

REACTION OF TETRACYANOCOBALTATE(I) WITH ARYL HALIDES. FORMATION OF σ -ARYLPENTACYANOCOBALTATES(III) AND CYANATION TO ARYL CYANIDES

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Summary

Tetracyanocobaltate(I), which is formed in strongly alkaline solutions of cyanocobaltate under H_2 at $CN:Co < 5:1$, reacts readily with aryl halides to form σ -arylpentacyanocobaltates(III). 1H and ^{13}C NMR spectra of these new and fairly stable complexes have been determined. In the reactions of some aryl halides, aryl cyanides as well as hydrogenolysis products are formed, and α -bromonaphthalene reacts selectively to give the highest yield of the nitrile. The reactions are explained by a mechanism involving an electron-transfer process.

Introduction

In the chemistry of cyanocobaltate, many types of organocyanocobalt complexes are known, e.g. σ -alkylcobalt(III) [1], σ -vinylcobalt(III) [1,2], π -allylcobalt(III) [1,3], and π -olefincobalt(I) [4] complexes, but little is known concerning the formation of σ -arylcobalt(III) complexes. Although σ -alkylpentacyanocobaltates(III) have been prepared via free radical intermediates [1,5] by the reaction of alkyl halides with $[Co(CN)_5]^{3-}$, aryl halides scarcely react with the cobalt(II) complex. σ -Phenyl- and σ -pyridyl-pentacyanocobaltates(III) have been prepared by the reaction of phenyldiazonium chloride [1c] and α -iodopyridine [5], respectively, with $[Co(CN)_5]^{3-}$, but the reaction has not been studied in detail. We report here that σ -arylpentacyanocobaltates(III) are readily formed by the reaction of aryl halides with a cobalt(I) species, $[Co(CN)_4]^{3-}$, which is formed at $CN:Co < 5:1$ in strongly alkaline solution under an atmosphere of hydrogen. The σ -aryl complexes form arylcyanides by the reaction analogous to the tetracyanocobaltate(I)-catalyzed cyanation of vinyl halides [2].

Experimental

General procedure

The solution of cyanocobaltate was prepared by mixing $CoCl_2$, KCN, and KOH

(mole ratio, Co : CN : OH = 1 : 4.95 : 2, [Co] = 0.2 *M*) in 2 ml of D₂O or 5 ml of H₂O in an atmosphere of hydrogen at 55°C. A 20-ml two-necked flask, which was equipped with a cold finger and connected to a gas buret, was used, and the solution was stirred magnetically. Liquid aryl halides (mole ratio, halide : Co = 2 : 1) were added with a microsyringe through a serum cap after preabsorption of hydrogen, but crystalline halides were mixed with metal salts before addition of the solvent. The progress of the reaction was followed by gas chromatographic analysis of samples extracted with dichloromethane, and the GLC yield was estimated by using an internal reference.

Determination of NMR spectra of the complexes in the reaction solutions

The solution prepared in D₂O was filtered through cotton packed in a glass tube into an NMR tube, and NMR spectra were measured on a Jeol FX-100 spectrometer. ¹H NMR spectra were taken at room temperature and ¹³C NMR under cooling to minimize the temperature rise caused by the pulse radiation.

Isolation of a stable σ-arylpentacyanocobaltate(III)

The solution from the reaction of *p*-bromobenzonitrile, which gives the most stable complex, was extracted with benzene, and the aqueous fraction was concentrated in vacuo to give a pale yellow powder. Chromatographic separation of the complexes was carried out on a column of alumina (200 mesh) using H₂O-MeOH (1 : 1) as the eluent. The σ-*p*-cyanophenylcobalt complex, which was contained in the last eluent, was characterized by IR and NMR spectroscopy and elemental analysis.

Results and discussion

Mono-substituted bromobenzenes and α- and β-halonaphthalenes reacted with cyanocobaltate at CN : Co < 5 : 1, but scarcely reacted at CN : Co > 5 : 1. The reactivity was greatly dependent on the substituent and the halogen. Bromobenzenes substituted by electron-donating groups were less reactive than those substituted by electron-withdrawing groups, and the reactivity of halonaphthalenes decreased, depending on the halide in the order of I ≥ Br ≫ Cl and α-Br ≫ β-Br.

