

Reduction of Cobalt Complexes by Carbon Monoxide and Synthesis of Mono- and Bis-organometallic Derivatives

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Cobalt(III) complexes of the type $[\text{Co}^{\text{III}}(\text{chel})(\text{OH})(\text{H}_2\text{O})]$, where chel is a tetradentate conjugated chelating ligand, react in water with CO yielding, in the pH range 4–13, $[\text{Co}^{\text{II}}(\text{chel})]$. Formation of $[\text{Co}^{\text{III}}(\text{chel})(\text{CO}_2\text{H})(\text{H}_2\text{O})]$ through nucleophilic attack of OH^- on the intermediate $[\text{Co}^{\text{III}}(\text{chel})(\text{CO})(\text{OH})]$ is assumed. The carboxy-derivative decomposes yielding CO_2 and $[\text{Co}^{\text{I}}(\text{chel})]^-$ species which, in turn, gives $[\text{Co}^{\text{II}}(\text{chel})]$ by different reaction paths depending on pH of the solution. The same mechanism operates for the complex with the 2,3,9,10-tetramethyl-1,4,8,11-tetra-azaundeca-1,3,8,10-tetraen-11-ol-1-olato anion (tn) up to pH 8. In more alkaline solution (pH 13) the corresponding carbonyl derivative $[\text{Co}^{\text{I}}(\text{chel})(\text{CO})]$ can be isolated. With all chel complexes investigated the reaction in alkaline solution appears to be autocatalytic. Mono- and di-organometallic derivatives can be prepared by the same reaction in the presence of organic halides.

THE equatorial ligands bound to cobalt in the complexes (I)–(IV) have a marked influence on the electronic, thermodynamic, and kinetic properties of the axial positions, compared with conventional ligands.

In these complexes the central metal atom is part of a conjugated system with a delocalised electronic structure, which changes the effective charge on the metal and the nature and energy of the orbital localised mainly along the z axis.

As a consequence, the relative stability of the formal oxidation states is profoundly modified¹ and the bonding properties of the axial positions give rise to stable cobalt-carbon bonds.

The thermodynamic effects of the equatorial ligands can be quantified by the equilibrium constants of substitution reactions at the axial positions. The extent of this effect is such that the co-operative *cis*- and *trans*-labilisation results in the preferred formation of five-co-ordinate cobalt(III).²⁻⁴

Finally the kinetic *cis*-effect can be shown even in cobalt(III) derivatives by the very fast exchange of the axial ligands, in marked contrast to the well known inertness of conventional cobalt(III) complexes.

Earlier papers have shown that all the above effects are sensitive to the nature of the equatorial ligand.^{1,5}

This paper is devoted to the investigation of the mechanism of carbonyl co-ordination in the axial positions which takes place in the insertion and reduction reactions.

RESULTS AND DISCUSSION

Reactions with Carbon Monoxide.—All cobalt(III) complexes (I)–(IV) of the type $[\text{Co}^{\text{III}}(\text{chel})(\text{H}_2\text{O})_2]^+$, where chel is one of the tetradentate chelating agents, were found to react with carbon monoxide at room temperature and atmospheric pressure in alcohol or water over a wide range of pH (4–13).†

† In the range of pH considered the dissociation products $[\text{Co}^{\text{III}}(\text{chel})(\text{OH})(\text{H}_2\text{O})]^0$ and $[\text{Co}^{\text{III}}(\text{chel})(\text{OH})_2]^-$ have to be considered as possible reacting species.

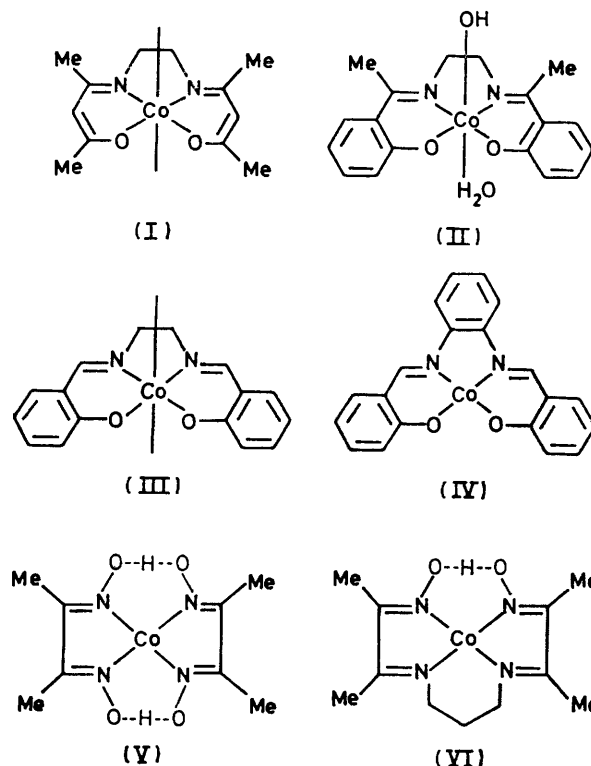
¹ G. Costa, G. Mestroni, A. Puxeddu, and E. Reisenhofer, *J. Chem. Soc. (A)*, 1970, 2870.

