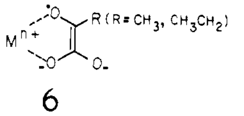
o-benzosemiquinone in DMF-water mixtures, since $\rho_4 + \rho_3$ (and therefore $\rho_1 + \rho_0$) is practically constant in their systems.

The hyperfine couplings to metal ions measured in this study may be compared with those measured[4] for semidiones from α-keto acids (**6**). For the ions Zn^{2+}, Al^{3+}, and La^{3+}, the hyperfine splittings in **5** are in each case about 50% greater than in the semidione (**6**), indicating slightly greater s-orbital spin population in the semiquinone. Couplings to group 2A metal ions Be^{2+} and Mg^{2+} in **6** are reported to be 0.3 G. However, we were unable to observe these couplings, which we would expect to be 0.4–0.5 G in the group 2A metal ion complexes of the *o*-semiquinone. This suggests that there is stronger association of the metal ion with the keto acid semidiones than with *o*-semiquinone, so that the residence time of the metal ion in the semidione complex is long enough for the coupling to the metal ion to be observed.



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The similarity between the couplings that we find at around neutral pH with those obtained in alkaline solution[1] suggest that the spectra are not very sensitive to hydrolysis of the metal ion, which must occur at high pH; i.e., whether the additional ligands to the metal ion are H_2O or OH^- does not appear to greatly influence the spin distribution.

Finally, it is notable that the hyperfine splitting to ^{111}Cd in the cadmium complex of *o*-benzosemiquinone (7 G) is larger than that estimated for cadmium complexes of free radicals in natural melanin from bovine eyes (ca. 3.2 G).[8] The reason for this may be that the melanin free radicals, although evidently possessing an *o*-semiquinone structure (complexation would not otherwise occur), are largely derived from units of 5,6-dihydroxyindole,[44] in which case they might be expected to possess rather less spin density in the *o*-semiquinone moiety.

Acknowledgment. This work was supported by National Institutes of Health Grants AM-26950, GM-29035, and 5-P41-RR01008.

Registry No. 1 (anionic radical), 20526-43-6; Mg, 7439-95-4; Al, 7429-90-5; Ca, 7440-70-2; Sc, 7440-20-2; Zn, 7440-66-6; Ga, 7440-55-3; Sr, 7440-24-6; Y, 7440-65-5; Cd, 7440-43-9; In, 7440-74-6; Ba, 7440-39-3; La, 7439-91-0; *o*-benzosemiquinone, 583-63-1; catechol, 120-80-9.

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(44) R. A. Nicolaus, "Melanins", Hermann, Paris, 1964, p 90.

(45) **Note Added in Proof**: We note that our assignments of ^{13}C hyperfine couplings in *o*-benzosemiquinone differ from the tentative assignments made for this radical in another solvent system (M. Brustolon, L. Pasimeni, and C. Corvaja, *J. Chem. Soc., Faraday Trans. 2*, 193–200 (1975)).

Stereoselective Cyanation of Vinyl Halides Catalyzed by Tetracyanocobaltate(I)

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Contribution from the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. Received July 3, 1980

Abstract: Tetracyanocobaltate(I), $[Co(CN)_4]^{3-}$, which is formed in an aqueous alkaline solution under a hydrogen atmosphere, catalyzes the cyanation of vinyl halides to form 2-alkenenitriles. The reaction is stereoselective, forming nitriles with retention of configuration, except for (*Z*)-2-bromobut-2-ene, which forms a mixture of nearly equimolar isomeric nitriles. Reactivity is dependent on the CN:Co ratio and is highest when the ratio is slightly lower than 5:1. Presence of excess cyanide ion inhibits the reaction, but a dropwise addition of the KCN solution to maintain CN:Co $\lesssim$ 5:1 is effective for the cyanation of a large excess of vinyl halides. σ-Vinyl complexes, $[\sigma\text{-vinyl-Co(CN)}_5]^{3-}$, were detected as intermediates by ^1H and ^{13}C NMR spectroscopy, indicating that the reaction proceeds stepwise. In the first step, the σ complex is formed by the oxidative addition of a vinyl halide to $[Co(CN)_4]^{3-}$ via a radical nonchain process; in this step stereoselectivity is determined. In the second step, which is rate determining, a 2-alkenenitrile is formed by the reductive coupling of the vinyl and cyano ligands, regenerating $[Co(CN)_4]^{3-}$. Clear NMR evidence has been obtained for the formation of $[\pi\text{-olefin-Co(CN)}_4]^{3-}$, where the olefin is (*E*)- or (*Z*)-cinnamonitrile. A high degree of electron transfer from $[Co(CN)_4]^{3-}$ to olefin was indicated by the large upfield shifts of the olefinic carbon atom resonances by coordination.

Since α,β-unsaturated nitriles serve as versatile intermediates in organic synthesis, efforts have been made to develop new methods of synthesis of the nitriles. Stereoselective cyanation of vinyl halides is one of the useful reactions developed in the last decade.[1] Some metal cyanides such as $NaCu(CN)_2$,[2] CuCN,[3] and $K_4Ni(CN)_6$[4] are known to be effective for stoichiometric synthesis of cinnamonitriles from β-bromostyrenes at elevated temperatures. Recently, Yamamura and Murahashi[5] reported that $Pd(PPh_3)_4$-KCN-crown ether catalyzed the cyanation of not only bromostyrenes but also alkenyl halides such as $C_4H_9CH{=}CHBr$ in benzene. However, no mechanistic study has been performed with these catalysts.

Pentacyanocobaltate(II), $[Co(CN)_5]^{3-}$, has been of interest for its high reactivity with various organic and inorganic substrates, but it has not been used as a catalyst for the synthesis of nitriles despite the complex having cyano ligands. Nitriles were formed by the decomposition of alkyl-, aryl-, and vinylpentacyanocobaltate(III) with acid and base,[6] but the reaction is far from being synthetically useful. We show here that cyanocobaltate is

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(1) (a) hydrocyanation of diolefins, e.g.: Albanese, P.; Benzoni, L.; Carnissio, G.; Crivelli, A. Italian Patent 869 900, 1970 (Chem. Abstr. **1973**, *78*, 135 701k). (b) Oxycyanation of olefins, e.g.: Nakajima, H. Japanese Patent 74·33 930, 1974 (*Chem. Abstr.* **1975**, *82*, 155 416g). (c) Peichucki, C. *Synthesis* **1974**, 869-870. (d) Loupy, A.; Sogadji, K.; Seyden-Penne, J. *Ibid.* **1977**, 126–127. (e) Tanaka, K.; Ono, N.; Kubo, Y.; Kaji, A. *Ibid.* **1979**, 890–891. (f) DiBiase, S. A.; Gokel, G. W. *Ibid.* **1977**, 629. (g) D'Incan, E.; Seyden-Penne, J. *Ibid.* **1975**, 516–517. (h) Westmijze, H.; Vermeer, P. *Ibid.* **1977**, 784–785. (i) Traas, P. C.; Takken, H. J.; Boelenes, K. *Tetrahedron Lett.* **1977**, 2027–2030. (j) Ono, N.; Tamura, T.; Hayami, J.; Kaji, A. *Ibid.* **1978**, 763–764. (k) Moriconi, E, J.; Jalandoni, C. C. *J. Org. Chem.* **1970**, *35*, 3796–3800. (1) Wilt, J. W.; Ho, A. J. *Ibid.* **1971**, *36*, 2026–2027. (m) Descamps, B.; Lefebre, G.; Seyden-Penne, J. *Tetrahedron* **1972**, *25*, 4209–4222. (n) Uemura, S.; Miyoshi, H.; Wakasugi, M.; Okano, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 553–554. (o) Uemura, S.; Wakasugi, M.; Okano, M. *J. Organomet. Chem.* **1980**, *194*, 277–283.

(2) House, H. O.; Fischer, W. F. *J. Org. Chem.* **1969**, *34*, 3626–3627.

(3) Lapouyad, R.; Deney, M.; Lapenue, M.; Bouas-Laurent, H. *Bull. Soc. Chim. Fr.* **1973**, 720–721.

(4) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 1233–1234.

(5) Yamamura, K.; Murahashi, S. *Tetrahedron Lett.* **1977**, 4429–4430.

(6) (a) Kwiatek, J.; Seyler, J. K. *J. Organomet. Chem.* **1965**, *3*, 433–437. (b) Kwiatek, J. *Catal. Rev.* **1967**, *1*, 38–72. (c) Johnson, M. D.; Tobe, M. L.; Lai Y. W. *J. Chem. Soc. A* **1967**, 491–497; **1968**, 923–928; 929–933.

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Table I. Formation of Nitriles from Vinyl Halides 1

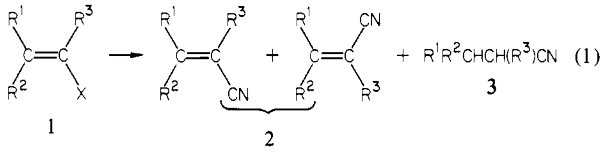
vinyl halide 1	method[a]	1/Co[b]	time, h	nitriles, % yield[c]	mole ratio of nitriles 2:3	mole ratio of nitriles (*Z*)-2:(*E*)-2
(*Z*)-MeCH=CHBr	A	2	4	52 (60)[d]	100:0	96:4
MeCH=CHBr (*Z*:*E* = 71:29)[e]	A	2	4	50 (60)[d]	100:0	70:30
(*Z*)-MeCH=CMeBr	A	2	1.7[f]	(60)	75:25	88:12
	A	2	24	65 (80)	47:53	51:49
	A[g]	2	22	60 (80)	100:0	54:46
Me_2C=CHBr	A	2	1	80 (89)	100:0	
	B	5	2	(76)	100:0	
	C	20	6	80 (89)	100:0	
Me_2C=CHCl	A	2	1	65 (75)	100:0	
	C	20	24	61 (81)	100:0	
	C	30	24	92 (98)	100:0	
Me_2C=CMeBr	A	2	1.5	80 (85)	100:0	
	C	10	3	86 (92)	100:0	
	C	20	6	80 (90)	100:0	
(*Z*)-PhCH=CHBr[h]	A	2	2	79 (89)	100:0	97:3
	B	2	2	68 (82)	100:0	96:4
	C	10	24	85 (95)	98:2	91:9
(*E*)-PhCH=CHBr	A	2	18	69 (75)	95:5	0:100
	B	2	18	50 (63)	98:2	0:100
	C	10	48	73 (78)	97:3	0:100
(*E*)-PhCH=CMeBr	A	2	8.5	90 (95)	97:3	18:82
PhC(Br)=CH_2	A[i]	1	12	34 (40)	77:23	
(*E*)-MeC(CO_2Me)=CHBr	A	2	24[k]	0		

