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REACTIONS OF (η^5-C_5Me_5)Co(CO)$_2$ WITH XCN (X = Br, I) AND INCO

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Summary

The pseudohalogens XCN (X = Br, I) and INCO react with (η^5-C_5Me_5)Co(CO)$_2$ to give the 18 electron complexes (η^5-C_5Me_5)Co(CO)X(CN) (X = Br, I) and (η^5-C_5Me_5)Co(CO)I(NCO). All the compounds have been characterized by elemental analysis and IR, electronic and ^{1}H NMR spectroscopy.

Introduction

The presence of substituents in the cyclopentadiene ring of cyclopentadienylmetal compounds bestows on these complexes properties different from those of similar unsubstituted complexes. Generally speaking, they are crystalline solids with a higher solubility than similar unsubstituted species.

In the cobalt group, Rh and Ir compounds of the type $C_5Me_5ML_2$ (L = neutral ligands, e.g. PPh_3, C_2H_4, CO) and $C_5Me_5M(L–L)$ (L–L = PhCHCHCOCHCHPh, $C_4Ph_2HCPhC_5Ph_2H_2$) have been obtained [1]. More recently, Kölle et al. [2] have synthesised the $C_5Me_5Co(C_2H_4)_2$ and $C_5Me_5Co(L–L)$, (L–L = C_4H_6, 1,5-C_8H_{12}, C_4Ph_4) complexes from the $C_5Me_5CoX_2$ dimer. These compounds were found to be more stable than the unsubstituted parent species.

Oxidative additions of pseudohalogens to $C_5H_5Co(CO)_2$, $C_2Me_4EtCo(CO)_2$ and $Me_3SiC_5H_4Co(CO)_2$ [3,4], have been studied, and elimination of a carbonyl group and oxidation of cobalt(I) to cobalt(III) was observed. The present work describes the oxidative addition reactions of $C_5Me_5Co(CO)_2$ with ICN, BrCN, and INCO.

Discussion of results

The addition of a solution of XCN (X = Br, I) or INCO in ether to solutions of $C_5Me_5Co(CO)_2$ in the same solvent under N_2 leads to release of CO and precipitation of solids with the following stoichiometry: $C_5Me_5Co(CO)X(CN)$ (X = Br, I) and $C_5Me_5Co(CO)I(NCO)$. These compounds were found to be hygroscopic, and fairly soluble in solvents such as $CHCl_3$, acetone, and CH_2Cl_2. Their IR spectra

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TABLE 1

ν(CN), ν(CO) AND FAR IR SPECTRA OF THE COMPLEXES [a]

RCo(CO)(CN)I	RCo(CO)(CN)Br	RCo(CO)(NCO)I	Assignment
2140 vs	2130 vs	2200 vs	ν(CN)
		2155 vs	
2060 vs	2065 m	2040 s	ν(CO)
		1330 w	ν(CO(NCO))
		595 m,sh	δ(NCO)
495 m	485 w	497 m	ν(Co–CO)
470 m	470 m	460 s	ν(Co–CN)
440 m	440 w	435 m	δ(Co–CO) and
410 vw	410 vw		δ(Co–CN)
325 m	325 m	345 s	ν(Co–ring)
		280 w	ν(CoNCO)
	260 m		ν(Co–Br)

[a] R = η^5-C_5Me_5.

show, in the 4000–200 cm^{-1} range, characteristic bands of the pentamethylcyclopentadiene ligand with C_{5v} symmetry [5,6]. Table 1 lists the bands arising from the cyanide, carbonyl and cyanate ligands, together with those corresponding to the metal–ligand bonds.

The range of the ν(CN) and ν(CO) bands in the case of ICN and BrCN, is typical of terminal ligands [7]. The ν(CO) values are lower than those observed for the analogous compounds with unsubstituted rings [3], (η^5-C_5H_5)Co(CO)X(CN) (X = Br, I), this being due to the inductive release of electrons by methyl groups.

The vibration frequencies ν(CO) (carbonyl), ν(CN) and ν(CO) (cyanate) are also characteristic of terminal ligands in the case of IOCN. The deformation vibration δ(NCO) was tentatively assigned to the band at 595 cm^{-1}, because at 585 cm^{-1} there is what appears to be the shoulder of another more intense band which is attributed to the χ(C–C) vibration of the ring. The ν(CN), ν(CO) and δ(NCO) values for the cyanate ligand indicate that the coordination with the metal is through the nitrogen [8]. The bands corresponding to ν(CoCN) and ν(CoCN) and to the deformation of these bonds [7] appear in the 500–410 cm^{-1} range.

The ν(Co–N) stretching vibration appears at 280 cm^{-1} and the ν(CoBr) at 255 cm^{-1}. The ν(CoI) stretching vibration was not observed, as its frequency is below 200 cm^{-1} [9].

The electronic spectra of the complexes in dichloromethane solution are given in Table 2. If we assume that the complexes are octahedral, the simultaneous presence

TABLE 2

ELECTRONIC SPECTRA OF THE COMPLEXES [a]

RCo(CO)(CN)I	RCo(CO)(CN)Br	RCo(CO)(NCO)I	Assignation
15863 sh,br	15873 sh,br	15625 br	*d*–*d*
18518 sh,br	19305 sh,br	19157 br	
21834 sh,br	21367 br		
27322	30303	27548	charge transfer

[a] In cm^{-1}; CH_2Cl_2 solution; R = η^5-C_5Me_5.

of CN or NCO, CO and X (X = Br, I) ligands reduces the O_h symmetry to C_s. Therefore, for interpretation purposes, we consider the C_5Me_5 and MLL′L″ fragments separately, following the procedure used for other complexes [10].

