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Homogeneous hydrogenations using pentacyanocobaltate(II) anion

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Abstract

The activation of hydrogen using soluble catalysts has gained importance because of their specificity and selectivity. Most of the soluble catalysts of importance are the derivatives of rhodium, iridium, ruthenium, cobalt and titanium and the like. The advantages of pentacyanocobaltate(II) anion as a soluble catalyst, the mechanism of addition, its scope and limitations are reviewed here.

Key words: Homogenous hydrogenation, pentacyanocobaltate(II) anion, α, β-unsaturated ketones, dienes.

1. Introduction

The saturation of double bonds in organic molecules, with molecular hydrogen, has been recorded from a very long time. Until recently the activation of molecular hydrogen was mainly due to hererogeneous catalysis involving finely divided metals such as nickel, platinum, palladium, metal salts, certain metal oxides and others, but in the last decade a wide range of metal ions and their complexes have been successfully used as homogeneous catalysts[1-10] for hydrogenation reactions of organic substrates. Despite the fact that as early as 1848, Roelen[11] did observe the olefins on treatment with carbon monoxide and hydrogen to give saturated compounds along with the expected aldehydes, the use of homogeneous catalysts to organic chemistry is of quite recent origin, if not altogether unknown.

These systems of homogeneous catalysis are, indeed, chemically and kinetically more versatile in comparison to the heterogeneous catalysts. Though the heterogeneous catalysts remain the major synthetic tool for catalytic hydrogenations, the appearance of increasing number of patents for the use of homogeneous catalysts shows a definite tendency to develop more selective and controlled hydrogenation systems. Thus, starting from the pioneering work of Calvin[12, 13] in 1938, who demonstrated, for the first time, the successful homogeneous catalytic hydrogenation of quinoline by cuprous

acetate, the accomplishments of Halpern[14–18], Vaska[19–21], Wilkinson[22] and a number of others[23–26] have established a new landmark in synthetic organic chemistry, in the use of metal ions and transition metal complexes as soluble homogeneous hydrogen activation catalysts for a number of organic substrates. These catalysts, efficient in hydrogenating a wide variety of organic substrates under mild conditions, promised far reaching developments which are still in progress. In most of these cases advantage is taken of the fact that the ligands employed, by virtue of their geometry around the metal ion, can exert both electronic and steric effects, to influence the catalytic activity. Similarly, the optical activity of ligands is also made use of in asymmetric hydrogenation reactions.

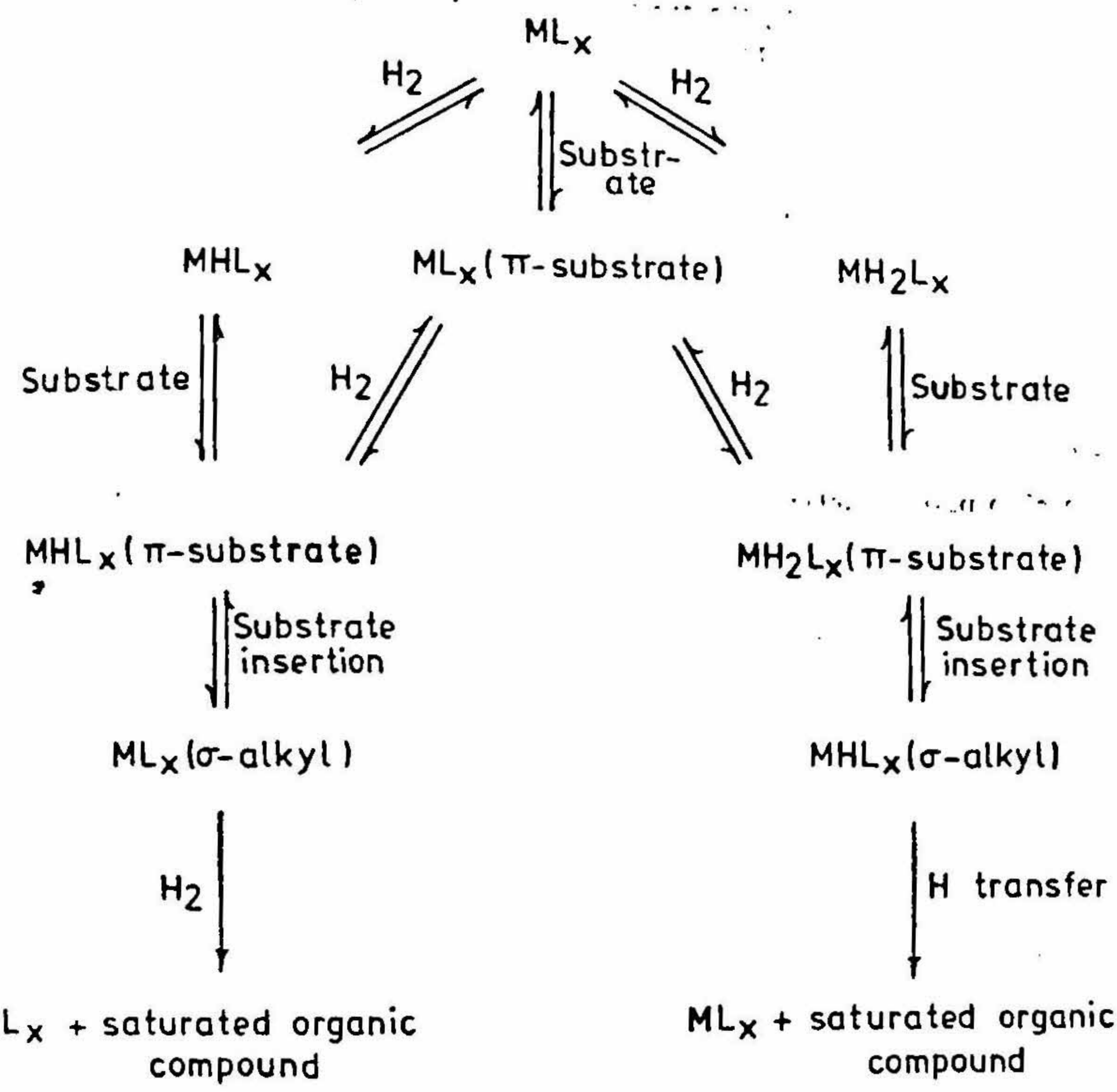
There are several transition metal complexes[1–10] available today for homogeneous hydrogenations, but not all of them are useful hydrogenation catalysts. Only a limited number find their applications in organic synthesis. Group VIII transition metals such as ruthenium, rhodium and iridium serve as the most useful ions and complexes as hydrogenation catalysts. To list a few of the very commonly used complexes : $RuCl_3$ (III)[3–27], $[Ru(CO)Cl_5]^{2-}$ (II)[28], $RuCl_4(bipy)^{2-}$ (II)[29], $RuCl_2(PPh_3)_4$(II)[30, 31], $RuCl_2(PPh_3)_3$ (II)[30], $HRuCl(CO)(PPh_3)_3$[32], $Co_2(CO)_8$ (II)[33], $[Co(CO)_3(PR_3)_2]^+$ $[Co(CO)_4]^-$, $[Co(CO)_3PR_3]_2$ (R = *n*-C_4H_9, Cyclo-C_6H_{11}, PPh_3)[34], $Co(CN)_5^{3-}$ (II)[35], $RhCl(PPh_3)_3$ (Wilkinson's catalyst)[36, 37], $Py_3RhCl_3/NaBH_4/DMF$[38] and $Ir(CO)Cl(PPh_3)_2$ (Vaska's complex)[39], etc. A comprehensive picture of the mechanistic pathways of hydrogenation using these transition metal ions and their coordination complexes is depicted[43] in Chart I.