¹H NMR spectra of the reaction solution in D₂O indicated clearly the formation of σ-arylcobalt complexes, most probably [ArCo(CN)₅]³⁻. Table 1 shows the NMR data for the various σ-arylcobalt complexes. ¹³C NMR spectra were also observed with some more stable complexes, and data are given in Table 2. In the reaction of *p*-dibromobenzene, in addition to doublets at 7.08 and 7.81 ppm ascribable to phenyl proton resonances of [BrC₆H₄Co(CN)₅]³⁻, a singlet at 7.42 ppm was observed, suggesting the formation of [(NC)₅CoC₆H₄Co(CN)₅]⁶⁻. The carbon resonance corresponding to the dicobalt complex was also observed at 143.4 ppm (d, *J* = 158 Hz). In the reaction of *p*-bromoacetophenone, the H-D exchange of the methyl protons of [CH₃COC₆H₄Co(CN)₅]³⁻ with D₂O was observed.

We have attempted to isolate [σ-arylCo(CN)₅]³⁻. Very few organocyanocobaltates have been isolated in a pure form, probably because of the instability of the complexes or the difficulty of separation of impurities [6]. The IR spectrum of the complex isolated from the reaction solution with *p*-bromobenzonitrile indicated clearly the presence of the *p*-cyanophenyl ligand (2239s(sh), 1620s(br), 1575s(sh), 1475s(sh), 1390w(br), 1180w(sh), 1040w(sh), 1010s(sh), 830s(sh), 550m(br) cm⁻¹).

TABLE 1

¹H NMR DATA FOR σ -ARYLPENTACYANOCOBALTATES(III)

Aryl ^a	δ (ppm) ^b (<i>J</i> , Hz)
<i>p</i> -NH ₂ C ₆ H ₄	6.65 (d, 6.5), 7.75 (d, 6.5)
<i>p</i> -CH ₃ OC ₆ H ₄	3.82 (s), 6.79 (d, 8.2), 7.67 (d, 8.2)
<i>p</i> -CH ₃ C ₆ H ₄	2.68 (s), 6.96 (d, 6.5), 7.67 (d, 6.5)
<i>m</i> -CH ₃ C ₆ H ₄	2.22 (s), 6.48 (s, br), 7.04 (q, br), 7.66 (q, br)
<i>o</i> -CH ₃ C ₆ H ₄	2.70 (s), 6.98 (s, br), 7.94 (d, br)
C ₆ H ₅	7.03 (s, br), 7.82 (s, br)
<i>p</i> -BrC ₆ H ₄	7.08 (d, 7.7), 7.81 (d, 7.7)
<i>p</i> -ClC ₆ H ₄	7.08 (d, 7.7), 7.76 (d, 7.7)
<i>p</i> -CH ₃ COC ₆ H ₄	2.55 (s), 7.58 (d, 8.5), 8.06 (d, 8.5)
<i>p</i> -NCC ₆ H ₄	7.34 (d, 8.5), 8.04 (d, 8.5)
α -C ₁₀ H ₇	7.26 (t), 7.54 (m), 7.82 (m), 8.25 (d), 8.91 (m)
β -C ₁₀ H ₇	7.45 (m), 7.63 (d, 8.5), 7.79 (d, 9.0), 7.88 (d, 9.0), 8.07 (d, 8.3), 8.29 (s)

^a C₁₀H₇ = naphthyl. ^b (CH₃)₃SiCD₂CD₂CO₂Na was used as an internal reference.

the CN ligands (2128m(sh), 2110vs(sh) cm⁻¹), and also H₂O (near 3500s(br) cm⁻¹). The elemental analysis of this hygroscopic complex was not satisfactory enough to conclude that the isolated complex was analytically pure, but the C : N ratio (Found: 1.74, calcd.: 1.72) indicated that the complex was σ -*p*-cyanophenylpentacyanocobaltate(III) rather than a tetracyanocobaltate(III) such as [NCC₆H₄Co(CN)₄-Co(CN)₄C₆H₄CN]⁶⁻: Found: C, 35.04; H, 2.15; N, 20.13; calcd. for K₃-[NCC₆H₄Co(CN)₅]: C, 35.29; H, 0.99; N, 20.58; calcd. for K₃[NCC₆H₄Co(CN)₅]·0.5H₂O: C, 34.53; H, 1.21; N, 20.13%.

