

Preliminary communication

A MASS SPECTRAL STUDY OF INTRAMOLECULAR REARRANGEMENTS IN *cis*-M(CO)₄(¹³CO)PIPERIDINE (M = Cr, W) DERIVATIVES

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Summary

Low voltage mass spectra of *cis*-M(CO)₄(¹³CO)piperidine (M = Cr, W) show the initial loss of CO to proceed with complete scrambling of the label between axial and equatorial sites.

There has been considerable interest in the mechanism of substitution reactions in M(CO)₅X species (I). Initial studies of CO exchange in I (M = Mn, X = Cl, Br, I) suggested a distinct kinetic preference for exchange of equatorial ligands [1,2], a finding that might be predicted from qualitative bonding arguments. These results were questioned by two groups [3,4], both of which reported no discernible steric differences in exchange rates. Atwood and Brown [5] have recently conclusively shown that exchange reactions between ¹³CO and M(CO)₅Br (M = Mn, Re) proceed by preferential dissociative CO loss from the *cis* position where the intermediate [M(CO)₄Br] species are fluxional.

As part of a continuing study of the mass spectral behaviour of metal carbonyl derivatives [6,7], it was, therefore, of interest to us to examine the behaviour of such an M(CO)₅X species, which had been stereospecifically labelled with ¹³CO, in order to ascertain if there was a preferred site for loss of CO from the molecular ion or if CO scrambling occurred prior to fragmentation.

Such labelled molecules are now available in the form of *cis*-M(CO)₄(¹³CO)-pip (M = Cr, W; pip = piperidine) [8] and although these may not show the same marked effect of enhancement of equatorial dissociation initially

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reported and suggested by Johnson et al. for $\text{Mn}(\text{CO})_5\text{X}$, C—O force constant calculations indicate a markedly stronger axial M—C bond in the chromium and tungsten complexes [9]. It is, of course, recognised that the behaviour of the mass spectral molecular ion cannot be directly compared to the neutral molecule and it is not the intention of this study to correlate the findings to the situation in the neutral molecules.

The mass spectrum of $\text{Cr}(\text{CO})_5\text{pip}$ shows the molecular ion to fragment only by CO loss. There is no competing loss of piperidine or any piperidine fragment. Furthermore, there is no ion at $(\text{M}-\text{CO}-\text{H})^+$ that may complicate scrambling calculations. Examination of the low voltage (nominal 10 eV ionising electrons) mass spectra of *cis*- $\text{Cr}(\text{CO})_4(^{13}\text{CO})\text{pip}$ and *cis*- $\text{W}(\text{CO})_4(^{13}\text{CO})\text{pip}$ show the loss of ^{12}CO to that of ^{13}CO to be $4.0 \pm 0.2/1$ for the former and $3.8 \pm 0.2/1$ for the latter (corrected for natural ^{13}C isotope abundance). Low energy ionising electrons were used in order that the molecular ions would be formed with the minimum excess energy over the activation energy for CO loss. Appearance potential measurements for the closely related molecules $\text{M}(\text{CO})_5\text{L}$ (M = Cr, W; L = CO, PPh_3 , PBU_3 , $\text{P}(\text{OMe})_3$, $\text{P}(\text{OEt})_3$) give values for the $\text{M}-\text{CO}^+$ ion for these molecules varying between 8.25 and 9.4 eV [10].

Thus, even at energies very close to the threshold for CO loss, complete scrambling of axial and equatorial CO groups occurs. In this case, of course, scrambling must precede CO loss and must, therefore, occur by a non-dissociative mechanism such as that suggested by Brown [11] or by the trigonal twist mechanism observed in other Group VIb metal derivatives [12–15]. In this context it is noteworthy that the barrier to rearrangement in these complexes is low (10–13 kcal mol⁻¹). Furthermore these results provide new examples of Group VIb seventeen electron species which undergo greatly enhanced rearrangement processes when compared to their eighteen electron neutral counterparts [14,16].

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