[a] [Co] = 0.2 M, Co:CN:OH = 1:4.95:2, in H_2O, at 45 °C, and under a hydrogen atmosphere. Method A, in 25 mL of H_2O; method B, in 5 mL of H_2O; method C, in 5 mL of H_2O, with a dropwise addition of the KCN–KOH solution. [b] Mole ratio of vinyl halides to cobalt. [c] Total isolated and GLC (in parentheses) yields of nitriles based on halides. [d] Low yield is partly due to the vaporization of the reactant and product in the reaction vessel. [e] Reagent from Aldrich Chemical Co. [f] Time for the maximal content of (*Z*)-MeCH=CMeCN. [g] Under a nitrogen atmosphere. [h] *Z*:*E* = 92:8. [i] Reaction at 55 °C with addition of 5 mL of benzene. [j] PhCH($CONH_2$)CH_3 was obtained as residue. [k] Rapid reaction was noticed by the color change of the solution.

useful as a catalyst for synthesis of 2-alkenenitriles from vinyl halides under mild conditions. We have studied the reaction mechanism by detecting intermediate complexes by NMR spectroscopy and revealed that the active species for this reaction is a cobalt(I) complex, $[Co(CN)_4]^{3-}$. In the chemistry of vitamin B_{12}[7] and cobaloxime,[8] the importance of a cobalt(I) species has well been noted, but little is known concerning the formation and reactivity of cyanocobaltate(I).[9,10] The results here will show new reactivity patterns for cyanocobaltate(I) and present new information on the oxidative addition and reductive elimination processes.

Results

Formation of Nitriles. 2-Alkenenitriles were readily obtained by the reaction of vinyl halide **1** with cyanocobaltate at CN:Co $< 5:1$ in an aqueous solution under a hydrogen atmosphere. Reactivity was first studied by reacting a twofold excess of vinyl halide in relation to the cobalt concentration at Co:CN:OH[11] = 1:4.95:2, and then a further excess of halide with a dropwise addition of the KCN solution. As shown in Table I, the reaction was highly stereoselective to form 2-alkenenitriles with retention of configuration, and yields of the inversion product and saturated nitrile **3** were generally low except for the case of (*Z*)-2-bromobut-2-ene.



(*Z*)-1-Bromopropene reacted rather slowly to give (*Z*)-2-butenenitrile, and a mixture of (*Z*)- and (*E*)-bromopropene formed a mixture of (*Z*)- and (*E*)-2-butenenitrile of the same *Z*:*E* ratio as that of the reactant. Butanenitrile was not formed. (*Z*)-2-Bromobut-2-ene on the other hand gave a mixture of (*Z*)- and (*E*)-2-methyl-2-butenenitriles and 2-methylbutanenitrile. The reaction formed initially the retention product (*Z*)-**2** and then (*E*)-**2** and **3** (R^1 = H, R^2 = R^3 = Me). Isomerization of the initial product (*Z*)-MeCH=CMeCN to the *E* isomer and hydrogenation of these nitriles were observed in the same reaction conditions. However, when the reaction of (*Z*)-MeCH=CMeBr was performed in a nitrogen atomosphere to control the isomerization and hydrogenation of the initial products by $[Co(CN)_5H]^{3-}$, nearly equimolar yields of (*Z*)- and (*E*)-MeCH=CMeCN were obtained, indicating that the cyanation was not stereospecific. 1-Bromo- and 1-chloro-2-methylpropenes and 2-bromo-3-methylbut-2-ene reacted rapidly to form only unsaturated nitriles Me_2C=CHCN and Me_2C=CMeCN, respectively. (*Z*)- and (*E*)-β-bromostyrenes formed selectively (*Z*)- and (*E*)-cinnamonitriles, respectively, and reactivity of the (*Z*)-bromide was much greater than that of the (*E*)-bromide. (*E*)-β-Methyl-β-bromostyrene formed mainly (*E*)-2-methylcinnamonitrile, (*E*)-PhCH=CMeCN, but formation of the *Z* isomer was relatively high. Reaction of α-bromostyrene was very slow, and yields of nitriles (α-cyanostyrene and α-phenylpropionitrile) were low. (*E*)-Methyl 3-bromomethacrylate reacted readily with cyanocobaltate, which was noted by the color changes of the solution, but no nitrile was formed. This is because the reaction proceeds stepwise via a rather stable intermediate (vide infra). We expected a dicyanation of dihalides, but only monocyanated nitriles without halogen were obtained: e.g., α,β-dibromostyrene (*E*:*Z* = 68:32) formed PhCH(CN)CH_3 and (*Z*)- and (*E*)-PhCH=CHCN, together with a fairly large amount of phenylacetylene.

Catalytic activity of cyanocobaltate for this reaction was studied with 1-bromo-2-methylpropene which formed only 3-methyl-2-butenenitrile, Me_2C=CHCN. Figure 1 shows the dependence of the initial rate and the yield of the nitrile on the CN:Co ratio. As observed in the hydrogenation of conjugated dienes[6b,12] and

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[7] Cf.: Pratt, J. M. "Inorganic Chemistry of Vitamin B_{12}"; Academic Press: London, 1972; pp 1–347.

[8] Cf.: Dodd, D.; Johnson, M. D. *J. Organomet. Chem.* **1973**, *52*, 1–232.

[9] Hanzlík, J.; Vlček, A. A. *Chem. Commun.* **1969**, 47–48; *Inorg. Chem.* **1969**, *8*, 669–672.

[10] Halpern, J.; Pribanič M. *J. Am. Chem. Soc.* **1971**, *93*, 96–98. Venerable, G. D., II; Halpern, J. *Ibid.* **1971**, *93*, 2176–2179. Guastalla, V.; Halpern, J.; Pribanič, M. *Ibid.* **1972**, *94*, 1575–1577.

[11] Mole ratio of $CoCl_2$, KCN, and KOH.

[12] Funabiki, T.; Matsumoto, M.; Tarama, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2723–2730. Funabiki, T.; Mohri, M.; Tarama, K. *J. Chem. Soc. Dalton Trans.* **1973**, 1813–1818.

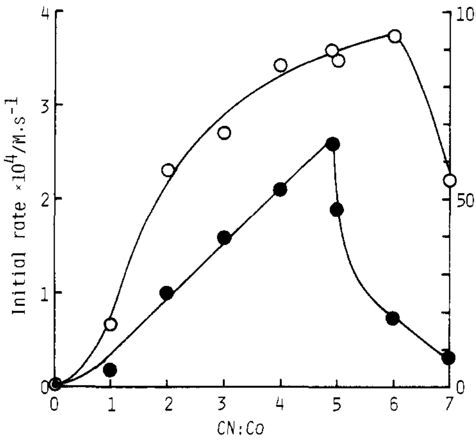

Figure 1. Effect of the CN:Co ratio on the cyanation of 1-bromo-2-methylpropene. (●) Initial rate estimated from the GLC yield of 3-methyl-2-butenenitrile in an initial 15-min period (left-hand scale); (○) the GLC yield of the nitrile after 1 h, based on the bromide (right-hand scale). [Co] = 0.2 M, Co:OH:bromide = 1:2:2, in 5 mL of H_2O, at 45 °C, in H_2.

the hydrogenolysis of unsaturated alcohols,[13] the catalytic activity abruptly changed at CN:Co = 5:1. The initial rate was maximal when the ratio was slightly lower than 5:1. It decreased gradually at CN:CO < 5:1 and abruptly at >5:1. Since the formation of nitrile brings about the decrease in the CN:Co ratio, a rapid reaction began even at >5:1 after conversion of some extent of halides. The time for the beginning of the rapid reaction was proportional to the extent of the cyanide ion, but too much excess of the cyanide ion inhibited the reaction, probably by forming a stable σ-alkylcobalt complex between unsaturated nitriles and $[Co(CN)_5H]^{3-}$. In the reaction at CN:Co < 5:1, the precipitate increased with the progress of the reaction. As shown in Figure 1, the nitrile was formed even at low CN:Co ratios, suggesting that the active species is formed in that region and that the cyanation of excess halides may proceed until the CN:Co ratio becomes very low. The reaction of $Me_2C{=}CHBr$ at CN:Co = 4.95:1 formed $Me_2C{=}CHCN$ in a 370% yield on the basis of the cobalt concentration. Further excess of the bromide was efficiently cyanated by a dropwise addition of the KCN solution so that the solution contained a small amount of precipitate. Chloride, $Me_2C{=}CHCl$, was also cyanated in the same way, but it took longer than in the reaction of the bromide. A large excess of $Me_2C{=}CMeBr$ was readily cyanated, but the reaction of (*Z*)-PhCH=CHBr was slow. Reactions of (*E*)-PhCH=CHBr and (*Z*)- and (*E*)-MeCH=CHBr were so slow that the addition of the KCN solution so as to maintain the CN:Co ratio at ≲5:1 was rather difficult.

We examined the effect of hydrogen and alkali on the reactivity. The initial rate of the cyanation of $Me_2C{=}CHBr$ was 2.6×10^{-4} and 8.0×10^{-5} M s^{-1} in H_2 and N_2, respectively, at $[Co]_0 = 0.2$ M and Co:CN:OH:**1** = 1:4.95:2:2, while the yield of $Me_2C{=}CHCN$ was comparable (~90%) in both cases. When KOH was not added in the reaction in H_2, the initial rate was 6.0×10^{-5} M s^{-1}, the yield was low (~57%), and a large amount of a yellow muddy precipitate was formed. These results indicated that the reaction was promoted by hydrogen and alkali, although too much excess of alkali, e.g., Co:OH = 1:10, was not useful.

