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ELECTRON TRANSFER REACTIONS INVOLVING COBALT(II) AND ORGANOMETALLIC COBALT(III) SCHIFF-BASE COMPLEXES

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Summary

Group exchange reactions have been studied between organocobalt(III) derivatives containing Schiff-base ligands and related cobalt(II) complexes. Reactions are fast in DMSO for cobalt(III) alkyls but very slow for fluoroalkyl and aryl derivatives. Measurably slow reactions occur with CF_3CH_2 substituents.

A mechanism is proposed involving nucleophilic attack of a cobalt(II) species on the carbon atom attached to cobalt(III).

Introduction

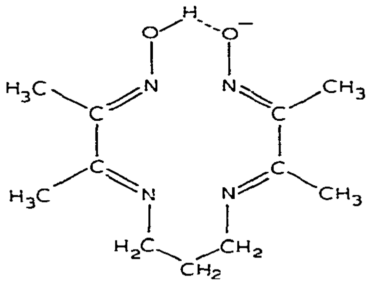
A number of reactions have been reported in which an alkyl group attached to a Co^{III} ion can be transferred to another metal or to another cobalt ion. Thus alkyl groups can be removed from alkyl cobalamins [1,2] and cobaloximes [3,4] by reaction with Hg^{II}, $Hg—CH_3$ species being formed. These reactions do not involve formal redox reactions and bimolecular, electrophilic substitution reactions have been suggested for the mechanistic pathways involved [2-4].

Costa and co-workers [5] have also demonstrated other $Co^{III}—R/Co^{III}$ exchanges by showing that $(CH_3)_2Co^{III}[(DO)(DOH)pn]$ can methylate other Co^{III} chelate complexes such as $[Co^{III}(Salen)(H_2O)_2]^+$, and $[Co(Acacen)(H_2O)_2]^+$. Alkyl exchange has also been reported [6] to be general between $Co^{III}(Chel)—CH_3$ and $[Co^{III}Chel(H_2O)_2]^+$ where Chel represents a tetradentate ligand of the Schiff-base type.

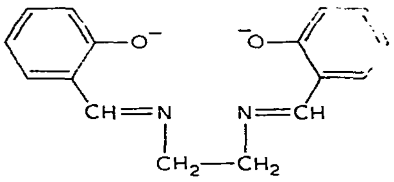
Structures for the ligands mentioned in the text are given in Table 1.

Electron transfer reactions are well established in which a ligand, initially coordinated to one metal ion, is transferred to the second metal ion involved in the reaction. In many instances the ligand concerned is believed to take part in the formation of a bridged intermediate [7]. The ligands previously known to be transferred in such reactions have included halide or similar ions or organic acid anions.

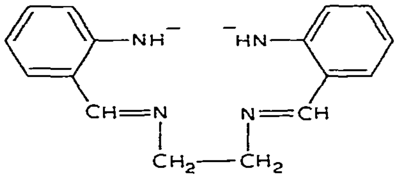
TABLE 1
STRUCTURES FOR LIGANDS



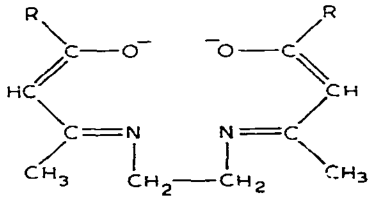
[(DO) (DOH) pn]



