PREPARATION OF ORGANOCYANOCOBALTATE(III) COMPLEXES

JACK KWIATEK AND JAY K. SEYLER
U.S. Industrial Chemicals Co., Division of National Distillers and Chemical Corp., Cincinnati, Ohio (U.S.A.)

(Received September 4th, 1964)

Organocobalt complexes were previously postulated as intermediates in the homogeneous hydrogenation of various substrates catalyzed by potassium pentacyanocobaltate(II)[1]. Two methods have now been found for the preparation and isolation of such complexes. The first involves addition of the hydride species, $[Co(CN)_5H]^{3-}$, to activated olefins. The second involves reaction of pentacyanocobaltate(II) anion, $[Co(CN)_5]^{3-}$, with organic halides. The latter method was found independently of Halpern who recently described the reaction with alkyl and benzyl halides[2].

RESULTS AND DISCUSSION

Stoichiometry

Method 1. The addition of $[Co(CN)_5H]^{3-}$ to butadiene was previously indicated to occur in the following manner[1]:

$$[Co(CN)_5H]^{3-} + C_4H_6 \longrightarrow [Co(CN)_5(C_4H_7)]^{3-}$$

It has now been found possible to isolate the butenyl complex so formed. α,β-Unsaturated carbonyls and nitriles, as well as vinyl halides, apparently add in a similar manner to yield the adducts characterized in Table 1. The product formed with vinyl chloride is formulated as a vinyl, rather than chloroethyl, complex on the basis of its infrared spectrum and reaction with iodine. Presumably, it is formed via the following addition–elimination sequence:

$$[Co(CN)_5H]^{3-} + CH_2{=}CHCl \longrightarrow [Co(CN)_5(CHClCH_3)]^{3-}$$
$$[Co(CN)_5(CHClCH_3)]^{3-} \longrightarrow [Co(CN)_5(CH{=}CH_2)]^{3-} + HCl$$

A vinyl analog of vitamin B_{12} coenzyme has been reported to be formed using vinyl bromide[3].

Method 2. The reaction of aqueous solutions of $[Co(CN)_5]^{3-}$ with allyl halides is formulated in the following manner[4,5]:

$$2[Co(CN)_5]^{3-} + CH_2{=}CHCH_2X \longrightarrow [Co(CN)_5(C_3H_5)]^{3-} + [Co(CN)_5X]^{3-}$$

Other organic halides are assumed to yield similar mixtures of halo- and organocobalt complexes, characterized in Table 2, on the basis of spectral evidence. Infrared spectra

TABLE 1

INFRARED ABSORPTION BANDS OF $[Co(CN)_5H]^{3-}$–OLEFIN ADDUCTS

Olefin	*C≡N Stretch (cm^{-1})*	*C=C Stretch (cm^{-1})*
$CH_2=CHCH=CH_2$	2092	1609
$CH_2=CHCOC_6H_5$	2103	1601
		1595[a]
		1570
$CH_2=CHCN$	2195	—
	2098	
$CH_2=CHCl$	2100	1562

[a] No assignment of these peaks can be made at present.

of the isolated products exhibit two main cyanide absorption bands of approximately equal strength in the vicinity of 2125 and 2095 cm^{-1}, respectively. The former band is characteristic of halocyanocobaltate(III) component, while the latter is characteristic of the organocyanocobaltate(III) complex (*cf.* Table 1 and ref. 2). While allyl chloride, bromide or iodide could be employed in formation of the allyl complex, the latter two substrates gave considerably faster reaction rates and better yields. Iodides were the only halides successfully employed in the formation of simple alkyl complexes. Reaction with ethylene dibromide led to the exclusive formation of ethylene. The separation of methyl and benzyl complexes from their co-formed halo-complexes has been reported[2].

TABLE 2

INFRARED ABSORPTION BANDS OF $[Co(CN)_5]^{3-}$–HALIDE PRODUCTS

Halide	*C≡N Stretch (cm^{-1})*	*C=C Stretch (cm^{-1})*
$CH_2=CHCH_2Br$	2124, 2092	1609
$CH_3CH=CHCH_2Br$	2124, 2092	1609
$C_6H_5COCH_2Br$	2128, 2103	1622 (sh)[a]
		1607, 1595 (sh)
		1571
$C_6H_5COCHBrCH_3$	2130, 2104	1601, 1595
		1570[a]
$NCCH_2Cl$	2208, 2201	—
	2127, 2103	
$C_6H_5CH_2Br$	2124, 2092	1593
CH_3I	2120, 2087	—
CH_3CH_2I	2122, 2085	—
$CH_3CH_2CH_2I$	2124, 2084	—
$CH_3CH_2CH_2CH_2I$	2124, 2083	—
$(CH_3)_2CHCH_2I$	2124, 2082	—
$C_6H_5N_2Cl$	2128, 2100	1562

[a] No assignment of these peaks can be made at present.

