Chemical Ionization Mass Spectra of some Allyl Carbonyl Nitrosyl Iron Derivatives

D. PERUGINI, G. INNORTA*, S. TORRONI and A. FOFFANI

Department of Chemistry 'G. Ciamician', University of Bologna, Via Selmi 2, 40126 Bologna, Italy

(Received October 6, 1987)

Abstract

Allylic iron carbonyls were studied by chemical ionization mass spectrometry using some protonating and non protonating reagent gases. The presence of specific fragmentation reactions gives information on the possible protonation site; some reactions, unknown in the condensed phase, are described.

Introduction

Following our investigation on the chemical ionization mass spectra of organometallic compounds [1], we present the results on some allylic iron derivatives. Once again in the mass spectrometer ion source, reactions of the substrates with the reagent gas system have been found, which resemble the behaviour in the condensed phase or which are new.

The idea that CI mass spectrometry could give useful hints for the synthesis of new derivatives seems to be reinforced.

*Author to whom correspondence should be addressed.

Electron Impact Mass Spectra

As a basic feature, in the mass spectra of these compounds of general formula $[(\eta^3\text{-}C_3H_4X)Fe(CO)(NO)L]$ (**I**: X = H, L = PPh_3; **II**: X = 1-CH_3, L = PPh_3; **III**: X = H, L = $P(OPh)_3$; **IV**: X = H, L = $P(OC_2H_5)_3$; **V**: X = H, L = $P(OCH_2)_3CC_2H_5$) the molecular ions have a rather low relative intensity (Tables I–V).

TABLE I. Mass Spectra of $(\eta^3\text{-}C_3H_5)Fe(CO)(NO)(PPh_3)$

m/z	EI	H_2	CH_4	i-Bu	Assignment
418		1.5	6.3	9.2	$[MH]^+$
417	3.3	5.7	5.6	9.1	$[M]^+$
390		6.1	22.6	17.3	$[MH-CO]^+$
389	100.0	100.0	100.0	100.0	$[M-CO]^+$
360		0.3		1.5	$[MH-CO-NO]^+$
359	46.6	26.6	12.7	5.1	$[M-CO-NO]^+$
349			0.4	0.9	$[MH-CO-All]^+$
348	53.3	22.0	88.4	5.0	$[M-CO-All]^+$
318	45.0	17.5		3.6	$[FeL]^+$
317	100.0	26.1	27.2	4.2	$[FeL-H]^+$

TABLE II. Mass Spectra of $(\eta^3\text{-}1\text{-}CH_3C_3H_4)Fe(CO)(NO)(PPh_3)$

m/z	EI	H_2	CH_4	i-Bu	Assignment
432		0.5		10.2	$[MH]^+$
431	4.8	1.0		8.7	$[M]^+$
404			70.1	12.8	$[MH-CO]^+$
403	100.0	100.0	100.0	100.0	$[M-CO]^+$
373	52.0	45.0	13.4	3.1	$[M-CO-NO]^+$
348	20.7	27.0	88.7	6.0	$[M-CO-All]^+$
319			88.7	47.2	$[FeLH]^+$
318	35.4	30.1	100.0		$[FeL]^+$
317	68.7	60.3			$[FeL-H]^+$

0020-1693/88/$3.50

TABLE III. Mass Spectra of $(\eta^3\text{-}C_3H_5)Fe(CO)(NO)[P(OPh)_3]$

m/z	EI	H_2	CH_4	i-Bu	Assignment
465	1.0	1.0	1.0	2.4	$[M]^+$
437	100.0	100.0	100.0	100.0	$[M-CO]^+$
407	17.5	19.2	12.5	4.1	$[M-CO-NO]^+$
396	34.7	38.5	80.7	22.6	$[M-CO-All]^+$
372			3.2	8.7	$[M-OPh]^+$
366	78.4	50.5			$[FeL]^+$
365	91.3	50.5			$[FeL-H]^+$
344			93.0	22.6	$[M-CO-OPh]^+$

