

# Concomitant Bond Formation and Bond Fission in the Mass Spectral Fragmentation of an Organometallic Molecule

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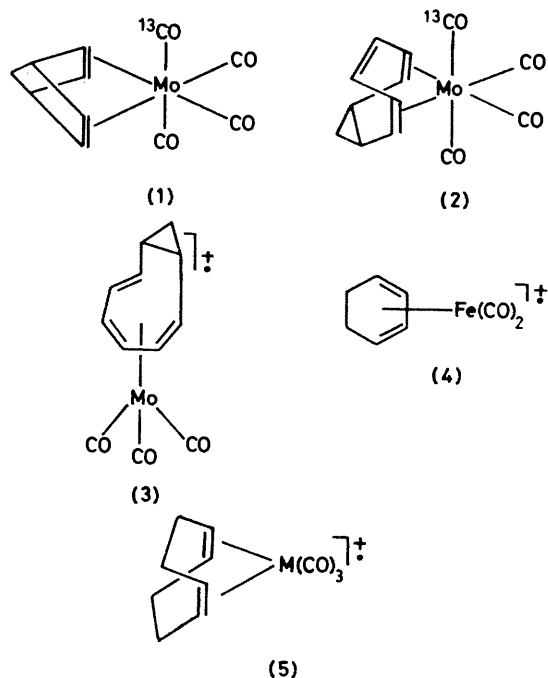
**Summary** Examination of the mass spectra of *fac*-(nbd)-Mo(<sup>13</sup>CO)(CO)<sub>3</sub> (nbd = norbornadiene) (1) and *fac*-(bcnt)Mo(<sup>13</sup>CO)(CO)<sub>3</sub> (bcnt = bicyclo[6.1.0]nona-2,4,6-triene) (2) shows that in the former loss of CO occurs with complete scrambling, while that in the latter is by almost exclusive loss of the labelled group; this is interpreted in terms of accompanying formation of a new metal-olefin bond on loss of CO from (2).

absence of scrambling, the loss of one of the CO groups bonded *cis* to the olefin might be predicted from qualitative bonding arguments, the exclusive nature of the loss suggests (a) that the molecular ion maintains the original stereochemistry of the neutral molecule and (b) that the CO group is replaced by the available carbon-carbon double bond in

THERE have been relatively few mass spectral studies of organotransition metal complexes directed towards elucidating detailed fragmentation mechanisms or the structure of gaseous ions,<sup>1</sup> and in contrast to the situation in organic mass spectrometry, the use of isotopic labelling towards these ends has only been reported in a few cases. We now report a study of the stereospecifically <sup>13</sup>CO labelled molecules (1) and (2)<sup>2</sup> which provides information concerning the stereochemistry of the molecular ions and details of the mechanism of loss of CO.

We have recently found that loss of CO from the molecules *cis*-M(CO)<sub>4</sub>(<sup>13</sup>CO)(piperidine) (M = Cr or W) proceeds with complete scrambling of the label between the axial and equatorial sites.<sup>3</sup> Similarly, the low voltage mass spectrum of (1) shows CO scrambling to be complete prior to loss of the first CO group (Table). It is likely that randomisation occurs either by a trigonal twist mechanism (involving a trigonal prismatic transition state) or by a mechanism involving chelate ring opening and rearrangement of the five-co-ordinate species by a Berry mechanism. The former mechanism has been demonstrated in solution for isomerisation of the cation *cis*-[Mo(CO)<sub>2</sub>(dmdpe)<sub>2</sub>]<sup>+</sup> (dmdpe = 1-dimethylphosphino-2-diphenylphosphinoethane)<sup>4</sup> and for CO scrambling in the neutral complexes (LL)M(CO)<sub>4</sub> (M = Mo, LL = substituted diazabutadienes;<sup>5</sup> M = Cr, LL = butadiene<sup>6</sup>), while CO scrambling in (nbd)W(CO)<sub>4</sub> (nbd = norbornadiene) proceeds by the latter route.<sup>7</sup>

However, the spectrum of (2) shows loss of the first CO group (metastable ion observed) to be almost specifically confined to the labelled *cis* position (Table). While, in the



the co-ordination sphere, thereby maintaining six-co-ordination in the fragment ion. We suggest structure (3) for the fragment ion and, indeed, the mass spectrum of (bcnt)Mo(CO)<sub>3</sub> (bcnt = bicyclo[6.1.0]nona-2,4,6-triene) is almost identical to that of (2). However, the observation

TABLE. Partial mass spectroscopic data of (1) and (2).

	Energy (eV)	Relative intensities <sup>a</sup>			
		<i>M</i> <sup>+</sup>	( <i>M</i> - <sup>12</sup> CO) <sup>+</sup>	( <i>M</i> - <sup>13</sup> CO) <sup>+</sup>	( <i>M</i> - <sup>12</sup> CO)/( <i>M</i> - <sup>13</sup> CO) <sup>b</sup>
(1)	70 eV	100	31	12	2.58
	15 eV	100	54	18	3.00
(2)	70 eV	5	11	100	0.11
	15 eV	11	22	100	0.22

<sup>a</sup> Relative intensities are corrected for natural isotope abundances and, for each spectrum, are normalised with respect to the most intense peak among those shown in the Table. <sup>b</sup> Complete randomisation requires 3.00.

of a metastable ion for the fragmentation  $M^+ \rightarrow (M-CO)^+$  in (2) precludes a thermally induced loss of CO. Intuitively, it would seem unlikely that the barrier to scrambling is much higher in (2) than in (1) and the differences in behaviour must therefore lie in a much easier loss of CO for (2). Presumably the co-ordination of the free olefinic bond in the triene assists this process in a manner analogous to an anchimerically assisted reaction. There has been some discussion of dehydrogenation processes in the mass spectra of organometallic species. Thus, it has been suggested<sup>8</sup> that  $H_2$  loss from ions of the types (4) and (5), where this is preceded by loss of another ligand such as CO, is accom-

panied by bond formation between the metal and the newly created unsaturated centre. There has, however, been no evidence to support this directly and  $H_2$  loss has been discussed in terms of other effects.<sup>9</sup> We believe the present results lend support to the suggestion of concomitant bond fission and bond formation in certain fragmentation processes.

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