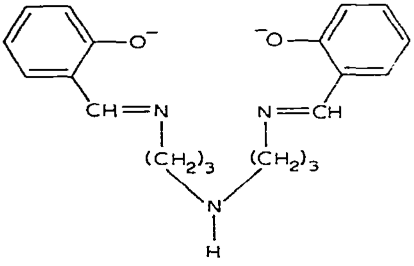
Salen



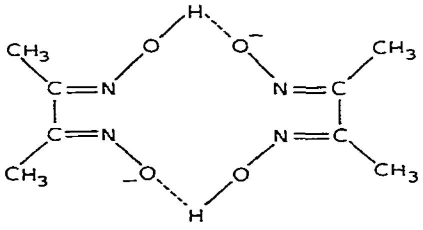
Amben



R = CH_3 , Acacen
R = CF_3 , Tfacen

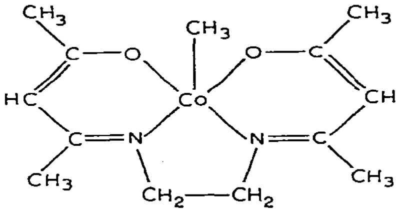


Saldpt



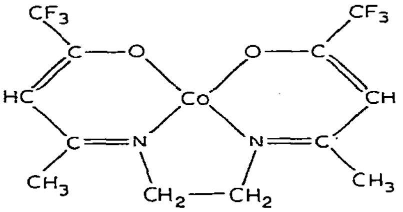
$(Dmg)_2$

It has now been established that rapid electron transfer can occur between various cobalt(III) organometallic compounds and related cobalt(II) complexes which is accompanied by the exchange of the organic group between the two cobalt ions. A preliminary communication [8] reported that Co^{III} (Acacen—CH_3) (I) reacted rapidly with Co^{II}(Tfacen) (II) at room temperature in dimethyl sulphoxide to form the products Co^{II} (Acacen) and Co^{III} (Tfacen—CH_3), *i.e.* a methyl group has exchanged between the cobalt ions, accompanying the formal electron transfer.



Co(Acacen—CH_3)

(I)



CoTfacen

(II)

$$Co^{III}(Acacen—CH_3) + Co^{II}\,Tfacen \rightleftharpoons Co^{II}\,Acacen + Co^{III}(Tfacen—CH_3)$$

The reverse reaction also proceeded readily.

This paper reports further investigations of the scope of these electron transfer reactions. Subsequent reports of formal electron transfer reactions involving Co^{I} and Co^{III} species have been made by Costa, Mestroni and Cocevar [5] and Dodd and Johnson [9].

Experimental

Co^{II} complexes were prepared by literature methods, *viz.* Co(Tfacen) [10], Co(Acacen) [11], Co(Salen) [12], Co(Amben) [13], $Co(Dmg)_2(H_2O)_2$ [14], Co(Saldpt) [15] (yellow brown product, dehydrated before use). Co^{III} alkyls [16,17] fluoroalkyls [10], sulphonyl [18], and acyl compounds [16] with Schiff-base ligands were prepared by the general method introduced independently by Costa and Mestroni [16], and Calderazzo and Floriani [19], in which an appropriate cobalt(II) complex was reduced with sodium sand or sodium amalgam in dry tetrahydrofuran followed by the addition of an appropriate organic halide. The resulting cobalt(III) compound was precipitated by water and subsequently recrystallised from aqueous methanol. The compounds were isolated in the main as aquo derivatives. Alkyl cobaloximes [20] and Co(Saldpt—CH_3) [21] were prepared by published methods.

Several mixed fluoro-hydrocarbon alkyls have been prepared and not previously reported, *viz.* $CF_3CH_2Co(Acacen)H_2O$, $CF_3CH_2Co(Tfacen)H_2O$ and $CH_2FCo(Acacen)H_2O$. They are all red crystalline products, prepared by the addition of CF_3CH_2I and CHF_2Cl to solutions of the Co^{I} species produced by Na/Hg reduction of the Co^{II} chelates in THF.

Exchange experiments

^1H and ^{19}F NMR spectra were measured using a Varian A-56-60A spectrometer.

