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PRELIMINARY COMMUNICATION

MASS SPECTRA OF SOME CYCLOPENTADIENYLRHODIUM OLEFIN COMPLEXES

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The mass spectra of several olefin derivatives of the metal carbonyls have been investigated[1,2,3]. I now wish to report the mass spectra of two carbonyl-free rhodium olefin complexes of the general formula $C_5H_5Rh(olefin)_2$. The monoisotopic nature of rhodium permits observation of metastable ions which lend further support to proposed fragmentation schemes.

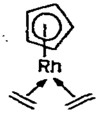
The first compound investigated was cyclopentadienyldiethylenerhodium, $C_5H_5Rh(C_2H_4)_2$ (I)[4]. Metastable ions were observed which indicated that the parent ion was converted to the bare Rh^+ ion by the following three-step process involving successive losses of the two ethylene groups followed by the π-cyclopentadienyl ring:

$$\text{(a)}\ \underset{m/e\ 224}{C_5H_5Rh(C_2H_4)_2^+} \xrightarrow{m^*\ 171.5} \underset{m/e\ 196}{C_5H_5RhC_2H_4^+} + C_2H_4$$

$$\text{(b)}\ \underset{m/e\ 196}{C_5H_5RhC_2H_4^+} \xrightarrow{m^*\ 144} \underset{m/e\ 168}{C_5H_5Rh^+} + C_2H_4$$

$$\text{(c)}\ \underset{m/e\ 168}{C_5H_5Rh^+} \xrightarrow{m^*\ 63.3} \underset{m/e\ 103}{Rh^+} + C_5H_5$$

The ethylene groups are thus lost stepwise much like the carbonyl groups in metal carbonyls. Indeed the rhodium ions in the mass spectrum of $C_5H_5Rh(C_2H_4)_2$ correspond closely to the cobalt ions in the reported[5] mass spectrum of $C_5H_5Co(CO)_2$.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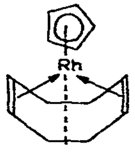
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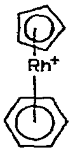
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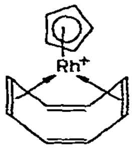
IV

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The other cyclopentadienylrhodium diolefin derivative investigated was cyclopentadienyl-1,5-cyclooctadienerhodium, $C_5H_5RhC_8H_{12}$ (II)[6]. The mass spectrum of this rhodium complex II exhibited enough metastable ions to permit elucidation of a detailed fragmentation scheme as depicted in Fig.1. Several pathways appear to be possible in going from the parent ion to the ion $C_5H_5Rh^+$ (*m/e* 168). The ion $C_5H_5Rh^+$ can then fragment to the "bare" rhodium ion Rh^+ (*m/e* 103) by cleavage of its C_5H_5 ring.

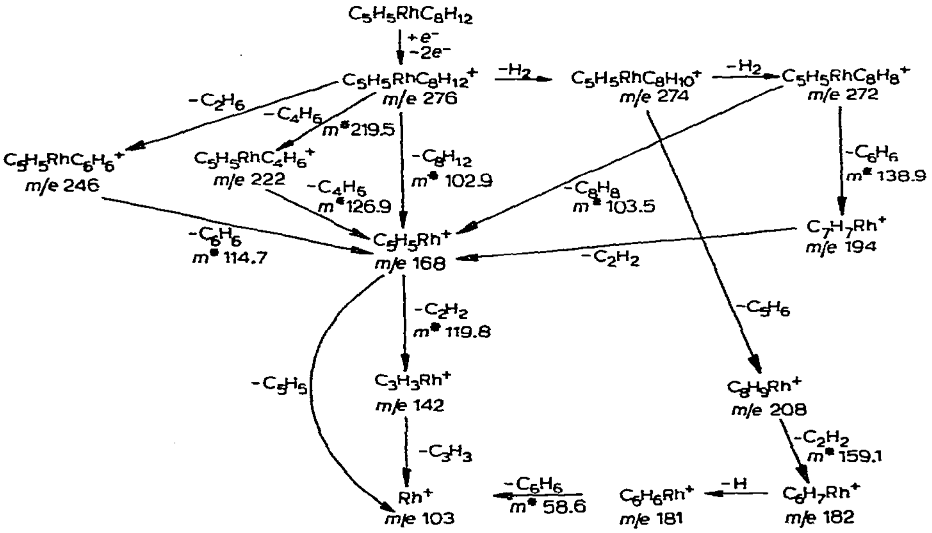

Fig.1. Fragmentation scheme of $C_5H_5RhC_8H_{12}$.

The parent ion $C_5H_5RhC_8H_{12}{}^+$ (*m/e* 276) can form the ion $C_5H_5Rh^+$ (*m/e* 168) by loss of the diolefin C_8H_{12} ligand in a single step. Alternatively the parent ion can lose the elements of ethane (C_2H_6 or $2CH_3$) to form the ion $C_5H_5RhC_6H_6{}^+$ (*m/e* 246), apparently with structure III containing a π-complexed benzene ring. This ion can then lose its C_6H_6 fragment in a further step forming the ion $C_5H_5Rh^+$ (*m/e* 168).

