The Reaction of Bis(dimethylglyoximato)(pyridine)cobalt(ı) Anion with CF$_2$=CFX (X = Cl or Br): Evidence for Competitive Reaction Paths

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The course of reaction of the 'supernucleophile' [pyCo(DH)$_2$]$^-$ (py = pyridine, DH = dimethylglyoximato) with CF$_2$=CFX depends upon the nature of X to give [pyCo(DH)$_2$(CF$_2$CFClH)] (X = Cl) and [pyCo(DH)$_2$(CF=CF$_2$)] (X = Br) as the major isolated products.

The nature and reactivity patterns of reduced cobalt(ı) 'supernucleophiles' have been the subject of intense study over the years.[1,2] Early investigations[3] suggested that bis(dimethylglyoximato)(pyridine)cobalt(ı) anion, [pyCo(DH)$_2$]$^-$ (1),† reacts with electrophiles such as alkyl halides *via* an S_N2 mechanism. Later studies involving bulky alkyl halides and methyl toluene-*p*-sulphonates[4] and a recent reinterpretation[5] of the previously obtained data have indicated that an electron-transfer pathway is also feasible for alkylation reactions of (1).

As part of a program aimed at synthesizing organo-cobalt(ııı) complexes containing highly fluorinated alkyl groups for the purpose of comparing their structural and spectroscopic properties to non-fluorinated analogues, we have investigated the interaction of (1) with CF$_2$=CFX (X = Cl or Br, see equation 1). In this Communication, we report a novel change in product distribution for equation 1 as a function of X.

$$(Co)^- + CF_2=CFX \rightarrow (Co)-CF_2CFXH + (Co)-CF=CF_2 + (Co)-X \quad (1)$$
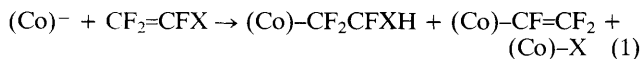
where (Co) = pyCo(DH)$_2$ fragment

The complex [pyCo(DH)$_2$]$^-$ (1) was prepared by reaction of [pyCo(DH)$_2$Cl] with one molar equivalent of sodium boro-hydride in strongly alkaline methanol under argon. When CF$_2$=CFCl was bubbled briefly through the resulting solution, an immediate colour change from green to deep red–orange occurred. Stirring overnight, concentration of the reaction mixture, and recrystallization from acetone–water afforded yellow–orange (2) in 60% yield.

The product (2) was tentatively identified as

† *Abbreviations*: py = pyridine, DH = dimethylglyoximato.

[pyCo(DH)$_2$(CF$_2$CFClH)]‡§ from its ^{1}H and ^{19}F n.m.r. spectra and their similarity to those of [(CO)$_5$M(CF$_2$CFClH)] (M = Mn, Re).[6,7] The two F nuclei on the α-C atom of the alkyl group are diastereotopic and appear as broadened doublets (*J* 205 Hz) due to incomplete averaging of coupling to the quadrupolar ^{59}Co nucleus.[8] The unequivocal geometry of the alkyl group in this complex was proved conclusively by the independent synthesis of (2) from (1) and BrCF$_2$CFClH.

On the other hand, treatment of (1) with CF$_2$=CFBr produced a red–brown solution. Shiny, golden-yellow (3) was isolated in 20% yield after concentration and acetone–water recrystallization. The purified material has resonances in its ^{1}H n.m.r. spectrum assignable only to py and DH ligands; its ^{19}F n.m.r. spectrum is wholly consistent with a σ-bonded trifluorovinyl structure, [pyCo(DH)$_2$(CF=CF$_2$)].[9]§
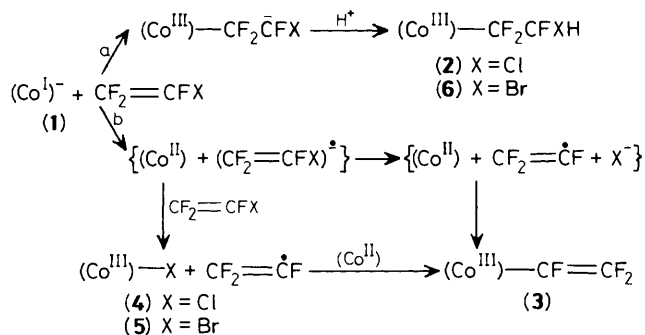
Significantly, before purification, trace amounts of (3) and [pyCo(DH)$_2$Cl] (4) were observed in the crude preparation of (2) from (1) and CF$_2$=CFCl, while minor impurities of [pyCo(DH)$_2$Br] (5) and [pyCo(DH)$_2$(CF$_2$CFBrH)] (6) were detectable in unrecrystallized (3) from (1) and CF$_2$=CFBr. In

Scheme 1. (Co) = pyCo(DH)$_2$; possible side reactions of radicals not shown.

vs. Cl. On the other hand, (1) is known to react with CH$_2$=CHY, where Y is an electron-withdrawing group such as CN or CO$_2$Me, to give the nucleophilic addition product [pyCo(DH)$_2$(CH$_2$CH$_2$Y)].[11] Consequently, we observe that nucleophilic addition predominates for CF$_2$=CFCl where substitution by (1) should be slow, while electron transfer-mediated substitution is observed for (1) and CF$_2$=CFBr. We note that formation of (5) *via* a direct bromophilic attack on CF$_2$=CFBr by (1) cannot be excluded at this time.[12]

fact, in some preparations of (3), nearly equimolar amounts of (3) and (5) were obtained (the different results are probably caused by differences in the rate of addition of the gaseous alkene). Furthermore, [pyCo^{II}(DH)$_2$] reacts with CF$_2$=CFBr in methanol to give (3) and (5). These results suggest that competitive nucleophilic addition (a) and single electron-transfer (b) reaction pathways are probably responsible for the formation of the observed products, with the former predominating for X = Cl and the latter for X = Br (see Scheme 1). To our knowledge this is the first example in which the structure of the major product, derived from the interaction of a transition metal nucleophile with CF$_2$=CFX, is determined by the nature of X.

For the present case of (1) and CF$_2$=CFX, if the radical anion (CF$_2$=CFX)$^{\bar{\cdot}}$ forms significantly faster or is able to dissociate more easily for X = Br than Cl, then the electron-transfer pathway may prevail over nucleophilic addition. Support for retardation of the rate for the electron-transfer reaction involving (1) and CF$_2$=CFCl may be derived from prior investigations[10] of (1) with PhCH=CHX where the ease of halogen substitution increased dramatically for X = Br

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