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Bromination of Tris(1,1,1-trifluoro-2,4-pentanediono)rhodium(III)

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Collman *et al.* have investigated a number of electrophilic substitution reactions of metal acetylacetonates, the products were isolated by classical chromatography and characterised by elemental and spectroscopic analysis [1]. It was also reported that metal chelates of trifluoro- and hexafluoroacetylacetones were inert to substitution reactions [2]. However, Joshi and Pathak investigated a number of fluoro-substituted metal acetylacetonates and halogenation of CF_3 substituted chelates was found to be slow [3, 4].

In a previous paper, we reported the preparation and gas chromatographic separation of the bromination products of tris(1,1,1-trifluoro-2,4-pentanediono)chromium(III) [5]. Samples of the tri- and bibrominated chelates were isolated by fractional crystallization and identified by mass spectrometry. Interestingly, there was little evidence for the presence of geometrical isomers in the gas chromatogram. In this paper, we wish to report our results on the bromination of tris(1,1,1-trifluoro-2,4-pentanediono)rhodium(III).

Experimental

Tris-(1,1,1-trifluoro-2,4-pentanediono)rhodium(III), $Rh(tfa)_3$, was prepared by the method of Fay and Piper [6] and purified by column chromatography on acid-washed alumina using chloroform as eluent. Bromination of $Rh(tfa)_3$ was performed at room temperature using excess bromine in chloroform. Gas chromatography was carried out using a Perkin-Elmer F-11 gas chromatograph fitted with a flame ionization detector. Mass spectra of the solid chelates were recorded on a JEOL JMS D-100 Mass Spectrometer using a direct insertion probe. Preparative scale liquid chromatography was carried out on a Waters Prep LC-system 500 liquid chromatograph using a PrepPAK-500 silica cartridge and refractive index detector. Proton NMR spectra were recorded on a JEOL JNM-FX200 Fourier transform NMR spectrometer at room temperature (22 °C) and samples were dissolved in deuterochloroform with TMS as internal standard.

Results and Discussion

As in the case of bromination of $Cr(tfa)_3$ reported previously [5], bromination of $Rh(tfa)_3$ was successfully achieved using bromine in chloroform at ambient temperatures. Using a 4:1 mole ratio of bromine to $Rh(tfa)_3$, the extent of the reaction was determined by gas chromatography and it was found that complete bromination of $Rh(tfa)_3$ was achieved in about 6 days, being three times longer than that reported for the corresponding reaction of $Cr(tfa)_3$ [5]. The chromatogram obtained for a 12 h bromination of $Rh(tfa)_3$ is shown in Fig. 1. Using an effluent splitter, samples of the two major peaks with retention times of 2.5 and 5.5 min were collected for mass spectral analysis. The pair of peaks around 12 - 14 min were collected individually after improving their resolution by decreasing the GC oven temperature to 155 °C.

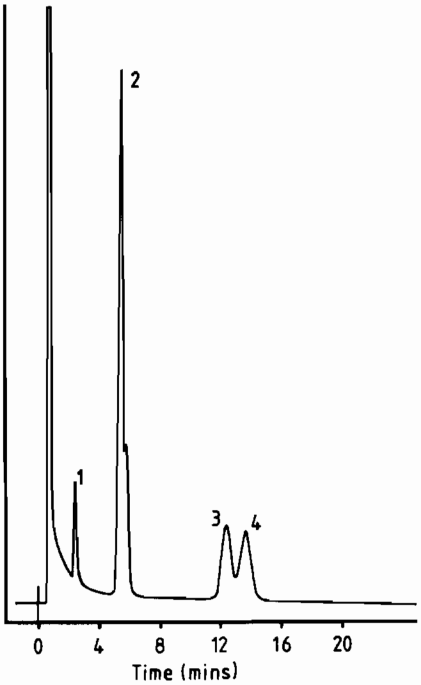

Fig. 1. Gas chromatogram of the reaction mixture from bromination of $Rh(tfa)_3$ after 12 h. Column: glass (1 m × 4 mm internal diameter) packed with 2.5% QF1 on Chromosorb 750. Conditions: oven, 170 °C; injector and detector, 220 °C; carrier (N_2) flow rate, 32 cm^3 min^{-1}. Peak identification: (1) $Rh(Brtfa)(tfa)_2$; (2) *mer*/*fac* $Rh(Brtfa)_2(tfa)$; (3) *mer*-$Rh(Brtfa)_3$; (4) *fac*-$Rh(Brtfa)_3$.

