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Mass Spectroscopic Study of π-Cyclopentadienyl Nickel Acetylene Complexes

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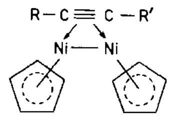
The mass spectra of several bis(nickel cyclopentadienyl)acetylene complexes ($Cp_2Ni_2RC_2R'$) are discussed. The major processes of decomposition of the parent ions can be satisfactorily described in terms of: a) loss of the alkyne ligand; b) loss of a cyclopentadiene molecule; c) loss of a NiCp fragment; d) fragmentation of the R groups. The effect of the R and R' groups is taken into account to explain the different breakdown pathways.

Introduction

The application of mass spectroscopy to the problems of structure and bonding in organometallic compounds has been widely developed in the last few years. Several reviews on this field have recently appeared[1].

As a part of a study on the reactivity of the acetylenic derivatives of metal carbonyls, this paper describes the fragmentation pattern of some $Cp_2Ni_2RC_2R'$ complexes, whose structure has been already determined[2]:



In this series only the mass spectrum of $Cp_2Ni_2HC_2CF_3$ has been reported[3]. By comparison, a detailed spectrum of $Cp_2Ni_2(CO)_2$ is also described: its major features have previously appeared[4].

We have recently reported the interesting features of the reactivity and of the IR and NMR spectroscopic properties of the above compounds, regarding the nature of the R and R' groups[5].

So it is possible to make a complete comparison with the analogous cobalt complexes of general formula $Co_2(CO)_6RC_2R'$ which exhibit an alkyne depending behaviour on the CO[6] and acetylene[7] substitution reaction, IR[8] and mass[9] spectroscopic properties.

Results and Discussion

$Cp_2Ni_2(CO)_2$ (I)

The main peaks are similar to those previously reported[4]. The different intensities are probably due to the different values of the ionizing energy.

As expected according to the very different lability of the CO and of the π-cyclopentadienyl group[1], the parent ion simply loses the two CO's to give the very intense ion $Ni_2Cp_2^+$ (246). It decomposes by loss either of a cyclopentadiene molecule to give $Ni_2C_5H_4^+$ (180) or of a nickel atom, giving $NiCp_2^+$ (188) as the base peak. Other ions containing two nickel atoms are $Ni_2C_{10}H_8^+$ (121), $Ni_2C_3H_2^+$ (154), $Ni_2C_2H^+$ (141), all presumably derived from the intense $Ni_2Cp_2^+$ and $Ni_2C_5H_4^+$ by loss of an hydrogen molecule or of hydrocarbon fragments.

$NiCp_2^+$ shows a decomposition pattern very similar to that of nickelocene[10] giving $NiC_{10}H_8^+$ (186), $NiCp^+$ (123), $NiC_3H_3^+$ (97), Ni^+ (58), $C_5H_5^+$ (65), $C_3H_3^+$ (39) as the most prominent ions.

Detailed data on the spectrum are given in Table I.

$Cp_2Ni_2C_2(CH_3)_2$ (II)

From the data reported in Table I it can be observed that this spectrum shows very similar features to those of the spectrum of (I). This is due to the fact that the parent ion decomposes only by loss of the alkyne ligand, to give $Ni_2Cp_2^+$ and, successively, $NiCp_2^+$ and $NiCp^+$. Their fragmentations, similar to those reported in (I), give the other ions in the spectrum.

$Cp_2Ni_2C_2H_2$ (III) and $Cp_2Ni_2HC_2CH_3$ (IV)

Two different paths appear to be competitive in the decomposition of both parent ions: the loss of the acetylene and the loss of a cyclopentadiene fragment to give $Ni_2CpC_2H^+$ (206) and $Ni_2CpC_2CH_3^+$ (220), respectively. The absence of these ions in the spectrum of (I) confirms that they are not produced by fragmentation of $Ni_2Cp_2^+$. Furthermore, both paths are supported by the presence of the relevant metastable peaks (see Table II).

The simple elimination of $C_5H_5\cdot$ radical is not observed: the driving force of this decomposition seems to be the great stability of the cyclopentadiene molecule, formed presumably by abstraction of an hydrogen atom from the alkyne.

The fragmentation of $Ni_2Cp_2^+$, $NiCp_2^+$ and $NiCp^+$ give rise to the same pattern as with (I) and (II).

