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Mass Spectra of Metal Tropolonates

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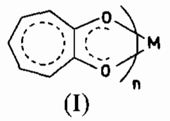
The mass spectra of the complexes MT_n (TH = tropolone; M = Co, Ni, Cu, Zn, Pd; n = 2. M = Al, Ga, In, Sc, Cr, Fe; n = 3) have been investigated. The main decomposition pathways involve loss of T· radicals and CO molecules. For complexes derived from transition metals loss of CO groups leads to cyclopentadienyl metal ions reflecting the ability of such metals to form complexes with unsaturated hydrocarbon ligands. In complexes of type MT_3 successive loss of T· radicals occurs only when M = Ga, In, Cr or Fe. This behaviour is rationalized in terms of the ability of these metals to change oxidation state. The spectrum of the copper complex exhibits several hydrogen-migration reactions.

Introduction

The mass spectrometric study of metal chelates, especially of those derived from β-diketones, has received considerable attention in recent years.[1] On the basis of these studies it has been established that the metal has a pronounced effect on the fragmentation behaviour of metal chelates. Following our studies[2,3] of various types of metal complexes we have now investigated several metal tropolonates of formula (I):



(I)

n = 2; M = Co, Ni, Cu, Zn, Pd
n = 3; M = Al, Ga, In, Sc, Cr, Fe

TABLE I. Ion Abundances[a] for MT_2.

Ion[b]	M in MT_2									
	Co m/e		Ni m/e[c]		Cu m/e		Zn m/e		Pd m/e	
$[MT_2]^+$	301	34(3)[d]	300	40(4)	305	21(1)	306	50(5)	346	35(5)
$[MT_2-H_2O]^+$	–		–		287	1	–		–	
$[MT_2-CO]^+$	273	4	272	5	277	1	278	11	318	1
$[MT_2-H_2O-CO]^+$	–		–		259	1	–		–	
$[MT_2-2CO]^+$	245	1	244	1	249	1	250	1	–	
$[MT_2-C_5H_4O]^+$	–		–		–		226	1	–	
$[MT_2-2CO-C_2H_2]^+$	219	1	218	1	223	1	–		–	
$[MT_2-3CO]^+$	–		216	1	221	1	222	1	262	2
$[MT_2-4CO]^+$	189	1	188	1	–		–		–	
$[MT+H]^+$	–		–		185	11	–		–	
$[MT]^+$	180	30	179	18	184	22	185	29	225	2
$[MT-H]^+$	–		178	1	183	8	–		–	
$[MT-CO]^+$	152	1	151	2	156	9	157	1	197	6
$[MT-HCO]^+$	–		150	1	155	1	–		–	
$[MTH-CO-H_2O]^+$	–		–		139	1	–		–	
$[MT-2CO]^+$	124	10	123	11	128	4	–		169	48
$[MC_5H_4]^+$	123		122		127	3	–		–	
$[MC_3H_3]^+$	98	3	97	4	102	1	–		–	
$[MC_3H_2]^+$	–		96	1	101	1	–		–	
$[M]^+$	59	6	58	4	63	23	64	1	104	6

[a] Abundances are expressed as percentage of the total ion current due to metal-containing ions. All species are corrected for isotopic abundance. [b] Only metal-containing ions are recorded. [c] m/e values are given for the ions containing ^{58}Ni, ^{63}Cu, ^{64}Zn and ^{104}Pd. [d] Figures in brackets indicate abundance of doubly charged species.

TABLE II. Metastable Ions in MT_2.

