

Evidence for $\sigma \rightarrow \eta^3$ Rearrangement Reaction in Gaseous Ions from Fe, Mn and Re Allylic Derivatives

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Abstract

The fragmentation pathways of $(\eta^3\text{-C}_3\text{H}_4\text{X})\text{Fe}(\text{CO})_2\text{NO}$, $(\sigma\text{-C}_3\text{H}_4\text{X})\text{Fe}(\text{CO})_2(\text{NO})\text{L}$, $(\eta^3\text{-C}_3\text{H}_4\text{X})\text{Fe}(\text{CO})(\text{NO})\text{L}$, $(\sigma\text{-C}_3\text{H}_4\text{X})\text{Fe}(\text{CO})_2(\text{NO})\text{L}'$, $(\eta^3\text{-C}_3\text{H}_4\text{X})\text{Fe}(\text{CO})(\text{NO})\text{L}'$, $(\sigma\text{-C}_3\text{H}_5)\text{M}(\text{CO})_5$, $(\eta^3\text{-C}_3\text{H}_5)\text{M}(\text{CO})_4$, $(\sigma\text{-CH}_2\text{-CH}=\text{C}(\text{Me})_2)\text{Mn}(\text{CO})_5$, $(\eta^3\text{-CH}_2\text{-CH}=\text{C}(\text{Me})_2)\text{Mn}(\text{CO})_4$, ($\text{X} = 2\text{-Cl}$; $\text{L} = \text{PPh}_3$; $\text{L}' = \text{P}(\text{OMe})_3$; $\text{M} = \text{Mn, Re}$) have been investigated by mass spectrometry. In the σ derivatives the molecular ion loses CO or the allylic ligand, while in the η^3 derivative loss of a CO group is the only fragmentation mode of the molecular ion. Electron impact as well as methane chemical ionization mass spectra have been reported. Kinetic energy release of selected metastable ions indicates that a $\sigma \rightarrow \eta^3$ rearrangement reaction occurs.

Introduction

It is well known that most of $\sigma\text{-}\pi$ rearrangement reactions are initiated by reaction at the metal center or at the ligand itself [1]. The change in electron density of the metal center, caused by addition or abstraction of a π acid ligand, generally results in a $\sigma \rightarrow \pi$ rearrangement [2] (e.g., loss of a ligand leaves a coordinatively unsaturated metal, and a rearrangement from σ to π satisfies the coordination requirement by donation of more than one electron pair). Moreover, creating or removing unsaturation at the ligand can initiate a $\sigma\text{-}\pi$ rearrangement; hydride abstraction and protonation reactions are perhaps the best elucidated examples [3].

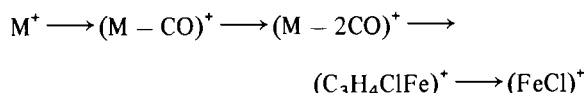
Results have been reported in the condensed phase, but, to our knowledge, no studies, have shown such a rearrangement for organotransition metal compounds in the gaseous phase. We now report a mass spectrometric study of some σ and η^3 allylic compounds, which also provides some information on the ionic structure of a selected ion whose formation could involve a σ to η^3 isomerization.

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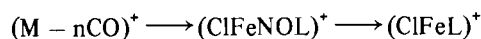
Electron Impact Mass Spectra