While hydroxopentacyanocobaltate(III) may be reduced by $[Co(CN)_5H]^{3-}$, certain organocyanocobaltate(III) complexes are not (see following section). Advantage of this difference in reactivities may be taken in preparing organocobalt complexes associated with lesser amounts of inorganic complexes without resorting to physical methods[2] for separation of these two types, formed in equimolar amounts in the reaction of organic halides with $[Co(CN)_5]^{3-}$. *E.g.*, the successive addition of small quantities of methyl iodide or benzyl bromide to $[Co(CN)_5H]^{3-}$ in a hydrogen atmosphere yields complexes rich in the organocobalt component. Under these conditions the inorganic component is reduced to $[Co(CN)_5]^{3-}$ which is then recycled by further reaction with organic halide. The reactions involved and the overall result are shown below:

$$\begin{array}{l} 2[Co(CN)_5]^{3-} + RX \longrightarrow [Co(CN)_5R]^{3-} + [Co(CN)_5X]^{3-} \\ \underline{[Co(CN)_5X]^{3-} + [Co(CN)_5H]^{3-} + OH^- \longrightarrow 2[Co(CN)_5]^{3-} + H_2O + X^-} \\ [Co(CN)_5H]^{3-} + RX + OH^- \longrightarrow [Co(CN)_5R]^{3-} + H_2O + X^- \end{array}$$

A side reaction is direct reduction of the organic halide to the corresponding hydrocarbon. The method can be employed where such side reactions occur to only a minor extent.

Cobalt analyses of the complexes prepared via the above methods showed them to be impure. However, analyses for carbon and nitrogen, calculated as carbon-to-nitrogen ratios, indicated the amount of organic radical incorporated and defined the stoichiometry of the complexes. These values, reported in Table 3 for selected stable complexes, correspond well with the values calculated for the structures assumed. Enrichment of the methyl and benzyl complexes formed by incremental addition of the respective halides to $[Co(CN)_5H]^{3-}$ in a hydrogen atmosphere may be clearly seen.

TABLE 3

ANALYSIS OF COMPLEXES

Substrate	*% C*	*% N*	*C/N, found*	*C/N, theory*
$CH_2=CHCN$	21.85	19.25	1.32	1.33[a]
$CH_2=CHCl$	20.27	16.29	1.45	1.40[a]
$C_6H_5COCH_2Br$	22.69	16.12	1.64	1.80[b,c]
$NCCH_2Cl$	16.95	18.15	1.09	1.09[b]
$C_6H_5CH_2Br$	21.89	15.76	1.62	1.70[b]
$C_6H_5CH_2Br$	25.80	15.38	1.96	2.40[a,d]
CH_3I	17.06	17.15	1.16	1.10[b]
CH_3I	18.35	17.46	1.23	1.20[a,d]
n-C_3H_7I	19.82	17.05	1.36	1.30[b]

[a] Calculated on the basis of $K_3[RCo(CN)_5]$. [b] Calculated on the basis of $K_3[RCo(CN)_5]$ + $K_3[XCo(CN)_5]$. [c] σ-Complex assumed. [d] Enriched complex prepared by incremental addition of substrate to $[Co(CN)_5H]^{3-}$ in a H_2 atmosphere.

Structure

A number of observations demonstrate the direct attachment of the organic grouping to the cobalt atom in the various complexes prepared by either method. The proton magnetic resonance spectrum of a freshly prepared deuterium oxide solution of allyl complex (Fig. 1) shows the presence of a σ-, as well as minor quantities of a π-, bonded structure. The σ-allyl group is gradually converted entirely to the π-allyl arrangement (Fig. 2), presumably through loss of a cyanide ligand; the σ-bonded structure immediately reformed upon addition of cyanide ion (Fig. 3)[4]. Although the exact location of the π-allyl group with respect to the metal and the arrangement of the cyanide ligands are not known, the structure of the π-allyl complex (II, R = H) is based on its proton spectrum[6], formation from the σ-allyl complex (I, R = H)[7] and conversion to the σ-allyl complex[8].

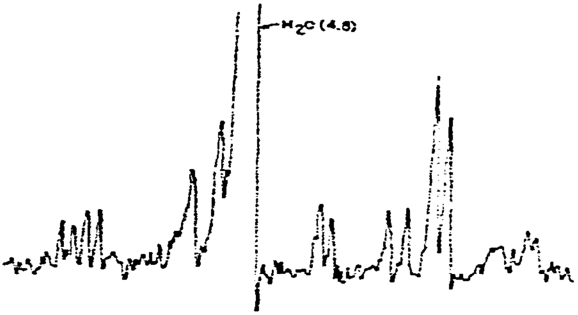


Fig. 1. Proton spectrum of allyl complex (freshly dissolved in D_2O).

