

## MASS SPECTRA OF PENTACARBONYLCHROMIUM-CARBENE COMPOUNDS CONTAINING HETEROCYCLIC AND VINYLIC SUBSTITUENTS

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### SUMMARY

Studies of a series of  $(\text{CO})_5\text{CrC}(\text{X})\text{Y}$  compounds ( $\text{Y}$  is  $\text{C}_4\text{H}_3\text{Z}$ ;  $\text{Z} = \text{S}, \text{NMe}, \text{O}$ , and vinyl) have shown that the abundance ratio parameter,  $R_I$ , does not necessarily bear an inverse, linear relation to the ionisation potential. When  $\text{Y}$  is vinyl, the formation in the spectrometer of a  $\pi$ -allyl complex is observed. The influence of the heteroatom,  $\text{Z}$ , upon the fragmentation of the ligand,  $\text{XCC}_4\text{H}_3\text{Z}$ , is discussed and compared with the conclusions of other studies. Carbene dimerisation to give olefins is observed when  $\text{X} = \text{OEt}$  but not when  $\text{X} = \text{OPh}$ .

### INTRODUCTION

The mass spectra of certain classes of substituted metal carbonyl complexes have shown that substantial support exists for an empirically based inverse linear relationship between the ionisation potential,  $IP$ , of the molecule and the abundance ratio,  $R_I$ . For a molecule  $\text{L}_n\text{M}(\text{CO})_q$ , the parameter  $R_I$  is defined as:

$$R_I = I(\text{L}_n\text{M}^+) / \sum_{x=1}^q I[(\text{CO})_x\text{ML}_n^+] \quad (I = \text{relative abundance}).$$

An earlier report<sup>2</sup> on compounds of the type  $(\text{CO})_5\text{CrC}(\text{X})\text{Y}$  ( $\text{X} = \text{OR}, \text{NR}_2, \text{SPh}; \text{Y} = \text{Me}, \text{Ph}$ ) has shown that, within a series of compounds containing  $\text{X} = \text{NHR}, \text{NR}_2$  groups, the variation in the directly measured  $IP$  was capable of simple explanation in terms of the results of other spectroscopic studies. As a consequence, it might have been assumed that the relative magnitude of  $R_I$  in a series of closely related compounds of this type would provide a reliable index of the  $IP$  in the absence of a direct measurement of the latter.

### EXPERIMENTAL

The preparation and characterisation of the compounds  $(\text{CO})_5\text{CrC}(\text{X})\text{C}_4\text{H}_3\text{Z}$  [ $\text{Z} = \text{S}, \text{NMe}; \text{X} = \text{OEt}, \text{NH}_2$ : (I)–(IV)],  $(\text{CO})_5\text{CrC}(\text{X})\text{C}_4\text{H}_3\text{O}$  [ $\text{X} = \text{OCOCH}_3, \text{OPh}, \text{OEt}, \text{SEt}, \text{SPh}, \text{NH}_2, \text{NC}_4\text{H}_8$ : (V)–(XI)] and  $(\text{CO})_5\text{CrC}(\text{OMe})\text{C}_2\text{H}_3$  (XII) (see Table 1) will be described elsewhere<sup>3</sup>. The mass spectra were recorded on an AEI MS-12 Spectrometer at a nominal beam energy of 70 eV. In order to achieve comparability

TABLE I  
RELATIVE ABUNDANCES OF THE PRINCIPAL CHROMIUM-CONTAINING IONS IN THE MASS SPECTRA OF  $(CO)_5CrC(X)Y$  COMPOUNDS<sup>a</sup>

Ion	(I) X=OEt Y=Th	(II) X=NH <sub>2</sub> Y=Th	(III) X=OEt Y=NMP	(IV) X=NH <sub>2</sub> Y=NMP	(V) X=OAc Y=Fu	(VI) X=OPh Y=Fu	(VII) X=OEt Y=Fu	(VIII) X=SEt Y=Fu	(IX) X=SPh Y=Fu	(X) X=NH <sub>2</sub> Y=Fu	(XI) X=NC <sub>4</sub> H <sub>9</sub> Y=Fu	(XII) X=OMe Y=Vi
$(CO)_5CrL^+$	4	7	0.4	10	7	4	15	2	1	29	0.3	21
$(CO)_4CrL^+$	13	10	7	12	72	15	3	43	14	7	3	13
$(CO)_3CrL^+$	15	8	6	7	9		9	26		14	4	6
$(CO)_2CrL^+$	14	10	4	3	38	48	7	33	25	8	3	37
$(CO)CrL^+$	28	17	14	10	105	33	15	67	26	31	16	23
$CrL^+$	100	100	100	100	100	100	100	100	100	100	100	100
$CrCO \cdot Y^+$	32		66		114	35	53					37
$CrCS \cdot Y^+$								310	54			
$CrY^+$	74		293		48	33	43	6	3		16	42
$CrNH_2^+$		2		6						2	5	
$Cr(CO)_2^+$	7	1	14	11	27	3	4	19	8	1	6	88
$Cr(CO)^+$	16	5	130	14	48	16	18	29	23	3	39	131
$Cr^+$	73	58	480	78	95	334	83	190	92	41	356	354
$R_i$	1.4	1.9	3.2	2.4	0.4	1.0	2.1	0.6	1.5	1.2	3.7	1.0

<sup>a</sup> Th = 2-thienyl; Fu = 2-furyl; NMP = 2-N-methyl-pyrrol; Vi = vinyl; Ac = acetyl.

between spectra, the ion  $[\text{CrC}(\text{X})\text{Y}]^+$  has been assigned a relative abundance of 100% in every case.

