

Intermediate complexes for formation of nitriles in the hydrocyanation and cyanation by cyanocobaltate

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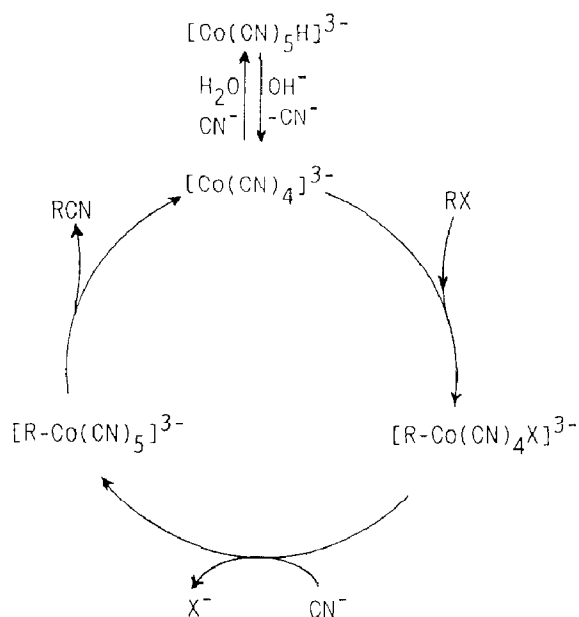
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Abstract

The proposed intermediate for the hydrocyanation of $\text{PhC}\equiv\text{CH}$ and cyanation of $\text{PhC}(\text{Br})=\text{CH}_2$ by cyanocobaltate has been isolated as $\text{K}_3[\text{CH}_2=\text{C}(\text{Ph})-\text{Co}(\text{CN})_5] \cdot 2\text{H}_2\text{O}$. The effect of the $\text{CN}:\text{Co}$ ratio on its formation from $\text{PhC}\equiv\text{CH}$ and on its decomposition to form nitriles has indicated that $[\text{CH}_2=\text{C}(\text{Ph})-\text{Co}(\text{CN})_5]^{3-}$ is not a real intermediate in formation of $\text{PhC}(\text{CN})=\text{CH}_2$, and that the importance of a ratio of $\text{CN}:\text{Co} < 5:1$ for the two reactions becomes manifest in the steps of formation of the σ -vinylcyanocobaltate in which the number of the CN ligand is less than 5 and of its decomposition to nitriles by reductive elimination.