Detection of Intermediate Complexes by ^{1}H and ^{13}C NMR. In many cases, the rate of formation of nitriles was lower than that of the disappearance of vinyl halides, and the yield of nitriles was less than that expected from the complete conversion of the halides. This suggested that rather stable intermediates were formed. We observed ^{1}H and ^{13}C NMR spectra of the reaction solution in D_2O. The pale yellow solution obtained by the reaction of (*Z*)-MeCH=CHBr showed resonances assigned to σ-propenylcobalt complex. The solution obtained by the reaction of a mixture of the *Z* and *E* isomers of the bromide gave spectra indicating the formation of two isomeric σ-propenyl complexes. Figure 2 shows the ^{13}C NMR spectra, in which slightly broad peaks were assigned to the resonances of carbons attached to cobalt. Since the coupling constant J_H for olefinic protons in the ^{1}H NMR spectrum of the same solution was 9.29 Hz with the complex obtained from the (*Z*)-bromide and 15.15 Hz with the isomeric complex, the complexes could be identified as those with retention and inversion of configuration, (*Z*)- and (*E*)-$[MeCH{=}CHCo(CN)_5]^{3-}$, respectively.[14] In the reaction of (*Z*)-MeCH=CMeBr, nearly equimolar isomeric complexes were formed in the initial stage, but one of them gradually diminished, as shown in Figure 3. The less stable complex could correspond to (*Z*)-$[MeCH{=}CMeCo(CN)_5]^{3-}$, because (*Z*)-MeCH=CMeCN with retention of configuration was selectively formed in the initial stage. In the

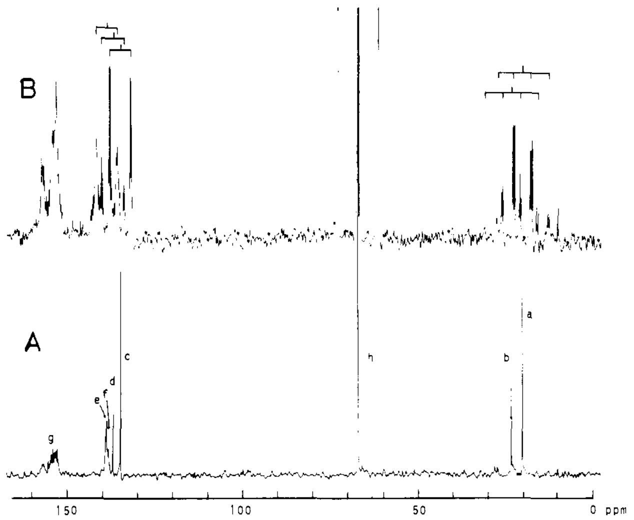

Figure 2. ^{13}C NMR spectra of the reaction solution of 1-bromopropene (*Z*:*E* = 71:29). A and B correspond to the completely decoupled and nondecoupled spectra, respectively. [(*Z*)-$MeCH{=}CHCo(CN)_5]^{3-}$: a, Me; c, C_α; e, C_β. [(*E*)-$MeCH{=}CHCo(CN)_5]^{3-}$: b, Me; d, C_α; f, C_β; g, cyano ligand; h, dioxane.

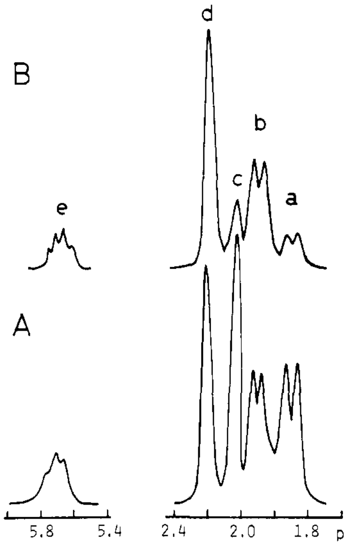

Figure 3. ^{1}H NMR spectra of the reaction solution of (*Z*)-2-bromobut-2-ene. A and B are the spectra observed after 15-min and 2-h reactions, respectively. [(*Z*)-$MeCH{=}CMeCo(CN)_5]^{3-}$: a, Me; c, Me; e, H. [(*E*)-$MeCH{=}CMeCo(CN)_5]^{3-}$: b, Me; d, Me; e, H. New peaks appeared with the elapse of time at the higher field,[15] but they are omitted in B to show clearly the spectral changes of the isomeric σ complexes.

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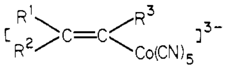
[13] Funabiki, T.; Yamazaki, Y.; Tarama, K. *J. Chem. Soc., Chem. Commun.* **1978**, 63–65.

[14] Although we have not obtained any evidence for the number of cyano ligands, pentacyanocobaltate(III) is the most likely as a stable σ complex even at CN:Co < 5:1.

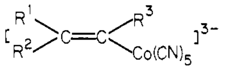
Table II. ^{1}H NMR Parameters of σ-Vinylpentacyanocobaltate(III) 4



$R^1R^2C{=}CR^3$	chemical shifts, δ (coupling constants, Hz)[a]
(Z)-MeCH=CH	1.91 (dd, J = 6.30, 1.2, Me), 6.10 (dq, J = 9.29, 6.30, H(R^1)), 6.41 (dd, J = 9.29, 1.2, H(R^3))
(E)-MeCH=CH	1.81 (dd, J = 6.11, 1.2, Me), 5.72 (dq, J = 15.15, 6.11, H(R^2)), 6.34 (dq, J = 15.15, 1.2, H(R^3))
(Z)-MeCH=CMe	1.71 (d, J = 6.4, Me(R^2)), 2.04 (s, Me(R^3)), 5.70 (br, H(R^1))[b]
(E)-MeCH=CMe	1.90 (d, J = 7.6, Me(R^1)), 2.22 (s, Me(R^3)), 5.70 (br, H(R^2))[b]
$Me_2C{=}CH$	1.91 (s, 2 Me), 5.91 (s, H(R^3))
$Me_2C{=}CMe$	1.02 (s, Me), 1.89 (s, Me), 2.02 (s, Me)
(Z)-PhCH=CH	7.23 (d, J = 11.2, H(R^1)), 7.29 (d, J = 11.2, H(R^3)), 7.23–7.92 (m, Ph)
(E)-PhCH=CH	6.84 (d, J = 16.4, H(R^2)), 7.80 (d, J = 16.4, H(R^3)), 7.40, 7.44 (2 s, Ph)
(E)-PhCH=CMe	2.38 (s, Me), 7.31 (s, H(R^2)), 7.36 (s, Ph)
$H_2C{=}C(Ph)$	5.15 (d, J = 3.0, H(R^2)), 5.55 (d, J = 3.0, H(R^1)), 7.30–7.34 (m, Ph)
(E)-MeC(CO_2Me)=CH	2.21 (s, Me(R^2)), 8.70 (s, H(R^3)), 3.74 (s, CO_2Me)
(E)-MeC(CO_2K)=CH[c]	2.15 (s, Me(R^2)), 7.95 (s, H(R^3))

[a] Observed in D_2O at room temperature. Chemical shifts are relative to $Na(O_2CC_2D_4SiMe_3)$. [b] Observed as a broad overlap peak. [c] Complex of the hydrolyzed species of (E)-MeC(CO_2Me)=CHBr.

Table III. ^{13}C NMR Parameters of σ-Vinylpentacyanocobaltate(III) 4



$R^1R^2C{=}CR^3$	chemical shift, δ (coupling constants, $^1J_{CH}$, Hz)[a]		
	C_α	C_β	others
(Z)-MeCH=CH	135.1 (d, 147.7)	139.1 (d, 148.9)	20.3 (q, 124.5, Me)
(E)-MeCH=CH	137.3 (d, 153)	148.6 (d, 148)[b]	23.5 (q, 123.3, Me)
(Z)-PhCH=CH	140.0 (d, 150.2)	145.2 (d, 144.9)	{140.6 (s), 130.3 (d, 158.7), 127.9 (d, 161.2), 126.4 (d, 161.1), Ph}
(E)-PhCH=CH	140.5 (d, 153.8)	147.4 (d, 141.6)	{140.3 (s), 129.7 (d, 157.8), 125.6 (d, 158.7), 126.7 (d, 162.3), Ph}
(E)-PhCH=CMe	137.3 (d, 149)	140.3 (s)	{130.7 (s), 128.9 (d, 156), 125.6 (d, 156), Ph}, 30.7 (q, 134, Me)
$H_2C{=}C(Ph)$	124.3 (dd, 149, 159)	158 (s)	{129.5 (s), 127.4 (d, 159), 127.8 (d, 158), 124.9 (d, 158), Ph}
(E)-MeC(CO_2Me)=CH	135.0 (s)	169.5 (d, 191.4)	168.9 (s, CO), 53.0 (q, 142.7, Me), 19.4 (q, 127.4, Me(R^2))
(E)-MeC(CO_2K)=CH	137.3 (s)	169.5 (d, 176)	176.8 (s, CO), 21.1 (q, 126.3, Me)

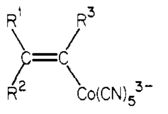
[a] Observed in D_2O under cooling at 0 °C. Chemical shifts were referred to dioxane (67.4 ppm). [b] Overlapped with the peaks of (Z)-MeCH=CH-Co.

