

## Redox Chemistry of Organobis(dimethylglyoximato)cobalt Complexes

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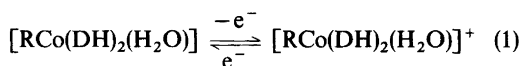
Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

Cyclic voltammetry measurements demonstrate that organobis(dimethylglyoximato)cobalt(III) complexes,  $[\text{RCo}(\text{DH})_2(\text{H}_2\text{O})]$ , (abbreviated  $[\text{CoR}]$ , where  $\text{DH}_2 = \text{dimethylglyoxime}$  and  $\text{R} = \text{alkyl}$  or  $\text{benzyl}$ ) undergo reversible one-electron oxidations to form the corresponding  $[\text{CoR}]^+$  radical cations which have been characterized as cobalt(IV) complexes. Kinetic studies confirm that the chemical oxidation of  $[\text{CoR}]$  complexes by  $[\text{IrCl}_6]^{2-}$  also proceeds through such radical cations which are formed through initial outer-sphere electron transfer reactions. Thermodynamic and kinetic measurements on these reactions are described. The  $[\text{CoR}]^+$  radical cations are stable in aqueous methanol solutions at  $-78^\circ\text{C}$  and have been characterized by electronic and EPR spectroscopy. Chemical reactions of  $[\text{CoR}]^+$ , including nucleophilic displacement of  $\text{R}^+$  and disproportionation, are described.

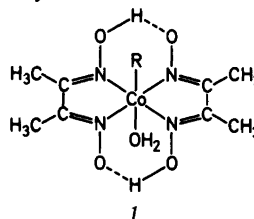
Whereas the simple redox chemistry of inorganic coordination compounds has been extensively investigated, and many of the mechanistic features of the electron transfer reactions of such complexes are now well understood, the corresponding redox chemistry of organometallic compounds is still largely unexplored. In contrast to inorganic complexes which often accommodate variable stable electron configurations connected by simple electron transfer processes, *e.g.*  $[\text{Fe}(\text{CN})_6]^{4-} \rightleftharpoons [\text{Fe}(\text{CN})_6]^{3-} + e^-$ , stable organometallic compounds and metal carbonyls usually correspond to closed shell con-

figurations (typically 18 or, in some cases, 16 electrons) which are severely destabilized by electron addition or removal with consequent accompanying chemical decomposition or transformation.

The present paper describes studies on the electrochemical and chemical oxidations of a series of organobis(dioximato)cobalt(III) complexes,  $[\text{RCo}(\text{DH})_2(\text{H}_2\text{O})]$  (*I*, abbreviated  $[\text{CoR}]$ , where  $\text{DH}_2 = \text{dimethylglyoxime}$  and  $\text{R} = \text{alkyl}$  or  $\text{benzyl}$ ). Evidence is deduced for the reversible formation of the corresponding radical cations,  $[\text{RCo}(\text{DH})_2(\text{H}_2\text{O})]^+$ , by electrochemical or outer-sphere one-electron oxidations according to eqn. (1). The studies reported in this paper



encompass the following themes: (a) cyclic voltammetry measurements on reaction 1, (b) thermodynamic and kinetic measurements on the oxidation of  $[\text{CoR}]$  complexes by  $[\text{IrCl}_6]^{2-}$ , (c) the spectral characterization of stable aqueous-methanol solutions of  $[\text{CoR}]^+$  radical cations, and (d) elucidation of some features of the chemical reactivity of such radical cations. Attention is directed to pertinent earlier publications on related themes including several preliminary communications from our own laboratory.<sup>1-9</sup>



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## RESULTS

**Electrochemical oxidations.** Fig. 1 depicts cyclic voltammograms for the oxidation of representative [CoR] complexes in aqueous solution at 25 °C. In most cases sufficiently high scan rates (*e.g.* >0.2 V/s for R=C<sub>2</sub>H<sub>5</sub> and >20 for R=iso-C<sub>3</sub>H<sub>7</sub>) yielded voltammograms characteristic of reversible one-electron oxidation processes according to eqn. (1) ( $E_c - E_a = 60 \pm 10$  mV,  $n = 1.0$ ), from which the reversible oxidation potentials,  $E_{\frac{1}{2}}$ , listed in Table 1 were determined. The trend of  $E_{\frac{1}{2}}$  values is in the expected direction of increasing ease of oxidation of [CoR] with increasing electron donor power of R. This trend is depicted in Fig. 2 for a series of *para*-substituted benzylcobalt complexes for which the data yield a good linear plot of  $E_{\frac{1}{2}}$  versus the Hammett substituent constant,  $\sigma_p$  ( $\rho = -1.2$ ). From the reversibility of the cyclic voltammograms (*e.g.* those in Fig. 1) it can be deduced that the lifetimes of the [CoR]<sup>+</sup> radical cations decrease in the order R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> > iso-C<sub>3</sub>H<sub>7</sub> and *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> > C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> ≫ *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> (oxidation of the latter organocobalt complex being irreversible at scan rates as high as 100 V/s). This is consistent with a decomposition mode involving nucleophilic attack on R [presumably leading to Co(II) and ROH, as found in the studies on chemical oxidation described below], as is the observation that the lifetime of [CoR]<sup>+</sup> is reduced by the addition of nucleophiles such as Cl<sup>-</sup>.

