Controlled Radical Production and Dimerisation Induced by Cobalt(III)

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Summary Rapid intramolecular oxidation of the carbanion $(NH_3)_5CoN{\equiv}C\bar{C}HPh$ generated in $[(NH_3)_5CoN{\equiv}C{-}CH_2Ph]^{3+}$ yields the nitrile radical which immediately dimerises to stilbene dinitrile.

WHEN base is added to solutions of complexes of the type $[(NH_3)_5CoN{\equiv}CCH_2R]^{3+}$ carbanions, $[(NH_3)_5CoN{\equiv}C\bar{C}HR]^{2+}$, are rapidly formed.[1] The Co^{III} fragment enhances the acidity of the nitrile methylene group by *ca.* 10^6 fold.[2]

One possibility for the reactions of these carbanions is an intramolecular oxidation by Co^{III} to give the Co^{II} pentaammine unit and the organic radical. For $[(NH_3)_5CoN{\equiv}C\text{-}CH_2Ph][ClO_4]_3$ in neutral aqueous solution at 25° immediate decomposition of the complex was observed with deposition of a white precipitate which analysed for $C_{16}H_{12}N_2$ (yield $>90\%$). ^1H N.m.r. and mass spectrometry showed that the product was primarily a 1 : 1 mixture of *meso* and racemic stilbene dinitrile, PhCH(CN)CH(CN)Ph. This presumably arises by deprotonation of the methylene group in the co-ordinated benzyl nitrile followed by rapid oxidation of the co-ordinated carbanion by Co^{III} to the radical $Ph\dot{C}HCN$ which then dissociates from the labile $[(NH_3)_5Co^{II}]^{2+}$ ion and dimerises. The radical also competes for other radicals such as 2,2-diphenyl-1-picrylhydrazyl and for radical trapping agents such as bromine and iodine in inert buffer solutions (pH 4—6).

The complex is stable in dilute aqueous acid solutions but decomposes rapidly in unbuffered neutral solution and in basic media. The rate of deprotonation and thereby the production of the radical may be controlled therefore by adjusting the acidity. The complex is also soluble in some organic solvents ($HCONMe_2$, Me_2SO, Me_2CO, MeCN) but decomposes rapidly unless acid is added. The same dinitrile dimer was obtained from decomposition in MeCN as in water.

The Co^{III} centre provides ready access to the co-ordinated carbanion and the intramolecular oxidation has the unusual property of generating a radical adjacent to a strong electron-withdrawing group. The process is an easily controlled one-electron transfer under mild conditions and complexes of this type might be useful reagents in organic synthesis for carbanion and radical generation. Also the strategy could be effective for any potential co-ordinating ligand capable of being deprotonated to give a carbanion attached to a metal ion. Whether subsequent electron transfer is observed or not would depend on the metal ion and its oxidation state.

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[1] D. A. Buckingham, F. R. Keene, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1973, **95**, 5649.
[2] F. R. Keene and J. MacB. Harrowfield, unpublished work.