Table IV. ^{1}H and ^{13}C NMR Parameters of (π-Cinnamonitrile)tetracyanocobaltate(I) 5[a]

complex	chemical shifts, δ, (coupling constants, J, Hz)					
	δ_C	($^1J_{CH}$)	$\Delta\delta_C$[b]	δ_H	(J_H)	$\Delta\delta_H$
$[\pi\text{-}(Z)\text{-}Ph\overset{\alpha}{C}H{=}\overset{\beta}{C}HCN\text{-}Co(CN)_4]^{3-}$						
$C_\alpha H{=}$	44.8	(d, 154)	103.8	3.85	(d, 8.8)	3.27
$C_\beta H{=}$	11.4	(d, 164)	83.5	2.34	(d, 8.8)	3.00
CN	133.1	(s)	−15.8			
C_1(Ph)[b]	149.1	(s)	−15.6			
$[\pi\text{-}(E)\text{-}Ph\overset{\alpha}{C}H{=}\overset{\beta}{C}HCN\text{-}Co(CN)_4]^{3-}$						
$C_\alpha H{=}$	47.7	(d, 156)	102.7	3.98	(d, 10.0)	3.40
$C_\beta H{=}$	10.9	(d, 162)	85.3	2.74	(d, 10.0)	3.12
CN	132.5	(s)	−14.4			
C_1(Ph)[c]	148.2	(s)	−14.8			

[a] Observed in D_2O under cooling at 0 °C. Chemical shift was referred to $Na(O_2CC_2D_4SiMe_3)$ (^{1}H NMR) or dioxane (67.4 ppm) (^{13}C NMR). Positive values of $\Delta\delta = \delta$(coordinated olefin) − δ(free olefin) indicate upfield shifts. [b] Other phenyl carbon resonances: 125.1 (d, 161), 128.0 (d, 160), 128.6 (d, 159); proton resonances: 7.29 (m), 7.64 (m). [c] Other phenyl carbon resonances: 123.6 (d, 159), 126.5 (d, 161), 128.6 (d, 157); proton resonance: 7.24 (s).

prolonged reaction, peaks for the isomeric σ-alkylcobalt complexes, which could be formed by the reaction of MeCH=CMeCN with $[Co(CN)_5H]^{3-}$, appeared at the higher field.[15] The σ-vinyl complexes **4** were detected in the reactions of $Me_2C{=}CHBr$ and $Me_2C{=}CMeBr$, but they were very unstable and decomposed while taking the ^{1}H NMR spectra. ^{1}H and ^{13}C NMR data of the σ-vinyl complexes are summarized in Tables II and III, respectively.



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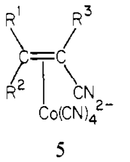

5

β-Bromostyrenes gave first yellow solutions and then dark red solutions after prolonged reaction. The change of color did not occur while bromostyrenes remained in the solution, and the red color was returned to yellow by addition of the KCN solution. The spectra observed with the yellow solutions indicated the stereospecific formation of (Z)- and (E)-σ-styryl complexes. As shown in Figure 4 (B and C), the yellow solution exhibited also peaks at the high field in addition to those assigned to the σ complex. As the color of the solution changed from yellow to dark red, the peaks of the σ complex disappeared to give finally the

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[15] Two σ complexes, $[\sigma\text{-}CH_3CH(CN)CH(CH_3)Co(CN)_5]^{3-}$ and $[\sigma\text{-}CH_3CH_2C(CH_3)(CN)Co(CN)_5]^{3-}$, could be formed, but peaks observed at 0.89, 1.05, 1.06, 1.29, and 1.45 ppm were broad and could not be assigned.

spectrum A. Similar changes of spectra were observed by ^{1}H NMR spectroscopy. The proton resonances of olefinic protons of the (*Z*)-styryl complex overlapped with those of phenyl protons, and we have found that the previous assignment[16] was erroneous. Data are corrected in Table II. Two peaks appearing at the high field are assigned to olefinic carbons or protons from the values of coupling constants (Table IV). Since the great upfield shifts of olefinic carbons and protons are characteristic of π-olefin complexes,[17] these spectra suggested the formation of π-olefin complexes of cyanocobaltate **5**. The following results clearly indicated that the complex was a π-(*Z*)- or -(*E*)-cinnamonitrile–Co(I) complex: (*i*) the dark red solution was also obtained when cinnamonitriles was added in place of β-bromostyrenes, and the spectra were identical with those obtained by the reaction of β-bromostyrenes; (*ii*) the reaction of β-bromostyrenes with use of ^{13}C-enriched KCN showed the great increase in the intensity of the resonance of the nitrile carbon. The very large upfield shift of the π-coordinated olefin carbon atom resonances was characteristic of these π complexes and indicates that the extent of the electron transfer from cyanocobaltate(I) to the olefins is very large. Downfield shifts of singlets of CN and C_1(Phenyl) were also characteristic of these π complexes. The spectra also indicated that no deuterium was incorporated in these complexes in spite of the ready formation of $[Co(CN)_5D]^{3-}$ in D_2O. Thus, a direct interaction of the hydrido complex with vinyl halides or cinnamonitriles to form a σ or π complex is not probable. When we used ^{13}C-enriched KCN, a large broad peak was observed at 152.7 ppm with the solution containing the σ complex, and it shifted to 162.7 ppm as the π complex was formed. The peaks corresponded to the cyano ligands of the σ and π complexes, respectively.

(*E*)-PhCH=CMeBr and PhC(Br)=CH_2 formed only σ complexes. The NMR spectra of the solution obtained by the reaction of (*E*)-MeC(CO_2Me)=CHBr were analyzed to those of two stable vinyl complexes having CH=CMeCO_2Me and CH=CMeCO_2K ligands and of free CH(Br)=CMeCO_2^- and MeOD. This is because the bromide is hydrolyzed in the strong alkaline solution as rapidly as the reaction with cyanocobaltate(I).

Discussion

Utility of Cyanocobaltate as a Catalyst for Synthesis of 2-Alkenenitriles. Direct synthesis of 2-alkenenitriles from vinyl halides by the present method is very useful for reasons such as experimental simplicity, very high stereoselectivity, and good yields, although the selectivity and yield depend on the vinyl halides. Thus, the catalyst is readily prepared, and isolation of products is very easy because they are generally insoluble in an aqueous solution. A phase-transfer catalyst, which was used in the Wittig–Horner synthesis,[1c,e] is not required because the rate-determining step is not the reaction of vinyl halides with cyanocobaltate but the process of the intramolecular product formation from the intermediate complexes (vide infra). The reaction is highly stereoselective, as observed in the reaction catalyzed by the palladium complex,[5] and generally more stereoselective than observed in the Wittig–Horner synthesis and other reactions.[1] Formation of MeCH=CMeCN from (*Z*)-MeCH=CMeBr was not stereoselective. Interestingly, no method has been reported for the stereoselective formation of the nitrile.[1a,18,19] Since the stereoselectivity of the formation of (*E*)-PhCH=CMeCN is lower than that of (*Z*)- and (*E*)-PhCH=CHCN from the corresponding bromides, the methyl substituent on the halogen-bearing carbon seems to reduce the stereoselectivity. 2-Alkenenitriles have been catalytically produced by using HCN,[1a,b] stoichiometrically by the method without using HCN.[1c–o,2–4] In the present reaction, a large excess of alkenyl halides such as Me_2C=CHBr, Me_2C=CHCl, Me_2C=CMeBr, and (*Z*)-PhCH=CHBr were readily cyanated by adding the KCN solution at a controlled rate to maintain CN:Co < 5:1. In the case of vinyl halides which form rather stable intermediate complexes, e.g., (*Z*)- and (*E*)-MeCH=CHBr, (*Z*)-MeCH=CMeBr, and (*E*)-PhCH=CHBr, the use of a larger amount of catalyst is advantageous for the synthetic purpose. The present method is not applicable to such a halide as MeC(CO_2Me)=CHBr, which forms a too stable σ complex. Generally, the cyanation of vinyl halides is promoted by electron-releasing or bulky substituents at the cis position, which are effective to destabilize the intermediate complexes. We have not studied in detail the effect of halide ion formed by the cyanation, but a retardation effect was observed in the reaction with 20 equiv of the chloride, Me_2C=CHCl, but not the bromides, Me_2C=CHBr and Me_2C=CMeBr. Thus, in the case of vinyl chlorides it is better to perform the reaction at the low ratio of the chlorides to the cobalt catalyst.

In addition, this method is very convenient to synthesize 2-alkenenitriles having a ^{13}C-enriched nitrile group, because it is achieved by using ^{13}C-enriched KCN. In the present study, the ^{13}C-enriched nitriles were useful to assign the peak of the nitrile group in the ^{13}C NMR spectra.

Mechanism. In the chemistry of cyanocobaltate, high reactivity has been ascribed to the radical nature of $[Co(CN)_5]^{3-}$ or the atomic hydrogen-like character of $[Co(CN)_5H]^{3-}$. This can be seen in the proposal that the reaction of vinyl halides forming σ-vinylcobalt complex proceeds by a two-step sequence in eq 2.[6]

$$H_2C{=}CHX + [Co(CN)_5H]^{3-} \rightarrow [Co(CN)_5CHXCH_3]^{3-} \xrightarrow{-HX} [Co(CN)_5CH{=}CH_2]^{3-} \tag{2}$$

$$H_2C{=}CHX + [Co(CN)_5]^{3-} \rightarrow [Co(CN)_5X]^{3-} + H_2C{=}CH\cdot \tag{3}$$

$$H_2C{=}CH\cdot + [Co(CN)_5]^{3-} \rightarrow [Co(CN)_5CH{=}CH_2]^{3-} \tag{4}$$

However, it is clear that the sequence is not operative in the present reaction because the formation of σ-vinylcobalt complexes proceeds mostly stereoselectively with retention of configuration and no deuterium is incorporated into the σ complex. It is also clear that the free-radical process by $[Co(CN)_5]^{3-}$ (eq 3 and 4) is not applicable, because homolytic splitting of a vinylic carbon–halogen bond is far less favorable than that of a alkyl carbon–halogen bond, a free vinylic radical intermediate is not compatible with the stereospecific formation of σ-vinyl complexes, and formation of an inactive species, $[Co(CN)_5X]^{3-}$, is in conflict with the fact that the reaction proceeds catalytically.