Because of limited solubility of the [CoR] complexes in water at low acidities, the electrochemical measurements (as well as the kinetic measurements

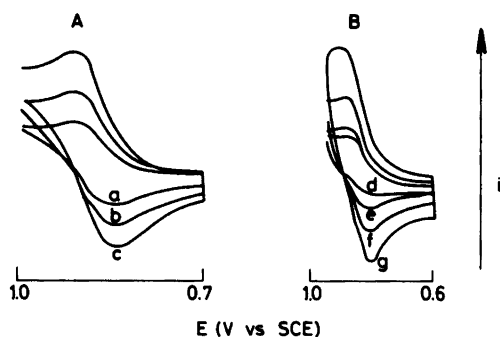


Fig. 1. Cyclic voltammograms of aqueous solutions of [RCo(DH)<sub>2</sub>(H<sub>2</sub>O)] (*ca.* 10<sup>-4</sup> mol/l) containing 1.0 mol/l NaClO<sub>4</sub>. A, R=C<sub>2</sub>H<sub>5</sub>; B, R=iso-C<sub>3</sub>H<sub>7</sub>. Scan rates (V/s): a, 0.2; b, 0.5; c, 1.0; d, 2.0; e, 5.0; f, 10; g, 20. (pH adjusted to 2.0 with HClO<sub>4</sub>).

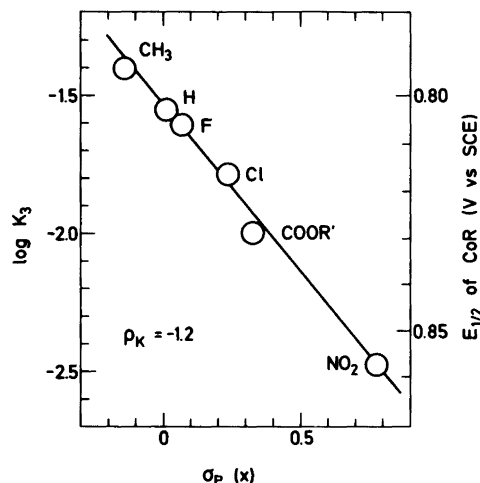


Fig. 2. Dependence of  $E_{\frac{1}{2}}$  (and of  $K_3$  computed according to eqn. 7) for the oxidation of [*p*-XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Co(DH)<sub>2</sub>(H<sub>2</sub>O)] on the Hammett substituent constant  $\sigma_p(X)$ . (Data for 1.0 mol/l NaClO<sub>4</sub> solutions; pH adjusted to 2.0 with HClO<sub>4</sub>).

described below) are most conveniently performed in solutions containing *ca.* 1 mol/l HClO<sub>4</sub>. However, the behaviour of such solutions is complicated by the susceptibility of the complexes to protonation,<sup>10</sup> *i.e.* to form [RCo(DH)<sub>2</sub>(DH)(H<sub>2</sub>O)]<sup>+</sup> ions (presumably with markedly lower susceptibilities

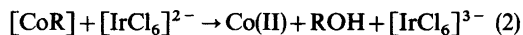
Table 1. Cyclic voltammetry data for the oxidation of [RCo(DH)<sub>2</sub>(H<sub>2</sub>O)].

R	$E_{\frac{1}{2}}$ (V versus SCE) <sup>a</sup>	
	1.0 mol/l HClO <sub>4</sub>	1.0 mol/l NaClO <sub>4</sub> <sup>b</sup>
CH <sub>3</sub>	0.902	—
C <sub>2</sub> H <sub>5</sub>	0.878	—
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	0.867	—
iso-C <sub>3</sub> H <sub>7</sub>	0.856	—
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	0.849	0.794
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	0.859	0.802
<i>p</i> -FC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	0.873	0.805
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	0.876	0.816
<i>p</i> -C <sub>2</sub> H <sub>5</sub> OCOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	—	0.829
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	0.907	0.858

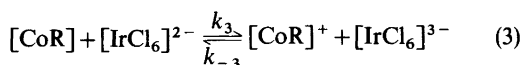
<sup>a</sup>  $E_{\frac{1}{2}} = \frac{1}{2}(E_a + E_c)$  measured at scan rates ranging from 0.2 to 100 V/s. Estimated accuracy  $\pm 0.002$  V. <sup>b</sup> pH adjusted to 2.0 with HClO<sub>4</sub>.

to oxidation). Typical  $pK_a$  values of such  $[\text{HCoR}]^+$  ions are 0.54 and 0.38 for  $\text{R}=\text{CH}_3$  and  $\text{C}_6\text{H}_5\text{CH}_2$ , respectively.<sup>10</sup> The consistent difference (Table 1) of ca. 0.06 V between the  $E_3$  values measured in 1 mol/l  $\text{HClO}_4$  solutions and those measured at  $\text{pH}=2$  (where such protonation is negligible) presumably reflects the influence of this effect. However, it is noteworthy that the *trend* of apparent  $E_3$  values for the various substituted benzyl complexes is virtually identical for the two sets of conditions.

