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Mass Spectra of Scandium(III) and Yttrium(III) Complexes of Trifluoromethyl-β-Diketones

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Introduction

Atom and group migration from the ligand to the metal occurs in the electron impact mass spectra (EIMS) of metal β-diketonates [1]. These rearrangement reactions are dependent on whether the metal belongs to class *a* or *b* [2, 3]. The migration of F in the EIMS of organometallics [4] and metal chelates [5] of $RCOCH_2COCF_3$ were discussed on the basis of the hard/soft/acid/base (HSAB) theory. Recently we have studied the EIMS of gallium and indium chelates of $RCOCH_2COCF_3$. These complexes showed both F and R migration [6]. These metals belong to class *a* group, and F migration was expected. The presence of d^{10} electrons in these metals are responsible for R migration, since the rearrangement involves d → R π bonding [7]. The EIMS of palladium(II) complexes of fluorinated β-diketones showed R (even alkyl) migration due to the presence of d electrons, and showed no F migration since the metal belongs to class *b* [8].

We have also studied the electron impact mass spectra of scandium(III) and yttrium(III) complexes of $RCOCH_2COCF_3$. These metals belong to class *a* and contain no d electrons. The EIMS of scandium(III) and yttrium(III) complexes of some non-fluorinated β-diketones have been reported [9–11], as have those of $Cs[Y(CF_3COCHCOCF_3)_4]$ [12].

Experimental

The preparation of scandium(III) complexes will be reported in a separate communication.

Preparation of Tris(β-diketonato)yttrium(III)

Yttrium oxide (0.5 g, 2.21 mmol; Koch-Light Lab.) was dissolved in 10 ml hot conc. HCl and evaporated to dryness, and the residue was dissolved in 25 ml water. A solution of β-diketone (13.26 mmol in 25 ml ethanol) was added to the aqueous solution of the metal chloride. The pH of the mixture was raised to 5–6 by adding conc. NH_3; the mixture was then digested for 10 min. The mixture was cooled in ice when the product separated as oil. The oil was separated and added to 25 ml of 50% ethanol. The mixture was allowed to stand in the refrigerator for 1–2 weeks, after which the product was solidified. The solid was powdered and washed with 50% ethanol. The compounds were solvated: $YL_3 \cdot C_2H_5OH$ when R = 2-thienyl and 2-furyl, and $YL_3 \cdot 2H_2O$ when R = phenyl. When R is CH_3, solid NH_4YL_4 was separated when the digested mixture was cooled in ice (no oily separation). Yttrium compounds found here were insoluble in benzene while the scandium complexes, all anhydrous, were soluble in benzene.

The EI mass spectra were obtained on an AEI MS-12 mass spectrometer at 70 eV and at a source temperature of 250 °C.

Results and Discussion

The relative intensities of the electron impact mass spectra of scandium(III) and yttrium(III) chelates of trifluoromethyl-β-diketones are shown in Table I. Since both scandium and yttrium are monoisotopic elements, the identification of metal-containing ions has some uncertainty. Both series of chelates gave similar ions in their EIMS. The thermal decomposition of $NH_4[Y(CH_3COCHCOCF_3)_4]$ in the mass spectrometer gave $Y(CH_3COCHCOCF_3)_3$ and a subsequent mass spectrum.

Most interesting were the $M - L - 2CF_2$ ions, a type of ion not previously reported in the mass spectra of metal chelates of trifluoromethyl-β-diketones. These ions have two fluorines migrated to the metals. During the process $M - L - CF_2 \xrightarrow{*} M - L - 2CF_2$, the first $L - CF_3$ breaks its oxygen–metal bond and the resulting neutral RC(O)–CH=C=O is linked to the metal through the coordination π bonding, the metals acting as acceptors since they have empty d orbitals.* The reaction $M - L - 2CF_2 \xrightarrow{*} MetLF - CF_2$, involves the loss of this weakly-bonded neutral RC(O)–CH=C=O. Other novel ions are M − L + 72 and MetL + 72. Their formations are not clear at this stage and 72 may be due to the neutral CH≡C–C(O)F which coordinates to the metal by π bonding, the metal acting as an acceptor.

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*Similar types of structure can be suggested for the $M - 2CF_3$ ion observed [1] in the EIMS of $Cu(RCOCHCOCF_3)_2$. In this case the copper(II) is reduced to copper(I) and one neutral $L - CF_3$(RCOCHCO) is linked to copper(I) through π bonding. The metal is acting as a donor in this case, since copper(I) has d^{10} electrons.