The third probable active species is a cobalt(I) species. Formation of $[Co(CN)_5]^{4-}$ and $[Co(CN)_4]^{3-}$ in a strong alkaline solution (eq 5, 6, and 7)[9,10] and reactions with *p*-benzoquinone[8]

$$[Co(CN)_5]^{3-} + 0.5H_2 \rightleftarrows [Co(CN)_5H]^{3-} \tag{5}$$

$$[Co(CN)_5H]^{3-} + OH^- \rightleftarrows [Co(CN)_5]^{4-} + H_2O \tag{6}$$

$$[Co(CN)_5]^{4-} \rightleftarrows [Co(CN)_4]^{3-} + CN^- \tag{7}$$

$$2[Co(CN)_5]^{3-} + H_2O \rightleftarrows [Co(CN)_5H]^{3-} + [Co(CN)_5OH]^{3-} \tag{8}$$

and carbon monoxide[10] have been reported. $[Co(CN)_5]^{4-}$ is regarded as the most reactive and basic cobalt(I) species studied so far[8] (rate constant for the reaction with water, 10^{-5} s^{-1}; formation constant, 10^{-6} M),[9,10] and dissociates very rapidly to $[Co(CN)_4]^{3-}$ (rate constant at 23 °C, 4.5×10^3 s^{-1}).[9] Since the present reaction is promoted by the presence of hydrogen and alkali as shown by the comparison of the initial rate of formation of Me_2C=CHCN from Me_2C=CHBr or the yield of the nitrile,

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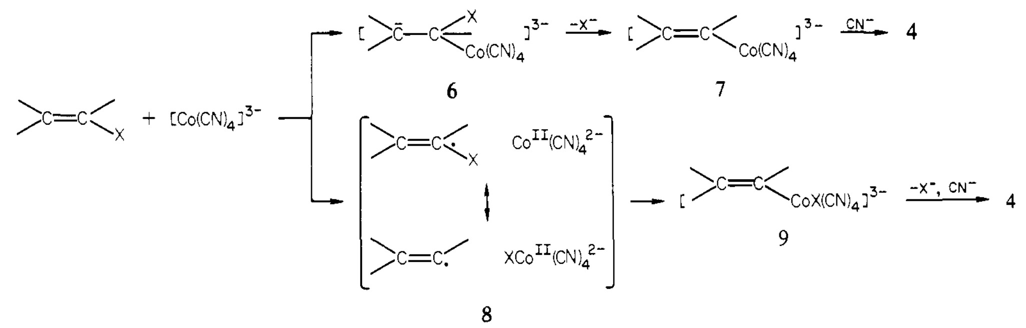
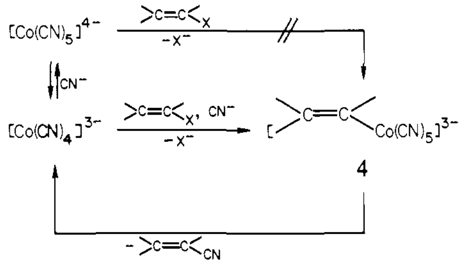


(10a)

(10b)

it is very probable that one of these two cobalt(I) species is an active species. The result that the cyanation occurs even in the absence of hydrogen and without addition of alkali is explained as follows: (i) in the absence of hydrogen, $[Co(CN)_5H]^{3-}$ is rapidly formed by the reaction with water (eq 8 at [Co] > 0.1 M),[20] but in this case half of the cobalt complex becomes inactive by forming $[Co(CN)_5OH]^{3-}$; (ii) the solution of cyanocobaltate is alkaline without addition of KOH, and the cobalt(I) species may be formed at high concentration of the complex. In this case, the cyanation is initiated but does not proceed catalytically because the complex becomes inactive, accompanied by the formation of a large amount of precipitate.

We have obtained clear NMR evidence for the intermediate formation of a σ-vinylcobalt complex. Since stereoselective, with retention of configuration, formation of a σ-vinylmetal complex from a vinyl halide is one of the typical organometallic reactions performed by low-valent metal complexes, it is very probable that the σ-vinylcobalt complex is formed by the reaction of cobalt(I) with vinyl halides. The σ-vinyl complex **4** may be formed either by eq 9 or 10, and the nitrile is formed probably by eq 11 with regenerating $[Co(CN)_4]^{3-}$. Since the reaction of vinyl halides with strong nucleophiles such as $[Co(dmgH)_2py]^-$[8] (dmgH = dimethylglyoximate(1−)) and $[Fe(CO)_4]^{2-}$[21] has been explained by the nucleophilic substitution mechanism, we have proposed that the complex **4** might be formed by the same mechanism by eq 9.[16] However, the mechanism cannot explain the facts that the σ complex **4** is hardly formed and the initial rate of formation of nitrile is very low at CN:Co > 5:1, at which the presence of $[Co(CN)_5]^{4-}$ is well expected. The ready formation of the complex **4** and the high catalytic activity at CN:Co < 5:1 suggest that the active species must be $[Co(CN)_4]^{3-}$. Since the decomposition of the complex **4** by eq 11 proceeds by the intramolecular reductive elimination mechanism (vide infra), the remarkable effect of the CN:Co ratio at CN:Co = 5:1 must be related to the formation and reactivity of the $[Co(CN)_4]^{3-}$ species. The reaction of vinyl halides with $[Co(CN)_4]^{3-}$ may proceed either by a nucleophilic substitution (eq 10a) or an oxidative addition (eq 10b) mechanism.



(9)

(10)

(11)

The nucleophilic substitution process (eq 10a) may be stereoselective if the cleavage of the carbon–halogen bond and the formation of carbon–cobalt bond proceed synchronously before the rotation of the carbon–carbon bond of the carbanion intermediate **6**.[8]

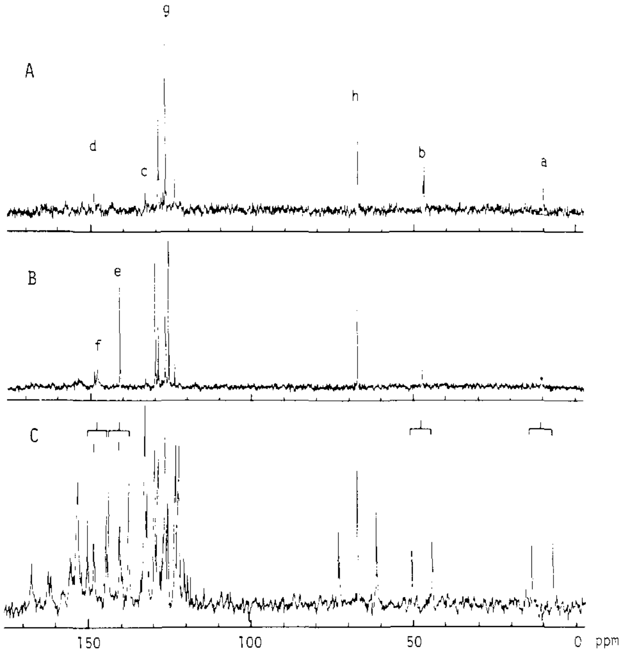


Figure 4. ^{13}C NMR spectra of the reaction solution of (*E*)-β-bromostyrene. A and B are the completely decoupled spectra and C is a nondecoupled spectrum of B. A corresponds to the spectrum of the dark red solution which involves only a π complex of (*E*)-cinnamonitrile. B and C correspond to the spectra of the yellow solution which involves a (*E*)-σ-styryl complex and the π complex. π complex: a, C_β; b, C_α; c, CN; d, C_1; σ complex: e, $C_\alpha + C_1$; f, C_β; g, phenyl carbons; h, dioxane.

Coordination of a cyanide ion to form **4** may occur after formation of **7**, but if it occurs after formation of the cobalt–halogen bond as in **9**, the reaction may be regarded as a type of oxidative addition process.[22] However, it seems rather difficult to explain, by the process via **6**, the high stereoselectivity with 1-bromopropene and nonstereoselectivity with 2-bromobut-2-ene. If the high degree of the stereoselectivity is ascribed to the bulkiness of a nucleophile which may inhibit the rotation in the carbanion intermediate,[21] the higher selectivity will be expected with 2-bromobut-2ene rather than with 1-bromopropene. In the nucleophilic vinylic substitution, stereoconvergence (i.e., formation of the same products from *E* and *Z* precursors) is expected only when the vinyl halide has a poor leaving group and electron-withdrawing substituents since, for the resulting long-lived carbanion **6**, the internal rotation in the intermediate may become faster than the leaving-group expulsion.[22] Vinyl halides studied here have a good leaving group (Br or Cl) and the reaction proceeds with exclusive retention when the vinyl halides have electron-withdrawing substituents rather than electron-donating substituents.

Alternatively, the process of an oxidative addition via an electron-transfer interaction (radical nonchain process) (eq 10b) seems more probable. A similar mechanism has been proposed for nickel(0) complexes,[23,24] and it has been suggested that electron

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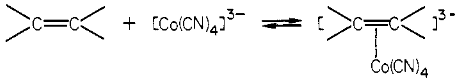
transfer may be involved in reactions of Co(I) complexes.[25] Requirement of $[Co(CN)_4]^{3-}$ rather than $[Co(CN)_5]^{4-}$ is reasonable in this process. When the formations of cobalt–carbon and cobalt-halogen bonds occur simultaneously or stepwise within the solvent cage, the reaction will proceed with retention of configuration. If the timing of the combination of the vinyl radical and Co(II) is such as to permit the rearrangement to the vinyl radical, stereoselectivity will become low. This is probably the case for the reaction of (*Z*)-MeCH=CMeBr because the nearly equimolar formation of isomeric σ complexes (Figure 3) suggests a free-radical intermediate. The α-methyl substituent of the bromide may promote a release of the bromide ion from the anion radical and inhibit sterically the formation of the carbon–cobalt bond. Reaction of alkenyl halides such as $Me_2C{=}CHX$ (X = Br or Cl) and $Me_2C{=}CMeBr$ may proceed in the radical process, and to some extent (*E*)-PhCH=CMeBr, which yielded a fairly large amount of the (*Z*)-nitrile (*E*:*Z* = 82:18). The low reactivity of $PhC(Br){=}CH_2$ is consistent with this explanation because the α-phenyl group may depress the release of the bromide ion. Thus, in this reaction cyanocobaltate(I) may take a role as an electron-transfer reagent rather than a nucleophile.[26]