1. *^{19}F resonance method.* Co^{II}(Tfacen) displayed a ^{19}F NMR spectrum in dimethyl sulphoxide (DMSO) consisting of a single broad peak due to the CF_3 fluorine atoms at δ 56 ppm (relative to $CFCl_3$). This resonance had been shifted from the region where the ^{19}F resonances of the diamagnetic Co^{III} (Tfacen) organometallic compounds occurred, ca. 70 ppm. Thus, both Co^{II} (Tfacen) and any Co^{III}(Tfacen—R) organometallic could be readily distinguished when present together in dimethyl sulphoxide solution. In order that the complexes could be detected, however, it was necessary to have relatively high concentrations of the species in solution particularly for Co^{II}(Tfacen). The variation in solubility among the Co^{III} compounds complicated the measurements and in a number of instances saturated solutions of unknown concentration had to be employed to obtain signals of the various fluorine-containing cobalt complexes. In general, however, the solubility of the compounds restricted the concentration range to 0.2 - 0.25 *M*.

The experiments were conducted by dissolving weighed amounts of each participating complex Co^{II} and Co^{III} in DMSO under a nitrogen atmosphere in glass tubes suitable for making NMR measurements. The tubes were then evacuated and sealed.

The shortest time between making up the solutions and completing an NMR spectral measurement in the ^{19}F mode was ca. 4 min. In the majority of systems examined attention was directed to identifying the particular fluorine-containing cobalt complex which was formed as a result of the appropriate exchange reaction. In the reactions involving Co^{II}(Tfacen) and Co^{III}(Acacen—R) when R = CH_3, C_2H_5, C_3H_7, C_4H_9, quantitative measurements of the equilibrium concentrations of the components were made.

Mixtures containing equimolar concentrations (0.25 *M*) of the Co^{II} and Co^{III} compounds in DMSO were prepared in sealed tubes under nitrogen and left for several hours at 20° to ensure that equilibrium had been achieved. The ^{19}F spectra of the solutions were then measured and the ratio of the areas under the ^{19}F resonance peaks obtained by integration using the spectrometer. These ratios were taken as proportional to the concentrations of the various ^{19}F containing species in the systems. If *x* represents the mole fraction of Co^{II}(Tfacen) converted to Co^{III}(Tfacen—R), then:

$$\underset{1-x}{\mathrm{Co^{II}(Tfacen)}} + \underset{1-x}{\mathrm{Co^{III}(Acacen{-}R)}} \rightleftharpoons \underset{x}{\mathrm{Co^{III}(Tfacen{-}R)}} + \underset{x}{\mathrm{Co^{II}(Acacen)}}$$

$$K = \frac{[(\mathrm{Co(Tfacen{-}R)})]\cdot[\mathrm{Co(Acacen)}]}{[(\mathrm{Co(Tfacen)})]\cdot[\mathrm{Co(Acacen{-}R)}]} = \frac{[\mathrm{Co(Tfacen{-}R)}]^2}{[\mathrm{Co(Tfacen)}]^2} = (\text{integrated ratio } \mathrm{Co^{III}/Co^{II}})^2$$

The values of *K* initially reported [8] were based on the average of 10 integrations carried out on the spectrum of each reaction mixture. The low solubility of the fluorine-containing complexes used in these studies made it difficult to obtain ^{19}F spectra and it was therefore necessary to use high amplitudes with consequent high S/N ratios to obtain the spectra. Attempts to reduce the noise level by increasing the power input to the sample caused saturation of signals particularly those due to Co^{III} complexes containing fluorine. This resulted in large errors in the relative integrals obtained so that the ratios of concentrations of Co^{II} and Co^{III} fluorine-containing species obtained from the integral ratios were considerably in error.

Subsequently a computer of average transients (Varian CAT 1024) was used in obtaining the integrations, thus allowing much better signal to noise ratios to be achieved and notably lowering or in several cases completely eliminating the saturation of the Co^{III} (Tfacen—R) signals by enabling much lower radio frequency power inputs to be used. Analysis of standard mixtures of Co^{II}(Tfacen) and Co^{III}(Tfacen- CH_3) gave an upper limit for the error in proportionality to concentration in these latter measurements of ± 20%.