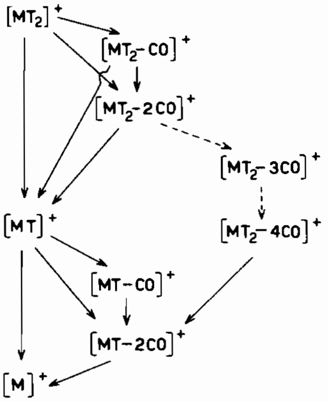
Transition	M in MT_2	m/e Values for Transition	m* Found[a]	m* Calcd.	Neutral Fragment
$[MT_2]^+ \rightarrow [MT_2-H_2O]^+$	Cu	305→287	270	270.06	H_2O
$[MT_2]^+ \rightarrow [MT_2-CO]^+$	Co	301→273	247.5	247.60	CO
	Ni	300→272	246.8	246.61	
	Cu	305→277	251.5	251.57	
	Zn	306→278	252.5	252.56	
$[MT_2]^+ \rightarrow [MT_2-2CO]^+$	Co	301→245	199.5	199.41	2×CO
	Zn	306→250	204	204.24	
$[MT_2]^+ \rightarrow [MT+H]^+$	Cu	305→185	112.1	112.21	[T–H]
$]MT_2]^+ \rightarrow [MT]^+$	Co	301→180	107.6	107.64	T
	Cu	305→184	111.0	111.00	
	Zn	306→185	112	111.85	
$[MT_2]^+ \rightarrow [MT-H]^+$	Cu	305→183	109.7	109.80	[T+H]
$[MT_2-CO]^+ \rightarrow [MT_2-2CO]^+$	Ni	272→244	219.0	218.88	2×CO
$[MT_2-CO]^+ \rightarrow [MT]^+$	Co	273→180	118.5	118.68	C_6H_5O
	Ni	272→179	117.6	117.80	
	Zn	278→185	123	123.11	
$[MT_2-2CO]^+ \rightarrow [MT]^+$	Co	245→180	132.2	132.24	C_5H_5
	Zn	250→185	136.7	136.90	
$[MT_2-4CO]^+ \rightarrow [MT-2CO]^+$	Co	189→124	81.2	81.35	C_5H_5
	Ni	188→123	80.5	80.47	
$[MT]^+ \rightarrow [MT-CO]^+$	Co	180→152	128.3	128.36	CO
	Ni	179→151	127.4	127.37	
	Cu	184→156	132.3	132.26	
$[MT]^+ \rightarrow [MT-2CO]^+$	Co	180→124	85.5	85.42	2×CO
	Ni	179→123	84.5	84.52	
$[MT]^+ \rightarrow [M]^+$	Co	180→ 59	19.3	19.34	T
$[MT-CO]^+ \rightarrow [MT-2CO]^+$	Co	152→124	101.2	101.16	2×CO
	Ni	151→123	100.2	100.19	
$[MT-2CO]^+ \rightarrow [MT-2CO-C_2H_2]^+$	Co	124→ 98	77.9	77.45	C_2H_2
	Ni	123→ 97	76.5	76.50	
$[MT-2CO]^+ \rightarrow [M]^+$	Co	124→ 59	28.0	28.07	C_5H_5
	Ni	123→ 58	27.3	27.35	

[a] For the compounds MT_2 (M = Cu, Ni, Zn) only transitions involving ^{63}Cu, ^{58}Ni, ^{64}Zn are given.

Experimental

All the compounds except ScT_3 (TH = tropolone) have been prepared as described in the literature.[4] The complex ScT_3 has been prepared by heating under reflux a mixture of scandium trichloride (0.1 g, 1 mol equiv.) and tropolone (3 mol equiv.) in ethanol. The crude product was purified by sublimation at 250° C /0.1 mm (Found: C, 61.6; H, 3.6. $C_{21}H_{15}O_6Sc$ requires: C, 61.8; H, 3.7%).

The mass spectra were obtained on a Hitachi RMS-4 spectrometer operating at 80eV, and by use of a direct insertion probe at *ca.* 250° C. Exact mass measurements and enhanced metastable spectra were obtained on an AEI MS-9 instrument at the Physico-Chemical Measurements Unit, Harwell.