(a) Iron Derivatives

The 70 eV mass spectra of compounds $(\eta^3\text{-CH}_2\text{-}\overline{\text{C}}\overline{\text{C}}\overline{\text{Cl}}\text{-}\overline{\text{C}}\overline{\text{H}}_2)\text{Fe}(\text{CO})_2\text{NO}$ (I), $(\sigma\text{-CH}_2\text{-CCl}=\text{CH}_2)\text{Fe}(\text{CO})_2(\text{NO})\text{PPh}_3$ (II), $(\eta^3\text{-CH}_2\text{-}\overline{\text{C}}\overline{\text{C}}\overline{\text{Cl}}\text{-}\overline{\text{C}}\overline{\text{H}}_2)\text{Fe}(\text{CO})(\text{NO})\text{PPh}_3$ (III), $(\sigma\text{-CH}_2\text{-CCl}=\text{CH}_2)\text{Fe}(\text{CO})_2(\text{NO})\text{P}(\text{OMe})_3$ (IV) and $(\eta^3\text{-CH}_2\text{-}\overline{\text{C}}\overline{\text{C}}\overline{\text{Cl}}\text{-}\overline{\text{C}}\overline{\text{H}}_2)\text{Fe}(\text{CO})(\text{NO})\text{P}(\text{OMe})_3$ (V) are very simple, showing low intensity molecular ions and fragment ions obtained by successive losses of the ligands (see Tables I, II and III); fragmentation involving the allyl ligand is accompanied by a Cl transposition leading to the loss of a neutral C_3H_4 moiety. From the mass spectra and the observed metastable ions, it is possible to ascertain that this rearrangement reaction follows the NO loss according to the reaction sequence for compound I



while for the other compounds the loss of C_3H_4 precedes the NO loss according to



The basicity of the phosphinic ligands can be invoked to explain this effect; it is indeed well known that the substitution of a CO group by a phosphinic ligand increases the bond strength between the

TABLE I. Relative Intensities of the Principal Ions in the Electron Impact Mass Spectra of Compound $(\eta^3\text{-CH}_2\text{-}\overline{\text{C}}\overline{\text{C}}\overline{\text{Cl}}\text{-}\overline{\text{C}}\overline{\text{H}}_2)\text{Fe}(\text{CO})_2\text{NO}$ (I).

Ion	<i>m/z</i>	Relative abundance (%)
$[(\text{C}_3\text{H}_4\text{Cl})\text{Fe}(\text{CO})_2\text{NO}]^+$	217	7
$[(\text{C}_3\text{H}_4\text{Cl})\text{Fe}(\text{CO})(\text{NO})]^+$	189	35
$[(\text{C}_3\text{H}_4\text{Cl})\text{FeNO}]^+$	161	20
$[(\text{C}_3\text{H}_4\text{Cl})\text{Fe}]^+$	131	55
$[\text{FeCl}]^+$	91	100

TABLE II. Relative Intensities of the Principal Ions in the Electron Impact Mass Spectra of Compounds (σ -CH₂-CCI=CH₂)Fe(CO)₂(NO)PPh₃ (II) and (η^3 -CH₂-CCl-CH₂)Fe(CO)(NO)PPh₃ (III)

Ion	m/z	Relative abundance (%)	
		II	III
[(C ₃ H ₄ Cl)Fe(CO) ₂ (NO)PPh ₃] ⁺	479	<0.1	
[(C ₃ H ₄ Cl)Fe(CO)(NO)PPh ₃] ⁺	451	<0.1	3
[(C ₃ H ₄ Cl)Fe(NO)PPh ₃] ⁺	423	1	14
[FeCl(NO)PPh ₃] ⁺	383	18	21
[FeClPPh ₃] ⁺	353	100	100
[Fe(NO)PPh ₃] ⁺	348	44	51
[FePPh ₃] ⁺	318	24	55
[PPh ₃] ⁺	262	(600)	(1200)

TABLE III. Relative Intensities of the Principal Ions in the Electron Impact Mass Spectra of Compounds (σ -CH₂-CCI=CH₂)Fe(CO)₂(NO)P(OMe)₃ (IV) and (η^3 -CH₂-CCl-CH₂)Fe(CO)(NO)P(OMe)₃ (V)