2. *Separation by thin layer chromatography.* The Co^{II} complexes used in this work do not elute readily when absorbed from DMSO solution on to silica-coated TLC plates. However, many of the Co^{III} organometallic compounds can be eluted with methanol/ether mixtures (1/9) and can be identified in mixtures from their R_F values. The method is slow and of limited use but was applied to separate the Co^{III} complexes from the reaction mixture containing known concentrations of Co^{II}(Tfacen) and Co^{III}(Acacen—CH_3). The compounds Co^{III}(Tfacen—CH_3) and Co^{III}(Acacen—CH_3) could be readily separated from the Co^{II} complexes and each other on silica-coated plates. The Co^{III} containing portions of the plate were separately extracted and analysed for Co content by atomic absorption spectroscopy.

In three successive runs K_{eq} values were measured as 1.13, 1.09, 1.19 averaging 1.14 at room temperature, 20°.

The method was also applied to the separation of the products of reaction of $Co(Dmg)_2CH_3.Py$ and Co^{II}(Tfacen).

Results and discussion

The results of the reactions investigated are given in Table 2. Reactions described as "fast" reached an equilibrium position or showed complete exchange of a group between cobalt species in the time taken to mix solutions of the reactants and measure the ^{19}F NMR spectrum of the mixture, ca. 4 - 5 mins. "Slow reactions" showed increasing concentrations of the species formed by group exchange when a reaction mixture was examined at intervals of time. In each such case measurement was extended until no further change in composition of the mixture could be detected.

"No reaction" means that NMR spectroscopic examination, together with thin layer chromatographic analysis of a reaction mixture did not show the presence of any compounds formed by a group exchange process. Any such reaction mixture was analysed at intervals up to 3 weeks after its preparation.

In general it can be concluded that alkyl groups can exchange very rapidly between cobalt(II) and -(III) ions coordinated with a variety of polydentate

TABLE 2

ELECTRON TRANSFER REACTIONS BETWEEN Co^{II} AND Co^{III} COMPLEXES IN DIMETHYL SULPHOXIDE

$Co^{II}(Chel) + Co^{III}(Chel'{-}R) \rightarrow Co^{II}(Chel') + Co^{III}(Chel{-}R)$

Co^{II}(Chel)	Co^{III}(Chel')[a]	R	Rate	Comment
Tfacen	Acacen	CH_3	Fast	Equilibrium reached
Acacen	Tfacen	CH_3	Fast	Equilibrium reached
Tfacen	Acacen	C_2H_5	Fast	Equilibrium reached
		C_3H_7	Fast	Equilibrium reached
		C_4H_9	Fast	Equilibrium reached
		CF_3	No reaction	
		CHF_2	No reaction	
		C_2F_5	No reaction	
		C_3F_7	No reaction	
		C_6H_5	No reaction	
		$COCH_3$	Slow	$t_{1/2}$ ca. 4 h at 0.12 *M*
Acacen	Tfacen	CH_2CF_3	Slow	$t_{1/2}$ ca. 3 days at 0.12 *M*
Tfacen	Salen	CF_3	No reaction	
		C_2F_5	No reaction	
		C_3F_7	No reaction	
Salen	Tfacen	C_3F_7	No reaction	
		C_6H_5	No reaction	
		C_2H_5	Fast	Equilibrium reached
	Bzacen	C_2H_5	Fast	Equilibrium reached
Acacen	Salen	C_2H_5	Fast	Equilibrium reached
Saldpt	Tfacen	CH_3	No reaction	No products detectable
Tfacen	Saldpt	CH_3	Fast	100% Exchange
$(Dmg)_2(H_2O)_2$	Tfacen	C_3H_7	Fast	Ca. 99% complete exchange
Tfacen	$(Dmg)_2Py$	CH_3	Fast	< 1% Co(Tfacen—CH_3)
Amben	Tfacen	CH_3	No reaction	
Pt^{II}(Salen)		CH_3	No reaction	
Fe^{II}(Salen)		CH_3	No reaction	Paramagnetic M^{II} species prevented ^{19}F resonances being detected. TLC was used to search for Co^{II} species
Mn^{II}(Salen)		CH_3	No reaction	

[a] Except for $CH_3Co(Dmg)_2Py$ all the Co^{III} organo compounds were obtained as aquo derivatives $RCo(Chel')H_2O$. When dissolved in DMSO the water was readily displaced by the solvent to form $RCo(Chel') \cdot DMSO$ as evidence by the single water ^1H resonance indicative of free H_2O.