An interesting difference is the remarkable intensities of $Ni_2C_2H^+$ (141) in the spectrum of (III) and of $Ni_2C_3H_3^+$ (155) in the spectrum of (IV). These ions

TABLE I. Mass Spectra of $Cp_2Ni_2RC_2R'$ Complexes.

m/e	Ion	Relative Intensity								
		I	II	III	IV	V	VI	VII	VIII	IX
424	$Ni_2Cp_2C_2(C_6H_5)_2^+$							37		
408	$Ni_2Cp_2C_2(CF_3)_2^+$					8				
389	$Ni_2Cp_2C_4F_5^+$					4				
388	$Ni_2Cp_2C_2(COOCH_3)_2^+$						32			
362	$Ni_2Cp_2CH_3C_2C_6H_5^+$								28	
360	$Ni_2Cp_2C_2OCH_3(COOCH_3)^+$						1			
357	$Ni_2Cp_2C_2CO(COOCH_3)^+$						1			
348	$Ni_2Cp_2HC_2C_6H_5^+$									39
330	$Ni_2Cp_2HC_2COOCH_3^+$						3			
329	$Ni_2Cp_2C_2COOCH_3^+$						2			
302	$Ni_2Cp_2(CO)_2^+$	12								
301	$NiCpC_2(C_6H_5)_2^+$							4		
300	$Ni_2Cp_2C_2(CH_3)_2^+$		20							
286	$Ni_2Cp_2HC_2CH_3^+$				19					
285	$NiCpC_4F_6^+$					3				
282	$Ni_2CpC_2C_6H_5^+$									3
274	$Ni_2Cp_2CO^+$	4								
272	$Ni_2Cp_2C_2H_2^+$			35			4			
271	$Ni_2Cp_2C_2H^+$						1			
270	$Ni_2Cp_2C_2^+$						3			
266	$NiCpC_4F_5^+$					5				
265	$NiCpC_2(COOCH_3)_2^+$ or $Ni_2Cp_2F^+$					9	3			
264	$Ni_2C_9H_8O_2^+$						6			
246	$Ni_2Cp_2^+$	48	46	65	44	27	90	100	77	70
245	$Ni_2C_{10}H_9^+$			4			3			
244	$Ni_2C_{10}H_8^+$	4		2		2	4	3	3	2
239	$C_{19}H_{11}^+$							4		
	$NiCpC_2CH_3C_6H_5^+$								4	
236	$NiC_{14}H_{10}^+$							5		
224	$NiCpC_2C_6H_5^+$									3
223	$NiC_{13}H_9^+$									3
220	$Ni_2CpC_2CH_3^+$				3					
219	$Ni_2C_8H_7^+$			1	2	1	1	2	1	
218	$Ni_2C_8H_6^+$	1		1	3	1	1		1	
217	$Ni_2C_8H_5^+$							1	3	9
215	$Ni_2C_8H_3^+$							3		
207	$NiC_9H_9O_2^+$						3			
206	$Ni_2CpC_2H^+$			10			10			
200	$Ni_2C_5H_5F^+$					1				
188	$NiCp_2^+$	100	100	100	100	86	100	90	100	64
186	$NiC_{10}H_8^+$	8		3	4	4	4	3	4	5
181	$Ni_2C_5H_5^+$	2	3		4	1	6		1	1
180	$Ni_2C_5H_4^+$	3	5	14	7	3	8	2	3	3
178	$C_{14}H_{10}^+$							50	2	
177	$C_{14}H_9^+$							5		
176	$C_{14}H_8^+$							10		
175	$NiC_8H_5O^+$						3			
173	$NiC_9H_7^+$	2							8	
172	$NiC_9H_6^+$								3	
169	$C_9H_4F_3^+$					4				
165	$C_{13}H_9^+$							5	3	9
162	$NiC_8H_8^+$		3							
160	$NiC_8H_6^+$	2	2							
155	$Ni_2C_3H_3^+$	2	7		13	2			2	
154	$Ni_2C_3H_2^+$	5	9	5	12	4	3		5	2
153	$Ni_2C_3H^+$	2	3	3	6		3		2	1
152	$C_{12}H_8^+$ or $C_9H_{12}O_2^+$					2		8		

TABLE I. (Cont.)