**Chemical oxidation by  $[\text{IrCl}_6]^{2-}$ .** Oxidation of several  $[\text{RCo}(\text{DH})_2(\text{H}_2\text{O})]$  complexes (*e.g.*  $\text{R}=\text{benzyl}$ ) by  $[\text{IrCl}_6]^{2-}$  in aqueous solution has previously been reported<sup>5</sup> to proceed according to the stoichiometry of eqn. 2 (modified in some cases by replacement of part of the ROH by other products formally derived from the latter, notably  $\text{RON}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{NOH}$ <sup>11</sup> or, in the case of  $\text{R}=\text{alkyl}$ , the corresponding olefins, *e.g.* some propylene together with isopropyl alcohol when  $\text{R}=\text{isopropyl}$ ). We have confirmed, for  $\text{R}=\text{iso-C}_3\text{H}_7$ ,  $\text{C}_6\text{H}_5\text{CH}_2$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2$  and  $p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2$ , over a wide range of initial concentrations with either reactant initially present in excess, that  $[\text{CoR}]$  and  $[\text{IrCl}_6]^{2-}$  consistently react in the ratio 1:1 and that the final  $\text{Co}^{2+}$  concentration is equal to the concentration of  $[\text{CoR}]$  oxidized in accord with eqn. (2).



Kinetic measurements provided convincing evidence for the mechanism depicted by eqns. 3–4, in which the first step involves *reversible* one-electron transfer between  $[\text{CoR}]$  and  $[\text{IrCl}_6]^{2-}$  in line with the usual role<sup>2,12,13</sup> of  $[\text{IrCl}_6]^{2-}$  as an outer-sphere one-electron oxidant. Thus, the observed kinetics conformed to eqns. (5) and (6) which are derived for this mechanistic scheme by assuming the steady state approximation for  $[\text{CoR}]^+$ .



$$\text{Rate} = \frac{-d[\text{CoR}]}{dt} = \frac{k_3 k_4 [\text{CoR}][\text{IrCl}_6^{2-}]}{k_{-3} [\text{IrCl}_6^{2-}] + k_4} \quad (5)$$

$$\frac{[\text{CoR}][\text{IrCl}_6^{2-}]}{\text{Rate}} = \frac{1}{k_{\text{obs}}} = \frac{k_{-3} [\text{IrCl}_6^{2-}]}{k_3 k_4} + \frac{1}{k_3} \quad (6)$$

The linear plots of  $k_{\text{obs}}^{-1}$  versus  $[\text{IrCl}_6^{2-}]$  in Fig. 3 are in accord with eqn. (6). Values of  $k_{-3}/k_3 k_4$  and of  $k_3$ , deduced from the slopes and intercepts of such plots, respectively, are listed in Table 2. Whereas the former values could usually be evalu-

Table 2. Kinetic and thermodynamic data for the oxidation of  $[\text{RCo}(\text{DH})_2(\text{H}_2\text{O})]$  by  $[\text{IrCl}_6]^{2-}$ .

R	Medium <sup>a</sup>	$k_3$ $\text{s}^{-1}$	$(k_{-3}/k_3 k_4)$ s	$(k_3/k_{-3})^b$	$k_4(\text{calc})$ $\text{s}^{-1}$	$k_4(\text{exp})$ $\text{s}^{-1}$
$p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2$	A	$3.4 \times 10^5$	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>
$p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2$	A	$1.4 \times 10^5$	$1.7 \times 10^{-2}$	$3.9 \times 10^{-2}$	$1.5 \times 10^3$	$> 10^2$
$\text{C}_6\text{H}_5\text{CH}_2$	A	$\sim 5 \times 10^4$ <sup>d</sup>	11.4	$2.8 \times 10^{-2}$	3.1	8.3
$p\text{-FC}_6\text{H}_4\text{CH}_2$	A	$\sim 5 \times 10^4$ <sup>d</sup>	4.3	$2.6 \times 10^{-2}$	9.1	9.1
$p\text{-ClC}_6\text{H}_4\text{CH}_2$	A	$\sim 1 \times 10^4$ <sup>d</sup>	35.8	$1.7 \times 10^{-2}$	1.7	1.7
$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2$	A	$\geq 10 \times 10^2$ <sup>d</sup>	$1.8 \times 10^4$	$3.2 \times 10^{-3}$	$1.7 \times 10^{-2}$	$1.7 \times 10^{-2}$
$\text{CH}_3$	A	<sup>d</sup>	$8.3 \times 10^4$	—	—	—
$\text{CH}_3$	B	<sup>d</sup>	$1.2 \times 10^5$	$4.6 \times 10^{-4}$	$1.8 \times 10^{-2}$	$1.6 \times 10^{-2}$
$\text{C}_2\text{H}_5$	B	<sup>d</sup>	$8.8 \times 10^4$	$1.1 \times 10^{-3}$	$1.0 \times 10^{-2}$	$0.9 \times 10^{-2}$
$n\text{-C}_3\text{H}_7$	A	<sup>d</sup>	$6.4 \times 10^3$	—	—	—
$n\text{-C}_3\text{H}_7$	B	<sup>d</sup>	$7.1 \times 10^4$	$1.9 \times 10^{-3}$	$7.3 \times 10^{-3}$	$9.3 \times 10^{-3}$
$\text{iso-C}_3\text{H}_7$	A	$3 \times 10^5$	$8.5 \times 10^{-1}$	—	—	—
$\text{iso-C}_3\text{H}_7$	B	—	9.7	$2.7 \times 10^{-3}$	38	32

<sup>a</sup> A, 1.0 mol/l  $\text{NaClO}_4$ ; pH adjusted to 2.0 with  $\text{HClO}_4$ . B, 1.0 mol/l  $\text{HClO}_4$ . <sup>b</sup> Computed from eqn. 7 using  $E_3([\text{IrCl}_6]^{2-})=0.711\text{V}$  and  $0.704\text{V}$  vs. SCE in medium A and B, respectively. <sup>c</sup> Measurement precluded by irreversibility of step (3), *i.e.* large values of  $k_4/k_{-3}$ . <sup>d</sup> Accurate measurement precluded by small value of intercept of plot of  $k_{\text{obs}}^{-1}$  versus  $[\text{IrCl}_6^{2-}]$ .

