Journal of Organometallic Chemistry, 249 (1983) 205–225
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE SYNTHESIS AND ELECTROCHEMISTRY OF SOME PERFLUOROALKYLCOBALT ORGANOMETALLIC COMPOUNDS *

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(Received January 27th, 1983)

Summary

Co^{II}(Salphen) reacts with R_FI in dimethylsulfoxide to yield $R_FCo^{III}(Salphen)H_2O$ complexes. The electrochemical reductions of such compounds together with the analogous alkyl derivatives $R_HCo^{III}(Salphen)H_2O$ and $R_FCo^{III}(Tfacen)H_2O$ and $R_FCo^{III}(Acen)H_2O$ compounds have been studied to examine the influence of the equatorial ligand on the stability of the $[RCo^{II}(Chel)]^{-1}$ species formed in the first stage of reduction.

Introduction

Perfluoroalkyl organometallics are generally found to be more thermally and photochemically stable than their alkyl counterparts and this has been a particular property observed for Co^{III}[1] and Cr^{III}[2] perfluoroalkyl compounds which also have coordinated to the metal a variety of tetradentate ligands of the salicylaldimine and β-diketodiimino types as well as Cr^{III} derivatives containing bidentate salicylaldimine [2] or dithiocarbamate ligands [3]. Indeed alkyl-Cr^{III} compounds containing these ligands have not yet been prepared ** although this may be more related to some mechanistic aspects of the synthetic procedures than the intrinsic instability of the Cr–alkyl bond.

Electrochemical studies on the perfluoroalkyl and alkyl complexes of Co containing the ligand, Salen, have established [6] that the perfluoroalkyl Co^{II} species, $[R_FCo^{II}(Salen)]^{-1}$, although readily undergoing dissociation, are notably more stable to dissociation than the analogous alkyl derivatives $[R_HCo^{II}(Salen)]^{-}$, providing

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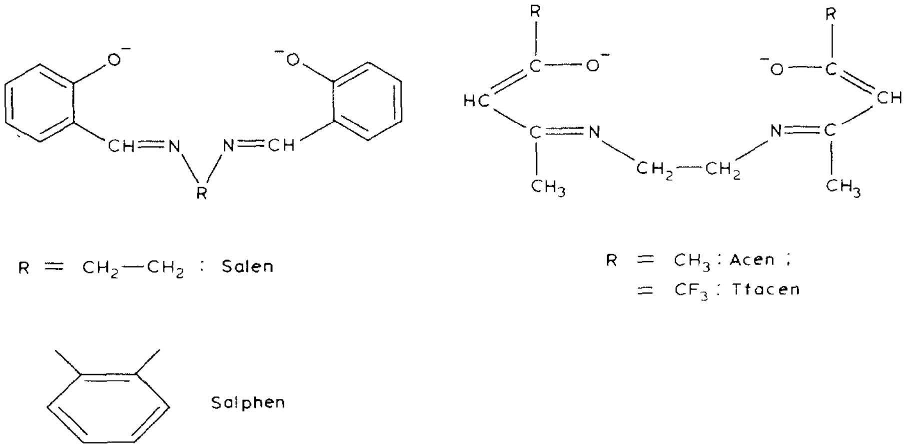
* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June, 1983. B.O. West was a research student at Cambridge under Professor Emeléus and R.N. Haszeldine during the period 1953–54.

** A report [4] claiming the synthesis of $CH_3Cr^{III}(Salen)$ by the alkyl hydrazine method of Goedken [5] has appeared. Few experimental details were given and we have been unable to obtain organometallic species in attempting to repeat the experiments.



SCHEME 1. Abbreviation of ligands.

further examples of the stabilizing influence of fluorine substitution in these types of organometallic complexes. The perfluoroalkyl-Co^{II} derivatives dissociate by a different route to that followed by the alkyl derivatives, giving Co^{II}(Salen) and R_F^- carbanions in contrast to the formation of $[Co^I(Salen)]^-$ and R_H radicals.

A further electrochemical study has been carried out to determine the influence of the equatorial ligand on the dissociative stability of $[RCo^{II}(Chel)]^-$ complexes where Chel = the dianions of Salphen, Acen and Tfacen (Scheme 1). This has also entailed an examination of the reduction stages of the Co^{II}(Chel) species in tetrahydrofuran, the solvent which allows for the largest negative potential range of reduction. Studies of the first reduction stages of Co^{II}(Salphen) [7,8] and Co^{II}(Acen) [7,9] have been reported in other solvents.

Results

Preparation of RCo^{III}(Salphen) complexes

Perfluoroalkyl-Co^{III} derivatives containing a variety of equatorial ligands have been prepared in good yields by the reaction of R_FI compounds with $[Co^I(Chel)]^-$ compounds in tetrahydrofuran (THF) [1]. However, when Salphen was the chelating ligand very low yields of the derived complexes were obtained [10], the larger part of the Co being regained as Co^{II}(Salphen) [and the iodo-Co^{III} derivative ICo^{III}(Salphen)] together with a variety of Co^{II} and Co^{III} species containing R_F groups substituted in the ligand itself, presumably due to attack by perfluorocarbanions. An alternative route to the R_FCo(Salphen) complexes was sought by examining the reaction of R_FI with Co^{II}(Salphen) in the presence of metallic Cu in dimethylsulphoxide (DMSO). McLoughlin and Thrower [11] have reported that Cu-perfluoroalkyl derivatives are produced when copper is heated with R_FI in polar aprotic solvents and that these compounds can act as perfluoroalkylating agents. It was anticipated that such Cu-perfluoroalkyl derivatives could act as appropriate sources of free R_F radicals and hence form the desired R_FCo^{III}(Salphen) derivatives. Successful radical transfer reactions of this type involving $Tl(C_6F_5)_2I$ and Co^{II}-Schiff base derivatives have been accomplished [12].

In the event perfluoroalkyl derivatives were obtained but subsequently it has been found that Co^{II}(Salphen) reacts directly with R_FI in DMSO at temperatures above 100°C to yield R_FCo^{III}(Salphen) and I-Co^{III}(Salphen) in good yields. Such reactions with Co^{II}(Salphen) have been reported by Halpern [13] to occur with substituted benzyl halides. Other Co^{II}(Chel) complexes of tetradentate Schiff bases or β-ketodiimines also react with R_FI to yield perfluoroalkyl derivatives.

Alkyl halides react under similar conditions to give green reaction mixtures which however do not yield organometallic-Co compounds.

The electrochemical studies to be described have subsequently shown that the reaction between $[Co^I(Salphen)]^-$ and R_FI does yield R_FCo^{III} compounds in good yields if care is taken to avoid the formation of substantial amounts of the lower valent species $[Co^0(Salphen)]^{2-}$.

The electrochemical reduction of Co^{II} chelates in tetrahydrofuran

Co^{II}(Salphen)

D.C. polarography of Co^{II}(Salphen) shows three consecutive reductions in tetrahydrofuran compared to the two stages found for Co^{II}(Salen) [6] (Table 1). The first reduction is a diffusion controlled ($i_l \propto h_{Hg}{}^{2/3}$), reversible (slope of E versus $\log_{10}[i/i_l - i] = -59 \pm 5$ mV), one-electronic process corresponding to

$$Co^{II}(Salphen) \overset{+e^-}{\rightleftharpoons} [Co^I(Salphen)]^-$$

as has been previously reported for studies in dimethylformamide and pyridine [7,8]. The reduction occurs at a more positive potential than the reduction of Co^{II}(Salen).