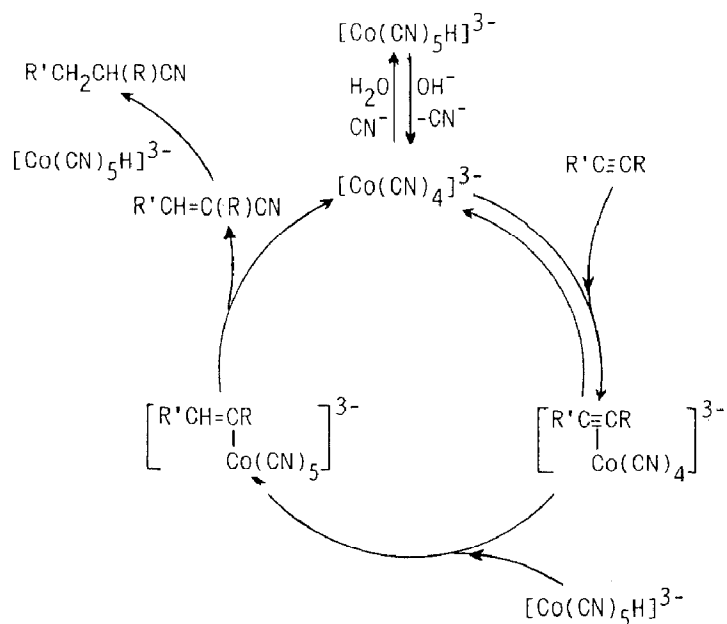
Introduction

The development of transition metal catalysis for the synthesis of nitriles is important, and the elucidation of the mechanism yields information useful in organometallic chemistry. Hydrocyanation is an important industrial process, and its mechanism has recently been studied in some detail, [1–6]. Previously, we found a new type of hydrocyanation catalyzed by cyanocobaltate [7] or cyanonickelate [8] which proceeds without the use of hydrogen cyanide. The active complex in the reaction by cyanocobaltate, $[\text{Co}(\text{CN})_5\text{H}]^{3-}$, is formed by activation of molecular hydrogen. The reaction is applicable only to acetylenes. In relation to this reaction we have also found that the stereoselective cyanation of vinyl and aryl halides is catalyzed by cyanocobaltate [9]. These results have indicated new reactions of cyanocobaltate for synthetic use. One characteristic feature is that the reaction proceeds only at $\text{CN}:\text{Co} < 5:1$ ($\text{CN}:\text{Co}$ denotes the mole ratio of CN^- and Co^{2+} used for the formation of cyanocobaltate). We have proposed Schemes 1 and 2 for cyanation [9] and hydrocyanation [7], respectively. The key points in these schemes are: (i) the formation of a Co^I species, i.e. $[\text{Co}(\text{CN})_4]^{3-}$ ($\text{CN}:\text{Co} = 4:1$), as an active species, (ii) the formation of σ -vinyl- and σ -aryl-pentacyanocobaltates as



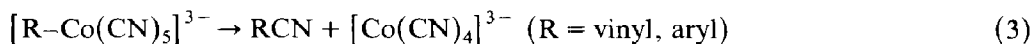
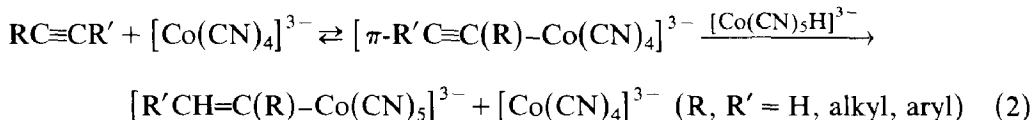
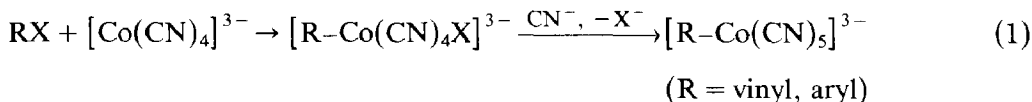
Scheme 1

intermediates, and (iii) the formation of nitriles from the σ -complexes by reductive elimination of the ligands. The oxidative addition of halides to the Co^I species (eq. 1) and formation of the π -acetylene- Co^I species (eq. 2) have been assumed because



Scheme 2

the reductive elimination (eq. 3) should not be affected by the CN : Co ratio.



Although the number of cyanide ligands remained uncertain, the formation of the σ -complexes in the reaction solution was shown by ^1H NMR (in the case of cyanation of halides) and it seemed reasonable to assume that $[\text{RCo}(\text{CN})_5]^{3-}$ was an intermediate since it regenerates $[\text{Co}(\text{CN})_4]^{3-}$ by eq. 3. However, it often happens that the detected species are not necessarily direct intermediates. In this work, we have isolated and identified $[\text{CH}_2=\text{C}(\text{Ph})-\text{Co}(\text{CN})_5]^{3-}$, which is a common intermediate for cyanation of $\text{PhC}(\text{Br})=\text{CH}_2$ and hydrocyanation of $\text{PhC}\equiv\text{CH}$, and studied the mechanisms of its formation in the hydrocyanation and its decomposition to form nitriles. We report here that the requirement of $\text{CN} : \text{Co} < 5 : 1$ is important in the decomposition of the intermediate rather than that of its formation, and we propose new processes in place of eqs. 2 and 3.