The second step of the cyanation is the formation of nitriles from σ-vinylcobalt complexes. In the case of the formation of nitriles by the treatment of alkylpentacyanocobaltate(III) with acid and base,[6] and by hydrocyanation of olefins catalyzed by metal complexes,[27] insertion of hydrogen isocyanide into a metal-alkyl bond has been proposed. But, the more plausible mechanism for the present reaction is the reductive coupling of the vinyl and cyano ligands forming a nitrile and $[Co(CN)_4]^{3-}$ (eq 11). Similar reactions have been reported with some vinylmetal complexes,[23] although a cyano ligand is not involved as a coupling ligand. The reverse reaction (oxidative addition of $CH_3C(CN)_3$ or PhCN to Pt(0) complexes) has been reported.[28] This step is rate determining, as indicated by the detection of stable σ-vinyl complexes, and the rate is dependent on the stability of the σ complexes. Thus, nitriles are readily obtained from vinyl halides which have electron-donating substituents and not from those having electron-withdrawing substituents. The greater reactivity of (*Z*)-β-bromostyrene than the *E* isomer indicates that the σ complex is destabilized also by a steric factor. The fact that the σ complexes $Me_2C{=}CHCo$ and $Me_2C{=}CMeCo$ are very unstable and (*Z*)-MeCH=CMeCo is less stable than the *E* isomer may be ascribed to the steric hindrance between the methyl substituent and the cyano ligands. Our previous work on the steric configuration of σ-alkyl- and π-crotylcyanocobaltate(III) supports the destabilization by the steric factor.[29]

We have obtained clear evidence for the formation of π-olefin complexes of cyanocobaltate. Formation of stable σ-alkyl- and π-allylcyanocobaltate(III) has been well-known,[5,30,31] but formation of a π-olefin complex has not been reported. Since examples of a stable π-monoolefin–cobalt(I) complex are very rare,[32] formation of a new type of π-olefin complex is of great interest. The extent of the upfield shift of the olefinic carbon atom resonances by coordination is remarkably large, and the resonances of carbon atoms bearing the nitrile group appear at very high field.[17,33,34] This indicates that the degree of the Co→olefin π back–bonding is very high, reflecting that cyanocbaltate(I) is a very strong nucleophile. It is reasonable to assume that the cobalt species is $[Co(CN)_4]^{3-}$ rather than $[Co(CN)_5]^{4-}$, because the π complex is formed only at CN:Co < 5:1, the 18-electron rule supports the former species, and cobalt(I), which has a d^8 electron configuration, forms a complex of coordination number five in a square-pyramidal structure.[35] Although we initially assumed that the π complex might be involved in a catalytic cycle,[16] it is not the case because the π complex was formed only when the concentration of reactants became low. Thus, the complex must be rather an incidental byproduct formed by eq 12 when the olefin



(12)

is cinnamonitrile. The formation of the π-olefin complex and the high degree of the π back-bonding may suggest that the electron-transfer in the oxidative addition process occurs via a prior coordination of vinyl halide to cobalt(I) as observed with platinum(0) complexes,[36] but we have not detected π complexes of vinyl halides.

Experimental Section

Materials. Commercial anhydrous $CoCl_2$ and KCN were dried under vaccum at 100 °C and at room temperature on P_2O_5, respectively. Commercial (*E*)-β-bromostyrene was purified by the method reported[37] (*E*:*Z* = 99:1). The following materials were prepared according to literature procedures: (*Z*)-β-bromostyrene from (*E*)-cinnamic acid[38] (*Z*:*E* = 92:8), α-bromostyrene from styrene[39] (>96% pure by GLC analysis), (*E*)-β-methyl-β-bromostyrene from benzaldehyde and methyl ethyl ketone[40] (*E*:*Z* = 96:4), α,β-dibromostyrene from phenylacetylene[41] (*E*:*Z* = 68:32), (*E*)-methyl 3-bromomethacrylate from methyl methacrylate[42] (>98% pure), and other alkenyl halides from corresponding unsaturated acids[43] (>99% pure). A mixture of (*Z*)- and (*E*)-1-bromopropene(*Z*:*E* = 71:29, Aldrich Chemical Co.) was also used.

Reaction of Vinyl Halides. General Procedure. The solution of cyanocobaltate was prepared by mixing $CoCl_2$, KCN, and KOH (ratio Co:CN:OH variable, [Co] = 0.2 M in 5 or 25 mL of water. A 20- or 100-mL cylindrical two-necked flask, which was connected to a gas buret, was used, and the solution was stirred magnetically at 45 °C in an atmosphere of hydrogen. After preabsorption of hydrogen for 30 min,

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a vinyl halide was added with a microsyringe through a rubber serum cap. The solution at CN:Co < 5:1, before addition of the vinyl halide, was pale yellow green and contained a small amount of green precipitate. When alkenyl halides were added, the solution became pale yellow and a small amount of pink precipitate appeared in place of the green. Completion of reaction was noted by the reappearance of the yellow green color of the solution. When β-bromostyrene was added, the color of the solution changed to yellow and finally to dark red, and the solution became almost homogeneous. Reaction of a large excess of vinyl halides was performed by adding the KCN solution dropwise by using a microtube pump (Tokyo Rika Co MP-201). It was very important that CN:Co < 5:1 was maintained throughout the reaction. The progress of the reaction was followed by the gas chromatographic analysis of the extracts with dichloromethane from small aliquots of the reaction solution by using 3 m of PEG 20M (20% on Celite 545 (60–80 mesh), carrier gas flow (nitrogen) 80 mL min^{-1}), or 3 m of Silcone SE-30 (10% on Uniport B (60–80 mesh), carrier gas flow 40 mL min^{-1}). A Shimadzu GC-4CM gas chromatograph was used, and data were analyzed by a Shimadzu Chromatopac E1A. Products were isolated directly from the aqueous solution or extracted with dichloromethane. The GLC yield was estimated by using *o*-xylene or benzonitrile as an internal reference in the separate reactions. The extract was dried by filtering through a cone of $MgSO_4$, and the solvent was removed at atmospheric pressure or on a rotary evaporator in vacuo. Bulb-to-bulb distillation was carried out with a Kugelrohr apparatus (Büchi's Glass Tube Oven GKR-50, oven temperatures are reported). Pure products were obtained by preparative gas chromatography on a Varian 90P gas chromatograph. Nitriles obtained here are all known compounds and gave satisfactory elemental analyses. Infrared spectra of the products were taken to detect C≡N stretching vibrations of nitriles, and products were identified by ^1H and ^{13}C NMR spectroscopy (JEOL FX-100 and Varian HR-220).

Reaction of (*Z*)-1-Bromopropene. (Method *A*) A 100-mL flask was charged with $CoCl_2$ (0.649 g, 5.00 mmol), KCN (1.612 g, 24.75 mmol), and KOH (0.56 g, 10 mmol). This was flushed with H_2, and 25 mL of O_2-free water was added by an injection syringe. After preabsorption of hydrogen, 0.84 mL (10 mmol) of (*Z*)-1-bromopropene was added. The bromide disappeared after 3 h, but the reaction was continued for 4 h because the intermediate complex is stable. The extract was concentrated at atmospheric pressure to colorless liquid, which was distilled at 130 °C (oven temperature). The distillate, 0.35 g (52%), contained >97% 2-butenenitrile (*Z*:*E* = 96:4). Since the (*Z*)-nitrile isomerized slowly to the *E* isomer, a prolonged reaction to obtain a good yield was not advantageous for the selective cyanation. The rather poor yield is partly due to the vaporization of the bromide and nitriles in the reaction vessel. Reaction of 0.84 mL of a mixture of the (*Z*)- and (*E*)-bromides (*Z*:*E* = 71:29) was performed in the same way, and the distillate was 0.34 g (50%) which contained >98% 2-butenenitriles (*Z*:*E* = 70:30). (*Z*)- and (*E*)-MeCH=CHCN:[1c] *Z* isomer: t_R (retention time in the GLC analysis, min) 7.2 (PEG 20M) at 90 °C; IR (neat) 2220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.05 (dd, *J* = 7.0, 1.5 Hz, Me), 5.33 (dq, *J* = 10.9, 1.5 Hz, =CH), 6.55 (dq, *J* = 10.9, 7.0 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ 17.5 (q, J_{CH} = 128.2 Hz, Me), 100.6 (d, J_{CH} = 158.7 Hz, =CH), 150.1 (d, J_{CH} = 175.9 Hz, =CH), 116.0 (s, CN); *E* isomer: t_R 10.3 (PEG 20M) at 90 °C; IR (neat) 2250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.92 (dd, *J* = 7.0, 1.8 Hz, Me), 5.34 (dq, *J* = 16.1, 1.8 Hz =CH), 6.73 (dq, *J* = 16.1, 7 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ 19.2 (q, J_{CH} = 128.2 Hz, Me), 101.0 (d, J_{CH} = 157.5 Hz, =CH), 151.3 (d, J_{CH} = 171.9 Hz, =CH), 117.6 (s, CN).

Reaction of (Z)-1-Bromobut-2-ene. Reaction of 1.0 mL (10 mmol) of the bromide was performed by method A as described above. (*Z*)-MeCH=CMeCN was rapidly formed in the initial stage, but proportions of the *E* isomer and $MeCH_2CHMeCN$ increased with the elapse of time. After 100 min, the bromide almost disappeared and the proportion of the *Z* nitrile became maximal (*Z*:*E*:$MeCH_2CHMeCN$ = 66:9:25, 60% GLC yield). On the following day the products were extracted and distilled at 150 °C. 0.54 g (65%) of colorless liquid contained only nitriles (*Z*:*E*:$MeCH_2CHMeCN$ = 24:23:53). When the reaction was performed in N_2 overnight, 0.50 g (60%) of unsaturated nitriles was obtained (*Z*:*E* = 54:46). The GLC analysis of products was performed by using in 5 m PEG 20M column with the rise of temperature (2 °C/min) from 90 °C. (*Z*)- and (*E*)-MeCH=CMeCN:[1a,18,19] *Z* isomer: t_R 25.0; IR (neat) 2211 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.81 (d, *J* = 6.8 Hz, Me), 1.87 (s, Me), 6.35 (q, *J* = 6.8 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ 14.3 (q, J_{CH} = 128.2 Hz, Me), 14.5 (q, J_{CH} = 129.4 Hz, Me), 110.0 (s, =C), 143.0 (d, J_{CH} = 157.5 Hz, =CH), 120.6 (s, CN); *E* isomer: t_R 28.4; IR (neat) 2211 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.93 (s, Me), 1.96 (d, *J* = 6.2 Hz, Me), 6.20 (q, *J* = 6.2 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ 17.1 (q, J_{CH} = 128.2 Hz, Me), 20.0 (q, J_{CH} = 130.6 Hz, Me), 110.2 (s, =C), 143.1 (d, J_{CH} = 157.5 Hz, =CH), 118.1 (s, CN). $MeCH_2CHMeCN$: t_R 17.8; IR (neat) 2238 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (t, *J* = 6.8 Hz, Me), 1.31 (d, *J* = 7.1 Hz, Me), 1.63 (m, CH_2), 2.57 (m, CH); ^{13}C NMR ($CDCl_3$) δ 11.4 (q, J_{CH} = 128.2 Hz, Me), 17.6 (q, J_{CH} = 128.8 Hz, Me), 27.0 (d, J_{CH} = 129.4 Hz, CH), 27.3 (t, J_{CH} = 129.4, CH_2), 122.9 (s, CN).