The second D.C. polarographic wave is not diffusion controlled and shows a larger limiting current than the first reduction process, the current being a function of the time a voltage is applied to the working electrode. This indicates that a further reaction involving the Co(Salphen) reduction product must be occurring. The second reduction process has been found to be chemically reversible using cyclic voltammetry on a Hg electrode (Table 2) and the process can be represented as

$$[Co(Salphen)]^- \overset{+e^-}{\rightarrow} [Co(Salphen)]^{2-}$$

The second reduction stage of Co^{II}(Salen) shows a similar large limiting current for i_l^2 and it was proposed that it was caused by reaction between $[Co(Salen)]^{2-}$ and $[NBu^n_4]^+$ from the supporting electrolyte to give $[Bu^nCo^{II}(Salen)]^-$ which could be reduced at the potential reached in the reduction of $[Co^I(Salen)]^-$ resulting in the cyclic redox process and a corresponding larger current [6]. A peak for the reoxidation of $[Bu^nCo^{II}(Salen)]^-$ was not detected up to a scanning rate of 50 V s^{-1} since the rate of dissociation of alkyl-Co^{II}(Salen) compounds to $[Co^I(Salen)]^-$ and alkyl radicals is very rapid even on the electrochemical time scale. Direct evidence for the formation of the $[Bu^nCo^{II}(Salphen)]^-$ species however is readily obtained from cyclic voltammetry of Co^{II}(Salphen) since the [alkyl-Co^{II}(Salphen)]$^-$ product is much more stable to dissociation than its Salen counterpart. A cyclic voltammogram at the rapid scan rate of 10 V s^{-1} (Fig. 1A) shows both first and second reduction stages with little or no evidence on the anodic sweep for a newly formed species. However, at the slower scan rate of 2 V s^{-1}, extended to include the third reduction stage (Fig. 1B) or with the potential held for a short time at a potential slightly more

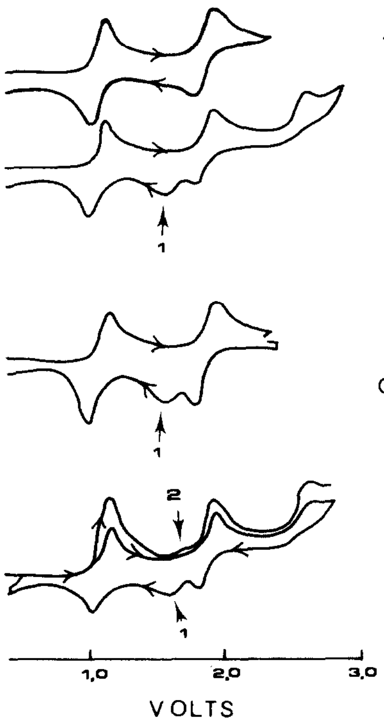


Fig. 1. Cyclic voltammograms for the reduction of Co^{II}(Salphen) in tetrahydrofuran at a Hg drop electrode (25°C).

Co^{II}(Salphen), 1×10^{-3} *M*; 0.1 *M* $[NBu^n_4][ClO_4]$;

(A) sweep range −0.5 to 2.3 V, including the first two reduction stages; scan rate 10 V s^{-1};

(B) sweep range −0.5 to 2.8 V, including the first three reduction stages; scan rate 2 V s^{-1}. Peak 1 is due to oxidation of $[Bu^nCo^{II}(Salphen)]^-$ formed by the reaction of $[Co^0(Salphen)]^{2-}$ with $[NBu^n_4]^+$;

(C) sweep range as in A but applied potential held at −2.3 V for 3 sec before commencing the anodic sweep; scan rate 2 V s^{-1}. Oxidation of $[Bu^nCo^{II}(Salphen)]^-$ is observed at peak 1;

(D) sweep range −0.5 to 2.8 V; scan rate 2 V s^{-1}. A second cathodic sweep is shown which displays the reduction of Bu^nCo^{III}(Salphen) (peak 2) formed during the first anodic sweep at peak 1. The increased current of the second cathodic sweep is due to the use of a growing Hg drop as electrode (see ref. [6]).

TABLE 1

D.C. POLAROGRAPHIC DATA FOR REDUCTION OF Co^{II}(Chel) COMPOUNDS IN TETRAHYDROFURAN AT 25°C [a]

Compound	$E^1_{1/2}$ (V)	i^1_l/c [b] (mA mol^{-1})	Slope [c] (mV)	$E^2_{1/2}$ (V)	i^2_l/c (mA mol^{-1})	i^2_l/i^1_l	$E^3_{1/2}$ (V)	i^3_l/c (mA mol^{-1})
Co^{II}(Salphen)	−1.054	1.33	−59	−1.861	1.68	1.26	−2.66	ca. 1.3
Co^{II}(Salen) [d]	−1.200	1.75	−57	−2.569	ca. 3	1.47	–	–
Co^{II}(Tfacen)	−1.215	1.69	−63	−2.53	ca. 6	ca. 3.6	–	–
Co^{II}(Acen)	−1.721	1.75	−57	–	–	–	–	–

[a] t_{Hg} 2.0 sec; conc. 1×10^{-3} *M*; 25°C; $[NBu^n_4][ClO_4]$, 0.1 *M*. [b] i^1_l, i^2_l, i^3_l are limiting currents for the first, second and third reduction stages. [c] Slope is of *E* versus $\log_{10}[i/i_l - i]$. [d] Data from Brockway, West and Bond [6].

negative than the second reduction step before beginning the anodic sweep (Fig. 1C) a new anodic peak is observed due to the oxidation of $[Bu^nCo^{II}(Salphen)]^-$ indicating a (relatively) slow rate of reaction between $[Co^I(Salphen)]^{2-}$ and the supporting electrolyte. The reduction of $Bu^nCo^{III}(Salphen)$ is observed on successive cycles of the voltammogram, the amount gradually increasing with time (Fig. 1D).

A sample of authentic $Bu^nCo^{III}(Salphen)$ was shown to have cyclic voltammetric potentials for reduction and subsequent reoxidation at the values observed for the new species detected in the $Co^{II}(Salphen)$ cyclic voltammograms.

The reaction is thus

$$[Co(Salphen)]^{2-} + [NBu^n_4]^+ \rightarrow [Bu^nCo^{II}(Salphen)]^- + NBu^n_3$$

Co^{II}(Acen) and Co^{II}(Tfacen)

The first D.C. polarographic reduction process for $Co^{II}(Tfacen)$ and $Co^{II}(Acen)$ (Table 1 and 2) is also diffusion controlled and reversible as for $Co^{II}(Salphen)$ and corresponds to the reaction

$$Co^{II}(Chel) \xrightarrow{+e^-} [Co^I(Chel)]^-$$

However, the demonstration that the processes were mono-electronic by controlled potential coulometry using 0.3 *M* sodium perchlorate as the supporting electrolyte was only possible for $Co^{II}(Tfacen)$. The electrolyte $[NBu^n_4][ClO_4]$ could not be used for this process because of the slow reaction between $[Co^I(Chel)]^-$ complexes of the type under study with $[NBu^n_4]^+$ to give $Bu^nCo^{III}(Chel)$ [9]. The reduction process for $Co^{II}(Acen)$, occurring as it does at large negative potentials, could not be resolved from the reduction of the electrolyte.

$Co^{II}(Acen)$ reduced at the most negative potential of the compounds examined and does not show a second reduction stage before the potential of solvent or electrolyte discharge is reached. $Co^{II}(Tfacen)$, however, does have a clearly defined second stage of reduction with the limiting current being considerably larger than that for the first reduction stage, just as was observed for Co(Salphen). The explanation is the same, viz. the formation of $[Bu^nCo^{II}(Tfacen)]^-$ by reaction of $[Co(Tfacen)]^{2-}$ with $[NBu^n_4]^+$. Repeated cyclic voltammograms of the $Co^{II}(Tfacen)$

TABLE 2

CYCLIC VOLTAMMETRY FOR Co^{II}(Chel) COMPLEXES IN TETRAHYDROFURAN, Hg DROP ELECTRODE [a]

Compound	E_p^{c1} (V)	E_p^{a1} (V)	ΔE_p (mV)	i_p^{c1}/i_p^{a1}	E_p^{c2} (V)	E_p^{a2} (V)	ΔE_p (mV)	i_p^{c2}/i_p^{a2}
Co^{II}(Salphen)	−1.090	−1.030	60	1.0	−1.889	−1.830	59	1.1 [b]
Co^{II}(Salen)	−1.222	−1.164	58	1.0	−2.612	−2.550	62	1.2
Co^{II}(Tfacen)	−1.222	−1.162	60	1.0	−2.73 [c]			
Co^{II}(Acen)	−1.750	−1.687	63	1.0	–	–	–	–

[a] Scan rates 10 V s^{-1}; Hg drop from DME, 1×10^{-3} *M*, 25°C; Co^{II}(Salphen) shows a third reduction process at E_p^{c3} −2.60 V. [b] This ratio has become 1 at a scan rate of 20 V s^{-1} with $\Delta E_p = 60$. [c] This reduction is not well resolved from solvent discharge but $i_p^{c2} > 3i_p^{c1}$.

system also show the appearance of a couple due to the butyl organometallics $Bu^nCo^{III}(Tfacen)/[Bu^nCo^{II}(Tfacen)]^-$. There is clearly a considerable increase in stability to dissociation for $[alkyl\text{-}Co^{II}(Tfacen)]^-$ species over that for analogous Salen compounds.

The constitution of $[Co(Chel)]^-$ and $[Co(Chel)]^{2-}$

There is little doubt that the products of the first reduction stages may be constituted as Co^I derivatives since each is formed by a consecutive one-electron process from a Co^{II} compound. The Na and Li salts of $[Co^I(Salen)]^-$ have also been structurally defined [14].