Experimental

UV spectroscopy of the formation of the intermediate in the hydrocyanation of phenylacetylene

An aqueous solution of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ was prepared by stirring CoCl_2 (0.2 mol dm^{-3}) and KCN (variable amounts) in water (20 cm^3) for 0.5 h at 45°C under 1 atm H_2 . Phenylacetylene ($\text{PhC}\equiv\text{CH} : \text{Co} = 2 : 1$ or $1 : 1$) was added by microsyringe through a rubber serum cap. The solution ($\text{CN} : \text{Co} > 5 : 1$) remained homogeneous, but green (before addition of $\text{PhC}\equiv\text{CH}$) and pink (after addition of $\text{PhC}\equiv\text{CH}$) precipitates were formed at $< 5 : 1$. Portions of the solution were then withdrawn by syringe and diluted with water to 0.02 mol dm^{-3} and filtered under N_2 . The diluted solutions were diluted further to 0.002 mol dm^{-3} in the UV cell (light path length = 0.1 cm). UV spectra were recorded with a Shimadzu UV-260 spectrometer at room temperature.

Isolation of σ -vinylcyanocobaltate

Reaction of phenylacetylene under the conditions of hydrocyanation was performed by stirring CoCl_2 , KCN, and phenylacetylene ($[\text{Co}] = 0.2$ mol dm^{-3} , $\text{Co} : \text{CN} : \text{PhC}\equiv\text{CH} = 1 : 5.2 : 1.1$) in water (40 cm^3) for 1 h at 45°C under 1 atm H_2 . The solution was added to 160 cm^3 acetone and stirred for 0.5 min. Aqueous acetone was decanted to give a dark-brown oil. 1-Propanol was added to the oily solution (ratio of volume of 1-propanol to that of oil = 3 : 7) and stirred vigorously. After filtration, the solution was chromatographed over the activated alumina with $\text{H}_2\text{O}/1\text{-propanol}$ (volume ratio = 7 : 3) as eluant. The fractions containing a yellow

solution were collected, and the solvent was evaporated in vacuo to give a yellow solid.

The data indicate that $K_3[H_2C=C(Ph)-Co(CN)_5] \cdot 2H_2O$ had formed, though the hygroscopic solid was not crystallized from solution. Found: C, 34.45; H, 2.12; N, 16.33. $C_{13}H_{11}CoK_3N_5O_2$ calcd.: C, 35.05; H, 2.49; N, 15.72%. ν_{max} (KBr) 2102 cm^{-1} ($C \equiv N$); λ_{max} 262 nm ($\epsilon\ 1 \times 10^4\text{ mol}^{-1}\text{ cm}^2$). $\delta_H(D_2O)$ 5.14 (d, 1H), 5.56 (d, 1H), 7.25–7.40 (m, 5H); $\delta_C(D_2O)$ 124.3 (dd, J_{CH} 149, 159), 158.1 (s), 124.9 (d, J_{CH} 158), 127.4 (d, J_{CH} 139), 127.8 (d, J_{CH} 158), 129.5 (s).

Kinetic study on the formation of $[H_2C=C(Ph)-Co(CN)_5]^{3-}$

The dependence of the initial rates of formation of $[H_2C=C(Ph)-Co(CN)_5]^{3-}$ on the initial concentration of $PhC \equiv CH$ ($[PhC \equiv CH]_0$) and $[Co(CN)_5H]^{3-}$ ($[Co(CN)_5H]_0^{3-}$) was studied spectroscopically by monitoring the peak intensity at 262 nm. Aqueous solutions of $[Co(CN)_5H]^{3-}$ were prepared by stirring $CoCl_2$ (15 mmol dm^{-3}) and KCN (78 mmol dm^{-3} ; CN : Co = 5.2 : 1) in water (20 cm^3) for 0.5 h at 25°C in 1 atm H_2 . After addition of $PhC \equiv CH$ (2.9 ~ 6.4 mmol dm^{-3}) by microsyringe, portions of the mixture were withdrawn at regular intervals to record the UV spectra in a cell of 0.1 cm light path length. Dependence of the initial rates on the $[Co(CN)_5H]_0^{3-}$ was determined at $[PhC \equiv CH]_0 = 6.4\text{ mmol dm}^{-3}$ by varying the $CoCl_2$ (10 ~ 20 mmol dm^{-3}) and KCN concentrations (CN : Co = 5.2 : 1). The initial concentration, $[Co(CN)_5H]_0^{3-}$, was estimated, before addition of $PhC \equiv CH$, from the height of its characteristic band (310 nm, $\epsilon\ 610\text{ mol}^{-1}\text{ cm}^2$) [10].