m/e	Ion	Relative Intensity								
		I	II	III	IV	V	VI	VII	VIII	IX
151	$C_{12}H_7^+$ or $C_9H_{11}O_2^+$						1	6		
	NiC_3F_3					4				
150	$C_{12}H_6^+$, $C_9H_4F_2^+$ or $C_9H_{10}O_2^+$					1	3	3		
149	$C_9H_9O_2^+$						6			
148	$C_9H_8O_2^+$						8			
147	$C_9H_7O_2^+$						16			
144	$C_8H_3F_3^+$					4				
143	$C_4F_5^+$					4				
142	$C_8H_8F_2^+$					7				
141	$C_{11}H_9^+$							3		
	$Ni_2C_2H^+$	7	17	40	27	6	18	5	9	7
139	$C_{11}H_7^+$ or $C_8H_5F_2^+$					3		4		
136	$NiC_6H_6^+$	1	4		9					
134	$NiC_6H_4^+$							3		
132	$NiC_3F_2^+$					7				
130	$C_{10}H_{10}^+$	5		1			1			21
129	$C_{10}H_9^+$	9	6	3	6	3	2	3		32
	Ni_2CH^+		2		5					
128	$C_{10}H_8^+$	7		3	6	3	2	4		19
127	$C_{10}H_7^+$	2								9
124	$NiC_5H_6^+$		3				4			
123	$NiCp^+$	45	100	37	83	100	56	45	70	27
122	$C_8H_7F^+$					4				
121	$NiC_5H_3^+$	2				2	2			
120	$C_8H_5F^+$ or $C_8H_8O^+$					5	2			
117	$C_9H_9^+$								3	
	Ni_2H^+		3		3		1			
116	$C_9H_8^+$								19	
	Ni_2^+	2	4		7		2		2	1
115	$C_9H_7^+$	6						3	54	23
112	$NiC_4H_6^+$		10							
110	$NiC_4H_4^+$ or NiC_3O^+		3				7			
104	$C_8H_8^+$							2		7
103	$C_8H_7^+$									21
102	$C_8H_6^+$	1						2		100
101	$C_8H_5^+$					3				8
100	$C_8H_4^+$									8
98	$C_8H_2^+$									8
	$NiC_3H_4^+$				6					
97	$NiC_3H_3^+$	10	29	8	26	20	8	5	8	4
96	$NiC_3H_2^+$ or NiF_2^+	5	12	6	16	8	4	2	4	2
95	NiC_3H^+	2	3	2	4	2	1			
91	$C_7H_7^+$								5	3
89	$C_7H_5^+$						11	6	7	3
87	$C_7H_3^+$							1		4
85	$NiC_2H_3^+$		3							
84	$C_5H_5F^+$					3				
	$NiC_2H_2^+$	2	6							
78	$C_6H_6^+$	1						3		14
77	$C_6H_5^+$	1	2					3		9
76	$C_6H_4^+$		1					8		86
75	$C_6H_3^+$							3		22
74	$C_6H_2^+$							3		31
73	C_6H^+									5
69	CF_3^+					3				
66	$C_5H_6^+$	9	4	17	6		4	6	4	20
65	$C_5H_5^+$	7	6	10	8	7	4	5	5	25

TABLE I. (Cont.)

m/e	Ion	Relative Intensity								
		I	II	III	IV	V	VI	VII	VIII	IX
64	$C_5H_4^+$								1	5
63	$C_5H_3^+$	3	3	4	7	3	2	4	6	23
62	$C_5H_2^+$	1		2					3	12
61	C_5H^+									8
58	Ni^+	15	62	20	56	31	17	20	34	15
54	$C_4H_6^+$		4							
53	$C_4H_5^+$		6					1		
52	$C_4H_4^+$				4			1		19
51	$C_4H_3^+$	1	6					4	3	37
50	$C_4H_2^+$	1	7		4			3	2	38
41	$C_3H_5^+$ or C_2HO^+	3					1	7		6
40	$C_3H_4^+$	3		5	9		2	2		7
39	$C_3H_3^+$	10	32	14	40	16	10	8	8	30
38	$C_3H_2^+$	2	6	3	10		1			8
37	C_3H^+			2	8					6

TABLE II. Metastable Ions.