However, multi-electron reductions of metal complexes containing highly conjugated ligands such as porphyrins and phthalocyanines result in products which

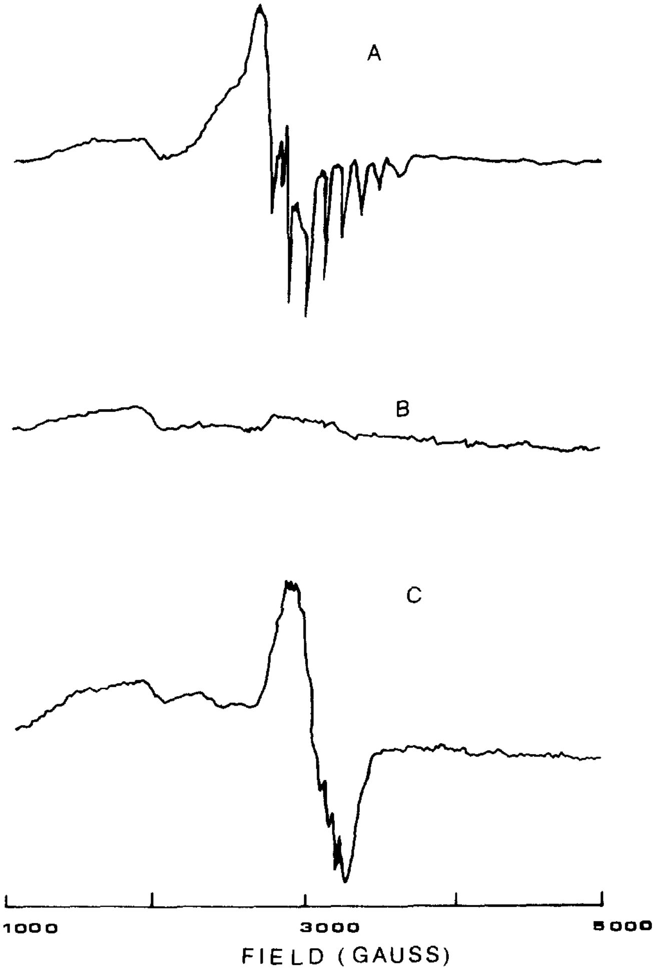


Fig. 2. X-band ESR spectra of Co(Salphen) complexes in tetrahydrofuran at 120 K.
(A) $Co^{II}(Salphen)$; (B) $[Co^I(Salphen)]^-$; (C) $[Co^0(Salphen)]^{2-}$.
(A) and (B) solutions 0.3 *M* in $NaClO_4$. $[Co^I(Salphen)]^-$ produced by electrochemical reduction; $[Co^0(Salphen)]^{2-}$ produced by reduction using Na amalgam. Microwave frequency 9.149 GHz.

appear to have the second and subsequent electrons residing in ligand-based orbitals rather than on the metal centre, as evidenced by ESR evidence [15].

The ESR spectra of Co^{II}(Salphen) and the two reduction products formed in the presence of sodium amalgam have been recorded to test the situation with these species which contain the most highly conjugated ligand of the series.

The initial Co^{II} d^7 spectrum (Fig. 2A) first changed to the featureless spectrum (Fig. 2B) expected for a diamagnetic d^8 Co^I complex, i.e. $[Co^I(Salphen)]^-$. As reduction proceeded a change to a new ESR spectrum occurred (Fig. 2C) which differed from that expected if the additional electron had been accommodated in a ligand based orbital, producing essentially an organic radical with an expected $g = 2.00$.

The observed spectrum has $g = 2.15$ and shows hyperfine splitting with A 46×10^{-4} cm^{-1} but has more than the eight lines expected for a low spin d^9 Co^0 system. Somewhat similar spectra have been reported for other d^9 metal systems when dissociation or association of the complex has taken place [16]. An iso-electronic species has been prepared by the one-electronic reduction of the d^8 complex Ni^{II}(Salphen) with sodium or lithium [17]. The product has been shown by X-ray crystallography to be a dimer linked through the CH methine carbons with the Ni still considered to be formally Ni^{II}. The dimer is reported to be diamagnetic however and hence such a process may not be occurring in the case of the reduction of the $[Co^I(Salphen)]^-$ species where the product is clearly paramagnetic. Alternate forms of association can be envisaged, however, which involve the phenolate oxygen atoms of the Co chelate as has been detected in the solid state for Na and Li salts of the $[Co^I(Salen)]^-$ anions [14].

The present ESR results are, therefore, tentatively interpreted as indicating that a formal Co^0, d^9 species is formed in the second reduction stage but is associated to some degree in solution.

The third reduction stage of Co(Salphen)

Co(Salphen) alone of the complexes studied showed a third stage of electrochemical reduction the assignment of which is at present uncertain. It is most likely that the process involves reduction of the ligand in some way rather than the metal since the parent ligand $(Salen)H_2$ shows a further reduction at -2.58 V following the initial reduction of the phenolic protons, very close to the potential observed for the third reduction stage of the Co complex. $(Salen)H_2$ on the other hand does not show such a reduction in addition to those associated with the phenolic protons and the different behaviour may relate to the highly conjugated nature of $(Salphen)H_2$. It is thought unlikely that a formal Co^{I-} species $[Co^{I-}(Salphen)]^{3-}$ could be produced for such a complex in any case. The third reduction step was not achieved using sodium amalgam reduction and could only be produced electrochemically at potentials more negative than the discharge of Na^+ in THF, i.e. when using $[NBu^n_4][ClO_4]$ as supporting electrolyte. The product reacted rapidly with such cations, however, and an ESR examination of the product could not be made.

TABLE 3

D.C. POLAROGRAPHIC REDUCTION OF PERFLUOROALKYL AND ALKYL COMPLEXES OF Co^{III} IN TETRAHYDROFURAN AT 25°C [a]

Compound	$E_{1/2}^1$ (V)	i_l^1/c (mA mol^{-1})	Slope (mV)	$E_{1/2}^2$ (V)	i_l^2/c (mA mol^{-1})	i_l^2/i_l^1	$E_{1/2}^3$ (V)	i_l^3/c (mA mol^{-1})
CH_3Co(Salen)	−1.563	1.44	−63	−2.20	0.6	0.42		
R_HCo(Salphen)								
$R_H = CH_3$	−1.477	1.4	−66	−1.912	1.2	0.86	−2.092	1.1
C_2H_5	−1.484	1.4	−54	−1.962	1.4	1.0	−2.102	1.4
C_3H_7	−1.509	1.2	−55	−1.982	1.1	0.92	−2.132	0.9
CF_3Co(Salen)	−0.989	1.42	−59	−2.04	1.1	0.79		
R_FCo(Salphen)								
$R_F = CF_3$	−1.032	1.3	−58	−1.842	ca. 1.2	0.92	−1.862	ca. 1
C_2F_5	−0.993	1.2	−64	−1.832	ca. 1.1	0.92	−1.862	ca. 1
C_3F_7	−0.921	1.5	−55	−1.802	ca. 1.4	0.93	−1.852	ca. 1.3
R_FCo(Acen)								
$R_F = CF_3$	−1.300	1.7	−57	−1.722	3.2	1.9		
C_2F_5	−1.205	1.7	−62	−1.722	2.1	1.2		
C_3F_7	−1.155	1.2	−57	−1.722	3.1	2.6		
R_FCo(Tfacen)								
$R_F = C_3F_7$	−0.857	1.4	−62	−2.202	5.4	3.9	−2.542	3.4
C_4F_9	−0.852	1.6	−55	−2.332	8.5	5.3	−2.582	4.5

[a] t_{Hg} 2.00 sec; slope of plot of E against $\log[i/i_l - i]$; $E_{1/2}^4$ ca. −2.6 V; $E_{1/2}^5$ ca. −2.7 V and $i_l^4 < i_l^5$ for R_HCo(Salphen); $E_{1/2}^4$ ca. −2.4 V; $E_{1/2}^5$ ca. −2.6 V and $i_l^4 \ll i_l^5$ for R_FCo(Salphen).

The electrochemical reduction of RCo^{III}(Chel) compounds *

Perfluoroalkyl and alkyl-Co^{III}(Salphen) compounds

D.C. polarographic data obtained in tetrahydrofuran are given in Table 3 for a series of complexes. The compounds each show five D.C. polarographic reduction waves compared to the four previously reported for the analogous Salen compounds [6]. In each case the second and third waves are not well resolved although the alkyl compounds show rather better resolution than the perfluoroalkyl. The limiting currents for the second and third waves are somewhat less than for the first reduction process. The fourth and fifth waves for the alkyl complexes are also not well resolved although using Tast polarography two waves could be distinguished for the ethyl derivative with $E^4_{1/2}$ ca. -2.58 V and $E^5_{1/2}$ ca. -2.68 V. The total current for these last two processes was of the order of that for the first reduction process and approximately equally divided between i^4_1/c and i^5_1/c. The fourth and fifth waves of the perfluoroalkyl complexes were better resolved ($E^4_{1/2}$ ca. -2.4, $E^5_{1/2}$ ca. -2.6 V) with a small limiting current for the fourth wave. The current for the fifth wave was only slightly less than for the first reduction wave.

