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PENTAFLUOROPHENYLCOBALT(II) COMPLEXES

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Summary

Complexes $(C_6F_5)_2CoL_2$ (L_2 = 2 PEt_3, 2 $Pn\text{-}Bu_3$, 2 PPh_3, $Ph_2PCH_2CH_2PPh_2$) have been obtained by adding the relevant ligands to solutions of $(C_6F_5)_2Co(dioxane)_2$. The *cis* and *trans* isomers have been separated and identified for the complexes having L = PEt_3 or $Pn\text{-}Bu_3$.

Structural and chemical behaviour for all the complexes is described.

Introduction

Several organocobalt(II) complexes $(C_6F_5)_2CoL_2$ are known. The complex L_2 = 2 PEt_3 was made to confirm the existence of $(\eta^6\text{-}C_6H_5CH_3)(C_6F_5)_2Co$ [1]. The complex with L_2 = $Ph_2PCH_2CH_2PPh_2$ (dpe) was prepared by the Grignard method [2] from the halo derivative. The complex with L_2 = 2 $Pn\text{-}Bu_3$ was isolated to confirm the existence of "$(C_6F_5)_2Co$" in THF or dioxane solutions [3]. We have used this last method to prepare the above phosphine complexes as well as that with L_2 = 2 PPh_3, and behaviour and structures of the various *cis* and *trans* isomers are described.

Results and discussion

Preparative results

The reaction of anhydrous $CoBr_2$ with C_6F_5MgBr in THF gave a blue solution (described [3] as containing solvated "$(C_6F_5)_2Co$") after precipitation and elimination of magnesium salt by addition of dioxane:

$$Br_2Co + 2\,C_6F_5MgBr \rightarrow (C_6F_5)_2Co + Br_2Mg \qquad (1)$$

The solvated species were not isolated.

When this blue solution was evaporated to dryness and the residue repeatedly washed with hexane and then extracted with dioxane, evaporation

TABLE 1

ANALYTICAL DATA FOR PENTAFLUOROPHENYLCOBALT(II) COMPOUNDS

Complex		Analysis found(calcd.)(%)		
		C	H	Co
I	$(C_6F_5)_2Co(dioxane)_2$	—	—	9.94
				(10.35)
II	*trans*-$(C_6F_5)_2Co(PEt_3)_2$	45.54	4.72	9.10
		(45.80)	(4.80)	(9.36)
III	*cis*-$(C_6F_5)_2Co(PEt_3)_2$	45.40	4.81	9.11
		(45.80)	(4.80)	(9.36)
IV	*trans*-$(C_6F_5)_2Co(Pn\text{-}Bu_3)_2$	54.00	6.73	7.20
		(54.21)	(6.82)	(7.39)
V	*cis*-$(C_6F_5)_2Co(Pn\text{-}Bu_3)_2$	54.10	6.60	7.16
		(54.21)	(6.82)	(7.39)
VI	*trans*-$(C_6F_5)_2Co(PPh_3)_2$	63.21	3.53	6.29
		(62.82)	(3.29)	(6.42)
VII	$(C_6F_5)_2Co$ dpe	57.91	4.00	7.26
		(57.67)	(3.06)	(7.45)

of the solvent gave a blue crystalline solid which was identified as $(C_6F_5)_2Co(dioxane)_2$ (I) from its IR spectrum and analytical data (Table 1). By comparison with the corresponding nickel derivative which has been unambiguously identified [4] we conclude that this cobalt complex has a square planar structure with monodentate dioxane [5]. Addition of various phosphine ligands to solutions of complex I gave complexes II—VII:

$$(C_6F_5)_2Co(dioxane)_2 + 2\,L \rightarrow (C_6F_5)_2CoL_2 + dioxane \qquad (2)$$

($L_2 = 2\,PEt_3$, *trans* (II), *cis* (III); $2\,Pn\text{-}Bu_3$; *trans* (IV), *cis* (V); $2\,PPh_3$; *trans* (VI); $Ph_2PCH_2CH_2PPh_2$ (VII)).

Analytical data are listed in Table 1.

The complexes with PEt_3 and $Pn\text{-}Bu_3$ were obtained as the separate *cis* and *trans* isomers, and the stereochemistries were assigned by comparison with data observed for complex VII.

The complex with $L_2 = 2\,PEt_2$ has been described [1] as a yellow-green crystalline solid, whereas that with $L_2 = 2\,Pn\text{-}Bu_3$ has been described [3] as a yellow solid which after recrystallization from hot hexane gives green crystals. We have isolated and identified the *cis* and *trans* isomers for each of these complexes. The yellow complexes II and IV were prepared by extracting with benzene the residue obtained by evaporation to dryness of the initial solution. Both were more soluble in benzene and had melting points higher than the corresponding complexes III and V. The complexes III and V were obtained by extracting the residue with hexane.

The *cis* and *trans* complexes had the same IR spectrum and their solutions were yellow-green in colour, suggesting the presence of an equilibrium between the two isomers. The electronic spectrum showed two shoulders, which can be interpreted in terms of the presence of both isomers.