Scheme 1

Results and Discussion

The spectra are given in Tables I–VI. Only the metal-containing ions are recorded. The spectra also showed the presence of non-metal species the most abundant of which had m/e values 122, 121, 94, 66, 65 and 39. In all cases, the sum of the intensities of these ions was less than 15% of the total ion-current.

MT_2 Complexes

The spectrum of each MT_2 complex is characterised by an intense molecular ion and exhibits a fairly intense doubly charged molecular ion. In general the molecular ions $[MT_2]^{+\cdot}$ fragment by loss of a ligand radical to give the even-electron ions $[MT]^+$ and by reactions involving elimination of CO groups (Scheme 1*).

The subsequent fragmentation of the ions $[MT]^+$ proceeds by similar routes except for the ion $[ZnT]^+$ which shows little tendency to decompose. The spectra of all compounds show fairly intense ions arising by loss of one CO group from the molecular ion and, except when M = Pd, weak ions due to loss of two such groups. The reactions leading to the ions $[MT_2–nCO]^+$ (n = 1 or 2) are strongly metastable supported in most cases.

TABLE III. Accurate Mass Measurements on Selected Peaks for MT_2.

Compound	Nominal Mass	Determined Mass	Ion Assignment	Calculated Mass
CoT_2	189	189.0710	$C_{10}H_{10}Co$	189.0114
	123[a]	122.9644	C_5H_4Co	122.9645
NiT_2	300	299.9937	$C_{14}H_{10}O_4{}^{58}Ni$	299.9932
	244	244.0001	$C_{12}H_{10}O_2{}^{58}Ni$	244.0034
	122[b]	121.9640	$C_5H_4{}^{57}Ni$	121.9666
CuT_2	287	286.9761	$C_{14}H_8O_3{}^{63}Cu$	286.9768
	277	277.9928	$C_{13}H_{10}O_3{}^{63}Cu$	276.9926
	259	258.9820	$C_{13}H_8O_2{}^{63}Cu$	258.9820
	186	185.9557	$C_7H_5O_2{}^{65}Cu$	185.9567
	185[c]	184.9642	$C_7H_6O_2{}^{63}Cu$	184.9664
	185[c]	184.9487	$C_7H_4O_2{}^{65}Cu$	184.9489
	184	183.9578	$C_7H_5O_2{}^{63}Cu$	183.9585
	183	182.9495	$C_7H_4O_2{}^{63}Cu$	182.9507
	156	155.9635	$C_6H_5O^{63}Cu$	155.9636
	139	138.9611	$C_6H_4{}^{63}Cu$	138.9609
	127	126.9608	$C_5H_4{}^{63}Cu$	126.9608
ZnT_2	250	249.9972	$C_{12}H_{10}O_2{}^{64}Zn$	249.9972
	226	225.9605	$C_9H_6O_3{}^{64}Zn$	225.9608
	157	156.9630	$C_6H_5O^{64}Zn$	156.9631
PdT_2	347	346.9626	$C_{14}H_{10}O_4{}^{105}Pd$	346.9630

[a] Peak overlaps with $[C_6{}^{13}CH_6O_2]^+$. [b] Peak overlaps with $[C_7H_6O_2]^+$. [c] Doublet intensity ratio $[C_7H_6O_2{}^{63}Cu]^+/[C_7H_4O_2{}^{65}Cu]^+ = 2$.

TABLE IV. Ion Abundances[a] for MT_3.

