Evidence for a Transient Intermediate in the Reaction between Tris(pentane-2,4-dionato)cobalt(III) and *N*-Chlorosuccinimide, from a Stopped-flow Pulse Fourier Transform ^{1}H Nuclear Magnetic Resonance Investigation

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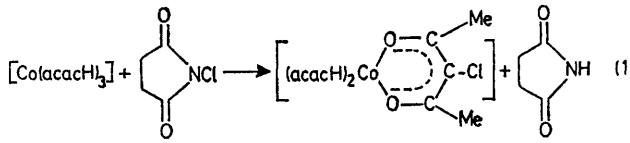
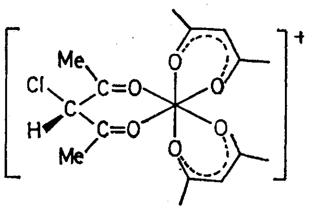
Summary A transient intermediate has been detected by stopped-flow pulse Fourier transform ^{1}H n.m.r. spectroscopy, during the reaction between excess of tris(pentane-2,4-dionato)cobalt(III) and *N*-chlorosuccinimide.

Recently two reports have appeared in which the stopped-flow technique has been combined with pulse Fourier transform n.m.r. spectroscopy to enable complete ^{1}H n.m.r. spectra to be obtained during the course of a moderately fast reaction.[1,2] In the first of these reports a static n.m.r. tube was used and therefore the spectra obtained were of relatively low resolution,[1] whereas in a more recent report a spinning n.m.r. tube was employed and the improvement in resolution was noticeable.[2] However, in the latter study a simple T-piece mixing device was used, with mixing outside the n.m.r. tube, and this produced undesirable features such as a large dead-volume and a dead-time of *ca.* 4 s. Recently we described an attachment for a Bruker WH90 spectrometer which largely overcomes these problems,[3] allowing rapid and efficient mixing *inside* a spinning 5 mm diameter n.m.r. tube in $< 0{\cdot}1$ s, and allowing free induction decays to be collected within *ca.* 0·2 s of mixing and at a repetition rate of *ca.* 0·6 s in favourable cases. We report here some results obtained in this way for the reaction between excess of tris(pentane-2,4-dionato)cobalt(III) [Co(acacH)$_3$] and *N*-chlorosuccinimide (NClS) in CDCl$_3$. In earlier[4] and recent[5] studies of this reaction by visible spectrophotometry no evidence of a transient intermediate was found, but ^{1}H n.m.r. spectra taken during the course of reaction (1) give clear evidence of a transient species. This species is tentatively assigned structure (**1**), in which the chlorinated carbon atom is tetrahedral, on the basis of the successive ^{1}H n.m.r. spectra obtained in the δ 5·5 region (Figure). The large resonance (δ 5·51) present in each of the spectra arises from the unchanged methine protons in position 3 of the acacH$^-$ ligands, and this resonance is relatively broad (*W ca.* 3 Hz)



(1)



(**1**)