Nitrile formation from $K_3[H_2C=C(Ph)-Co(CN)_5] \cdot 2H_2O$

Decomposition of the complex was monitored by UV spectroscopy. Thus, the complex (0.046 g, 0.1 mmol) and $CoCl_2$ (variable amounts, 0 ~ 0.2 mmol) were placed in a 5- cm^3 flask. Water (2 cm^3) was added under H_2 or N_2 and the solution was stirred at 45°C . Portions of the solution were withdrawn, diluted with water, and filtered. UV spectra were recorded in a cell of 0.1 cm light path length.

The formation of nitriles was monitored by GLC analysis of extracts from the reaction solution. Thus, the complex (0.113 g, 0.25 mmol) and $CoCl_2$ (variable, 0 ~ 0.5 mmol) were placed in a flask. Water (5 cm^3) was added under H_2 or N_2 , and the solution was stirred at 45°C . Aliquots (0.2 cm^3) of the solution were withdrawn at regular intervals, and benzonitrile (0.008 cm^3) added as an internal reference and dichloromethane (0.5 cm^3) added for extraction. A 3-m column of PEG-20M was used for GLC analysis.

Results and discussion

In the nitrile formation by cyanation of vinyl and aryl halides [9], we detected the σ -vinyl and σ -aryl complexes at CN : Co < 5 : 1, but not at CN : Co > 5 : 1. For the hydrocyanation of acetylenes, we did not study the formation of the intermediate, but presumed the same situation as that in the cyanation of halides, since nitriles are also only formed at CN : Co < 5 : 1 [7]. Since formation of the π -acetylene complex before that of the σ -complex was assumed, in order to explain the formation of σ -complex only at CN : Co < 5 : 1 (eq. 2), it is first important to make sure of the formation of the σ -complex in the hydrocyanation of acetylenes and the effect of the CN : Co ratio on that formation.

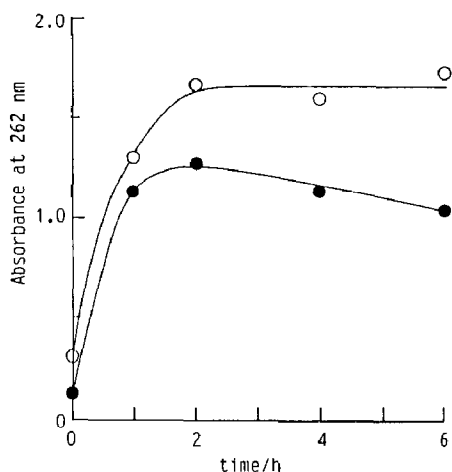
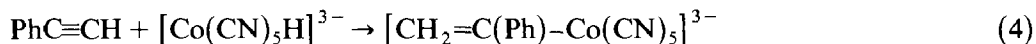


Fig. 1. Effect of the CN:Co ratio on the formation of the intermediate complex, monitored at 262 nm. At 45°C, 1 atm H₂, [Co]₀ = 0.2 mol dm⁻³, [PhC≡CH]₀ = 0.4 mol dm⁻³. CN:Co = (○) 5.5:1, (●) 4.5:1. Spectra were measured after dilution.

We first studied the formation of the intermediate in the hydrocyanation of phenylacetylene by UV spectroscopy. We found that the change in the band at 262 nm corresponds to that of an intermediate complex. As shown in Fig. 1, the intensity of the band increases both at CN:Co > 5:1 and < 5:1, indicating that the complex is formed regardless of the CN:Co ratio. The intensity remains constant after it attains the maximal intensity at CN:Co = 5.5:1, and begins to decrease at CN:Co = 4.5:1. This result indicates that the complex is stable at CN:Co ratios greater than 5:1 and less stable at CN:Co < 5:1. The formation of the intermediate complex at CN:Co > 5:1 strongly suggests that the intermediate complex is formed without prior formation of the π -acetylene complex.

We have isolated the complex which exhibits the 262 nm band from the reaction solution. The complex was identified as K₃[CH₂=C(Ph)-Co(CN)₅] · 2H₂O, indicating clearly the formation of [CH₂=C(Ph)-Co(CN)₅]³⁻ in solution.

