Nuclear Magnetic Resonance and Electronic Spectral Studies on the Formation of π-Olefin–Tetracyanocobaltate(I) Complexes

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Cyanocobaltate prepared at CN : Co <5 : 1 in water in the presence of alkali and under an atmosphere of hydrogen reacts readily with mono-olefins having electron-withdrawing substituents to give a dark red solution. Hydrogen-1 and ^{13}C n.m.r. spectra of the solutions in D_2O clearly indicate that π-olefin complexes of cyanocobaltate are formed. The solutions also exhibit characteristic bands near 450 nm. The stoicheiometry of complex formation has been studied using $PhCH{=}C(CN)_2$ and monitored by the absorbance of the complex at 440 nm. These results indicate that a new type of π-olefin–cobalt(I) complex, $[Co(CN)_4(olefin)]^{3-}$, is formed, where olefin is $(NC)_2C{=}C(CN)_2$, $PhCH{=}C(CN)_2$, *cis*- and *trans*-PhCH=CHCN, *E*-PhCH=C(CN)CO_2Et, *E*-PhCH=C(CN)CO_2K, or *cis*- and *trans*-$RO_2CCH{=}CHCO_2R$ (R = Me, Et, or Na). The π complex of dialkyl maleate isomerises to that of dialkyl fumarate, probably by an electron-transfer mechanism.

In the chemistry of cyanocobaltate, the reactivities of $[Co(CN)_5]^{3-}$ and $[Co(CN)_5H]^{3-}$, which are readily formed by equations (1)—(3), with various organic and inorganic reagents have been studied extensively.[1] The results have been useful not only in the development of homogeneous catalysis, but also in understanding the chemistry of vitamin B_{12}.[2,3] It is well known that cobalt(I) species, which are strong nucleophiles, play important roles in the reactions of vitamin B_{12} and its model

$$Co^{2+} + 5CN^- \rightleftharpoons [Co(CN)_5]^{3-} \quad (1)$$

$$[Co(CN)_5]^{3-} + \tfrac{1}{2}H_2 \rightleftharpoons [Co(CN)_5H]^{3-} \quad (2)$$

$$2[Co(CN)_5]^{3-} + H_2O \rightleftharpoons [Co(CN)_5H]^{3-} + [Co(CN)_5(OH)]^{3-} \quad (3)$$

complexes such as bis(dimethylglyoximato)cobalt (cobaloximes). The formation of a moderately stable π-olefin complex of cobaloxime(I) with activated olefins was first reported by Schrauzer *et al.*[4] and confirmed recently by Ramasami and Espenson,[5] based on the measurement of electronic spectra[4,5] and kinetic studies.[5] Attempts to detect the complexes by n.m.r. have not been successful.[5] On the other hand, few studies have been carried out on the formation and reactivity of cyanocobaltate(I). Hanzlik and Vlček[6] first reported that $[Co(CN)_5]^{4-}$ was formed by equation (4) in a strong alkaline solution, and the formation of $[Co(CN)_4]^{3-}$ by equation (5) was suggested by Halpern and co-workers[7] in the reaction with carbon monoxide.

$$[Co(CN)_5H]^{3-} + OH^- \rightleftharpoons [Co(CN)_5]^{4-} + H_2O \quad (4)$$

$$[Co(CN)_5]^{4-} \rightleftharpoons [Co(CN)_4]^{3-} + CN^- \quad (5)$$

Although one of the characteristics of catalysis by pentacyanocobaltate(II) is the remarkable dependence of reactivity and selectivity on the CN : Co ratio,[1,8] reactions have been studied mostly at CN : Co >5 : 1 probably because precipitates are formed at CN : Co < 5 : 1. Recently, we found that cyanation of vinyl halides to form unsaturated nitriles proceeds catalytically only at CN : Co ratios <5 : 1, and proposed that $[Co(CN)_4]^{3-}$ must be an active species for the reaction.[9] In the studies of intermediate complexes by n.m.r., π-*cis*- and -*trans*-cinnamonitrilecobalt(I) complexes were incidentally found in the reactions of *cis*- and *trans*-β-bromostyrenes.[9] Since the complexes were also formed by the reaction of cinnamonitriles with cobalt species under the same conditions, the formation of π-olefin–cyanocobaltate(I) with some other olefins has been studied in more detail using ^1H and ^{13}C n.m.r. and electronic spectroscopy.

It is interesting to note that examples of stable or metastable mono-olefin π-complexes of cobalt are few in comparison with those of other transition metals.[10] π-Mono-olefin–cobalt(I) complexes already reported include: $[Co(\eta\text{-}C_5H_5)(PR_3)(olefin)]$, R = Ph or alkyl;[11] $[Co(\eta\text{-}C_5R_5)(olefin)_2]$, R = alkyl or H;[12] $[CoR(PR'_3)_m(olefin)_n]$, R = H or alkyl, R' = Ph or alkyl, $m = 0$—3, $n = 1$—3;[13,14] $[Co(Hdmg)_2L(olefin)]^{-4}$ or $[Co(Hdmg)_2(olefin)]^-$,[5] Hdmg = dimethylglyoximate, L = pyridine or PR_3; and $[Co(CNCH_3)_5(olefin)]^+$.[15] The results presented here provide another example of a moderately stable π-olefin–cobalt(I) complex.

EXPERIMENTAL

Materials.—Commercial anhydrous $CoCl_2$ and K[CN] were dried *in vacuo* at 100 °C and at room temperature over P_2O_5 respectively. *cis*-Cinnamonitrile and *cis*- and *trans*-$PhCH{=}CH^{13}CN$ were synthesised from *cis*- and *trans*-β-bromostyrenes by the method reported previously.[9] Other olefins were of commercial origin and purified by distillation or recrystallisation before use.