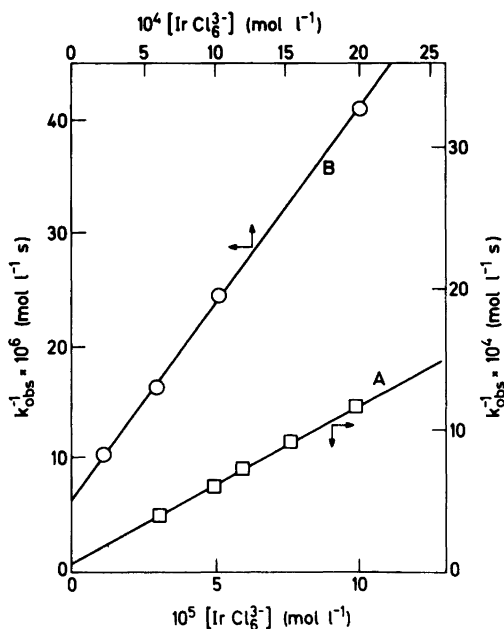


Fig. 3. Plots of  $k_{\text{obs}}^{-1}$  versus  $[\text{IrCl}_6^{3-}]$  for the oxidation of  $[\text{RCo}(\text{DH})_2(\text{H}_2\text{O})]$  by  $[\text{IrCl}_6]^{2-}$ . A,  $\text{R} = \text{C}_6\text{H}_5\text{-CH}_2$ ; B,  $\text{R} = p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2$ .

ated with considerable accuracy (typically better than  $\pm 5\%$ ), only in a few cases (as noted in Table 2) were the intercepts of plots such as those in Fig. 3 sufficiently large to permit accurate evaluation of  $k_3$ . Values of the equilibrium quotients of reaction 3,  $K_3 (=k_3/k_{-3})$ , determined from the cyclic voltammetry measurements [*i.e.* according to eqn. (7)], also are listed in Table 2 together with the values of  $k_4$ , *i.e.*  $k_4(\text{calc})$ , yielded by combination of such electrochemically determined values of  $(k_3/k_{-3})$  and the corresponding kinetically determined values of  $(k_{-3}/k_3k_4)$ .

$$\log K_3 = [E_{\frac{1}{2}}(\text{IrCl}_6^{3-}) - E_{\frac{1}{2}}(\text{CoR})]/0.059 \quad (7)$$

In most cases, the lifetimes of the  $[\text{CoR}]^+$  radical ions in aqueous solution, even at room temperature, were sufficiently long (*ca.* 1 min) that aqueous solutions of  $[\text{CoR}]^+$  could be prepared directly by oxidizing  $[\text{CoR}]$  rapidly, either chemically, *e.g.* with Ce(IV), Co(III) or tris(bipyridyl)iron(III), or electrochemically (using a Pt mesh electrode). The spectrum of the transient  $[\text{n-C}_3\text{H}_7\text{Co}(\text{DH})_2(\text{H}_2\text{O})]^+$  ion, determined in a stopped-flow experiment using

Ce(IV) as oxidant, was found to be similar to that of the corresponding stable ion in aqueous-methanol at  $-78^\circ\text{C}$  (see below). Such experiments also yielded direct spectrophotometric measurements of the first-order rate constants for the decomposition of  $[\text{CoR}]^+$  according to eqn. (4), *i.e.* the  $k_4(\text{exp})$  values in Table 2; these are generally in excellent agreement with the values deduced, as explained above, from the combination of equilibrium measurements on reaction 3 and kinetic measurements on the overall reaction 2. The proposed mechanistic scheme thus derives support from a considerable body of mutually consistent independently determined equilibrium and kinetic data as well as the direct detection of the proposed  $[\text{CoR}]^+$  intermediates.

*Generation and characterization of stable  $[\text{CoR}]^+$  ions at low temperatures.* The oxidation of  $[\text{CoR}]$  complexes to the corresponding  $[\text{CoR}]^+$  ions could be quantitatively effected in acidified aqueous methanol solutions (*ca.* 80 vol % methanol) using cerium(IV) nitrate as oxidant. The resulting  $[\text{CoR}]^+$  solutions ( $10^{-4}$  to  $10^{-3}$  mol/l), which were stable for many hours at  $-78^\circ\text{C}$ , absorbed throughout the visible-UV region. A typical spectrum (for  $\text{R} = \text{C}_2\text{H}_5$ ), depicted in Fig. 4, exhibits an absorption maximum at 400 nm ( $\epsilon \sim 3 \times 10^3$  mol/l cm) and shoulders at 450 and 525 nm ( $\epsilon \sim 2.5 \times 10^3$  and  $1.5 \times 10^3$  mol/l cm, respectively). The results of spectral titrations (exemplified by Fig. 5) for several  $[\text{CoR}]$  complexes confirmed, in each case, the 1:1 stoichiometry of eqn. (8)

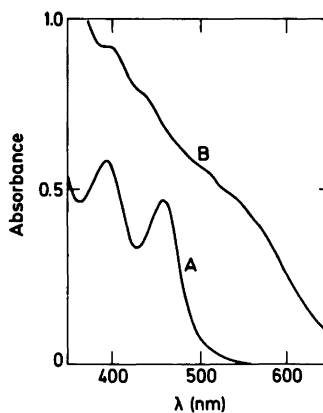


Fig. 4. Spectra in aqueous methanol (80 vol % methanol; 0.5 mol/l  $\text{H}_2\text{SO}_4$ ) at  $-78^\circ\text{C}$ . A,  $3.0 \times 10^{-4}$  mol/l  $[\text{C}_2\text{H}_5\text{Co}(\text{DH})_2(\text{H}_2\text{O})]$ ; B, after oxidation with Ce(IV).