In the C_5Me_5 fragment, orbitals, with a_1 and e_1 symmetry, are involved [11]. Photoelectronic studies indicate that the $M(CO)_3$ group (M is a d^6 metal) contains three orbitals with a_1 and e symmetry (where the 6 e^- are located), which result from the splitting of the t_{2g} orbitals when the O_h symmetry reduced to C_{3v}. The same group also contains three frontier orbitals, with an a and e symmetry, which act as acceptors and are well matched with the a_1 and e_1 orbitals of the C_5Me_5 ring [12].

Such a study was not carried out on complexes of the type synthesised in the present work namely CpCo(CO)L′L″. Because of the lesser symmetry of the Co(CO)L′L″ (C_s) fragment a greater percentage of splitting can be expected, with the subsequent increase in the width of the adsorption bands. The electronic spectra therefore display wide bands, poorly resolved, in the 15500–21800 cm^{-1} range, due to d–d transitions. An intense band appears in the 30300–27500 cm^{-1} range as a result of charge transfer from the metal to the π^* orbital of the CN, CO or NCO. The substituents in the cyclopentadiene ring exert an influence on the position of this band. Consequently, the donor effect of the methyl group increases the negative charge on the cobalt and the $M \rightarrow \pi^*$ transition requires less energy. This is evident, for example, in the case of the $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$ compounds [11].

In the present study, a similar decrease was observed when the position of this band was compared with that for related unsubstituted compounds of the type $(\eta^5\text{-}C_5H_5)Co(CO)(CN)(X)$ (X = NCS, NCSe) [3].

The ^1H NMR spectra display a single signal that can be attributed to the 15 equivalent protons of the 5 substituted methyl groups in the ring.

Experimental

All reactions were carried out under oxygen-free N_2. The pentamethylcyclopentadiene [13], $(\eta^5\text{-}C_5Me_5)Co(CO)_2$ [14] and the pseudohalogens ICN, BrCN [15] and INCO [16] were prepared by published procedures.

The cobalt was determined by titration of the Co-EDTA complex in presence of NET as indicator.

The IR spectra were recorded in the range 4000–200 cm^{-1} on a Perkin–Elmer model 325, using Nujol and Hostaflon mulls between CsI windows. ^1H NMR spectra were recorded on a Varian model XL-100/15.

The visible spectra were recorded on a Pye Unicam SP8-100 ultraviolet spectrophotometer.

Preparation of $(\eta^5\text{-}C_5Me_5)Co(CO)I(CN)$

In a two-neck flask (100 cm^3) fitted with a N_2 inlet, magnetic stirrer and pressure equalized dropping funnel, $\eta^5\text{-}C_5Me_5Co(CO)_2$ (1.5 g, 6 mmol) was dissolved in Et_2O (30 cm^3) saturated with oxygen-free N_2. A solution of ICN (1 g, 6 mmol) in Et_2O (10 cm^3) was slowly added dropwise. A dark brown solid immediately appeared, and evolution of CO was observed. The solid was filtered off, washed with Et_2O, and dried in vacuum. The yield is 2 g (90%). (Found: C, 38.10; H, 4.07; N, 3.69; Co, 15.80. $C_{12}H_{15}CoNOI$ calcd.: C, 38.41; H, 4.00; N, 3.73; Co, 15.72%. ^1H NMR ($CDCl_3$): δ 2.15 (15H, C_5Me_5)).

Preparation of (η^5-C_5Me_5)Co(CN)Br

Following the procedure described above, solutions of η^5-$C_5Me_5Co(CO)_2$ (1.5 g, 6 mmol) in Et_2O (30 cm^3) and BrCN (0.6 g, 6 mmol) in Et_2O (10 cm^3) were mixed. A dark brown solid was obtained. The yield is 1.75 g (90%. (Found: C, 43.71; H, 4.60; N, 4.12; Co, 18.03. $C_{12}H_{15}CoNOBr$ calcd.: C, 43.92; H, 4.57; N, 4.27; Co, 17.97%. ^1H NMR ($CDCl_3$): δ 2.10 (15H, C_5Me_5)).

Preparation of (η^5-C_5Me_5)Co(CO)(NCO)I

To a solution of η^5-$C_5Me_5Co(CO)_2$ (1.5 g, 6 mmol) in Et_2O (30 cm^3) at −10°C was added a solution of IOCN in EtO_2 (80 cm^3), made from 2.9 g (19 mmol) of AgNCO and 3.8 g (14 mmol) of I_2. A dark green solid rapidly appears, and this is filtered off, washed with Et_2O, and dried in vacuum. The yield is 2 g (90%). (Found: C, 36.38; H, 3.87; N, 3.50; Co, 15.10. $C_{12}H_{15}CoNO_2I$ calcd.: C, 36.84; H, 3.83; N, 3.58; Co, 15.07%. ^1H NMR ($CDCl_3$): δ 2.35 ppm (15H, C_5Me_5)).

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