Stereochemistry of the Nucleophilic Cleavage of Cobalt–Carbon Bonds in Organocobalt(IV) Compounds

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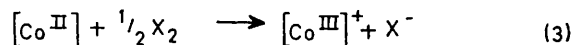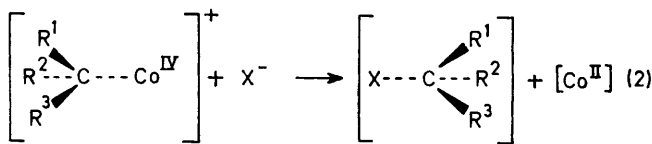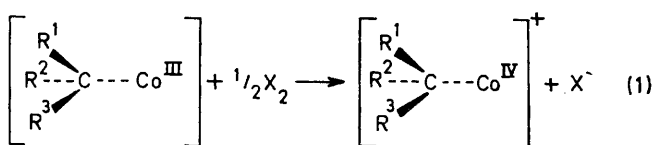
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Summary The nucleophilic decomposition of 1-methyl-heptylbis(dimethylglyoximato)cobalt(IV) by Cl⁻ to form 2-chloro-octane occurs with inversion of configuration at the cobalt-bonded carbon; this is consistent with the view that such a process is a step in the halogen cleavage of metal–carbon bonds.
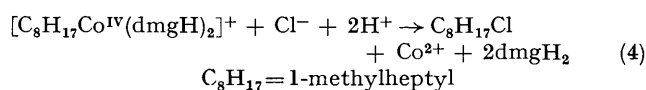
We have recently demonstrated the reversible one-electron oxidation of alkyl(chelate)cobalt(III) complexes [where chelate = a bis(dioxime) or Schiff's base] and have characterized the resulting radical cations as organocobalt(IV) complexes.[1-5] One of the distinctive chemical properties of these organocobalt(IV) complexes is their susceptibility to nucleophilic attack at the metal-bonded carbon atom by species such as water, halide ions, pyridine, or the chelating ligand itself. This class of reactions is of considerable interest, both because nucleophilic displacement at metal–carbon bonds is uncommon,[6] and because of the possible role of such reactions as steps in the halogen-cleavage of metal–carbon bonds.[7-10] Thus, the observation of *inversion* at the carbon centre during the halogen-cleavage of certain metal–carbon (including cobalt–alkyl) bonds has been alternatively interpreted as (a) direct electrophilic (S_E2) attack at carbon[8] or (b) one-electron oxidation followed by nucleophilic attack of halide on the resulting radical cation,[9] *i.e.*, according to equations (1)—(3).

Our demonstration[3] that organobis(dimethylglyoximato)-cobalt(III), [RCo(dmgH)$_2$], [H$_2$dmg = MeC(:NOH)C(:NOH)Me], can be oxidized to yield corresponding cobalt(IV) radical cations which are *stable* in aqueous methanol at low temperatures ($<$—50 °C) opens up the opportunity to examine reaction (2) *directly*, to confirm its occurrence, and to

$$\left[\begin{array}{c} R^1 \\ R^2\text{---}C\text{---}Co^{III} \\ R^3 \end{array}\right] + {}^{1}/_{2}X_2 \longrightarrow \left[\begin{array}{c} R^1 \\ R^2\text{---}C\text{---}Co^{IV} \\ R^3 \end{array}\right]^{+} + X^{\cdot} \quad (1)$$

$$\left[\begin{array}{c} R^1 \\ R^2\text{---}C\text{---}Co^{IV} \\ R^3 \end{array}\right]^{+} + X^{-} \longrightarrow \left[\begin{array}{c} R^1 \\ X\text{---}C\text{---}R^2 \\ R^3 \end{array}\right] + [Co^{II}] \quad (2)$$