Reactions.—Generally, reactions were performed in a 10-cm^3 flask with a rubber serum cap, which was connected to a gas burette. The compounds K[CN] (0.1313 g, 2.02 mmol), $CoCl_2$ (0.0623 g, 0.48 mmol), and K[OH] (0.054 g, 0.96 mmol) were placed in the flask and the atmosphere replaced with hydrogen. Pre-absorption of hydrogen by the complex was initiated by the addition of solvent (1.2 cm^3) (H_2O or D_2O) with stirring at 30 °C. The solution became pale yellow with a pink precipitate after absorption of hydrogen. Olefin (0.58 mmol) was added through the serum cap with a syringe in the case of liquid olefins or directly under an atmosphere of hydrogen in the case of crystalline olefins. The solution became red or dark red and almost homogeneous, the rate of colour change and the amount of precipitate depending on the nature of the olefin.

A solution of the complex was also prepared without the pre-absorption of hydrogen: solvent was added to a mixture of K[CN], $CoCl_2$, K[OH], and olefin. This method was more convenient when the olefins were crystalline, although it promoted the hydrolysis of esters before co-ordination to cobalt.

N.M.R. Spectra.—The solution prepared in D_2O was filtered into n.m.r. tubes under a nitrogen atmosphere. Hydrogen-1 n.m.r. spectra were recorded on either Varian 220-HR or JEOL FX-100 spectrometers at room temperature, while ^{13}C n.m.r. spectra were recorded on the latter instrument with cooling. Difficulties were sometimes encountered in the measurement of ^{13}C n.m.r. spectra, since the temperature of the solution rose even though the temperature of the probe was maintained at 0 °C. Dioxan and sodium 3-(trimethylsilyl)[$^2H_4$]propionate were used as references in the measurements of ^{13}C and ^1H n.m.r. spectra respectively.

Electronic Spectra.—A solution of the complex in water was filtered in a nitrogen atmosphere and diluted using syringes. Thus, the filtrate (0.1 cm^3) was added to water (19.9 cm^3) ([Co] = *ca.* 2×10^{-3} mol dm^{-3}, the concentration was affected by amounts of precipitate), and the visible spectrum was measured. A sample of the above solution (1 cm^3) was added to water (19 cm^3) and the u.v. spectrum was measured. Spectra were recorded using a JASCO UVIDEC-1 instrument at room temperature.

RESULTS

N.M.R. Spectra.—Crystalline tetracyanoethylene, $(NC)_2C=C(CN)_2$, reacted rapidly with the cobalt-containing solution to give a dark red colouration. The ^{13}C n.m.r. spectrum showed two strong peaks due to quaternary carbons in the high- (9.1 p.p.m.) and low-field (135.1 p.p.m.) regions together with some minor peaks. Since large upfield shifts of olefinic carbon resonances are generally observed with π-olefin–metal complexes,[16] the former two peaks must correspond to a π-tetracyanoethylene–cobalt complex. The peaks were assigned as shown in the Table. Downfield shifts of the resonances due to the carbons attached to the olefinic carbons (the nitrile carbon in this case) were generally observed in the present series of complexes. The other small peaks may be ascribed to unco-ordinated mono- or di-meric anionic species of the olefin.[17] In fact *ca.* 10 peaks were observed between 59.2 and 161.8 p.p.m. when the olefin was dissolved in alkaline D_2O to give the dark brown solution.

Crystalline benzylidenemalononitrile, $PhCH=C(CN)_2$, reacted very rapidly to give an almost homogeneous dark red solution at a ratio of CN : Co : OH = 4 : 1 : 2 (the mole ratio of added K[CN], $CoCl_2$, and K[OH]). As shown in Figure 1, formation of the π-complex was clearly indicated by the large upfield shifts of the olefinic carbon resonances and the downfield shifts of the nitrile and phenyl C^1 carbon resonances. Resonances of the two nitrile groups were distinguished by measuring the off-resonance spectrum. The coupling constant of the co-ordinated olefinic carbon ($^1J_{CH} = 156$ Hz) is slightly smaller than that of the free olefin (161 Hz), but consistent with sp^2 carbon. This olefin also dissolved in an alkaline solution, in the absence of the cobalt complex, to give a pale yellow solution probably due to the formation of anionic species.[18] The resonances observed from this solution are just evident in the spectra shown in Figure 1. Interestingly, however, the π complex was also formed when the filtrate from the alkaline solution of the olefin was added to the solution of cyanocobaltate. The possibility of formation of a π-olefin complex between the anionic species and cyanocobaltate will be discussed later. An upfield shift of the olefinic proton resonance was also observed in the ^1H n.m.r. spectrum.

The *trans*- and *cis*-cinnamonitriles, PhCH=CHCN, reacted rapidly to give dark red solutions, and the n.m.r. spectra were similar to those observed previously in the reactions of *trans*- and *cis*-β-bromostyrenes.[9] The previous assignments of the olefinic proton resonances of the *cis*-cinnamonitrile complex [9] which overlap with phenyl proton resonances are corrected in the Table. The nitrile carbon resonances were assigned by using $PhCH=CH^{13}CN$, which was synthesised from β-bromostyrene and K[^{13}CN].[9] The olefins were slowly hydrogenated to β-propionitriles, into which deuterium became incorporated in the reactions in D_2O, although the olefinic protons in the recovered olefins and the π-olefin complexes underwent little exchange with deuterium in D_2O.

