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NOTE

MASS SPECTRA AND APPEARANCE POTENTIALS OF SOME 1,5-CYCLOOCTADIENE–RHODIUM COMPLEXES

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We wish to report some exploratory studies of the mass spectra of the complexes $[RhX(C_8H_{12})]_2$, (X = Cl, Br, I) which show some novel fragmentations not previously observed in metal–olefin complexes[1].

Approximate appearance and ionisation potentials were determined by a technique accurate to ± 0.1 eV[2]. The results are given in Table 1. The simplest explanation for the appearance potential of $C_8H_{12}^+$ from each complex being equal to the ionisation potential of 1,5-cyclooctadiene is that each complex decomposed thermally in the mass spectrometer, giving some free 1,5-cyclooctadiene. It is therefore impossible to draw any conclusions about the strength of the bonds between 1,5-cyclooctadiene and rhodium from the present data. However, since the three complexes $[RhX(C_8H_{12})]_2$ have essentially the same ionisation potential it would appear that the ionisation involves a molecular orbital which has little halogen character.

TABLE 1

APPEARANCE POTENTIALS AND IONISATION POTENTIALS

Molecule	Ion A^+	A.P.(A^+)(eV)
$(C_8H_{12}RhCl)_2$	$(C_8H_{12}RhCl)_2^+$	7.1 ± 0.1
	$C_8H_{12}^+$	9.1 ± 0.1
$(C_8H_{12}RhBr)_2$	$(C_8H_{12}RhBr)_2^+$	7.2 ± 0.1
	$C_8H_{12}^+$	9.2 ± 0.1
$(C_8H_{12}RhI)_2$	$(C_8H_{12}RhI)_2^+$	7.1 ± 0.1
	$C_8H_{12}^+$	9.1 ± 0.1
C_8H_{12}	$C_8H_{12}^+$	9.1 ± 0.1

In Table 2 the general features of the mass spectrum of each complex are given. Only those ions containing rhodium are listed since all the complexes $[RhX(C_8H_{12})]_2$ decompose thermally by differing amounts to give C_8H_{12} and fragmentation of this species gives prominent peaks at and below *m/e* 108.

The intensities of the ions shown in Table 2 are percentages of the total ion current carried by those ions listed. It should also be noted that for each ion containing chlorine or bromine, only the lowest possible mass is recorded (*i.e.* corresponding to ^{35}Cl or ^{79}Br) but the intensity given in the Table is the sum of the intensities of all ions of that formula.

The general features of the mass spectrum of each complex are similar, although the various fragmentation paths differ in their relative importance. The most interesting feature, common to all three spectra, is the successive loss of two (H_3X) units from the molecular ion. These fragmentations are well supported by metastable transitions as shown in Table 3. The simplest way to rationalise this unusual type of fragmentation is to assume that the initial step is the elimination of HX from the molecule ion, followed by loss of H_2 from the same cyclooctadiene. Since no

TABLE 2

MASS SPECTRA

$(C_8H_{12}RhCl)_2$		$(C_8H_{12}RhBr)_2$		$(C_8H_{12}RhI)_2$		Formula
Mass	Int. (%)	Mass	Int. (%)	Mass	Int. (%)	
492	34.0	580	40.5	676	3.2	$C_{16}H_{24}Rh_2X_2$
462	0.17	550	0.71	646	0.89	$C_{14}H_{18}Rh_2X_2$
454	11.1	498	9.3	546	0.94	$C_{16}H_{21}Rh_2X$
452	2.7	496	4.9	544	1.4	$C_{16}H_{19}Rh_2X$
450	0.68	494	1.7	542	0.35	$C_{16}H_{17}Rh_2X$
346	3.5	390	6.9	438	11.3	$C_8H_9Rh_2X$
344	0.87	388	1.7	436	4.9	$C_8H_7Rh_2X$
416	10.8	416	6.2	416	9.2	$C_{16}H_{18}Rh_2$
414	3.5	414	2.5	414	2.7	$C_{16}H_{16}Rh_2$
412	5.8	412	3.5	412	4.3	$C_{16}H_{14}Rh_2$
410	2.4	410	1.5	410	2.3	$C_{16}H_{12}Rh_2$
310	5.5	310	5.8	310	12.0	$C_8H_8Rh_2$
308	5.0	308	4.7	308	11.2	$C_8H_6Rh_2$
284	0.95	284	0.40	284	0.13	$C_6H_6Rh_2$
283	0.70	283	0.62	283	0.20	$C_6H_5Rh_2$
282	1.7	282	1.04	282	0.33	$C_6H_4Rh_2$
232	1.8	232	~0	232	3.4	$C_{10}H_9Rh$
218	1.0	218	0.62	218	2.9	C_9H_7Rh
211	0.30	211	1.04	211	1.9	$C_8H_{12}Rh$
210	0.23	210	~0	210	0.57	$C_8H_{11}Rh$
209	0.30	209	1.04	209	1.9	$C_8H_{10}Rh$
208	0.50	208	1.04	208	1.3	C_8H_9Rh
207	0.90	207	0.82	207	2.8	C_8H_8Rh
206	0.55	206	0.42	206	1.6	C_8H_7Rh
205	1.1	205	1.04	205	5.1	C_8H_6Rh
182	0.90	182	0.62	182	2.3	C_6H_7Rh
181	1.2	181	1.24	181	4.3	C_6H_6Rh
168	0.87	168	0.82	168	4.5	C_5H_5Rh
157	0.87	157	~0	157	1.9	C_4H_6Rh
144	0.05	144	~0	144	0.17	C_3H_5Rh
143	0.07	143	~0	143	2.3	C_3H_4Rh
142	0.23	142	~0	142	0.58	C_3H_3Rh
241	0.23	285	0.60	333	2.0	Rh_2X

The mass spectrometer was an MS 9 (A.E.I. Ltd.) operated at a resolution of 1,000, which was sufficient to enable all fragment ions to be identified from isotope ratios. The temperature of the ionisation chamber was between 100° and 150°. Mass spectra are at 70 eV.

