Bimolecular Nucleophilic Displacement as a Mechanism of Alkyl Transfer from Cobalt

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Summary Alkyl groups are transferred from cobalt to cobalt and from cobalt to rhodium by the bimolecular nucleophilic displacement of one metal ion by the other; some reactions that apparently proceed by attack of cobalt(II) on saturated carbon are shown to proceed through cobalt(I) intermediates.

THOUGH several cobalt(I) species have been shown to have remarkable nucleophilic properties and are capable, for example, of displacing halide ions from alkyl halides extremely rapidly,[1] no indication has been given so far as to their capacity as fugal groups.

We report that some cobalt(I) species are not only strongly nucleophilic, but are themselves readily displaced by nucleophiles from saturated carbon. When methylbis-(dimethylglyoximinato)pyridinecobalt(III) [shown in equations below as R(Co)](0·01M) is treated with an equivalent amount of the bis(cyclohexanedionedioximinato)pyridinecobalt(I) ion [(Co′)$^-$] in mildly alkaline methanol at 0°, an equilibrium mixture with methylbis(cyclohexanedionedioximinato)pyridinecobalt(III) [R(Co′)] and the bis(dimethylglyoximinato)pyridinecobalt(I) ion [(Co)$^-$] is obtained within 5 minutes [equation (1), R = Me]. Similar exchange of ethyl groups is also very rapid but exchange of secondary alkyl groups and of the isobutyl group was not observed even over much longer periods. However, n-octyl groups exchange at a convenient rate and, as the corresponding n-octylcobalt(III) compounds (I and II, R = n-octyl) can together be recovered in almost quantitative yield, the rate of the exchange may be determined from changes in the character of the total n-octylcobalt(III) as a function of time.

$$\underset{\text{(I)}}{\text{R(Co)}} + \text{(Co}')^- \rightleftharpoons \underset{\text{(II)}}{\text{R(Co}')} + \text{(Co)}^- \tag{1}$$

The position of equilibrium differs with each alkyl group, but for the n-octyl group it contains *ca.* 50% of each component. Consequently, it is possible to treat the rates of reaction in the same manner as for isotopic exchanges.[2] The results show that the reaction is first order in each component and that the second order rate coefficient is $1{\cdot}5 \pm 0{\cdot}3 \times 10^{-2}\,\text{M}^{-1}\text{s}^{-1}$ at 23° and $6 \pm 2 \times 10^{-3}\,\text{M}^{-1}\text{s}^{-1}$ at 0°, implying that the activation energy is low and the entropy of activation is negative. This indicates strong steric compression on the alkyl group between the two large metal-containing groups in the transition state. Branching at either the α- or β-carbon is sufficient to prevent the attainment of the appropriate configuration in the transition state. The ease of displacement of the cobalt(I) species is exemplified by the fact that the rate coefficients shown above lie between those for the displacement of chloride ion and of bromide ion from saturated carbon by the same nucleophiles.[1]

Whilst apparently bis(dimethylglyoximinato)pyridinecobalt(II) [(Co)·] also reacts with alkylbis(cyclohexanedionedioximinato)pyridinecobalt(III) compounds under mildly alkaline conditions in methanolic solution, to give a similar equilibrium mixture, equation (2), we believe that this reaction also proceeds *via* equation (1). The kinetics of this exchange show that, under conditions identical with those described above, the reaction is first order in each component, but the rate coefficients are, within experimental error, one half of those for the cobalt(I) promoted exchange, at each temperature and at each of two alkali concentrations (0·033 and 0·066M). Since the cobalt(II) species are known to be completely disproportionated in strongly alkaline solution, equation (3),[3] it is apparent from the kinetics that the disproportionation is sufficiently complete under the present conditions for the reaction to proceed through the cobalt(I) species whose concentration is approximately one half of that of the cobalt(II) species added.

$$\text{R(Co}') + \text{(Co)}^{\bullet} \rightleftharpoons \text{R(Co)} + \text{(Co}')^{\bullet} \tag{2}$$

$$2\text{(Co)}^{\bullet} \rightleftharpoons \text{(Co)}^+ + \text{(Co)}^- \tag{3}$$

Two recent communications[4,5] are relevant to these results. First the formation of a dimethylcobalt(III) compound (V) from the reaction of a methylcobalt(III) compound (IV) with a methylcobalt(I) anion [(III), equation (4)] has been observed, but was described in terms of methyl carbanion transfer *from* the methylcobalt(I) ion (III). The present results indicate that nucleophilic attack of the methylcobalt(I) species (III) on the methyl group of the methylcobalt(III) compound (IV), might bring about methyl transfer *to* the methylcobalt(I) species with displacement of the unmethylated cobalt(I) fugal group.

$$\underset{\text{(III)}}{\text{Me–(Co:)}^-} + \underset{\text{(IV)}}{\text{Me–Co}^+} \longrightarrow \underset{\text{(V)}}{\text{Me–Co–Me}} + \text{:Co} \tag{4}$$

Another example of alkyl group transfer apparently promoted by a cobalt(II) species in dimethyl sulphoxide has been reported.[5] This may represent the first clear case of a bimolecular homolytic displacement at saturated carbon, and show that cobalt(II) and cobalt(I) can promote similar alkyl transfers, but it would be interesting to investigate the role of cobalt(I).

The reactions described here are important not only because of their relationship with the alkyl transfer reactions of the cobalamins,[6] but also because they provide information about the relative basicity of metal ions towards saturated carbon[7] and about carbon–metal bond strengths. Thus, with two dissimilar metal ions, the position of equilibrium of equation (5) provides a direct measure of the relative basicity of the two metal ions towards saturated carbon, and the position of equilibrium of equation (6) provides a direct measure of the relative bond strengths of the two carbon metal bonds. Preliminary results for (M)⁻ = the bis(dimethylglyoximinato)pyridinerhodium(I) ion, show that, though the rhodium(I) ion is the poorer nucleophile[8] it is much the superior carbon base, and that this is due largely to the higher bond strength of the carbon–rhodium bond.

$$\text{R(Co)} + \text{(M)}^- \rightleftharpoons \text{R(M)} + \text{(Co)}^- \tag{5}$$

$$\text{R(Co)} + \text{(M)}\cdot \rightleftharpoons \text{R(M)} + \text{(Co)}\cdot \tag{6}$$

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