² G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *J. Organometallic Chem.*, 1966, **6**, 181.

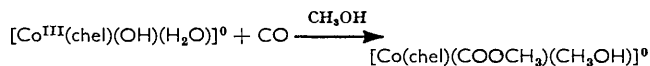
³ G. Costa, G. Mestroni, and L. Stefani, *J. Organometallic Chem.*, 1967, **7**, 943.

The corresponding cobalt(II) complexes under the same conditions do not absorb carbon monoxide.

In methanol 1 molar equivalent of CO is taken up per molar equivalent of complex and, as previously reported,⁶



the corresponding methoxycarbonyl-derivative is formed in quantitative yield.



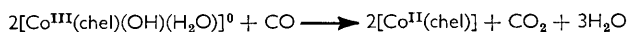
In aqueous tetrahydrofuran (THF) only a half molar equivalent of CO is absorbed per molar equivalent of complex. This stoichiometry holds over the pH range

⁴ S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 1969, **3**, 308.

⁵ A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Tauzher, *Inorg. Chim. Acta Rev.*, 1970, **4**, 41.

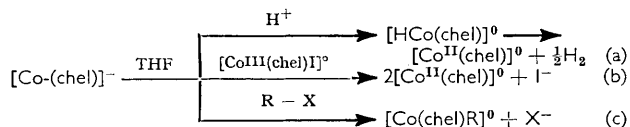
⁶ G. Costa, G. Mestroni, and G. Pellizer, *J. Organometallic Chem.*, 1968, **15**, 187.

4—13. In this case the reaction products are invariably carbon dioxide and the corresponding Co^{II} complex:

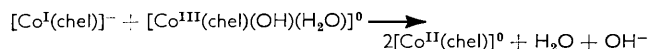


When this reaction is performed in the presence of a large excess of methyl iodide the complex $[\text{CH}_3\text{Co}(\text{chel})\text{H}_2\text{O}]^0$ was isolated in quantitative yield in the range of $\text{pH} \geq 13$, while at pH values ≤ 8 the cobalt(II) complex was obtained, also in quantitative yield. At intermediate pH the reaction products are mixtures of the organometallic and the cobalt(II) compounds.

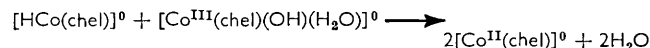
The formation of the methyl-derivative from methyl iodide strongly suggests that the cobalt(I) complex is an intermediate of the reaction. Only the cobalt(I) species reacts with alkyl halides.^{7,8} Furthermore, this strongly nucleophilic⁵ intermediate can react as follows: as was previously reported^{7,8} the $[\text{Co}^{\text{I}}(\text{chel})]^-$ complex reacts rapidly with H^+ yielding molecular hydrogen and $[\text{Co}^{\text{II}}(\text{chel})]^0$. This reaction involved the homolytic cleavage of the intermediate $[\text{HCo}(\text{chel})]^0$. This cobalt(I) complex reacts rapidly with cobalt(III) species, giving again the cobalt(II) as the final product.



In the reduction of $[\text{Co}^{\text{III}}(\text{chel})(\text{OH})(\text{H}_2\text{O})]^0$ with CO in an alkaline medium ($\text{pH} \geq 13$), the formation of $[\text{Co}^{\text{II}}(\text{chel})]^0$ can thus be explained by a reaction between the cobalt(I) intermediate and the unchanged cobalt(III) complex.



This reaction is irreversible. In fact the $[\text{Co}^{\text{II}}(\text{chel})]^0$ does not disproportionate even in 1M-NaOH solution. In neutral or acid solution reaction (a) prevails even in the presence of methyl iodide. The evolution of molecular hydrogen which should occur by reaction (a) was not observed.* However, if molecular hydrogen were to be evolved, the redox balance would require that 1 molar equivalent of carbon monoxide would react per molar equivalent of cobalt(III) complex, whereas only 0.5 molar equivalent is consumed over the whole pH range. Both results can be reconciled assuming that the intermediate $[\text{HCo}(\text{chel})]^0$ reacts with the cobalt(III) complex:



* The evolution of H_2 was erroneously reported in G. Costa, G. Mestroni, G. Pellizer, G. Tazzer, and T. Licari, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 515.

⁷ G. Costa and G. Mestroni, *J. Organometallic Chem.*, 1968, **11**, 325.

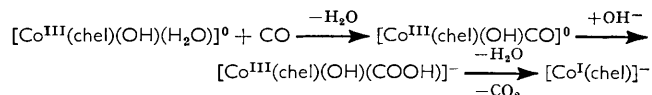
⁸ G. Costa, G. Mestroni, and G. Pellizer, *J. Organometallic Chem.*, 1968, **11**, 333.

⁹ R. Barnett, H. P. G. Hogenkamp, and R. H. Abeles, *J. Biol. Chem.*, 1966, **241**, 1483.

¹⁰ G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 1967, **89**, 143.

¹¹ J. Kruck and M. Noak, *Chem. Ber.*, 1964, **97**, 1693.