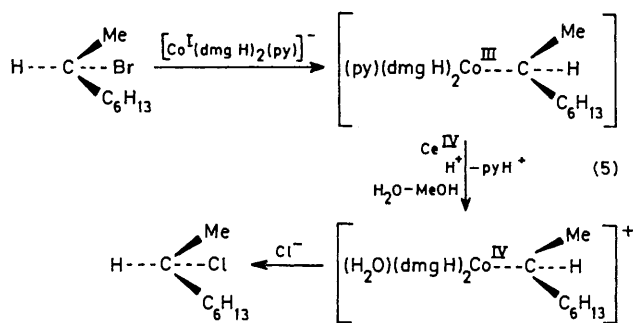$$[Co^{II}] + {}^{1}/_{2}X_2 \longrightarrow [Co^{III}]^{+} + X^{-} \quad (3)$$

establish the stereochemistry of reaction at the cobalt-bonded carbon atom. We report here the results of such a study on the reaction of Cl^- with optically active 1-methylheptylbis(dimethylglyoximato)cobalt(IV) [equation (4)].

$$[C_8H_{17}Co^{IV}(dmgH)_2]^{+} + Cl^{-} + 2H^{+} \rightarrow C_8H_{17}Cl$$
$$+ Co^{2+} + 2dmgH_2 \quad (4)$$
$$C_8H_{17} = 1\text{-methylheptyl}$$

Earlier related observations[9] bearing on the same theme, based on the stereochemistry of oxidative cleavage of $[C_8H_{17}Co^{III}(dmgH)_2]$ by $[Ir^{IV}Cl_6]^{2-}$ in the presence of Br^- may be subject to some ambiguity in view of the similarities of the $[RCo^{IV}(dmgH)_2]^{+}/[RCo^{III}(dmgH)_2]$ reduction potentials (ca. 0·86 V vs. SCE for R = 1-methyl alkyl, in aqueous solution)[3] and that of the Br_2/Br^- couple (ca. 0·82 V), with the resulting likelihood of formation of some $[RCo^{III}(dmgH)_2]$ and Br_2 through oxidation of Br^- by $[RCo^{IV}(dmgH)_2]^{+}$ (or $[Ir^{IV}Cl_6]^{2-}$). The corresponding Cl_2/Cl^- potential ($E^{\circ} = ca. 1·1$ V vs. SCE) is sufficiently high to preclude oxidation of Cl^- to Cl_2 under the conditions of our experiments.

The sequence of steps encompassed by our study is depicted in equation (5). $[(-)$-1-MethylheptylCo(dmgH)$_2$ (py)], $[\alpha]_D^{25}$ (CHCl$_3$) -43° (py = pyridine),† was prepared from $(+)$-2-bromo-octane $\{[\alpha]_D^{25}$ (neat) $+29·0^{\circ}$, (pentane) $+30·9^{\circ}$; ca. 72% optically pure$\}$ by reaction with $[Co^{I}(dmgH)_2(py)]^{-}$ (known to proceed stereospecifically with inversion)[11] and

oxidized to $[1\text{-methylheptylCo}^{IV}(dmgH)_2]^{+}$ (identified spectrophotometrically) in acidified $(HClO_4)$ aqueous methanol at $-60\ ^{\circ}C$ with a stoicheiometric amount of Ce^{IV}. The reaction of $[1\text{-methylheptylCo}^{IV}(dmgH)_2]^{+}$ with Cl^- was initiated by adding a cold methanolic solution of HCl (final concentration, 2·5 M) and allowed to proceed to completion at $-50\ ^{\circ}C$. Kinetic measurements confirmed that the disappearance of $[C_8H_{17}Co(dmgH)_2]^{+}$ was strictly first-order in $[C_8H_{17}Co(dmgH)_2]^{+}$ (k ca. 1×10^{-2} s^{-1}), thus ruling out any significant contribution from the second-order disproportionative decomposition pathway observed for the corresponding $[EtCo(dmgH)_2]^{+}$ complex.[3] Analysis of the solution after completion of the reaction {i.e., decomposition of all the $[C_8H_{17}Co(dmgH)_2]^{+}$} yielded the following composition {all percentages based on the original $[C_8H_{17}Co^{III}(dmgH)_2]$ concentration, ca. $2·5 \times 10^{-3}$ M}: unchanged $[C_8H_{17}Co^{III}(dmgH)_2]$, 33% (spectrophotometric); $C_8H_{17}Cl$, 16% (g.l.c.); octenes, ca. 50% (g.l.c.); Co^{II}, 61% [spectrophotometric, as $Co(SCN)_4^{2-}$]; dmgH$_2$, 53% [gravimetric, as $Ni(dmgH)_2$]. Thus, about 25% of the nucleophilically induced decomposition of $[C_8H_{17}Co^{IV}(dmgH)_2]^{+}$ yields $C_8H_{17}Cl$ according to equation (4), while the remaining 75% yields octenes according to the stoicheiometry of equation (6).‡

