

## Mass Spectral Studies of Some Mixed Chromium and Manganese Tricarbonyl of Benzocyclopentadienyl Derivatives

Chit-Kay Chu

NSAG/Nanyang Technological University, Singapore, # 1 Nanyang Walk, Singapore.  
Fax: (65)68969432; Tel: (65)67903828; E-mail: ckchu@nie.edu.sg

**Abstract :** The mass spectral fragmentation patterns of some derivatives containing both  $[\pi\text{-C}_6\text{H}_5]\text{Cr}(\text{CO})_3$  and  $[\pi\text{-C}_5\text{H}_5]\text{Mn}(\text{CO})_3$  moieties are discussed. In cases where the two groups are joined together by a ketonic CO, the loss of carbon monoxide molecules involves a combination of a three-step and a two-step process. In cases where the phenyl and cyclopentadienyl rings are connected through an alcohol or olefinic group, ring fusion becomes more important, and the stepwise loss of carbon monoxide seems less important. The ions  $[\text{C}_6\text{H}_5\text{Cr}]^+$  and  $[\text{C}_5\text{H}_4\text{Cr}]^+$  are more stable than  $[\text{C}_6\text{H}_5\text{Mn}]^+$  and  $[\text{C}_5\text{H}_4\text{Mn}]^+$ ; the latter ions are often not observed. The higher abundance of  $[\text{C}_6\text{H}_5\text{COC}_5\text{H}_4\text{Cr}]^+$  relative to the ion  $[\text{C}_6\text{H}_5\text{COC}_5\text{H}_4\text{Mn}]^+$  not only suggests a higher stability of the former but also that there is significant 'across rings' metal participation within the fragments; the  $\pi$ -bonding between the rings and Cr being much stronger than those between the rings and Mn. An intermediate bimetallic species must necessarily be formed in order to facilitate the loss of the ketonic CO. A mechanism for the fragmentation is proposed.

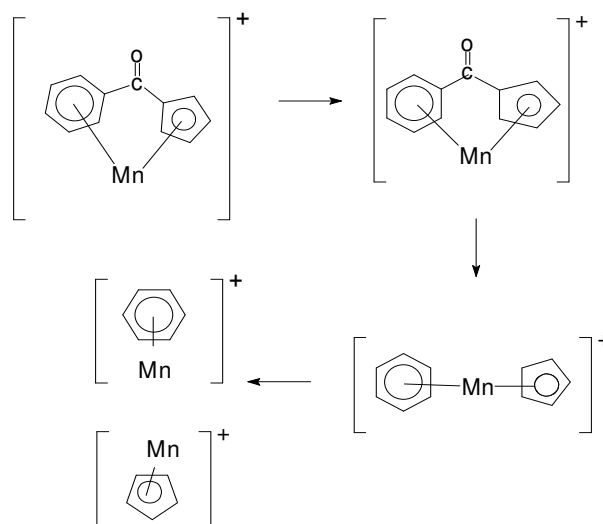
**Abstrak :** Beberapa sebatian organologam yang mengandungi kedua-dua  $[\pi\text{-C}_6\text{H}_5]\text{Cr}(\text{CO})_3$  dan  $[\pi\text{-C}_5\text{H}_5]\text{Mn}(\text{CO})_3$  dalamnya disediakan dan dikaji secara spektroskopi jisim. Mekanisma pemecahan sebatian ini melibatkan pembentukan spesi 'intermediate' yang mempunyai ikatan Cr-Mn. Didapati ion  $[\text{C}_6\text{H}_5\text{Cr}]^+$  dan ion  $[\text{C}_5\text{H}_4\text{Cr}]^+$  adalah lebih stabil daripada ion  $[\text{C}_6\text{H}_5\text{Mn}]^+$  dan ion  $[\text{C}_5\text{H}_4\text{Mn}]^+$  dalam keadaan spektroskopi. Juga proses pemisahan dimana keton CO disingkirkan dari molekul memerlukan babitan 'cross-linking' antara Cr dengan  $[\text{C}_6\text{H}_5\text{COC}_5\text{H}_4\text{Mn}]^+$ , dan Mn dengan  $[\text{CrC}_6\text{H}_5\text{COC}_5\text{H}_4]^+$ . Mekanisma pemecahan sebatian jenis tersebut dicadangkan.