The formation of the $[\text{Co}^{\text{I}}(\text{chel})]^-$ from $[\text{Co}^{\text{III}}(\text{chel})(\text{OH})(\text{H}_2\text{O})]^0$ and carbon monoxide can be seen as a nucleophilic attack of the OH^- on an intermediate cobalt(III) carbonyl derivative, formation of an unstable carboxy-derivative which then decomposes giving the reduced complex and carbon dioxide.



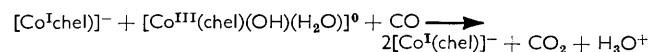
The reaction in methanol gives the corresponding stable methoxycarbonyl derivative. The easy decomposition of $[\text{HO}\cdot\text{CO}\cdot\text{Co}(\text{chel})\text{H}_2\text{O}]$ complexes could be related to the reaction of β -cyanoethyl-derivatives of cobalamin⁹ and of β -hydroxyalkyl and β -cyanoethyl-bis(dimethylglyoximate)cobalt complexes in alkaline media¹⁰ yielding acetaldehyde and acrylonitrile respectively. These reactions require the presence of an acidic hydrogen in the organic group bound to cobalt.

The attack of RO^- on carbonyl derivatives is a possible mechanism in the synthesis of alkoxy-carbonyl-derivatives of Mn, Ir, and Pt complexes.¹¹⁻¹³

The attack of OH^- by the same type of mechanism was assumed in the case of the reduction of $[\text{Mn}(\text{CO})_6]^+$ to $[\text{Mn}(\text{CO})_5]^-$ ¹¹ and of Rh^{III} to Rh^{I} in aqueous HCl .^{14,15} The same reaction was observed for the reduction¹⁶ of vitamin $\text{B}_{12\text{a}}$ to vitamin $\text{B}_{12\text{r}}$ with carbon monoxide. Analogous reactions were observed by absorption of carbon monoxide from L-Ag-OH and $\text{Hg}^{2+}, \text{H}_2\text{O}$.¹⁷ A stable carboxy-derivative $\text{IrCl}_2(\text{CO}_2\text{H})(\text{CO})(\text{PMe}_2\text{Ph})_2$ has also been obtained.¹⁸

By a preliminary kinetic investigation it was ascertained that the overall reaction is pseudo-first order in the Co^{III} complex at constant CO pressure and pH 8. However, at pH 10—13 an autocatalytic path was observed. The initial rate of reduction increases with decreasing pH , which excludes the possibility that either formation or decomposition of the $[\text{Co}(\text{chel})(\text{COOH})(\text{OH})]^-$ is the rate-determining step. Therefore formation of the carbonyl-derivative must be the rate-determining step.

The autocatalytic path could be explained by the overall reaction:



The detailed mechanism of this apparently termolecular reaction can be envisaged as involving a mixed valence bridge compound between the Co^{I} and

¹² L. Malatesta, M. Angoletta, and G. Caglio, 'Proc. 8th Int. Conf. on Coord. Chem.', Vienna, 1964.

¹³ H. C. Clark, R. K. Dixon, and W. J. Jacobs, *Chem. Comm.*, 1968, 548; H. C. Clark and W. J. Jacobs, *Inorg. Chem.*, 1970, **9**, 1229.

¹⁴ B. R. James and G. L. Rempel, *Chem. Comm.*, 1967, 158.

¹⁵ J. A. Stanko, G. Petrov, and C. K. Thomas, *Chem. Comm.*, 1969, 1100.

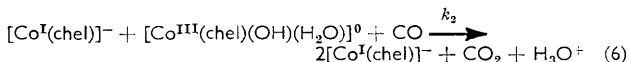
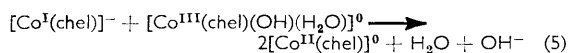
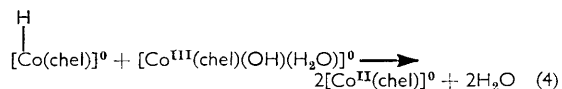
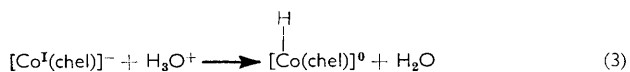
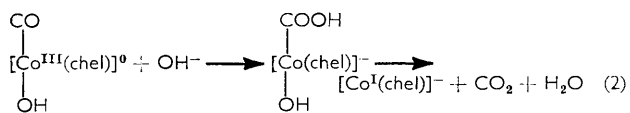
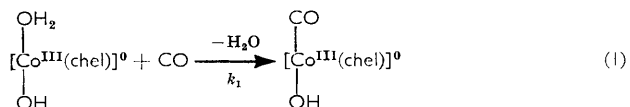
¹⁶ J. N. Bayston and M. E. Winfield, *J. Catalysis*, 1967, **9**, 217.

¹⁷ S. Nakamura and J. Halpern, *J. Amer. Chem. Soc.*, 1961, **83**, 4102; A. C. Harkness and J. Halpern, *ibid.*, p. 1258.

¹⁸ A. J. Deeming and B. L. Shaw, *J. Chem. Soc. (A)*, 1969, 443 and references cited therein.

Co^{III} complexes as was proposed by James and Rempel¹⁴ for the similar reaction of Rh^{III} complexes with CO (see below).

