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## Novel Organometallic Anions Generated by Electrochemical Reversible Reduction

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**Summary** The electrochemical reduction of organometallic  $\text{Co}^{\text{III}}$  chelates in aprotic solvents yields organometallic anions whose stability depends on the nature of the organic group.

THE mechanism by which the Co-C bond in the enzyme-bound C-5 deoxyadenosylcorrinoids is broken is not yet known. Availability of a series of model organo-cobalt chelates<sup>1</sup> should offer the opportunity to establish the role of ligands, organic group, and environment, in determining or influencing the preferred mechanism of cleavage. The reductive cleavage is particularly interesting because when the equatorial ligand is a monoanion it gives rise to a strongly nucleophilic  $\text{Co}^{\text{I}}$  species. This moiety is highly reactive, and this could explain the catalytic activity of corrinoids.

We report some novel organometallic anions containing  $\text{Co}^{\text{I}}$ , e.g.,  $[\text{PhCo}^{\text{I}}\{\text{(do)(doh)pn}\}]^-$  where  $\{\text{(do)(doh)pn}\}^-$  is the monoanion 1-diacetylmonoximateoimino-3-diacetylmonoximeiminopropane, or  $\text{Co}^{\text{II}}$  as in  $[\text{PhCo}^{\text{II}}(\text{chel})\text{dmf}]^-$  where  $(\text{chel})^{2-}$  is a quadridentate equatorial chelating dianion [e.g., *salen*: *NN'*-ethylenebis(salicylideneiminato); 7,7'-*salen*: *NN'*-ethylenebis-(7,7'-dimethylsalicylideneiminato); *bae*: *NN'*-ethylenebis(acetylacetoniminato)]. These organometallic anions can be obtained by electrochemical reduction of the corresponding  $[\text{R}-\text{Co}^{\text{III}}\{\text{(do)(doh)pn}\}-\text{H}_2\text{O}]^+$ <sup>2</sup> and  $[\text{R}-\text{Co}^{\text{III}}(\text{chel})\text{H}_2\text{O}]^0$ ,<sup>1,3</sup> respectively. The phenyl derivatives are stable for several hours under nitrogen in an aprotic environment at room temperature.† Evidence was obtained for the formation of unstable  $[\text{R}-\text{Co}^{\text{I}}\{\text{(do)(doh)pn}\}]^-$ <sup>5</sup> and  $[\text{R}-\text{Co}^{\text{II}}(\text{chel})\text{dmf}]^-$  when  $\text{R} = \text{Me}$  or  $\text{Et}$ . All these anions can be considered as precursors of the final products of the reductive cleavage.

The first polarographic wave of  $[\text{R}-\text{Co}^{\text{III}}(\text{chel})\text{dmf}]^0$  in

dimethylformamide corresponds to a diffusion-controlled, reversible one-electron transfer ( $\Delta E/\Delta \log i/i_d - i = 54$  mv at  $0^\circ$ ). The same polarographic behaviour was observed in pyridine and in dimethyl sulphoxide. The stability of the primary reduction product depends on the nature of the organic group.  $[\text{PhCo}^{\text{III}}(\text{chel})(\text{py})]^0$  was exhaustively reduced in pyridine at  $0^\circ$  at controlled potential (C.P.R.) at a potential corresponding to the first wave, yielding a green solution. Coulometry confirmed a one-electron reduction. Chemical reversibility was demonstrated by electrochemical one-electron re-oxidation, yielding the starting organometallic complex. The reduced species can thus be formulated as  $[\text{PhCo}^{\text{II}}(\text{chel})(\text{py})]^-$ . The lability of the phenyl group in the reduction product is shown by the rapid reaction with protons, yielding  $[\text{Co}^{\text{II}}(\text{chel})(\text{py})_2]^0$  which was identified by its polarographic behaviour.<sup>4</sup> The reactivity of  $[\text{PhCo}^{\text{II}}(\text{chel})\text{py}]$  is in contrast to the inertness of the  $\text{Ph}-\text{Co}^{\text{III}}$  bond towards strong acids.<sup>1</sup> When  $\text{R} = \text{Me}$  or  $\text{Et}$ , the reduction process is electrochemically reversible, and the  $i_d/c$  values as compared with that of  $[\text{PhCo}^{\text{III}}(\text{chel})(\text{dmf})]^0$  confirm that the process is one-electron. Cyclic voltammetry shows that the transient primary reduction product, assumed to be  $[\text{R}-\text{Co}^{\text{II}}(\text{chel})\text{dmf}]^-$ , is unstable. The second polarographic wave occurring at about  $-2.2$  v is less dependent on the nature of the organic group, and is not discussed here.

When the equatorial chelating ligand is  $\{\text{(do)(doh)pn}\}$  the first wave is still one-electron and reversible in all cases examined (see Table). The second wave corresponds to the acceptance of one more electron, giving rise to the monoanion  $[\text{R}-\text{Co}^{\text{I}}\{\text{(do)(doh)pn}\}]^-$ . When  $\text{R} = \text{Ph}$ , the anion can be prepared in dmf by C.P.R. at  $-1.1$  v (at the second wave) at  $0^\circ$ . The resulting green solution is stable for several hours under nitrogen. The visible spectrum shows the characteristic absorption of  $\text{Co}^{\text{I}}$  species:  $15.4$  kK (log

† In dimethylformamide (dmf) or pyridine (py) the water molecule is assumed to be displaced by the solvent. The parent compounds being light-sensitive, all experiments were performed in the dark.

$\epsilon_{\max}$  3.90 instead of 14.4 kK (3.77) as in the blue solution of  $[\text{Co}^{\text{I}}\{\text{(do)(doh)pn}\}]^0$ .

