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A Pivotal Application of Field Desorption Mass Spectrometry to Distinguish between Molecular and Ionic Organometallic Complexes

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The development of field desorption (FD) mass spectrometry for thermally labile ionic compounds has opened the question of its providing a simple test of ionicity or molecularity of organometallic compounds. In FD ions are formed in the solid state [1], and the thermal energy required to produce an ion current is in general only that needed to provide adequate surface mobility of the species being analyzed [2]. The FD spectra of molecular comcompounds are often dominated by the molecular ion M^+. For salts the base peak is usually the unipositive cation C^+ or a cluster ion $(nM + C)^+$ that corresponds to addition of n formula weights M of the salt to the cation. Spectra of complex organic salts are dominated by C^+, but cluster ions often dominate spectra of salts of simple inorganic cations [3].

The thermally labile organometallic salts generally give C^+ as the base peak in FD; fragments of the cation are also found, especially when C^+ contains metal–carbonyl bonds [4–6]. Covalent organometallic compounds generally give a prominent M^+ ion, in contrast [4–8]. Our results, which were obtained by coating samples on metal emitters [9] rather than the more common carbon microneedles used in FD, were universally in agreement with the previously obtained model; Tables I and II indicate typical results. With metal emitters we did not observe fragmentation. This result is similar to the more satisfactory spectra obtained for organic cations on metal dendrite emitters [10], and is probably related to the lower field developed at the tips of metal emitters [11].

TABLE I. Mass Spectra of Typical Covalent Organometallic Complexes.

Compound	Ion observed	Heating current (mA)
$(\eta^5\text{-}C_5H_5)Mn(CO)_3$	M^+	0
$(\eta^6\text{-}(CH_3)_2NC_6H_5)Cr(CO)_3$	M^+	0
$(\eta^4\text{-}Ph_4C_4)Fe(CO)_3$	M^+	0
$(\eta^5\text{-}C_6D_6H)Mn(CO)_3$	M^+	0
$(\eta^5\text{-}C_5H(C_3)_5)Fe(CO)_2CH_3$	M^+	0
$(\eta^4\text{-}C_8H_{10})Fe(CO)_3$ [a]	M^+	0

[a] Ligand = 1,3,5-cyclooctatriene.

TABLE II. Mass Spectra of Typical Ionic Organometallic Complexes.

Compound	Ion observed	Heating current (mA)
$[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+BF_4^-$	C^+	35
$[(\eta^5\text{-}C_7H_9)Fe(CO)_3]^+BF_4^-$ [a]	C^+	38
$[(\eta^5\text{-}CH_3C_6H_6)Fe(CO)_3]^+BF_4^-$	C^+	33
$[(\eta^5\text{-}CH_3OC_6H_6)Fe(CO)_3]^+BF_4^-$	C^+	33
$[(\eta^6\text{-}C_6H_6)Mn(CO)_3]^+PF_6^-$	C^+	23

[a] Ligand = 1,3-cycloheptadienyl.

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The triflate complex $(\eta^5\text{-}C_5(CH_3)_5)Fe(CO)_2(O_3SCF_3)$ allows a crucial test of the predictive value of the spectrum with respect to the kind of bonding in organometallic complexes. The Fe–O bond must possess a substantial amount of ionic character, and triflate should be a good leaving group in mass spectral reaction mechanisms. The crystal structure indicates that the compound is covalent, however: the Fe–O bond length is 200.7(3) pm [12]. The problem is thus reduced to whether the molecular ion M^+ of the covalent compound is observed or whether the $(\eta^5\text{-}C_5(CH_3)_5)Fe(CO)_2^+$ cation is formed because of the driving force to cleave the Fe–O bond heterolytically. In the event the M^+ ion was the only one observed. The result confirms the prediction of the crystal structure and demonstrates that FD analysis of covalent organometallics is successful even in a case of this extreme delicacy, which is a new kind of test of the limits of the FD technique. On the basis of this critical experiment and other results quoted herein, it is apparent that FD mass spectrometry can offer a more rapid test for the nature of bonding in questionable organometallics than determination of crystal structure, with the limitation that the putative cation should be unipositive. Because FD spectra using metal emitters indicate no decomposition of M^+ and C^+ in contrast to electron ionisation and chemical ionisation spectra [13, 14], they may also be used to identify components of mixtures, as we have done repeatedly.

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