Gas Phase Electron Attachment Reactions with Organometallic Compounds; Molecular Anion Formation and Negative Ion Mass Spectra of a Series of η^4-Dienetricarbonyliron Compounds

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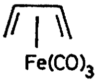
Summary Electron attachment by secondary electron capture in the gas phase with a series of conjugated η^4-dienetricarbonyliron compounds yields molecular anions which decompose by CO and diene eliminations; however, η^4-cyclobutadienetricarbonyliron, which undergoes dissociative electron capture to give the $[M - CO]^{\overline{\cdot}}$ ion at the highest *m/e* in its negative ion mass spectrum, decomposes only by elimination of CO ligands.

Whereas gas phase electron interaction with monomeric group 6 and 8 transition metal carbonyls occurs dissociatively and yields ions of highest *m/e* $[M - CO]^{\overline{\cdot}}$ in the negative ion mass spectra of these compounds, it is possible, by appropriate replacement of CO ligands in the parent metal carbonyl, to incorporate an electron capture species in the molecule which can facilitate the attachment of a secondary electron by a resonance capture process.[1,2] Such processes can give rise to structurally informative negative ion mass spectra at high primary electron beam energies (70 eV).[3-5] For example, there now exist numerous examples of metal complexes which can capture secondary or thermalized electrons in the gas phase and form molecular anions of low internal energies which then may undergo relatively simple fragmentations.[4–6] Few metal carbonyl derivatives, however, are known to form molecular anions under these conditions.[1,4,7]

We now report data for a series of η^4-dienetricarbonyliron compounds (**1**)—(**6**) (Table) where, for the first time with such compounds, secondary electron capture in the gas phase has resulted in the formation of molecular radical anions. With four conjugated members of the series, compounds (**1**)—(**4**), molecular anions are given in high abundance in the negative ion mass spectra. The $[M - CO]^{\overline{\cdot}}$ ion is the base peak in the spectra for all compounds, and few fragment ions are present.



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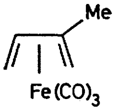

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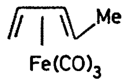

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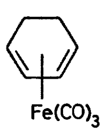

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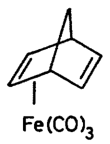

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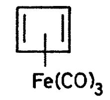

(6)

The major fragmentation pathway involves both consecutive and simultaneous elimination of neutral CO ligands. However, an important minor fragmentation pathway also involves loss of the diene ligand for four of the compounds, (**1**)—(**4**), from either their $[M]^{\overline{\cdot}}$ or $[M - CO]^{\overline{\cdot}}$ ions. For compound (**4**) additional fragmentations, for which metastable ion peaks were obtained, involve the loss of H_2 together with two CO ligands from either $[M]^{\overline{\cdot}}$ or $[M - CO]^{\overline{\cdot}}$, as well as the elimination of C_6H_6, or at least its elements, from the $[M - CO]^{\overline{\cdot}}$ ion. The formally non-conjugated compound (**5**)[8,9] gives a molecular anion of much lower intensity than compounds (**1**)—(**4**), together with a $[M - CO]^{\overline{\cdot}}$ ion carrying 96% of the total ion current, which may reflect the increasing importance of a dissociative capture process with this compound.

In contrast, η^4-cyclobutadienetricarbonyliron (**6**) gave significantly different results. No evidence for molecular anion formation could be found, the ion of highest *m/e* in its negative ion mass spectrum is $[M - CO]^{\overline{\cdot}}$ and $[M - \text{diene}]^{\overline{\cdot}}$ or $[M - CO - \text{diene}]^{\overline{\cdot}}$ fragment ions are not observed. This is consistent with the presence of the aromatic 6 π-system associated with the cyclobutadiene ligand in this compound[9] which is not readily reduced. We have also obtained similar electron capture and fragmentation data with η^6-benzenetricarbonylchromium, which gives a $[M - CO]^{\overline{\cdot}}$ ion of highest *m/e* in its negative ion mass spectrum, from which successive CO eliminations occur.

Electron attachment to the η^4-conjugated dienetricarbonyliron complexes may be rationalized in terms of a η^4 to η^3 conversion and reduction in the diene–iron bond order together with development of a radical site on the diene ligand, with the charge localized on the iron atom. This is consistent with the observation of only iron containing charged species in the negative ion mass spectra. The trend towards increasing molecular anion stability with compounds (**1**)—(**4**) (Table) may be indicative of the development of the more stable secondary radical sites on the diene ligands within this series, particularly with compounds (**3**) and (**4**).

TABLE. Percentage of the total ion current carried by the principal ions in the 70 eV negative ion mass spectra of η^4-dienetricarbonyliron compounds[a]

	Compound					
Ion	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)	(**6**)
$[M]^{\overline{\cdot}}$	20	22	27	33	2	0
$[M - CO]^{\overline{\cdot}}$	74	76	72	66	96	97
$[M - 2CO]^{\overline{\cdot}}$	1	0·3	0·1	< 0·1	0·4	2
$[M - 2CO - H_2]^{\overline{\cdot}}$	—	—	0·1	0·1	—	—
$[M - 3CO]^{\overline{\cdot}}$	1	—	—	—	—	1
$[M - \text{Diene}]^{\overline{\cdot}}$	1	1	1	2	1	—
$[M - C_6H_6 - CO]^{\overline{\cdot}}$	—	—	—	0·3	—	—
$[M - \text{Diene} - CO]^{\overline{\cdot}}$	1	0·1	—	0·3	0·3	—

[a] All atoms of all isotopes in the various clusters are considered. Intensities of ions in this Table refer to reproducible spectra by the all-glass inlet or solid insertion method, with inlet and ion source temperatures set at 50 °C, compound pressures in the range 4—8 × 10^{-6} Torr, electron energy 70 eV, filament current 3·2 A, target voltage 110 V, target current 35 μA, total emission 50 μA, ion accelerating voltage 3·2 kV, and ion source repellers at 0 V.

Thermolysis processes[10] contribute in part to the yield of $[M - CO]^{\overline{\cdot}}$ ions, even under the low temperature ion source conditions employed (Table). Increased yields of molecular anions are presently being sought at lower ion source temperatures and with the use of electron energy moderating gases such as methane to generate low energy electrons independently of the compounds, under high pressure ion source conditions.

The negative ion mass spectra were obtained with a modified Hitachi RMU-6L mass spectrometer under conditions described in the Table.

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