## RESULTS AND DISCUSSION

The fragmentation of the molecules (I)–(XII) is generally comparable to that of other  $(\text{CO})_5\text{CrC}(\text{X})\text{Y}$  molecules<sup>2</sup>. We have shown<sup>3</sup> that electron release to the empty *p*-orbital on the carbene carbon atom in the compounds (I)–(XII) occurs from both X and Y and that, in the case of the compounds (I)–(IV), (VII), (X), this release increased in the sense  $\text{X} = \text{OEt} < \text{NH}_2$  and  $\text{Z} = \text{O} < \text{S} < \text{NMe}$ .

A surprising feature of the spectra of the phenoxy (VI) and thiophenyl (IX) complexes and also of the analogous methylthiophenyl complex,  $(\text{CO})_5\text{CrC}(\text{SPh})\text{Me}^2$ , is the absence of the  $(\text{CO})_3\text{CrL}^+$  ion; this absence is characteristic of complexes in which X is OPh or SPh, since in the anilino complex,  $(\text{CO})_5\text{CrC}(\text{NHPh})\text{Me}$ , this particular ion is observed<sup>2</sup>. This may perhaps be explained in terms of a  $\pi$ -aryl structure (Fig. 1) for the ion  $\text{LCr}(\text{CO})_2^+$  with the probable enhanced stability of this ion facilitating the double carbonyl loss from the  $(\text{CO})_4\text{CrL}^+$  ion.

In the case where  $\text{X} = \text{NHPh}$ , a mixture of isomers is formed such that the phenyl group in both is *cis* and *trans* to the Cr atom<sup>4</sup>. For the *trans* isomer, stabilisation of the ion,  $(\text{CO})_2\text{CrC}(\text{NHPh})\text{Me}^+$  by the above mechanism is less likely: this is consistent with the appearance of a  $(\text{CO})_3\text{CrL}^+$  ion.

The values of  $R_I$  (Table 1) suggest that for  $\text{Y} = 2\text{-}N\text{-methylpyrrol}$  and 2-furyl, the *IP* of the complexes (III) and (VII) ( $\text{X} = \text{OEt}$ ) are lower than those of the complexes (IV) and (X) ( $\text{X} = \text{NH}_2$ ). However, the  $R_I$  value for (XI) is greater than that of (VII), as would have been expected.

Closer examination of the data (Table 1) shows that the spectrum of (III) contains the ions  $[\text{CrCOY}]^+$  and  $[\text{CrY}]^+$  of high relative abundance which are absent from the spectrum of (IV); also, the spectra of the former contain the ions  $[\text{Cr}(\text{CO})_n]^+$  ( $n = 1, 2$ ) of much greater relative abundance than the spectra of the latter. We consider that the contribution of these two types of fragment to the ionisation process involving the metal ion in these compounds is not negligible. Failure to account for this ionisation in calculating  $R_I$  leads to an overestimate of the parameter for the alkoxycarbene complex (III) with the result that  $R_I$  cannot be used as an index of *IP* under these circumstances. The  $R_I$  value for the amino compound (X) is anomalous due to the fact that the relative abundance of the parent ion is relatively high while those of the  $[\text{Cr}(\text{CO})_n]^+$  ( $n = 1, 2$ ) ions are low. This anomaly can be explained

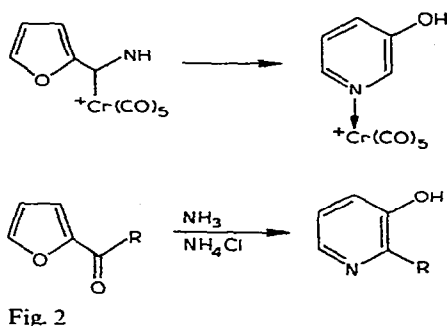
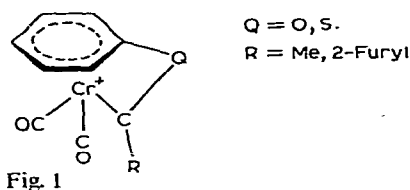


TABLE 2

RELATIVE ABUNDANCES OF IONS IN FIG. 3

Ion	Relative abundance
$(\text{CO})_4\text{CrC}(\text{OMe})\text{C}_2\text{H}_3^+$	13 <sup>a</sup>
$(\text{CO})_4\text{CrC}_3\text{H}_5^+$	3
$(\text{CO})_3\text{CrC}_3\text{H}_5^+$	3
$(\text{CO})_2\text{CrC}_3\text{H}_5^+$	6
$(\text{CO})\text{CrC}_3\text{H}_5^+$	40
$\text{CrC}_3\text{H}_5^+$	208
$\text{C}_3\text{H}_5^+$	94

<sup>a</sup> See Table 1.

by an impact induced isomeric transformation of (X) to give the complex (3-hydroxypyridine)Cr(CO)<sub>5</sub> (Fig. 2); this is supported by the observation of a very similar mass spectrum for pyridine Cr(CO)<sub>5</sub>. The conversion of a 2-acylfuran to a (2-alkyl-3-hydroxypyridine) by the action of ammonia/NH<sub>4</sub>Cl is known to occur in fairly good yield<sup>5</sup>.