Complex	Observed (m/c)	Calculated (m/e)	Process
I	144	143.7	$Ni_2Cp_2^+ \rightarrow NiCp_2^+ + Ni$
	80.5	80.5	$NiCp_2^+ \rightarrow NiCp^+ + Cp\cdot$
	76.5	76.5	$NiCp^+ \rightarrow NiC_3H_3^+ + C_2H_2$
II	144	143.7	$Ni_2Cp_2^+ \rightarrow NiCp_2^+ + Ni$
	81	80.5	$NiCp_2^+ \rightarrow NiCp^+ + Cp\cdot$
III	222.5	222.5	$M^+ \rightarrow Ni_2Cp_2^+ + C_2H_2$
	156.5	156.0	$M^+ \rightarrow Ni_2CpC_2H^+ + C_5H_6$
	144	143.7	$Ni_2Cp_2^+ \rightarrow NiCp_2^+ + Ni$
	80.5	80.5	$NiCp_2^+ \rightarrow NiCp^+ + Cp\cdot$
	76.5	76.5	$NiCp^+ \rightarrow NiC_3H_3^+ + C_2H_2$
IV	211	211.6	$M^+ \rightarrow Ni_2Cp_2^+ + C_3H_4$
	144	143.7	$Ni_2Cp_2^+ \rightarrow NiCp_2^+ + Ni$
	81	80.5	$NiCp_2^+ \rightarrow NiCp^+ + Cp\cdot$
V	370	370.9	$M^+ \rightarrow Ni_2Cp_2C_4F_5^+ + F\cdot$
	148	148.3	$M^+ \rightarrow Ni_2Cp_2^+ + C_4F_6$
	80.5	80.5	$NiCp_2^+ \rightarrow NiCp^+ + Cp\cdot$
	76.5	76.5	$NiCp^+ \rightarrow NiC_3H_3^+ + C_2H_2$
	27.5	27.3	$NiCp^+ \rightarrow Ni^+ + Cp\cdot$
VI	335	334.0	$M^+ \rightarrow Ni_2Cp_2C_2OCH_3(COOCH_3)^+ + CO$
	281	280.7	$M^+ \rightarrow Ni_2Cp_2C_2HCOOCH_3^+ + COOCH_2\cdot$
	144	143.7	$Ni_2Cp_2^+ \rightarrow NiCp_2^+ + Ni$
VII	144	143.7	$Ni_2Cp_2^+ \rightarrow NiCp_2^+ + Ni$
	76.5	76.5	$NiCp^+ \rightarrow NiC_3H_3^+ + C_2H_2$
	27.5	27.3	$NiCp^+ \rightarrow Ni^+ + Cp\cdot$
VIII	167.5	167.2	$M^+ \rightarrow Ni_2Cp_2^+ + C_9H_8$
	144	143.7	$Ni_2Cp_2^+ \rightarrow NiCp_2^+ + Ni$
IX	28	27.3	$NiCp^+ \rightarrow Ni^+ + Cp\cdot$

can be considered in part as fragments of $Ni_2Cp_2^+$, but mainly as the products of the $C_5H_5\cdot$ ejection from $Ni_2CpC_2H^+$ and $Ni_2CpC_2CH_3^+$ respectively, which are typical ions of these spectra.

$Cp_2Ni_2C_2(CF_3)_2$ (V)

The parent ion shows primarily the usual loss of the alkyne. It can also lose successively F· and NiCp·, or NiCp· and F· in reverse order, or CpNiF in a sole step, giving rise to $Ni_2Cp_2C_4F_5^+$ (389), $NiCpC_4F_6^+$ (285) and $NiCpC_4F_5^+$ (266).

The spectrum exhibits also other nickel–fluorine ions (*e.g.* $Ni_2Cp_2F^+$ (265), NiF_2^+ (96) *etc.*), probably due to the migration of F on Ni, as usual feature of fluoro-organometallic compounds. A large number of fluoro hydrocarbon ions is present (*e.g.* $C_9H_4F_3^+$ (169), $C_8H_3F_3^+$ (144), $C_8H_5F^+$ (120) *etc.*). They appear to be the result of a condensation of the alkyne on the Cp ligand during the fragmentation; the nickel-containing ions as (285) and (266) could present such condensed structure.

$Cp_2Ni_2C_2(COOCH_3)_2$ (VI)

The main path of the decomposition of the parent ion is the dissociation of the acetylene moiety to give the very strong ion $Ni_2Cp_2^+$. This ion follows probably the same breakdown pattern reported in the previous spectra, giving rise in particular to $NiCp_2^+$, $NiCp^+$, $Ni_2C_5H_4^+$, $NiC_3H_3^+$ *etc.* Minor paths regard the fragmentation on the ester groups of the alkyne ligand. This breakdown was reported in some detail in the case of $Fe_2(CO)_6C_4(COOCH_3)_4$[11] and $Co_3(CO)_9CCOOCH_3$[9] and implies the ejection of a CO molecule, with migration of a methoxyl group, and the elimination of OCH_2 or of $COOCH_2$ with the transfer of an hydrogen atom. In this way probably weak ions as $Ni_2Cp_2C_2OCH_3(COOCH_3)^+$ (360), $Ni_2Cp_2C_2CO(COOCH_3)^+$ (357), $Ni_2Cp_2C_2HCOOCH_3^+$ (330), $Ni_2Cp_2C_2H_2^+$ (272) are obtained.