Formation of the σ -complex was studied kinetically at 25°C, CN:Co = 5.2:1, and 1 atm H₂. As shown in Fig. 2, the initial rate is dependent on the [Co(CN)₅H]³⁻ and [PhC≡CH]. The first order dependence on each concentration supports the direct formation of the intermediate by eq. 4 rather than eq. 2.



Next, we studied the decomposition of the σ -complex. The effect of the CN:Co ratio on the decomposition of the complex was studied by addition of CoCl₂. As shown in Fig. 3, the intensity of the band at 262 nm scarcely decreases when no CoCl₂ is added to the solution of the complex (CN:Co = 5:1), but upon addition of CoCl₂ (CN:Co = 3:1) it decreased very rapidly in the initial stage and then slowly. This indicates that [CH₂=C(Ph)-Co(CN)₅]³⁻ is resistant to spontaneous decomposition and that the less stable complex is formed by the addition of CoCl₂.

Figure 4 shows the effect of the addition of CoCl₂ on the formation of nitriles (PhC(CN)=CH₂ + PhCH(CN)CH₃) from the σ -vinyl complex in H₂. Nitriles were formed only after the addition of CoCl₂. Curves indicate that the initial rates and yields increase in the order of CN:Co = 4:1 < 3:1 < 2:1 = 1:1 and 4:1 < 1:1 <

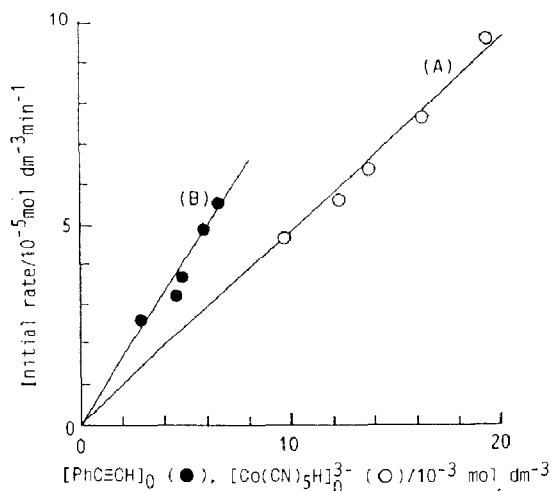


Fig. 2. Dependence of initial rates of formation of $[\text{CH}_2=\text{C}(\text{Ph})-\text{Co}(\text{CN})_5]^{3-}$ on the initial concentrations of $\text{PhC}\equiv\text{CH}$ and $[\text{Co}(\text{CN})_5\text{H}]^{3-}$. $\text{CN}:\text{Co} = 5.2:1$, at 25°C , 1 atm H_2 . (A) $[\text{PhC}\equiv\text{CH}]_0 = 6.4 \times 10^{-3}$ mol dm^{-3} ; (B) $[\text{Co}(\text{CN})_5\text{H}]_0^{3-} = 1.5 \times 10^{-2}$ mol dm^{-3} . Concentration of $[\text{CH}_2=\text{C}(\text{Ph})-\text{Co}(\text{CN})_5]^{3-}$ was determined spectroscopically.