The first reduction wave for each complex showed the characteristics of a diffusion controlled process and the magnitude of the slopes of the waves are in

TABLE 4

CYCLIC VOLTAMMETRY AT MERCURY AND PLATINUM ELECTRODES FOR THE FIRST REDUCTION COUPLE OF ALKYL- AND PERFLUOROALKYL-Co^{III} CHELATE COMPLEXES IN TETRAHYDROFURAN AT 25°C [a]

Compound	Hg [b]				Pt [c]			
	E_p^c (V)	E_p^a (V)	ΔE_p (mV)	i_p^c/i_p^a	E_p^c (V)	E_p^a (V)	ΔE_p (mV)	i_p^c/i_p^a
R_HCo(Salphen)								
$R_H = CH_3$	-1.547	-1.487	60	2.2	-1.556			
C_2H_5	-1.552	-1.472	80	1.7	-1.572			
C_3H_7	-1.557	-1.547	60	1.7	-1.557	-1.477	80	3.0
R_FCo(Salphen)								
$R_F = CF_3$	-1.062	-0.992	70	1.0	-1.094	-1.01	84	1.05
C_2F_5	-1.002	-0.932	70	1.0	-1.024	-0.948	86	1.03
C_3F_7	-0.972	-0.892	80	1.0	-1.012	-0.872	140	1.01
R_FCo(Acen)								
$R = CF_3$	-1.385	-1.297	88	0.95				
C_2F_5	-1.288	-1.196	92	0.95				
C_3F_7	-1.23	-1.157	73	0.90				
C_3F_7Co(Tfacen)	-0.932	-0.824	130	1.0				

[a] Solution concentrations 10^{-3} *M*, supporting electrolyte [NBu$^n_4$][ClO$_4$]. [b] Voltage scan rate for Co(Salphen) complexes, 5.0 V s^{-1}. Voltage scan rate for Co(Acen) and Co(Tfacen) complexes, 10.0 V s^{-1}. Hg drop electrode. [c] Voltage scan rate. 0.5 V s^{-1}, 1 cm Pt wire electrode.

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* The complexes used were all mono-aqua derivatives RCo^{III}(Chel)H$_2$O but for convenience the water molecule is omitted in all formulae. It may well be replaced by a THF molecule at the concentrations used in the experiments.

agreement with the reversible one electron process

$$\mathrm{RCo^{III}(Salphen)} \xrightarrow{+e^-} [\mathrm{RCo^{II}(Salphen)}]^-$$

Although $\mathrm{Co^{II}}$(Salen) reduces at a larger negative potential than $\mathrm{Co^{II}}$(Salphen) the corresponding pairs of analogous $\mathrm{Co^{III}}$ organometallic compounds reduce at rather similar potentials, the alkyl complexes having $E_{1/2}$ values at notably more negative potentials than the first $\mathrm{Co^{II}}$(Chel) reduction potentials. The perfluoroalkyl-$\mathrm{Co^{III}}$ complexes reduce at much less negative potentials than the alkyl derivatives.

While the $\mathrm{R_FCo^{III}}$(Salen) derivatives reduce at potentials 0.2–0.3 V more positive than $\mathrm{Co^{II}}$(Salen), the $\mathrm{R_FCo^{III}}$(Salphen) complexes have their first reduction potentials only marginally more positive than that for $\mathrm{Co^{II}}$(Salphen). The $\mathrm{CF_3}$ complex has an $E_{1/2}$ value which is virtually coincident with that for the $\mathrm{Co^{II}}$(Salphen)/[$\mathrm{Co^{I}}$(Salphen)]$^-$ reduction process.

Cyclic voltammetry has shown a notable difference between the first reduction stages of $\mathrm{R_HCo^{III}}$(Salphen) and $\mathrm{R_HCo^{III}}$(Salen) compounds. Some data are given in Table 4.

The reductions of the alkyl-Salen complexes were irreversible at a Pt electrode at all voltage scan rates up to 50 V s^{-1} and no anodic peak was observed corresponding to the reoxidation process.

$$[\mathrm{R_HCo^{II}(Salen)}]^- \xrightarrow[-e^-]{} \mathrm{R_HCo^{III}(Salen)}$$

However, the use of a Hg drop electrode did result in the observation of this reoxidation process at scan rates above 5 V s^{-1} indicating that the process was reversible or at least quasi-reversible. Nevertheless, it was clear that the anions [$\mathrm{R_HCo^{II}}$(Salen)]$^-$ dissociated very rapidly [6].

By contrast each of the alkyl-Co(Salphen) complexes examined by cyclic voltammetry using a Pt electrode showed evidence for anodic peaks at much lower scan rates of the order of 2 V s^{-1}. Indeed an anodic peak could be detected for the oxidation of [n-$\mathrm{C_3H_7Co^{II}}$(Salphen)]$^-$ species at a rate as low as 0.5 V s^{-1}.

However, at the comparative scan rate of 5 V s^{-1} used for all the compounds reported in Table 4 the n-$\mathrm{C_3H_7}$ compound, although giving the lowest i_p^c/i_p^a ratio measured for the alkyl compounds still had a ratio much greater than unity indicating that a considerable degree of reaction was occurring to remove the product of the reduction, [n-$\mathrm{C_3H_7Co^{II}}$(Salphen)]$^-$. The perfluoroalkyl derivatives on the other hand all showed ratios close to unity with ΔE_p values indicating that the reductions for these complexes were at least quasi-reversible with products consider-

TABLE 5

CYCLIC VOLTAMMMETRY OF $\mathrm{C_3F_7Co^{III}}$(Salphen) AT VARYING SCAN RATES ON Pt (1 cm Pt wire electrode)

Rate (V s^{-1})	E_p^c (V)	E_p^a (V)	ΔE_p (mV)	i_p^c/i_p^a
0.05	−0.972	−0.892	80	1.08
0.10	−0.972	−0.892	80	1.03
0.20	−0.982	−0.887	95	1.02
0.50	−1.012	−0.872	140	1.01

ably more stable than the analogous alkyl-Co^{II}(Salphen) anions. Indeed at scan rates less than 5 V s^{-1} the presence of $[Co^{I}(Salphen)]^{-}$ was detected following the first reduction of the alkyl derivatives confirming that the path of dissociation already identified for $[R_HCo^{II}(Salen)]^{-}$ species [6] is also followed by the alkyl-Co^{II}(Salphen) derivatives.

$$[R_HCo^{II}(Salphen)]^{-} \rightarrow [Co^{I}(Salphen)]^{-} + R_H$$

The perfluoroalkyl-Salphen derivatives dissociate more slowly than their alkyl counterparts as is seen from the data of Table 5 for a representative compound $C_3F_7Co^{III}$(Salphen) which shows that i_p^c/i_p^a slowly increases from unity as the scan rate decreases 10-fold indicating that although more dissociation occurs when the scan rate becomes slower the perfluoro complexes are very stable on the electrochemical time scale.

The product of dissociation however is not $[Co^{I}(Salphen]^{-}$ but Co^{II}(Salphen) since the complete electrolysis of a perfluoroalkyl-Co^{III}(Salphen) complex at the appropriate first reduction potential gives Co^{II}(Salphen) as the major electroactive product. This mode of dissociation is thus the same as detected for $[R_FCo^{II}(Salen)]^{-}$ [6].

$$[R_FCo^{II}(Salphen)]^{-} \rightarrow Co^{II}(Salphen) + R_F^{-}$$

Cyclic voltammetry at a Hg electrode gives generally similar results to the Pt data indicating that the reductions of perfluoroalkyl- and alkyl-Co^{III}(Salphen) derivatives are reversible or bordering on quasi-reversible at a scan rate of 5 V s^{-1} (ΔE_p 60–80 mV). The i_p^c/i_p^a ratios indicate some degree of following reaction (i.e. dissociation) for the alkyl but gives no indication of this for the perfluoroalkyl on the voltammetric time scale.

The second reduction process for both the perfluoroalkyl and alkyl derivatives has been assigned to

$$[RCo^{II}(Salphen)]^{-} \xrightarrow{+e^{-}} [RCo^{I}(Salphen)]^{2-}$$

The D.C. polarographic reduction potentials show only small variations with respect to the number of carbon atoms in the chain but the alkyl derivatives show a shift to more negative potentials with increasing chain length while the perfluoroalkyl derivatives show the reverse effect.