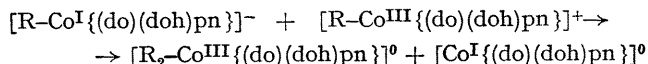
Half-wave potentials of the first cathodic wave for some representative  $[\text{R}-\text{Co}(\text{salen})(\text{dmf})]^0$  complexes show a linear

Half-wave potentials (in v at 0°) of  $\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$  and  $\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}}$  redox couples, vs. S.C.E. aq., and diffusion current constants (in  $\mu\text{A}/\text{mmol}$ ); conc. of the complex  $\times 10^{-3}$  M/l. in dmf-tetraethylammonium perchlorate 0.2M

	$\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$		$\text{p}K_{\text{a}}^6$ RH	$\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}}$		
	$E_{\frac{1}{2}}$	$i_{\text{a}}/c$		$E_{\frac{1}{2}}$	$i_{\text{a}}/c$	
$[\text{Ph}-\text{Co}^{\text{III}}(\text{do})(\text{doh})\text{pn}(\text{dmf})]^+$	.. ..	-0.84	0.50	37	-0.93	0.50
$[\text{Me}-\text{Co}^{\text{III}}(\text{do})(\text{doh})\text{pn}(\text{dmf})]^+$	.. ..	-0.85	0.54	39	ill-defined	
$[\text{Et}-\text{Co}^{\text{III}}(\text{do})(\text{doh})\text{pn}(\text{dmf})]^+$	.. ..	-0.93	0.57	40.5	ill-defined	
$[\text{Ph}-\text{Co}^{\text{III}}(\text{salen})(\text{dmf})]^0$	.. ..	-1.42	0.82			
$[\text{Me}-\text{Co}^{\text{III}}(\text{salen})(\text{dmf})]^0$	.. ..	-1.57	0.80			
$[\text{Et}-\text{Co}^{\text{III}}(\text{salen})(\text{dmf})]^0$	.. ..	-1.71	0.75			
$[\text{CH}_2=\text{CH}-\text{Co}^{\text{III}}(\text{salen})(\text{dmf})]^0$	.. ..	-1.54	0.78			
$[\text{CH}_2=\text{CH}-\text{Co}^{\text{III}}(7,7'\text{-salen})(\text{dmf})]^0$	.. ..	-1.59	0.74			
$[\text{CH}_2=\text{CH}-\text{Co}^{\text{III}}(\text{bae})(\text{dmf})]^0$	.. ..	-1.77	0.70			

The reactivity of  $\text{Ph}^-$  in the  $[\text{PhCo}^{\text{I}}\{\text{(do)(doh)pn}\}]^-$  is shown by the quantitative rapid formation of  $[\text{Co}^{\text{III}}\{\text{(do)(doh)pn}\}(\text{dmf})_2]^+$  and of benzene by reaction with protons. The  $\text{Co}^{\text{III}}$  complex was identified by its polarographic behaviour.

When  $\text{R} = \text{Me}$  or  $\text{Et}$  the corresponding anion obtained by C.P.R. (second wave) reacts with the parent species giving the bis-organometallic complex<sup>5</sup> as in the chemical reduction with CO



The latter product was identified by visible spectrum and by the half-wave potential of the reversible anodic waves due to the oxidation  $\text{Co}^{\text{I}} \rightarrow \text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{III}}$  as compared with the anodic waves obtained after C.P.R. of  $[\text{Co}^{\text{III}}\{\text{(do)(doh)pn}\}(\text{dmf})_2]^+$ :  $E_{\frac{1}{2}}(\text{Co}^{\text{I}}-\text{Co}^{\text{II}}) - 0.79$  v,  $E_{\frac{1}{2}}(\text{Co}^{\text{II}}-\text{Co}^{\text{III}}) + 0.16$  v vs. S.C.E. aq.

The height of the wave indicates that, in agreement with the suggested reaction, only half of the cobalt atoms are reduced to  $\text{Co}^{\text{I}}$ .

correlation with the  $\text{p}K_{\text{a}}$  of the corresponding hydrocarbon acid RH, suggesting that the electron affinity is governed by the stability of  $\text{R}^-$  and that the redox orbital is mainly localized on the  $\text{R}-\text{Co}$  bond.<sup>6</sup> On the other hand the  $E_{\frac{1}{2}}(\text{Co}^{\text{III}}-\text{Co}^{\text{II}})$  values for the same organic group, e.g. vinyl (see Table), indicate increasing negative charge on the cobalt atom (lower electron affinity) going from  $(\text{do})(\text{doh})\text{pn}$  complexes to bae derivatives, in agreement with the trend of  $E_{\frac{1}{2}}$  values in the cations  $[\text{Co}^{\text{III}}(\text{chel})(\text{PhNH}_2)_2]^+$ <sup>4</sup> and  $[\text{Co}^{\text{III}}\{\text{(do)(doh)pn}\}(\text{PhNH}_2)_2]^{2+}$  [ $E_{\frac{1}{2}}(\text{Co}^{\text{III}}-\text{Co}^{\text{II}}) - 0.11$  v] and the nucleophilicity of the corresponding  $\text{Co}^{\text{I}}$  derivatives.

The electron transfer from the electrode enhances reactivity of the co-ordinated organic group in electrophilic substitution at carbon, and at the same time leaves the metal in the reactive  $\text{Co}^{\text{I}}$  oxidation state. The formation of an intermediate organometallic anion and the release of the organic group as a carbanion was postulated in the reduction of  $\{\text{(do)(doh)pn}\}$  complexes with carbon monoxide.<sup>7</sup>

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