Ion	m/z	Relative abundance (%)	
		IV	V
[(C ₃ H ₄ Cl)Fe(CO) ₂ (NO)P(OMe) ₃] ⁺	341	1	
[(C ₃ H ₄ Cl)Fe(CO)(NO)P(OMe) ₃] ⁺	313	4	2
[(C ₃ H ₄ Cl)Fe(NO)P(OMe) ₃] ⁺	285	30	20
[(C ₃ H ₄ Cl)Fe(NO)P(OMe) ₂] ⁺	254	4	3
[FeCl(NO)P(OMe) ₃] ⁺	245	12	12
[FeClP(OMe) ₃] ⁺	215	100	100
[Fe(NO)P(OMe) ₃] ⁺	210	28	9
[FeP(OMe) ₃] ⁺	180	13	6
[P(OMe) ₃] ⁺	124	15	7
[FeCl] ⁺	91	18	18

central metal and strongly π acceptor ligands like CO or NO; since this effect is likely to hold also in the ionic state, it follows that in the phosphinic derivatives the increased Fe-NO bond strength makes the NO loss a process that demands more energy than the C₃H₄ loss. There are no substantial differences in the mass spectra of the two σ and η^3 couples; thus it seems that the different mode of bonding of the allylic ligand does not affect the decomposition reactions of these molecular ions.

(b) Manganese and Rhenium Derivatives

The 70 eV mass spectra of (σ -C₃H₅)Mn(CO)₅ (VI), (η^3 -C₃H₅)Mn(CO)₄ (VII), (σ -C₃H₅)Re(CO)₅ (VIII), (η^3 -C₃H₅)Re(CO)₄ (IX), (σ -CH₂-CH=CMe₂)Mn(CO)₅ (X) and (η^3 -CH₂-CH=CMe₂)Mn(CO)₄ (XI) (see Tables IV, V and VI) reflect the different

TABLE IV. Relative Intensities of the Principal Ions in the Electron Impact Mass Spectra of Compounds (σ -C₃H₅)Mn(CO)₅ (VI) and (η^3 -C₃H₅)Mn(CO)₄ (VII)

Ion	m/z	Relative abundance (%)	
		VI	VII
[(C ₃ H ₅)Mn(CO) ₅] ⁺	236	5	
[(C ₃ H ₅)Mn(CO) ₄] ⁺	208	49	32
[Mn(CO) ₅] ⁺	195	12	
[(C ₃ H ₅)Mn(CO) ₃] ⁺	180	13	15
[Mn(CO) ₄] ⁺	167	33	-
[(C ₃ H ₅)Mn(CO) ₂] ⁺	152	24	19
[Mn(CO) ₃] ⁺	139	26	2
[(C ₃ H ₅)MnCO] ⁺	124	29	23
[Mn(CO) ₂] ⁺	111	20	2
[(C ₃ H ₅)Mn] ⁺	96	100	100
[MnCO] ⁺	83	29	9
[(C ₃ H ₅)CO] ⁺	69	11	11

TABLE V. Relative Intensities of the Principal Ions in the Electron Impact Mass Spectra of Compounds (σ -C₃H₅)Re(CO)₅ (VIII) and (η^3 -C₃H₅)Re(CO)₄ (IX)

Ion	m/z	Relative abundance (%)	
		VIII	IX
[(C ₃ H ₅)Re(CO) ₅] ⁺	368	27	
[(C ₃ H ₅)Re(CO) ₄] ⁺	340	84	54
[Re(CO) ₅] ⁺	327	44	
[(C ₃ H ₅)Re(CO) ₃] ⁺	312	54	26
[Re(CO) ₄] ⁺	299	85	2
[(C ₃ H ₅)Re(CO) ₂] ⁺	284	47	42
[(C ₃ H ₃)Re(CO) ₂] ⁺	282	100	100
[Re(CO) ₃] ⁺	271	77	7
[(C ₃ H ₅)ReCO] ⁺	256	15	13
[(C ₃ H ₃)ReCO] ⁺	254	41	42
[Re(CO) ₂] ⁺	243	33	6
[(C ₃ H ₅)Re] ⁺	228	15	13
[(C ₃ H ₃)Re] ⁺	226	59	52
[(C ₃ H)Re] ⁺	224	53	51
[ReCO] ⁺	215	18	5
[(C ₂ H)Re] ⁺	212	9	8
[(CH ₂)Re] ⁺	201	11	10
[(CH)Re] ⁺	200	36	34
[CRe] ⁺	199	20	14
[Re] ⁺	187	37	21

type of bonding of the allylic ligand; this behaviour was already noted for the rhenium derivatives [4] and it is now confirmed for the two manganese couples. In the σ derivatives the molecular ion loses CO or the allylic ligand, while in the η^3 derivatives loss of a CO group is the only fragmentation mode of the molecular ion.