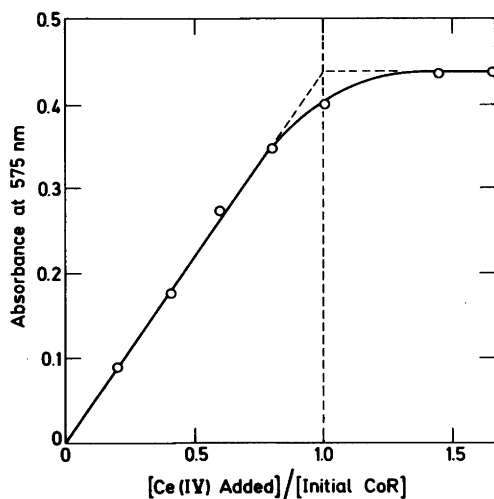
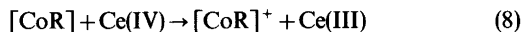


Fig. 5. Spectral titration of an aqueous methanol solution (80 vol % methanol; 0.5 mol/l  $\text{H}_2\text{SO}_4$ ) containing  $3.0 \times 10^{-4}$  mol/l  $[\text{C}_2\text{H}_5\text{Co}(\text{DH})_2(\text{H}_2\text{O})]$  with Ce(IV) at  $-78^\circ\text{C}$ .



Solutions of  $[\text{CoR}]^+$  ions prepared in this way were sufficiently stable to permit characterization by EPR spectroscopy in both the liquid and frozen states. The results of such studies, which we have previously reported, convincingly support the formulation of these radical cations as organocobalt(IV) complexes.<sup>6</sup>

**Chemical reactivity of  $[\text{CoR}]^+$  ions.** Warming aqueous methanol solutions of  $[\text{CoR}]^+$  ions, prepared by oxidation with Ce(IV) at  $-78^\circ\text{C}$ , resulted in decomposition of the ions. Such decomposition, which usually set in below  $-20^\circ\text{C}$ , followed two distinct patterns, the first characteristic of benzyl and secondary alkyl (e.g.  $\text{R} = \text{iso-C}_3\text{H}_7$  and  $2\text{-C}_8\text{H}_{17}$ ) cobalt complexes and the second of primary alkyl cobalt complexes ( $\text{R} = \text{C}_2\text{H}_5$ ,  $n\text{-C}_3\text{H}_7$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$ ).

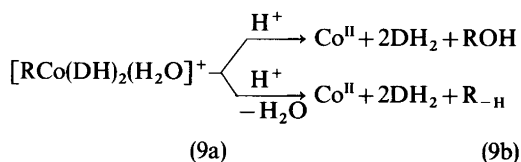
Decomposition of  $[\text{C}_6\text{H}_5\text{CH}_2\text{Co}]^+$ ,  $[\text{iso-C}_3\text{H}_7\text{Co}]^+$  and  $[2\text{-C}_8\text{H}_{17}\text{Co}]^+$  in aqueous methanol (80 vol % methanol) at  $-23^\circ\text{C}$ , monitored spectrophotometrically at 575 nm, exhibited first order kinetics, i.e.  $-\text{d}[\text{CoR}]^+/\text{d}t = k_0 [\text{CoR}]^+$ , with  $k_0$  values (listed in Table 3) of approximately  $3 \times 10^{-4}$ ,  $1 \times 10^{-4}$  and  $2 \times 10^{-2} \text{ s}^{-1}$ , respectively (all at 1.0 m/l ionic strength, maintained with  $\text{NaClO}_4$ ). In the case of  $\text{R} = \text{iso-C}_3\text{H}_7$  it was

Table 3. Kinetic data for the decomposition of  $[\text{CoR}]^+$  according to eqn. (9)<sup>a</sup>.

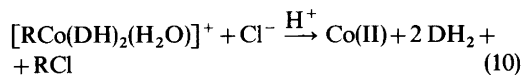
R	$10^3 [\text{CoR}^+]$ mol/l	$[\text{HClO}_4]$ mol/l	$10^3 k_0$ $\text{s}^{-1}$
iso- $\text{C}_3\text{H}_7$	0.7	1.0	1.0
iso- $\text{C}_3\text{H}_7$	0.7	0.2	1.3
iso- $\text{C}_3\text{H}_7$	0.7	0.06	1.2
iso- $\text{C}_3\text{H}_7$	0.7	0.01	1.4
iso- $\text{C}_3\text{H}_7$	4.2	1.0	0.7
iso- $\text{C}_3\text{H}_7$	4.2	1.0	0.8 <sup>b</sup>
$2\text{-C}_8\text{H}_{17}$	0.7	1.0	19
$\text{C}_6\text{H}_5\text{CH}_2$	0.7	0.02	0.26

<sup>a</sup> Rate constants measured at  $-23^\circ\text{C}$  in aqueous methanol solutions containing 80 vol % methanol; ionic strength maintained at 1.0 mol/l with  $\text{NaClO}_4$ .  
<sup>b</sup> 0.05 mol/l HCl added.