Received : 01.08.02; accepted : 28.04.03

### Introduction

The fragmentations of organic molecules under mass spectral conditions are very different from those of organometallic molecules. In a previous paper (1), we observed that the metal ion, both sigma- and pi- bonded to the organic substrate, plays a very significant role in the fragmentation of the molecule. The metal ion stabilises the organic moiety through direct participation of the vacant  $d\pi$  orbitals with the  $p\pi^*$  orbitals of the organic moiety, often triggering non-classical reactions and fragmentations. Half sandwiched  $\pi$ -arenechromium tricarbonyl derivatives and  $\pi$ -cyclopentadienylmanganese tricarbonyl derivatives have been studied by several workers (2,3,4). Bursley et al (4) have found that the mass spectrum of  $[\pi\text{-C}_6\text{H}_6]\text{Cr}(\text{CO})_3$  shows high abundances of the molecular ion,  $[\text{P}]^+$ ,  $[\pi\text{-C}_6\text{H}_6\text{Cr}]^+$ , and  $[\text{Cr}]^+$ , while those of  $[\pi\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_n]^+$  ( $n = 1$  or  $2$ ) species, are relatively low. A stepwise loss of CO molecules has been proposed. It is also observed that the fragmentation of the ring is not very significant and no thermal decomposition is evident at temperatures below  $300^\circ\text{C}$ . Rearrangement processes involving the migration of  $\alpha$ -substituents of ligands to the metal has been observed in  $\alpha$ -ketonic derivatives of anisolechromium tricarbonyl (5). The loss of CO molecules in derivatives of  $[\pi\text{-C}_5\text{H}_5]\text{Mn}(\text{CO})_3$  is a two step process in which two

CO molecules are simultaneously removed followed by the loss of a third.



**Scheme 1**  
Proposed Participation of Manganese Ion in Fragmentation

In our previous papers (6,7), we have described the synthesis and characterisation of some benzocyclopentadienylmanganese tricarbonyl derivatives. We have also discussed the mass spectra of some of these compounds (1). The

fragmentation involves the loss of the three CO molecules from the  $\text{Mn}(\text{CO})_3$  moiety by a two step mechanism; the loss of two CO simultaneously followed by the loss of a third CO. Subsequent fragmentation involves the formation of an intermediate where the manganese ion is  $\pi$ -bonded with both the phenyl and the cyclopentadienyl ring. This is to be followed by the ejection of the ketonic carbonyl group from the organic substrate (Scheme 1).

Very few mass spectral studies of bimetallic complexes have been reported (9) and no attempts have been made to interpret the fragmentation results. This may be attributed to the insufficient volatility of these compounds for study with the conventional electron-impact technique. Some attempts have been made to correlate metal-metal bond strengths with applied ionisation potentials. More recently, some noncovalent (10) metal-ligand bond energies have been determined using threshold collision-induced dissociation (CID) techniques. In this paper, we prepare and examine the mass spectra of  $[\pi\text{-Cr}(\text{CO})_3]\text{C}_6\text{H}_4\text{XCOC}_5\text{H}_4$   $[\pi\text{-Mn}(\text{CO})_3]$  (X = H, *ortho*-, *meta*-, and *para*- $\text{CH}_3$ , *para*- $\text{OCH}_3$ ),  $[\pi\text{-Cr}(\text{CO})_3]\text{C}_6\text{H}_5\text{CH}=\text{CHC}_5\text{H}_4$   $[\pi\text{-Mn}(\text{CO})_3]$ ,  $[\pi\text{-Cr}(\text{CO})_3]\text{C}_6\text{H}_5\text{CH}_2\text{COC}_5\text{H}_4$   $[\pi\text{-Mn}(\text{CO})_3]$ ,  $[\pi\text{-Cr}(\text{CO})_3]\text{C}_6\text{H}_5\text{CH}_2\text{C}_5\text{H}_4$   $[\pi\text{-Mn}(\text{CO})_3]$  and  $[\pi\text{-Cr}(\text{CO})_3]\text{C}_6\text{H}_5\text{C}_5\text{H}_4$   $[\pi\text{-Mn}(\text{CO})_3]$ .