An equally important and very useful catalyst as those mentioned above is the pentacyanocobaltate(II) complex anion, $Co(CN_5)^{3-}$ [35], the role of which in homogeneous catalysis is quite promising. While the $(PPh_3)_3RhCl$ and others are selective in the hydrogenation of isolated double bonds, the pentacyanocobaltate(II) system appears to hydrogenate only the conjugated systems and does not reduce the isolated double bonds. This review is, therefore, mainly devoted to demonstrate the importance and potential usefulness of this catalyst to organic chemists.

2. Pentacyanocobaltate(II), $Co(CN)_5^{3-}$

Unlike the other transition metal complexes already referred to, pentacyanocobaltate(II) complex anion is prepared *in situ* by adding potassium cyanide solution to a solution of cobaltous chloride.

Iguchi[40] in 1942 observed the great facility with which the pentacyanocobaltate(II), $Co(CN)_5^{3-}$ species reacts with hydrogen. Later it was shown[41, 42] to form a hydrido complex, $HCo(CN)_5^{3-}$. Since then this complex, $Co(CN)_5^{3-}$ has been quite successfully employed in the homogeneous catalytic hydrogenations of a wide variety of organic substrates with a fair amount of selectivity. Its property of facile hydrogenation of conjugated systems, such as dienes, α,β-unsaturated acids, esters, aldehydes, ketones



M = Metal, L_x = Ligand (x may change during reaction)

Chart I : Hydrogenation Pathways

and styrenes, etc. (except monoenes) is well known. Many reviews have appeared in literature[1-3, 16, 43, 44] about $Co(CN)_5^{3-}$ as a soluble catalyst. A brief account is presented below.

3. Reaction of $Co(CN)_5^{3-}$ with hydrogen

Solutions of pentacyanocobaltate(II) complex anion prepared in an atmosphere of hydrogen rapidly absorbs hydrogen[41, 42]. Though there is some doubt concerning the

mechanisms of this process, the overall reaction is considered to take place *via* homolytic cleavage of hydrogen molecule giving a hydrido complex, $HCo(CN)_5^{3-}$.

$$2Co(CN)_5^{3-} + H_2 \rightleftharpoons 2HCo(CN)_5^{3-}. \quad (1)$$

Careful spectroscopic studies of this reaction by King and Winfield[41, 45] showed that $Co(CN)_5^{3-}$ has an absorption peak at 967 nm which is a quantitative measure of Co(II) species. As it is converted to $HCo(CN)_5^{3-}$, the 967 nm absorption falls off in intensity and finally only one absorption at 305 nm is observed which is attributed to $HCo(CN)_5^{3-}$, characteristic of Co(III) species. The same workers prepared $HCo(CN)_5^{3-}$ by reacting cobaltous cyanide solution with sodium borohydride. In this reaction on side products were obtained and the resulting species had the same characteristic peak at 305 nm.

The absorption at 305 nm also appears when the species $Co(CN)_5^{3-}$ was kept in aqueous solution. This has been attributed to the homolytic cleavage of water with $Co(CN)_5^{3-}$ leading to the formation of $HCo(CN)_5^{3-}$ and $(HO)Co(CN)_5^{3-}$ (eqn. 2).

$$2Co(CN)_5^{3-} + H_2O \rightarrow HCo(CN)_5^{3-} + Co(CN)_5OH^{3-}. \quad (2)$$

This was substantiated[41] from spectroscopic data wherein the absorption at 967 nm due to $Co(CN)_5^{3-}$ species disappears yielding two absorptions at 305 and 380 nm attributable to $HCo(CN)_5^{3-}$ and $Co(CN)_5OH$, respectively.

Fresh $Co(CN)_5^{3-}$ solutions absorb hydrogen rapidly. As the solution is allowed to age, the rate of hydrogen uptake slows down. The mechanism of this reaction in dilute solutions involves a slow initial step and is first order with respect to cobalt. This is followed by the second step with the formation of $HCo(CN)_5^{3-}$, which is a bimolecular reaction.

$$Co(CN)_5^{3-}(II) + H_2 \overset{\text{slow}}{\rightleftharpoons} H_2Co(CN)_5^{3-} \quad (3)$$

$$H_2Co(CN)_5^{3-} + Co(CN)_5^{3-} \rightleftharpoons 2HCo(CN)_5^{3-}(II) \quad (4)$$

The transition metal complexes which are used as homogeneous hydrogenation catalysts were shown to form hydrido complexes with hydrogen and show abnormally large chemical shifts (14–22 ppm on high field side relative to water as reference)[46–48] which are characteristic of hydrogen bound to transition metal atoms. Hence PMR of such complexes provides a basis for detecting such systems.

The hydrido complex, $HCo(CN)_5^{3-}$ obtained by the reaction of hydrogen with $Co(CN)_5^{3-}$, has a proton signal at δ, 17·4 with respect to water as reference[46]. However, even the fresh aqueous solutions of $Co(CN)_5^{3-}$ show a signal at the same position with 1/10 to 1/4 its intensity[47]. This shows that hydrido complex is formed rapidly at the beginning even without hydrogen being present. This process is enhanced by adding 2M sodium hydroxide solution[49] to 0·25 M $[Co(CN)_5]^{3-}$ solution and the reaction was found to reach completion within 10 minutes. This large elevation of rate has led to the

suggestion[50] that the ions involved in the hydrogenation of $Co(CN)_5^{3-}$ may be $KCo(CN)_5^{2-}$ and $KH_2Co(CN)_5^{3-}$.

Based on the spectroscopic data, Griffith and Wilkinson[47, 51] and King and Winfield[41] suggested that the cobalt in the hydrido complex, $HCO(CN)_5^{3-}$ exists in 3 + oxidation state. But Vlcek[52], and Simandi and Nagy[53] on the basis of polarographic measurements suggested that cobalt exists essentially in 2+ oxidation state with hydrogen as stabilized atom, that is, Co(II) $(CN)_5(\cdot H)^{3-}$ rather than Co(III) $(CN)_5(:H)^{3-}$.