The course of the reaction can be now summarised as follows:



The pseudo-first-order reaction at pH 8 takes place mainly through reactions (1)–(4). The Co^I species is essentially consumed *via* reaction (3). At higher pH reactions (5) and (6) compete with reaction (3) and the rate of absorption of carbon monoxide is accounted for both by reactions (1) and (6). The latter is responsible for the autocatalytic process.

Reaction of Complex (VI) with Carbon Monoxide.—When the parent complex [Co^{III}(tn)Br₂]¹⁹ is dissolved in aqueous THF it easily aquates giving [Co^{III}(tn)(H₂O)₂]²⁺. This is in equilibrium with its dissociation products hydroxo-aquo- and dihydroxo-derivatives (pK₁ = 4.17, pK₂ = 7.70).

In the pH range 6–8 this cobalt(III) complex reacts with carbon monoxide giving, as final product, [Co^{II}(tn)(H₂O)₂]⁺ with the same stoichiometry as the above discussed complexes. On the other hand, at pH 13 two moles of carbon monoxide are absorbed and the uncharged carbonyl derivative [Co^I(tn)CO] can be isolated in high yields. In the pH range 8–13, intermediate stoichiometries were observed.

The reactivity of the key intermediate [Co^I(tn)H₂O] was investigated independently of the above reaction. This complex can be easily obtained in aqueous THF solution by reduction with a small excess of NaBH₄ starting from the [Co^{III}(tn)(H₂O)₂]²⁺ complex. Its formation is indicated by the intense blue colour of the solution. Up to pH 10 the [Co^I(tn)H₂O] is very labile giving [Co^{II}(tn)(H₂O)₂]⁺ as final product, while at pH 13 the blue colour is permanent in a nitrogen atmosphere. In the presence of *N*-methylimidazole or triphenylphosphine¹⁹ the corresponding Co^I complex was isolated

as a deep blue product stable in an atmosphere of nitrogen at room temperature. The reduction with NaBH₄ performed from pH 7 to 13 in the presence of carbon monoxide gives mixtures of [Co^I(tn)CO] and [Co^{II}(tn)(H₂O)₂]⁺ and the yield of the former increases with increasing pH. If [Co^{III}(tn)(H₂O)₂]²⁺ is reduced in the presence of methyl iodide and in the absence of carbon monoxide the [CH₃Co(tn)H₂O]⁺ complex is obtained in good yield at any pH.

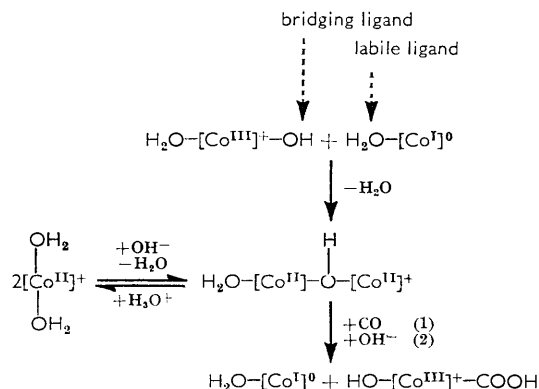
From the above results it can be concluded that [Co^I(tn)H₂O] clearly shows both the oxidative addition of CH₃I or H⁺ and co-ordinative addition reaction of CO.

The co-ordinative addition of CO gradually prevails over the oxidative addition of H⁺ with increasing pH. Furthermore the oxidative addition of H⁺ to [Co^I(tn)CO] is much slower than in the case of the corresponding aquo-complex.

In the pH range from 8 to 13 the autocatalytic path of the reaction of [Co^{III}(tn)(H₂O)₂]²⁺ with CO is even more pronounced than in the case of the complexes (I)–(IV). Moreover an induction time was always observed. Addition of [Co^I(tn)CO] shortens the induction time at pH 13.

It was previously observed¹⁹ that the [Co^{II}(tn)(H₂O)₂]⁺ complex disproportionates in alkaline solution giving equimolecular mixtures of the corresponding Co^I and Co^{III} complexes. The same phenomenon was found for the cobalt dimethylglyoximates.²⁰ When 1 mmol of [Co^{III}(tn)Br₂] is treated with CO at pH 8, the Co^{II} complex is formed quantitatively by absorption of 0.5 mol of CO. If at this stage the alkalinity is adjusted to pH 13, the absorption of CO starts again without any induction time and continues autocatalytically until complete formation of [Co^I(tn)CO] and absorption of 1.5 mmol of CO. These results suggest that the induction period is due to the low reactivity of the parent Co^{III} complex toward CO and that even in the case of tn complexes the autocatalysis arises from the reaction of parent Co^{III} with Co^I species.

The role of Co^I intermediate in the autocatalysis could be tentatively explained by the following scheme.



