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LIGAND OXIDATION IN MACROCYCLIC COBALT, NICKEL AND COPPER COMPLEXES: A SIMPLE SYNTHESIS OF CORRIN ANALOGUES

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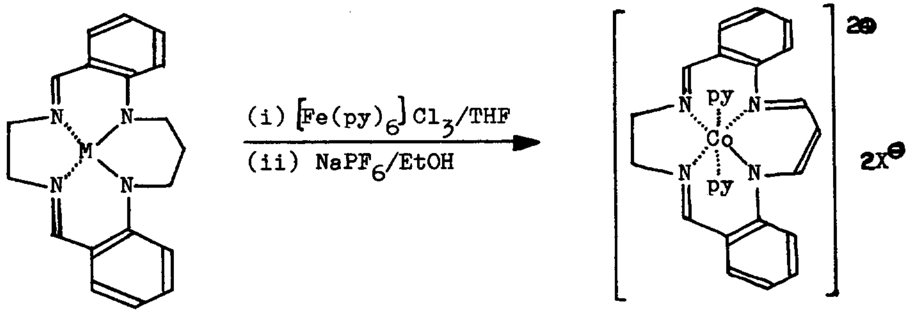
The oxidative dehydrogenation of coordinated amine ligands in a variety of nickel and iron complexes[1] and several ruthenium complexes[2] has been reported, and electrochemical oxidative dehydrogenation of a copper complex has also been suggested[3]. In addition, nickel-coordinated ß-amino ketimine anions[4,5] are susceptible to oxidative dehydrogenation. So far, attempts to effect this type of reaction with cobalt complexes have failed[1g], presumably because of the stability of the cobalt(III) oxidation state, and in a discussion of metal ion specificity, it has been stated that "cobalt does not appear to work at all"[4].

We have found that the red air-sensitive cobalt(II) complex (1) undergoes reaction with iron(III) chloride and excess pyridine in anhydrous tetrahydrofuran, followed by addition of ethanolic sodium hexafluorophosphate, to yield the green dibenzocorromin complex $[Co(dbc)py_2](PF_6)_2$ (4) in 80% yield together with hexapyridinatoiron(II) dichloride[6].

The dibenzocorromin cobalt(III) complex (4) was characterised by analytical and spectral data (as were all other new compounds mentioned) and by its conversion to $[Co(dbc)(CN)_2]$ and $[Co(dbc)(SCN)_2]$, which have been prepared previously by a different route[7].



(1) M=Co

(2) M=Ni

(3) M=Cu

(4) X=PF$_6$

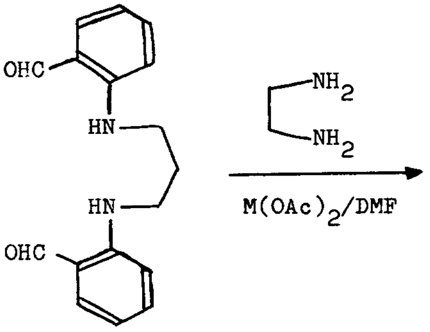
(5) X=I

The complex (1) can also be oxidised in high yield by oxygen or hydrogen peroxide with similar work-up conditions to afford the complex (4), or by iodine and pyridine in tetrahydrofuran to afford [Co(dbc)py$_2$] I$_2$ (5). The nickel(II) complex (2) was similarly converted to [Ni(dbc)] Cl.H$_2$O[7] by oxidation with iron(III) chloride in 95% yield and to [Ni(dbc)] I by oxidation with iodine in 80% yield, and was also slowly oxidised by oxygen in dimethylformamide solution.

The copper(II) complex (3) can also be converted by iron(III) chloride to [Cu(dbc)] ClO$_4$[7].

The various oxidation mechanisms are as yet unclear, but it is possible that the great ease of these reactions is partly a consequence of the presence of a coordinated amine anion in the starting materials and a highly conjugated chromophore in the products.

These oxidative dehydrogenation reactions are doubly important as they provide a versatile alternative to the direct metal template synthesis[7] of dibenzocorromin metal complexes. The complexes (1-3) can be readily prepared from the dialdehyde (6)[8] by a modification of a previously described metal template process[9].



(6)

(1-3)

A study of the effects of ligand and metal ion variation on the scope of the oxidative dehydrogenation reactions, coupled with an investigation of the redox properties of the metal complexes, is in progress.

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