Schiff-base ligands in dimethyl sulphoxide. The type of ligand coordinated to cobalt can greatly influence the extent of exchange. Thus an equilibrium mixture is obtained when Co^{II}(Tfacen) reacts with Co^{III}(Acacen—CH_3) or when the reverse reaction is carried out, i.e. Co^{II}(Acacen) and Co^{III}(Tfacen—CH_3). However, Co^{II}(Tfacen) reacts so rapidly and completely with Co^{III}(Saldpt—CH_3) that only the exchange product Co^{III}(Tfacen—CH_3) and Co^{II}(Saldpt) can be detected in the final solution. No evidence can be obtained from ^{19}F resonance examination or from TLC that the reverse reaction of Co^{II}(Saldpt) with Co^{III}(Tfacen—CH_3) proceeds at all, in line with the equilibrium position being displaced completely in favour of these two compounds.

$$Co^{II}(Tfacen) + Co^{III}(Saldpt{-}CH_3) \rightarrow Co^{II}(Saldpt) + Co^{III}(Tfacen{-}CH_3)$$

In a similar reaction $Co^{II}(Dmg)_2(H_2O)_2$ was found to react almost completely with Co^{III}(Tfacen—C_3H_7) forming Co^{II}(Tfacen) and $Co^{III}(Dmg)_2C_3H_7$. Less than 1% of Co^{III}(Tfacen—C_3H_7) could be detected at equilibrium.

The nature of the alkyl group is also of importance, however, in determining the position of equilibrium as can be seen from the equilibrium constants given below for the reaction

$$Co^{II}(Tfacen) + Co^{III}(Acacen{-}R) \rightleftharpoons Co^{III}(Tfacen{-}R) + Co^{II}(Acacen)$$

$$R = CH_3, K_{eq}\ (44°) = 0.90; C_2H_5, 0.27; C_3H_7, 0.25; C_4H_9, 0.22.$$

The value of 1.14 was obtained for the $R = CH_3$ system after separating the components chromatographically at room temperature and directly analysing the cobalt species.

The values were obtained by using ^{19}F NMR to determine concentrations in solution though with limited accuracy.

Thus the $R = CH_3$ reaction would indicate that $Co^{III}(Acacen{-}CH_3) < Co^{III}(Tfacen{-}CH_3)$ in terms of ability of donate CH_3 groups to a Co^{II} complex.

Several unsuccessful attempts have been made to use the apparent lability of the CH_3 group in Co^{III} organometallic complexes to synthesise other organometallic compounds not previously known, e.g. Co^{II}(Amben) does not react with $Co^{III}(Tfacen{-}CH_3)$ in DMSO. Several earlier attempts have also failed to prepare Co^{III}(Amben—R) compounds using the reduction of Co^{II}(Amben) to $[Co^{I}(Amben)]^-$ by Na/Hg [22] or alkaline $BH_4/[PdCl_4]^{2-}$ [23] followed by addition of an alkyl or fluoroalkyl halide. Co^{II}(Amben) was reformed in these reactions and suggestions have been made by Green, Smith and Tasker [22] to explain the probable instability of the alkyl derivatives of this Co complex. Similarly $Co^{III}(Tfacen{-}CH_3)$ did not react with Mn^{II}(Salen) or Fe^{II}(Salen) which might well have been expected to yield the presently unknown compounds, $Mn^{III}(Salen{-}CH_3)$ and $Fe^{III}(Salen{-}CH_3)$. Paramagnetic interaction due to Mn^{II} and Fe^{II} species caused notable broadening of the ^{19}F resonance due to the Co^{III} complex making detection difficult. However, TLC examination of the mixtures failed to show evidence for any Co^{II} species, the Co^{III} complex, together with the M^{II} species being the only compounds observed.