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TABLE I. Relative Intensities of Metal Containing Ions in the EI Mass Spectra of Scandium(III) and Yttrium(III) Complexes of $RCOCH_2COCF_3$.

Ion	$Sc(RCOCHCOCF_3)_3$				$Y(RCOCHCOCF_3)_3$			
R =	Methyl	Phenyl	2-Thienyl	2-Furyl	Methyl	Phenyl	2-Thienyl	2-Furyl
M^a	58.3	100	100	100	100	100	100	100
$M - R^b$	1.5^a				4.3^a			
$M - F$	1	1.2	3	5		1.7	1.2	2.5
$M - 44$					7.6	8.3	17	8.5
$M - CF_3{}^c$	40^a	66^a	53.6^a	34.5^a	47.6^a	83.3^a	64^a	52.5^a
$M - CF_3 - 44$	–				3.3	5.8	8.5	2.9
$M - L + 72$	10	4	2	0.8	10.7	5	2.4	1.2
$M - L^d$	100^c	66^{ac}	67.9^{ac}	100^{ac}	61.9^{bc}	29.2^c	41.5^c	50^c
$M - L - CO$	6.6^d	6^d	26.8^d	20.7^d	6^d	11.7	14	17.5
$M - L - 44$					6	6.6	13	2.7
$M - L - CF_2{}^e$	91.7^d	40^d	34^d	55.2^d	47.6^d	32.5	24	42.5
$M - L - CF_2 - CO$	4.1	3.8^e	6^e	6	3.3	7.5	3.6	4.5
$M - L - 2CF_2{}^f$	30^e	8^e	8^e	9^e	10^e	10	4.6	6
MetLF + 72	4.5			1.5	31	10	9.5	10
$MetLF^g$	4.7	10	18	4	5	21.7	18	5
MetL	3.7	1.4	2.1	1.9	1.7			1.6
MetLF – CO	2.1	6	8.6	5.2	1.2	11.7	8.5	7
$MetLF - CF_2$	56.7^g	44^g	4.6^{fg}	43.1^{fg}	8.8^g	62.5	36.6	45
$MetF_2$	6.7	5.4	*	3.8	1.3	21.6	15	7.5

The symbols M, L and Met stand for molecule (complex), ligand and metal, respectively. Identified metastable transitions are indicated by superscripts which relate the daughter to its parent ion. * Could not be calculated due to the presence of R(83).

The spectra of these two classes of compounds showed some differences. The yttrium complexes showed $M - 44$, $M - CF_3 - 44$ and $M - L - 44$ ions. Such ions were absent in the EIMS of scandium complexes. Loss of CO_2(44) from $M - CF_3$ ions were observed in various metal complexes of $RCOCH_2COCF_3$ [3, 15]. This involves the organometallic bond formation, and the mechanism for such reactions was discussed in [14]. The comparable loss of COS from zinc, nickel and platinum complexes of monothio-β-diketones ($RCSCH_2COCF_3$) have also been observed [16, 17].

However, $M - 44$ and $M - L - 44$ ions have not been reported previously. The mechanism for the loss of 44(CO_2) from the unfragmented ligand coordinated to the metal is not clear. These ions also have an organometallic bond. Loss of CO_2 is probably in two stages; first the CO adjacent to CF_3 is lost, followed by the oxygen and the resulting $RC(-)CHCF_3$ is linked to the metal through the carbon atom adjacent to R.

These complexes showed no R migration to the metals. This is probably due to the absence of d electrons in Sc(III) and Y(III), since the migration of R is assumed to be due to d → R π bonding [7]. The metal fluoride ions ($ScF_2{}^+$ and $YF_2{}^+$) were confirmed by high resolution mass measurements. Such ions were only observed in the chelates of strong class *a* metals with no d electrons. The mass spectra of lanthanide chelates of $RCOCH_2COCF_3$, also showed these ions [18, 19]. A doubly charged ion, $M - L - CF_3$ (1.2%), at 224.5 (m/e) was observed in the spectrum of yttrium complex with R as 2-thienyl. Recently we haxe reported the presence of dipositive ions in the EIMS of palladium(II) complexes of fluorinated β-diketons [8].

Conclusion

The influences of class *a* and class *b*, and d electrons in the rearrangement reactions in EIMS of metal chelates of $RCOCH_2COCF_3$, are important. The class *a* metals (Sc and Y) with no d electrons show F but not R migration, whereas class *a* metals (Ga and In) with d^{10} electrons show both F and R migrations [6]. The chelates of strong class *b* metal (Pd) shows R but not F migration [8].

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