TABLE IV. Mass Spectra of $(\eta^3\text{-}C_3H_5)Fe(CO)(NO)[P(OC_2H_5)_3]$

m/z	EI	H_2	CH_4	i-Bu	Assignment
322		2.0	3.9	1.5	$[MH]^+$
321	3.9	7.9	6.1	17.0	$[M]^+$
294			12.0	16.2	$[MH-CO]^+$
293	77.8	100.0	100.0	100.0	$[M-CO]^+$
276		5.7	8.3	21.7	$[M-OC_2H_5]^+$
263	24.4	13.1	8.8	1.1	$[M-CO-NO]^+$
252	100.0	55.3	55.0	14.7	$[M-CO-All]^+$
248	12.2	18.4	89.0	11.0	$[M-CO-OC_2H_5]^+$

TABLE V. Mass Spectra of $(\eta^3\text{-}C_3H_5)Fe(CO)(NO)[P(OCH_2)_3CEt]$

m/z	EI	H_2	CH_4	i-Bu	Assignment
318		0.3	1.9	12.8	$[MH]^+$
317	5.0	6.7	5.0	16.0	$[M]^+$
290		3.0	51.7	22.0	$[MH-CO]^+$
289	100.0	100.0	100.0	100.0	$[M-CO]^+$
259	56.0	44.7	17.0	5.6	$[M-CO-NO]^+$
248	16.2	19.5	24.0	9.8	$[M-CO-All]^+$
217	62.7	46.0	17.1	5.7	$[FeL-H]^+$

These ions fragment only by loss of the carbonyl group; indeed the M–CO bond is the weakest and the loss of the allyl group is competitive, with respect to the loss of CO, only when the allyl is η^1 bonded [2].

As is well known, the coordinated phosphynic ligand doesn't show any fragmentation except when $L = P(OC_2H_5)_3$ which easily loses the $\cdot OC_2H_5$ group [3].

Chemical Ionization Mass Spectra

As shown in Tables I–V ions formed both by charge exchange and by proton transfer reactions are observed when protonating gases are used. Although chemical ionization is a soft ionization technique leading to a reduced fragmentation, these compounds show M^+ and $[MH]^+$ ions of low relative abundance while the $[M-CO]^+$ ion remains the base peak; this confirms that loss of the CO group requires a very low activation energy.

The existence of specific fragmentation pathways induced by protonation allows us to hypothesize about the site of proton attack. In fact, as the relative abundance of ions obtained by loss of allylic groups is lower in chemical ionization than in electron impact conditions, it may be inferred that the allylic ligand is not a site of proton attack; otherwise after the proton attack followed by a charge transfer to the metal, the loss of the ligand as the stable neutral molecule (C_3H_6) should be very likely.

Compound **III** shows an interesting feature: there is no evidence of the presence of a protonated molecule but a new fragmentation is observed leading to the loss of the $\cdot OC_6H_5$ fragment from the molecular ion. In this case, the site of proton attack should be

TABLE VI. Mass Spectra of $(\eta^3\text{-}C_3H_5)Fe(CO)(NO)L$ using NO as Reagent Gas

Ion	L = PPh_3	L = $P(OPh)_3$	L = $P(OC_2H_5)_3$	L = $P(OCH_2)_3CEt$
All-$Fe(NO)_2L^+$	1.5	36.0	39.0	47.6
$Fe(NO)_3L^+$			5.6	12.5
All-$Fe(NO)L^+$	100.0	100.0	100.0	100.0
$Fe(NO)_2L^+$	2.9	20.5	18.7	5.3
All-$Fe\text{-}L^+$	6.5		3.6	
$Fe(NO)L^+$	4.2	4.0	15.0	15.0

the oxygen atom of the phosphynic ligand; a very fast and unique fragmentation reaction then occurs, leading to loss of the phenol while the charge remains on the metal containing fragment.

A similar fragmentation pathway is also likely in compound **IV**, since the fragments obtained by loss of $(\cdot OC_2H_5)$ are of higher relative intensity; nevertheless, the protonated molecule and its fragments are well represented.

The other compounds do not show any clear reaction induced by the proton transfer.

