Oxidatively Induced Carbonyl Insertion and Nucleophilic Cleavage Reactions of Alkylmetal Carbonyl Compounds

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Summary Oxidation of several alkylmetal carbonyl compounds by cerium(IV) ion in methanol takes place extremely rapidly to give the methyl ester of the next higher homologous carboxylic acid, in some cases in quantitative yield.

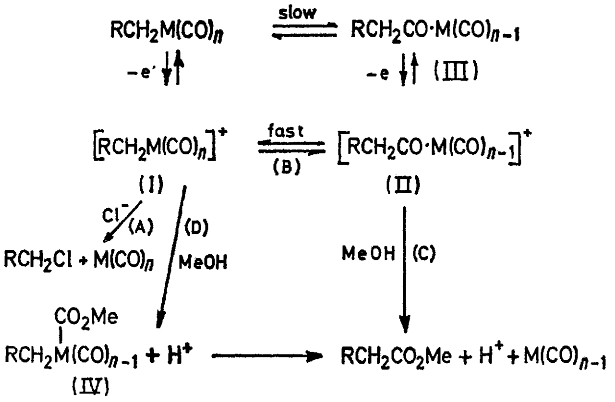
We have recently described the ready oxidatively induced nucleophilic cleavage[1] of some alkylcobalt(III) complexes, in which the one-electron oxidation[2] greatly increases the susceptibility of the α-carbon atom to nucleophilic attack [equation (1)]. We now describe novel oxidatively induced carbonyl insertion reactions of several alkylmetal carbonyl compounds and oxidatively induced nucleophilic cleavage reactions of corresponding acylmetal carbonyl compounds. In some cases the carbonyl insertion reaction may completely dominate the alternative oxidatively induced nucleophilic cleavage of the alkylmetal carbonyl compound.

$$\mathrm{RCo(dmgH)_2L} - e \rightarrow [\mathrm{RCo(dmgH)_2L}]^+ \xrightarrow{X^-} \mathrm{RX} + \mathrm{Co(dmgH)_2L} \qquad (1)$$

Thus, when a solution of tricarbonyl-π-cyclopentadienyl-4-fluorobenzylmolybdenum (10^{-3} M) and lithium chloride (10^{-1} M) in methanol is treated with a five-fold excess of cerium(IV) ion at room temperature, methyl 4-fluorophenylacetate is formed rapidly and quantitatively at a rate too fast for measurement by standard spectrophotometric techniques. Similar reaction of tricarbonyl-π-cyclopentadienyl-4-fluorobenzyltungsten and dicarbonyl-π-cyclopentadienyl-4-fluorobenzyliron give the same product together with some 4-fluorobenzyl chloride and 4-fluorobenzyl methyl ether. Neither methyl 4-fluorophenylacetate nor 4-fluorobenzyl chloride were obtained from the corresponding reaction of pentacarbonyl-4-fluorobenzylmanganese.

The ester formation is not confined to benzylmetal complexes, for dicarbonyl-π-cyclopentadienyl-2-(4-fluorophenyl)ethyliron and tricarbonyl-π-cyclopentadienyl-3-pyridylmethylmolybdenum rapidly give almost quantitative yields of methyl 3-(4-fluorophenyl)propionate and methyl 3-pyridylacetate, respectively.

The formation of the alkyl chloride is almost certainly the result of a cleavage of the oxidised alkyl metal carbonyl complex (I) by chloride ion, (Scheme, path A), for the rate of reaction of the starting complexes with chloride ion and the rate of oxidation of chloride ion are negligible under the reaction conditions. The formation of the ester probably involves a carbonyl insertion reaction which, because the overall rate of the reaction greatly exceeds those of other ligand- and solvent-induced carbonyl insertion reactions,[3] must take place in the oxidised species (I) (Scheme, path B). The oxidised acyl complex (II) formed by such an insertion reaction is itself highly susceptible to nucleophilic attack at the α-acyl carbon, particularly by the mildly nucleophilic solvent which gives the observed product methyl ester (Scheme, path C). Some attack by chloride ion may also occur, but the resulting acid chloride would be hydrolysed to the ester under the conditions used. Oxidatively induced nucleophilic cleavage of acylmetal carbonyl complexes (III) has also been demonstrated by the rapid formation of methyl 4-fluorophenylacetate and methyl benzoate from the reaction of tricarbonyl-4-fluorophenylacetyltriphenylphosphinecobalt and dicarbonyl-π-cyclopentadienylbenzoyliron, respectively, with lithium chloride and Ce^{4+} in methanol.



Scheme

An alternative but less likely path might involve the nucleophilic attack of methanol on a carbonyl group of the oxidised alkylmetal complex (Scheme, path D), to give the methoxycarbonyl derivative (IV) which undergoes a reductive elimination reaction.

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