Reaction of 1-Bromo-2-methylpropene. The bromide (1.0 mL, 10 mmol) was cyanated by method A. Reaction proceeded very rapidly, and the bromide disappeared within about 0.5 h. Workup of the reaction mixture after 1 h and distillation ((50 °C (20 mm)) of the concentrated solution gave 0.64 g (79%) of pure Me_2C=CHCN. The reaction was also performed in 5 mL of the aqueous solution of cyanocobaltate, which was prepared in at 20-mL flask by mixing $CoCl_2$ (0.130 g, 1.00 mmol), KCN (0.322 g, 4.95 mmol), and KOH (0.11 g, 2.0 mmol) (method B). When 0.5 mL (5 mmol) of the bromide was added, the yield of Me_2C=CHCN was 76% based on the bromide (370% based on the cobalt complex). The bromide (2.0 mL, 20 mmol) was cyanated by 1 mmol of the cobalt complex (method C). Thus, the aqueous solution of KCN 1.30 g (20 mmol) of KCN, 0.11 g (2 mmol) of KOH in 5 mL of H_2O) was added dropwise so as to remain a small amount of precipitate. Workup of the reaction mixture after 6 h gave 1.3 g (80%) of the nitrile, which contained 2% of the bromide. Me_2C=CHCN:[1c,k,18] t_R 2.6 (PEG 20M) at 140 °C; IR (neat) 2213 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.94 (s, Me), 2.06 (s, Me), 5.09 (m, *J* ≲ 0.1 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ 22.5 (q, J_{CH} = 128.2 Hz, Me), 25.0 (q, J_{CH} = 128.2 Hz, Me), 95.8 (d, J_{CH} = 172.1 Hz, =CH), 161.7 (s, =C), 117.1 (s, CN).

The effect of the CN:Co ratio on the reactivity was studied by varying the amount of KCN from 0 to 0.256 g (7.00 mmol) when other materials are $CoCl_2$ (0.130 g, 1 mmol), KOH (0.11 g, 2 mmol), Me_2C=CHBr (0.1 mL, 1 mmol), and H_2O (5 mL). The initial rate was estimated from the GLC yield in a 15-min period. Since reactions in the liquid–liquid heterogeneous solution are sensitive to the diffusion of liquids, the rates we obtained here may refer to the relative activity in our condition. At CN:Co < 5:1, the solution contained a precipitate, which increased with the progress of the reaction, and the product was formed without an induction period. The maximal yield increased with the CN:Co ratio. At CN:Co > 5:1, the solution was homogeneous and yellow green in the initial stage, and the formation of the nitrile was very slow. After the induction period, the rapid reaction started when the solution became yellow and the precipitate appeared. The induction period became longer with increasing concentration of the cyanide ion, and the bromide remained even after 4 h at CN:Co = 7.0.

Reaction of 1-Chloro-2-methylpropene. The chloride (1.0 mL, 10 mmol) was cyanated by method A, and workup of the reaction mixture after 1 h gave 0.52 g (65%) of pure Me_2C=CHCN. The reaction of 2.0 mL (20 mmol) of the chloride was performed by method C as described for the bromide, but the reaction did not proceed as rapidly as that of the bromide. On the following day the organic layer was separted from the aqueous layer, which was then extracted with dichloromethane. The organic layer was nearly pure Me_2C=CHCN. The organic layer and the extract were combined and worked up to give Me_2C=CHCN 1.0 g (61%)(>98% pure). In a similar way, 3.0 mL (30 mmol) of the chloride was converted to the nitrile by adding dropwise the aqueous solution of 1.95 g of KCN and 0.22 g of KOH in 10 mL of H_2O (yield, 2.24 g, 92%).

Reaction of 2-Bromo-3-methylbut-2-ene. Me_2C=CMeBr (1.18 mL, 10 mmol)was readily cyanated by method A, and workup of the reaction mixture after 1.5 h as described for 1-bromopropene gave 0.76 g (80%) of pure Me_2C=CMeCN after distillation at 65 °C (20 mm). The bromide (1.18 mL and 2.36 mL (20 mmol) was cyanated by method C to give 0.82 g (86%) and 1.52 g (80%) of the nitrile, respectively. Me_2C=CMeCN:[1j,k,19] t_R 4.4 (PEG 20M) at 140 °C; IR (neat) 2210 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.84 (s, Me), 1.85 (s, Me), 2.06 (s, Me); ^{13}C NMR ($CDCl_3$) δ 16.2 (q, J_{CH} = 129.5 Hz, Me), 20.0 (q, J_{CH} = 127.0 Hz, Me), 24.4 (q, J_{CH} = 127.0 Hz, Me), 103.6 (s, =C), 152.1 (s, =C), 119.8 (s, CN).

Reaction of (*Z*)-β-Bromostyrene. The bromide (1.28 mL, 10 mmol) (*Z*:*E* = 92:8) was added to the aqueous solution of cyanocobaltate prepared in 25 mL of H_2O (method A). The color of the solution changed as follows: yellow green → pale yellow → yellow → orange → dark red. The pink precipitate after formation almost disappeared in the dark red solution. Before extraction with dichloromethane after 2 h, the aqueous solution of KCN ([CN] = ca. 0.2 M) was added to decompose the π-cinnamonitrile complex complex which showed the dark red color. The GLC analysis of the extract indicated the formation of (*Z*)-cinnamonitrile (93%), (*E*)-cinnamonitrile (3%), 3-phenylpropanenitrile (<1%), styrene (2%), ethylbenzene (<1%). The extract was concentrated in vacuo and distilled at 100 °C (1 mm) to give 1.02 g (79%) of cinnamonitriles (*Z*:*E* = 97:3). Reaction of 1.28 mL of the bromide was performed by method C by adding dropwise the KCN-KOH solution (0.65 g of KCN, 0.06 g of KOH in 2.5 mL of H_2O) to keep the color of the solution pale yellow or yellow. On the following day >99% of the bromide was converted and the solution became dark red. The reaction mixture was worked up as described above to give 1.23 g (85%) of nitriles

(Z:E:$PhCH_2CH_2CN$ = 89:19:2). (Z)- and (E)-PhCH=CHCN:[1c,d,2,3] Z isomer: t_R 7.1 (Silicone SE-30) at 150 °C; IR (neat) 2215 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.43 (d, J = 12.2 Hz, =CH), 7.12 (d, J = 12.2 Hz, =CH), 7.43, 7.80 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 94.9 (d, J_{CH} = 174.5 Hz, =CH), 148.6 (d, J_{CH} = 157.5 Hz, =CH), 117.3 (s, CN) [128.8 (d), 130.8 (d), 133.5 (s), Ph]. E isomer: t_R 8.7 (Silicone SE-30) at 150 °C; IR (neat) 2218 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.86 (d, J = 16.6 Hz, =CH), 7.38 (d, J = 16.6 Hz, =CH), 7.42 (s, Ph); ^{13}C NMR ($CDCl_3$) δ 96.2 (d, J_{CH} = 170.1 Hz, =CH), 150.4 (d, J_{CH} = 157.5 Hz, =CH), 118.1 (s, CN) [127.1 (d), 129.0 (d), 131.1 (d), 133.4 (s), Ph]. $PhCH_2CH_2CN$: t_R 6.6 (Silicone SE-30) at 150 °C; IR (neat) 2220 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.67 (m, CH_2), 2.90 (m, CH_2), 7.20 (s, Ph); ^{13}C NMR ($CDCl_3$) δ 19.3 (t, J_{CH} = 136.5 Hz, CH_2), 31.6 (d, J_{CH} = 138.5 Hz, CH), 119.0 (s, CN) [127.2 (d), 128.2 (d), 128.8 (d), 131.1 (s), Ph].

Reaction of (*E*)-*β*-Bromostyrene. Conversion of 1.28 mL (10 mmol) of the bromide by method A took 18 h at 45 °C and 8 h at 55 °C. Workup of the reaction mixture as described for the (Z)-bromide gave a colorless extract which contained (E)-cinnamonitrile (93%), 3-phenylpropanenitrile (5%), and styrene (2%). Distillation at 100 °C (1 mm) gave 0.89 g (69%) of nitriles ((E)-PhCH=CHCN:$PhCH_2CH_2CN$ = 95:5). Reaction of 1.25 mL (10 mmol) of the bromide by method C was tried, but the reaction was so slow that the addition of the KCN solution in a controlled rate was difficult. After 2 days, the bromide was converted and 0.94 g (73%) of nitriles was obtained after distillation ((E)-PhCH=CHCN:$PhCH_2CH_2CN$ = 97:3).