This scheme implies a redox process in a rapidly formed binuclear bridged complex in which the carbon monoxide

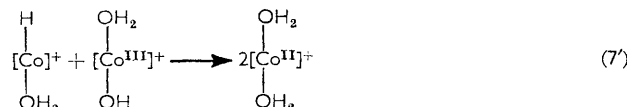
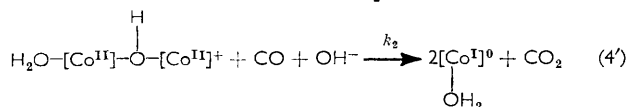
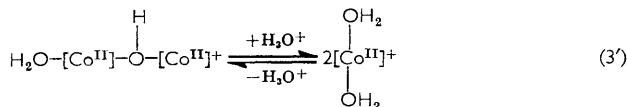
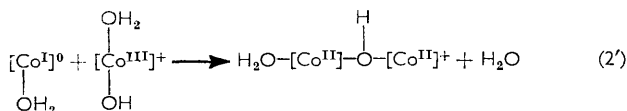
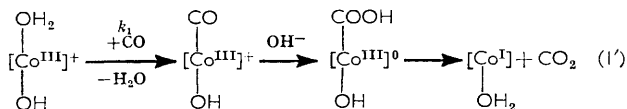
¹⁹ G. Costa, G. Mestroni, and E. de Savognani, *Inorg. Chim. Acta*, 1969, **3**, 322.

²⁰ G. N. Schrauzer and R. J. Windgassen, *Chem. Ber.*, 1966, **99**, 602.

can be easily co-ordinated and converted into an equimolecular mixture of Co^{I} and $\text{Co}^{\text{III}}\text{-COOH}$.

This scheme accounts for the autocatalysis, the reactivity of Co^{II} with CO in alkaline medium and for the disproportionation reaction.

From the above considerations the reaction scheme can be now written as follows:



[] indicates the tn monoanion ligand

At pH 13 the reduction to $[\text{Co}^{\text{I}}(\text{tn})\text{CO}]^0$ takes place through reactions (1')—(5'). At lower pH values the reactions (3') and (6') compete with the reactions (4') and (5') respectively. At pH 8 reaction (5') is negligible and only Co^{II} is formed as final product.

The formal oxidation states of the examined cobalt complexes which react with CO appear to be the Co^{III} and Co^{II} (only as a binuclear complex) except for the dimethylglyoximates which were proposed to react only as Co^{II} complexes.²¹

The results published for the dimethylglyoximates²¹ including the induction time and autocatalysis would be in agreement with the scheme proposed here for tn complexes. The diaquobis(dimethylglyoximato)cobalt(III) complex is slowly reduced by CO. On the other hand, the aquocobalamine seems to behave more like the derivative of the salen type. In fact Bayston and Winfield¹⁶ pointed out that the reduction is pseudo-first order with respect to vitamin $\text{B}_{12\text{a}}$ (Co^{III}). Induction time and autocatalysis were not observed (neutral and acid solution) as in the case of $[\text{Co}^{\text{III}}(\text{salen})(\text{H}_2\text{O})_2]^+$.

²¹ Lian-Pin Lee and G. N. Schrauzer, *J. Amer. Chem. Soc.*, 1968, **90**, 5274.

Bis-organometallic Derivatives of Complex (VI).—It was previously reported²² that derivatives of the type $[\text{Co}(\text{tn})\text{R}_2]$ ($\text{R} = \text{CH}_3$ or PhCH_2) can be obtained at pH 13 by reaction of the corresponding diaquo-complexes with CO in the presence of organic halides (see Experimental section). We have found that the cobalt(I) carbonyl complex undergoes an oxidation addition reaction with alkyl halides, in benzene or neutral aqueous THF solution, to give the corresponding mono-organometallic complex. The bis-organometallic complexes are obtained in alkaline aqueous THF solution by the action of alkyl halide on the cobalt(I) carbonyl complex or the mono-organometallic derivative. By the latter reaction a different organic radical can be introduced in the *trans*-position (see Table 1).

The existence of the species $\text{R}[\text{Co}]^-$ which undergoes oxidative addition is indicated by the formation of asymmetrical bis-organometallic derivatives.

Side reactions were observed by the reduction of mono-organometallic derivatives in the absence of organic halides with CO in alkaline solution: (a) If carbon monoxide absorption is stopped before the reaction is complete, the symmetrical bis-organometallic derivative is obtained. (b) In the presence of an excess of CO the main product is the cobalt(I) carbonyl complex.

The bisorganometallic complexes can also be obtained by these different routes (see Experimental section): (a) Grignard reaction on $[\text{Co}^{\text{III}}(\text{tn})\text{Br}_2]^0$. (b) Reduction of the cobalt(III) complex or of the mono-organometallic derivatives with excess NaBH_4 in the presence of RX . (c) Reduction of mono-organometallic derivatives with Na-Hg in THF followed by addition of RX .

Intermediates of the type $[\text{R-Co}]^-$ obtained by a two-electron reduction of $[\text{R-Co-H}_2\text{O}]^+$ could be involved in the synthesis of $\text{CH}_3\text{CO}_2\text{H}$ from the methylcobalamin and CO_2 .²³ We are currently investigating all these aspects of the problem on the model complexes.

EXPERIMENTAL

Reduction of Cobalt(III) Complexes of the Dianions with Carbon Monoxide.— $[\text{Co}(\text{salen})(\text{OH})\text{H}_2\text{O}]$ (0.36 g, 1 mmol) was dissolved in deaerated aqueous THF (50%) and CO was bubbled through the solution for 2 min in the dark, at room temperature and atmospheric pressure.