Parent ions were observed for all four samples and the isotopic splitting patterns for bromine allowed identification of the mono-, bi- and tribrominated chelates. As expected, the order of

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elution in gas chromatography is Rh(Brtfa)(tfa)$_2$ < Rh(Brtfa)$_2$(tfa) < Rh(Brtfa)$_3$ where Brtfa is the brominated trifluoroacetylacetone ligand anion. It was also concluded from the mass spectra that the two peaks around 12 - 14 min in the chromatogram could be assigned to the tri-brominated chelate and the two components probably arise from the existence of geometrical isomers of Rh(Brtfa)$_3$.

Further evidence for the presence of geometrical isomers was obtained by NMR studies on samples of the two components after their separation by prepLC. Using the conditions outlined above, bromination of Rh(tfa)$_3$ yielded a reaction mixture which contained about 95% Rh(Brtfa)$_3$ after 5 days and the components of the mixture were separated on a PrepPAK-500 silica cartridge using 10% dichloromethane in hexane as the eluent at a flow-rate of 100 cm^3 min^{-1}. One isolated component gave a single GC peak with retention time t_R = 12.4 min corresponding to the first-eluting peak of the pair attributed to Rh(Brtfa)$_3$. The second isolated sample gave two GC peaks with retention times matching the pair of peaks at 12–14 mins in Fig. 1; however gas chromatography indicated that the sample was initially enriched in the second-eluting component and that the composition of the sample changed with time, reverting back to the 50:50 mixture observed for Rh(Brtfa)$_3$ in Fig. 1. In proton NMR spectroscopy, the sample from the GC peak at t_R = 12.4 min gave three methyl group resonances at 2.72–2.75 ppm consistent with non-equivalent methyl groups in the meridional isomer. The sample containing two components yields four methyl group resonances at 2.72–2.76 ppm which indicates that the mixture contains the meridional and facial isomers. The difficulty in isolating a pure sample of the facial isomer by prepLC is attributed to its rapid isomerization in solution and, at equilibrium, GC shows that the mixture contains about equal proportions of each isomer. The order of elution is in agreement with that previously reported for metal trifluoroacetylacetonates [7].

Figure 1 indicates that the bi-brominated rhodium chelate (t_R ~ 5.5 min) also contains two components. The predominant species was isolated by prepLC in sufficient quantity to run NMR spectra. ^{1}H NMR gave three methyl resonances at 2.30–2.32 ppm consistent with a meridional configuration and a single resonance at 5.96 ppm was observed for the methine proton on the ligand which has not been brominated. In comparison to the above spectra data, the meridional isomer of Rh(tfa)$_3$ has three methyl resonances at 2.36–2.41 ppm and the three methine proton resonances at 5.97–6.04 ppm.

In earlier investigations [1, 3, 4], it is interesting to note that geometrical isomers were not observed in the products derived from electrophilic substitution reactions of tris-chelates of unsymmetrical β-diketones. Furthermore, in a previous report on the bromination of Cr(tfa)$_3$, GC separation of the reaction mixture gave little evidence for the existence of geometrical isomers in the products of this reaction although the starting material, Cr(tfa)$_3$, contained a mixture of isomers (~92% meridional) [5]. The results described in this paper on the bromination of Rh(tfa)$_3$ were achieved using an initial mixture of 85% *mer*/15% *fac,* however, in this case the gas chromatogram clearly showed the presence of geometrical isomers in the bi- and tri-brominated derivatives, the latter containing about 50% of each isomer at equilibrium.

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