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Preliminary communication

GAS PHASE MOLECULAR ANION FORMATION BY η^4- AND η^6-CYCLOHEPTATRIENE DERIVATIVES OF ZEROVALENT IRON, CHROMIUM, MOLYBDENUM, AND TUNGSTEN TRICARBONYLS

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Summary

The title compounds form molecular anions in high abundance in their negative ion mass spectra in apparent violation of the rare-gas rule.

Monomeric η^5-cyclopentadienyl transition metal carbonyls possessing a rare-gas valence shell electronic configuration undergo, in general, reductive decarbonylation upon interaction with low energy secondary electrons, as evidenced by the appearance of $[M-CO]^{-\bullet}$ radical anions as the base peaks in their negative ion mass spectra.[1] The seventeen electron $[M-CO]^{-\bullet}$ species are formally isoelectronic with the positively charged molecular ions, $[M]^{+\cdot}$, formed by electron detachment from these compounds. However, in the negative ion mass spectrum of $(\eta^5-C_5H_5)Co(CO)_2$ a molecular anion was observed as the base peak. This result was rationalised in terms of reduction in the bond order of the η^5-cyclopentadienyl interaction to an η^3-allylic configuration during the electron capture process, thereby avoiding violation of the rare-gas rule. This mechanism also appears to apply to η^4-diene iron tricarbonyls, where molecular radical anions were observed[2] in the negative ion mass spectra of compounds capable of being reduced to relatively stable η^3-allyl derivatives. Molecular anions are also observed in the mass spectra of complexes containing metals with saturated valence shell configurations if an electron capture moiety, for example, an ester group, is attached to the precursor molecules.[3]

As a continuation of our study concerning the generation and reactivity of organometallic radical anions in the gas phase, we now report some preliminary details concerning the negative ion mass spectra of η^4- and η^6-cycloheptatriene derivatives of iron, chromium, molybdenum, and tungsten carbonyls (Table 1). Molecular radical anions have been observed for these zerovalent complexes in the gas phase, in apparent violation of the rare-gas rule. For tricarbonyl(1-4-η-cyclohepta-1,3,5-triene)iron(0), I, two distinct fragmentation pathways were identified as a result of the assignment of metastable peaks in the various reproducible spectra:

$$\begin{tikzcd}
{[\text{M}]} \arrow[r, "+e"] & {[\text{M}]^{-\cdot}} \arrow[r] \arrow[rr, bend left] \arrow[dr] & {[\text{M-CO}]^{-\cdot}} \arrow[r] & {[\text{M-2CO}]^{-\cdot}} \arrow[r] & {[\text{M-3CO}]^{-\cdot}} \\
 & & {[\text{M-triene}]^{-\cdot}} \arrow[r] & {[\text{M-triene-CO}]^{-\cdot}} &
\end{tikzcd}$$

We suggest that electron capture by the parent molecule (I) is concomitant with reduction in the η^4-diene bond order of the triene-metal system, affording a 17-electron molecular carbanion or an 18-electron di-radical, both of which contain an η^3-allyl-iron bond (Figure 1). The appearance of a significant peak due to $[\text{M-triene}]^{-\cdot}$ (7%) is strong evidence for the existence of the di-radical form of the molecular anion. However, since $[\text{M-CO}]^{-\cdot}$ is the base peak

