PENTAFLUOROPHENYL COMPLEXES OF COBALT(III) WITH 1-(DIACETYLMONOXIMATOIMINO)-3-(DIACETYLMONOXIMEIMINO)-PROPANE (dotnH)

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Summary

The treatment of $Br_2Co(dotnH)$ with the C_6F_5MgBr Grignard reagent leads to the isolation of $(C_6F_5)BrCo(dotnH)$. Substitution reactions of this substance make it possible to isolate neutral complexes $((C_6F_5)CoX(dotnH)$ (X = CN^-, SCN^-, I^-, NO_2^-)), mononuclear cationic complexes $([(C_6F_5)Co(dotnH)L]Y$ (L = H_2O, NH_3, py; Y = ClO_4^-, BPh_4^-) and binuclear cationic complexes $(\{(C_6F_5)Co(dotnH)]_2X\}^+BPh_4^-$ (X = CN^-, SCN^-)).

The new complexes were studied by IR, visible-UV and NMR spectroscopy.

Introduction

We recently described the preparation of pentafluorophenyl complexes of cobalt(III) with acacen [1] and dimethylsalen [2]. Because they involved dianionic tetradentate ligands, all the isolated complexes were neutral, of the type $(C_6F_5)CoL_4B$, except for the anionic complexes which are formed when B is CN^-. In order to extend the previous study by inserting into the axial position various kinds of base, including anionic ligands, we had to use a Schiff base which would behave like a monoanionic ligand. We chose 1-(diacetylmonoximatoimino)-3-(diacetylmonoximeimino)propane (abbreviated to "dotnH"), which has been subject of previous studies [3].

The complexes isolated by use of this ligand display great versatility, since it is now possible to insert practically any substituent into the axial position and thus to study its effect on the stability of the Co—C_6F_5 bond. Furthermore, it is possible to determine the effects of a tetradentate ligand substantially different from those previously studied.

## Results and discussion

(a) Preparative results

The reaction between $Br_2Co(dotnH)$ and an excess of C_6F_5MgBr in THF

produces complex I (see analytical data in Table 1). Only one C_6F_5 group is introduced whatever excess of the Grignard reagent is used. By interchange reactions in aqueous methanol complexes II—IV are obtained. When such reactions are carried out with salts of anions with low coordinative ability the cationic aquo complexes VI and VII are obtained. The addition of Lewis bases to these aquo complexes leads to substitution with elimination of water. The same result is obtained when the solutions of $(C_6F_5)BrCo(dotnH)$ to which the base has been previously added, are treated in aqueous methanol with $NaBPh_4$. Finally, when an equimolar quantity of III or IV is added to a suspension in chloroform of the cationic complex VI the latter immediately disolves and complexes X and XI are obtained.

All the neutral complexes are very soluble in chloroform and dichloromethane, soluble in acetone, ethanol and THF and insoluble in water and ethyl ether. In contrast, the cationic complexes are less soluble than previous ones in methanol, ethanol and acetone and insoluble in non-polar solvents.

(b) Conductivity

The solutions of the neutral complexes in methanol display significant conductivity, which shows that they dissociate, possibly in accord with the equilibrium
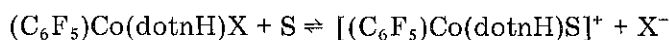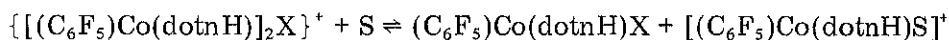
$$(C_6F_5)Co(dotnH)X + S \rightleftharpoons (C_6F_5)Co(dotnH)S^+ + X^-$$
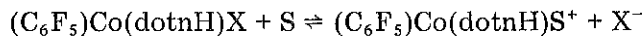
The position of this equilibrium depends on the nature of X, and from the