Attempts to isolate the hydrido complex by addition of alcohol resulted in the precipitation of $K_6Co_2(CN)_{10}$. The 3+ state of cobalt in $HCo(CN)_5^{3-}$ is stabilized by the cyanide ligand.

4. Mechanism of $HCo(CN)_5^{3-}$ formation

Kind and Winfield[41] suggested the following mechanism on the basis of kinetic studies.

$$Co(CN)_5^{3-} + H_2 \overset{k_1}{\rightleftharpoons} \underset{(I)}{[H_2Co(CN)_5^{3-}]} \tag{3}$$

$$\underset{(I)}{[H_2Co(CN)_5^{3-}]} + Co(CN)_5^{3-} \overset{k_2}{\rightleftharpoons} 2HCo(CN)_5^{3-}. \tag{4}$$

The reversibility of this reaction was shown by Mills *et al*[46] by deuterium exchange studies.

DeVries[33] proposed the following mechanism based on equilibrium and IR studies. The kinetic and equilibrium studies of Burnett *et al*[54] is in accord with this.

$$2Co(CN)_5^{3-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{(II)}{[Co_2(CN)_{10}^{6-}]} \tag{5}$$

$$\underset{(II)}{[Co_2(CN)_{10}^{6-}]} + H_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2HCo(CN)_5^{3-} \tag{6}$$

But it was difficult to distinguish between these two sequences because the intermediate species, *i.e.*, $CO_2(CN)_{10}^{6-}$ or $H_2Co(CN)_5^{3-}$ is said to be in low steady state concentration.

Simandi and Nagy[55, 56] confirmed the results of DeVries[33] by measuring the rate of absorption of molecular hydrogen by $Co(CN)_5^{3-}$ solution under non-equilibrium conditions. The mechanism proposed by Simandi and Nagy is similar to the one proposed by Kind and Winfield[41] with the difference that a bimolecular hydrogen complex III was proposed.

$$Co(CN)_5^{3-} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2Co(CN)_5^{3-} \tag{7}$$

$$H_2Co(CN)_5^{3-} + Co(CN)_5^{3-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [(CN)_5Co \cdot\cdot \underset{(III)}{H} \cdot\cdot H \cdot Co(CN)_5^{6-}] \cdot\cdot \quad (8)$$

$$[(CN)_5Co \cdot\cdot \underset{(III)}{H} \cdot\cdot H \cdot\cdot Co(CN)_5^{6-}] \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} 2HCo(CN)_5^{3-}. \quad (9)$$

Here the pentacyanocobaltate(II) species is called the 'hydrogen carrier'[56].

On closer observation of the above mechanisms serious objections can be raised against eqns. (3), (4), (7), (8) and (9) since the chemical bonding in the intermediates I and III is very unstable due to two hydrogens binding to the electronegative atoms. On the other hand, formation of the intermdiate $[Co_2(CN)_{10}^{6-}]$ in eqns. (5) and (6) as proposed by DeVries[42] seems feasible since dicobalt and dimanganese complexes are known. The intermediate $[Co_2(CN)_{10}^{6-}]$ can react with H_2 in a cyclic transition state as in eqn. (10) to give the hydrido complex.

$$(CN)_5Co\text{–}Co(CN)_5^{6-} + H_2 \rightarrow H_2(NC)_5Co \overset{H \cdots H}{\cdot\cdot\cdot\cdot} Co(CN)_5 \rightarrow 2HCo(CN)_5^{3-}. \quad (10)$$

A third order kinetics has been proposed by the above workers for this reaction.

$$\text{Rate} = k(Co)^2(H_2). \quad (11)$$

The catalytic hydrogenation of substrates has generally been discussed in terms of the hydride, $HCo(CN)_5^{3-}$. The hydrido complex, $HCo(CN)_5^{3-}$, may be prepared from cobaltous cyanide solution by reaction with hydrogen[41, 44, 57] borohydride or by the aging reaction[49, 57]. Hydrazine has also been used as a hydride source[47].

5. Mechanism of hydrogenation with $HCo(CN)_5^{3-}$

Hydridopentacyanocobaltate(III), $HCo(CN)_5^{3-}$ complex anion exclusively hydrogenates activated double bonds, *i.e.*, conjugated dienes[68], α,β-unsaturated acids, esters, ketones, nitriles, aldehydes, etc., but not isolated double bonds. The mehanism of these hydrogenations depends upon the group activating the double bond to be hydrogenated. Two mechanisms have been postulated; one of them involves the formation of organocobalt complex [eqns. (12) and (13)] as the intermediate while the other a radical species as the intermediate[56] [eqns. (14) and (15)].

Mechanism I :

$$HCo(CN)_5^{3-} + C_4H_6 \rightleftharpoons Co(CN)_5(C_4H_7)^{3-} \quad (12)$$

$$Co(CN)_5(C_4H_7)^{3-} + HCo(CN)_5^{3-} \rightleftharpoons 2Co(CN)_5^{3-} + C_4H_8. \quad (13)$$

Mechanism II

$$CoH + S \rightarrow Co + HS \quad (14)$$

$$HS\cdot + CoH \rightarrow Co + H_2S \quad (15)$$

$$HS\cdot + Co \rightleftharpoons CoSH \quad (16)$$

where S = substrate, and Co = $Co(CN)_5^{3-}$.

The direction of addition was determined by the percentage incorporation of deuterium, in the deuteriogenated products and recovered substrates. Depending upon the quantity of deuterium involved in the deuterations by $DCo(CN)_5^{3-}$, of butadiene[44], sorbates[58], styrene, methyl methacrylate[59], etc., the initial deuterium addition has been suggested to take place at the β-carbon (relative to the activating group). A general scheme[3, 60, 61] involving both the above mechanisms is shown in Chart II.