The potentials are all very close to that for the second reduction of Co^{II}(Salphen) (i.e. $Co^{I} \rightarrow Co^{0}$) but this process can be eliminated as a possible second reduction because of the demonstration by cyclic voltammetry that both R_H- and R_F-Co^{II}(Salphen) anions are relatively stable to dissociation and thus formation of a sufficient amount of $[Co^{I}(Salphen)]^{-}$ would not occur in the electrochemical time period involved in the measurements to account for the waves observed. It is notable that the values of i_l^2/i_l^1 for both alkyl- and perfluoroalkyl-Salphen complexes are closer to unity than for the analogous Salen complexes indicating that less dissociation is occurring with these compounds than those derived from Salen. (Some comparative values included in Table 3.) Furthermore, the difference in these ratios between the perfluoroalkyl- and alkyl-Co(Salphen) complexes is much less than for the Salen series. The remaining reduction processes observed for both perfluoroalkyl and alkyl complexes do not involve cobalt-organometallic species. The third and fifth D.C. polarographic waves occur at the potentials corresponding to the processes already established in the reduction of Co^{II}(Salphen) viz.

$$[Co^{I}(Salphen)]^{-} \xrightarrow{+e^{-}} [Co^{0}(Salphen)]^{2-}$$

and

$$[Co^{0}(Salphen)]^{2-} \xrightarrow{+e^{-}} [Co(Salphen)]^{3-}$$

The $[Co^{I}(Salphen)]^{-}$ arises from the evidently very fast dissociation of $[R_FCo^{I}(Salphen)]^{2-}$ formed upon reduction of $[R_FCo^{II}(Salphen)]^{-}$, in turn the first product of reduction of R_FCo^{III}(Salphen).

Cyclic voltammetry has not succeeded in showing any clear evidence for the reoxidation of the $[R_FCo^{I}(Salphen)]^{2-}$ product at any voltage scan rate. Only the anodic peaks for the oxidation stages $[Co^{0}(Salphen)]^{2-}/[Co^{I}(Salphen)]^{-}$ and $[Co^{I}(Salphen)]^{-}/Co^{II}(Salphen)$ are observed. This has reinforced the concept of the rapid dissociation of $[RCo^{I}(Chel)]^{2-}$ species first observed for the Salen compounds [6]. The cyclic voltammetric results for the R_FCo(Salphen) systems however are complicated by the closeness of the reduction potentials for the $[R_FCo^{II}(Salphen)]^{-}/[R_FCo^{I}(Salphen)]^{2-}$ and $[Co^{I}(Salphen)^{-}/[Co^{0}(Salphen)]^{2-}$ stages. Figure 3 shows a cyclic voltammogram obtained with a Pt electrode of the $C_3F_7Co^{III}$(Salphen) compound, a typical example of the series. The scan has been extended to the potential region of the fifth reduction stage detected by D.C. polarography. The fourth reduction process found in D.C. polarography is not observed on Pt and is related to the reduction of subvalent Hg alkyl derivatives formed by similar processes to those described in the RCo(Salen) studies [6].

The second cathodic peak has a value of i_p^{c2} almost twice as large as i_p^{c1} and results from the virtual coincidence of the reduction potentials for the two processes

$$[R_FCo^{II}(Salphen)]^{-} \xrightarrow{+e^{-}} [R_FCo^{I}(Salphen)]^{2-}$$

and

$$[Co^{I}(Salphen)]^{-} \xrightarrow{+e^{-}} [Co^{0}(Salphen)]^{2-}$$

such that $i_p^{c2} = i_p^{c}\,[R_FCo^{II}]^{-}/[R_FCo^{I}]^{2-} + i_p^{c}\,[Co^{I}]^{-}/[Co^{0}]^{2-}$.

The latter process arising because of the rapid dissociation

$$[R_FCo^{I}(Salphen)]^{2-} \rightarrow [Co^{I}(Salphen)]^{-} + R_F^{-}$$

When the cyclic voltammogram is restricted to the voltage region around this peak the anodic peak corresponding to the 'double' cathodic peak shows a peak current approaching half the value of the cathodic current as the overall scan rate increases, e.g. $i_p^{c}/i_p^{a} = 2.5$ at a rate of 0.05 V s^{-1}, reaching 2.1 at 0.50 V s^{-1}. This is consistent with the reoxidation of $[Co^{0}(Salphen)]^{2-}$ to $[Co^{I}(Salphen)]^{-}$ with little or no component due to reoxidation of $[R_FCo^{I}(Salphen)]^{2-}$. However, the process is further complicated because of the reaction of $[Co^{0}(Salphen)]^{2-}$ with $[NBu^{n}_4]^{+}$ to form $[Bu^{n}Co^{II}(Salphen)]^{-}$ which will undergo further electrochemical reduction at these potentials. The reoxidation step on the anodic sweep is shown in Fig. 3.

The appearance of an anodic peak for the process $[R_FCo^{II}(Salphen)]^{-}/R_FCo^{III}$

(Salphen) following a cathodic scan which ends with the reduction process $[Co^0(Salphen)]^{2-}/[Co(Salphen)]^{3-}$ is due to the diffusion of $R_FCo^{III}(Salphen)$ into the volume immediately surrounding the electrode during the time taken to complete the total cathodic and anodic sweeps.

The molecules will be immediately reduced to $[R_FCo^{II}(Salphen)]^-$ at potentials less negative than -1.8 V and hence will be detected by an anodic peak at around -1.0 V.

A cyclic voltammogram of an alkyl $Co^{III}(Salphen)$ complex is more complex and shows not one but three unresolved peaks on the cathodic sweep in the potential region corresponding to the expected $[R_HCo^{II}]^-/[R_HCo^I]^{2-}$ and $[Co^I]^-/[Co^0]^{2-}$ processes ($-1.98 \rightarrow -2.18$ V) which again occur at rather similar potentials. The total value of i_p^c for all three peaks is close to $2 \times i_p^{c1}$. Two of the peaks are no doubt due to the reductions already described for the R_F species viz. $[R_HCo^{II}(Salphen)]^-/[R_HCo^I(Salphen)]^{2-}$ followed by $[Co^I(Salphen)]^-/[Co^0(Salphen)]^{2-}$ with $[Co^I(Salphen)]^-$ being formed by rapid dissociation of $[R_HCo^I(Salphen)]^{2-}$. The lack of resolution follows the D.C. polarographic observations that reduction stages 2 and 3 overlap. A further reduction was not anticipated in the same potential region as judged by the polarographic results. The peak has tentatively been ascribed to an adsorption of one of the reduced organometallic products on the Pt electrode. This is

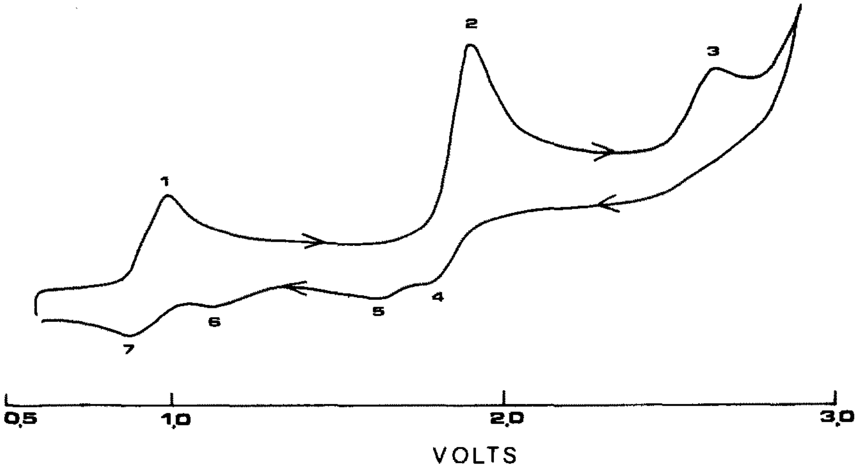

Fig. 3. Cyclic voltammogram for $C_3F_7Co^{III}(Salphen)$ in tetrahydrofuran at a Pt electrode (25°C). conc. 1×10^{-3} *M*; scan rate 0.10 V s^{-1}; 0.1 $M[NBu^n_4][ClO_4]$;

(1) $R_FCo^{III}(Salphen) \xrightarrow{+e^-} [R_FCo^{II}(Salphen)]^-$

(2) $[R_FCo^{II}(Salphen)]^- \xrightarrow{+e^-} [R_FCo^I(Salphen)]^{2-}$

and $[Co^I(Salphen)]^- \xrightarrow{+e^-} [Co^0(Salphen)]^{2-}$

(3) $[Co^0(Salphen)]^{2-} \xrightarrow{+e^-} [Co(Salphen)]^{3-}$

(4) $[Co^0(Salphen)]^{2-} \xrightarrow{+e^-} [Co^I(Salphen)]^-$

(5) $[Bu^nCo^{II}(Salphen)]^- \xrightarrow{-e^-} Bu^nCo^{III}(Salphen)$

(6) $[Co^I(Salphen)]^- \xrightarrow{-e^-} Co^{II}(Salphen)$

(7) $[R_FCo^{II}(Salphen)]^- \xrightarrow{-e^-} R_FCo^{III}(Salphen)$

at least consistent with the 2/1 ratio of the total current for all three reduction processes, to i_p^{c1}.

