

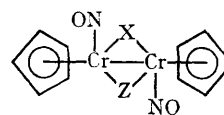
## Mass-spectral Studies of Binuclear Metal Complexes

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IN the course of an extended investigation<sup>1,2</sup> into the behaviour of organometallic compounds under electron impact we have had occasion to study a selection of cyclopentadienyl  $\mu$ -mercaptide-,  $\mu$ -alkoxo-, and  $\mu$ -dialkylamido-derivatives of the metals Cr, Fe, and Ni.<sup>†</sup> Growing interest in the use of mass spectrometry as a physical tool in the study of organometallic chemistry prompts us to report some of the more unusual features in the spectra of these compounds.

The complexes of chromium (I—V) which involves a chromium–chromium bond show fragmentation patterns consistent with their structures, *i.e.*, systematic losses (with the exception of V)

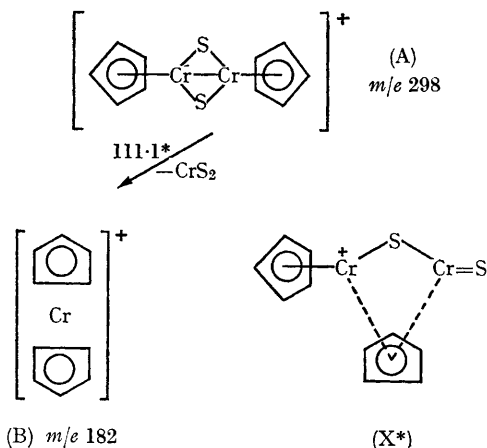


- |       |             |      |                      |
|-------|-------------|------|----------------------|
| (I)   | X=Z=SMe     | (IV) | X=Z=OMe              |
| (II)  | X=Z=SPh     | (V)  | X=Z=NMe <sub>2</sub> |
| (III) | X=SMe, Z=OH |      |                      |

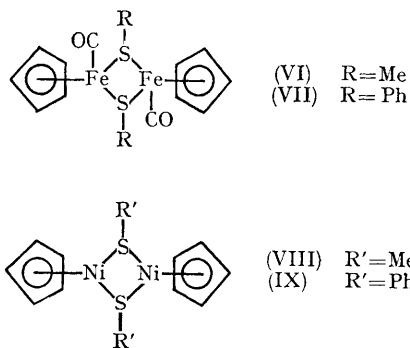
of the two NO groupings, followed by simple losses of alkyl, alkyl-(thio,oxy), and cyclopentadienyl radicals. However, in all cases, there exists the ion  $m/e$  182 which must be attributed to

the positively-charged ion of chromocene, since further fragmentations to yield ions at  $m/e$  117, 65, and 52 occur, *cf.* ferrocene.<sup>1,3</sup>

If, in particular, we examine the cracking pattern of (I), which is the simplest, we find a metastable ion at  $M/e = 111.1$  (calc. 111.2) representing the decomposition, (A)  $\rightarrow$  (B).



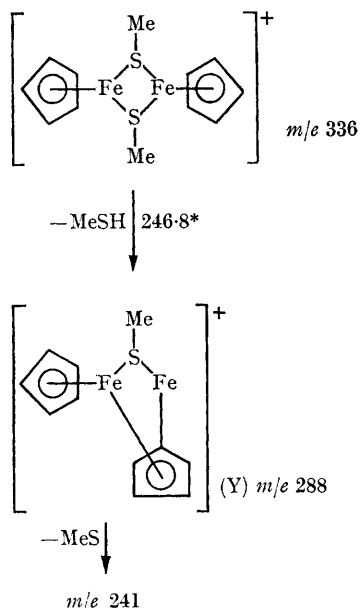
Such a fragmentation involves the breaking of one Cr-Cr bond and two Cr-S bonds together with the simultaneous transfer of a cyclopentadienyl ring, and intermediates such as (X\*) cannot be ruled out entirely. Except for compound (V), the ion  $m/e = 182$  arises from the base peak of the



spectrum, all transitions being supported by the appropriate metastables and exact mass measurements.

Within the iron and nickel analogues studied (VI-IX) an additional fragmentation process occurs.

Although the dissociation of (VI) appears similar to that of (I), the observed metastables require that a further mechanism operate. Hence not only does the ion  $m/e$  336 ( $P - 2CO$ )<sup>+</sup> eliminate two methyl groups as expected, but dissociation also occurs, by the loss of MeSH to give the ion  $m/e$  288 which further dissociates to the ion  $m/e$  241 by the loss of MeS.



It is suggested that  $m/e = 288$  has the "structure" Y, on an analogy with the ion  $m/e$  425 in the spectrum of bis(chloridodicyclopentadienylzirconium).<sup>4</sup> An ion for the corresponding metallocene occurs in the spectra of (VI-IX), but it is here thought to occur by a thermal process. This seems consistent since it is well known that bridged carbonyls decompose to ferrocenes.<sup>5</sup>

Further work is in progress to demonstrate the transfer of hydrogen in the loss of  $C_6H_6$  and RSH units for these systems.

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<sup>1</sup> R. I. Reed and F. M. Tabrizi, *Appl. Spectroscopy*, 1963, 17, 124.

<sup>2</sup> M. M. Bagga, P. L. Pauson, F. J. Preston, and R. I. Reed, *Chem. Comm.*, 1965, 543.

<sup>3</sup> L. Friedman, A. P. Izra, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1955, 77, 3689.

<sup>4</sup> A. F. Reid, J. S. Shannon, J. M. Swan, and P. C. Wailes, *Austral. J. Chem.*, 1965, 18, 173.

<sup>5</sup> B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 1956, 3030.

† These new classes of complexes will be described by Dr. G. R. Knox and his co-workers (University of Strathclyde).