Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

The occurrence of binuclear species in the mass spectra of arene chromium tricarbonyl derivatives

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(Received May 24th, 1971)

The occurrence, in mass spectrometers, of ion-molecule reactions which result in the formation of ions with higher mass than that of the parent molecule is well known for organic substances and has recently been reported for organo-compounds of transition metals[1,2,3]. We report here on a series of such ions formed in a mass spectrometer from parent compounds of the type $ArCr(CO)_3$.

The mass spectra were measured with an A.E.I. MS 12 instrument with an ionising potential of 70 eV, a trap current of 100 μA and an ion accelerating voltage of 8 kV. The samples were introduced into the mass spectrometer by means of a direct insertion probe. In all cases binuclear ions of the type $Ar_2Cr_2(CO)_n^+$ were detected, where $n = 0, 1, 2$ and 3; ions with $n > 3$ were not detected. Ion source pressures, measured on an A.E.I. V.C.9 ionisation gauge, were between 5 and 8×10^{-6} mm. Table 1 shows the relative intensities of these ions observed in the mass spectra of mesitylene, toluene and methyl benzoate chromium tricarbonyl. The intensities of the binuclear ions were all of the order of 0.01 to 0.1% of the parent ions.

TABLE 1

Ion type	Ar = mesitylene		Ar = toluene		Ar = methyl benzoate	
	m/e	rel. peak height	*m/e*	rel. peak height	*m/e*	rel. peak height
$(Ar)_2Cr_2(CO)_3^+$	428	33.3	372	15.0	460	3.6
$(Ar)_2Cr_2(CO)_2^+$	400	19.2	344	6.0	432	19.3
$(Ar)_2Cr_2(CO)^+$	372	0.7	316	0.5	404	0.2
$(Ar)_2Cr_2^+$	344	10.5	288	5.0	376	8.9
$(Ar)_1Cr_2(CO)_3^+$	308	53.8	280	37.5	324	13.9
$(Ar)_1Cr_2(CO)_2^+$	280	100	252	100	296	100
$(Ar)_2Cr^+$	292	9.5	236	4.0	324	13.9

The observed ions could be due to reaction either in the solid sample or in the gas phase. However, the introduction of two physically separate mono-nuclear carbonyls with different arene ligands produced binuclear ions containing both ligands (*e.g.* (mesitylene)-(methylbenzoate)$Cr_2(CO)_3^+$ ions), which rules out the possibility of reactions in the solid sample being solely responsible for the binuclear ions. This is confirmed by a plot of the intensity of (mesitylene)$_2$Cr$_2$(CO)$_3$$^+$ peak against the square of the intensity of the parent ions shown in Fig. 1. The quadratic dependence indicates that a bimolecular gas phase reaction is responsible for the appearance of the binuclear ions. Figure 2 shows a plot of the ratio of intensities for binuclear to parent ions *versus* electron energy; the maximum in the curve at 16 eV (nominal) is typical of an ion-molecule reaction and excludes the possibility that the precursor to the binuclear ion is a binuclear molecule formed in a gas phase molecule–molecule reaction.

The appearance potential of (mesitylene)$_2$Cr$_2$(CO)$_3$$^+$ was found to be 7.35 eV which is just above the appearance potential of the (mesitylene)Cr(CO)$_2$$^+$ ion from the parent molecule and suggests that one or both of reactions (1) and (2) are the major routes to the binuclear ion:

$$\text{(mesitylene)Cr(CO)}_3 + \text{(mesitylene)Cr(CO)}_3{}^+ \rightarrow \text{(mesitylene)}_2\text{Cr}_2\text{(CO)}_3{}^+ + 3\text{CO} \quad (1)$$

$$\text{(mesitylene)Cr(CO)}_3 + \text{(mesitylene)Cr(CO)}_2{}^+ \rightarrow \text{(mesitylene)}_2\text{Cr}_2\text{(CO)}_3{}^+ + 2\text{CO} \quad (2)$$