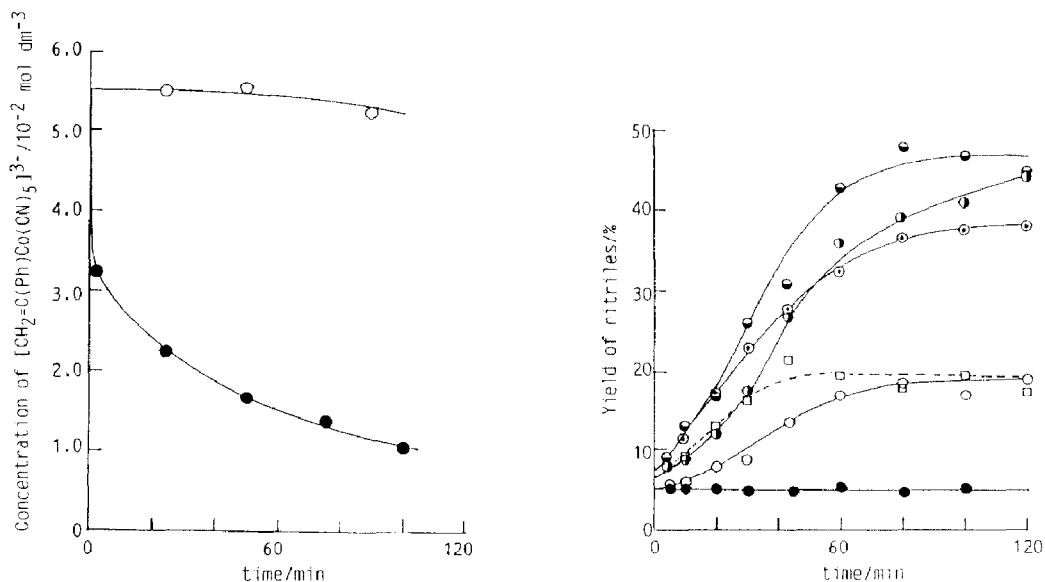
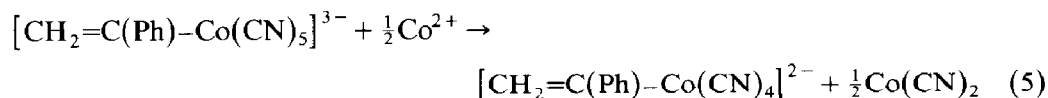


Fig. 3. Effect of addition of $[\text{Co}]^{2+}$ on the decomposition of $[\text{CH}_2=\text{C}(\text{Ph})-\text{Co}(\text{CN})_5]^{3-}$. $[\text{CH}_2=\text{C}(\text{Ph})-\text{Co}(\text{CN})_5]_0^{3-} = 5.5 \times 10^{-2}$ mol dm^{-3} , at 45°C , 1 atm H_2 . $\text{CN}:\text{Co}$ after addition of $[\text{Co}]^{2+}$: (○) 5:1, (●) 3:1. Concentration of $[\text{CH}_2=\text{C}(\text{Ph})-\text{Co}(\text{CN})_5]^{3-}$ was determined spectroscopically.

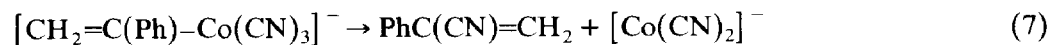
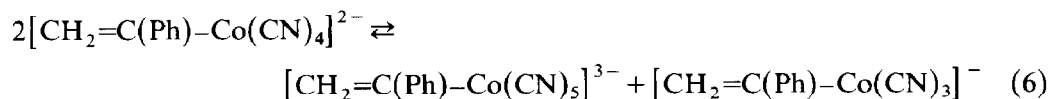
Fig. 4. Effect of the addition of $[\text{Co}]^{2+}$ on the formation of nitriles from $[\text{CH}_2=\text{C}(\text{Ph})-\text{Co}(\text{CN})_5]^{3-}$. $[\text{CH}_2=\text{C}(\text{Ph})-\text{Co}(\text{CN})_5]_0^{3-} = 6 \times 10^{-2}$ mol dm^{-3} , at 45°C , 1 atm H_2 . $\text{CN}:\text{Co}$ after addition of $[\text{Co}]^{2+}$: (○) 5:1, (●) 4:1, (◐) 3:1, (◑) 2:1, (◒) 1:1, (◓) 2:1 under N_2 . Yield of nitriles ($\text{PhC}(\text{CN})=\text{CH}_2 + \text{PhCH}(\text{CN})\text{CH}_3$) is based on the complex.

3:1 < 2:1, respectively, but differences at CN:Co \leq 3:1 are small. The curve at CN:Co = 4:1 indicates that decomposition of the complex ceases at the lower level of yield.

As for the structure of the complex which decomposes to give nitriles, we can assume a σ -vinylcyanocobaltate with a CN:Co ratio of less than 5:1. Since the addition of CoCl₂ immediately forms pink precipitates, probably of Co(CN)₂, formation of [CH₂=C(Ph)-Co(CN)₄]²⁻ is expected by the following reaction.