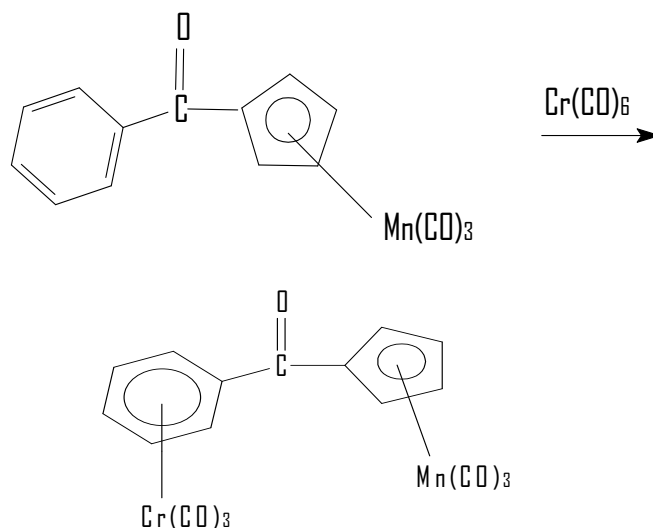
The fragmentations and the participation of the metals in these mixed systems, in which there is a  $\text{Mn}(\text{CO})_3$  moiety on the cyclopentadienyl ring and a  $\text{Cr}(\text{CO})_3$  moiety on the arene ring, will be discussed.

### Experimental

The synthesis of mixed  $\text{Cr}(\text{CO})_3$  and  $\text{Mn}(\text{CO})_3$  derivatives have been reported earlier (7). Basically, it involves the Friedel-Crafts arylation of cyclopentadienylmanganese tricarbonyl, followed by refluxing with  $\text{Cr}(\text{CO})_6$  in *n*-butylether. The products obtained are either purified by vacuum distillation, sublimation or recrystallisation, and characterised using IR, NMR spectroscopies, and elemental analysis. The mass spectra are recorded using a GC/MS Finnigan Mat GCQ spectrometer using a direct inlet system at ionisation potential 70eV at a chamber temperature of 90°C. The percentage abundance quoted is taken relative to the most intense peak.

### Results and Discussions

#### 1. Fragmentations of $[\pi\text{-Cr}(\text{CO})_3]$



Metastables for the loss of one CO molecule from their respective parents are observed in all the fragmentations of  $[\text{P}]^+ \rightarrow [\text{P-CO}]^+$  processes except for the  $[\text{M}]^+ \rightarrow [\text{P-CO}]^+$  where M is the molecular ion,  $[\pi\text{-Cr}(\text{CO})_3\text{C}_6\text{H}_4\text{XCOC}_5\text{H}_4\text{-Mn}(\text{CO})_3]^+$ . Metastables for the initial loss of two CO molecules,  $[\text{P}]^+ \rightarrow [\text{P-2CO}]^+$  have also been observed in most of the derivatives. However, it cannot be ruled out that the initial loss of one CO has not taken place merely from the non-observed or absence of metastables since both the parent and daughter ions are only present in low abundances and the fact that sometimes such metastables are not observable. The presence of  $[\text{M-CO}]^+$  ion (ca 4%) also suggests that there is also present a stepwise fragmentation process. The initial fragmentation of derivatives studied, therefore, appears to be a combination of a stepwise and a two-step loss of CO molecules.

No cleavage of the C-O bond is observed as opposed to metal carbonyls in which there are no aromatic ligands  $\pi$ -bonded to the metals as observed in  $\text{W}(\text{CO})_6$  (11). In such cases, metal carbides have been reported.

The fragmentation patterns for these  $\{[\pi\text{-Cr}(\text{CO})_3]\text{C}_6\text{H}_4\text{XCOC}_5\text{H}_4[\pi\text{-Mn}(\text{CO})_3]\}^+$  ions are very characteristic; bearing ions corresponding to  $[\text{P-nCO}]^+$  ions where n = 0 to 6. A typical spectrum of  $[\pi\text{-Cr}(\text{CO})_3]\text{C}_6\text{D}_5\text{COC}_5\text{H}_4[\pi\text{-Mn}(\text{CO})_3]$  is shown in Figure 1.