Ion[b]	M in MT_3											
	Al m/e		Ga m/e[c]		In m/e		Sc m/e		Cr m/e		Fe m/e	
$[MT_3]^+$	390	8.0(0.4)[d]	432	2.3	478	3.6(0.5)	408	20.0	415	16.6(1.7)	419	8.7(0.4)
$[MT_2]^+$	269	75.0	311	90.7	357	59.0	287	74.0	294	57.6(0.6)	298	66.0(0.6)
$[MT_2–C_2H_2]^+$	243	0.6		–		–	261	w		–		–
$[MT_2–CO]^+$	241	0.6(0.3)	283	w	329	w	259	1.0	266	0.1	270	1.0
$[MT_2–HCO]^+$	240	0.3		–		–	258	w		–		–
$[MT_2–2CO]^+$		–		–		–		–	238	0.2		–
$[MT_2–2CO–C_2H_2]^+$		–		–		–		–	214	0.5	218	0.1
$[MT_2–3CO]^+$		–		–		–		–	212	0.5	216	0.2
$[MT_2–C_5H_4O]^+$	189	3.4	231	2.2		–	207	2.0		–		–
$[MT_2–C_5H_4O_2]^+$	173	1.8		–		–	191	1.0		–		–
$[MTOH]^+$	165	3.5	207	1.1		–	183	0.6		–		–
$[MT]^+$	148	1.7	190	2.1	236	15.4	166	0.4	173	20.0	177	21.0
$[MT–C_2H_2]^+$		–		–		–		–	147	0.6		–
$[MT–CO]^+$		–	162	0.5	208	0.2		–	145	0.4	149	0.3
$[MT–HCO]^+$		–		–	207	0.2	137	1.0		–		–
$[MT–2CO]^+$		–		–		–		–	117	0.2	121	0.1
$[M]^+$		–	69	3.9	115	18.2		–	52	2.5	56	1.7

[a] Abundances are expressed as percentage of the total ion current due to metal-containing ions. All species are corrected for isotopic abundance. [b] Only metal-containing ions are recorded. [c] m/e values are given for the ions containing ^{69}Ga, ^{115}In, ^{52}Cr and ^{56}Fe. [d] Figures in brackets indicate abundance of doubly charged species.

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* In the fragmentation schemes solid arrows represent processes confirmed by presence of metastable peaks whilst the dotted arrows represent unconfirmed but possible processes.

TABLE V. Metastable Ions in MT_3.

Transition	M in MT_3	m/e Values for Transition	m* Found[a]	m* Calcd.	Neutral Fragment
$[MT_3]^+ \rightarrow [MT_2]^+$	Al	390→269	185.5	185.54	T
	Ga	432→311	224	223.89	
	In	478→357	267	266.66	
	Sc	408→287	202	201.88	
	Cr	415→294	208	208.27	
	Fe	419→298	212	211.94	
$[MT_2]^+ \rightarrow [MT_2\text{–}CO]^+$	Al	269→241	216	215.90	CO
	Ga	311→283	257.5	257.51	
	Sc	287→259	234	233.73	
	Cr	294→266	241	240.66	
	Fe	298→270	245	244.63	
$[MT_2]^+ \rightarrow [MT_2\text{–}HCO]^+$	Al	269→240	214	214.13	HCO
$[MT_2]^+ \rightarrow [MT_2\text{–}2CO]^+$	Ga	294→238	193	192.66	2 × CO
$[MT_2]^+ \rightarrow [MT_2\text{–}C_5H_4O]^+$	Al	269→189	132.8	132.79	C_5H_4O
	Ga	311→231	171.6	171.58	
	Sc	287→207	149.3	149.30	
$[MT_2]^+ \rightarrow [MTOH]^+$	Al	269→165	101.0	101.20	C_7H_4O
	Sc	287→183	116.5	116.68	
$[MT_2]^+ \rightarrow [MT]^+$	Ga	311→190	116	116.08	T
	In	357→236	156	156.00	
	Cr	294→173	101.8	101.79	
	Fe	298→177	105.0	105.13	
$[MT_2\text{–}CO]^+ \rightarrow [MTOH]^+$	Al	241→165	113	112.96	C_6H_4
	Sc	259→183	129	129.30	
$[MT_2\text{–}CO]^+ \rightarrow [MT]^+$	Cr	266→173	112.5	112.51	C_6H_5O
	Fe	270→177	116.0	116.03	
$[MT_2\text{–}2CO]^+ \rightarrow [MT]^+$	Cr	238→173	125.5	125.75	C_5H_5
$[MT_2\text{–}C_5H_4O]^+ \rightarrow [MT]^+$	Ga	231→190	156.3	156.27	C_2HO
$[MTOH]^+ \rightarrow [MT]^+$	Al	165→148	132.8	132.75	OH
	Sc	183→137	102.6	102.56	
$[MT]^+ \rightarrow [MT\text{–}CO]^+$	Ga	190→162	138	138.12	CO
	Cr	173→145	121.5	121.53	
	Fe	177→149	125.5	125.42	
$[MT]^+ \rightarrow [MT\text{–}2CO]^+$	Fe	177→121	82.7	82.71	
$[MT]^+ \rightarrow [M]^+$	Ga	190→ 69	25.1	25.06	T
	In	236→115	56	56.03	
$[MT\text{–}CO]^+ \rightarrow [MT\text{–}2CO]^+$	Fe	149→121	98.2	98.26	CO
$[MT\text{–}2CO]^+ \rightarrow [M]^+$	Fe	121→ 56	25.9	25.91	C_5H_5