TABLE VI. Relative Intensities of the Principal Ions in the Electron Impact Mass Spectra of Compounds (σ -CH₂-CH=CMe₂)Mn(CO)₅ (X) and (η^3 -CH₂-CH=CMe₂)Mn(CO)₄ (XI)

Ion	<i>m/z</i>	Relative abundance (%)	
		X	XI
[(C ₅ H ₉)Mn(CO) ₅] ⁺	264	6	
[(C ₅ H ₉)Mn(CO) ₄] ⁺	236	20	26
[(C ₅ H ₉)Mn(CO) ₃]	208	12	30
[Mn(CO) ₅] ⁺	195	4	4
[(C ₅ H ₉)Mn(CO) ₂] ⁺	180	20	55
[Mn(CO) ₄] ⁺	167	10	—
[(C ₅ H ₇)MnCO] ⁺	152	18	36
[Mn(CO) ₃] ⁺	139	12	3
[(C ₅ H ₉)Mn] ⁺	124	100	100
[(C ₅ H ₇)Mn] ⁺	122	14	32
[Mn(CO) ₂] ⁺	111	13	6
[MnCO] ⁺	83	19	14
[C ₅ H ₉] ⁺	69	164	107
[C ₅ H] ⁺	67	15	11
[MnH] ⁺	56	80	100
[Mn] ⁺	55	124	105

TABLE VII. Relative Intensities of the Principal Ions in the Methane Chemical Ionization Mass Spectra of Compounds (σ -CH₂-CCl=CH₂)Fe(CO)₂(NO)P(OMe)₃ (IV) and (η^3 -CH₂-CCl=CH₂)Fe(CO)(NO)P(OMe)₃ (V)

Ion	<i>m/z</i>	Relative abundance (%)	
		IV	V
[(C ₃ H ₄ Cl)Fe(CO) ₂ (NO)P(OMe) ₃] ⁺	341	0.2	
[H(C ₃ H ₄ Cl)Fe(CO)(NO)P(OMe) ₃] ⁺	314	—	0.8
[(C ₃ H ₄ Cl)Fe(CO)(NO)P(OMe) ₃] ⁺	313	1.3	2.2
[(C ₃ H ₄ Cl)Fe(NO)P(OMe) ₃] ⁺	285	7.8	5.1
[(C ₃ H ₄ Cl)Fe(CO)(NO)P(OMe) ₂] ⁺	282	3.8	3
[(C ₃ H ₄ Cl)Fe(NO)P(OMe) ₂] ⁺	254	5.5	1.7
[(C ₃ H ₄)Fe(NO)P(OMe) ₃] ⁺	250	—	1.2
[Fe(NO)P(OMe) ₃] ⁺	210	6.3	1.9
[FeP(OMe) ₃]	180	2.2	—
[Fe(NO)P(OMe) ₂]	179	10	3.9
[HP(OMe) ₃]	125	100	100
[P(OMe) ₃]	124	33	7.3

The successive fragmentations involve chiefly successive losses of CO groups, while fragments due to loss of the allylic ligand occur with high probability only from the molecular ions of the σ derivatives; this was confirmed by a search for the metastable ions of the (M - CO)⁺ ions which were found to decompose only through the loss of a CO ligand.