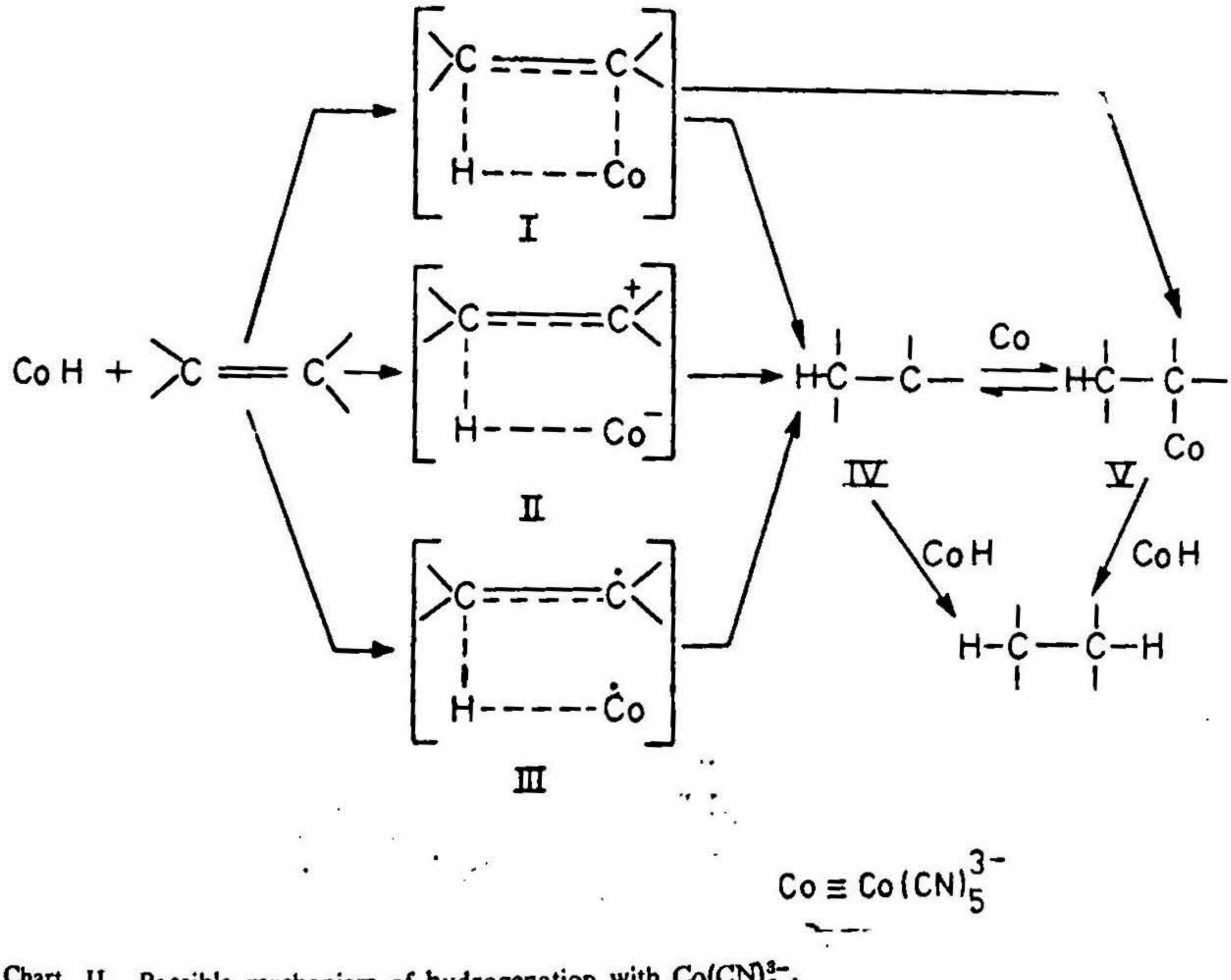


Chart II. Possible mechanism of hydrogenation with $Co(CN)_5^{3-}$.

The hydrogen of the hydrido complex approaches the β-carbon of the activated double bond which looks like a four centre transition state (I). This may rearrange either to a radical (IV) or to an organo-cobalt complex (V) which subsequently reacts with more of the hydrido complex to form saturated product. Alternatively, it may disproportionate to give equal amounts of reduced product and the starting material when no excess $HCo(CN)_5^{3-}$ is present. This scheme explains well the results obtained for the hydrogenations of butadiene, cinnamates, α, β-unsaturated nitriles, etc.

The structure of substrate determines whether stable organocobalt complex is formed during the hydrogenation[16]. Primary organocobalt complexes[16] formed from organic halides, (*e.g.*, benzyl, primary alkyl, etc.) are stable. The secondary[16] organocobalt complexes having an *a*-substituted carbonyl or a nitrile group and also tertiary organocobalt complexes[16] having a nitrile substituent form stable complexes. Hence it seems that electronegative groups stabilize metal carbon bonds to form stable complexes while the electropositive groups destabilize the metal carbon bonds to give saturated products by hydrogen transfer or disproportionation.

6. Hydrogenation of organic substrates with $Co(CN)_5^{3-}/H_2$

Many reviews have appeared on the catalytic hydrogenation of olefinic bonds by pentacyanocobaltate(II), $Co(CN)_5^{3-}$ solutions in water. It is interesting to note that while the $(PPh_3)\cdot RhCl$ is selective in the hydrogenation of double bonds, the pentacyanocobaltate(II) system appears to hydrogenate only the conjugated systems and does not touch the isolated double bonds. Activation through conjugation is a necessary requirement. Two basic mechanisms discussed earlier have been put forward. The intermediates for dienes and α,β-unsaturated acids are organocobalt complex and radical respectively. These reactions said to depend upon the CN/Co ratio. Water is the usual solvent in these reactions with alcohol as cosolvent sometimes. The following illustrative examples are discussed.

6.1. *Hydrogenation of dienes*[16]

Reduction of butadiene with hydrogen at 1 atmosphere pressure and at 20° gave 1-butene at CN/Co > 5 and *trans*-but-2-enes > but-1-ene > *cis*-but-2-ene at CN/Co ratio $\leqslant 5$.

The following mechanism[44] was put foward for the butadiene hydrogenation with $HCo(CN)_5^{3-}$.

$$HCo(CN)_5^{3-} + C_4H_6 \rightleftharpoons Co(CN)_5(C_4H_7)^{3-} \quad (17)$$

$$Co(CN)_5(C_4H_7)^{3-} + HCo(CN)_5^{3-} \rightarrow 2Co(CN)_5^{3-} + C_4H_8 \quad (18)$$

The butenyl complex, $Co(CN)_5(C_4H_7)^{3-}$ was isolated by Kwiatek and coworkers[62] and was shown to be identical to the organocobalt complex obtained by the reaction of crotylbromide with $HCo(CN)_5^{3-}$ (eqn. 19).

$$2Co(CN)_5^{3-} + CH_3CH=CHCH_2Br \rightarrow (CN)_5CoCH_2CH=CHCH_3^{3-} + Co(CN)_5Br^{3-}. \quad (19)$$

The presence of σ-butenyl complex was supported by NMR studies[62, 63] in D_2O solutions. On protonation it gave 1-butene (eqn. 20).

$$(CN)_5CoCH_2CH=CHCH_3^{3-} \xrightarrow{H^+} Co(CN)_5-CH_2\overset{+}{C}HCH_2CH_3^{3-} \rightarrow Co(CN)_5^{3-} + CH_2=CH-CH_2CH_3 \quad (20)$$

The σ-butenyl complex with $HCo(CN)_5^{3-}$ gave 1-butene or *trans*-2-butene as major product depending upon the high or low cyanide concentration[68, 69]. This was also proved by the easy cleavage of allyl complexes[44, 63] with $HCo(CN)_5^{3-}$. The steric control[16, 44, 54, 62] of this reaction is explained on the basis of the equilibrium between the σ-complexes and allylic complexes involved [eqn. (21)]. Based on these equilibria, Kwiatek and coworkers[16] assumed that at high cyanide concentration only σ-butenyl complexes were present. Therefore, at high cyanide concentrations γ-attack at the allylic carbon leads to 1-butene [eqn. (22), Chart III], and at low cyanide/cobalt ratio *trans*-2-butene is obtained [eqn. (23), Chart III].