GLC analysis of the extract from the solution in H₂O indicated that aryl cyanides were formed from some aryl halides; the results are shown in Table 3. Aryl halides which form stable σ -complexes, e.g. *p*-BrC₆H₄Br, *p*-CH₃COC₆H₄Br and *p*-NCC₆H₄Br, did not give nitriles, whereas C₆H₅Br, *o*-, *m*-, and *p*-CH₃C₆H₄Br, and *p*-CH₃OC₆H₄Br formed nitriles, but the yields were very low. *p*-NH₂C₆H₄Br, which has a strong electron-donating substituent, formed *p*-NH₂C₆H₄CN in a considerable

TABLE 2

¹³C NMR DATA FOR σ -ARYLPENTACYANOCOBALTATES(III)

Aryl	δ (ppm) ^a (<i>J</i> (CH) Hz)
C ₆ H ₅	123.2 (d, 159), 127.2 (d, 154), 143.7 (d, 158)
<i>p</i> -BrC ₆ H ₄	127.4 (d, 158), 144.0 (d, 161)
<i>p</i> -ClC ₆ H ₄	126.6 (dd, 165, 4) 145.0 (dd, 163, 9)
<i>p</i> -CH ₃ COC ₆ H ₄	26.8 (q, 128), 125.9 (dd, 159, 6), 132.0 (s), 144.6 (dd, 161, 9), 205.8 (s)
<i>p</i> -NCC ₆ H ₄	105.5 (s), 123.1 (s), 129.9 (dd, 165, 6), 145.4 (dd, 165, 9)

^a Dioxane was used as an internal reference. Resonances due to the carbon atoms linked to the cobalt atom could not be observed.

TABLE 3

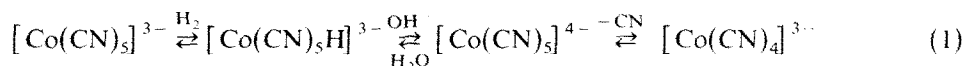
CYANATION AND HYDROGENOLYSIS OF ARYL HALIDES CATALYZED BY TETRACYANOCOBALTATE(I)^a

Aryl-X	Conversion ^b (mol %)	Yield (mol%) ^b	
		Aryl-CN	Aryl-H
<i>p</i> -NH ₂ C ₆ H ₄ Br	62	25	15
<i>p</i> -CH ₃ OC ₆ H ₄ Br	21	4	1
α -C ₁₀ H ₇ I	66	24	27
	69 ^c	0	55
α -C ₁₀ H ₇ Br	82	64	4
	93 ^d	84	4
α -C ₁₀ H ₇ Cl	26	18	trace
β -C ₁₀ H ₇ Br	39 ^e	7	2

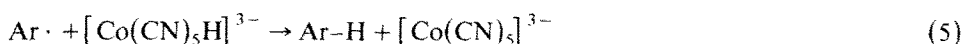
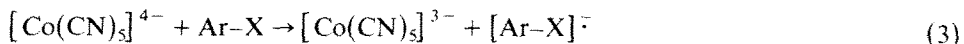
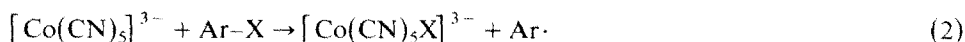
^a CoCl₂ (1 mmol), KCN (4.95 mmol), KOH (2 mmol), Aryl-X (2 mmol) in 5 ml H₂O, at 55°C and under H₂. Reaction time: 24 h. ^b Determined by GLC analysis, based on added aryl halides. ^c KCN (6 mmol) was used. ^d Reaction time: 48 h. ^e 0.1 ml of toluene was added to dissolve the crystalline bromide.

yield together with C₆H₅NH₂. Cyanation and hydrogenolysis were also observed in the reaction with α -iodonaphthalene, but the formation of naphthalene was observed only in the initial stage. α -Bromonaphthalene yielded selectively α -naphthonitrile in a good yield (more than the stoichiometric yield). The reaction of α -chloronaphthalene was also selective, but very slow. β -Bromonaphthalene also formed β -naphthonitrile, although the reactivity was very low. Interestingly, α -iodonaphthalene reacted at CN:Co = 6:1 to give selectively naphthalene. The bromo and chloro compounds scarcely reacted under the same conditions, and the detectable product was α -naphthonitrile.