Crystalline ethyl α-cyano-β-phenylacrylate, $PhCH=C(CN)CO_2Et$, reacted rapidly, but the n.m.r. spectra were complicated by the ester hydrolysing or dimerising in alkaline solution.[17] Two doublets due to olefin-carbon resonances in the ^{13}C n.m.r., and two singlets in the ^1H n.m.r., were observed in the high-field region. This indicated the formation of two π-olefin complexes; one must be that of the ester and the other that of the hydrolysed species, probably the potassium salt of the acrylate rather than the anionic acrylate. Peaks other than phenyl groups were assigned by comparison of the relative intensities.

Dialkyl fumarates and maleates, $RO_2CCH=CHCO_2R$ (R = Me or Et), reacted rapidly to give dark red solutions, the n.m.r. sepctra of which showed peaks due to π-olefin complexes (peaks due to alkyl groups and olefinic protons and carbons in the high-field region) together with peaks due to unco-ordinated fumarate and maleate anions (peaks due to MeOD or EtOD and olefinic protons and carbons in the low-field region). The hydrolysed species was mainly the dicarboxylate at olefin : Co ratios of 1.2 : 1, but the mono-carboxylate at olefin : Co = 2 : 1. Interestingly, the singlet resonance of the olefinic proton of the co-ordinated maleate ester shifted to that of the co-ordinated fumarate ester without a change in the total peak intensities (Figure 2).[19] The rate of isomerisation increased with temperature, but the effect of excess of cyanide ion [19] was rather obscure. A preliminary kinetic study was not successful. Since the shift occurred during the measurements of ^{13}C n.m.r. spectra of π-dialkyl maleate complexes, ^1H n.m.r. spectra were taken just after the measurements of the ^{13}C n.m.r. spectra to ascertain the presence of these complexes. To examine the co-ordination of the hydrolysed species, disodium fumarate and maleate (R = Na) were added in place of the esters. The reaction was rather slow and the colour of the resulting solution was orange or dark yellow. N.m.r. spectra indicated the formation of π complexes, but the intensities of the singlets of the co-ordinated olefin protons were much lower than those of the free olefins, especially in the case of maleate.

Ethyl cinnamate, $PhCH=CHCO_2Et$, reacted relatively slowly and the filtrate was orange-red The complex was very unstable and its ^{13}C n.m.r. spectrum was barely observable. The ^1H n.m.r. spectrum showed resonances due to two ethyl groups, one of which corresponded to EtOD, suggesting that the π complex of the ester might be

Carbon-13 and ^1H n.m.r. data for olefins and $[Co(CN)_4(olefin)]^{3-}$ [a]

Olefin	$\delta(C_{free})(^1J_{CH})$	$\delta_{(co\text{-}ord.)}(^1J_{CH})$	$\Delta\delta_C$ [b]	$\delta(H_{free})(J_H)$	$\delta(H_{co\text{-}ord.})(J_H)$	$\Delta\delta_H$ [b]
(*a*) $(NC)_2C{=}C(CN)_2$						
=C–	109.6	9.1	100.5			
CN	113.5	135.1	−21.6			
(*b*) $PhCH{=}C(CN)_2$						
=C–	82.6	5.6	77.0			
=CH–	160.0 (161)	48.1 (156)	111.9	7.78	4.23	3.55
CN	112.6	125.2	−12.6			
CN	113.7	125.4	−11.7			
C^1(Ph) [c]	130.8	145.9	−15.1			
(*c*) *trans*-PhCH=CHCN						
=CH–(CN)	96.2 (170)	10.9 (162)	85.3	5.86 (16.6)	2.74 (10.0)	3.12
=CH–(Ph)	150.4 (158)	47.7 (156)	102.7	7.38	3.98	3.40
CN	118.1	132.5	−14.4			
C^1(Ph) [d]	133.4	148.2	−14.8			
(*d*) *cis*-PhCH=CHCN						
=CH–(CN)	94.9 (175)	11.4 (164)	83.5	5.43 (12.2)	2.43 (8.8)	3.00
=CH–(Ph)	148.6 (162)	44.8 (154)	103.8	7.12	3.85	3.27
CN	117.3	133.1	−15.8			
C^1(Ph) [e]	133.5	149.1	−15.6			
(*e*) *E*-$PhCH{=}C(CN)CO_2Et$ [f]						
=C–	103.0	27.3	75.7			
=CH–	154.9 (159)	44.2 (155)	110.7	8.24	4.53	3.71
CN	115.4	124.5	−9.1			
C^1(Ph) [g]	131.4	146.1	−14.7			
CO_2	162.4	174.8	−12.4			
(*f*) *E*-$PhCH{=}C(CN)CO_2K$ [h]						
=C–	109.8	30.5	79.3			
=CH–	153.3 (160)	46.7 (153)	106.6	7.96	4.65	3.31
CN	119.9	124.1	−4.2			
C^1(Ph) [g]	137.0	147.4	−10.4			
CO_2	170.3	180.3	−10.0			
(*g*) *trans*-$EtO_2CCH{=}CHCO_2Et$ [i]						
=CH–	133.7 (169)	34.7 (159)	99.0	6.84	3.19	3.65
CO_2	164.9	179.9	−15.0			
(*h*) *trans*-$MeO_2CCH{=}CHCO_2Me$ [j]						
=CH–	133.4 (161)	34.7 (159)	98.7	6.86	3.21	3.65
CO_2	165.3	180.8	−15.5			
(*i*) *trans*-$NaO_2CCH{=}CHCO_2Na$ [k]						
=CH–	136.1 (162)	42.5 (153)	93.6	6.50	3.08	2.42
CO_2	175.5	[l]				
(*j*) *cis*-$EtO_2CCH{=}CHCO_2Et$ [m]						
=CH–	129.8 (166)	34.5 (157)	95.3	6.24	2.89	3.35
CO_2	165.2	178.2	−13.0			
(*k*) *cis*-$MeO_2CCH{=}CHCO_2Me$ [n]						
=CH–	129.7 (166)	34.1 (155)	95.6	6.27	2.92	3.35
CO_2	165.6	179.0	−13.4			
(*l*) *cis*-$NaO_2CCH{=}CHCO_2Na$ [k]						
=CH–	131.3 (160)	41.5 (152)	89.8	6.00	3.06	2.94
CO_2	176.2	[l]				