In the case of Fe^{III} derivatives, successful synthesis of $Fe^{III}(Salen{-}C_6H_5)$ and $Fe^{III}(Salen{-}CH_2C_6H_5)$ and related studies by Calderazzo and Floriani [24] has indicated that Fe^{III} alkyls will be very unstable molecules as might be anticipated also for Mn^{III} compounds. This should not be the case with Pt^{IV} alkyls, however, but the exchange route has not proved successful, Pt^{II}(Salen) showing no indication of reaction with $Co^{III}(Tfacen{-}CH_3)$ even at elevated temperatures.

An alternative route leading to the formation of the anionic complexes $[\{(CH_3)_2PtBr_2\}_2(Salen)]^{2-}$ has been developed nevertheless [25] while $Pt(CH_3)_3SB$ compounds [26] have been recently reported.

Exchange reactions involving the perfluoroalkyl groups CF_3, C_2F_5 and C_3F_7 have not been found to proceed, whereas the 1,1,1-trifluoroethyl group has been found to exchange slowly in the system $Co^{II}(Tfacen)/Co^{III}(Acacen{-}CH_2CF_3)$. The perfluoroalkyl Co^{III} Schiff-base complexes are more resistant to decomposition by heat and light than their alkyl counterparts [17] just as perfluoroalkyl - transition metal compounds are noted as being more generally stable than alkyl derivatives [27].

The behaviour of mixed fluoro-hydrocarbon substituents is most interesting in that a slow rate of exchange is observed between Co^{II}(Tfacen) and $Co^{III}(Acacen{-}CH_2CF_3)$. In this reaction the growth of the ^{19}F triplet due to the CH_2CF_3 chain in $Co^{III}(Tfacen{-}CH_2CF_3)$ can be observed growing at δ 55.6

ppm alongside that due to the $Co^{III}(Acacen—CH_2CF_3)$ compound at 56.3. Both triplets have J 16 Hz. Substitution of one hydrogen by F in CH_3, however, removes the lability of the methyl group, Co^{II}(Tfacen) and $Co^{III}(Acacen—CH_2F)$ showing no reaction over several days.

No exchange was observed involving an aryl group.

A related reaction to those reported here but involving formal group exchange between Co^{I} and Co^{III} species has been described by Costa, Mestroni and Cocevar [5] *viz.*,

$$[CH_3Co^{I}\{(DO)(DOH)pn\}]^- + [CH_3Co^{III}\{(DO)(DOH)pn\}H_2O]^+ \rightarrow$$

$$\rightarrow [(CH_3)_2Co^{III}\{(DO)(DOH)pn\}]^0 + [Co^{I}\{(DO)(DOH)pn\}]^0$$

These workers have suggested that a carbanion transfer mechanism could be involved.

Costa [28] and coworkers have also studied the electrochemical reduction of a variety of Co^{III}—methyl derivatives having Schiff-base, dimethylglyoxime or related ligands coordinated to the metal and have related the "methyl donating" ability of such compounds in transmethylation reactions to the polarographic $E_{1/2}$ value for the process $Co^{III}—R \rightarrow (Co^{II}—R)^-$. The more negative the potential the more readily can the alkyl group be "donated" or exchanged.

Dodd and Johnson [9] have also reported fast alkyl group exchange reactions between the pyridinebis(cyclohexanedionedioximato)cobalt(I) anion and pyridinebis(dimethylglyoximato)cobalt(III)—alkyl complexes in alkaline methanol whereby the appropriate alkylbis(cyclohexanedionedioximato) cobalt(III) species are produced. Exchange of secondary alkyl or isobutyl groups could not be observed. Kinetic measurements on the slow reaction involving n-octyl group exchange indicated a second order rate law. The authors suggested a reaction mechanism involving nucleophilic attack of the Co^{I} species on the α-carbon atom of the organometallic Co^{III} compound. These authors also considered that a reaction between bis(dimethylglyoximinato)Co^{II} and alkylbis(cyclohexanedionedioximinato)Co^{III} in alkaline methanol proceeded via a Co^{I} species formed by disproportionation of Co^{II}.