[a] For the compounds MT_3 (M = Cr, Fe, Ga, In) only transitions involving ^{52}Cr, ^{56}Fe, ^{69}Ga, ^{115}In are given.

When M = Co or Ni loss of all four CO groups from $[MT_2]^+$ leads to the biscyclopentadienylmetal ion $[M(C_5H_5)_2]^+$ ($[MT_2\text{–}4CO]^+$) which decomposes to the ion $[MC_5H_5]^+$ ($[MT\text{–}2CO]^+$) by the metastable-supported elimination of a cyclopentadienyl radical. The ions $[MC_5H_5]^+$, which are present in high abundance, are also formed by elimination of two CO groups from $[MT]^+$. This process is metastable-supported, occurs when M = Cu or Pd also but is not observed for the zinc compound. The formulation of the ions $[MT_2\text{–}4CO]^+$ and $[MT\text{–}2CO]^+$ as cyclopentadienyl metal ions is supported by their fragmentation behaviour (Scheme 2) which involves processes, such as the metastable-supported elimination of $C_5H_5^{\cdot}$ and C_2H_2 species, analogous to those observed in the spectra of metal cyclopentadienyl compounds.[5] The formation of these ions in all cases except when M = Zn is in accord with the ability of transition metals to form complexes with unsaturated hydrocarbon ligands. However, the zinc

$$\begin{tikzcd}
 & & {[MC_3H_3]^+} \arrow[dr] & \\
{[M(C_5H_5)_2]^+} \arrow[r] & {[M(C_5H_5)]^+} \arrow[ur] \arrow[rr] & & {[M]^+} \\
{([MT_2\text{–}4CO]^+)} & {([MT\text{–}2CO]^+)} & &
\end{tikzcd}$$

Scheme 2

TABLE VI. Accurate Mass Measurements on Selected Peaks for MT_3.