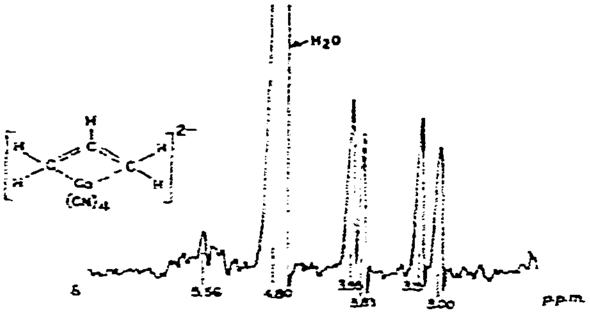


Fig. 2. Proton spectrum of allyl complex (after 2.5 hours in D_2O).

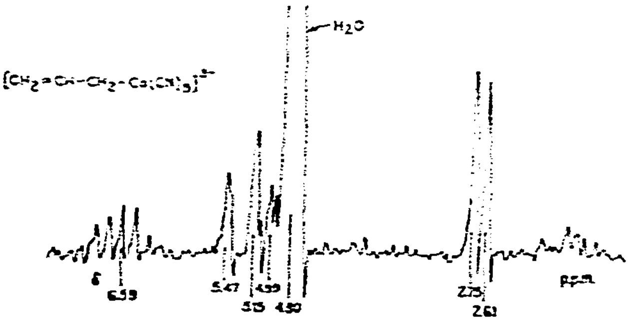
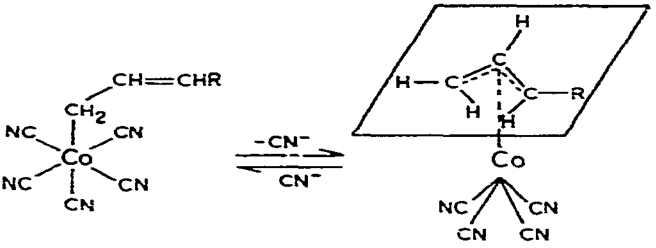


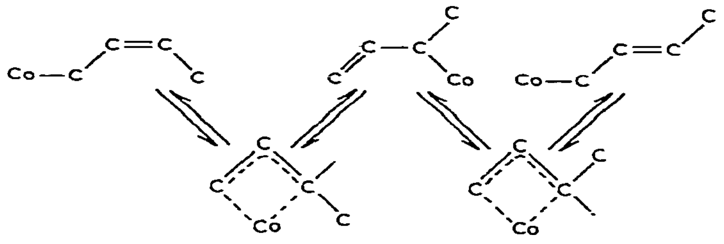
Fig. 3. Proton spectrum of allyl complex (KCN added after 2.5 hours in D_2O).

Analogous σ- and π-structures have been proposed as determining the "stereoselectivity"[9] of the butene product obtained in the pentacyanocobaltate(II)-catalyzed hydrogenation of butadiene[1,4]. Thus, 1-butene, the predominant product obtained in the presence of excess cyanide ion, is believed to derive exclusively from a σ-butenyl complex intermediate. *trans*-2-Butene, the greatest amount of which is formed in the



(I) R = H or CH_3 (II)

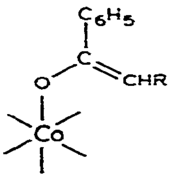
absence of excess cyanide, may derive from either a π-butenyl complex or an isomeric σ-butenyl complex in equilibrium with the π-structures shown below.



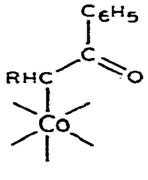
The butene products formed by reacting isolated butenyl complex with $[Co(CN)_5H]^{3-}$ prepared at various cyanide-to-cobalt ratios also show this stereoselectivity.

The proton spectrum of a fresh solution of butenyl complex in deuterium oxide displays three resonance groups and is similar to that of an iron-σ-2-butenyl complex[10], but not to that of π-(1-methylallyl)-cobalt tricarbonyl[11]. The exclusive formation of 1-butene on protonation of the butenylcyanocobalt complex provides evidence for the σ-2-butenyl structure (I, R = CH_3)[5], such also being obtained in the addition of other transition metal hydrides to butadiene[7,10]. Decomposition of the complex in solution renders the observation of σ-π rearrangement difficult.

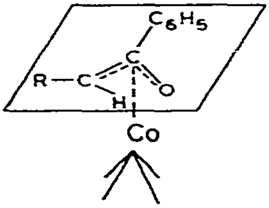
Formulae (III), (IV) or (V) may be used to represent the phenacyl complexes. Since they have not been obtained in a pure state, only spectral analysis may be relied on in attempting to distinguish between them.