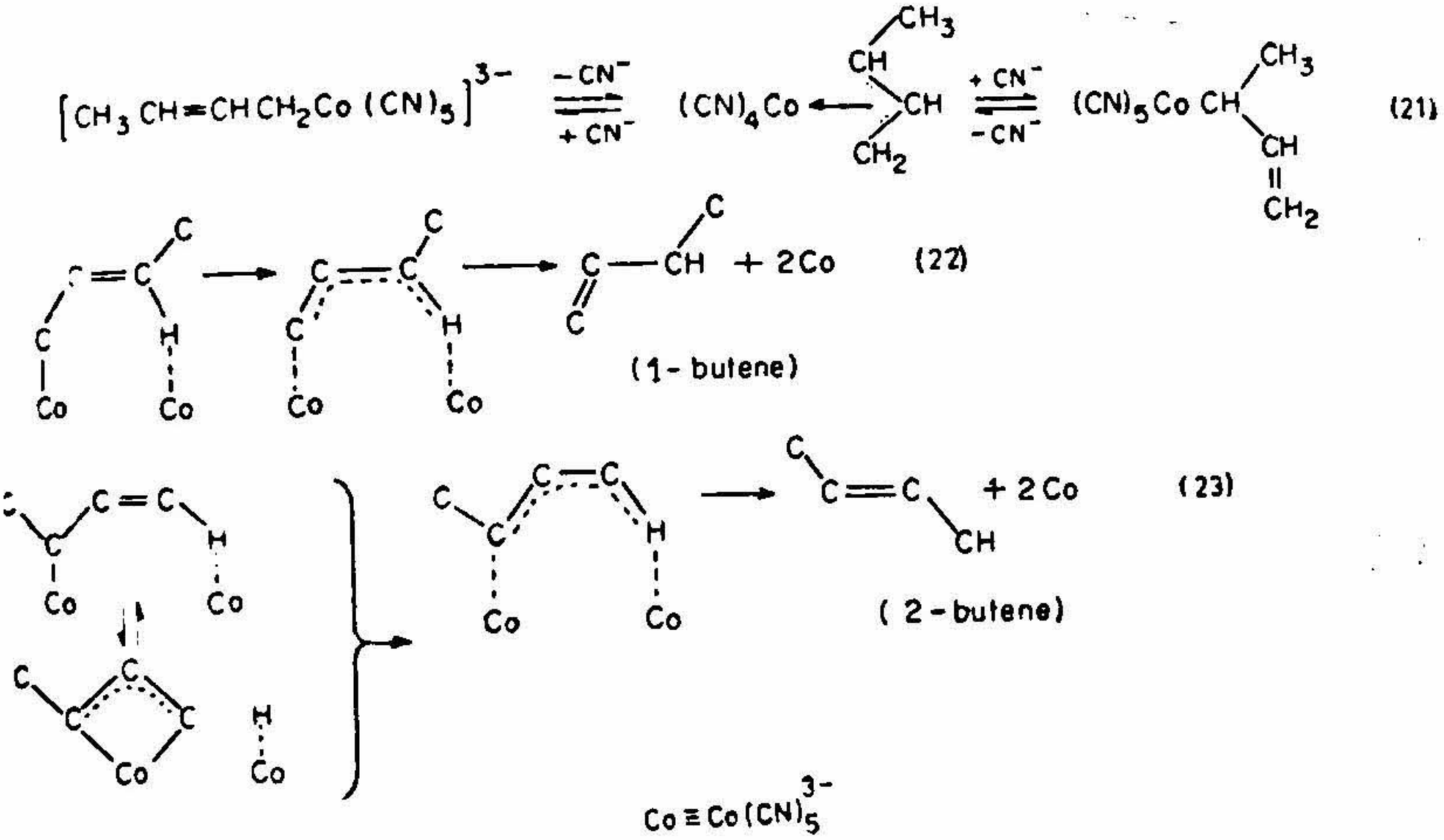


Chart III. Hydrogenation of σ- butenyl complexes

Table I depicts several dienes which were successfully reduced with $HCo(CN)_5^{3-}$.

Table I

Hydrogenation of conjugated diene [$Co(CN)_5^{3-}$ as catalyst]

Substrate	Product	References
Butadiene	1-Butene, *trans*-2-butene	16, 62, 44
Isoprene	2-Methylbut-1 and 2-enes	2. 16
2, 4-Hexenes	Hex-2-enes	59
Cyclopentadiene	Cyclopentene	44, 64
1, 3-Cyclohexadiene	Cyclohexene	44

6.2. *α, β-Unsaturated aldehydes*

Not much work has been done on the α, β-unsaturated aldehydes and the reported hydrogenations[59] were not very efficient. Methacrolein[59] was hydrogenated with difficulty. Both propionaldol and propionaldehyde gave α-methylvaleraldehyde[44], the latter probably through aldol condensation and subsequent reduction.

$$2H_3CCH_2CHO \xrightarrow{\text{base}} C_2H_5CH(OH)CH(CH_3)CHO$$

$$\xrightarrow{-H_2O} C_2H_5CH=CH(CH_3)CHO \quad (24)$$

$$C_2H_5CH=C(CH_3)CHO \xrightarrow{H_2} C_2H_5CH_2CH(CH_3)CHO. \quad (25)$$

Benzaldehyde was reduced to benzylalcohol in presence of added base[44]; the possible mechanism being :

$$HCO(CN)_5^{3-} + C_6H_5CHO \rightarrow Co(CN)_5(C_6H_5CH_2O^-)^{3-} \quad (26)$$

$$Co(CN)_5(C_6H_5CH_2O^-)^{3-} + H_2O \xrightarrow{OH^-} Co(CN)_5OH^{3-} + C_6H_5CH_2OH. \quad (27)$$

Triglaldehyde[62] was hydrogenated without the base. Mixed aldehydes gave condensation–hydrogenation products, for example, benzaldehyde with acetaldehyde gave α-benzylcinnamaldehyde[44], and cinnamladehyde yielded the reduced condensation product 2-benzyl-5-phenyl-pent-2-en-1-al.

6.3. *α, β-Unsaturated acids, esters and amides*

Like conjugated diene systems, these were studied extensively by a number of groups using the pentacyanocobaltate(II) catalyst. Table II shows different acid systems which were hydrogenated using $Co(CN)_5^{3-}$ as catalyst.

From Table II we can infer that α-substituted α, β-unsaturated acids are reduced readily by $H_2/Co(CN)_5^{3-}$ system, whereas acids with no α-substituents such as acrylic, maleic, crotonic, fumaric, etc., are not hydrogenated under usual experimental conditions of 1 atmosphere hydrogen pressure and 25° temperature; but stable organocobalt complexes such as $RCH_2CH(CO_2^-)Co(CN)_5^{3-}$ were isolated. For their reductions much stringent conditions (higher hydrogen pressures and temperatures) were necessary. Acids which have activating groups at β-carbon of the α, β-unsaturated acid systems such as cinnamic acid are readily hydrogenated.