The colour of the solution changed from brown to brownish-red, after 15 min a microcrystalline red-brown precipitate was formed and identified (analysis, i.r. spectrum) as $[\text{Co}^{\text{II}}(\text{salen})]$.

Carbon dioxide in the exit gas was identified by reaction with $\text{Ba}(\text{OH})_2$. Formation of hydrogen was excluded by g.c. analysis. The same reaction was performed starting from 1 mmol of $[\text{Co}(\text{salen})(\text{OH})\text{H}_2\text{O}]$ in a buffered mixture of THF (25 ml) and water (25 ml) at pH 4, 6, 7, 8, 10, and 13. In each instance the product was isolated and identified as $[\text{Co}^{\text{II}}(\text{salen})]$. Complex (II) (0.372 g, 1 mmol) was dissolved in aqueous THF (50 ml), treated with NaOH (0.2 g),

²² G. Costa, G. Mestroni, T. Licari, and E. Mestroni, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 561.

²³ H. P. C. Hogenkamp, *Ann. Rev. Biochem.*, 1969, **37**, 225, and references cited therein.

and saturated with CO at room temperature and atmospheric pressure. An orange solid was precipitated and collected after concentration of the solution by evaporation *in vacuo*. The product was identified as *NN'*-ethylenebis(α -methylsalicylideneiminato)cobalt(II).

$[(\text{HO})\text{Co}(\text{saloph})\text{H}_2\text{O}]$ (0.49 g, 1 mmol) was treated by the same procedure with CO; the brown precipitate obtained was identified as $[\text{Co}^{\text{II}}(\text{saloph})\text{H}_2\text{O}]$.

$[\text{BrCo}(\text{bae})(\text{Ph}_3\text{P})]$ (1.25 g, 2 mmol) was dissolved in a mixture of THF (75 ml) and H_2O (25 ml), NaOH (0.1 g) added and then saturated with CO. After 20 min the yellow solution was concentrated by evaporation *in vacuo* and the yellow solid was recrystallised from benzene and identified as $[\text{Co}^{\text{II}}(\text{bae})]$.

Reduction of the Cobalt(III) Complexes with CO in the Presence of Methyl Iodide.— $[(\text{HO})\text{Co}(\text{salen})\text{H}_2\text{O}]^0$ (0.36 g, 1 mmol) was dissolved in a mixture of THF (50 ml) and water (30 ml) and treated with solid NaOH (1 g) and

When the same reaction was performed in a buffered solution at pH 7 and 8 the $[\text{Co}^{\text{II}}(\text{tn})(\text{H}_2\text{O})_2]^+$ was obtained as the main product. It was precipitated and identified as the tetraphenylborate.¹⁹

The formation of the cobalt(I) carbonyl derivative, as a by-product, was shown by extraction into benzene, in which the complex shows the characteristic intense blue colour. At pH 10 the cobalt(I) carbonyl derivative was obtained as the main product.

Reduction by NaBH_4 in the Absence of CO.— $[\text{Co}(\text{tn})\text{Br}_2]^0$ (0.5 g, 1 mmol) was dissolved in THF (25 ml)– H_2O (25 ml) buffered solution at pH values of 13, 10, and 7 and then reduced with an excess of NaBH_4 . At pH 13 the blue colour characteristic of cobalt(I) derivative was noticed lasting for ca. 0.5 h. At pH 10 and 7 the cobalt(I) colour was fleeting and the final product was $[\text{Co}^{\text{II}}(\text{tn})(\text{H}_2\text{O})_2]^+$.

The same reaction carried out at pH 13 in the presence of *N*-methylimidazole gave, after evaporation of the solvent,

Complexes	C (%)		H (%)		N (%)	
	Found	Calc.	Found	Calc.	Found	Calc.
$[\text{Co}^{\text{I}}(\text{tn})\text{CO}]^0$	43.55	44.2	5.85	5.85	17.0	17.2
$[\text{Co}^{\text{I}}(\text{tn})(\text{C}_4\text{H}_8\text{N}_2)]^0$	46.7	47.35	6.75	6.65	21.9	22.1
$[\text{Co}^{\text{III}}(\text{tn})\text{Me}_2]^0$	47.95	47.55	7.80	7.7	17.15	17.1
$[\text{Co}^{\text{III}}(\text{tn})(\text{C}_7\text{H}_7)_2]^0$	62.2	62.5	6.90	6.9	11.65	11.65
$[\text{Co}^{\text{III}}(\text{tn})(\text{Ph}_2)]^0$	61.05	61.05	6.45	6.45	12.3	12.4
$[\text{Co}^{\text{III}}(\text{tn})(\text{Me})\text{Ph}]^0$	55.10	55.4	7.15	6.95	14.4	14.35
$[\text{Co}^{\text{III}}(\text{tn})(\text{C}_7\text{H}_7)\text{Ph}]^0$	61.7	61.8	6.75	6.7	12.15	12.0

methyl iodide (2 ml). The solution was saturated with CO. After 24 h an orange precipitate was obtained, and identified as $[\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}]$ (analysis, i.r. spectrum).