It should be noted that although the third reduction process observed for the R_HCo^{III}(Salphen) compounds has been ascribed to the $[Co^I(Salphen)]^-/[Co^0(Salphen)]^{2-}$ reduction step the actual D.C. polarographic $E_{1/2}$ value found for the process is some 0.2–0.3 V more negative than that measured when reducing Co^{II}(Salphen). The alternate hypothesis that in the alkyl series this third process represents the couple $[R_HCo^I(Salphen)]^{2-}/[R_HCo(Salphen)]^{3-}$ does not seem reasonable since $[R_HCo^I(Salphen)]^{2-}$ anions are obviously so dissociatively unstable. It is suggested that the process is the Co^I/Co^0 reduction with its potential shifted because of an alteration in the surface characteristics of the Hg drop brought about by the interaction of alkyl radicals or carbanions formed in the rapid dissociation of $[R_HCo^I(Salphen)]^{2-}$ in close proximity to the surface.

The fourth polarographic wave detected for both R_H and R_F species is certainly due to Hg-alkyl species being reduced and is of substantial size in the case of the alkyl-cobalt compounds indicating that a considerable amount of surface reaction must have occurred. Reduction of $[Co^I(Salphen)]^-$ at a surface containing a substantial portion of R_H-Hg species should result in a different potential being observed than at pure Hg.

The corresponding fourth wave in the D.C. polarographic reduction of the R_F species is relatively small in line with the likely formation of Bu^n–Hg species by exchange between R_F-Hg and $[NBu_4^n]^-$ since R_F-Hg compounds are not expected to be reduced in this region [6].

Perfluoroalkyl-Co^{III}(Acen) and (Tfacen) compounds

Perfluoroalkyl-Co^{III}(Acen) compounds show only two D.C. polarographic waves in contrast to the 5 waves observed for the Salphen complexes while three waves are detected for the Tfacen compounds (Table 3).

The first reduction stage for each complex examined was shown to be diffusion controlled and can be assigned to the reduction step

$$R_FCo^{III}(Chel) \xrightarrow{+e^-} [R_FCo^{II}(Chel)]^-$$

where Chel = Acen or Tfacen. Constant potential coulometry established that a single electron was involved in the reduction.

The second reduction stage for the Acen series is not diffusion controlled however. The half wave potential for the process indicates that it is the reduction

$$Co^{II}(Acen) \xrightarrow{+e^-} [Co^I(Acen)]^-$$

There is no evidence for any further reduction before the solvent discharge region. The ratio i_l^2/i_l^1 being greater than unity for the organometallic compounds and the use of Tast polarography shows that the value of the limiting current depends on the time the voltage is applied to the drop indicating that a chemical reaction is occurring, following the reduction of Co^{II}(Acen), which essentially reforms more Co^{II}(Acen).

Although the cyclic voltammetric studies on perfluoroalkyl-Co^{III}(Salen) and Salphen complexes have established that $[R_FCo^{II}(Chel)]^-$ ions dissociate to give Co^{II}(Chel) as one product, this complex has not been detected in D.C. polarograms of the former compounds but only in cyclic voltammetric studies. Thus the D.C. polarographic results for the Acen complexes indicate that $[\mathrm{R_FCo^{II}(Acen)}]^-$ species must dissociate more rapidly than any of the analogous Salen or Salphen complexes.

Cyclic voltammetry of the $\mathrm{C_3F_7Co^{III}(Acen)}$ complex confirms that the first reduction process is reversible or quasi-reversible at high scan rates (> 50 V s^{-1}) while at the low rate of 1 V s^{-1} there is no evidence for the reoxidation of $[\mathrm{C_3F_7Co^{II}(Acen)}]^-$ on the anodic sweep, when the overall range of the voltammogram is allowed to include the $\mathrm{Co^{II}(Acen)}/[\mathrm{Co^{I}(Acen)}]^-$ redox stage indicating that $[\mathrm{C_3F_7Co^{II}(Acen)}]^-$ dissociates to $\mathrm{Co^{II}(Acen)}$ and, presumably $\mathrm{C_3F_7}^-$ carbanions at a very fast rate. Cyclic voltammograms of Salen and Salphen species show considerable evidence for the analogous $[\mathrm{C_3F_7Co^{II}(Chel)}]^-$ species at such low scan rates.

The Tfacen complexes show two further D.C. polarographic reductions following the initial $\mathrm{R_FCo^{III}(Tfacen)}/\mathrm{R_FCo^{II}(Tfacen)}]^-$ reductions. The second wave is due to the process

$$[\mathrm{R_FCo^{II}(Tfacen)}]^- \xrightarrow{+e^-} [\mathrm{R_FCo^{I}(Tfacen)}]^{2-}$$

while the third occurs at the potential corresponding to the reduction

$$[\mathrm{Co^{I}(Tfacen)}]^- \xrightarrow{+e^-} [\mathrm{Co^{0}(Tfacen)}]^{2-}$$

The formation of the $[\mathrm{Co^{I}(Tfacen)}]^-$ species is considered to arise by the rapid dissociation of $[\mathrm{R_FCo^{I}(Tfacen)}]^{2-}$ as observed for the Salen and Salphen systems. There is no D.C. polarographic evidence for the formation of $\mathrm{Co^{II}(Tfacen)}$ in the complexes examined. The ratios of i_l^2/i_l^1 and i_l^3/i_l^1 are however considerably greater than 1 and indicate some following reactions involving the products of each reduction step. Cyclic voltammograms obtained for the $\mathrm{R_FCo^{III}(Tfacen)}$ compounds showed no evidence for the dissociation of the $[\mathrm{R_FCo^{II}(Tfacen)}]^-$ complexes to $\mathrm{R_F}^-$ and $\mathrm{Co^{II}(Tfacen)}$ on the electrochemical time scale and make these complexes the most stable to dissociation of the various species studied.

The second and third reduction stages are also detected in cyclic voltammetric studies. The second reduction process is electrochemically reversible with peak currents considerably larger than for the first process, and is considered due to the $[\mathrm{R_FCo^{II}(Tfacen)}]^-/[\mathrm{R_FCo^{I}(Tfacen)}]^{2-}$ couple with an additional reoxidative reaction involved. The third process assigned to the $[\mathrm{Co^{I}(Tfacen)}]^-/[\mathrm{Co^{0}(Tfacen)}]^{2-}$ couple has a peak current close to that of the first reduction process and agrees with the concept of very rapid decomposition of $[\mathrm{R_FCo^{I}(Tfacen)}]^{2-}$ to $[\mathrm{Co^{I}(Tfacen)}]^-$ and $\mathrm{R_F}^-$.

Satisfactory explanations for the large ($\gg 1$) ratios of i_l^2/i_l^1 in the reduction of $\mathrm{R_FCo^{III}(Acen)}$ or $\mathrm{R_FCo^{III}(Tfacen)}$ cannot be given. It is known that $[\mathrm{Co^{I}(Acen)}]^-$ reacts with $[\mathrm{NBu^n_4}]^+$ to form $\mathrm{Co^{II}(Acen)}$ and alkyl radicals in contrast to the formation of $\mathrm{RCo^{III}(Chel)}$ complexes when: Chel = Salen or other related ligands [9]. Such a process could be envisaged as providing the cyclic reaction needed to account for the large limiting current in the second reduction stage

$$\mathrm{R_FCo^{III}(Acen)} \xrightarrow{+e^-} [\mathrm{R_FCo^{II}(Acen)}]^- \xrightarrow[\text{rapid}]{} \mathrm{Co^{II}(Acen)} + \mathrm{R_F}^-$$

$$\mathrm{Co^{II}(Acen)} \underset{[\mathrm{NBu^n_4}]^+}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Co^{I}(Acen)}]^-$$

However the rate of reaction of $[NBu^n_4]+$ with $[Co^I(Acen)]^-$ as reported appears too slow to account for the large limiting current observed. One alternative hypothesis that has yet to be tested involves a possible rapid redox reaction between $[Co^I(Acen)]^-$ as these ions are formed and molecules of $R_FCo^{III}(Acen)$ in the layer of solution immediately surrounding the 'electrode' layer. Thus providing a mechanism for reoxidation.

$$R_FCo^{III}(Acen) + [Co^I(Acen)]^- \rightarrow [R_FCo^{II}(Acen)]^- + Co^{II}(Acen)$$

Related redox reactions involving $Co^{II}(Chel)$ and $RCo^{III}(Chel')$ species have been examined where Chel and Chel′ are ligands such as Acen, Salen, Tfacen etc. Fast reactions were observed when R = alkyl but slow reactions for R_F compounds [18].