(III)



(IV)

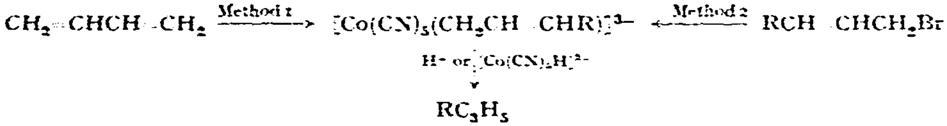


(V)

The infrared absorptions occurring in the range 1570–1622 cm^{-1} may be assigned to either C=O or C=C stretching frequencies. This range is considerably lower than the carbonyl region of alkyl aryl ketones (1685 cm^{-1}) but includes that of certain dibenzoylmethane chelates (Ni^{II}, 1595 cm^{-1}).

Although interpretation of the proton spectra is difficult due to the unknown effects of the cyanocobalt group on the organic ligand, the data obtained from the σ- and π-allyl and (cyanomethyl)cyanocobaltate complexes indicate that methylene protons adjacent to the cobalt atom have chemical shifts 0.4–0.9 ppm further downfield than those in comparable iron[10,22] and cobalt[7,11] carbonyls. Thus, the single peak at 3.05 ppm obtained for the CH_2 group of the phenacyl complex is that expected for (V, R = H) rather than (III) or (IV), although two proton peaks are required for such a formulation. A possible explanation for the single peak is that a solution of the phenacyl complex in D_2O may consist of structures (III) and (IV) in rapid equilibrium[12]. Addition of cyanide ion did not affect the proton spectra. Similarly, the multiline resonance at 4.4 ppm obtained for the CH group of the methylphenacyl complex is that expected for (III, $R = CH_3$) or (V, $R = CH_3$) rather than (IV). In summary, no definite conclusion can be reached about the bonding in these complexes with the data at hand, and their representation[4] as (V) is arbitrary.

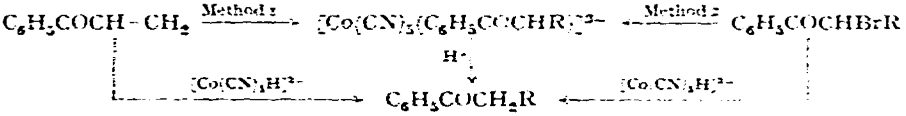
The identity of the complexes prepared by either method, as well as the cobalt–carbon bonding present, is evidenced by the ready release of RC_3H_5 from $[Co(CN)_5(CH_2CH{=}CHR)]^{3-}$, where R = H or CH_3, upon treatment with acid[5] or $[Co(CN)_5H]^{3-}$:



$$\begin{tikzcd}
CH_2{=}CHCH{=}CH_2 \arrow[r, "\text{Method 1}"] & {[Co(CN)_5(CH_2CH{=}CHR)]^{3-}} \arrow[d, dashed, "H^+ \text{ or } {[Co(CN)_5H]^{3-}}"] & RCH{=}CHCH_2Br \arrow[l, "\text{Method 2}"'] \\
 & RC_3H_5 &
\end{tikzcd}$$

The reaction with $[Co(CN)_5H]^{3-}$ supports the intermediacy of such organocobalt complexes in the catalytic hydrogenation and hydrogenolysis of the respective substrates[1,4,13].

An alternate pathway, not involving organocobalt intermediates, is indicated in the reduction of phenyl vinyl ketone and phenacyl halides catalyzed by pentacyanocobaltate(II)[14]. Although the identity of the complexes prepared by either method is evidenced by the ready release of $C_6H_5COCH_2R$ from $K_{x-2}[Co(CN)_x(C_6H_5COCHR)]$ (R = H or CH_3; x = 4 or 5) upon treatment with acid[5], addition of $[Co(CN)_5H]^{3-}$ gives only low yields of $C_6H_5COCH_2R$:



$$\begin{tikzcd}
C_6H_5COCH{=}CH_2 \arrow[r, "\text{Method 1}"] \arrow[dr, dashed, "{[Co(CN)_5H]^{3-}}"] & {[Co(CN)_5(C_6H_5COCHR)]^{3-}} \arrow[d, dashed, "H^+"] & C_6H_5COCHBrR \arrow[l, "\text{Method 2}"'] \arrow[dl, dashed, "{[Co(CN)_5H]^{3-}}"'] \\
 & C_6H_5COCH_2R &
\end{tikzcd}$$

These results indicate that either an organocobalt intermediate is not involved in the catalytic hydrogenation and hydrogenolysis of the respective substrates or that an initially formed σ-bonded complex (III) or (IV), is capable of reaction with $[Co(CN)_5H]^{3-}$ while the π-oxaallyl complex (V) is not.