The same amount of $[\text{HOCO}(\text{salen})\text{H}_2\text{O}]$ was reacted in buffered solution THF– H_2O (50%). At pH 7 only the $[\text{Co}^{\text{II}}(\text{salen})]$ and at pH 13 only $[\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}]$ were isolated.

Complex (II) (0.372 g, 1 mmol) was dissolved in aqueous THF (50%), treated with NaOH (0.3 g) and with CH_3I (2 ml) and saturated with CO. The product was isolated as above, crystallised from CH_2Cl_2 – CH_3OH and identified as $[\text{CH}_3\text{Co}(\text{NN}'\text{-ethylenebis}(\alpha\text{-methylsalicylideneiminato})\text{-CH}_3\text{OH})]$.

The complex $[\text{Co}^{\text{I}}(\text{salen})]^- \text{Na}^+$ (1 mmol) treated in anhydrous THF with 1 mmol of $[\text{ICo}^{\text{III}}(\text{salen})]^0$ gave 2 mmol of $[\text{Co}^{\text{II}}(\text{salen})]^0$.

Reduction of Cobalt(III) Complexes of the 2,3,9,10-Tetramethyl-1,4,8,11-tetra-azaundeca-1,3,8,10-tetraen-11-ol-1-olato-anion with Carbon Monoxide.— $[\text{Co}(\text{tn})\text{Br}_2]$ (0.229 g, 0.5 mmol) was dissolved in a mixture of THF (50 ml) and H_2O (35 ml) and treated with 0.3 g NaOH. After saturation with CO the solution became deep blue. By evaporation *in vacuo* a microcrystalline precipitate was obtained. It was filtered in a nitrogen atmosphere, washed with deaerated water, and dried *in vacuo*. Analysis and i.r. spectra ($\nu_{\text{CO}} = 1950 \text{ cm}^{-1}$) agree with the formula $[\text{Co}^{\text{I}}(\text{tn})\text{CO}]^0$. The diamagnetic product is soluble in benzene, diethyl ether, THF, only slightly soluble in ethanol and insoluble in water. The solution of the complex is quite sensitive to oxygen. The product dissolved in buffered solution of THF (50 ml) and H_2O (50%) at pH 7 was found to be stable for several days.

Reduction by NaBH_4 in the Presence of CO.—The same product was obtained from $[\text{Co}(\text{tn})\text{Br}_2]$ (0.5 g, 1 mmol) dissolved in THF (50 ml)– H_2O (35 ml) and treated with 0.3 g NaOH. When the solution had been saturated with CO an excess of NaBH_4 was added.

a deep blue microcrystalline precipitate identified as $[\text{Co}^{\text{I}}(\text{tn})(\text{C}_4\text{H}_8\text{N}_2)]$.

Organometallic Derivatives formed by Reduction of $[\text{Co}^{\text{III}}(\text{tn})\text{Br}_2]$ with CO in the Presence of Organic Halides, $[(\text{CH}_3)_2\text{Co}(\text{tn})]$.— $[\text{Co}(\text{tn})\text{Br}_2]^0$ (0.229 g, 0.5 mmol) was dissolved in THF (50 ml)– H_2O (35 ml) and NaOH (0.3 g, 7.5 mmol) and CH_3I (2 ml) were added to the solution. After saturation with CO the colour slowly turned to orange-yellow. Upon concentration under reduced pressure, a microcrystalline solid was precipitated; this was recrystallised from water–acetone. The product was soluble in ether and benzene, but insoluble in water.

$[(\text{C}_7\text{H}_7)_2\text{Co}(\text{tn})]^0$.—The orange crystalline benzyl-derivative was prepared by the same procedure.

Bis-organometallic Derivatives formed by Reduction of $[\text{RCo}(\text{tn})]^+$ with CO in the Presence of Organic Halides.— $[(\text{C}_7\text{H}_7)\text{Co}(\text{tn})\text{H}_2\text{O}]^+\text{ClO}_4^-$ (0.5 g, 1 mmol) was dissolved in aqueous THF (50%) (100 ml), treated with NaOH (0.1 g), $\text{C}_7\text{H}_7\text{Cl}$ (0.5 ml), and saturated with CO. By evaporation of the solvent, the $[(\text{C}_7\text{H}_7)_2\text{Co}(\text{tn})]^0$ complex was precipitated. It was recrystallised from water–acetone.

$[(\text{CH}_3)_2\text{Co}(\text{tn})]$ was obtained by the same procedure from $[\text{CH}_3\text{Co}(\text{tn})\text{H}_2\text{O}]^+\text{ClO}_4^-$ and CH_3I .

$[(\text{C}_6\text{H}_5)\text{Co}(\text{tn})\text{H}_2\text{O}]^+\text{ClO}_4^-$ (0.25 g, 0.5 mmol) was dissolved in THF (50 ml)–water (35 ml) and treated with NaOH (0.3 g, 7.5 mmol) and with CH_3I (2 ml). The solution was saturated with CO. After 4 h the solvent was evaporated and the microcrystalline product $[(\text{C}_6\text{H}_5)(\text{CH}_3)\text{Co}(\text{tn})]^0$ was recrystallised from aqueous acetone.

