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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

VIII. CrS^+ IONS IN THE MASS SPECTRUM OF π-THIOPHENECHROMIUM TRICARBONYL

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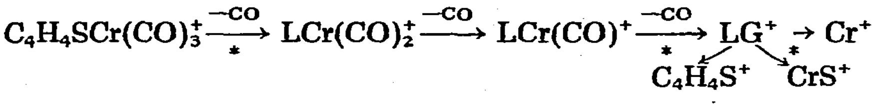
Summary

The fragmentation of π-thiophenechromium tricarbonyl under electron impact has been examined. The formation of the rearrangement ion CrS^+ has been observed.

Fragmentation of thiophenechromium tricarbonyl (I) under electron impact is similar to the degradation of benzenechromium tricarbonyl (II) [1,2] in that successive elimination of three carbonyl groups and of the ligand molecule occurs and results in the ions $C_4H_4SCr(CO)_n^+$ (n is 0 to 2) and Cr^+, respectively (Table 1, Scheme 1). It should be noted that mass spectra of thiophene and benzenechromium tricarbonyls are very similar (Table 1).

SCHEME 1



$$\begin{tikzcd}
C_4H_4SCr(CO)_3^{+} \arrow[r, "-CO", "*"'] & LCr(CO)_2^{+} \arrow[r, "-CO"] & LCr(CO)^{+} \arrow[r, "-CO", "*"'] & LG^{+} \arrow[r] \arrow[d] \arrow[dr, "*"] & Cr^{+} \\
 & & & C_4H_4S^{+} & CrS^{+}
\end{tikzcd}$$

TABLE 1

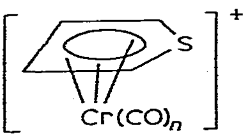
MASS SPECTRA OF THIOPHENECHROMIUM TRICARBONYL (I) AND BENZENECHROMIUM TRICARBONYL (II) (70 eV)

	Ion	P^+	$(P-CO)^+$	$(P-2CO)^+$	LCr^+	L^+	$(CrS)^+$	Cr^+
I	m/e	220	192	164	136	84	84	52
	% Σ	0.093	0.021	0.028	0.138	0.050	0.025	0.438
II	m/e	214	186	158	130	78	—	52
	% Σ	0.120	0.007	0.014	0.180	0.066		0.510

TABLE 2

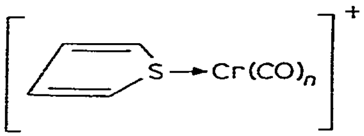
EXACT MASSES AND THE $CrS^+/C_4H_4S^+$ RATIOS IN THE MASS SPECTRUM OF TIOPHENECHROMIUM TRICARBONYL

	Masses Found (calcd.)	Δ	$CrS^+/C_4H_4S^+$ at	
			70 eV	15 eV
$C_4H_4S^+$	84.0083 (84.0034)	0.0044	0.5	1
CrS^+	83.9167 (83.9126)	0.0041		
$SCr(CO)^+$	111.9028 (111.9075)	0.0047		



$n = 0-1$

(III)



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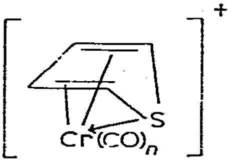
(IV)



$n = 0-1$

(V)

The mass spectrum of thiophenechromium tricarbonyl displays intense ions at *m/e* of 84 assignable to the ligand ion C_4H_4S. Measuring the exact masses has shown, however, that the peak is a doublet consisting of $C_4H_4S^+$ and CrS^+, the CrS^+ contribution in the *m/e* 84 peak increasing with a decrease in the ionising electron energy (Table 2). The formation of CrS^+ ions suggests that, along with the expected π-coordination of $C_4H_4CrS^+$ (III), at least part of the $C_4H_4SCr^+$ is subject to σ-type coordination (IV), or that both π- and σ-coordination (V) operate in the ion $C_4H_4SCr^+$.

Ions containing a Cr—S bond may arise not only following the complete decarbonylation of the parent ion but also at intermediate steps of the elimination. This agrees with the $SCr(CO)^+$ ion found in the spectrum. The $SCr(CO)_n^+$ ion (*n* is 2 or 3), if they exist at all, are of very low intensity.

Experimental

Mass spectra were recorded on an AEI MS-30/DS-50 mass spectrometer at 20°C. The ionising chamber temperature was 100°C and the ionising energy was 70 or 15 eV.

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