Reaction of (*E*)-*β*-Methyl-*β*-bromostyrene. The bromide (1.46 mL, 10 mmol) (E:Z = 96:4) was cyanated by method A. The bromide disappeared within 7 h, and products were extracted after 8.5 h. The concentrated solution on distillation (100 °C, 1 mm) gave 1.29 g (90%) of colorless liquid containing (E)-PhCH=CMeCN (80%), (Z)-PhCH=CMeCN (17%), and $PhCH_2CHMeCN$ (3%). The E:Z ratio was smaller in the initial stage of the reaction, indicating that the intermediate complex for the Z isomer was less stable than that for the E isomer. (E)- and (Z)-PhCH=CMeCN:[1g,k,m] E isomer: t_R 20.0 (PEG 20M) at 190 °C; IR (neat) 2210 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.14 (d, J = 1.5 Hz, Me), 7.20 (q, J = 1.5 Hz, =CH), 7.36 (s, Ph); ^{13}C NMR ($CDCl_3$) δ 16.7 (q, J_{CH} = 130.6 Hz, Me), 109.5 (s, =C), 121.1 (s, CN) [128.6 (d), 129.2 (d), 129.7 (d), 134.0 (s), Ph]. Z isomer: t_R 18.0 (PEG 20M) at 190 °C; IR (neat) 2210 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.14 (d, J = 1.6 Hz, Me), 6.92 (q, J = 1.6 Hz, =CH), 7.2–7.6 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 22.1 (q, J_{CH} = 130.6 Hz, Me), 106.0 (s, =C), 143.9 (d, J_{CH} = 156.3, =CH), 118.7 (s, CN) [128.6 (d), 128.8 (d), 129.2 (d), 133.8(s), Ph]. $PhCH_2CHMeCN$: t_R 16.2 (PEG 20M) at 190 °C; IR (neat) 2240 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (m, Me), 2.85 (br, CH, CH_2), 7.27 (s, Ph); ^{13}C NMR ($CDCl_3$) δ 17.6 (q, J_{CH} = 130.5 Hz, Me), 27.5 (d, J_{CH} = 135.5 Hz, CH), 39.9 (t, J_{CH} = 136.7 Hz, CH_2), 122.6 (s, CN) [127.3 (d), 128.6 (d), 128.9 (d), 140.0 (s), Ph].

Reaction of *α*-Bromostyrene. Since the reaction of the bromide with cyanocobaltate was very slow and the product, α-cyanostyrene, was likely to polymerize or to be hydrogenated, the reaction was performed with addition of benzene at 55 °C. It took 12 h for the complete conversion of 0.65 mL (5 mmol) of the bromide dissolved in 5 mL of benzene by method A. Extraction with dichloromethane and concentration left yellow oil. Distillation at 100 °C (1 mm) gave 0.22 g (34%) of colorless oil containing nitriles (97%): $PhC(CN){=}CH_2$ (73%) and $PhCH(CN)CH_3$ (23%). From the yellow residue after the distillation, 0.05 g of $PhCH(CONH_2)CH_3$ was isolated. $PhC(CN){=}CH_2$:[44] t_R 8.5 (PEG 20M) at 200 °C; IR (neat) 2210 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.81 (s, =CH), 6.04 (s, =CH), 7.07 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 128.0 (dd, J_{CH} = 163.7, 166.0, =CH_2), 117.6 (s, =C), 122.8 (s, CN) [125.6 (d), 128.9 (d), 129.9 (d), 132.2 (s), Ph]. $PhCH(CN)CH_3$: t_R 7.9 (PEG 20M) at 200 °C; IR (neat) 2235 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.60 (d, J = 11.3 Hz, Me), 3.80 (q, J = 11.3 Hz, CH), 7.27 (s, Ph); ^{13}C NMR ($CDCl_3$) δ 21.4 (q, J_{CH} = 130.9 Hz, Me), 31.2 (d, J_{CH} = 133.9 Hz, CH), 121.6 (s, CN) [126.6 (d), 128.0 (d), 129.0 (d), 137.1 (s), Ph]. $PhCH(CONH_2)CH_3$: mp 96 °C; IR (KBr) 1685 cm^{-1} (ν_{CO}); ^{1}H NMR ($CDCl_3$) δ 1.40 (d, J = 11.3 Hz, Me), 3.43 (q, J = 11.3 Hz, CH), 7.17 (s, Ph); ^{13}C NMR ($CDCl_3$) δ 18.4 (q, J_{CH} = 130.9 Hz, Me), 47.3 (d, J_{CH} = 132.4 Hz, CH), 177.1 (s, CO) [127.3 (d), 127.6 (d), 129.0 (d), 141.3 (s), Ph].

Reaction of (*E*)-Methyl 3-bromomethacrylate. The bromide (1.2 mL, 10 mmol) was added to the solution of cyanocobaltate prepared in 25 mL of H_2O (method A). The color of the solution changed immediately from yellow green to yellow brown and a large amount of precipitate appeared. After 24 h, the reaction mixture was extracted with dichloromethane, but the bromide and products were not involved in the extract. Ethanol (150 mL) was added to the aqueous solution and the precipitate was separated by filtration. The filtrate was concentrated in vacuo, 50 mL of ethanol was added, and a yellow crystalline solid was separated. The white solid obtained after concentration of the ethanol solution was dissolved in 20 mL of water, which was made acidic with 1 N HCl and extracted with dichloromethane. Removal of dichloromethane gave 0.3 g of colorless oil, which did not show the C$\equiv$N band in the IR spectrum. The product was identified as CH(Br)=CMeCOOH.

Reaction of *α*,*β*-Dibromostyrene. The dibromide (0.75 mL, 5 mmol)(E:Z = 68:32) was added to 25 mL of an aqueous solution of cyanocobaltate (method A). The solution became yellow and a large amount of yellow precipitate appeared. The (E)-dibromide disappeared after 1 h, but the (Z)-dibromide after 3 h. In an initial stage, phenylacetylene and (Z)-PhCH=CHCN were mainly formed, but $PhCH(CN)CH_3$ and (E)-PhCH=CHCN were slowly formed. After 15 h, the composition of products in the extract was $PhCH(CN)CH_3$ (40%), (Z)-PhCH=CHCN (27%), (E)-PhCH=CHCN (19%), PhC$\equiv$CH (14%) (GLC yield of the nitriles, 31%). Concentration of the extract gave a yellow oil, which was distilled at 100 °C (1 mm) to give 0.17 g (27%) of the mixture of the nitriles. The residue was trace amounts of yellow oil, which contained $PhCH(CONH_2)CH_3$ (detected by IR). Phenylacetylene was hydrocyanated to $PhCH(CN)CH_3$ by cyanocobaltate.[13]

Observation of NMR Spectra of the Reaction Solution. $CoCl_2$ (0.062 g), KCN (0.155 g), and KOH (0.054 g) were dissolved in 1.2 mL of D_2O in a hydrogen atomsphere at 30 °C. After the preabsorption of hydrogen, vinyl halides (**1**:Co = 1.2:1) was added, and the reaction was continued until the solution became pale yellow or dark red. The solution was filtered through cotton packed in a glass tube into a NMR tube in a nitrogen atmosphere. ^{1}H NMR spectra were taken at room temperature, and ^{13}C NMR under cooling at 0 °C to minimize the temperature rise by the pulse radiation, but the temperature of the solutions in the NMR tube (^{13}C NMR) often became high enough to bring about decomposition of the complexes. The complexes were generally stable except for those obtained from $Me_2C{=}CHBr$ and $Me_2C{=}CMeBr$.

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Registry No. $[Co(CN)_4]^{3-}$, 80612-25-5; (Z)-MeCH=CHBr, 590-13-6; (E)-MeCH=CHBr, 590-15-8; (Z)-MeCH=CMeBr, 3017-68-3; $Me_2C{=}CHBr$, 3017-69-4; $Me_2C{=}CHCl$, 513-37-1; $Me_2C{=}CMeBr$, 3017-70-7; (Z)-PhCH=CHBr, 588-73-8; (E)-PhCH=CHBr, 588-72-7; (E)-PhCH=CMeBr, 54624-37-2; $PhC(Br){=}CH_2$, 98-81-7; (E)-$MeC(CO_2Me){=}CHBr$, 40053-01-8; (E)-α,β-dibromostyrene, 27786-05-6; (Z)-α,β-dibromostyrene, 29707-57-1; (Z)-MeCH=CHCN, 1190-76-7; (E)-MeCH=CHCN, 627-26-9; (Z)-MeCH=CMeCN, 20068-02-4; (E)-MeCH=CMeCN, 30574-97-1; $MeCH_2CHMeCN$, 18936-17-9; $Me_2C{=}CHCN$, 4786-24-7; $Me_2C{=}CMeCN$, 4786-37-2; (Z)-PhCH=CHCN, 24840-05-9; (E)-PhCH=CHCN, 1885-38-7; $PhCH_2CH_2CN$, 645-59-0; (E)-PhCH=CMeCN, 53587-72-7; (Z)-PhCH=CMeCN, 26157-51-7; $PhCH_2CHMeCN$, 33802-51-6; $PhC(CN){=}CH_2$, 495-10-3; $PhCH(CN)CH_3$, 1823-91-2; $PhCH(CONH_2)CH_3$, 1125-70-8; [(Z)-$MeCH{=}CHCo(CN)_5]^{3-}$, 80612-26-6; [(E)-$MeCH{=}CHCo(CN)_5]^{3-}$, 80657-43-8; [(Z)-$MeCH{=}CMeCo(CN)_5]^{3-}$, 80612-27-7; [(E)-$MeCH{=}CMeCo(CN)_5]^{3-}$, 80657-44-9; $[Me_2C{=}CHCo(CN)_5]^{3-}$, 80612-28-8; $[Me_2C{=}CMeCo(CN)_5]^{3-}$, 80612-29-9; [($Z$)-$PhCH{=}CHCo(CN)_5]^{3-}$, 69486-70-0; [($E$)-$PhCH{=}CHCo(CN)_5]^{3-}$, 69501-45-7; [($E$)-$PhCH{=}CMeCo(CN)_5]^{3-}$, 80612-30-2; $[H_2C{=}C(Ph)Co(CN)_5]^{3-}$, 80630-25-7; [($E$)-$MeC(CO_2Me){=}CHCo(CN)_5]^{3-}$, 80630-26-8; [($E$)-$MeC(CO_2K){=}CHCo(CN)_5]^{3-}$, 80612-31-3; [$\pi$-($Z$)-$PhCH{=}CHCN\text{-}Co(CN)_4]^{3-}$, 69486-76-6; [$\pi$-($E$)-$PhCH{=}CHCN\text{-}Co(CN)_4]^{3-}$, 69501-42-4; $CoCl_2$, 7646-79-9; KCN, 151-50-8.

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