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CARBONYL FLUORIDES OF MANGANESE

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Summary

The first carbonyl fluorides of manganese $Mn(CO)_3F_3$ and $[Mn(CO)_4F]_2$ have been prepared by treating $Mn(CO)_5Br$ with AgF. The compounds have been characterized by elemental analysis, conductance measurement, IR and mass spectrometric studies.

Introduction

Studies on the fluorides of metal carbonyls is one of the areas of recent interest in transition metal carbonyl chemistry [1—6]. Although the molecular carbonyl halides of manganese and rhenium where the halogen is chlorine, bromine or iodine have been known for about twenty years [7,8], the two carbonyl fluorides of rhenium $Re(CO)_5F$ [6] and $Re(CO)_3F_3$ [4,6] have been reported only recently. To our knowledge no carbonyl fluoride of manganese has previously been prepared. We now wish to report the preparation and characterisation of two fluorides of manganese carbonyl, viz., $Mn(CO)_3F_3$ and $[Mn(CO)_4F]_2$.

Experimental

Unless otherwise stated all reactions and other manipulations were carried out under nitrogen or argon. All solvents were degassed before use. Analyses were performed by the Analytical Laboratories of this institute. IR spectra of the two compounds were obtained in Nujol-mulls using a Perkin—Elmer model 125 spectrometer. Mass spectrometric measurements were taken on a CH-5 Varian-MAT mass spectrometer at 70 eV electron energies. Molar conductances were determined in acetone at room temperature using a LBR-Conductivity Bridge (WTW; West-Germany). $Mn(CO)_5Br$ was prepared by the method of Wilkinson and coworkers [7]. The compounds were characterised by elemental analyses, IR and mass spectroscopic studies and by molar conductance measurements.

Preparation of $Mn(CO)_3F_3$

0.7 g (2.55 mmol) $Mn(CO)_5Br$ and 2.0 g (15.75 mmol) AgF were mixed intimately in a porcelaine mortar, and triturated for 18 to 20 min in presence of CH_2Cl_2 (replacing CH_2Cl_2 from time to time to compensate loss due to evaporation). The mixture was transferred to a 100 ml Pyrex round bottom flask and stirred vigorously with a magnetic stirrer for 80 min in a closed system. The course of the reaction was followed by taking IR spectra at 10 min intervals. The evolved gas was pumped off from time to time.

The mixture was then filtered and cooled at −80° C for half an hour followed by filtration. The filtrate was dried under vacuum and extracted with acetone. The acetone extract was then concentrated and to it was added 7 ml n-pentane followed by scratching the walls of the container for 10 min, whereby the orange-yellow micro-crystalline $Mn(CO)_3F_3$ was obtained.

Yield 0.17 g (31.4%); m.p. 137° C (dec.). (Found: C, 18.15; F, 28.72; Mn, 28.13; *M* (by mass spec.) 196. $C_3F_3MnO_3$ calcd.: C, 18.38; F, 29.08; Mn, 28.03; *M* 195.97.) IR (nujol mull): ν(CO) 2037vs, 1944vs(br), 1922(sh), molar conductance (acetone, 21° C): 1.15 $cm^2\ ohm^{-1}\ mol^{-1}$.

Preparation of $[Mn(CO)_4F]_2$

0.7 g (2.55 mmol) $Mn(CO)_5Br$, 0.65 g (5.10 mmol) AgF and 15—18 ml CH_2Cl_2 were taken in a 100 ml pyrex round bottom flask and stirred vigorously for 75 min in a closed system at room temperature. The course of the reaction was followed by taking the IR spectra at 7 min intervals. The evolved gas was released from time to time. After the reaction was complete the mixture was filtered and concentrated in a vacuum system, whereby a light orange-yellow coloured product was obtained. The product $[Mn(CO)_4F]_2$ was purified by recrystallisation from dichloromethane and acetone mixture.