$$[C_8H_{17}Co^{IV}(dmgH)_2]^{+} + H^{+} \rightarrow C_8H_{16} + Co^{2+}$$
$$+ 2dmgH_2 \quad (6)$$
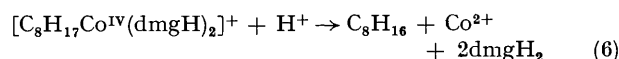
The specific optical rotation of the isolated $C_8H_{17}Cl$ product in pentane was found to be $+23^{\circ}$. Using the known[12] ratio (0·82:1) of specific rotation of $C_8H_{17}Cl$ to $C_8H_{17}Br$, this corresponds to $90 \pm 10\%$ inversion of configuration at the cobalt–bonded carbon during the Cl^--induced cleavage.

In the absence of Cl^-, the nucleophilic decomposition of $[C_8H_{17}Co^{IV}(dmgH)_2]^{+}$ in acidified (0·12 M $HClO_4$) aqueous methanol occurred more slowly yielding analogous products, i.e., predominantly octenes together with ca. 25% octan-2-ol. However, the specific rotation of the latter $(+2·7^{\circ})$ corresponded to only about 30% inversion. Related experiments on optically active $[C_6H_{13}Co(dmgH)_2(py)]$ also were attempted using pyridine as the attacking nucleophile in acetonitrile solution. However, while controlled potential oxidation at 0·90 V at 25 $^{\circ}C$ demonstrated the requirement of 2-electron equivalents per mole according to the stoicheiometry of equation (7), attempts to determine the stereochemistry yielded inconclusive results.

$$[RCo^{III}(dmgH)_2(py)] + 2py \rightarrow [Rpy]^{+}$$
$$+ [Co^{III}(dmgH)_2(py)_2]^{+} + 2e^{-} \quad (7)$$
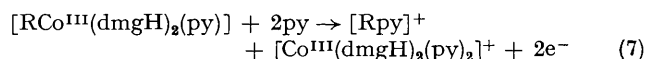
In summary, our results demonstrate directly that Cl^- does induce the nucleophilic decomposition of $[RCo^{IV}]^{+}$ radical cations produced by oxidation of organocobalt(III) compounds and that cleavage of the cobalt–carbon bond occurs with virtually quantitative inversion at carbon.

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† This value was determined for a relatively dilute solution (ca. 5×10^{-3} M) and is consistent with the determination of Dodd and Johnson (ref. 7). Other workers (F. R. Jensen and R. C. Kiskis, J. Organometallic Chem., 1973, 49, C46) have noted difficulty in detecting optical activity for alkylcobaloximes; the explanation for this is unclear.

‡ This product distribution is comparable with that reported for the bromination of 1-methylheptylbis(dimethylglyoximato) cobalt(III), i.e. ca. 30% $C_8H_{17}Br$, together with mainly the bromides of oct-1-ene and oct-2-ene (D. Dodd and M. D. Johnson, J. Organometallic Chem., 1973, 52, 80, and references therein).

Such a process therefore does appear to be a viable step in the halogen-cleavage reactions of metal–carbon bonds which occur with inversion at carbon.

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