[CH₂=C(Ph)-Co(CN)₄]²⁻ must be sufficiently unstable to decompose spontaneously, but the rate of decomposition and the yield of nitriles are poor at CN:Co = 4:1, compared with those at CN:Co \leq 3:1. Cessation of decomposition of the complex at low reaction levels at CN:Co = 4:1 indicates that the decomposition of [CH₂=C(Ph)-Co(CN)₄]²⁻ is only partial. The result that the yield at CN:Co = 4:1 is nearly one half of those at CN:Co \leq 3:1 indicates that the equilibrium (6) exists at CN:Co = 4:1. [CH₂=C(Ph)-Co(CN)₃]⁻ may decompose more readily (eq. 7), to leave the stable complex [CH₂=C(Ph)-Co(CN)₅]³⁻. At CN:Co \leq 3:1, the formation of [CH₂=C(Ph)-Co(CN)₅]³⁻ is less probable and this is supported by the higher yield of nitriles and the similar rates of nitrile formation.



The cessation of decomposition at low yields of nitriles was also observed in the reaction under N₂ as shown in Fig. 4. This indicates that the presence of hydrogen is important for the decomposition of the complex. As shown in Fig. 5, the time course of the product formation in H₂ indicates that the initial product,

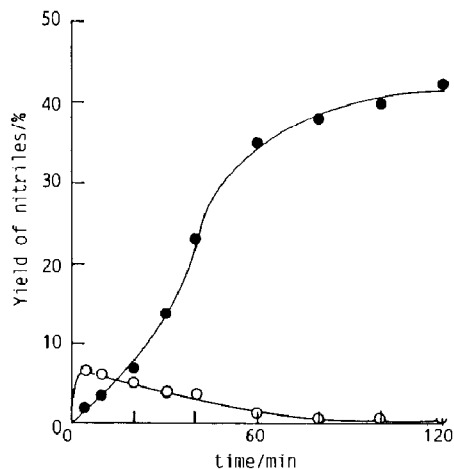
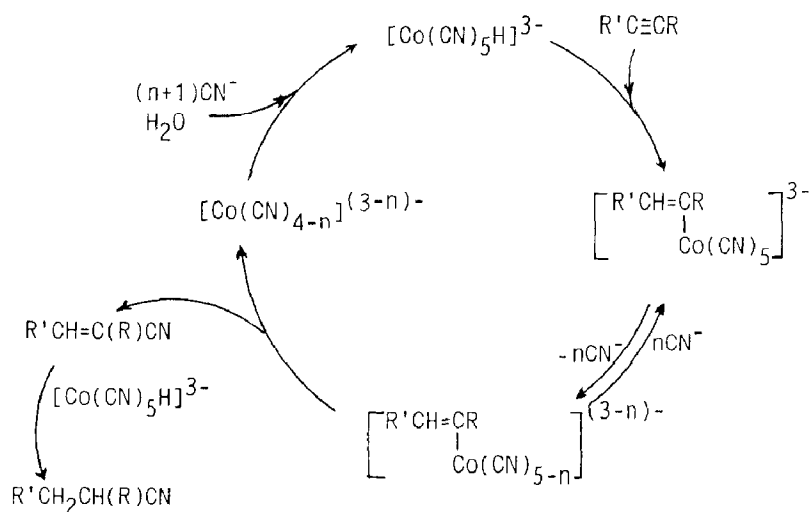
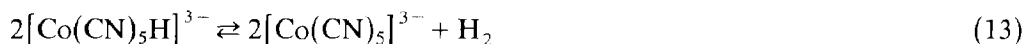
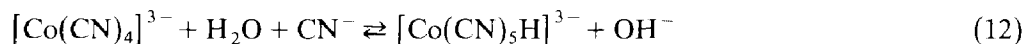
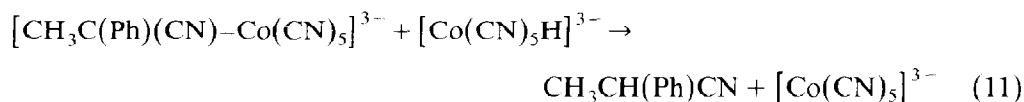
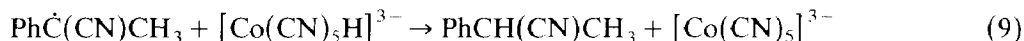
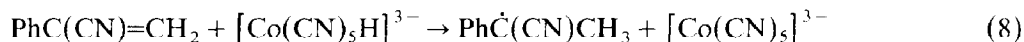