[a] Chemical shifts δ (p.p.m.) were referred to $SiMe_4$ in $CDCl_3$, dioxan (67.4 p.p.m. for ^{13}C n.m.r.), and $NaO_2CC_2D_4SiMe_3$ (for ^1H n.m.r.) in D_2O. $^1J_{CH}$ and J_H denote coupling constants (Hz). [b] $\Delta\delta_C = \delta(C_{free}) - \delta(C_{co\text{-}ord.})$, $\Delta\delta_H = \delta(H_{free}) - \delta(H_{co\text{-}ord.})$; positive values correspond to upfield shifts. [c] Phenyl carbon attached to the olefinic carbon. δ_C values of *ortho* (*o*), *meta* (*m*), and *para* (*p*) carbons are 129.5, 130.6, 134.5 (free); 128.5, 128.7, 125.3 (co-ordinated). Phenyl protons were observed as multiplets. [d] *o* 129.0, *m* 127.3, *p* 131.3 (free); *o* 126.5, *m* 128.6, *p* 123.6 (co-ordinated). [e] *o*, *m* 128.8, *p* 130.8 (free); *o* 128.6, *m* 127.9, *p* 124.1 (co-ordinated). [f] $\delta_C(CH_3)$ 14.2 (free), 14.1 (co-ordinated), $\delta_H(CH_3)$ 1.39 (free), 1.32 (co-ordinated); $\delta_C(CH_2)$ 62.7 (free), 61.6 (co-ordinated), $\delta_H(CH_2)$ 4.38 (free), 3.65 (co-ordinated). [g] Peaks of *o*, *m*, and *p* carbons were not assigned except for the free ester (129.2, 131.0, and 133.2 respectively). [h] Observed in the reaction of the ester. Peaks of EtOD were observed: $\delta_C(CH_3)$ 17.8, $\delta_H(CH_3)$ 1.20; $\delta_C(CH_2)$ 58.3, $\delta_H(CH_2)$ 3.66. [i] $\delta_C(CH_3)$ 14.2 (free), 14.6 (co-ordinated), $\delta_H(CH_3)$ 1.32 (free), 1.27 (co-ordinated); $\delta_C(CH_2)$ 61.4 (free), 61.0 (co-ordinated), $\delta_H(CH_2)$ 4.26 (free), 4.11 (co-ordinated). [j] $\delta_C(CH_3)$ 52.3 (free), 52.1 (co-ordinated), $\delta_H(CH_3)$ 3.81 (free), 3.63 (co-ordinated). [k] May be potassium salts in the solution. [l] Not detected. [m] $\delta_C(CH_3)$ 14.0 (free), 14.2 (co-ordinated), $\delta_H(CH_3)$ 1.31 (free), 1.26 (co-ordinated); $\delta_C(CH_2)$ 61.2 (free), 60.3 (co-ordinated), $\delta_H(CH_2)$ 4.25 (free), 4.08 (co-ordinated). [n] $\delta_C(CH_3)$ 52.1 (free), 52.0 (co-ordinated), $\delta_H(CH_3)$ 3.79 (free), 3.63 (co-ordinated).