Reactions between Co^I and R_FCo^{III} species have not so far been examined although reactions involving R_H systems are also known to proceed readily [19] and the greater difference in redox potentials for these systems could encourage rapid electron transfer.

In the case of the $R_FCo(Tfacen)$ reductions the large i_l^3/i_l^1 values can be explained as for the Salen and Salphen systems by the rapid reaction of $[NBu^n_4]^+$ with the $[Co^0(Tfacen)]^{2-}$ species formed from $[Co^I(Tfacen)]^-$ to yield $[Bu^nCo^{II}(Tfacen)]^-$ which would reduce in the voltage range of the $[Co^I(Tfacen)]^-/Co^0(Tfacen)]^{2-}$ couple as previously described.

The $i_l^2/i_l^1 > 1$ result cannot be explained so readily. The reaction of $[NBu^n_4]^+$ with $[Co^I(Tfacen)]^-$ will be too slow to provide sufficient $[Bu^nCo^{II}(Tfacen)]^-$ to account for the size of the limiting current in the second reduction stage. Once again the hypothesis that $[Co^I(Tfacen)]^-$, formed by the rapid dissociation of $[R_FCo^I(Tfacen)]^{2-}$, might react sufficiently rapidly with the 'boundary' layer of $R_FCo^{III}(Tfacen)$ to form $Co^{II}(Tfacen)$ might be considered. Certainly any $Co^{II}(Tfacen)$ formed at these potentials would be immediately reduced to $[Co^I(Tfacen)]^-$ and would result in an increased amount being observed. It might be expected however that if such a reaction could occur for Tfacen complexes it ought to have resulted in $Co^{II}(Tfacen)$ being detected by D.C. polarography or cyclic voltammetry which it has not or that a similar process would have occurred with the Salen or Salphen systems and caused larger i_l^2/i_l^1 values than actually observed.

Discussion

These studies provide further evidence that $RCo^{III}(Chel)$ complexes can undergo reduction in two stages forming Co^{II} and Co^I organo compounds of varying degrees of dissociative stability depending on the attached R groups and the equatorial ligand.

$$RCo^{III}(Chel) \xrightarrow{+e^-} [RCo^{II}(Chel)]^- \qquad \text{Stage 1}$$

$$[RCo^{II}(Chel)]^- \xrightarrow{+e^-} [RCo^I(Chel)]^{2-} \qquad \text{Stage 2}$$

The dissociative stabilities of each $[RCo^I(Chel)]^{2-}$ complex formed are extremely low however, and $[Co^I(Chel)]^-$ species are rapidly formed on the electrochemical time scale so that a third stage is detected for most systems examined corresponding to

$$[Co^{I}(Chel)]^{-} \xrightarrow{+e^{+}} [Co(Chel)]^{2-}$$

The exception is in the reductions of R_FCo^{III}(Acen) compounds where $[R_FCo^{II}(Acen)]^-$ is so unstable with respect to dissociation to R_F^- and Co^{II}(Acen) that D.C. polarography for example shows as the second reduction stage the reduction of

$$Co^{II}(Acen) \xrightarrow{+e^{-}} [Co^{I}(Acen)]^{-}$$

Other features of the electrochemical studies arise from the reactivity of the various reduced RCo(Chel) species. Thus the polarographic studies show evidence for the formation of R-Hg species as secondary products of the decompositions by the various Co species and in cyclic voltammetric studies Bu^nCo(Chel) compounds can be detected in a number of instances formed by the rapid reaction of $[Co^0(Chel)]^{2-}$ species with $[NBu^n_4]^+$ ions from the supporting electrolyte.

The electrochemical studies provide further clear evidence that $[R_FCo^{II}(Chel)]^-$ anions, formed by the reduction of R_FCo^{III}(Chel) complexes, dissociate to give perfluorocarbanions and Co^{II}(Chel) in contrast to the behaviour of alkyl derivative which dissociate giving alkyl radicals $R_H\bullet$ and $[Co^I(Chel)]^-$ ions. Other studies have previously reported the formation of alkyl radicals in dissociations of $[RCo^{II}(Chel)]^-$ species for various Schiff base tetradentate ligands [20,21] as well as methyl derivatives of cobalamin, cobinamide and tetraphenylporphin [22].

The complex $[C_6H_5Co^{II}(Salen)]^-$ has however been reported to dissociate giving the carbanion $C_6H_5^-$ and Co^{II}(Salen) [23]. Overall these results indicate that the electronegativity of the organo group plays a major role in determining the route of decomposition of a Co^{II} organo species, the more electronegative groups dissociating as carbanions.

However, the rates of dissociation are also clearly influenced by the nature of the organo group. The ratios of the diffusion currents for the first and second reduction stages for the various complexes studied provide a qualitative measure of the relative stabilities of the $[R_FCo^{II}(Chel)]^-$ complexes towards dissociation and clearly show the enhanced stabilities of perfluoroalkyl derivatives $[R_FCo^{II}(Chel)]^-$ over alkyl derivatives $[R_HCo^{II}(Chel)]^-$ for a given ligand. Thus the more electronegative is R the slower is the rate of dissociation of the complex. The $[C_6H_5Co^{II}(Salen)]^-$ complex has been stated [21] to be considerably more resistant to dissociation than $[alkyl\text{-}Co^{II}(Salen)]^-$ compounds and the $C_6H_5^-$ ions can be considered as a notably more electronegative group than CH_3^- etc.

The order of stability for the R_F and R_H complexes of Salen and Salphen can thus be compared giving an order of decreasing stability $[R_FCo^{II}(Salphen]^- \approx [R_HCo^{II}(Salphen)]^- > [R_FCo^{II}(Salen)]^- \gg [R_HCo^{II}(Salen)]^-$.

The cyclic voltammetric data in turn have allowed a comparison to be made of the dissociative stabilities of $[R_FCo^{II}(Chel)]^-$ anions containing a series of different equatorial ligands such that their dissociative stabilities decrease in order $[R_FCo^{II}(Tfacen)]^- > [R_FCo^{II}(Salphen)]^- > [R_FCo^{II}(Salen)]^- > [R_FCo^{II}(Acen)]^-$

An attempt has been made to obtain estimates of the orders of magnitude of the rates of dissociation of the series of C_3F_7-Co^{II} anions using the double step chronoamperometric technique developed by Schwartz and Shain [24]. This has yielded the following approximate first order rate constants and half lives such that

Chel	(Tfacen)	(Salphen, Salen)	(Acen)
k (s^{-1})	0.5	3	40
$t_{1/2}$ (s)	1.4	0.1	0.02

The approximations necessary for the application of the technique to these systems did not result in a significant separation between the Salphen and Salen systems although it was possible to distinguish between the complexes of these ligands qualitatively by D.C. polarographic and cyclic voltammetric data as shown previously.

The results seem to infer that those ligands which are highly conjugated or best able to bear enhanced electron density by virtue of electronegative substituents help to stabilize $[R_FCo^{II}(Chel)]^-$ species against dissociation. Lexa and Savéant [22] have reported a considerable dissociative stabilisation for the highly conjugated $[CH_3Co^{II}(TPP)]^-$ species (TPP-dianion of tetraphenylporphin) over $[CH_3Co^{II}(Salen)]^-$ which in turn is more stable than the methyl-cobinamide complex.

The Co^I organo species $[R_FCo^I(Chel)]^{2-}$ were found to undergo extremely rapid dissociation in every case examined and no examples were found in the present series of complexes where the further reduction of such species was detected. However, a combination of R and equatorial ligand has been reported to yield an RCo^I(Chel) species, stable for some hours at room temperature viz. the $[C_6H_5Co^I(Chel)]^-$ complex where Chel = the monoanion of *N,N'*-1,3 propylene-(bisacetylmonoximediimine) [20].

The synthesis of R_FCo^{III}(Salphen) complexes

The problems met in earlier attempts to synthesise R_FCo^{III}(Salphen) compounds [10] can now be understood in the light of the electrochemical studies on Co^{II}(Salphen) and the R_FCo^{III}(Salphen) compounds themselves. Firstly, the reduction potential of Co^{II}(Salphen)/$[Co^I(Salphen)]^-$ is relatively close to the second reduction step $Co^I \rightarrow Co^0$. This $Co^I \rightarrow Co^0$ stage is thus readily accessible using sodium amalgam as the reducing agent in THF. Under the experimental conditions of the earlier work excess amalgam was used along with variable times of reduction, and therefore quantities of $[Co^0(Salphen)]^{2-}$ could be easily formed. These ions would react with perfluoroalkyl iodides to yield $[R_FCo^{II}(Salphen)]^-$ which would dissociate rapidly during the reaction period to yield Co^{II}(Salphen) and R_F^-, the carbanions being able to substitute the ligand.