Yield 0.3 g (31.5%); no sharp melting point was observed; the compound starts to decompose at 210° C. (Found: C, 25.94; F, 10.09; Mn, 29.15. $C_8F_2Mn_2O_8$ calcd.: C, 25.83; F, 10.22; Mn, 29.54; *M* 371.96.)

Results and discussion

Manganese pentacarbonyl bromide $Mn(CO)_5Br$ reacts with AgF in different ways under slightly different reaction conditions. One of our aims was to obtain $Mn(CO)_5F$, but various attemps were unsuccessful.

By changing the reaction conditions two different carbonyl fluorides could be obtained. Using an excess of AgF (about 7—8 times) and by trituration for about 20 min followed by stirring in a closed system the compound $Mn(CO)_3F_3$ was obtained. From the reaction of $Mn(CO)_5Br$ and AgF in 1:2 mole proportion without prior trituration the compound $[Mn(CO)_4F]_2$ was obtained.

In the second case at least, it is believed, that the reaction proceeds through the intermediate formation of $[Mn(CO)_5F]$, which perhaps because of its instability dimerises to $[Mn(CO)_4F]_2$ even though the reaction conditions are not very extreme. The molar conductance of $Mn(CO)_3F_3$ in acetone at 21° C was 1.15 $cm^2\ ohm^{-1}\ mol^{-1}$ suggesting it to be a molecular species [9]. Possibly because of its low vapour pressure, a good mass spectrum of the compound could only be obtained at a relatively high temperature. The mass spectrum at 200° C shows the molecular peak at *m/e* 196 followed by the peaks due to successive loss of CO groups until *m/e* 112 due to MnF_3^+. Furthermore the appearance of the peaks at *m/e* 111 and 83 due to Mn(CO)$_2^+$ and Mn(CO)$^+$, respectively, suggests that a simultaneous fragmentation path due to the loss of F groups might be possible as well. Similar observations could also be made in the case of Mn(CO)$_5$X (X = Cl, Br) [10].

The IR spectrum of Mn(CO)$_3$F$_3$ in ν(CO) region was virtually the same as that of Re(CO)$_3$F$_3$ [4]. In principle [11] for a compound of the type *cis*-Mn(CO)$_3$L$_3$ two ν(CO) peaks, a_1 sharp at higher and *e* broad at a relatively lower energy, are to be expected. This compound showed two ν(CO) bands, one at 2037 cm^{-1} (sharp) and the other at 1944 cm^{-1} a very strong but broad peak. A very weak shoulder at 1922 cm^{-1} complicated the pattern slightly. A similar effect was observed with Re(CO)$_3$F$_3$, and in the present case we believe that the appearence of a shoulder is due to crystal effects and the compound possesses a structure similar to that of Re(CO)$_3$F$_3$ [4,6].

Although a satisfactory mass spectrum could not be obtained for [Mn(CO)$_4$F]$_2$ some fragments at *m/e* 269, 214, 213, 205 and 185 due to the ions Mn$_2$(CO)$_5$F$^+$, Mn(CO)$_5$F$^+$, Mn$_2$(CO)$_3$F$^+$, Mn(CO)$_4$F$_2^+$ and Mn$_2$(CO)$_2$F$^+$, respectively, support the formula. The molar conductance at 21°C in acetone, 0.66 cm^2 ohm^{-1} mol^{-1}, suggested the molecular nature of the compound [9]. The IR spectrum in ν(CO) region shows four bands, that at the high energy side being relatively weak. Since the frequencies all lie in the 2100—1900 cm^{-1} range, it is safe to assume that the compound is a dimer with no bridging carbonyl groups. This assumption is in accord with observations made on other tetracarbonyl halide dimers of manganese and its congeners, technetium and rhenium. In view of the expected octahedral local symmetry around each metal atom with the fluorine atoms acting as the bridging atoms, it is suggested that this molecule [Mn(CO)$_4$F]$_2$ has a structure similar to the other tetracarbonyl halide dimers of manganese [12].

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