The hydrogenolysis of alkyl and benzyl halides catalyzed by pentacyanocobaltate(II)[14] does not involve organocobalt intermediates as shown by the lack of RH formation from $[Co(CN)_5R]^{3-}$, where R = alkyl or benzyl, upon treatment with $[Co(CN)_5H]^{3-}$. The reaction of these complexes with acid[5] also does not result in the formation of RH. Attachment of the organic group to the cobalt atom in these complexes is indicated by the following reactions: (*1*) isobutyl complex releases isobutene on standing; (*2*) halogenation of methyl[2] and propyl complexes yields the corresponding alkyl halide; (*3*) the complex obtained from vinyl chloride and $[Co(CN)_5H]^{3-}$ yields vinyl iodide on treatment with iodine. The latter evidence, as well as the infrared spectrum of the complex which exhibits a carbon–carbon double bond stretching frequency at 1562 cm^{-1}, supports its formulation as a vinyl complex. The iodination may take place either by direct cobalt–carbon cleavage or a two-step addition–elimination as follows:

$$[Co(CN)_5(CH{=}CH_2)]^{3-} \xrightarrow{I_2} [Co(CN)_5(CHI{\cdot}CH_2I)]^{3-} \longrightarrow [Co(CN)_5I]^{3-} + CH_2{=}CHI$$

Stabilities

The butenyl complex is unstable. Its solution in water under a nitrogen atmosphere gradually evolves an equimolar mixture of butenes and butadiene, suggesting the following mode of decomposition[1]:

$$[Co(CN)_5(C_4H_7)]^{3-} \rightleftharpoons [Co(CN)_5H]^{3-} + C_4H_6$$

$$[Co(CN)_5H]^{3-} + [Co(CN)_5(C_4H_7)]^{3-} \longrightarrow 2[Co(CN)_5]^{3-} + C_4H_8$$

The mixture of organo- and halo-complexes obtained from allyl bromide and pentacyanocobaltate(II) slowly evolves propene when dissolved in water. Addition of alkali prevents this decomposition but does not affect that of butenyl complex. Presumably aquation of the accompanying halo-complex releases protons which effect decomposition of the allyl complex. An attempt to convert the allyl complex to the *n*-propyl complex by hydrogenation in the presence of 10 % Pt on carbon resulted in cleavage of the allyl group (*cf.* ref. 10).

Primary *n*-alkyl and benzyl complexes are stable, their infrared spectra showing little change after long periods of time. They, as well as vinyl complex, are unaffected by treatment with hydrogen in the presence of Adam's catalyst. Isobutyl complex, however, slowly formed isobutene, presumably with elimination of hydride complex:

$$\{Co(CN)_5[CH_2CH(CH_3)_2]\}^{3-} \longrightarrow [Co(CN)_5H]^{3-} + CH_2{=}C(CH_3)_2$$

Attempts to prepare isopropyl or *tert*-butyl complexes from the corresponding iodides yielded predominantly the respective dehydrohalogenation products, propylene and isobutene. Either such complexes are unstable or the elimination reaction does not involve organocobalt intermediates. It is noteworthy that while the isopropyl complex, $C_5H_5W(CO)_3(iso\text{-}C_3H_7)$, is stable below 60°, it could not be prepared by the reaction of $Na[C_5H_5W(CO)_3]$ with isopropyl halides[15]. In another series of alkyl complexes, $C_5H_5Fe(CO)_2R$, the isopropyl complex was found to be less stable thermally than the *n*-propyl analog, while a *tert*-butyl complex could not be prepared[16].

Mechanism

A plausible mechanism for the reaction of pentacyanocobaltate(II) with organic halides involves radical intermediates:

$$[Co(CN)_5]^{3-} + RX \longrightarrow [Co(CN)_5X]^{3-} + R^\bullet$$

$$[Co(CN)_5]^{3-} + R^\bullet \longrightarrow [Co(CN)_5R]^{3-}$$

Isolation of alkyl–acrylonitrile adducts from the reactions of either *n*-propyl or isopropyl iodide with pentacyanocobaltate(II) in the presence of excess acrylonitrile supports this mechanism (*cf.* ref. 17). Furthermore, dimeric species are formed from benzhydryl, trityl or tropylium halides. Reaction with benzenediazonium chloride results in the evolution of nitrogen and formation of a complex which appears to contain a phenyl–cobalt bond[5]; aryl radicals are involved in similar processes[18]. Radical intermediates have also been proposed in the homogeneous reduction of alkyl halides by chromous salts[19,20].

Further work on the formation and reactions of organocyanocobaltate(III) complexes and clarification of the role of certain of these in catalytic hydrogenations is being carried out.

EXPERIMENTAL

Method 1

$K_3[Co(CN)_5(C_4H_7)]$. An aqueous solution of $K_3[Co(CN)_5H]$ was prepared as previously described[1], 200 ml of $K_3[Co(CN)_5]$ solution (0.15 *M* cobalt, 0.15 *M* KOH, CN/Co = 6.0) absorbing 349 ml hydrogen at 0–5°. A total of 188 ml of this cold solution was injected in approximately 30 ml increments via a hypodermic syringe into a flask, equipped with a stirring bar magnet, surrounded by an ice bath and containing a butadiene atmosphere. After absorption of butadiene was complete, the resultant solution was added to 800 ml of acetone and the aqueous layer decanted from the brown oil which settled out. Addition of ethanol to the oil yielded a tan powder which was collected on a sintered-glass filter, washed with several portions of ethanol followed by ether and dried briefly *in vacuo*.