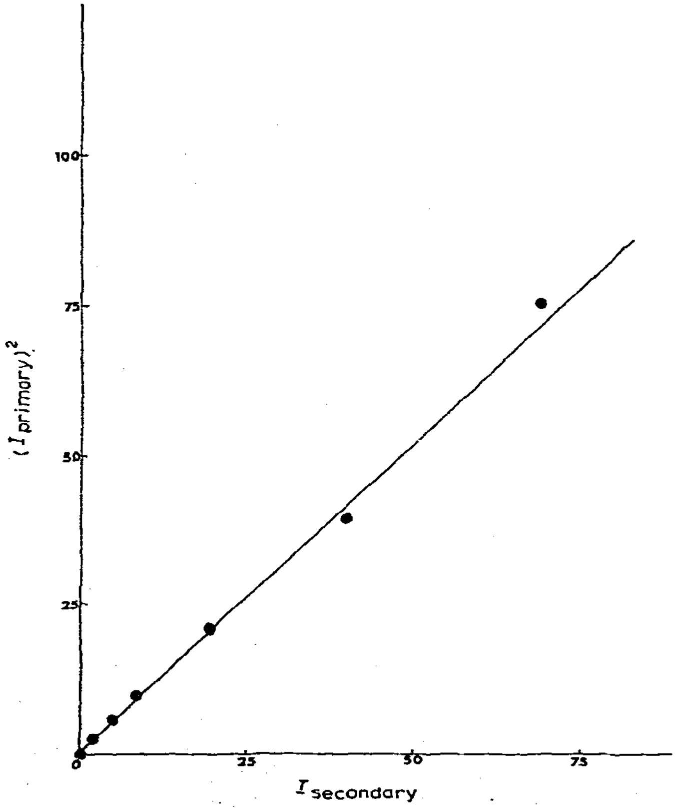

Fig. 1. Plot of the intensity of (mesitylene)$_2$Cr$_2$(CO)$_3$$^+$ against the square of the intensity of the parent ions.

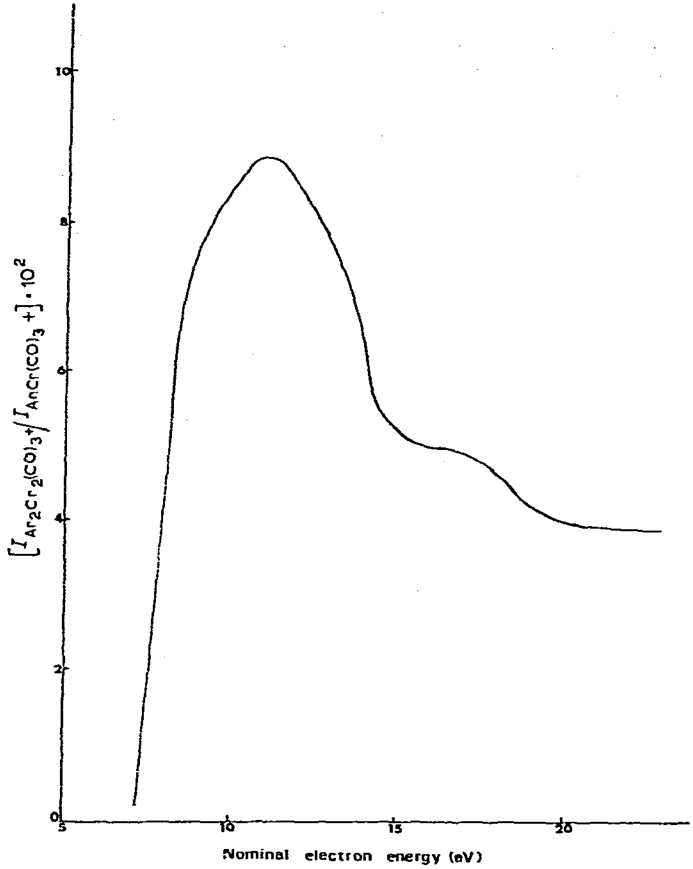

Fig.2. Plot of the ratio of intensities for binuclear to parent ions *vs.* electron energy.

Metastable peaks at *m/e* 374.0, 318.1,405.8 for arene as mesitylene toluene and methyl benzoate respectively show that ions of the type $(Ar)_2Cr_2(CO)_2^+$ are formed by loss of CO from the $(Ar)_2Cr_2(CO)_3^+$ ions, although this does not exclude the possibility of ion-molecule reactions of the type (3):

$$(Ar)Cr(CO)_3 + ArCr^+ \rightarrow (Ar)_2Cr_2(CO)_2^+ + CO \qquad (3)$$

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