Some of the daughter ions have been identified by comparison with spectra obtained under similar spectral conditions for the deuterated  $\{[\pi\text{-Cr}(\text{CO})_3]\text{C}_6\text{D}_5\text{COC}_5\text{H}_4[\pi\text{-Mn}(\text{CO})_3]\}^+$  ion. No attempt has been made to compare the relative metal-CO bond strengths of the two metal moieties though IR studies have shown that the Mn-CO stretching frequencies are lower than those of the Cr-CO bond. This may be attributed to the increased back-donation from the  $\pi$ -orbitals of the manganese to the cyclopentadienide ligand

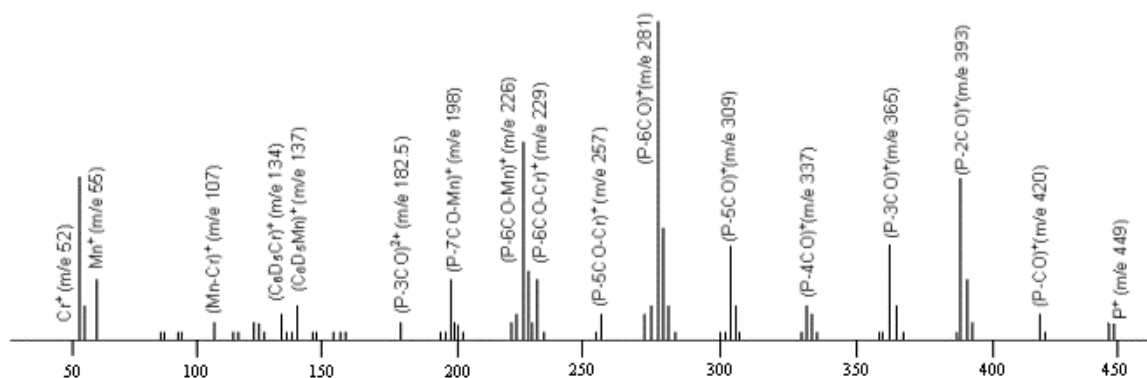


Figure 1

resulting in a weaker Mn-CO bond. The loss of CO molecules is not a random process. Perhaps, the first CO comes from the  $\text{Mn}(\text{CO})_3$  moiety, to be followed by the loss of CO from the  $\text{Cr}(\text{CO})_3$  moiety. The relative abundances of  $[\text{P}-n\text{CO}]^+$  ions in the complexes studied appear to follow a general trend and of decreasing order;

$$[\text{P}-6\text{CO}]^+ > [\text{P}-2\text{CO}]^+ > [\text{P}-5\text{CO}]^+ \approx$$

$$[\text{P}-3\text{CO}]^+ \approx [\text{P}-4\text{CO}]^+ > [\text{P}-\text{CO}]^+ \approx [\text{P}]^+$$

Labelling studies will be required to identify the origins of the CO molecules. The most significant observation is the high abundance of the  $[\text{P}-6\text{CO}]^+$  ion which, in all cases, forms the most intense peak.

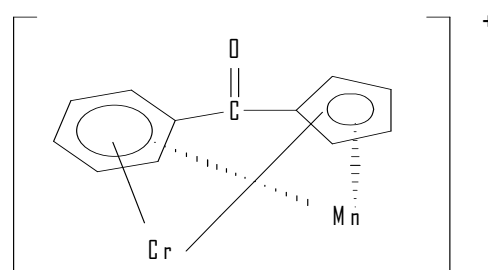
This suggests that the  $[\text{P}-6\text{CO}]^+$  is a very stable ionic species with the positive charge largely residing on the chromium ion. This is rationalised from the fact that chromium has a lower ionisation potential than that of manganese.

Incidentally, these bimetallic species are observed to be the most stable and therefore most abundantly present in the mass spectra. The bare metals, now devoid of CO ligands, are grossly electron deficient and very readily stabilise themselves by bonding with the electron-rich aromatic ligands. Two possible structures for the species formed are proposed; a structure where the manganese and chromium atoms are  $\pi$ -bonded to the two ring systems, (structure I) and a bimetallic species containing a manganese-chromium bond, (structure II).

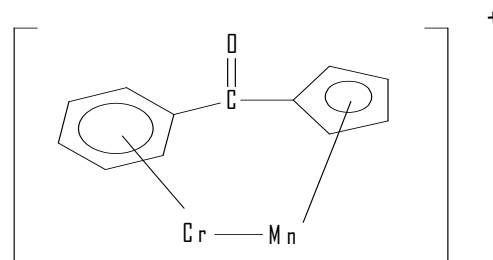
This is supported by the presence of the species  $[\text{Cr}-\text{Mn}]^+$  ( $m/e$  107, 5.3%) in all the compounds studied. Bimetallic ions such as  $[\text{Cr}-\text{Cr}]^+$ ,  $\{\text{Cr}-\text{Fe}\}^+$  have been reported by Cais *et al* (5) but no attempt has been made to account for their formation.