The strongly alkaline solution of cyanocobaltate in H₂ may contain the following active species which are in equilibria (eq. 1) [2,7]:

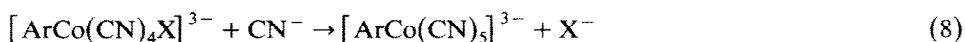
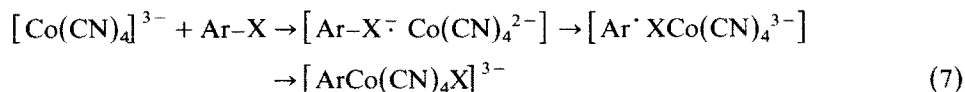


The reaction of [Co(CN)₅]³⁻ with aryl halides to form aryl radicals (eq. 2) seems to be less probable since homolytic splitting of a aryl carbon-halogen bond is far less favorable than that of a alkyl carbon-halogen bond. The formation of the hydrogenolysis products from aryl iodides even at CN:Co > 5:1 suggests the formation of the aryl radicals and the subsequent reaction with [Co(CN)₅H]³⁻. The aryl radicals may be formed by the reaction of aryl halides with [Co(CN)₅]⁴⁻ (eqs. 3 and 4), and the hydrogenolysis product and the σ -complex may be formed by eqs. 5 and 6. However, the reactions 3,4 and 6





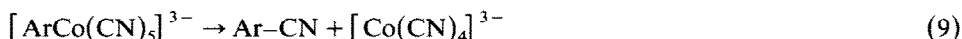
cannot explain the result that the σ -aryl complex is formed at $\text{CN}:\text{Co} < 5:1$ rather than at $\text{CN}:\text{Co} > 5:1$. The effect of the $\text{CN}:\text{Co}$ ratio suggests that the active species for the formation of the σ -aryl complex is $[\text{Co}(\text{CN})_4]^{3-}$. The reaction must proceed by the oxidative addition of aryl halides to $[\text{Co}(\text{CN})_4]^{3-}$ via a one electron-transfer process (eq. 7), followed by a rapid ligand substitution (eq. 8):



Reaction 7 may proceed in the solvent cage without forming a free aryl radical, but if diffusion from the cage is sufficiently competitive, the hydrogenolysis product may be formed by reaction 5.

Known examples of σ -aryl complexes of cobalt are few in comparison with those of other transition metals [8]. Some of them were prepared by the reaction of aryl halides with cobalt(I) complexes [9], but the reaction mechanism have been scarcely studied. It has been reported that aryl halides are generally less reactive than vinyl halides in oxidative addition to nickel(0) and platinum(0) [10], but the present results indicate that aryl halides react with cobalt(I) in a similar way to the reaction of vinyl halides [2]. The fact that most aryl bromides react to give σ -aryl complexes without forming the hydrogenolysis products, in spite of the presence of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ supports the oxidative addition process without formation of the free radical intermediate. The formation of the free radical may be likely only when departure of a halide anion from the anion radical is facile; this must be the case for iodonaphthalene and *p*-aminobromobenzene. The fact that the reactivity of aryl halides increases with the increasingly electron-withdrawing substituents is consistent with the electron-transfer process.

Transformation of aryl halides to aryl cyanides has been performed with nickel [11], palladium [12] and copper [13] complexes or salts, but the present reaction is the first to show the cyanation of aryl halides by a cobalt complex. The reaction probably proceeds by the reductive coupling of the aryl and cyanide ligands of the σ -aryl complexes (eq. 9):



The regeneration of $[\text{Co}(\text{CN})_4]^{3-}$ may explain the catalytic reaction. The reaction is facilitated by the relatively weak aryl-Co bond, but σ -arylpentacyanocobaltates(III) seem to be much more stable than σ -arylnickel complexes.

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