Fig. 5. Time-course of the formation of nitriles from [CH₂=C(Ph)-Co(CN)₅]³⁻. [CH₂=C(Ph)-Co(CN)₅]₀³⁻ = 5.5 × 10⁻² mol dm⁻³, at 45°C, 1 atm H₂, CN:Co = 3:1 after addition of [Co]²⁺. (○) PhC(CN)=CH₂, (●) PhCH(CN)CH₃.



Scheme 3

$\text{PhC}(\text{CN})=\text{CH}_2$, is readily hydrogenated to $\text{PhCH}(\text{CN})\text{CH}_3$. Hydrogenation of $\text{PhC}(\text{CN})=\text{CH}_2$, either by the radical process (eqs. 8, 9) [11] or by the process involving the intermediate, $[\text{CH}_3\text{C}(\text{Ph})(\text{CN})-\text{Co}(\text{CN})_5]^{3-}$ (eqs. 10, 11), requires the presence of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$. Since reductive elimination of the Co^{III} species forms the Co^{I} species, see eqs. 3 and 7, the Co^{I} species should be reoxidized to $[\text{Co}(\text{CN})_5\text{H}]^{3-}$. This step probably follows reaction (12). Hydrogen effectively inhibits the conversion of the $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ thus formed into $[\text{Co}(\text{CN})_5]^{3-}$ (eq. 13).



The hydrocyanation of acetylenes by cyanocobaltate is summarized in Scheme 3, in which n may be 2 or 3. The effect of the $\text{CN}:\text{Co}$ ratio is manifested in the equilibrium between σ -vinylcyanocobaltates. This equilibrium is probably also present in the catalytic cyanation of vinyl and aryl halides in Scheme 1.

It is useful to compare the hydrocyanation of acetylenes with the cyanation of vinyl halides. Hydrocyanation proceeds non-catalytically to give saturated nitriles as the main product, and is inhibited by the presence of excess acetylene. On the other hand, cyanation proceeds catalytically to give acrylonitriles as the main product, and is not inhibited by the presence of excess vinyl halides. The difference between the two reactions is probably attributable to differing reactivities of the active species towards the substrates and initial products. In the case of hydrocyanation,

the active species is $[\text{Co}(\text{CN})_5\text{H}]^{3-}$, which reacts with both acetylene and acrylonitrile; the latter reaction seems faster than the former as indicated by the formation of the saturated product as a main product. This hydrogenation requires two moles of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ to give saturated products. In addition, the active species can be reproduced by oxidation of the Co^{I} species (eq. 12) in the absence of excess cyanide ion. Thus, excess acetylene inhibits the hydrocyanation by decreasing the concentration of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$. On the other hand, in the cyanation, the active species is $[\text{Co}(\text{CN})_4]^{3-}$, and $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ is not involved in the catalytic cycle. The active species is readily regenerated after reductive elimination of acrylonitriles from the Co^{III} species. Formation of acrylonitrile as a main product suggests that the reaction of the active species with vinyl halides is faster than that of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ with acrylonitrile. This is also reflected by the absence of inhibition by excess substrate. The presence of excess vinyl halides effectively inhibits the formation of stable π -olefin complexes between $[\text{Co}(\text{CN})_4]^{3-}$ and acrylonitriles [9,12].

Hydrocyanation of acetylene under activation by molecular hydrogen is a useful process for the synthesis of nitriles, but the reaction requires a supply of acetylene at a concentration lower than that of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$. Since the CN : Co ratio decreases as the reaction progresses—conversion of the cyanide ligand to nitrile—the cyanide ion concentration should be kept at the optimum condition of CN : Co < 5 : 1. It is difficult to develop cyanocobaltate into a good catalyst for substrates which form fairly stable σ -vinyl and alkyl complexes. The catalytic process may be developed by other metal cyanide complexes which can activate hydrogen.

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