Inversion of Configuration in the Nucleophilic Displacement of Cobalt from Alkylcobalt(IV) Complexes and its Relevance to the Halogenation of the Corresponding Alkylcobalt(III) Complexes

By S. N. Anderson, D. H. Ballard, J. Z. Chrzastowski, D. Dodd, and M. D. Johnson*
(*Department of Chemistry, University College, 20 Gordon Street, London* WCIH OAJ)

Summary Nucleophilic displacement of cobalt from alkylcobalt(IV) complexes takes place with inversion of configuration at the α-carbon and probably accounts for the inversion of configuration found in alkyl halides obtained from the reaction between the corresponding alkylcobalt(III) complexes and halogens.

The inversion of configuration at the α-carbon, observed when some alkyl transition metal complexes react with halogens,[1–3] has not so far been satisfactorily explained. It has been suggested[2] that bimolecular electrophilic substitution, unlike bimolecular nucleophilic substitution, may proceed with either retention or inversion of configuration, depending upon the size and character of the electrophile. However, an alternative explanation might be that the electrophile does not directly attack the α-carbon, but oxidises the complex so that the actual carbon–metal bond cleavage is caused by a rapid subsequent nucleophilic attack at the α-carbon.

We here demonstrate that the oxidation products of alkylcobalt(III) complexes readily undergo nucleophilic substitution with inversion of configuration at the α-carbon, and that the products of these reactions bear a remarkable similarity to those obtained in the halogenation of the same alkylcobalt(III) complexes.

Thus benzylaquobis(dimethylglyoximato)cobalt(III) (**1**) is rapidly oxidised by one equivalent of $IrCl_6^{2-}$ to the unstable benzylcobalt(IV) complex (**2**).[4] In the absence of added nucleophiles, (**2**) decomposes predominantly to the corresponding *O*-benzyl ether† of dimethylglyoxime (**3**) for which a free radical mechanism has been suggested. However, we find that, in the presence of an excess of halide ion, the corresponding benzyl halide is the main product (equation 3) together with some compound (**3**). For example, with 5×10^{-3}M reagents in the presence of 1·7M chloride ion in aqueous methanol, the product is 87% benzyl chloride and 13% (**3**).

$$\underset{(\mathbf{1})}{PhCH_2Co(dmgH)_2aq} + IrCl_6^{2-} \rightarrow \underset{(\mathbf{2})}{[PhCH_2Co(dmgH)_2aq]^+} + IrCl_6^{3-} \qquad (1)$$

$$[PhCH_2Co(dmgH)_2aq]^+ \rightarrow \underset{(\mathbf{3})}{PhCH_2ON{:}CMe{\cdot}CMe{:}NOH} + Co^{II} + dmgH_2 \qquad (2)$$

$$[PhCH_2Co(dmgH)_2aq]^+ + X^- \rightarrow PhCH_2X + Co(dmgH)_2aq \qquad (3)$$

X = Cl, Br, I; dmgH = monoanion of dimethylgloxime

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† In ref. 4 this is incorrectly referred to as the *N*-benzyl ether.

When the oxidation is carried out by iodine chloride (1 equiv) in acetic acid containing chloride ion (1·2M), the product is *ca.* 75% benzyl chloride and *ca.* 25% (**3**), but little benzyl iodide can be detected. In the absence of the added chloride ion, the product is mainly (**3**) (60%), together with benzyl chloride (15%) and benzyl iodide (25%). These reactions are not influenced by the presence of anisole, which would have reacted rapidly with any chlorine that might have been formed during the reaction.[5]

Similar reactions with bromine in the presence of chloride ion also give appreciable proportions of benzyl chloride in the products.

(+)-s-Octylbis(dimethylglyoximato)pyridinecobalt(III), prepared from (−)-s-octyl bromide ($[\alpha]_D = -10 \pm 2°$; $CHCl_3$), reacts with a two fold excess of $IrCl_6^{2-}$ in aqueous methanol in the presence of bromide ion (2M) to give (−)-s-octyl bromide ($[\alpha]_D = -8 \pm 2°$; $CHCl_3$) in 37% yield. Similarly, the same (+)-s-octylbis(dimethylglyoximato)-pyridinecobalt(III) reacts with bromine in acetic acid to give (−)-s-octyl bromide ($[\alpha]_D = -7 \pm 2°$; $CHCl_3$) in *ca.* 30% yield.[1] When this reaction is carried out in the presence of bromide ion, better yields of s-octyl bromide are obtained.

This very ready displacement of cobalt from alkylcobalt-(IV) complexes with inversion of configuration at the α-carbon should be compared with the known, if much slower, displacements from alkylcobalt(III) complexes.[6] Since these reactions involve the displacement of cobalt(II) and cobalt(I) nucleofugal groups respectively, it is not surprising that the latter proceeds only with the most effective nucleophiles[6] whereas the former proceeds with even mild nucleophiles such as chloride ion. Moreover, that such displacements occur is an indication that alkylcobalt(IV) species have a finite lifetime in solution.

The intermediate formed on oxidation of the alkylcobalt(III) complex by oxidants such as iodine chloride or bromine should therefore be sufficiently reactive that even the low concentration of halide ion liberated into the solvent cage during the oxidation would be an effective nucleophile able to react at the α-carbon with inversion of configuration. It is perhaps significant that, in the reaction of s-octylcobalt(III) complexes with bromine in several protic solvents in the absence of added halide ion, the main products include oct-1-ene and oct-2-ene (as their halogen addition products). These olefins would be expected if, as is usual with nucleophilic substitution reactions at saturated carbon, attack of the nucleophile competes with solvent promoted elimination reactions.

It seems probable that more than one mechanism may be possible for apparent electrophilic displacements of organo-transition metal complexes, and radical mechanisms may well intrude in those of the organocobalt(III) species. However, the high stereospecificity of these reactions and the close similarity between the nucleophilic displacements and the halogenations do suggest that oxidation induced nucleophilic substitution may be an important mechanism in the halogenation of alkylcobalt(III) complex.

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[1] D. Dodd and M. D. Johnson, *Chem Comm.*, 1971, 571.
[2] F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, 1971, **93**, 5283.
[3] G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, 1971, **93**, 1529.
[4] P. Abley, E. R. Dockal, and J. Halpern, *J. Amer. Chem. Soc.*, 1972, **94**, 659.
[5] S. N. Anderson, D. H. Ballard, and M. D. Johnson, *J.C.S. Perkin II*, 1972, 311.
[6] D. Dodd and M. D. Johnson, *Chem. Comm.*, 1971, 1371.