TABLE VIII. Relative Intensities of the Principal Ions in the Methane Chemical Ionization Mass Spectra of Compounds (σ -C₃H₅)Mn(CO)₅ (VI) and (η^3 -C₃H₅)Mn(CO)₄ (VII)

Ion	<i>m/z</i>	Relative abundance (%)	
		VI	VII
[H(C ₃ H ₅)Mn(CO) ₅] ⁺	237	6	
[(C ₃ H ₅)Mn(CO) ₅] ⁺	236	10	
[H(C ₃ H ₅)Mn(CO) ₄] ⁺	209	30	100
[(C ₃ H ₅)Mn(CO) ₄] ⁺	208	54	51
[HMn(CO) ₅] ⁺	196	11	
[Mn(CO) ₅] ⁺	195	84	
[H(C ₃ H ₅)Mn(CO) ₃] ⁺	181	93	85
[(C ₃ H ₅)Mn(CO) ₃] ⁺	180	4	—
[Mn(CO) ₄] ⁺	167	47	—
[H(C ₃ H ₅)Mn(CO) ₂] ⁺	153	100	61
[(C ₃ H ₅)Mn(CO) ₂] ⁺	152	34	—
[Mn(CO) ₃] ⁺	139	8	—
[H(C ₃ H ₅)MnCO] ⁺	125	19	57
[(C ₃ H ₅)Mn(CO)] ⁺	124	7	—
[Mn(CO) ₂] ⁺	111	4	—
[(C ₃ H ₅)Mn] ⁺	96	8	—
[MnCO] ⁺	83	11	—

TABLE IX. Relative Intensities of the Principal Ions in the Methane Chemical Ionization Mass Spectra of Compounds (σ -C₃H₅)Re(CO)₅ (VIII) and (η^3 -C₃H₅)Re(CO)₄ (IX)

Ion	<i>m/z</i>	Relative abundance (%)	
		VIII	IX
[(C ₃ H ₅)(C ₃ H ₅)Re(CO) ₅] ⁺	397	3	
[(CH ₃)(C ₃ H ₅)Re(CO) ₅] ⁺	383	3	
[H(C ₃ H ₅)Re(CO) ₅] ⁺	369	18	
[(C ₃ H ₅)Re(CO) ₅] ⁺	368	5	
[(CH ₃)(C ₃ H ₅)Re(CO) ₄] ⁺	355	14	—
[(CH ₃)(C ₃ H ₃)Re(CO) ₄] ⁺	353	14	—
[H(C ₃ H ₅)Re(CO) ₄] ⁺	341	100	100
[(C ₃ H ₅)Re(CO) ₄] ⁺	340	17	34
[Re(CO) ₅] ⁺	327	12	12
[(CH ₃)(C ₃ H ₃)Re(CO) ₃] ⁺	325	—	12
[H(C ₃ H ₅)Re(CO) ₃] ⁺	313	20	63
[(C ₃ H ₅)Re(CO) ₃] ⁺	312	13	32

Chemical Ionization Mass Spectra

The presence of the molecular ion in the CH₄ chemical ionization mass spectra is a common feature for these allylic compounds; it is indeed expected that the ionization energy of most transition metal organometallic compounds be lower than the recombination energy of the reactant primary ions so that the

TABLE X. Kinetic Energy Release ($\text{eV} \times 10^2$) in some Metastable Ion Transitions of Compounds IV–XI

	σ -Compounds				η^3 Compounds			
	IV	VI	VIII	X	V	VII	IX	XI
$M^+ \rightarrow (M - CO)^+$		13.0	7.9	2.8	1.9	1.9	5.4	2.4
$(M - CO)^+ \rightarrow (M - 2CO)^+$	2.1	1.9	5.3	2.4	3.0		5.7	