Compound	Nominal Mass	Determined Mass	Ion Assignment	Calculated Mass
AlT_3	390	390.0680	$C_{21}H_{15}O_6Al$	390.0684
	243	243.0240	$C_{12}H_8O_4Al$	243.0237
	241	241.0442	$C_{13}H_{10}O_3Al$	241.0445
	240	240.0365	$C_{13}H_9O_3Al$	240.0366
	189	189.0135	$C_9H_6O_3Al$	189.0183
	173	173.0182	$C_9H_6O_2Al$	173.0183
	165	165.0128	$C_7H_6O_3Al$	165.0132
GaT_3	432	432.0127	$C_{21}H_{15}O_6{}^{69}Ga$	432.0125
	231	230.9591	$C_9H_6O_3{}^{69}Ga$	230.9573
	207	206.9567	$C_7H_6O_3{}^{69}Ga$	206.9573
InT_3	478	477.9908	$C_{21}H_{15}O_6{}^{115}In$	477.9908
	207	207.9370	$C_{16}H_5O^{115}In$	207.9379
ScT_3	408	408.0405	$C_{21}H_{15}O_6Sc$	408.0428
	259	259.0187	$C_{13}H_{10}O_3Sc$	259.0189
	207	206.9877	$C_9H_6O_3Sc$	206.9876
	183	182.9877	$C_7H_6O_3Sc$	182.9876
CrT_3	415	415.0274	$C_{21}H_{15}O_6{}^{52}Cr$	415.0274
	52	51.9408	^{52}Cr	51.9405
FeT_3	270	269.9970	$C_{13}H_{10}O_3{}^{56}Fe$	269.9979
	149[a]	148.9960	$C_{14}H_{10}O_4{}^{56}Fe$[b]	297.9928
	149[a]	148.9682	$C_6H_5O^{56}Fe$	148.9689

[a] Doublet intensity ratio $[C_{14}H_{10}O_4Fe]^{2+}/[C_6H_5OFe]^+ = 2$.
[b] Doubly charged ion.

compound exhibits the ion $[ZnT_2\text{–}3CO]^+$, which might be represented as $[C_6H_5O\cdot Zn\cdot C_5H_5]^+$, in higher abundance than any of the other compounds.

In addition to loss of a ligand radical and CO elimination the molecular ion of the copper compound exhibits several other reactions which involve hydrogen transfer. These reactions lead to the ions $[CuT_2\text{–}H_2O]^+$, $[CuT+H]^+$ and $[CuT\text{–}H]^+$ (Scheme 3). The reaction $[CuT_2]^+ \rightarrow [CuT_2\text{–}H_2O]^+$

$$\begin{tikzcd}
 & {[CuT_2\text{–}H_2O]^+} \arrow[r, dotted] & {[CuT_2\text{–}H_2O\text{–}CO]^+} \\
{[CuT_2]^+} \arrow[ur, bend left] \arrow[r] \arrow[dr, bend right] & {[CuT+H]^+} \arrow[r, dotted] & {[CuTH\text{–}CO\text{–}H_2O]^+} \\
 & {[CuT\text{–}H]^+} \arrow[r, dotted] & {[CuT\text{–}H\text{–}CO]^+}
\end{tikzcd}$$

Scheme 3

is metastable-supported and a grouping of metastable peaks at m/e 109–112 is probably due to the reactions $[CuT_2]^+ \rightarrow [CuT]^+$, $[CuT_2]^+ \rightarrow [CuT+H]^+$ and $[CuT_2]^+ \rightarrow [CuT\text{–}H]^+$. Ions analogous to $[CuT_2\text{–}H_2O]^+$, $[CuT+H]^+$ and $[CuT\text{–}H]^+$ have been observed in the spectra of several copper(II) β-diketonates and ions analogous to $[CuT+H]^+$ have also been observed in the spectra of cobalt(II) and nickel(II) β-diketonates.[1,6,7] The ions $[CuT_2\text{–}H_2O\text{–}CO]^+$, $[CuTH\text{–}CO\text{–}H_2O]^+$ and $[CuT\text{–}H\text{–}CO]^+$ may originate as indicated in Scheme 3.