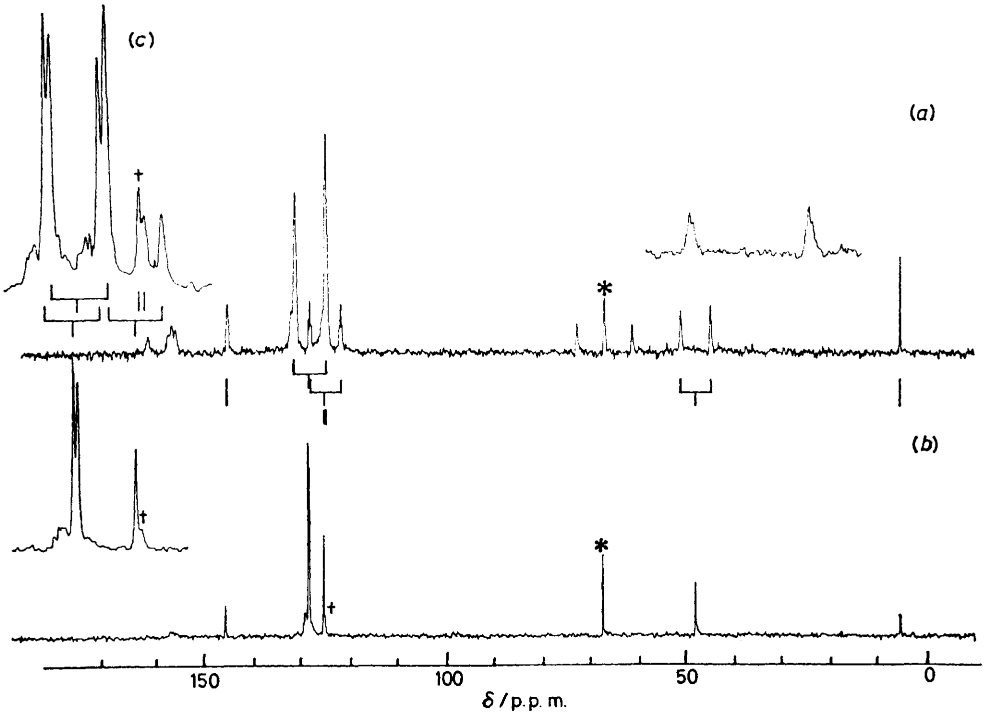


FIGURE 1 Carbon-13 n.m.r. spectra of $[Co(CN)_4\{PhCH{=}C(CN)_2\}]^{3-}$ in D_2O. (*a*) Non-decoupled spectrum, (*b*) completely decoupled spectrum, (*c*) off-resonance spectrum. Peaks marked with an asterisk are due to dioxan, those marked with a dagger are due to CN groups

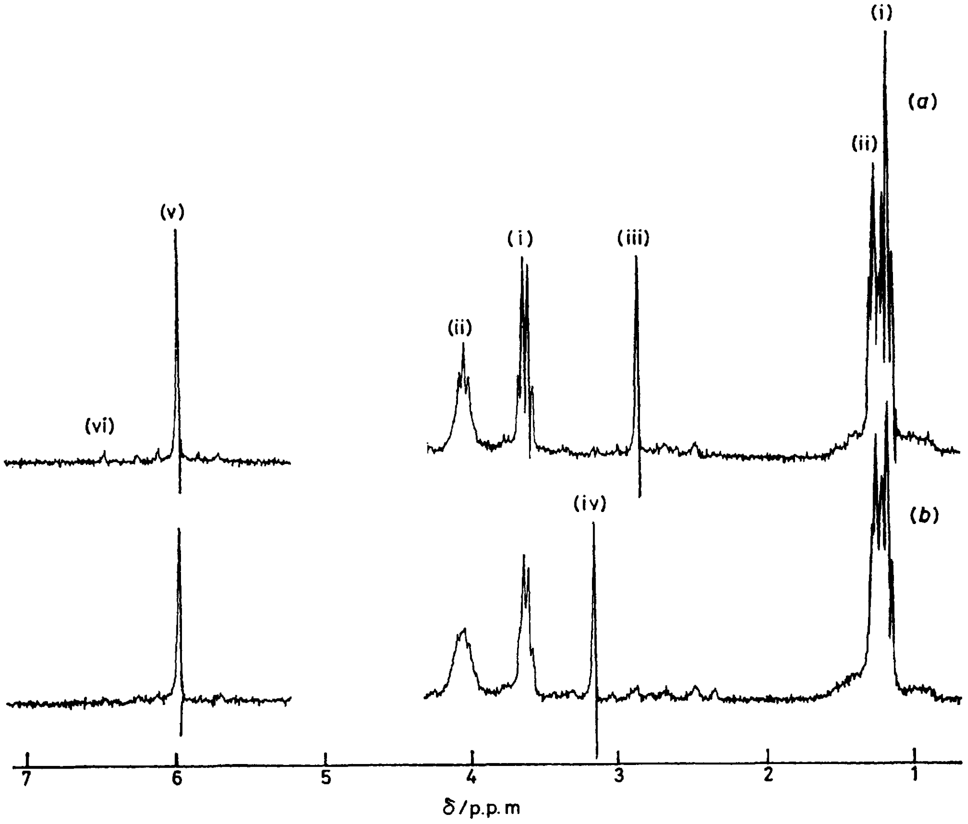


FIGURE 2 Hydrogen-1 n.m.r. spectra of the reaction of diethyl maleate in D_2O. (*a*) Observed after 1 h, (*b*) after being left overnight. (*i*) EtOD, (*ii*) ethyl group of co-ordinated ester; (*iii*), (*iv*) olefinic protons of co-ordinated diethyl maleate and fumarate respectively; (*v*), (*vi*) olefinic protons of free maleate and fumarate respectively

formed, although the resonances due to olefinic protons of the complex could not be distinguished. On the other hand, peaks due to the hydrogenated (or deuteriated) product of the hydrolysed cinnamate were detected and their intensity increased with time. Ethyl benzylidenemalonate, $PhCH{=}C(CO_2Et)_2$, and *trans*-stilbene, $PhCH{=}CHPh$, barely reacted with the cobalt complex. Fumaronitrile, $NCCH{=}CHCN$, was expected to form a stable π complex, but the solution was dark brown and peaks due to co-ordinated and unco-ordinated olefins were scarcely observable. Radical species may have been formed, but the reaction requires to be studied in more detail.

Electronic Spectra.—As shown in Figure 3, the solutions of π-olefin complexes exhibited characteristic bands near 450 nm: 440 [$PhCH{=}C(CN)_2$], 460 [$PhCH{=}C(CN)CO_2Et$], 460 (*trans*-$EtO_2CCH{=}CHCO_2Et$), 450 nm (*cis*-$EtO_2CCH{=}CHCO_2Et$), and shoulders (cinnamonitriles). A typical band for the π complex of tetracyanoethylene was not characterised, since the alkaline solution of the olefin exhibited strong bands both in the visible and u.v. regions. Unstable complexes formed from disodium fumarate or maleate and ethyl cinnamate decomposed rapidly on dilution. Dilution with a strongly alkaline solution was effective in slowing down the decomposition, and shoulders were observed with less dilute solutions, together with bands due to $[Co(CN)_5]^{3-}$. The solution obtained by the reaction with fumaronitrile exhibited bands at 248 and 333 nm, but a shoulder at 440 nm was almost insignificant.