Although alkyl-Co^{II}(Salphen) derivatives have also been made by [25,26] the oxidative addition of RI to $[Co^I(Salphen)]^-$ solutions the yields of such compounds can vary with amount of sodium amalgam and time of reduction for the reasons given above.

Most other commonly studied ligand systems used in synthesising Co^{III}-organometallics e.g. Co^{II}(Salen) have such widely spaced potentials for the Co^{II}/Co^I and Co^I/Co^0 stages that this problem has not arisen.

Solutions of $[Co^I(Salphen)]^-$ can be produced by electrolysis on a suitable scale for synthetic work and addition of R_FI to such solutions is found to result in high yields (> 60%) of the desired R_FCo^{III}(Salphen) complexes. The electrochemical production of $[Co^I$(Salphen)] on a preparative scale infact provides an excellent synthetic procedure for making both perfluoroalkyl- and alkyl-Co^{III} derivatives, the alkyl complexes being obtained in almost quantitative yields.

Experimental

Co^{II} compounds

Co^{II}(Acen) and Co^{II}(Tfacen) were prepared by literature methods [1]. Co^{II}(Salphen) was prepared by warming stoichiometric quantities of cobalt acetate tetrahydrate and the pre-formed ligand in a small amount of dimethylformamide (30 ml per 0.3 g of ligand) in the presence of a slight excess of KOH. The complex readily crystallised, was filtered, washed with warm dimethylformamide and vacuum-dried. It was used without further purification.

Co^{III} organometallic compounds

R_FCo(Acen) and R_FCo(Tfacen) compounds were prepared as previously described [1] by the reaction of the appropriate R_FI and [Co^I(Acen)]$^-$ or [Co^I(Tfacen)]$^-$, prepared in tetrahydrofuran by the reduction of the corresponding Co^{II} complexes with 1% sodium amalgam. They were precipitated as the mono-aqua compounds R_FCo(Chel)H_2O by the addition of water to the tetrahydrofuran solution and recrystallized from water/tetrahydrofuran before use.

R_HCo(Salphen) compounds were also prepared by the addition of alkyl iodides in slight excess to a solution of [Co^I(Salphen)]$^-$ prepared by reduction of Co^{II}(Salphen)] with a stoichiometric quantity of 1% sodium amalgam.

R_FCo(Salphen) derivatives were obtained by either (A) the reaction of R_FI with Co^{II}(Salphen) in dimethylsulphoxide or (B) the reaction of R_FI with [Co^I(Salphen)]$^-$ prepared by controlled potential electrolysis in a dimethylformamide/tetrahydrofuran mixture or by reduction of Co^{II}(Salphen) with a stoichiometric amount of Na/Hg.

Method A. Co^{II}(Salphen) (0.5 g) was placed in a Carius tube fitted with a Rotoflow tap. The tube was flushed with oxygen-free nitrogen and dry dimethylsulfoxide (5 ml) added followed by a slight stoichiometric excess of the appropriate perfluoroalkyl iodide. The addition of a small amount (0.5 ml) of dry pyridine increased the rate of reaction and aided in eventual isolation of the complex. A small magnetic stirrer bead was placed in the tube to aid mixing. The tube was sealed and heated at 120°C for 30 min with continual stirring. The initial red-violet suspension changed to an orange-red solution during the period of heating. After cooling the contents of the vessel were poured into water (100 ml) with vigorous stirring. The precipitated complex was purified by recrystallization from methanol/water as the mono-aqua derivatives R_FCo^{III}(Salphen)H_2O. Yields of 40–50% based on Co^{II} were readily obtained.

Method B. In a typical experiment Co^{II}(Salphen) (0.3g) was shaken with dimethylformamide (10 ml) until much of the solid had dissolved. The slurry was then added to an electrochemical cell containing dimethylformamide and tetrahydrofuran (1/10) (50 ml) with sodium perchlorate (0.5 *M*) as supporting electrolyte. The solution was then carefully deoxygenated with a stream of purified nitrogen passing through it for 15 min. Reduction was commenced at -1.18 V, a potential (0.1 V) more negative than the maximum voltage of the diffusion wave for the Co^{II} $\rightarrow$ Co^I reduction process. Reduction was continued until only a small residual current remained. A slight excess of perfluoroalkyl iodide was then added to the solution causing a rapid change in colour to red. The reaction mixture was removed from the cell and water added to precipitate the organometallic complex as the mono-aqua compound. The product was filtered and recrystallised twice from tetrahydrofuran/water mixtures to completely remove traces of $NaClO_4$. Yields of up to 70% of organometallic were obtained in this way.

Similar procedures have been used to prepare perfluoroalkyl compounds using Co^{II}(Salen), Co^{II}(Tfacen) and Co^{II}(Acen).

$C_3F_7Co(Salphen)H_2O$: Found: F, 23.8. $C_{23}H_{16}CoF_7N_2O_3$ calcd.: F, 23.7%;

$C_2F_5Co(Salphen)H_2O$: Found: F, 18.6. $C_{22}H_{16}CoF_5N_2O_3$ calcd.: F, 18.6%;

$CF_3Co(Salphen)H_2O$: Found: F, 12.2. $C_{21}H_{16}CoF_3N_2O_3$ calcd.: F, 12.4%;

$C_3F_7Co(Acen)H_2O$: Found: F, 20.0. $C_{15}H_{20}CoF_7N_2O_3$ calcd.: F, 28.4%;

$C_4F_9Co(Tfacen)H_2O$: Found: C, 30.9; H, 2.37. $C_{16}H_{14}CoF_{15}N_2O_3$ calcd.: C, 30.7; H, 2.25%;

$C_3F_7Co(Tfacen)H_2O$: Found: C, 32.9; H, 2.68. $C_{15}H_{14}CoF_{13}N_2O_3$ calcd.: C, 32.3; H, 2.45%

$C_3F_7Co(Salen)H_2O$: Found: C, 44.6; H, 3.43. $C_{19}H_{16}CoF_7N_2O_3$ calcd.: C, 44.6; H, 3.15%.

ESR measurements were recorded using a Varian E12 spectrometer with THF solutions, usually about 10^{-3} *M* in the complex, and frozen to a glass at liquid nitrogen temperatures. The experiments on the reduction of Co^{II}(Salphen) were carried out by gently agitating a THF solution of Co^{II}(Salphen) with 1% sodium amalgam in excess of the amount necessary to reduce Co^{II}(Salphen) by a two-electron process. The flask in which the reduction was carried out had an ESR cell attached to it by a ground glass joint and samples could be removed directly into a cell for examination. Observations were made at intervals until a fixed spectrum was obtained indicating a particular phase of the reduction.

Electrochemical techniques and purification of tetrahydrofuran were as previously described [6]. All measurements were carried out under an atmosphere of nitrogen in a light tight cabinet. High grade nitrogen was used ($O_2 < 10$ ppm) further purified by passage through a tetrahydrofuran solution containing $[Co^I(Salen]^-$ (0.1 *M*), and sodium amalgam (1%). This purification procedure was found most effective in reducing the oxygen content of nitrogen to a level at which it would no longer be detected polarographically in the systems examined.

The reference cell was Ag/Ag^+, the silver salt being silver pentafluoropropionate (0.01 *M*) dissolved in tetrahydrofuran containing $[NBu^n_4][ClO_4]$ (0.1 *M*). The electrode had a potential of +0.618 V with respect to the saturated calomel electrode (S.C.E.). All results are quoted with respect to the latter electrode.

The silver salt was prepared by dissolving silver carbonate (freshly precipitated by mixing solutions of Na_2CO_3 and $AgNO_3$, filtering the yellow solid and washing with water until free of soluble salts) in a slight excess of pentafluoropropionic acid. The solution was evaporated under reduced pressure to crystallization. The salt was recrystallized three times from low boiling (30–40°C) petroleum before use. The solid was stored in the dark. Solutions for the standard cell were freshly prepared each day since occasional unavoidable exposure to light occurred during use and the solutions gradually darkened with deposition of Ag if kept in use for several days continuously.

Supporting electrolytes. $[NBu^n_4][ClO_4]$ (Eastman Kodak) was used for all polarographic and cyclic voltammetric measurements at a concentration of 0.1 *M*. It allowed measurements to be made to -3.0 V without evidence for discharge of the cation. $NaClO_4$ however was used for constant potential coulometry or synthetic procedures where Co^I species would be produced since $[NBu^n_4]^+$ ions react slowly with such Co^I species.

Acknowledgement

This work was supported by grants from the Australian Research Grants Scheme (to B.O.W.) to whom grateful acknowledgement is made.

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