By comparison with complex VII and the differences observed in their solu-

TABLE 2

PHYSICAL DATA, CONDUCTIVITIES AND MAGNETIC MEASUREMENTS OF PENTAFLUOROPHENYLCOBALT(II) COMPLEXES

Complex	Colour	M.p.(°C)	Λ(ohm^{-1} cm^2 mol^{-1}) (c = 10^{-4} mol l^{-1})	$10^6\chi_M$	μ_{eff}(B.M.) (298° K)
II	yellow	130(dec.)	1.2(Acetone)	2396	2.39
III	green	125(dec.)	1.1(Acetone)	2380	2.39
IV	yellow	136—142(dec.)	0.0(Chloroform)	2362	2.38
V	green	130—140(dec.)	0.0(Chloroform)	2341	2.37
VI	yellow	60(dec.)	—	—	—
VII	yellow	150—175(dec.)	0.9(Nitromethane)	2195	2.29

bility, melting point and comparative stability we suggest the *cis* configuration for the green and *trans* configuration for the yellow complexes.

Complex VI was obtained only as the yellow *trans* isomer. It is thermally unstable, and its solutions decompose on handling. A *cis* configuration must of course be assigned to complex VII.

Chemical and structural behaviour

Table 2 shows several properties of the isolated complexes. All the complexes are non-conductors in acetone.

The IR spectra of all the complexes show absorptions characteristic of the C_6F_5 groups [6,7] located at 1490—1500s, 1050—1070s, 1035—1050s, 945—955vs and 780—800s cm^{-1}. The electronic absorption spectrum of complex VII (Table 3) shows only one band, at 406 mμ, which must be assigned to the $d_{xy} \rightarrow d_{x^2y^2}$ transition in a square planar environment. The solution spectra of complexes with PEt_3 and $Pn\text{-}Bu_3$ show two shoulders at 412 and 379 mμ, probably due to the presence of both *cis* and *trans* isomers. Complex VI is unstable in solution, and its spectral properties were not studied.

All the complexes are paramagnetic with μ_{eff} = 2.29—2.39 BM at room temperature (298 K), suggesting a high orbital contribution.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer at 4000—250 cm^{-1} using Nujol mulls between CsI or KBr plates. Near IR and vis—

TABLE 3

ELECTRONIC SOLUTION SPECTRA OF THE PENTAFLUOROPHENYLCOBALT(II) COMPLEXES

Complex	λ_{max}(mμ) {ϵ(l^{-1} mol^{-1} cm^{-1})} (in chloroform)
II *trans*-$(C_6F_5)_2Co(PEt_3)_2$	412(sh), 379(sh), 325 {2840}, 316 {9141}, 266 {8954}, 247 {12423}
III *cis*-$(C_6F_5)_2Co(PEt_3)_2$	
IV *trans*-$(C_6F_5)_2Co(Pn\text{-}Bu_3)_2$	412(sh), 379(sh), 320(sh), 287 {11241}, 265 {10071}, 246 {19590}
V *cis*-$(C_6F_5)_2Co(Pn\text{-}Bu_3)_2$	
II $(C_6F_5)_2$Codpe	406 {887}, 319(sh), 244 {15796}

UV spectra were recorded on a Perkin-Elmer 330 spectrophotometer at 186—2600 mμ. Conductivities were measured with a Phillips PW 9501/01 conductimeter. Magnetic measurements were carried out by the Faraday method employing a Bruker magnet system with variable temperature control unit. C, H, N analyses were carried out with a Perkin-Elmer 204 B microanalyzer. Cobalt was determined according to ref. 8. Melting points were determined with a Reichert Thermopan microscope.

$(C_6F_5)_2Co(dioxane)_2$ (I)

A blue solution of "$(C_6F_5)_2Co$" [3] (15.4 mmol) in THF (70 ml) was evaporated to dryness and the resulting blue residue was washed with hexane (4 × 20 ml) then dissolved in THF (70 ml), and the solution was filtered. The blue filtrate yielded I as a dark blue solid after addition of anhydrous dioxane (15 ml) and concentration under vacuum. Yield 60%.

trans- and cis-$(C_6F_5)_2CoL_2$ (L_2 = 2 PEt_3 (II, III); 2 Pn-Bu_3 (IV, V))

PEt_3 (4.5 ml, 30.5 mmol) was added rapidly to a blue solution of complex I (15.4 mmol) in THF (70 ml) to give a dark green mixture. After 20 minutes of stirring at room temperature the solvent was removed under reduced pressure. The resulting green-yellow powder was washed with pentane and extracted with benzene (2 × 30 ml) to give a yellow solution and a green residue. The yellow solution yielded the *trans* isomer II as yellow crystals after concentration, addition of hexane, and cooling. Yield 40%. The green residue was recrystallized from hot hexane to give the *cis* isomer as green crystals. Yield 25%.

The compounds IV and V with L = Pn-Bu_3 were similarly obtained.

trans-$(C_6F_5)_2Co(PPh_3)_2$ (VI)

PPh_3 (4.039 g, 15.4 mmol) was added rapidly to a blue solution of I (7.7 mmol) in THF (70 ml) to give a green mixture. After 10 minutes of stirring at 0°C the solvent was carefully removed at 0°C under reduced pressure. The green-yellow residue was repeatedly washed with hexane and diethyl ether at 0°C to give yellow crystals of VI. Yield 30%.

$(C_6F_5)_2$Codpe (VII)

When dpe (6.136 g, 15.4 mmol) was added to a solution of complex I (15.4 mmol) in THF (70 ml) the original blue solution rapidly became green. After stirring at room temperature for 30 minutes the solvent was removed under reduced pressure. The residue was recrystallized from chloroform/ethanol to give yellow crystals of VII. Yield 65%.

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