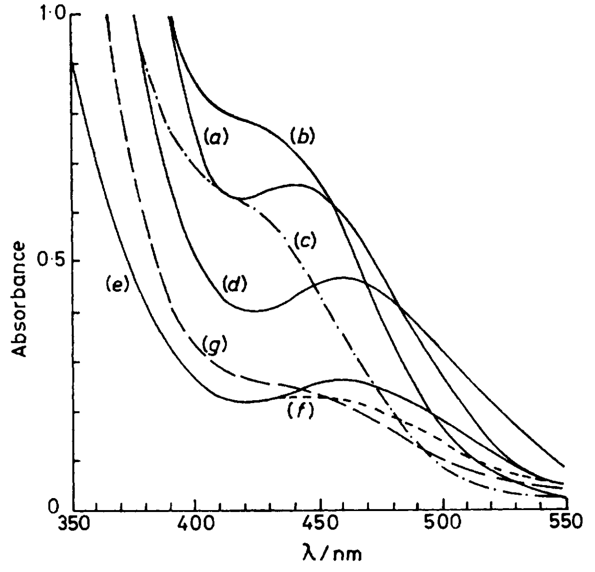


FIGURE 3 Absorption spectra of π-olefin tetracyanocobaltates(I) in water. Olefins are $PhCH{=}C(CN)_2$ (*a*), *trans*-$PhCH{=}CHCN$ (*b*), *cis*-$PhCH{=}CHCN$ (*c*), *E*-$PhCH{=}C(CN)CO_2Et$ (*d*), *trans*-$EtO_2CCH{=}CHCO_2Et$ (*e*), *cis*-$EtO_2CCH{=}CHCO_2Et$ (*f*), and *E*-$PhCH{=}CHCO_2Et$ (*g*). The solutions were prepared at CN : Co : OH : olefin ratio of 4.2 : 1 : 2 : 1.2 with $CoCl_2$ (0.48 mmol) in water (1.2 cm^3). They were filtered and diluted 200 times [(*a*)—(*f*)] or 20 times [(*g*)] with water

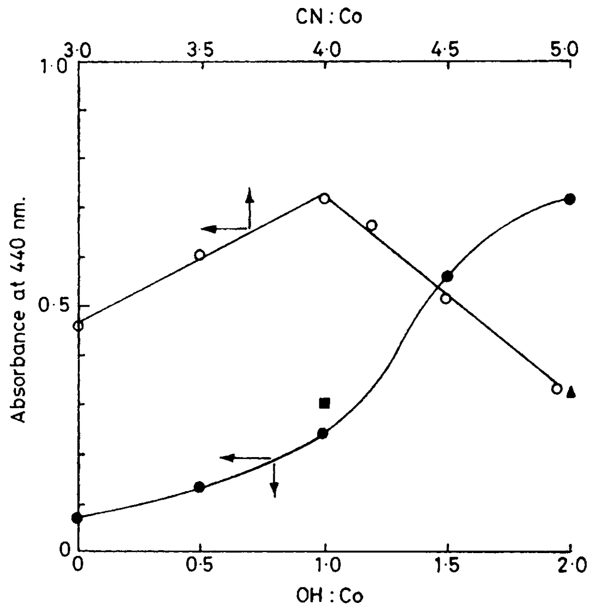


FIGURE 4 Effects of alkali, CN : Co ratio, and hydrogen on the formation of the π complex of $PhCH{=}C(CN)_2$ at a Co : olefin ratio of 1 : 1.2. (○), Co:OH = 1:2 in H_2; (●), CN:Co = 4.0 : 1 in H_2; (▲), CN : Co : OH = 4.0 : 1 : 2 in N_2; (■), CN : Co : OH = 4.95 : 1 : 1 in H_2

The stoicheiometry of formation of the π complex was studied using the complex of $PhCH{=}C(CN)_2$, monitored by the absorbance at 440 nm. Figure 4 shows the effects of the alkali concentration, the CN : Co ratio, and the absence of hydrogen on the formation of the complex. At CN : Co : olefin = 4 : 1 : 1.2 ($[Co]_0$ = 0.4 mol dm^{-3}), the precipitate increased and absorbance decreased with decreasing alkali concentration. It seems noteworthy that a small peak due to the π complex was detected even in the absence of alkali, although a large amount of yellow precipitate was formed. A slight precipitate was observed at CN : Co : OH : olefin = 4 : 1 : 2 : 1.2 which disappeared on increasing the cyanide concentration. However, the absorbance decreased with increasing CN : Co ratio from 4.0 : 1 to 4.95 : 1. The solution was homogeneous at CN : Co : OH : olefin = 4.95 : 1 : 1 : 1.2 and heterogeneous at 4 : 1 : 1 : 1.2, but the absorb-

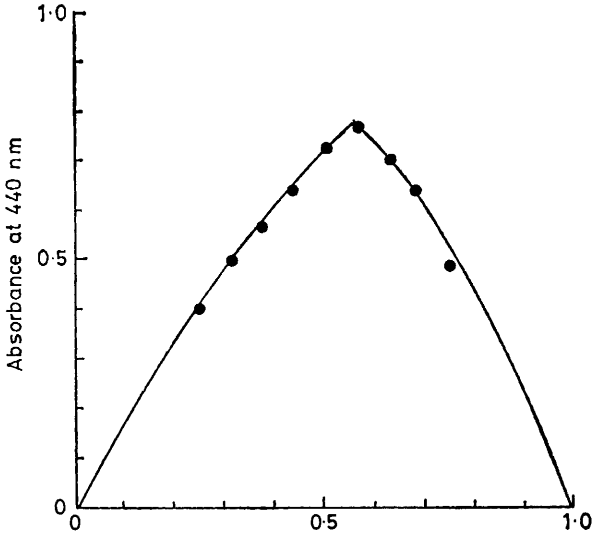


FIGURE 5 Effect of Co : olefin ratio on the formation of the π complex of $PhCH{=}C(CN)_2$. The compounds K[OH] (1.2 mmol), K[CN] (CN : Co = 4 : 1), and $CoCl_2$ + olefin (0.96 mmol in total) were mixed in water (1.2 cm^3) under hydrogen at 30 °C. After 30 min, the solution was filtered and diluted 200 times