The proton spectrum of a solution of the complex in D_2O displayed an unresolved doublet at $\delta = 1.74$ (rel. intensity 3), an unresolved triplet at $\delta = 2.56$ (rel. intensity 2) and a multiline resonance centered at $\delta = 5.8$.

The solid in a sealed vial evolved gases, noted by pressure release on opening the vial. An aqueous solution in a nitrogen atmosphere gradually evolved the following compounds in the relative amounts shown: 1-butene (36), *trans*-2-butene (55), *cis*-2-butene (9) and butadiene (101). Addition of aqueous solutions of $K_3[Co(CN)_5H]$ to the solid yielded butenes, the composition of which depended on the CN/Co ratio present. *E.g.*, a solution of $K_3[Co(CN)_5H]$ prepared at CN/Co = 5.1 yielded 1-butene (47), *trans*-2-butene (52) and *cis*-2-butene (1); at CN/Co = 6, 1-butene (82), *trans*-2-butene (17) and *cis*-2-butene (1); and at CN/Co = 7, 1-butene (97), *trans*-2-butene (2) and *cis*-2-butene (1). Addition of hydrochloric acid to the solid yielded 1-butene, exclusively.

$K_{x-2}[Co(CN)_x(C_6H_5COCHCH_3)]$. A similar addition of $K_3[Co(CN)_5H]$ solution (CN/Co = 5.1) to 4 g phenyl vinyl ketone[21] in an inert atmosphere followed by isolation of the complex in the above manner gave a gelatinous yellow precipitate which was difficult to dry. The proton spectrum of a D_2O solution of the complex consisted of a multiresonance peak centered at $\delta = 4.30$ (CH), a doublet at $\delta = 1.69$ (CH_3) and aromatic peaks at $\delta = 8.01$.

Acidification yielded propiophenone, identified by IR and VPC. Addition of 6.8 g of the complex to an aqueous $K_3[Co(CN)_5H]$ solution (CN/Co = 5.1) with stirring in a hydrogen atmosphere followed by ether extraction yielded 0.17 g propiophenone.

Acidification of the resultant solution yielded an additional 0.78 g propiophenone.

$K_3[Co(CN)_5(CH_3CHCN)]$. Addition of $K_3[Co(CN)_5H]$ solution to 20 ml acrylonitrile in like manner yielded a solid, the IR spectrum of which displayed two cyanide absorption bands at 2195 and 2098 cm^{-1}, the former being due to the cyanoalkyl group. A similar addition of an iron hydride to acrylonitrile has been reported[22]. Pyrolysis yielded propionitrile as the major product, identified by IR and VPC. The proton spectrum of a D_2O solution consisted of a multiresonance peak at $\delta = 2.47$ (CH) and a doublet at $\delta = 1.73$ (CH_3).

$K_3[Co(CN)_5(CH{=}CH_2)]$. Introduction of $K_3[Co(CN)_5H]$ solution into a flask containing a vinyl chloride atmosphere resulted in the absorption of approximately one mole of substrate per mole hydride complex. Isolation of the resulting complex gave a yellow solid, the IR spectrum of which exhibited a carbon–carbon double bond stretch at 1562 cm^{-1}. Treatment with aqueous KI_3 at room temperature followed by ether extraction yielded vinyl iodide, identified by mass spectrum (parent peak 154). There was essentially no change in the IR spectrum of the complex on treatment of an aq.–alc. solution with hydrogen (30 psi) in the presence of PtO_2. Pyrolysis yielded ethylene.

Method 2

$K_3[Co(CN)_5(CH_2CH{=}CHR)]$ ($R = H$ or CH_3). An aqueous solution of $K_3[Co(CN)_5]$ (200 ml, 0.25 *M* cobalt, 0.075 *M* KOH, CN/Co = 5.1) was prepared in the manner employed in the preparation of hydride complex except that a nitrogen atmosphere was used. Immediately after the potassium cyanide solution had been added, 0.03 mole allyl bromide was injected into the stirred solution of $K_3[Co(CN)_5]$, the reaction mixture changing from dark green to orange within two minutes. The mixture of complexes so formed was isolated in the previously described manner. Proton spectra of the solid product dissolved in D_2O are shown in Figs. 1, 2 and 3, the latter illustrating π–σ conversion on addition of KCN. Addition of KOH or KCl did not cause this change to take place.