established that  $k_0$  is substantially independent of the initial  $[\text{CoR}]^+$  concentration (between  $7 \times 10^{-4}$  and  $4.2 \times 10^{-3}$  mol/l) and of the  $\text{H}^+$  concentration (between 0.01 and 1.0 mol/l). In typical experiments, about 10–20% of the cobalt could be recovered as unconverted  $[\text{CoR}]$  following complete decomposition of the  $[\text{CoR}]^+$  and the remaining (ca. 80%) as Co(II). The stoichiometries of decomposition of  $[\text{C}_6\text{H}_5\text{CH}_2\text{Co}]^+$  and  $[2\text{-C}_8\text{H}_{17}\text{Co}]^+$  are approximated by eqns. (9a) and (9b), respectively (where  $\text{R}_{-\text{H}} = 1\text{-}$  and/or  $2\text{-}$ octene)



In related studies we have also demonstrated that in solutions containing ca. 2.5 M HCl reaction 9(b) of  $[2\text{-C}_8\text{H}_{17}\text{Co}]^+$  is accompanied by ca. 25%  $\text{Cl}^-$ -induced nucleophilic decomposition according to eqn. (10) and have established that this occurs with inversion of configuration at the cobalt-bonded carbon atom.<sup>7</sup>



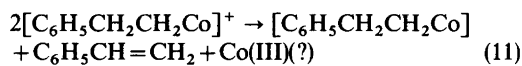
Decomposition of  $[\text{C}_2\text{H}_5\text{Co}]^+$  and  $[\text{C}_6\text{H}_5\text{CH}_2\text{-CH}_2\text{Co}]^+$  followed a quite different pattern. The

Table 4. Kinetic data for the decomposition of  $[\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Co}(\text{DH})_2(\text{H}_2\text{O})]^+$  according to eqn. 11<sup>a</sup>.

$10^3[\text{CoR}^+]$ mol/l	$10^3[\text{CoR}]$ mol/l	$[\text{HCl}]$ mol/l	$2k_{12}$ $\text{l mol}^{-1} \text{s}^{-1}$
1.4	2.8	0	0.28
2.1	3.8	0	0.27
2.8	2.8	0	0.27
2.8	1.4	0	0.23
2.8	3.5	0	0.26
0.7	1.4	0.050	8.8
0.7	2.1	0.050	7.6
0.7	2.8	0.050	5.9
0.7	3.5	0.050	4.9
0.7	4.2	0.050	4.2
0.7	5.6	0.050	3.7

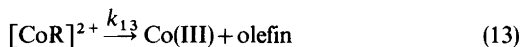
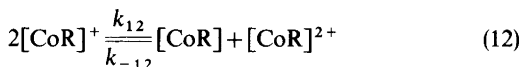
<sup>a</sup> Rate constants measured in aqueous methanol solutions (80 vol % methanol) containing 1.0 mol/l  $\text{HClO}_4$  at  $-23^\circ\text{C}$ .

stoichiometry in the latter case is represented by eqn. (11),



in which the oxidation state of the inorganic cobalt product cannot be definitively specified. The latter is ultimately identified as  $\text{Co}^{2+}$ ; however, this does not necessarily correspond to its initial oxidation state since  $\text{Co}^{3+}$  (*i.e.* the product expected from the overall stoichiometry) is unstable and readily undergoes reduction to  $\text{Co(II)}$  under the reaction workup conditions. This reaction exhibited *second order* kinetics, *i.e.*  $-\text{d}[\text{CoR}^+]/\text{d}t = 2k_{12}[\text{CoR}^+]^2$ , with  $2k_{12} = 2.6 \times 10^{-1} \text{ l mol}^{-1} \text{ s}^{-1}$  (at  $-23^\circ\text{C}$  in solutions containing 1.0 mol/l  $\text{HClO}_4$ ), unaffected by variation of the initial  $[\text{CoR}^+]$  concentration ( $1.4 \times 10^{-3}$  to  $2.8 \times 10^{-3}$  mol/l) or added  $[\text{CoR}]$  ( $1.4 \times 10^{-3}$  to  $4.5 \times 10^{-3}$  mol/l). The decomposition reaction was strongly accelerated by added  $\text{HCl}$  ( $k_{12} > 10$  at 0.05 mol/l  $\text{HCl}$ ) and, in the presence of  $\text{HCl}$ , the second order rate constants (*i.e.*  $k_{12}$ ) exhibited an inverse dependence on the  $[\text{CoR}]$  concentration (see Table 4). Qualitatively similar kinetics (including catalysis by  $\text{Cl}^-$ ) were observed for the decomposition of  $[\text{C}_2\text{H}_5\text{Co}]^+$ , except that in the latter case the inverse dependence on the concentration of  $[\text{CoR}]$  was evident even in the absence of  $\text{Cl}^-$ .