ance was similar in both solutions. These results suggest that the CN : Co ratio of the active complex is 4 : 1 rather than 5 : 1. The formation of the π complex was slower under a nitrogen atmosphere than under hydrogen at CN : Co : OH : olefin = 4 : 1 : 2 : 1.2, and the absorbance of the former solution was nearly half that of the latter. This indicated that the formation of $[Co(CN)_5H]^{3-}$ was essential for the formation of the π complex.

Figure 5 shows the effect of the Co : olefin ratio on the absorbance at CN : Co = 4 : 1; the alkali concentration and the total concentration of cobalt and olefin were held constant. It can be clearly seen that the Co : olefin ratio in the complex was 1 : 1.

DISCUSSION

Large upfield shifts of n.m.r. resonances of olefinic protons and carbons are known for many transition-metal π-olefin complexes.[16,20] As for the π-mono-olefin–cobalt(I) complex, ^1H n.m.r. data have been reported for η-cyclopentadienyl–π-mono-olefin–cobalt(I) complexes,[11,12] but only one result appears to be available for the carbon resonance shift with $[Co(\eta\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}CH_2{=}CH_2)]$.[11c,21,*] Although the explanation for the proton resonance shifts does not seem simple, the shifts of olefinic carbon resonances and the values of coupling constants, $^1J_{CH}$, are characteristic of the formation of π-olefin complexes. As seen in the Table, resonances of olefinic protons and carbons are shifted to high field on complexation with cyanocobaltate. This shift indicates that the π-olefin–cobalt bond is formed mainly from electron transfer from cobalt to olefin. This is reflected in the downfield shifts of resonances of neighbouring carbons, *e.g.* carbons of CN and C^1(Ph) in PhCH=CHCN, and in the increasing stability of the complex with electron-withdrawing substituents. That the values of $^1J_{CH}$ due to the olefinic carbons decreased only slightly after complexation indicates clearly that the sp^2 hybridisation of the carbons is little affected by complexation.

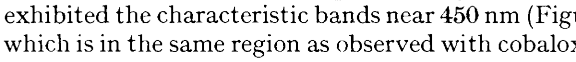
It is clear that the cobalt species which forms the π-olefin complex is an electron-rich cobalt(I) species rather than cobalt(II) or cobalt(III) species. Broadening of peaks due to paramagnetic cobalt(II) species was not observed in the ^1H n.m.r. spectra. Two cobalt(I) species have been reported, as shown in reactions (4) and (5), but support for $[Co(CN)_4]^{3-}$ rather than $[Co(CN)_5]^{4-}$ as the species active in complexation is as follows: (*i*) the complex was formed only at CN : Co <5 : 1, (*ii*) the formation was optimum at CN : Co = 4 : 1 (Figure 4), (*iii*) the importance of alkali and hydrogen (Figure 4) is consistent with the suggestion that the cobalt(I) species is formed *via* reactions (1), (2), (4), and (5), and (*iv*) the formation of the π complex under a nitrogen atmosphere is nearly half of that under hydrogen and is due to the formation of $[Co(CN)_5H]^{3-}$ *via* reaction (3). The data in Figure 5 clearly indicate that $[Co(CN)_4]^{3-}$ and olefin form a 1 : 1 complex. This is consistent with the suggestion

$$[Co(CN)_4]^{3-} + \text{olefin} \rightleftharpoons [Co(CN)_4(\text{olefin})]^{3-} \quad (6)$$

that cobalt(I), which has a d^8 electron configuration, forms a complex of co-ordination number five with a square-pyramidal structure.[5,22]

In the present reaction, olefins, which are not soluble in aqueous solution, become soluble by forming the π complexes, but complicating features occur in very basic solution. Esters are readily hydrolysed in the solution to form anionic species. The hydrolysed species can then form new π complexes, which are less stable than those of esters and liable to decompose on dilution. It is assumed that the carboxylates co-ordinate as neutral salts rather than anionic olefins, since cyanocobaltate(I) is an electron-rich anionic species. It is interesting to note that esters are barely hydrolysed after co-ordination to cobalt(I). This is because the electron transfer from cobalt(I) to olefins makes the olefins sufficiently electron-rich to inhibit hydrolysis. Unsaturated nitriles such as $(NC)_2C{=}C(NC)_2$ and $PhCH{=}C(CN)_2$ also become soluble, probably by forming anionic species in basic solution. Hydrolysis and dimerisation *via* the anions have been reported.[17,18] That the π complex of $PhCH{=}C(CN)_2$ was formed by mixing the filtrate of the aqueous alkaline solution of the olefin with the solution of cyanocobaltate suggests that the π complex is formed by interaction of the anionic species in an equilibrium (7) with $[Co(CN)_4]^{3-}$, but we prefer reaction (8) for the reason described in the co-ordination of carboxylates.