Addition of only 0.02 mole allyl bromide in a similar manner led to the quantitative evolution of propene. Allyl iodide and crotyl bromide reacted rapidly with $K_3[Co(CN)_5]$, while allyl chloride reacted slowly, the reaction mixture turning yellow after approximately 30 minutes. Acidification of the solids so obtained yielded propene and 1-butene, respectively. Treatment of an aq.–alc. solution of allyl complex with hydrogen (44 psi) in the presence of 10% Pt on carbon led to the formation of a propylene–propane (2:1) mixture. Addition of an aqueous solution of $K_3[Co(CN)_5H]$ to allyl complex produced propene, while such addition to the butenyl complex yielded butenes, the composition of which depended on the CN/Co ratio present, as noted previously for that complex prepared via Method 1. Thus, a solution of $K_3[Co(CN)_5H]$ prepared at CN/Co = 5.1 yielded 1-butene (50), *trans*-2-butene (49) and *cis*-2-butene (1), while that prepared at CN/Co = 7 yielded 1-butene (96), *trans*-2-butene (3) and *cis*-2-butene (1).

$K_{x-2}[Co(CN)_x(C_6H_5COCHR)]$ ($R = H$ or CH_3). Phenacyl bromide (0.03 mole dissolved in 10 ml benzene) or α-bromopropiophenone reacted rapidly with a solution of $K_3[Co(CN)_5]$ in a similar manner to yield complexes which released acetophenone and propiophenone, respectively, upon addition of acid. The ketones were identified by IR and 2,4-dinitrophenylhydrazine derivatives. Only traces of the ketones were formed on treatment with excess $K_3[Co(CN)_5H]$ solution. The proton spectrum of a D_2O solution of the phenacyl complex consisted of a broad peak at $\delta = 3.25$ (CH_2) and aromatic peaks at $\delta = 8.45$. That of the methylphenacyl complex consisted of a quartet at $\delta = 4.54$ (CH), a doublet at $\delta = 1.80$ (CH_3) and aromatic peaks at $\delta = 8.12$.

$K_3[Co(CN)_5(CH_2CN)]$. Reaction of chloroacetonitrile in a similar manner yielded a complex with four cyanide absorption bands. The proton spectrum of a D_2O solution consisted of a broad peak at $\delta = 1.83$. A cyanomethyl–iron complex has also been prepared from chloroacetonitrile[22].

$K_3[Co(CN)_5R]$ (R = n-alkyl or benzyl). Methyl, ethyl and *n*-propyl iodides reacted rapidly in the above manner, while *n*-butyl iodide reacted slowly, the reaction mixture turning orange-yellow after approximately one hour, during which time small quantities of 1-butene and *n*-butane were formed. Isobutyl iodide reacted after two hours with some formation of isobutene and isobutane. Benzyl bromide and benzyl iodide reacted rapidly. The complexes, isolated in the usual manner, did not form RH on treatment with acid or $K_3[Co(CN)_5H]$. The methyl, propyl and benzyl complexes in aq.–alc. solution also did not form RH when treated with hydrogen in the presence of Adam's catalyst or when treated with aqueous sodium borohydride.

Isobutyl complex slowly evolved isobutene. Pyrolysis of the methyl complex yielded methane, the propyl complex gave a propene–propane (1.2:1) mixture and the benzyl complex yielded toluene as the main product with a minor amount of benzaldehyde (*cf.* ref. 2). Chlorine passed through an aqueous solution of propyl complex yielded a trace of propyl chloride; the addition of aqueous KI_3 yielded a trace of propyl iodide, the quantity of which increased considerably on heating.

Alternate Method 2

Cyanocobaltate(II) was formed in a hydrogen atmosphere, 200 ml of solution (0.15 *M* cobalt, CN/Co = 5.1, 0.225 *M* KOH) absorbing 310 ml of H_2. A total of 0.045 moles of benzyl bromide was injected in 0.003 mole increments over 90 minutes, time being allowed for complete H_2 absorption after each addition (total, 360 ml H_2). The color of the reaction mixture gradually changed from medium green to orange-yellow. Extraction with ether yielded 0.013 moles toluene. The complex isolated from the aqueous medium in the usual manner showed a large 2092 cm^{-1} peak compared with a relatively minor absorption at 2124 cm^{-1}. Methyl iodide similarly formed a complex rich in the component absorbing at 2087 cm^{-1}. In the latter run, by-product methane was removed and hydrogen was added after each addition of halide.

Dehydrohalogenation

Isopropyl iodide (0.03 mole) was injected into 200 ml of an aqueous solution of $K_3[Co(CN)_5]$ (0.25 *M* cobalt, 0.10 *M* KOH, CN/Co = 5.1) prepared in a nitrogen atmosphere, immediately after addition of the cyanide solution. The dark green solution became brown-red in five minutes and evolved a propene–propane (5.1:1) mixture in nearly quantitative yield. Final color of the reaction mixture was light green. *tert*-Butyl iodide similarly formed an isobutene–isobutane (5.4:1) mixture. Ethylene dibromide yielded ethylene, exclusively.