Kwiatek *et al*[33, 34], Murakami *et al*[65] and Simandi and Nagy[63] studied the cinnamic acid hydrogenation with $Co(CN)_5^{3-}$ as catalyst. The mechanism involves the formation of free radical intermediates as seen in eqns. (28), (29) and (30).

$$HCo(CN)_5^{3-} + S \rightarrow Co(CN)_5^{3-} + HS. \quad (28)$$

$$HS. + HCo(CN)_5^{3-} \rightarrow Co(CN)_5^{3-} + H_2S \quad (29)$$

$$HS. + Co(CN)_5^{3-} \rightleftharpoons Co(SH)(CN)_5^{3-} \quad (30)$$

where S is Cinnamate and $C_6H_5\text{-}CH=CHCOO^-$.

Making use of the deuterido cobalt complex, $DCo(CN)_5^{3-}$, the direction of hydrogen additions and the σ-complexes (for acrylates, etc., with no α-substituents) were investigated[16, 61] and the deuterations were found to be irreversible[59].

Table II

α, β-Unsaturated acids and their derivatives hydrogenated by $H_2/Co(CN)_5^{3-}$

Substrate	Product	References
Cinnamic acid	β-Phenylpropionic acid	33, 44, 53, 59
Sorbic acid	2, 3 and 4-hexenoic acids	33, 59
Acrylic acid	Not reduced	33, 44, 61
Methacrylic acid	α-Methylbutyric acid	61
Tiglic acid	Not reduced	61
Angelic acid	Isomerisation to tiglic acid	61
Maleic acid	Not reduced	65
Acetylene dicarboxylic acid	Fumaric acid	65
Methylmethacrylate	Methyl isobutyrate and isobutyric acid	44, 63

6.4. α, β-*Unsaturated nitriles*

Acrylonitriles with α-ethoxy or α-phenyl groups were hydrogenated at the double bond when they were added to $HCo(CN)_5^{3-}$ solutions[44]. If nitrile is added in excess, N-amidocobalt complex is formed. Similar to acids, these also involve radical intermediates[2, 16].

$$CH_2 = CRCN = HCo(CN)_5^{3-} \longrightarrow CH_3CRCN + Co(CN)_5^{3-} \quad (31)$$

$$CH_3\dot{C}RCN + HCo(CN)_5^{3-} \longrightarrow CH_3CHRCN + Co(CN)_5^{3-} \quad (32)$$

$$CH_3CRCN + Co(CN)_5^{3-} \longrightarrow CH_3CR = C = NCo(CN)_5^{3-} \xrightarrow{H_2O} CH_3\dot{C}HRCONHCo(CN)_5^{3-}. \quad (33)$$

Table III presents hydrogenations of several nitriles and related compounds using $HCo(CN)_5^{3-}$ system. In these hydrogenations, at higher temperatures and pressures, nitrile group was found to get hydrolysed[66]. As we see from Table III, oxime gets reduced to an amine[66] and hydrazone to a substituted hydrazine[66].

Table III

$Co(CN)_5^{3-}$ catalyzed hydrogenations of nitriles, oximes and hydrazones

Substrate	Product	References
α-Phenylacrylonitrile	α-Phenylpropionitrile	16
α-Ethoxyacrylonitrile	α-Ethoxypropionitrile	16
Phenylacetonitrile	Phenylacetic acid	65
Acetoxime	Isopropylamine	65
Phenylpyruvic acid oxime	Phenylalanine	65
Phenylacetylcyanide phenylhydrazone	2 (Phenylhydrazino)-3-phenyl-propionic acid	66

6.5. *Styrenes*

α-Substituted styrenes were readily reduced but not β-substituted styrenes[16]. They form no complexes with cobalt. Table IV shows several styrenes hydrogenated using $Co(CN)_5^{3-}$ as catalyst.

Table IV

Styrenes hydrogenated by $H_2/Co(CN)_5^{3-}$

Substrate	Product	References
Styrene	Ethylbenzene	33, 44
α-Methylstyrene	Isopropylbenzene	44
Propenylbenzene	No reduction	33, 44
Stilbene	No reduction	44

It is worth mentioning that although acetylenes are not hydrogenated by $HCo(CN)_5^{3-}$ they form bridged complexes such as $(NC)_5CoCH=CHCo(CN)_5^{6-}$ with $HCo(CN)_5^{3-}$; but phenylacetylenes[59] and phenylacetylenic acids[16, 59] are hydrogenated to the corresponding olefinic compounds.

6.6. *Reductive amination reactions*

Reductive amination of activated keto groups by $HCo(CN)_5^{3-}$ system in presence of excess of ammonia is a useful method for preparing amines. α-Amino acids can be readily obtained from the α-keto acids or esters using $H_2/Co(CN)_5^{3-}$ system in the presence of excess of ammonia. Imines are the likely intermediates[67] in these reactions. Table V shows the substrates and the products obtained in reductive aminations.

$$\rangle C{=}O \underset{-H_2O}{\overset{NH_3}{\rightleftharpoons}} \rangle C = NH \xrightarrow{H_2} \rangle CH - NH_2. \quad (34)$$

Table V

Reductive amination reactions catalyzed by $Co(CN)_5^{3-}$

Substrate	Product	Reference
Pyruvic acid	Alanine	67
Phenylpyruvic acid	Phenylalanine	67
α-Ketoglutaric acid	Glutamic acid	67
Ethylacetoacetate	No reaction	67
Benzalacetone	3-Amino-1-phenylbutane	67

6.7. *Hydrogenolysis of organic halides*

Organic halides[2, 16] are readily reduced by alkaline solutions of $Co(CN)_5^{3-}$ system. The first step of this reaction[16] is believed to involve $Co(CN)_5^{3-}$ with the formation of a radical.

$$Co(CN)_5^{3-} + RX \longrightarrow XCo(CN)_5^{3-} + R \quad (35)$$

$$R\cdot + HCo(CN)_5^{3-} \longrightarrow Co(CN)_5^{3-} + RH \quad (36)$$

The radical formed may react with $Co(CN)_5^{3-}$ to form an organocobalt complex or direct addition may take place as :

$$RX + 2Co(CN)_5^{3-} \longrightarrow RCo(CN)_5^{3-} + XCo(CN)_5^{3-}. \quad (37)$$

Many stable organocobalt complexes have been prepared. These organocobalt complexe. give disproportionate products in the absence of the hydrido complex, $HCo(CN)_5^{3-}$.

$$2Co(CN)_5^{3-} + 2(CH_3)_2CHI \longrightarrow 2Co(CN)_5I^{3-} + CH_3CH{=}CH_2 + CH_3CH_2CH_3 \quad (38)$$

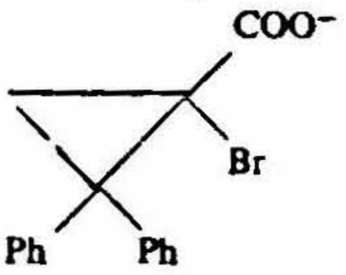
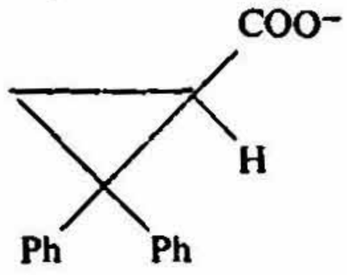
The evidence for the radical intermediate was obtained by trapping the radicals[16] with acrylonitrile. Methyl methacrylate[2] gave compounds of the following structures : $(CH_3)_2CHCH_2CH(CH_3)COOCH_3$ and $Me_2CHCH{=}C(CH_3)COOCH_3$. In addition to these, dimers were also isolated. All these prove that the reaction proceeds through the formation of radical intermediates.

