from THF. Yields \cong 70%.

Reactions with CO were carried out by passing CO gas through a THF solution of the dioxane complex for 8-10 h at room temperature until the color changed to pale yellow and following the course of the reaction by IR spectroscopy. The same reaction was also performed on the solid dioxane complex placed over a sintered glass plate.

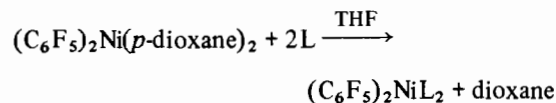
Results and Discussion

We concluded in a previous paper [1] that the THF-dioxane solution of (C₆F₅)₂Ni obtained from C₆F₅MgBr and anhydrous NiBr₂ contained small amounts of unreacted NiBr₂ and C₆F₅MgBr as well as MgBr₂ formed in the reaction. The addition of ligands to this solution gives not only the bis-pentafluorophenyl nickel(II) but also the dibromonickel(II) complexes, so that it is not possible to obtain directly pure samples of the organocomplex when the solubilities of the organo and halo complexes are similar. This difficulty was found when attempts were made to prepare complexes I, II, VI, VII following the preceding method. We always obtained mixtures which could not be resolved by recrystallization.

On the other hand, similar attempts to isolate

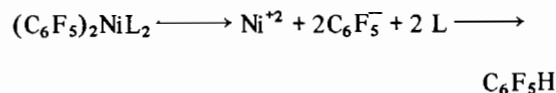
complexes III-V by the same method gave only decomposition products with occasionally low yields of the organocomplexes.

In order to avoid these difficulties we carried out substitution reactions using the dioxane complex previously isolated as the starting material:



The method presents several advantages. (C₆F₅)₂Ni(p-dioxane)₂ is very soluble and stable in polar solvents. Although this dioxane complex is not stable in nondonor solvents, these types of solvents can also be used if ligands have been added previously. All the substitutions are rapid at room temperature. The bis-pentafluorophenyl nickel(II) complex is the unique product of the reaction so that if stoichiometric amounts of reagents are used, the solid obtained does not need any further purification. In this way complexes I, II, VI, VII can be prepared easily as pure crystalline solids.

Moreover, using the solid dioxane complex, it is possible to know the exact amount of ligand needed to maintain the desired stoichiometric ratio. Using a molar proportion 1/2 for Ni/pyridine or an equimolar 1/1 proportion for Ni/en, complexes IV and V are respectively obtained. However, we observed that the addition of an excess of these ligands produces the rupture of the C-Ni bond to give Ni⁺² solvated by the ligand and/or the solvent and C₆F₅⁻ finally trans-



formed into C₆F₅H by its reaction with the solvent.

This reaction explains the observed behaviour when the ligand was directly added to the initial solution.

The same behaviour is observed for NH₃. In order to prepare the diamine complex, passing of NH₃ gas must be reduced to a few seconds as an excess produces the decomposition of the complex.

The different ability of ligands to effect the nucleophilic attack to the C-Ni bond with subsequent bond rupture is in agreement with their K_A values. Ligands with lower acid equilibrium constants such as pyridine, ammonia and ethylenediamine, produce the bond rupture while ligands such as 1,10-phenanthroline and 2,2'-bipyridine with higher K_A values do not affect the C-Ni bond.

We have also studied the reaction of the dioxane complex with CO in order to isolate possible pentafluorophenyl nickel carbonyl complexes. When CO is bubbled into a THF solution of the dioxane complex the initial orange color becomes pale yellow after 8-10 h at room temperature. IR spectra of

samples of the solution at different times show the presence of an absorption at 2035 cm^{-1} . The solution is stable under CO but immediately decomposes in air. It is not possible to obtain a solid by evaporation. When the solution is evaporated to dryness the solid residue results to be a mixture containing increasing amounts of $(\text{C}_6\text{F}_5)_2$. The solid initially shows an IR absorption at 2060 cm^{-1} in nujol, which disappears with time. Any attempt to isolate the carbonyl complex gives only $(\text{C}_6\text{F}_5)_2$ as the unique decomposition product.

When the reaction was carried out passing CO through the solid dioxane complex placed over a sintered glass plate, a colorless solid was obtained. Its IR spectrum in nujol gives intense absorptions at 2135 and 2160 cm^{-1} along with less intense peaks at 2040 and 2095 cm^{-1} . It is neither possible to isolate the carbonyl complex as the solid loses CO with time and increasing amounts of $(\text{C}_6\text{F}_5)_2$ are produced. Similar results were obtained also at lower temperatures. We could not isolate a carbonyl complex but our observations strongly suggest that the complex is formed and easily decomposes giving $(\text{C}_6\text{F}_5)_2$.

All the isolated complexes are stable in the presence of air in the solid. They decompose on heating except for complexes I–II which melt without decomposition. The new complexes are nonconductors in acetone. They are soluble in THF, dioxane, chloroform, carbon tetrachloride, acetone and benzene and insoluble in alcohols and hexane.

Characteristic vibrations of the pentafluorophenyl groups [4] and the corresponding ligands are present in all the complexes.

All the complexes present a square planar structure according with the diamagnetism measured at room temperature. Visible–UV spectra for complexes I–V are similar to those described [1] for other bis-pentafluorophenyl nickel(II) derivatives. The absorption observed in the range $27,000$ – $23,800\text{ cm}^{-1}$ ($\log\epsilon = 2$ – 3) is assigned to the ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ transition. Complexes VI–VII show a different visible–UV spectral behaviour. Both present a broad absorption with maxima located at $22,800$, $24,400$ and $25,900\text{ cm}^{-1}$ in benzene. These absorptions are displaced at higher frequency when the spectra are recorded in THF.

The frequency of the d–d transition increases in the order $\text{NH}_3 < \text{en} < \text{py} < \text{PPh}_2\text{Cl} < \text{dpe}$ without regard to the bidentate N-ligands. In comparison with the behaviour observed for other similar organo-complexes [1] the splitting produced by monodentate N-ligands is between that of AsPh_3 and PPh_3 while PPh_2Cl and dpe produce the highest orbital splitting in these compounds.

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