

CYANOMETHYL CYCLOPENTADIENYL COMPLEXES OF COBALT

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Summary

The reactions of the complexes $\text{CpCo}(\text{CO})\text{L}$ (Cp = cyclopentadienyl, L = CO , PPh_3) with ClCH_2CN have been investigated. Chloroacetonitrile reacts with $\text{CpCo}(\text{CO})\text{PPh}_3$ to give the cationic complex $[\text{CpCo}(\text{CH}_2\text{CN})(\text{CNCH}_2\text{Cl})\text{PPh}_3]^+$, which has been isolated and characterized. Compounds of the type $[\text{CpCo}(\text{CH}_2\text{CN})(\text{bipy})]^+ \text{BPh}_4^-$ and $\text{CpCo}(\text{CH}_2\text{CN})\text{PPh}_3\text{CN}$ have been obtained by substitution reactions.

Introduction

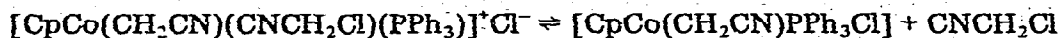
Several transition metal organo complexes containing the CH_2CN group have been reported [1–4]. Among the cobalt group elements, Faraone et al. [5] have prepared complexes of the type $[\text{CpRh}(\text{CO})(\text{CH}_2\text{CN})\text{PPh}_3]^+$ by oxidative addition of chloroacetonitrile to $[\text{CpRh}(\text{CO})\text{PPh}_3]$. In this paper we report the reactions of the $[\text{CpCo}(\text{CO})_2]$ and $[\text{CpCo}(\text{CO})\text{PPh}_3]$ with chloroacetonitrile, and describe the preparation and properties of several new acetonitrile complexes.

Results and discussion

$[\text{CpCo}(\text{CO})_2]$ does not react with chloroacetonitrile at room temperature, but a slow reaction takes place at 70°C to give a completely insoluble brown solid, which presumably contains impure $[\text{CpCo}(\text{CH}_2\text{CN})(\text{CNCH}_2\text{Cl})_2]\text{Cl}$. We cannot yet identify this product, but we note that the behaviour observed is different from that described for the rhodium analogue.

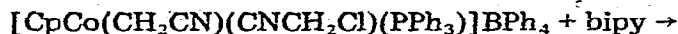
In contrast, $[\text{CpCo}(\text{CO})\text{PPh}_3]$ reacts with an excess of chloroacetonitrile to give the cobalt(III) complex $[\text{CpCo}(\text{CH}_2\text{CN})(\text{CNCH}_2\text{Cl})\text{PPh}_3]^+ \text{Cl}^-$ (I). This substance is stable to air at room temperature. On standing, dilute cyclohexane/benzene solutions of this complex give some violet crystals which have been identified as $[\text{CpCo}(\text{CH}_2\text{CN})\text{PPh}_3\text{Cl}]$, (II). This transformation reveals that the limited coordinating capacity of chloroacetonitrile is surpassed by the chloride when

the solution contains only a small excess of the ligand.



When I is treated with NaBPh_4 in methanol, $[\text{CpCo}(\text{CH}_2\text{CN})(\text{CNCH}_2\text{Cl})\text{PPh}_3]\text{BPh}_4$, (III) is obtained. On the other hand, the cyanide complex $[\text{CpCo}(\text{CH}_2\text{CN})(\text{PPh}_3)\text{CN}]$ (IV) is obtained from I on treatment with a methanolic solution of potassium cyanide. In this case, because of the high coordinating ability of the anion, only the neutral species is isolated.

Finally, in the presence of non coordinating anions, chloroacetonitrile can be replaced by other ligands, and when donor bidentate ligands are used not only the chloroacetonitrile but also the triphenylphosphine is displaced.



Thus, addition of 2,2'-bipyridine to complex III gives $[\text{CpCo}(\text{CH}_2\text{CN})(\text{bipy})]\text{BPh}_4$ (V).