It is not suggested that structure II is more favoured than structure I since 'across rings' fragments, such as  $[\text{C}_6\text{H}_5\text{M}]^+$  and  $[\text{C}_5\text{H}_4\text{M}]^+$ , ( $\text{M} = \text{Cr}$  and  $\text{Mn}$ ), have been observed. Perhaps a rearrangement within the system, involving the participation of the orbitals of the metals with the ring system has taken place prior the breaking of

the ring system and subsequent metal-metal bond cleavage. Apparently, the fragmentation of the aromatic ring system requires more drastic conditions than those observed in this study.

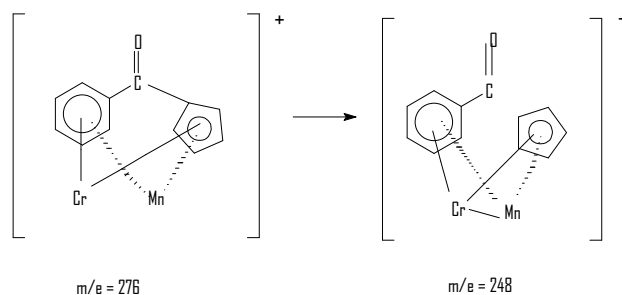


Structure I



Structure II

The relative abundance of the species  $[\text{P}-7\text{CO}]^+$  species is almost non-observed; quite unlike the benzocyclopentadienylmanganese tricarbonyl system,  $\text{C}_6\text{H}_4\text{XCOC}_5\text{H}_4[\pi\text{-Mn}(\text{CO})_3]$  where the  $[\text{P}-4\text{CO}]^+$  abundance is very significant.

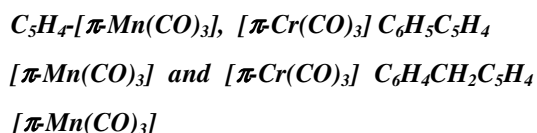


The reluctance of the ketonic CO to break away in these mix metal carbonyls is due to the Mn and Cr metals stabilising the organic substrate. The  $[\text{C}_6\text{H}_5\text{COCr}]^+$  and  $[\text{C}_6\text{H}_5\text{Cr}]^+$  abundances are significantly higher than those of  $[\text{C}_5\text{H}_4\text{COMn}]^+$   $[\text{C}_5\text{H}_4\text{Mn}]^+$  in all the spectra studied.

Interestingly, very low abundances (< 1%) of the species  $[\text{C}_5\text{H}_4\text{Cr}]^+$  or  $[\text{C}_5\text{H}_4\text{Mn}]^+$  have been observed and higher abundances (ca 8%) of the species  $[\text{C}_6\text{H}_5\text{Cr}]^+$  and  $[\text{C}_6\text{H}_5\text{Mn}]^+$  species have been detected. This suggests, therefore, that there is 'across rings' participation of the manganese and chromium ions during the fragmentation process and that the metal-cyclopentadienide bonds are much weaker than the metal-phenyl bonds. This may be attributed to the availability of  $\pi$ -electron or higher Lewis basicity of the phenyl ring which is consistent with our previous observations for the single metal carbonyl complexes. It is noteworthy that, Goser (8) and Denning *et al* (12), in a somewhat similar system, observed that the benzene complexes,  $[\text{C}_6\text{H}_6\text{M}]^+$  (M = Mn or Cr) are less stable than those of the cyclopentadiene complexes  $[\text{C}_5\text{H}_5\text{M}]^+$ , in metallocenes. However, the comparisons made are for single metal systems and are quite different from mix metal systems as in our case.

The fragmentations of methyl substituted derivatives of the type  $[\pi\text{-Cr}(\text{CO})_3]\text{C}_6\text{H}_4\text{RCO-C}_5\text{H}_3\text{R}$   $[\pi\text{-Mn}(\text{CO})_3]$  (R = H or  $\text{CH}_3$ ) are essentially the same; the relative abundances of the fragments suggest the same mode of fragmentations. Stable ionic species such as  $[\text{C}_7\text{H}_7\text{Cr}]^+$  and  $[\text{C}_7\text{H}_7\text{Mn}]^+$  are also observed for the toluoyl derivatives.