TABLE 3

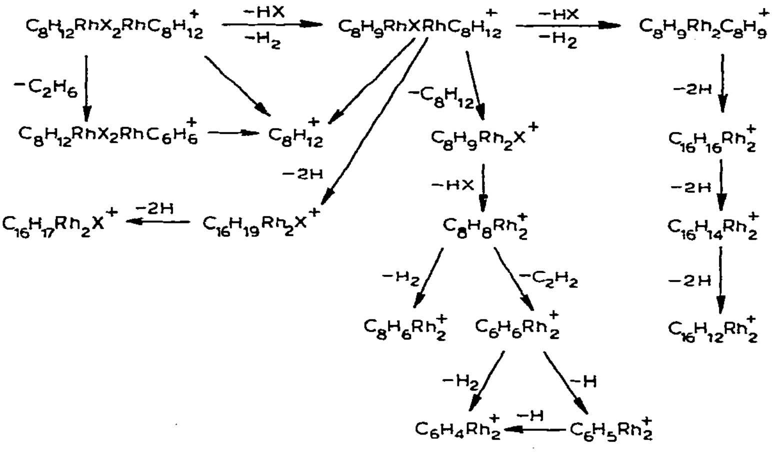
METASTABLE TRANSITIONS FOR LOSS OF H_3X

Transition			m^* $(=m_2^2/m_1)$ (calcd.)	
m_1	m_2			
$(C_8H_{12}RhCl)_2^+$	$\rightarrow C_8H_{12}Rh_2ClC_8H_9^+$	$+(H_3Cl)$	417.4–421.0[a]	Observed
$(C_8H_{12}Rh_2ClC_8H_9)^+$	$\rightarrow (C_8H_9Rh)_2^+$	$+(H_3Cl)$	379.5–381.2[a]	Observed
$(C_8H_{12}RhBr)_2^+$	$\rightarrow (C_8H_{12}Rh_2BrC_8H_9)^+$	$+(H_3Br)$	426.2–429.5[a]	Observed
$(C_8H_{12}Rh_2BrC_8H_9)^+$	$\rightarrow (C_8H_9Rh)_2^+$	$+(H_3Br)$	346.1–347.5[a]	Not observed[b]
$(C_8H_{12}RhI)_2^+$	$\rightarrow (C_8H_{12}Rh_2IC_8H_9)^+$	$+(H_3I)$	441.0	Not observed[b]
$(C_8H_{12}Rh_2IC_8H_9)^+$	$\rightarrow (C_8H_9Rh)_2^+$	$+(H_3I)$	317.0	Observed

[a] Range of values due to halogen isotopes. [b] Intensities of m_1^+ and m_2^+ very low.

metastable peaks corresponding to the loss of HX (or H_2) alone were observed, these steps must be essentially concerted. This behaviour contrasts with that of some bridged metal carbonyl halides, where the M_2X_2 unit persists until loss of carbonyl groups is complete[3].

An outline scheme for some of the further fragmentation of the $[RhX(C_8H_{12})]_2$ complexes is given in Fig. 1, but few metastable transitions relating to these fragmentations were observed. The low mass ions from $C_8H_{11}Rh^+$ to $C_3H_3Rh^+$ (Table 2) are not included since they could be formed from several of the ions in Fig. 1. Since the mass spectrum of 1,5-cyclooctadiene has no significant peaks from $C_8H_{11}^+$ to $C_8H_6^+$ it is possible that the ions in Table 2 between $C_8H_{11}Rh^+$ and $C_8H_6Rh^+$ contain two hydrocarbon fragments attached to rhodium. The formation of dinuclear ions such as $C_{16}H_{18}Rh_2^+$ and $C_8H_8Rh_2^+$ is unusual but it is not possible as yet to comment further on these species. The formation of the ion $C_5H_5Rh^+$ is also interesting since treatment of $[RhCl(C_8H_{12})]_2$ with iodine has recently[4] been shown to give the π-cyclopentadienyl complex $[C_5H_5RhI_2]_n$.



All the complexes $[RhX(C_8H_{12})]_2$ give approximately equal amounts of $C_{16}H_{18}Rh_2^+$ but the precursors $(C_8H_{12}RhX)_2^+$ and $C_8H_9RhXRhC_8H_{12}^+$ are of very low abundance in the iodide. In this complex the alternative fragmentation path from $C_8H_9RhXRhC_8H_{12}^+$ through $C_8H_9Rh_2X^+$ to $C_8H_8Rh_2^+$ is favoured.

A minor fragmentation of the molecule ion, of decreasing importance from iodide to chloride, is the loss of uncharged C_2H_6:

$$C_8H_{12}RhX_2RhC_8H_{12}^+ \longrightarrow C_8H_{12}RhX_2RhC_6H_6^+ + C_2H_6$$

In the spectrum of the iodide and bromide there are metastable peaks (at 617.3 and centred around 524 respectively) but in the chloride this fragmentation was too insignificant for a metastable peak to be observed. This type of fragmentation is known[1]. There is also evidence in the spectrum of the bromide only for loss of neutral C_3H_8 from the parent ion and this fragmentation appears to be more favoured than the loss of C_2H_6.

The mass spectra of similar compounds with different organic ligands or different metals are being investigated.

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