These observations can be accommodated by the mechanistic scheme,



for which the steady-state rate law,

$$\frac{-\text{d}[\text{CoR}^+]}{\text{d}t} = \frac{2k_{12}k_{13}[\text{CoR}^+]^2}{k_{-12}[\text{CoR}] + k_{13}} \quad (14)$$

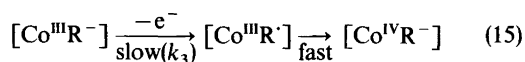
is consistent with the observed kinetic behaviour. The effect of  $\text{Cl}^-$  can be accommodated within this scheme if  $\text{Cl}^-$  catalyzes reaction (12), *i.e.* increases the effective values of both  $k_{12}$  and  $k_{-12}$ . Such catalysis by  $\text{Cl}^-$  and other anions is quite common for electron transfer reactions between metal complexes.<sup>14</sup> Furthermore, the reversible disproportionation of  $[\text{CoR}^+]$  according to eqn. (12), also finds close analogies in reactions of other organometallic radical cations, for example  $[\text{Cr}(\text{CO})_6]^+$  generated by electrochemical oxidation of  $[\text{Cr}(\text{CO})_6]$ .<sup>15</sup> Failure to detect the disproportionative pathway in the case of the benzyl and secondary alkyl cobalt complexes presumably reflects the much higher reactivity of these complexes toward nucleophilically-induced decomposition [*i.e.* according to eqn. (9)].

## DISCUSSION

A principal objective of these studies has been the physical and chemical characterization of the novel cations,  $[\text{CoR}^+]$ , produced by the reversible chemical or electrochemical oxidation of organobis(dimethylglyoximate)cobalt(III) complexes. In the absence of close precedents, the electronic structures of such radical cations are not initially obvious, especially with respect to the extent of contributions from the two limiting formulations,  $[\text{Co}^{\text{III}}\text{R}^+]^+$  and  $[\text{Co}^{\text{IV}}\text{R}^-]^+$ . The evidence provided by the EPR studies convincingly supports the latter formulation, *i.e.* the description of these radical cations as cobalt(IV) complexes.<sup>6</sup> Some support for this conclusion also is provided by the results of the electrochemical studies reported in this paper, *i.e.* the cyclic voltammetry measurements on the series of *p*-substituted benzyl compounds,  $[p\text{-X}-\text{C}_6\text{H}_4\text{CH}_2\text{Co}(\text{DH})_2(\text{H}_2\text{O})]$ . These yielded a dependence of the

equilibrium constants ( $K_3$ ) for the reversible one-electron oxidation on the Hammett substituent constant of X, corresponding to a  $\rho$  value of only ca. -1.2. This value would appear to be too small to be compatible with "R-" being the principal site of electron removal, *i.e.* with formulation of the resulting radical cation as  $[\text{Co}^{\text{III}}\text{R}^\cdot]$ .

Examination of the data in Table 2 reveals an unusual pattern of relationships between the rate constants ( $k_3$ ) and equilibrium constants ( $K_3$ ) for reaction 3. Although the difficulties cited (*i.e.* the small intercepts of the plots of  $k_{\text{obs}}^{-1}$  versus  $[\text{IrCl}_6^{3-}]$ ) limit the accuracy of determination of some of the  $k_3$  values, it is nevertheless apparent that, for the series of *p*-substituted benzylcobalt complexes examined, the rate constant  $k_3$  exhibits a significantly larger dependence on the variation of R than the corresponding equilibrium constant,  $K_3$ . These data give rise to a Marcus plot<sup>16</sup> of  $\log k_3$  versus  $\log K_3$  with an anomalously large slope of ca. 2-3 instead of the slope of ca. 0.5 expected for a simple outer-sphere electron transfer reaction (and found, for example, in the closely-related oxidations of  $\text{PbR}_4$  compounds by  $[\text{IrCl}_6^{2-}]$ ).<sup>17,2</sup> This result suggests that reaction 3 may actually be a stepwise process of the type depicted by eqn. (15) in which the second step presumably involves a structural rearrangement as well as internal electron transfer. In such a case the measured rate-constant and equilibrium constant would not refer to the same process. The testing of this suggestion calls for measurements on a faster time scale than can be achieved by the electrochemical and chemical oxidation procedures employed in these studies, *e.g.* pulse radiolysis.



Finally it is of interest to note that, notwithstanding the evidence favouring formulation of the ground states of the  $[\text{CoR}]^+$  radical cations as organocobalt(IV) complexes (*i.e.* formally as  $\text{Co}^{\text{IV}}\text{R}^-$ ), the principal reactivity patterns exhibited by these ions (*e.g.* reactions 4, 9 and 10) reflect marked susceptibility of nucleophilic attack on R leading to products formally derived from  $\text{Co}^{\text{II}}$  and  $\text{R}^\cdot$ .

## EXPERIMENTAL

**Materials.** (a)  $\text{CoR}$  complexes. The procedure used to prepare the starting  $[\text{RCo}(\text{DH})_2(\text{pyridine})]$  compounds and the corresponding aqueous solutions of  $[\text{RCo}(\text{DH})_2(\text{H}_2\text{O})]$  have previously been described.<sup>10</sup> (b)  $\text{K}_2[\text{IrCl}_6]$  was prepared by dissolving commercial  $\text{Na}_2[\text{IrCl}_6] \cdot 6\text{H}_2\text{O}$  in ca. 1 mol/l HCl and heating while bubbling  $\text{Cl}_2$  through the solution to oxidize any Ir(III) or reducing impurities. KCl was added to precipitate  $\text{K}_2[\text{IrCl}_6]$  which was recrystallized from hot aqueous HCl (ca. 1 mol/l) - KCl (ca. 2 mol/l) while passing  $\text{Cl}_2$  through the solution. For some of the kinetic experiments the  $[\text{IrCl}_6]^{2-}$  was further purified by electrolysis with a Pt electrode at 0.85 V vs. SCE until the concentration of Ir(III) (as estimated from the limiting current) was less than  $10^{-8}$  mol/l. (c)  $\text{K}_3[\text{IrCl}_6]$  was prepared with (i) by recrystallizing the commercial salt from hot aqueous HCl (ca. 1 mol/l) - KCl (ca. 2 mol/l), followed by repeated washing with boiling methanol and, finally, with ether; or (ii) by reducing  $\text{K}_2[\text{IrCl}_6]$  in 0.1 mol/l HCl with a slight excess of  $\text{FeSO}_4$ , eluting through a cation exchange column and precipitating the product salt by addition of KCl to the eluate. (d)  $\text{NaClO}_4$  was prepared as a concentrated stock solution (ca. 5 mol/l) by neutralizing sodium carbonate with perchloric acid (both analytical reagent grade).