When the reaction was carried out in the absence of CH_3I the solution became intensely blue after 2 h. Successive addition of CH_3I (2 ml) gave, instead of the methyl-phenyl-derivative, the orange microcrystalline dimethyl-derivative identified by analysis and i.r. spectrum.

$[(\text{C}_6\text{H}_5)(\text{C}_7\text{H}_7)\text{Co}(\text{tn})]^0$ was prepared from the phenyl derivative in the same way. When the reduction was

performed in the absence of C_7H_7Cl and the latter successively added to the blue Co^I solution the dibenzyl-derivative was obtained.

The same product resulted also starting from the $[CH_3Co(tn)]^+ClO_4^-$ under the same experimental conditions as described above, when the C_7H_7Cl was added after 12 h.

Organometallic Derivatives from $[Co^I(tn)CO]$.—The complex $[Co^I(tn)CO]$ (1 mmol) dissolved in deaerated benzene (50 ml) was treated with CH_3I (1 ml). After 1 h an orange-yellow solution was obtained. By addition of aqueous $NaClO_4$ and evaporation of the solvent the $[CH_3Co(tn)H_2O]^+ClO_4^-$ was isolated. The carbon monoxide evolved was identified by g.l.c.

The same reaction occurs also in neutral aqueous THF solution. The $[(CH_3)_2Co(tn)]$ was formed instead at pH 13.

Reduction of $[RCo(tn)H_2O]^+$ with CO.— $[CH_3Co(tn)H_2O]^+ClO_4^-$ (0.430 g, 1 mmol) was dissolved in THF (100 ml)– H_2O (70 ml), treated with $NaOH$ (0.6 g), and saturated with CO. After 12 h the solvent was evaporated and the microcrystalline, deep blue, carbonyl-derivative $[Co^I(tn)CO]^0$ was filtered off, washed with water under a nitrogen atmosphere, and identified as previously described.

$[C_6H_5Co(tn)H_2O]^+ClO_4^-$ (1 g, 2 mmol) was treated with CO by exactly the same procedure. The Co^I carbonyl derivative was filtered off from the concentrated solution under nitrogen. From the filtered solution left in contact with air a small amount of a yellow microcrystalline solid was obtained. It was recrystallised from aqueous acetone and identified as the $[(C_6H_5)_2Co(tn)]^0$.

$[CH_3Co(tn)H_2O]^+ClO_4^-$ (0.860 g, 2 mmol) was treated as above but as soon as the solution turned green the carbon monoxide was removed by a stream of nitrogen. The solution was set aside overnight. The solution turned orange and after concentration gave an orange-yellow precipitate identified as $[(CH_3)_2Co(tn)]^0$.

$[(C_6H_5)Co(tn)H_2O]^+ClO_4^-$ gave by the same procedure the $[(C_6H_5)_2Co(tn)]^0$ complex.

Bis-organometallic Derivatives via Reduction with $NaBH_4$ or $Na-Hg$ and Reaction with Organic Halides or via Grignard

Reaction.—The following procedures are reported as examples of general methods. $[Co^{III}(tn)I_2]^0$ (2 g, 4 mmol) was suspended in aqueous EtOH (50%, 100 ml) and treated with C_7H_7Cl (1 ml) and an excess of $NaBH_4$ under nitrogen. The bis-benzyl derivative $[(C_7H_7)_2Co(tn)]^0$ was immediately formed as an orange-red precipitate.

Starting from $[Co^{III}(tn)I_2]^0$ and CH_3I the bis-methyl-derivative $[(CH_3)_2Co(tn)]^0$ was obtained while by the same procedure from $[(C_6H_5)Co(tn)H_2O]^+ClO_4^-$ the $[(C_6H_5)(CH_3)Co(tn)]$ was formed.

$[(C_6H_5)Co(tn)I]^0$ was suspended in anhydrous THF (100 ml) and reduced with $Na-Hg$. The blue solution was withdrawn under nitrogen and CH_3I was added at $-80^\circ C$. An orange solution was formed. By addition of water and concentration of the solution an orange solid was precipitated and identified as $[(C_6H_5)(CH_3)Co(tn)]^0$.

$[Co(tn)Br_2]^0$ (0.92 g, 2 mmol) was suspended in anhydrous THF (100 ml), 8 mmol of $RMgX$ ($R = CH_3, C_6H_5,$ or $C_6H_5CH_2$) were added under nitrogen at $-80^\circ C$ yielding an orange solution.

The solution was poured into water, neutralised, and concentrated by evaporation of THF. The corresponding bis-organometallic derivative was obtained in each case and recrystallised from aqueous acetone.

Carbon Monoxide Absorption Measurements.—The reactions were carried out in a reactor thermostatted at $25^\circ C$. The carbon monoxide absorption or its rate of absorption were determined by a gasometric burette connected to the reactor. 50 ml in the range from 10^{-3} to $10^{-2}M$ solutions of the complexes were used, the solvent being formed by mixing equal amounts of THF and the suitable buffers.

Buffers.—The following buffers were used: pH 4, 5, phthalate– $NaOH$ mixture; pH 6, 7, 8, KH_2PO_4 – $NaOH$ mixture; pH 10, boric acid– $NaOH$ mixture; pH 13, solution 0.1M– $NaOH$.

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