Another evidence for the radical mechanism is the loss of optical activity. When 1-bromo 2,2-diphenylcyclopropylcarboxylic acid was hydrogenated over $H_2/Co(CN)_5^{3-}$ system, the active acid was reduced to optically inactive (racemic) acid[16].

Table VI shows some of the organic halides hydrogenated using $H_2/Co(CN)_5^{3-}$.

Table VI

Hydrogenolysis of organic halides by $H_2/Co(CN)_5^{3-}$

Halide, RX	Products	References
CH_3I	CH_4	16
iso-C_3H_7I	C_3H_8, C_3H_6	16
neo-$C_5H_{11}I$	neo-C_5H_{12}	59
$PhCH_2Br$	$PhCH_3$	2
$Ph_3C \cdot Cl$	Ph_3CH	16, 59
$PhCH=CHCH_2Br(Cl)$	$PhCH=CHCH_3$	59
$HC \equiv CCH_2Cl$	$CH_3C \equiv CH$, $CH_3CH=CH_2$	59
		16
[α] + 103°	[α] 0°	

6.8. *Hydrogenation of α, β-unsaturated ketones*

As in the previous cases, olefinic bonds conjugated to keto group are reduced by $HCo(CN)_5^{3-}$ system. Also keto groups are reduced when they are conjugated with suitable activating groups. Several such hydrogenations of α, β-unsaturated ketone are listed in Table VII.

Table VII

$Co(CN)_5^{3-}$ catalyzed hydrogenations of ketones

Substrate	Product	References
Methylisopropenyl ketone	Methylisopropyl ketone	59, 63
Phenylisopropenyl ketone	Phenylisopropyl ketone	59
Benzil	Benzoin	33
Indigo	Indigowhite	59
Mesityl oxide	4-Methylpentan-2-one	70
Benzalacetone	4-Phenylbutan-2-one	70
Citral	Citronellol	70

It may be noted that the isopropenyl ketones are readily reduced. The mechanism in these cases was found to be similar to that of bromoallyl or 1-bromoisopropyl ketones[44]. Phenyl-vinyl ketones form stable adducts which have to be protonated to yield the hydrogenated product[62], whereas α, β-diketo compounds are hydrogenated to the corresponding α-hydroxy ketones.

Further, it is quite significant to mention that most of the substrates investigated so far with $Co(CN)_5^{3-}$ appear to be acyclic conjugated compounds. Until about 1977, when work from this laboratory[70] has shown the usefulness of this reagent as a homogeneous hydrogenation catalyst for cyclic systems too, cyclohexenone was the only known example of the cyclic compound that was hydrogenated. These examples are summarised in Table VIII.

Table VIII

$Co(CN)_5^{3-}$ catalyzed hydrogenations of cyclic ketones

Substrate	Product	Reference
Cyclohexenone	Cyclohexanone	70
l-Carvone	Dihydrocarvone	70
β-Ionone	4-(2′,6′,6′-trimethyl-cyclohexyledene) butan-2-one	70
3, 5-Dimethyl-cyclohexenone	Starting material	70

The results in these cases are consistent with the mechanism of hydrogenation of acyclic conjugated α, β-unsaturated ketones. However, it is quite interesting to note that the β-substitution on the α, β-unsaturated carbonyl compounds has a profound effect on the hydrogenation with $Co(CN)_5^{3-}$. Apart from mesityl oxide, none of the substrates carrying a β-substituent seem to be hydrogenated with this catalyst. This may be due to the fact that β-substitution hinders the approach of a bulky moiety like the hydridopentacyanocobaltate(II). Similarly, for the same reason steroid molecules like testosterone, its acetate, androst-4-en-3,17-dione, androst-1,4-diene-3,17-dione and dienobol, which have a β-substituent, do not undergo hydrogenation, although 17-acetoxyandrost-1-en-3-one gets readily hydrogenated. It may be mentioned that this is the first successful attempt of hydrogenating steroids with this reagent.

Cross conjugated dienones also do not get hydrogenated with this reagent, which may probably be due to the formation of a stable π-complex between the reagent and the substrate. This six electron system π-complex can prevent hydrogen transfer and thereby hydrogenation.

Lastly, the formation of the α, δ-dihydro compound may be envisaged from the initial hydrogenation of the α, β-double bond followed by isomerisation leading to the final product. Thus, the equilibration of the double bond of the dihydro compound can result in the formation of a mixture of the *trans*- and *cis*-isomers.