## 2. Fragmentations of $[\pi\text{-Cr}(\text{CO})_3]\text{C}_6\text{H}_5\text{CHCH}$



The relative abundances of  $[\text{P-nCO}]^+$  no longer follow the relative abundances of the keto-derivatives. The spectra generally show a significant drop in the relative abundances of the  $[\text{P-CO}]^+$  and  $[\text{P-2CO}]^+$  ions. However, the  $[\text{P}]^+$  ion seems to have increased significantly. This seems to suggest that the metal-CO bonds are relatively stronger than those in the keto-derivatives where a stepwise decarbonylation fragmentation is observed. This is supported by infrared studies which show that the stretching frequencies of CO for both the  $\text{Cr}(\text{CO})_3$  and  $\text{Mn}(\text{CO})_3$  moieties are lower than those of the keto-derivatives. Another significant difference with the keto derivatives is the simplicity of the spectra. Apparently, there is significant amount of ring condensation resulting in less fragmentation of the organic substrates.

The spectrum of  $[\pi\text{-Cr}(\text{CO})_3]\text{C}_6\text{H}_5\text{C}_5\text{H}_4[\pi\text{-Mn}(\text{CO})_3]$  shows that the peak at m/e 193,

attributed to the ion,  $[\text{CrC}_6\text{H}_5\text{C}_5\text{H}_4]^+$ , is about 7X more intense than the peak at m/e 196, attributed to the ion  $[\text{C}_6\text{H}_5\text{C}_5\text{H}_4\text{Mn}]^+$ . This again suggests that the Cr-carbon bond is stronger than the Mn-carbon bond.

## Conclusions

The loss of the carbonyl groups is largely a stepwise process except perhaps in complexes where the rings are not connected by a ketonic group. Apparently, the ketonic CO tends to strengthen the  $\pi$ -aromatic ring-metal bond at the expense of the metal-CO bond, i.e. the ketonic CO is an electron withdrawing group rendering the rings less Lewis basic and therefore reducing the back-donation from the rings to the metal.

This results in less back-donation from the rings to the CO  $p\pi$  antibonding orbitals with concomitant ease of breaking of the M-CO bond. The fragmentation process resulting in the loss of the keto carbonyl fragment must necessarily involve 'across rings' participation of the metals which are now devoid of CO molecules. The participation of the two metals in the benzoylcyclopentadienyl stabilises the ketonic CO group more than the single manganese metal in the same organic system. The chromium ion appears to form more stable intermediates with the rings than the manganese ion.

## Acknowledgements

The author acknowledges the National Institute of Education, Nanyang Technological University, Singapore for financial support.

## References

1. N.J. Gogan and Chit-Kay Chu (1977) *Organic Mass Spectrometry*, **12**(6), 343.
2. S. Pignataro and F.P. Lossing (1968) *J. Organometal Chem.*, **11**, 571.
3. R.E. Winters and R.W. Kiser (1965) *J. Organometal Chem.*, **4**, 190.
4. M.M. Bursey, F.E. Tibbetts, W.F. Little, Rausch and G.A. Moser (1969) *Tetrahedron Lett.*, **3469**.
5. M. Cais and M.S. Lupin (1970) *Adv. In Organometal Chem.*, **8**, 211.
6. N.J. Gogan and Chit-Kay Chu (1975) *J. Organometal Chem.*, **93**, 343.
7. N.J. Gogan and Chit-Kay Chu (1977) *J. Organometal Chem.*, **103**, 132.
8. J. Muller and P. Goser (1968) *J. Organometal Chem.*, **12**, 163.
9. M. Maoz, A. Mendelbaum and M., Cais (1965) *Tetrahedron Lett.*, **2087**.
10. M.T. Rodgers and P.B. Armentrout (2000) *Mass Spectroscopy Review*, **19**(4), 215.
11. R.E. Winters and R.W. Kiser (1965) *Inorg. Chem.*, **4**, 157.
12. R.G. Denning and W.A.D. Wentworth (1966) *J. Am. Chem. Soc.*, **88**, 4619.