charge exchange reaction can compete with the proton transfer reaction. As a consequence, the mass spectra presented in Tables VII, VIII and IX are the superposition of the spectra, due to the proton transfer and to the charge exchange reactions, respectively, so that the ratio between the sum of the relative abundances of the protonated and the unprotonated ions roughly measures the relative probability of the two reactions. Under this assumption it follows that the η^3 compounds should have a stronger tendency to acquire a proton than the corresponding σ derivatives. The analysis of the decomposition pathway shows that, for all the compounds, the protonated molecule loses only CO or the allylic group; this, according to a generally accepted suggestion [5], should indicate a protonation to the central metal. These results are in agreement with the ESCA study in gaseous phase [6] of compounds VI and VII, where it has been found that the $\eta^3\text{-C}_3\text{H}_5$ group has a lower negative charge density than the $\sigma\text{-C}_3\text{H}_5$ group and that the manganese atom in the η^3 compound is more negative than in the σ derivative; it follows that the greater tendency of the η^3 compounds to acquire the proton can be only justified by an initial protonation to the central metal. A different conclusion has been reported [7] for the solution protonation of compound VI by strong acids which gives, as the final product, a propene compound $(\text{CH}_3\text{CH}=\text{CH}_2)\text{Mn}(\text{CO})_6^+$. Indeed, protonation to the central metal [8] or to the organic moiety has been reported for various organometallic derivatives, but their behaviour to the acid attack has not yet been rationalized.

Ionic Structures

The comparison of the mass spectra of the σ and η^3 couples suggests that after the loss of a CO group a σ compound rearranges to an η^3 compound; this follows from the observation that in a σ compound the losses of CO and allylic ligands are competitive in the molecular ion, while the ion $(M - \text{CO})^+$ has a unique fragmentation pathway, *i.e.*, loss of CO group. However, since this argument is not decisive, we turned to the study of the metastable characteristics of ions with the same elemental composition (for

information on the use of metastable characteristics in structure elucidation see refs. 9 and 10).

For each $\eta^3\text{-}\sigma$ couple we examined the kinetic energy released in the metastable transitions $M^+ \rightarrow (M - \text{CO})^+$ and $(M - \text{CO})^+ \rightarrow (M - 2\text{CO})^+$ for η^3 and σ compounds, respectively. The data reported in Table X, mean values of at least four measurements, clearly indicate that for each couple the two ions have the same structure, very likely that of η^3 compound. It seems, therefore, that in the σ compound the loss of a CO group induces a rearrangement of the allylic ligand from σ to η^3 ; this isomerization is very fast, since the sampled ions have lifetimes around 10^{-5} s.

It can be argued that the fragmentation reaction $M^+ \rightarrow (M - \text{CO})^+$ in the σ compounds is a rearrangement reaction in which, when the CO group begins to leave its coordination position, it is replaced by the allylic ligand. This suggestion is supported by the higher kinetic energy release associated with this metastable ion decomposition. Also, the fact that in the chemical ionization mass spectra of the σ compounds there are many more ions (in fact, they resemble more EI than CI spectra) than in the η^3 compounds might indicate that after this rearrangement the resultant ion has an high energy content, which is used to induce extensive fragmentation of the molecular ion. It can be concluded that the gaseous phase σ to η^3 isomerization is a thermodynamically and kinetically favoured process.

Moreover, the stability of σ derivatives may be linked to the stability of the metal–CO bond; low bond dissociation energy or low activation energy for a substitution reaction should make a σ derivative unstable; it would rearrange to η^3 with elimination of a CO molecule. The influence of these factors is probably responsible for the absence of a σ compound corresponding to compound I; only when one CO group is substituted by a phosphinic ligand, thus reinforcing the remaining Fe–CO bonds, can a σ derivative be isolated.

Experimental

The samples were prepared according to previously published procedures: (I–V) [11], (VI, VII) [12], (VIII, IX) [4], (X, XI) [13]. Mass spectra

were recorded on Finnigan-MAT 112S mass spectrometer at 70 eV (EI) or 100 eV and *ca.* 0.5 torr methane pressure (CI); the ion source temperature was fixed at 150 °C while the sample inlet temperature was at 20 °C. The mean kinetic energy release was evaluated in the usual way [9].

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