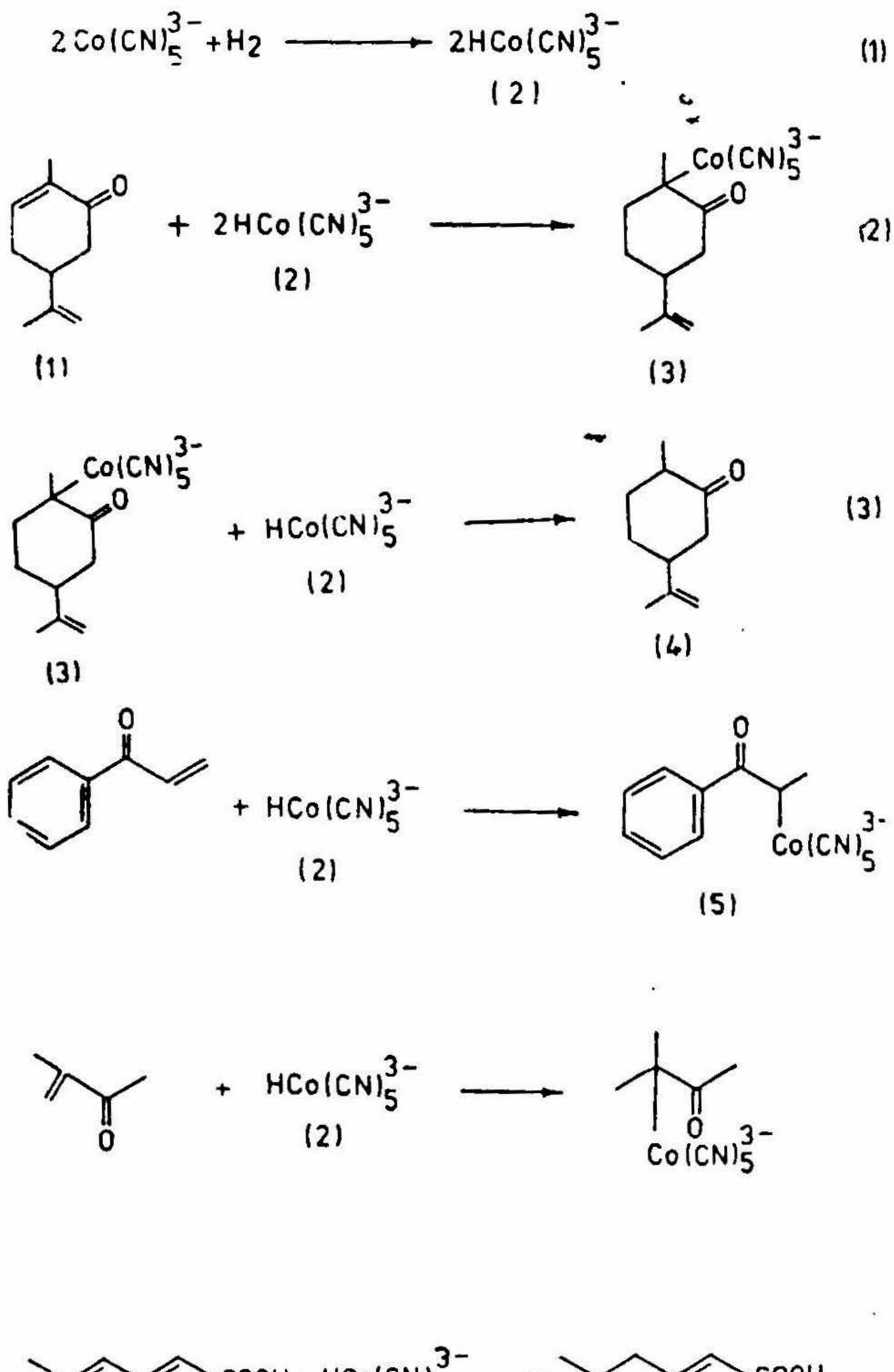


Chart IV

6.9. *Mechanism*

The mechanism of hydrogenations in the above discussed cases is quite interesting and the same is projected in Chart IV, considering the hydrogenation of *l*-carvone (1) as the general case and then extending the same to all other successful hydrogenations.

The $Co(CN)_5^{3-}$ formed by the addition of a solution of potassium cyanide to a solution of cobaltous chloride reacts with a molecule of hydrogen forming a hydridopentacyanocobaltate(III) complex anion, $HCo(CN)_5^{3-}$ (2) as shown in eqn. (1), Chart IV.

The hydridopentacyanocobaltate(III), $HCo(CN)_5^{3-}$ then reacts with *l*-carvone (1) to give the organocobalt complex (3) which reacts subsequently with another mole of $HCo(CN)_5^{3-}$ (2) to give the dihydrocarvone (4). The reaction proceeds smoothly. These results are consistent with the results obtained for the hydrogenation of isopropenyl ketones[59, 62, 63] which are reduced by the $H_2/Co(CN)_5^{3-}$ system. Since no complex of the type, $(CN)_5Co(CH_3)_2CCR^{-3}$ (with C=O) was observed[62], the formation of (3)

seems to be transient. This unstable adduct (3) is reactive enough to be hydrogenated by another mole of $HCo(CN)_5^{3-}$ (2), giving the final dihydro compound (4). The hypothesis of unstable adduct formation is also supported[44] by the observation that the hydrogenation proceeds to near completion with the added base whereas in the absence of the base the reaction is only partial.

It is known[21, 41, 49] that even in the absence of hydrogen an aqueous solution of $Co(CN)_5^{3-}$ contains a small concentration of the hydrido complex (2). However, when the base is present[49], the concentration of the hydrido complex (2) considerably increases as shown from the NMR studies of the sodium hydroxide solution of $Co(CN)_5^{3-}$. The same observations have been found to be true in the presence of hydrogen. In the absence of the base, the amount of $HCo(CN)_5^{3-}$ (2) available for the second hydrogen transfer to the organocobalt complex (3) may not be sufficient and hence the unstable complex may disproportionate, as observed in the case of dienes[44] to give the starting material (1) and the dihydro product (4). In the presence of base, excess of the hydrido complex is present which reacts with the organocobalt complex (3) affording exclusively the dihydro compound (4) in good yield (90%).

It has been reported[44] that α-substituted unsaturated acids are readily hydrogenated with $Co(CN)_5^{3-}$, whereas acids with no α-substituents such as acrylic, crotonic, maleic, fumaric, etc., are not hydrogenated under the usual experimental conditions. This is also supported by the fact that isopropenyl ketones do not form stable organocobalt complexes, while phenylvinyl ketones with an unsubstituted α-position form stable adducts[2, 44] of the type (5). These stable adducts are hydrolysed to give the final dihydro compound. Our results are consistent with this observation. Thus *l*-carvone (1), an α-substituted α, β-unsaturated compound is reduced readily, whereas cyclohexenone could not be hydrogenated without the added base.

It is also interesting to note that the β-substitution on the α, β-unsaturated carbyonl compound has profound effect on the hydrogenation with $Co(CN)_5^{3-}$. Thus apart from mesityl oxide none of the substrates carrying a β-substituent could be hydrogenated with this catalyst. This may be due to the fact that substitution at the β-position hinders the approach of a bulky moiety like the hydridopentacyanocobaltate(III). Similarly the steroid hormones, testosterone, its acetate, adrost-4-en-3, 17-dione, adrost-1, 4-diene-3, 17-dione and dienobol which have a β-substituent could not be hydrogenated with this catalyst; although 17-acetoxyandrost-1-en-3-one is readily hydrogenated.

It has been reported[33, 42] that the hydrogenation of sorbic acid (6) using this catalyst affords 2-hexenoic acid (7) wherein the γ, δ-double bond is hydrogenated. Unlike this, hydrogenation of β-ionone, an $\alpha, \beta, \gamma, \delta$-unsaturated ketone affords the corresponding α, δ-dihydro compound.

The formation of the α, δ-dihydro compound may be envisaged from the initial hydrogenation of the α, β-double bond of β-ionone and the subsequent isomerisation of the resulting compound to the final product under the reaction conditions. Thus equilibration of the double bond of the dihydro-β-ionone results in the formation of a mixture of the *trans*- and *cis*-isomers.

The hydrogenation of citral to citronellol is not unexpected, since benzaldehyde is known to get hydrogenated to beznyl alcohol under similar basic conditions[44].

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