TABLE 1

ANALYTICAL RESULTS FOR ORGANOCOBALT(III) COMPLEXES WITH dotnH

	Complex	Analysis found (calcd.) (%)			
		C	N	H	Co
I	$(C_6F_5)Co(dotnH)Br$	37.51	10.31	3.10	10.73
		(37.41)	(10.28)	(3.48)	(10.81)
II	$(C_6F_5)Co(dotnH)I$	34.10	9.52	2.97	10.06
		(34.44)	(9.46)	(3.21)	(9.95)
III	$(C_6F_5)Co(dotnH)(CN)$	43.53	14.20	4.14	11.95
		(43.96)	(14.25)	(3.86)	(12.00)
IV	$(C_6F_5)Co(dotnH)(SCN)$	42.62	13.52	4.02	11.12
		(41.27)	(13.37)	(3.63)	(11.26)
V	$(C_6F_5)Co(dotnH)(NO_2)$	39.97	13.92	3.43	11.56
		(39.90)	(13.69)	(3.71)	(11.53)
VI	$[(C_6F_5)Co(dotnH)(H_2O)]ClO_4$	35.14	9.73	4.06	9.98
		(35.04)	(9.61)	(3.60)	(10.11)
VII	$[(C_6F_5)Co(dotnH)(H_2O)]BPh_4$	61.12	6.84	5.01	7.42
		(61.33)	(6.98)	(5.11)	(7.35)
VIII	$[(C_6F_5)Co(dotnH)(NH_3)]BPh_4$	62.03	9.44	5.02	7.55
		(62.03)	(8.82)	(5.29)	(7.43)
IX	$[(C_6F_5)Co(dotnH)(py)]BPh_4$	63.28	8.62	5.25	6.64
		(63.95)	(8.11)	(5.10)	(6.83)
X	$\{[(C_6F_5)Co(dotnH)]_2(CN)\}ClO_4$	38.92	11.17	3.12	11.25
		(39.77)	(11.93)	(3.60)	(11.16)
XI	$\{[(C_6F_5)Co(dotnH)]_2(SCN)\}BPh_4$	53.70	9.58	4.49	9.22
		(54.13)	(9.64)*	(4.43)	(9.01)

conductivity values shown in Table 2 we conclude that the bromo and iodo complexes are almost completely dissociated and the complex with NO_2 less so, while the complexes with CN and SCN are even less dissociated.

The conductivities exhibited by the cationic complexes in which L = H_2O, NH_3 and py correspond to the values expected for this type of substances [4]. However the conducitivities of binuclear cationic complexes in which L = CN and SCN are markedly higher, showing that such species must be dissociated in accord with the equilibria:

$$\{[(C_6F_5)Co(dotnH)]_2X\}^+ + S \rightleftharpoons (C_6F_5)Co(dotnH)X + [(C_6F_5)Co(dotnH)S]^+$$

$$(C_6F_5)Co(dotnH)X + S \rightleftharpoons [(C_6F_5)Co(dotnH)S]^+ + X^-$$

Thus, in the presence of a polar solvent the bridge system breaks and the neutral complex formed dissociates in turn, as indicated giving a substantial increase in conductivity.

(c) IR spectra

The IR spectra of these substances show many absorption bands and we discuss only the more structurally significant. The bands characteristic of the C_6F_5 group are situated at 1600—1630m, 1495vs, 1050—1070vs and 950—960vs cm^{-1} [5]. The tetradentate ligand also shows an absorption, due to $\nu(C=N)$ stretching vibration of the imino group, at 1500vs cm^{-1} [6]. In this region there is a broad band, produced by the superposition of this with the previously mentioned band of the C_6F_5 group. In addition to the bands mentioned which are present in all the complexes, other bands are noted for the ligand in the axial position. Thus $(C_6F_5)Co(dotnH)CN$ has an absorption band at 2138 cm^{-1}, which for $\{[(C_6F_5)Co(dotnH)]_2CN\}ClO_4$ appears at 2182 cm^{-1}. Both absorptions must be assigned to $\nu(C\equiv N)$ stretching vibration; the first corresponds to a $C\equiv N$ terminal group whereas the second is in the region corresponding to a $C\equiv N$ bridge group. The separation between the two is only 44 cm^{-1}, but similar behaviour has been observed for other complexes of this type [7].