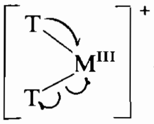
MT_3 Complexes

All the MT_3 complexes show the molecular ion $[MT_3]^{+\cdot}$ which fragments exclusively by loss of a ligand radical to give the even-electron ion $[MT_2]^+$. This ion is present as the most intense ion in all cases. Further fragmentation is dependent on the nature of the metal and reflects primarily its oxidation state characteristics and its ability to form complexes with unsaturated hydrocarbon ligands. When M = Cr, Fe, Ga or In decomposition of $[MT_2]^+$ leads to the ions $[MT]^+$ and $[M]^+$ (Scheme 4).

$$[MT_3]^+ \rightarrow [MT_2]^+ \rightarrow [MT]^+ \rightarrow [M]^+$$

Scheme 4

The presence of these ions in high abundance and the successive loss of odd-electron species from even-electron ions in the spectra of the MT_3 complexes (M = Cr, Fe, Ga or In) can be correlated with the ability of these metals to undergo reduction and the stability of their lower oxidation states. For example the loss of a ligand radical from $[M^{III}T_2]^+$ (M = Ga or In) can be correlated with the stability of oxidation state +I by assuming that this is accompanied by transfer of one electron from the remaining ligand to the metal.



$\rightarrow [M^{I}T]^{+\cdot} + T^{\cdot}$

The very low abundance of $[MT]^+$ and the absence of $[M]^+$ in the spectra of MT_3 (M = Al or Sc) is in accord with the high stability of aluminium(III) and scandium(III).

When M = Ga, In, Cr or Fe the reaction $[MT_2]^+ \rightarrow [MT]^+$ is supported by the appropriate metastable ions. The detection of metastable ions for this reaction does not necessarily suggest that it occurs in a single step *i.e.* by loss of an intact ligand radical. The transition could also proceed stepwise as indicated in the case of the chromium and iron compounds by the presence of the ions $[MT_2\text{–}n\ CO]^+$ (n = 1 or 2) and the occurrence of the reactions given in Scheme 5.

$$\begin{tikzcd}
 & {[MT_2\text{–}CO]^+} \arrow[r, dotted] \arrow[drr, bend right] & {[MT_2\text{–}2CO]^+} \arrow[dr, bend left] & \\
{[MT_2]^+} \arrow[ur, bend left] \arrow[rrr] & & & {[MT]^+}
\end{tikzcd}$$

Scheme 5

For the aluminium and scandium compounds the reaction $[MT_2]^+ \rightarrow [MT]^+$ also occurs stepwise but in these cases the loss of CO from $[MT]^+$ is followed by loss of another even-electron species, C_6H_4. The ion $[MTOH]^+$ thus produced then gives $[MT]^+$ by loss of an $OH^{\cdot}$ radical (Scheme 6).

$$\begin{tikzcd}
& {[MT_2-CO]^+} & \\
{[MT_2]^+} \arrow[ur] \arrow[r] \arrow[dr] & {[MTOH]^+} \arrow[r] & {[MT]^+} \\
& {[MT_2-C_5H_4O]^+} \arrow[r, dashed] & {[MT_2-C_5H_4O_2]^+}
\end{tikzcd}$$

Scheme 6

All these steps, as well as the step $[MT_2]^+ \rightarrow [MTOH]^+$ are metastable supported. Ions analogous to $[MTOH]^+$ have been observed in the spectra of the acetylacetonate complexes of aluminium and scandium.[8] Another interesting metastable-supported reaction of $[MT_2]^+$ (M = Al or Sc) involves loss of 80 mass units to give $[MT_2-C_5H_4O]^+$. This ion is also present in the spectra of the compounds GaT_3 and ZnT_2.

In close similarity to the decomposition of the ions $[MT]^+$ (M = Co, Ni, Cu or Pd) the analogous iron- and chromium-containing ions undergo elimination of one or two CO groups to form the ions $[MT-CO]^+$ and $[MT-2CO]^+$ ($[MC_5H_5]^+$). As in the spectra of $M(C_5H_5)_2$ (M = Cr or Fe), further decomposition of the cyclopentadienylmetal ions leads to the bare metal ions. In contrast when M = Ga or In only one CO group is lost from $[MT]^+$. For these metals the reaction $[MT]^+ \rightarrow [MT-CO]^+$ is weak and the main decomposition pathway is $[MT]^+ \rightarrow [M]^+$.

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