**Electrochemical measurements.** The cyclic voltammetry measurements were made with a PAR 173/175/179 assembly using a conventional three-electrode circuit. The reference electrode was either a saturated potassium chloride calomel electrode (SCE) or a saturated sodium chloride calomel electrode (to eliminate formation of  $\text{KClO}_4$  in the reference junction) in which case the measured potentials were referred to SCE by relating them to the measured  $E_3$  values for the  $[\text{IrCl}_6^{3-}]/[\text{IrCl}_6^{2-}]$  couple (0.711 V vs. SCE). The auxiliary electrode was either (a) a platinum disc, or (b) a carbon paste capillary. Because of its lower residual current the latter electrode was preferred for the experiments at pH ~2 where the concentrations of  $[\text{CoR}]$  were limited by solubility to ca.  $10^{-4}$  to  $10^{-3}$  mol/l. The cell was thermostatted at 25 °C and flushed with  $\text{N}_2$  to remove  $\text{O}_2$ . The cyclic voltammograms were recorded on a Tektronix storage oscilloscope and the potentials measured with a Fluke digital voltmeter.

**Analytical procedures.** The product solutions following oxidation of  $[\text{CoR}]$  and decomposition of  $[\text{CoR}]^+$  were analyzed as follows: (a)  $[\text{CoR}]$  was determined spectrophotometrically using the characteristic absorption bands in the 400-500 nm region ( $\epsilon \sim 10^3$  l/mol cm; *e.g.* see Fig. 1). (b)  $\text{Co}^{2+}$  was determined spectrophotometrically as the thiocyanate complex.<sup>18</sup> (c) Dimethylglyoxime was deter-

mined gravimetrically as the nickel salt following removal of  $\text{Co}^{2+}$  by passing the solution over a cation exchange resin. (d) Organic products (2-propanol, 1- and 2-octene, benzyl alcohol and styrene) were identified and estimated by gas chromatography or (in the case of propylene) mass spectrometrically.

**Kinetic measurements.** Kinetic measurements on the oxidation of the  $[\text{CoR}]$  complexes by  $[\text{IrCl}_6]^{2-}$  were made by monitoring the disappearance of  $[\text{CoR}]$  spectrophotometrically at ca. 500 nm. The measurements were performed at 25 °C using either a Cary 16 spectrophotometer or (in most cases) a Durrum stopped flow spectrophotometer. The most extensive measurements were made on reaction solutions containing known concentrations of added  $[\text{IrCl}_6]^{3-}$  in order to obtain data which could be analyzed by plotting  $k_{\text{obs}}^{-1}$  vs.  $[\text{IrCl}_6^{3-}]$  (see, for example, Fig. 3). These experiments were performed under pseudo-first-order conditions with either reactant present in excess. Typical initial concentration ranges were:  $1 \times 10^{-5}$  to  $2 \times 10^{-4}$  mol/l  $[\text{CoR}]$ ,  $1 \times 10^{-5}$  to  $5 \times 10^{-4}$  mol/l  $[\text{IrCl}_6]^{2-}$  and up to  $10^{-3}$  mol/l  $[\text{IrCl}_6]^{3-}$ . Such experiments with added  $[\text{IrCl}_6]^{3-}$  consistently gave results in excellent accord with eqns. 5 and 6 (see, for example, Fig. 3) and yielded reliable values of  $k_{-3}/k_3k_4$ . However, only in a few cases (e.g.  $\text{R} = p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2$  and  $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2$ ) were the intercepts of such plots sufficiently large to permit accurate evaluation of  $k_3$  by this procedure. Where this difficulty was encountered (e.g. for  $\text{R} = \text{C}_6\text{H}_5\text{-CH}_2$ ,  $p\text{-FC}_6\text{H}_4\text{CH}_2$  and  $p\text{-ClC}_6\text{H}_4\text{CH}_2$ ) the direct estimation of  $k_3$  also was attempted at very low initial reactant concentrations (to prevent accumulation of significant concentrations of  $[\text{IrCl}_6]^{3-}$ ), typically ca.  $10^{-6}$  mol/l  $[\text{CoR}]$ . The approximate values of  $k_3$  yielded by these experiments were consistent with those estimated from the intercepts of plots of  $k_{\text{obs}}^{-1}$  vs.  $[\text{IrCl}_6^{3-}]$  and are listed in Table 2.

Kinetic measurements on the decomposition of  $[\text{CoR}]^+$  in aqueous methanol at low temperatures were performed spectrophotometrically (Cary 14), monitoring the disappearance of  $[\text{CoR}]^+$  at 575 nm. A vacuum-jacketed cell was used for these experiments in which the temperature was maintained at  $-23$  °C with a  $\text{CCl}_4$  slush bath. The same cell, thermostatted at  $-78$  °C with dry ice-acetone, was used for the spectral titrations of  $[\text{CoR}]$  with  $\text{Ce(IV)}$ .

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