Although Co^{II} dimethylglyoxime is reported to disproportionate in alkaline solution [29] thus: $2Co^{II} \rightarrow Co^{III} + Co^{I}$, there is no evidence to indicate that such reactions can occur for the Schiff-base complexes used in the present work, either in the solvent used (DMSO) or other basic solvents such as pyridine or methanol. Indeed, such Co^{I} species are unstable in alkaline solution [31]. A test for the formation of Co^{I} species was carried out on a DMSO solution containing Co^{II}(Tfacen) and $Co^{III}(Acacen—CH_3)$ by sealing solutions under nitrogen together with C_3F_7I and leaving the systems for 3 days. It has been established synthetically that R_FI reacts readily with Co^{I} species [10] to yield $Co(Chel—R_F)$ derivatives and hence such somplexes should have been readily detected in the reaction mixtures if any were formed. No evidence of such complexes was found by infra-red or ^{19}F NMR spectroscopic examination of the solution.

In fact, the extreme readiness with which Co^{I} species are oxidised to Co^{II} makes it imperative that any mechanism based on Co^{I} intermediates can clearly demonstrate the absence of any Co^{II} species in solution.

A further possible mechanism to explain the exchange results could involve a photochemically catalysed reaction in which radicals are produced by homolysis of the Co—C bond which can then react with other Co^{II} species in solution. Halpern [30] has demonstrated that free radicals can react with Co^{II} Schiff-base compounds to give $R—Co^{III}$(Chel).

$$R - Co^{III}L \xrightarrow{h\nu} Co^{II}L + R\bullet \qquad (i)$$

$$R\bullet + Co^{II}L' \rightarrow Co^{III}L' - R \qquad (ii)$$

Co^{III} alkyls are known to be decomposed by light [31] and thus a possible mechanistic pathway may be proposed. However, experiments on the system Co^{II}(Tfacen)/Co^{III}(Acacen—CH_3) in which the reaction mixture was prepared and its ^{19}F NMR spectrum measured with careful exclusion of light up until the measuring tube was in position in the spectrometer gave exactly the same results as for mixtures prepared and examined in the normal light of the laboratory. It is possible that a mixture of Co^{II}(Chel) and Co^{III}(Chel′—R) may reach some form of equilibrium which would inhibit photochemical decomposition by the very existence of such reactions as (*i*) and (*ii*). However, a sample of Co^{III}(Acacen—CH_3) in DMSO gave the same amount of CH_4 over a period of 24 hours as was evolved by solution containing Co^{III}(Acacen—CH_3) and Co^{II}(Tfacen), each equivalent in concentration to the Co^{III} complex alone. The amount of gas was slight being equal to the decomposition of $< 1\%$ of the Co^{III} alkyl in 24 h.

Group exchange reactions between Co^{III} species or between Hg^{2+} and alkyl cobaloximes have been categorised as electrophilic substitutions at a saturated carbon atom since no valence change occurs in the metal species involved.

At the present stage of investigation, however, the available evidence for group exchange reactions involving a change in metal valence appears to favour a reaction mechanism which can be described as essentially nucleophilic substitution by a Co^{II} species at a saturated carbon atom to which is bonded another cobalt atom, formally Co^{III}. Lack of reactivity in the case of a Co^{III}—phenyl derivative would then be in line with the rarity of nucleophilic substitutions at aryl carbon atoms. The extent to which the carbon atom initially bonded to cobalt gains a ‘share’ in the pair of electrons forming the Co—C bond will influence the ease with which another cobalt(II) moiety can approach the carbon and offer an alternative electron to be shared with a carbon electron. Thus, powerful electronegative substituents on the carbon atom should cause a displacement of electron density away from cobalt towards carbon in the Co—C bond making it more difficult for a second Co to compete for the carbon electron. This seems in line with the slow exchange found for a CH_2CF_3 group and the total lack of exchange of R_F groups. The situation with regard to exchange of acyl groups may be anticipated to be somewhat different with regard to the formation of the intermediate transition state. The oxygen atom attached to C could be expected to form weak donor bonds to an attacking cobalt species and hence provide an alternative bridging arrangement to allow electron rearrangement and group exchange to occur.