Similarly, $\{[(C_6F_5)Co(dotnH)]_2(SCN)\}ClO_4$ shows an absorption band at

TABLE 2

MOLAR CONDUCTIVITIES OF ORGANOCOBALT(III) COMPLEXES IN METHANOL

Complex	$c \times 10^4$ (mol/l)	Λ (ohm^{-1} cm^2 mol^{-1})
$(C_6F_5)Co(dotnH)Br$	6.16	58.1
$(C_6F_5)Co(dotnH)I$	5.72	62.2
$(C_6F_5)Co(dotnH)(CN)$	4.68	17.0
$(C_6F_5)Co(dotnH)(SCN)$	4.93	22.4
$(C_6F_5)Co(dotnH)(NO_2)$	5.12	38.5
$[(C_6F_5)Co(dotnH)(H_2O)]ClO_4$	2.37	67.5
$[(C_6F_5)Co(dotnH)(H_2O)]BPh_4$	4.27	59.0
$[(C_6F_5)Co(dotnH)(NH_3)]BPh_4$	4.09	60.1
$[(C_6F_5)Co(dotnH)(py)]BPh_4$	2.01	58.8
$\{[(C_6F_5)Co(dotnH)]_2(CN)\}ClO_4$	2.29	110.0
$\{[(C_6F_5)Co(dotnH)]_2(SCN)\}BPh_4$	2.16	107.3

2158 cm^{-1} which must be assigned to the ν(C≡N) stretching vibration of an
SCN bridge group. In contrast, the complex (C$_6$F$_5$)Co(dotnH)(SCN) shows two
absorption peaks at 2064 and 2086 cm^{-1}. This band corresponds to the ν(C≡N)
stretching vibration of an SCN terminal group, but the presence of two absorp-
tion peaks indicates that there are two superimposed bands, arising from two
SCN groups in different bonding situations. From the separation between the
bands we conclude that the difference stems from the existence of two isomers
with Co—SCN and Co—NCS bonds [8]. It was impossible to separate the two
isomers by repeated recrystallization.

The spectrum of the substance in chloroform shows a single absorption
band at 2102 cm^{-1} which indicates a displacement produced by the solvent
and the existence of a unique type of bond.

The complex (C$_6$F$_5$)Co(dotnH)(NO$_2$) shows three absorptions at 1390—1395vs,
1305—1310vs and 812 cm^{-1} which correspond to the ν_{as}(NO$_2$), ν_s(NO$_2$) and
δ(ONO), respectively, of a Co—NO$_2$ nitro group.

(d) Visible-UV spectra

The study of analogous complexes of DMG [9] has disclosed the presence of
three absorption bands assignable to d—d transitions, generally situated at 16—
18, 19—21 and 23—25 × 10^3 cm^{-1}, although it is possible that the first of these
absorptions has two components, as observed in the complex with acacen [1].

All the complexes isolated display a very intense absorption band at about 33.3
× 10^3 cm^{-1}, which corresponds to a charge transfer. The overlapping of this
absorption with those due to d—d transitions is so intense that the latter mostly
appear as shoulders whose exact position is difficult to allocate. The observed
absorptions and their intensity and assignments are given in Table 3. For reasons
already given it is not always possible to locate the three transitions, and in
some cases only two shoulders can be seen.

(e) NMR spectra

The spectra of the studied complexes should show five types of resonances.
The peak due to protons of the C—CH$_2$—C group can never be seen because it is
a very small absorption, which is overlapped by absorption peaks of the CH$_3$

TABLE 3

NEAR ULTRAVIOLET AND VISIBLE SPECTRA OF (C$_6$F$_5$)Co(dotnH)X^{n+} COMPLEXES (n = 0, 1) (in
chloroform)

X	Frequencies (10^3 cm^{-1}) and log ϵ_{max} (in brackets)		
	ν_{IE} (^{1}A$_1$ → ^{1}E^a)	ν_{IA} (^{1}A$_1$ → ^{1}A$_2$)	ν_{II} (^{1}A$_1$ → ^{1}B$_2$, E^b)
Br	17.7(2.06)	21.1(3.35)	26.7(sh)
I	17.8(2.13)	21.1(3.37)	26.7(sh)
CN	17.5(sh)	22.7(sh)	27.4(sh)
SCN	17.5(sh)	22.7(sh)	27.4(sh)
NO$_2$		21.7(sh)	26.7(sh)
H$_2$O		21.7(sh)	25.7(sh)
NH$_3$		21.7(sh)	25.6(sh)
py	17.6(2.37)	21.3(3.48)	26.8(sh)

groups [10]. The resonance corresponding to the protons of the N—CH_2—C group invariably appears at 6.03 ppm. The protons of the two kinds of CH_3 groups present produce two very close peaks at τ 7.60 and 7.64 ppm. Moreover, the position of these peaks does not noticeably modify with the different nature of the axial base. It is obvious that the effect produced by this base cannot be very important because it must pass through the cobalt atom to the methyl group.