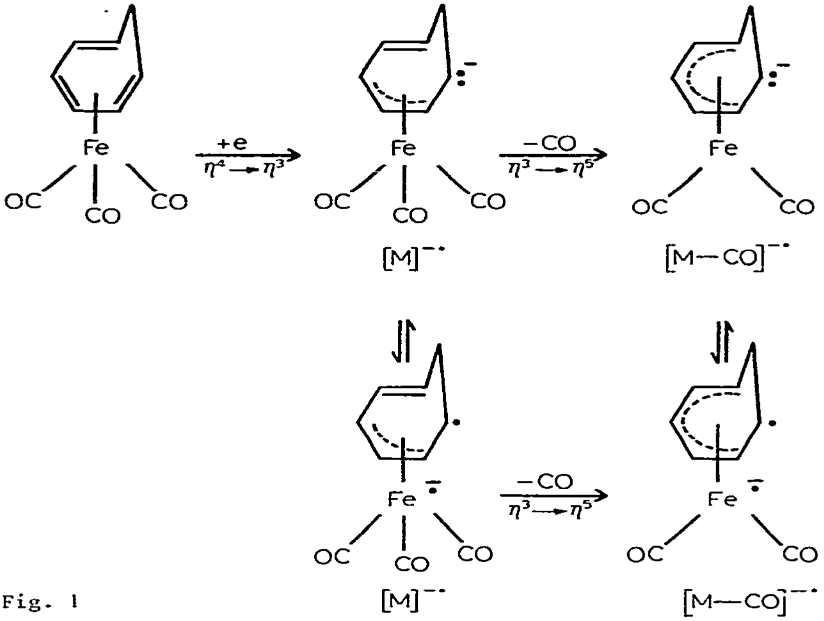

Fig. 1

in the spectrum of this compound, the alternative mechanism involving reductive decarbonylation of the parent molecule presumably also takes place. It is significant that decarbonylation of either form of the molecular anion allows, on the basis of the rare-gas rule, the formation of a stable η^5-dienyl-metal bond involving a 17- or 18-electron metal atom. Decarbonylation of $[M\text{-triene}]^{-\cdot}$ leads to $[Fe(CO)_2]^{-\cdot}$. A metastable peak corresponding to the alternative transition $[M\text{-}CO]^{-\cdot} \rightarrow [M\text{-}CO\text{-triene}]^{-\cdot}$ was not observed.

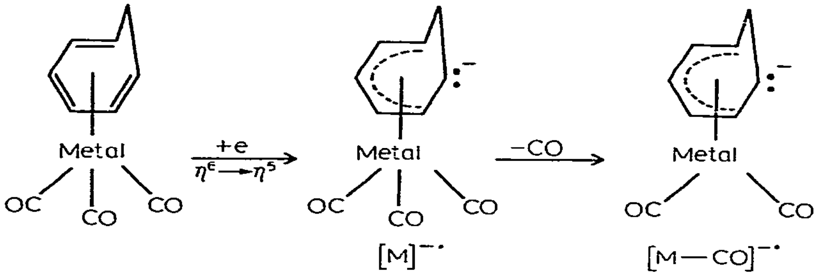

Fig. 2

TABLE 1. Percentage of the Total Ion Current Carried by the Significant Ions in the Negative Ion Mass Spectra of η^4- and η^6-Cycloheptatriene Tricarbonyl Metal Compounds[a,b].

Compound	I	II	III	IV
Metal	Fe	Cr	Mo	W
Metal-triene Bond	η^4	η^6	η^6	η^6
$[M]^{-\cdot}$ [c] (%)	41	67	76	90
$[M - CO]^{-\cdot}$	48	13	6	3
$[M - 2CO]^{-\cdot}$	2	13	18	7
$[M - 3CO]^{-\cdot}$	0.1	6	0	0
$[M - \text{triene}]^{-\cdot}$	7	0	0	0
$[M - \text{triene} - CO]^{-\cdot}$	1	0	0	0

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[a] All atoms of all isotopes in the various clusters are considered.

[b] 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, and with compound pressures $4\text{-}8\times10^{-6}$ torr, primary electron beam energy 70 eV, filament current 3.2A, regulated total emission 50 µA, target current 35-40 µA, ion accelerating voltage 3.2 kV, and with ion source repellers set at 0 V.

[c] The symbol M refers to the molecular ion for each of the compounds.

The η^6-triene-metal complexes (II) - (IV) show an increasing tendency to form stable molecular anions (Table 1). Here, electron capture by an antibonding orbital associated with the triene ligand results in the ready formation of a carbanion containing an η^5-dienyl-metal bond. Consequently, the molecular anions derived from (II) - (IV) show much less tendency to decarbonylate (Figure 2).

Assignment of metastable peaks indicates that both simultaneous and consecutive decarbonylation of the molecular anion occurs for (II) - (IV):

$$\begin{tikzcd}{[M]^{-\cdot}} \arrow[r] \arrow[rrr, bend left] \arrow[rr, bend right] & {[M\text{-}CO]^{-\cdot}} \arrow[r] & {[M\text{-}2CO]^{-\cdot}} \arrow[r] & {[M\text{-}3CO]^{-\cdot}} \\ & & & \text{(II only)}\end{tikzcd}$$

Ions corresponding to the loss of the neutral triene were not observed for (II) - (IV), and the loss of the first CO molecule was shown, in part, to involve a thermolysis component. Thermal decarbonylation of metal carbonyls and their derivatives in the gas phase is well documented,[4] and in view of this the ion intensity data for (II) - (IV) were obtained with mass spectrometer ion source temperatures of 50° C.

It is noteworthy that the η^6-arene metal bond in η^6-arene chromium tricarbonyls (where arene = benzene or mesitylene) is not reduced by electron capture in the gas phase: these compounds undergo reductive decarbonylation to produce 17-electron $[M\text{-}CO]^{-\cdot}$ radical ions as their base peaks.[5] We have also found that tricarbonyl(1-4-η-cyclohepta-1,3,5-trienone)iron(0) and tricarbonyl(1-4-η-cyclooctatetraene)iron(0) undergo reductive decarbonylation under the same conditions to yield $[M\text{-}CO]^{-\cdot}$ radical anions as base peaks in 76% and 68% abundance, respectively.

The negative ion mass spectra were obtained using a modified Hitachi RMU-6L mass spectrometer under the conditions described in Table 1.

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