The parent ion $C_5H_5RhC_8H_{12}{}^+$ (*m/e* 276) can also undergo dehydrogenation forming the ion $C_5H_5RhC_8H_8{}^+$ (*m/e* 272)★. This ion may have a structure IV containing a π-complexed cyclooctatetraene ring. A related compound $C_5H_5RhC_8H_8$ has been reported[8]. The ion $C_5H_5RhC_8H_8{}^+$ (*m/e* 272) can lose a neutral C_8H_8 fragment (presumably cyclooctatetraene) forming the ion $C_5H_5Rh^+$ (*m/e* 168).

Another possible route from $C_5H_5RhC_8H_{12}{}^+$ to $C_5H_5Rh^+$ involves the intermediate ion $C_5H_5RhC_4H_6{}^+$ (*m/e* 222). Metastable ions are observed corresponding to the following reactions:

★Similar dehydrogenations have been noted in the mass spectra of other olefin–metal complexes with hydrogens attached to sp^3 hybridized carbon atoms which in turn are attached to an sp^2 carbon atom π-bonded to the metal atom[7].

$$\underset{m/e\ 276}{C_5H_5RhC_8H_{12}{}^+} \xrightarrow{m^*\ 219.5} \underset{m/e\ 222}{C_5H_5RhC_4H_6{}^+} + C_4H_6$$

$$\underset{m/e\ 222}{C_5H_5RhC_4H_6{}^+} \xrightarrow{m^*\ 126.9} \underset{m/e\ 168}{C_5H_5Rh^+} + C_4H_6$$

There is thus some evidence that a 1,5-cyclooctadiene ligand can break down into a butadiene ligand in the mass spectrometer. This can occur by breaking the two allylic carbon–carbon bonds as indicated by dotted lines in structure II. This process is the reverse reaction to the synthesis of 1,5-cyclooctadiene by dimerization of butadiene. In addition it resembles fragmentations related to the reverse Diels–Alder reaction observed in the mass spectra of certain metal carbonyl complexes of bicyclo[2,2,1]-heptadiene and dicyclopentadiene[7].

The mass spectrum of $C_5H_5RhC_8H_{12}$ also exhibited the ion $C_8H_9Rh^+$ (*m/e* 208), possibly formed by elimination of a neutral cyclopentadiene (C_5H_6) fragment from the ion $C_5H_5RhC_8H_{10}{}^+$ (*m/e* 274). The $C_8H_9Rh^+$ (*m/e* 208) ion loses an acetylene (C_2H_2) fragment giving the ion $C_6H_7Rh^+$ (*m/e* 182). The occurrence of this elimination process is supported by a metastable ion at *m/e* 159.1 ($182^2/208 = 159.1$). The ion $C_6H_7Rh^+$ appears to undergo dehydrogenation giving $C_6H_6Rh^+$ (*m/e* 181) which eliminates a C_6H_6 fragment giving the "bare" Rh^+ (*m/e* 103) ion. This C_6H_6 elimination process is confirmed by the presence of a metastable ion at *m/e* 58.6 ($103^2/181 = 58.6$). The fact that the ion $C_5H_5Rh^+$ (*m/e* 168) is bypassed upon further fragmentation of the ion $C_8H_9Rh^+$ (*m/e* 208) suggests that the latter ion is not $C_5H_5RhC_3H_4{}^+$ still containing a π-cyclopentadienyl ring.

These observations suggest that in different fragmentation modes of the parent ion of $C_5H_5RhC_8H_{12}$ either the C_5H_5 ring or the C_8H_{12} ring may be lost. This indicates that the fragmentation pattern of $C_5H_5RhC_8H_{12}$ in the mass spectrum is intermediate between those of typical π-cyclopentadienyl derivatives of iron, manganese, chromium, vanadium, and their heavier congeners and those of π-cyclopentadienyl derivatives of nickel and palladium such as $C_3H_5PdC_5H_5$, $C_{10}H_{12}OCH_3PdC_5H_5$, and $C_5H_5NiC_{13}H_{17}$. In the former cases the ligands other than π-cyclopentadienyl are lost more readily in the mass spectrum resulting in relatively high abundances of the $C_5H_5M^+$ ions. In the latter cases an important fragmentation pathway of the parent ion is loss of the π-cyclopentadienyl rings as C_5H_6 resulting in relatively high abundances of cyclopentadienyl-free metal ions.

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REFERENCES

1 R.E. Winters and R.W. Kiser, *J. Phys. Chem.*, 69 (1965) 3198.
2 R.B. King, *J. Am. Chem. Soc.*, 88 (1966) 2075.
3 R.B. King and A. Fronzaglia, *Inorg. Chem.*, 5 (1966) 1837.
4 R.B. King, *Inorg. Chem.*, 2 (1963) 528.
5 R.E. Winters and R.W. Kiser, *J. Organometal. Chem.*, 4 (1965) 190.
6 J. Chatt and L.M. Venanzi, *J. Chem. Soc.*, (1957) 4735.
7 R.B. King, unpublished results.
8 A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, (1962) 4821.