The mass spectrum of compound (XII) shows a number of ions, in addition to those mentioned in Table 1, in which allyl groups are present. These are detailed in Table 2 and their possible mode of formation shown in Fig. 3. Clearly, the vinyl carbene ligand in (XII), which can be regarded as a pseudo  $\sigma$ -allyl group in certain respects, is here converted to a  $\pi$ -allyl ligand. The well-known photochemically induced  $\sigma \rightarrow \pi$  transformation<sup>6</sup> in  $\text{C}_5\text{H}_5(\text{CO})_3\text{MoCH}_2\text{CH}=\text{CH}_2$  provides a possible parallel to this unusual process. The mass spectral rearrangement (Fig. 3) is exceptional since a combination of both alkyl- and H-transfer followed by elimination of both CO and H must be invoked to explain the formation of the ion  $[\text{C}_3\text{H}_5\text{Cr}(\text{CO})_4]^+$ . A comparable process has been suggested for the partial fragmentation of ethyl isopropylcyanoacetate<sup>7</sup>. Although  $\pi$ -allyl complexes of chromium are known<sup>8</sup>,  $[\pi\text{-C}_3\text{H}_5\text{Cr}(\text{CO})_4]^+$  has not been observed hitherto. We reject an alternative formulation of the  $\text{C}_3\text{H}_5$  moiety as a  $\sigma$ -cyclopropyl ligand as implausible.

The fragmentation of the  $\text{C}_4\text{H}_4\text{Z}$  ring from various 2-substituted heterocycles  $\text{RC}_4\text{H}_3\text{Z}$  has been shown<sup>9</sup> to depend on the nature of Z and upon the previously attached 2-substituent. We find that for any ring fission of  $\text{C}_4\text{H}_4\text{Z}^+$  derived from the compounds (I)–(XI) the relative abundance of the resulting fragment ions is usually greater when  $\text{Y} = \text{O}, \text{S}$  than when  $\text{X} = \text{NMe}$ . This is consistent with the presence of

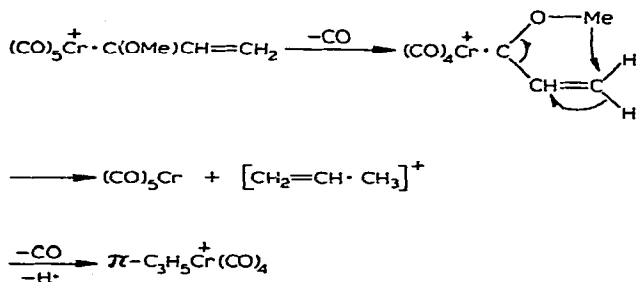


Fig. 3

TABLE 3

RELATIVE ABUNDANCES OF FREE AND COMPLEXED FRAGMENT IONS

Compound	Z	$C_3H_3^+$	$CrC_3H_3^+$	$Z\equiv CH^+$	$CrZ\equiv CH^+$	$C_2H_2Z^+$	$CrC_2H_2Z^+$
(I)	S	88	8	63	39	100	32
(II)	S	38	0.4	11	1	58	1
(III)	NMe	115	36	43	10	4	7
(IV)	NMe	15	3	9	2	4	
(V)	O	5	19				
(VI)	O	131	24				
(VII)	O	9	26				
(VIII)	O	57	9				
(IX)	O	139	8				
(X)	O	1	1				
(XI)	O						

lesser electron release from a particular Z for the former than for the latter complexes. Some of the ions derived by ring fission are observed as constituents of chromium containing ions (Table 3) and the relative abundance of the complexed ions with relation to X follow the same pattern as for the non-complexed ions. The high relative abundance of the  $[C_3H_3]^+$  ion in complexes (VI) and (IX) can be accounted for by the additional fragmentation of the phenyl ring in both cases.

The mass spectra of the ethoxy complexes (I), (III) and (VII) are further characterised and distinguished from other complexes by the appearance of ions due to the dimerisation of the free carbene ligand to give an olefin. The formation of the olefin as a product of the thermal decomposition of the ethoxycarbene complex was established by continuous monitoring of the spectrum usually showed only the pure complex  $(CO)_5CrC(OEt)C_4H_3Z$  ( $Z=S, NMe, O$ ) and no olefin. Subsequent scans showed the gradual disappearance of the complex and appearance of the olefin and its fragment ions.

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