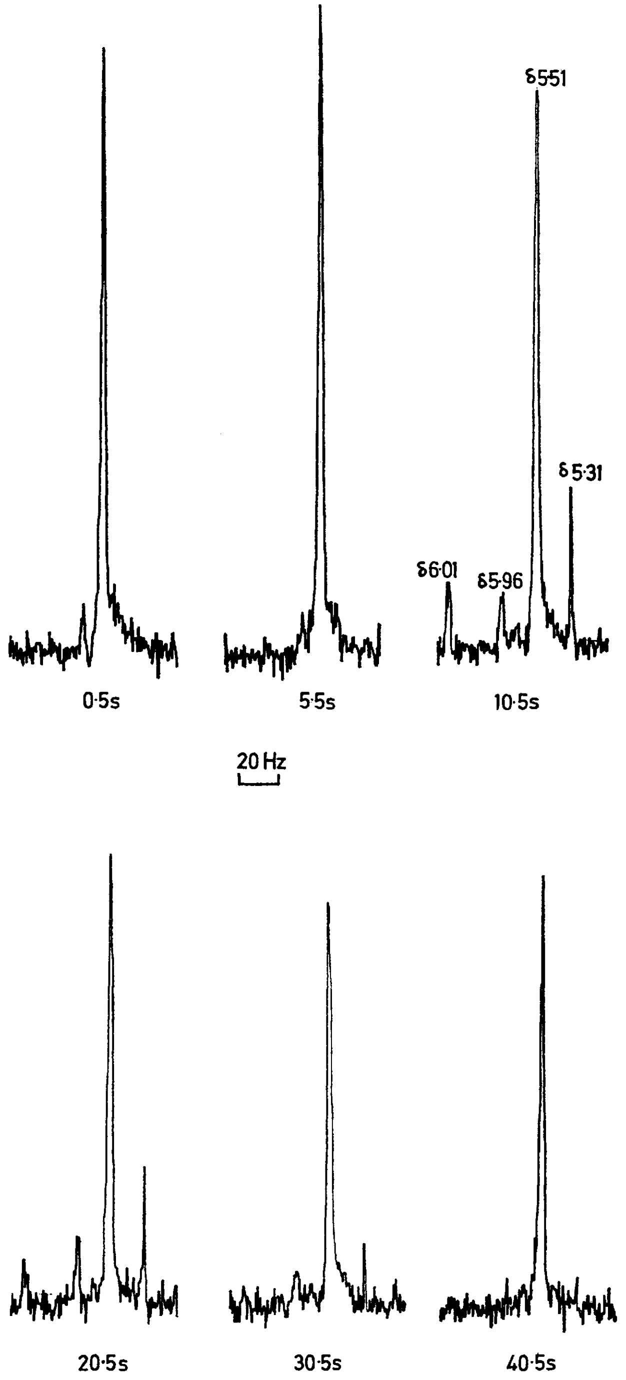


Figure. Parts of some of the ^{1}H n.m.r. spectra obtained at 5 s time intervals during the course of reaction (1); [Co(acacH)$_3$] = [NClS] = 0·15 mol l^{-1}; at 295 K in CDCl$_3$.

possibly through coupling to the cobalt atom (^{59}Co has a nuclear spin of 7/2) *via* the delocalised pentane-2,4-dionate rings or through some residual paramagnetism from traces of Co$^{\mathrm{II}}$ species. During the course of reaction (1) three new resonances appear, and then disappear, in the same region of the spectrum, as shown by the successive spectra (Figure). Two of these resonances (at δ 5·96 and 6·01) are relatively broad like the main methine proton resonance, and the third resonance (δ 5·31) is noticeably narrower. We tentatively assign this sharper resonance to the proton attached to the chlorinated carbon atom in the proposed structure (**1**), the formation of a tetrahedral structure preventing delocalisation within that pentane-2,4-dionate ring. The other two small resonances which are still broad can be assigned to the other two methine protons which are present in the two unchlorinated pentane-2,4-dionate ligands of the same intermediate.

The rate of reaction (1) may be conveniently investigated by following the disappearance of the NClS resonance (δ 2·90) in the presence of excess of [Co(acacH)$_3$]. Preliminary results indicate a second-order rate law: $-\mathrm{d}[\mathrm{NClS}]/\mathrm{d}t = k[\mathrm{NClS}][\mathrm{Co(acacH)_3}]$. At 295 K the pseudo-first-order rate constants when $[\mathrm{Co(acacH)_3}] = 7{\cdot}5 \times 10^{-2}$ and 15×10^{-2} mol l^{-1} are $(1{\cdot}65 \pm 0{\cdot}03) \times 10^{-2}$ s^{-1} and $(3{\cdot}53 \pm 0{\cdot}33) \times 10^{-2}$ s^{-1} respectively; hence $k = 0{\cdot}22 \pm 0{\cdot}01$ l mol^{-1} s^{-1} at 295 K in CDCl$_3$. A second-order rate law has been reported previously for this reaction.[5]

There seems little doubt that this new technique will enable considerable mechanistic information to be obtained for reactions which are moderately fast (half-lives > 0·1 s). Other reactions which we have already found amenable to study in this way include rapid hydrogen–deuterium exchange[3] and a direct study of solvent exchange with solvated metal ions {*e.g.* between (CD$_3$)$_2$SO and the [Al(Me$_2$SO)$_6$]$^{3+}$ ion}.

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