Alkyl halides and acrylonitrile

The reaction of isopropyl iodide with $K_3[Co(CN)_5]$ was carried out as in the above example except that 10 ml acrylonitrile was injected just before the cyanide solution was added. Gas evolution took place as before. However, it consisted exclusively of propene and the solution remained a deep red. Extraction of the reaction mixture with ether, followed by drying and evaporation gave a concentrate containing a small quantity of $(CH_3)_2CHCH{=}CHCN$ and $(CH_3)_2CHCH_2CH_2CN$ (separated by VPC and identified by mass spectroscopy). A similar run with *n*-propyl iodide gave a very low yield of propyl-acrylonitrile adducts (parent masses 95 and 97, respectively).

Dimerization

Benzhydryl, trityl and tropylium bromides, upon reaction with $K_3[Co(CN)_5]$, yielded tetraphenylethane, hexaphenylethane (isolated as the peroxide) and bitropyl[23], all products being identified by m.p. and IR spectra.

Preparation of $K_3[Co(CN)_5(C_6H_5)]$

An aqueous solution of benzenediazonium chloride prepared from 2 ml (0.02 mole) aniline in aq. HCl (6 ml concd. HCl + 10 ml H_2O) added dropwise to aq. $NaNO_2$ (2 g in 10 ml H_2O) at 0°, was injected into a solution of $K_3[Co(CN)_5]$ in a nitrogen atmosphere. An immediate blood-red color formed and > 300 ml of gas was evolved. The mixture was filtered after standing overnight, and the white complex was precipitated from the filtrate in the usual manner. The IR spectrum displayed two cyanide bands at 2133 and 2105 cm^{-1} as well as a carbon–carbon double bond stretch at 1566 cm^{-1}.

Infrared spectra

Measurements were made with a Perkin-Elmer model 421 spectrometer on Nujol mulls of the various complexes.

Proton spectra

Measurements were made with a Varian V-4302 DP-60 spectrometer at 60 Mc on D_2O solutions of the various complexes. All δ values were related to water at 4.8 ppm from tetramethylsilane.

ACKNOWLEDGEMENT

Support of this work by the Directorate of Chemical Sciences, Air Force Office of Scientific Research (Contract No. AF 49(638)-1214) is gratefully acknowledged.

SUMMARY

Two methods have been found for the preparation of organocyanocobaltate(III) complexes. The first involves addition of $[Co(CN)_5H]^{3-}$ to activated olefins. The second involves reaction of $[Co(CN)_5]^{3-}$ with organic halides.

Studies show the mode of attachment of the organic groupings and indicate the role of certain of these complexes in hydrogenations and hydrogenolyses cata-

lyzed by pentacyanocobaltate(II) anion. Allylic conversions of the type σ–π and π–σ have been demonstrated. A mechanism for the cleavage of organic halides is discussed.

REFERENCES

1 J. Kwiatek, I. L. Mador and J. K. Seyler, *Advan. Chem. Ser.*, No. 37 (1963) 201.
2 J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, 86 (1964) 2311.
3 A. W. Johnson, L. Mervyn, N. Shaw and E. L. Smith, *J. Chem. Soc.*, (1963) 4146.
4 J. Kwiatek and J. K. Seyler, *Proceedings, VIII I.C.C.C.*, Vienna, 1964, p. 308.
5 J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, 3 (1965) 433.
6 E. L. Muetterties and W. D. Phillips, *Advan. Inorg. Chem. Radiochem.*, 4 (1962) 253.
7 W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties and B. W. Howk, *J. Am Chem. Soc.*, 83 (1961) 1598.
8 J. C. W. Chien and H. C. Dehm, *Chem. Ind.* (*London*), (1961) 745.
9 P. B. Wells, *Chem. Ind.* (*London*), (1964) 666.
10 M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, (1963) 189.
11 J. A. Bertrand, H. B. Jonassen and D. W. Moore, *Inorg. Chem.*, 2 (1963) 601.
12 J. E. Norlander and J. D. Roberts, *J. Am. Chem. Soc.*, 81 (1959) 1769.
13 J. Kwiatek, I. L. Mador and J. K. Seyler, *J. Am. Chem. Soc.*, 84 (1962) 304.
14 Unpublished results.
15 M. L. H. Green and A. N. Stear, *J. Organometal. Chem.*, 1 (1964) 230.
16 M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, 1 (1963) 58.
17 J. K. Kochi and D. D. Davis, *Abstracts, 145th Am. Chem. Soc. Meeting*, New York, 1963, p. 24 Q.
18 H. Zollinger, *Azo and Diazo Chemistry*, Interscience, New York, 1961, p. 159.
19 C. E. Castro and W. C. Kray, *J. Am. Chem. Soc.*, 85 (1963) 2768.
20 L. H. Slaugh and J. H. Raley, *Tetrahedron*, 20 (1964) 1005.
21 K. W. Bentley and J. C. Ball, *J. Org. Chem.*, 23 (1958) 1720.
22 J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, (1963) 2976.
23 W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, 79 (1957) 352.