The spectrum shows many other examples of this kind of fragmentation. The mass of several ions differs from that of others by 28, 30, 31, 57, 58, indicating losses of CO, OCH_2, OCH_3, $COOCH_2$ and $COOCH_3$ respectively.

The parent ion can lose also the CpNi· radical giving $CpNiC_2(COOCH_3)_2^+$ (265), but not a cyclopentadiene molecule: this probably requires an hydrogen atom on the acetylene moiety as observed in the spectra of (III) and (IV). This condition presumably is satisfied by the (330) and (272) ions because of the hydrogen transfer: so the following transition could probably occur;

$$\underset{(m/e\ 330)}{Cp_2Ni_2C_2HCOOCH_3^+} \xrightarrow{-C_5H_6} \underset{(m/e\ 264)}{CpNi_2C_2COOCH_3^+}$$

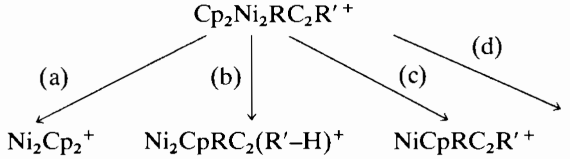
$$\underset{(m/e\ 272)}{Cp_2Ni_2C_2H_2^+} \xrightarrow{-C_5H_6} \underset{(m/e\ 206)}{CpNi_2C_2H^+} \xrightarrow{-C_5H_6} \underset{(m/e\ 140)}{C_2Ni_2^+}$$

$Cp_2Ni_2C_2(C_6H_5)_2$ (VII), $Cp_2Ni_2CH_3C_2C_6H_5$ (VIII) and $Cp_2Ni_2HC_2C_6H_5$ (IX)

The great stability of the acetylenic ligands characterizes these spectra. It is suggested by the large intensities of the relevant alkyne ions and of other organic fragments, most of which are probably originated from the condensation process between the alkyne and the cyclopentadienyl group. (VII) and (VIII) show also the (alkyne)Ni^+, which can derive directly from the parent ion by loss of a $NiCp_2$ molecule.

In all three cases, of course, the main decomposition path of the parent ion is the elimination of the alkyne; minor paths are in (VII) and (VIII) the ejection of an NiCp· radical and in (IX) the loss of C_5H_6 and NiC_5H_6. This confirms that the presence of an acetylenic hydrogen is in part responsible for the fragmentation pathways of the parent ion.

The fragmentation of the parent ions in the $Cp_2Ni_2RC_2R'$ complexes could be rationalised in terms of different pathways, as shown in the following scheme:



Scheme 1

They can be described as: a) loss of the alkyne; b) loss of a cyclopentadiene molecule; c) dissociation of $NiC_5H_5\cdot$ and/or NiC_5H_6 fragments; d) fragmentation of the R and R' groups. In many cases the appearance of the relevant metastable ions supports these mechanisms.

Path (a) is the most important, as confirmed by the intensity of the $Ni_2Cp_2^+$ ion, which is one of the most prominent in the spectra. All the compounds follow this mechanism, which agrees with their chemical reactivity, as reported elsewhere[5]. In effect the possibility to substitute the acetylenic ligand is comparable with the facility to dissociate the same ligand in the ionizing process.

The other mechanisms are much less important than the previous one. Path (b) is followed only by (III), (IV) and (IX). As discussed previously the presence of an acetylenic hydrogen is required to dissociate Cp as cyclopentadiene molecule, but it is not sufficient: *e.g.*, $Cp_2Ni_2HC_2CF_3$ is reported[3] to follow the mechanisms (a) and (c) but not (b). The remaining compounds, *i.e.* (V), (VI), (VII), (VIII) together with (IX) show the pathway (c) (in the case of (V) the fragment lost is CpNiF instead of C_5H_6Ni).

This behaviour can be tentatively rationalised in terms of the electron attracting power of the R and R′ groups: the complexes with the less electronegative groups, like H and CH_3, lose preferably the cyclopentadiene fragment, whereas with the most electron attracting groups (C_6H_5, $COOCH_3$, CF_3) cyclopentadienylmetal is the lost fragment. The results are of course inadequate to draw some definite conclusions, nevertheless it is noteworthy that the decomposition of the parent ions of this series of complexes depends in some way on the properties of the R and R′ groups, as occurs with regard to their chemical reactivity[5].

Experimental Part

The preparations of the complexes have been described[5].

Mass spectra were obtained with an Hitachi RMU 6H single focusing mass spectrometer, using an ionizing energy of 75ev. Samples were introduced via a direct inlet system.

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