We can rationalize these observations on admitting that the protonation site changes with the bonding properties of the phosphynic ligands. The ionization potentials of free phosphynic ligands $P(OC_6H_5)_3$, $P(OC_2H_5)_3$ and $P(C_6H_5)_3$ are 8.60, 8.40 and 8.20 respectively [4]; the electronic density on the iron atom when bonded to phosphynic ligand should follow the same trend, so that the proton attack to the metal center should be favoured by a decrease of the ionization energy of the ligand. This agrees with our observation on the specific proton attack to the ligand in compound **III**, to the ligand and metal center in compound **IV** and to the metal center in compounds **I**, **II** and **V**. To our knowledge, this is the first example where, with reasonable confidence, the change of the site of proton attack to a compound by changing a ligand is displayed.

Lastly we can observe that, except for **III**, the proton affinity of these compounds is higher than 857 kJ/mol since the protonation reaction occurs.

When ammonia is used as the reagent gas, apart from the well known addition reactions of $(NH_4)^+$ ion (compounds **III** and **IV**), interesting substitution reactions are observed. Ions of the type $[(C_3H_5)Fe(NO)(NH_3)L]^+$ are obtained by CO substitution reactions; these ions also seem very reactive towards a further substitution of the allyl group by ammonia; in fact, often, ions such as $[Fe(NO)(NH_3)_2L]^+$ are observed with high relative abundance.

The above ions should derive from substitution reactions since, in some cases, we do not observe the NH_4^+ addition ions which could give the same ions by fragmentation. It seems also that the allyl substitution by NH_3 becomes likely only after CO substitution; this behaviour resembles the reactivity in the condensed phase.

It is well known [5] that both CO and the allylic ligands are easily substituted by V group ligands, and that CO is replaced first; moreover, the ammonia ligand favours the subsequent substitution of the allylic group, which is perturbated towards a more weak structure in the presence of strongly electron withdrawing ligands [6].

When carbon monoxide or ethylene are used as the reagent gas, only charge transfer reaction is observed; substitution of allyl by the hydrocarbon ligand as well as the addition of carbon monoxide, do not seem to be possible reactions.

However, an interesting reaction is observed when nitric oxide is used as the reagent gas; as shown in Table VI, the molecular ion is absent while an ion due to CO ligand exchange reaction by NO is well represented; this ion, then, should be fairly stable considering the low relative abundance of the respective molecular ion obtained by different ionization techniques.

A search of metastable ions shows that the base peak $[(C_3H_5)Fe(NO)L]^+$ is not due to charge exchange reaction followed by CO loss, but is generated by the reaction

$$[(C_3H_5)Fe(NO)_2L]^+ \longrightarrow [(C_3H_5)Fe(NO)L]^+ + NO$$

A similar exchange reaction is known [7] between these compounds and $NOPF_6$ in the condensed phase.

Experimental

The iron complexes were prepared by published procedures [8]. Mass spectra were obtained with a Finnigan-Mat 112S Mass Spectrometer equipped with a chemical ionization ion source.

The reactant gases were reagent grade products and their pressure in the ionization box was kept between 0.05 and 0.1 torr; significant variation of the mass spectra was not observed over this pressure range. The ion source temperature was 170 °C.

Acknowledgement

This work was supported financially by the Italian Ministero della Pubblica Istruzione.

References

1 D. Perugini, G. Innorta, S. Torroni and A. Foffani, *J. Organomet. Chem., 308,* 167 (1986); *Inorg. Chim. Acta, 133,* 243 (1987).
2 G. Innorta, S. Torroni, A. Foffani and D. Perugini, *Inorg. Chim. Acta, 112,* 183 (1985).
3 S. Torroni, G. Innorta, A. Foffani and G. Distefano, *J. Organomet. Chem., 65,* 209 (1974).
4 G. Distefano, G. Innorta, S. Pignataro and A. Foffani, *J. Organomet. Chem., 14,* 165 (1968); J. Muller and K. Fenderl, *19,* 123 (1969).
5 H. C. Volger and K. Vriege, *J. Organomet. Chem., 6,* 297 (1966).
6 K. C. Ramey and G. L. Statton, *J. Am. Chem. Soc., 88,* 4387 (1966).
7 P. K. Baker and N. G. Connelly, *J. Organomet. Chem., 178,* C33 (1979).
8 G. Cardaci and A. Foffani, *J. Chem. Soc., Dalton Trans.,* 1808 (1974).