$$PhCH{=}C(CN)_2 + OH^- \rightleftharpoons PhCH(OH){-}\bar{C}(CN)_2 \quad (7)$$



$$PhCH{=}C(CN)_2 + [Co(CN)_4]^{3-} \rightleftharpoons \left[\begin{array}{c} PhCH{=}C(CN)_2 \\ | \\ Co(CN)_4 \end{array}\right]^{3-} \quad (8)$$

It has been reported that the electronic spectra of cobaloxime(I) exhibits characteristic low-energy bands which have been assigned to ligand-modified *d–d* transitions, and that the π-olefin complexes of cobaloxime(I) exhibit two or three bands from 360 to 530 nm,[4] or from 390 to 620 nm.[5] The π complexes of cyanocobaltate(I) exhibited the characteristic bands near 450 nm (Figure 3), which is in the same region as observed with cobaloximes. Bands for $[Co(CN)_4]^{3-}$ or $[Co(CN)_5]^{4-}$ have not been observed in the visible region ($\lambda_{max.} = 280$ nm has been reported for the latter).[7] In the case of cobaloxime(I), the band of the longest wavelength, which is the most intense, appears at longer wavelengths in complexes with diminished co-ordination power of the in-plane ligands.[4] It is difficult to comment on the wavelength of the band but the fact that the wavelengths of the π complexes of cyanocobaltate(I) are shorter than those of cobaloximes(I) may indicate that the co-ordination power of a cyano-ligand is stronger than that of a glyoximato-ligand and the electron density on cobalt is higher in cyanocobaltates(I) than in cobaloximes(I). The effect of the co-ordinated olefin on the wavelength was discussed for cobaloximes,[4] but the present data are not sufficient to enable us to comment on the small shift observed on changing olefins.

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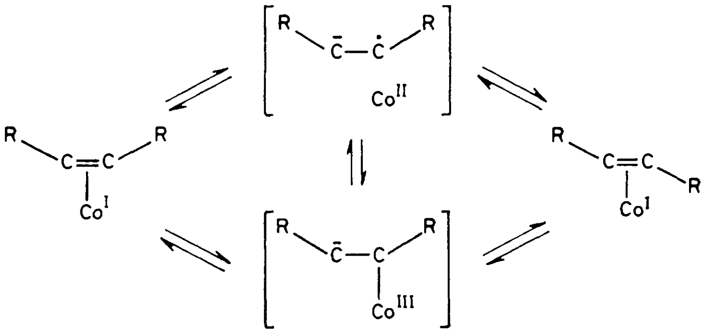
[*] Data have been reported for complexes of the type, σ,π-alkyl-cobalt(I), *e.g.* $[Co(CO)_2(PMe_2Ph)(CF_2CF_2CH_2CH{=}CH_2)]$, see ref. 21.

One of the interesting results observed here is the isomerisation of the π complex of dialkyl maleate to that of fumarate. Jackman *et al.*[23] have reported that α,β-unsaturated carboxylates are hydrogenated or isomerised by pentacyanocobaltate(II) at CN : Co = 6 : 1 *via* half-hydrogenated intermediates [reaction (9)], but the

$$\begin{aligned} cis\text{-R-CH=CH-R} + [\mathrm{Co(CN)_5H}]^{3-} &\rightleftharpoons \\ [\mathrm{Co(CN)_5(CHR{-}CH_2R)}]^{3-} &\rightleftharpoons \\ [\mathrm{Co(CN)_5H}]^{3-} + trans\text{-R-CH=CH-R} & \quad (9) \end{aligned}$$

present isomerisation seems to proceed by a different mechanism. Thus, the isomerisation *via* a half-hydrogenated intermediate requires that dialkyl maleate first dissociates from the π-complex, isomerises to dialkyl fumarate, and then co-ordinates to cobalt(I). These steps may permit the hydrolysis of dissociated esters, hydrogen–deuterium exchange of the olefinic protons, and hydrogenation (or deuteriation) of the esters in D_2O. As shown in Figure 2, isomerisation did not accompany these reactions. Since cyanocobaltate(I) is thought to be the most basic cobalt(I) species and a strong electron donor,[4,24] electron transfer from cobalt(I) to olefin seems probable. This may result in an anion radical and cobalt(II) species (Scheme), and the present results may be explained if the formation and recombination of these species occur more slowly than rotation about the carbon–carbon bond. Balch [15] has reported that the complex of tetracyanoethylene with $[Co(CNCH_3)_5]^+$ is formed by a stepwise outer-sphere electron-transfer mechanism, which involves a free anion-radical intermediate. The mechanism does not explain the selective formation of π complexes of olefins with retention of configuration in the initial stage, but may support the electron-transfer process shown in the Scheme. The other possible process for the isomerisation is that *via* a σ complex of a carbanion, as shown in the Scheme. A similar intermediate has been proposed in the nucleophilic substitution of vinyl halides by cobaloxime(I).[25] The present data are insufficient to enable us to decide which of the two probable intermediates is preferred.



SCHEME

This report affords another example of organocyanocobaltate in addition to the previously described σ-alkyl–pentacyanocobaltate(III) and η³-allyl–tetracyanocobaltate(III). Only a limited number of olefins has been studied, but it is very probable that a π complex will be formed with other olefins. One of the problems is that the complex is formed only in a strongly alkaline solution, while olefins having electron-withdrawing substituents are mostly sensitive to base. The facts that a precipitate is usually formed at CN : Co <5 : 1, that olefins are mostly insoluble in aqueous solution, and that the complex is liable to decompose on dilution do not favour kinetic studies. Stable complexes may be isolated, although preliminary attempts at such isolation have not been successful. Since π-olefin–cobalt(I) complexes have been proposed as intermediates in homogeneous catalysis, the π complexes reported here may be used as intermediates or starting materials for catalytic reactions.

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