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References

1 J.M. Wood, F. Scott Kennedy and C.G. Rosen, Nature, 220 (1968) 123.
2 H.A.O. Hill, J.M. Pratt, S. Ridsdale, F.R. Williams and R.J.P. Williams, J. Chem. Soc. D., (1970) 341.
3 G.N. Schrauzer, J.H. Weber, T.M. Beckham and R.K.Y. Ho, Tetrahedron Lett., (1971) 275.
4 A. Adin and J.H. Espenson, J. Chem. Soc. D., (1971) 653.
5 G. Costa, G. Mestroni and C. Cocevar, J. Chem. Soc. D, (1971) 706.
6 G. Costa, G. Mestroni and C. Cocevar, Tetrahedron Lett. (1971) 1869.
7 H. Taube, "Electron transfer reactions of complex ions in solution", Academic Press, New York and London, 1970, Ch. 3.
8 A. van den Bergen and B.O. West, J. Chem. Soc. D, (1971) 52.
9 D. Dodd and M.D. Johnson, J. Chem. Soc. D, (1971) 1371.
10 K.S. Murray, A. van den Bergen and B.O. West, J. Organometal. Chem., 33 (1971) 89.
11 G. Morgan and J. Main Smith, J. Chem. Soc., (1925) 2030.
12 B.O. West, J. Chem. Soc., (1954) 395.
13 M. Green and P.A. Tasker, J. Chem. Soc. A, (1970) 3105.
14 M. Green and P.A. Tasker, Inorg. Syn., 11 (1968) 6.
15 L. Sacconi and I. Bertini, J. Amer. Chem. Soc., 88 (1966) 5180.
16 G. Costa and G. Mestroni, J. Organometal. Chem., 11 (1968) 325.
17 G. Costa, G. Mestroni and G. Pelliger, J. Organometal. Chem., 11 (1968) 333.
18 R.J. Cozens, G.B. Deacon, P.W. Felder, K.S. Murray and B.O. West, Aust. J. Chem., 23 (1970) 481.
19 C. Floriani, M. Puppis and F. Calderazzo, J. Organometal. Chem., 12 (1968) 209.
20 G.N. Schrauzer and R.J. Windgassen, J. Amer. Chem. Soc., 88 (1966) 3738.
21 W.M. Coleman and L.T. Taylor, J. Amer. Chem. Soc., 93 (1971) 5446.
22 M. Green, J. Smith and P.A. Tasker, Disc. Faraday Soc., 47 (1969) 172.
23 A. van den Bergen and B.O. West, unpublished work.
24 F. Calderazzo and C. Floriani, J. Chem. Soc. A, (1971) 3665.
25 K.S. Murray, B.E. Reichert and B.O. West, J. Organometal. Chem., 63 (1973) 461.
26 V. Romano, R. Badalamenti, T. Pizzino and F. Maggio, J. Organometal. Chem., 42 (1972) 199.
27 P.M. Treichel and F.G.A. Stone, Advan. Organometal. Chem., 1 (1964) 143 and references therein.
28 G. Costa, A. Puxeddu and E. Reisenhofer, J. Chem. Soc., Dalton Trans., (1972) 1519.
29 G.N. Schrauzer, R.J. Windgassen and J. Kohnle Chem. Ber., 98 (1965) 3324.
30 G. Marzilli, P.A. Marzilli and J. Halpern, J. Amer. Chem. Soc., 93 (1971) 93.
31 G.N. Schrauzer, J.W. Sibert and R.J. Windgassen, J. Amer. Chem. Soc., 90 (1968) 6681.