In spite of this, we observe that both peaks in our complexes with C_6F_5 are situated at lower values of τ than in analogous methyl derivatives [11], in which they are located at τ 7.73 and 7.28 ppm, respectively. This is a clear indication that the C_6F_5 group exhibits a greater π-acceptor capacity, leading to a decrease in density of electronic charge on the cobalt atom which is transmitted to the methyl groups.

Experimental

$Br_2Co(dotnH)$ and C_6F_5MgBr were prepared by published methods [12,13]. The IR spectra were recorded on a Perkin—Elmer 457 spectrophotometer (over the range 4000—250 cm^{-1}) using KBr tablets. The visible-UV spectra were recorded in solution in chloroform with a Perkin—Elmer 124 spectrophotometer The NMR spectra were recorded on a 60Hz Perkin—Elmer R12 spectrometer in CDCl$_3$ and the chemical shifts are relative to TMS as internal standard. The C, H and N analyses were made with a Perkin—Elmer 240 microanalyzer. Cobalt was determined with EDTA using murexide as indicator. All the reactions involving Grignard reagents were carried out under dry nitrogen.

$(C_6F_5)CoBr(dotnH)$ (I)

A freshly prepared solution of C_6F_5MgBr (5 mmol) in THF (50 ml) was slowly added to a suspension of $Br_2Co(dotnH)$ (0.92 g, 2 mmol) in THF (100 ml) and the mixture stirred at —70°C for 4 h. It was allowed to warm up and stirred at room temperature for 3 h. After hydrolysis it was neutralized with 2 M HBr and the solid obtained after evaporation was recrystallized from dichloromethane/ethyl ether. Reddish-orange crystals. Yield 60%.

$(C_6F_5)CoX(dotnH)$ (II—V) and $[(C_6F_5)Co(dotnH)(H_2O)]Y$ (VI—VII)

Solutions of KI, NaNO$_2$, KNC, NaClO$_4$ or NaBPh$_4$ in water were added to a hot solution of complex I (0.54 g, 1 mmol) in methanol. After stirring for 1 h the solvent was evaporated to give solids which were recrystallized from chloroform/ethyl ether and dried under vacuum over P_2O_5. Yield 50—55%.

$[(C_6F_5)Co(dotnH)(NH_3)]BPh_4$ (VIII)

A current of NH$_3$ gas was passed for 0.5 h through a solution containing a mixture of complex I (0.54 g, 1 mmol) and NaBPh$_4$ (0.34 g, 1 mmol) in methanol (60 ml). After filtering, a yellow crystalline solid is obtained by evaporation and cooling. Yield 65%.

$[(C_6F_5)Co(dotnH)(py)]BPh_4$ (IX)

An excess of pyridine (1 ml) was added to a solution of complex VII (0.4 g)

in methanol and the mixture was stirred at 50°C for half an hour. A red crystalline solid was obtained by partial evaporation and cooling. Yield 40%.

$\{[(C_6F_5)Co(dotnH)]_2(CN)\}ClO_4$ (X)
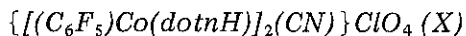
Complex VI (0.29 g, 1 mmol) was added to a solution of III (0.24 g, 1 mmol) in chloroform (40 ml) and the mixture was stirred for 2 h until VI, which is insoluble in chloroform, completely dissolves. Evaporation gave a solid which was recrystallized from chloroform/ethyl ether to give orange crystals. Yield 40%.

$\{[(C_6F_5)Co(dotnH)]_2(SCN)\}BPh_4$ (XI)
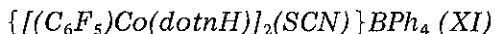
The same method gave a reddish-orange crystalline solid from complexes IV and VII. Yield 30%.

Acknowledgement

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