Infrared spectra

The IR spectra of I and III show two strong bands at 2196 and 2237 cm^{-1} , which can be assigned to $\nu(\text{CN})$. These two bands indicate the presence of the cyanomethyl group and the N-bonded chloroacetonitrile. Only the first band appears in complex II and V. The first band is in the region observed for other cyanomethyl complexes [5], and the position of the second, due to the N-bonded chloroacetonitrile, is in accord with the expected displacement with respect to the free ligand. Complex IV shows, along with this band, a second at 2110 cm^{-1} , which corresponds to the $\nu(\text{CN})$ of a terminal cyano group.

Experimental

$[\text{CpCo}(\text{CO})\text{PPh}_3]$ was prepared as described in the literature [6], and $[\text{CpCo}(\text{CO})_2]$ was prepared from $\text{Co}_2(\text{CO})_8$ (Strem Chemicals) and cyclopenta-

TABLE I
ANALYTICAL RESULTS FOR CYANOMETHYLCOBALT COMPLEXES

No Complex	Analysis found (calcd.) (%)		
	C	H	N
I $[\text{CpCo}(\text{CH}_2\text{CN})(\text{NCCH}_2\text{Cl})\text{PPh}_3]\text{Cl}$	60.28 (60.35)	4.62 (4.50)	5.17 (5.21)
II $[\text{CpCo}(\text{CH}_2\text{CN})\text{PPh}_3\text{Cl}]$	64.44 (65.02)	4.48 (4.80)	3.01 (3.03)
III $[\text{CpCo}(\text{CH}_2\text{CN})(\text{NCCH}_2\text{Cl})\text{PPh}_3]\text{BPh}_4$	73.71 (74.60)	5.73 (5.40)	3.40 (3.41)
IV $[\text{CpCo}(\text{CH}_2\text{CN})\text{PPh}_3\text{CN}]$	68.86 (69.03)	4.85 (4.90)	5.84 (6.19)
V $[\text{CpCo}(\text{CH}_2\text{CN})\text{bipy}]\text{BPh}_4$	77.02 (77.01)	5.42 (5.52)	6.31 (6.57)

diene [7]. The other chemicals used were commercial Reagent Grade materials.

IR spectra were recorded with a Perkin-Elmer 457 spectrophotometer using KBr pellets. Melting points were determined with a Reichert Thermopan microscope. Elemental analysis were carried out with a Perkin-Elmer 240 micro-analyzer. Conductivities were measured with a Phillips PW 9501/01 conductimeter.

The analytical data of complexes I-V are shown in Table 1.

Complexes I and II

An excess of chloroacetonitrile (1 ml) was added to a solution of $[\text{CpCo}(\text{CO})\text{PPh}_3]$ (414 mg; 1 mmol) in benzene (100 ml). A precipitate appeared immediately. The solution was stirred for 4 h. The solid was filtered off and dissolved in dichloromethane. The solution was filtered, and addition of cyclohexane gave $[\text{CpCo}(\text{CH}_2\text{CN})(\text{CNCH}_2\text{Cl})\text{PPh}_3]\text{Cl}$ as a violet brown solid, m.p. 144°C.

When cyclohexane was added to a sample of this solution of I in benzene, violet crystals of II formed on standing.

Complexes III and V

When a solution of sodium tetraphenylborate (0.17 g; 0.50 mmol) in methanol was added to a solution of I (0.268 g; 0.50 mmol) in this solvent, a brown precipitate was immediately formed. The solid was filtered off, and recrystallized from dichloromethane/ethyl ether to give IV as red-brown crystals, m.p. 146-150°C. Molar conductivity $55.64 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

When the same procedure was carried out after addition of 2,2'-bipyridine (0.078 g; 0.50 mmol) to the solution of I and stirring for 0.5 h, a brown precipitate was formed rapidly, and red crystals of V were obtained, m.p. 176°C. Yield 65%. Molar conductivity $63.70 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Complex IV

A solution of I (0.268 g; 0.50 mmol) and KCN (0.066 g; 1.0 mmol) in methanol was vigorously stirred for 10 h. The yellow red solution was evaporated to dryness, and the solid residue extracted with dichloromethane, filtered off and recrystallized from dichloromethane/cyclohexane to give orange crystals of IV, m.p. 140°C. Yield 40%.

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