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COMPARATIVE MASS SPECTROMETRIC INVESTIGATION OF TRANSITION METAL POLYMETHYLCYCLOPENTADIENYLCARBONYL COMPLEXES

II ** MASS SPECTRA OF $R_nC_5H_{5-n}Mn(CO)_3$ ($R = CH_3$, $n = 0$–5; $R = t\text{-}C(CH_3)_3$, $n = 1$)

I.R. LYATIFOV *, G.I. GULIEVA

Institute of Inorganic and Physical Chemistry, Azerbaijan SSR Academy of Sciences, 29 Pr.Narimanova, Baku 370143, USSR

E.I. MYSOV, V.N. BABIN and R.B. MATERIKOVA

Institute of Organoelement Compounds, USSR Academy of Sciences, 28 Vavilov St., Moscow, USSR

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Summary

Investigation of π-$(CH_3)_nC_5H_{5-n}Mn(CO)_3$ (Me_n-CpMnT) $n = 0$–5 and t-butyl CpMnT mass spectra showed that Me_nCpMnT molecular ion (M^+) fragmentation occurs by a simpler scheme than that for Me_nCpReT M^+ molecular ions. The reason is that the Mn–Cp and Mn–CO bonds are not as strong as the Re–Cp and Re–CO bonds, and the relative "inertness" (compared to Re) of the Mn atom (ion), coordinated to the methylcyclopentadienyl ligand. Variations of M^+ molecular ion intensity with different values of n are probably due to a complexity of electronic and spatial methyl-carbonyl group interactions in M^+.

In an earlier paper [1] we studied mass spectra of cyclopentadienyl tricarbonylrhenium methyl homologues; the results indicated active Re atom participation in the fragmentation of the associated polymethyl cyclopentadienyl ligand. This resulted in the predominance of cyclopentadienyl ring methyl group dehydrogenation, following elimination of the second CO group from Me_nCpReT molecular ions. Here we describe a mass spectrometric investigation of cyclopentadienyl tricarbonyl manganese (Me_nCpMnT) methyl analogues, revealing the effect of location of the transition metal in the first row on the fragmentation nature of Me_nCpMT molecular ions.

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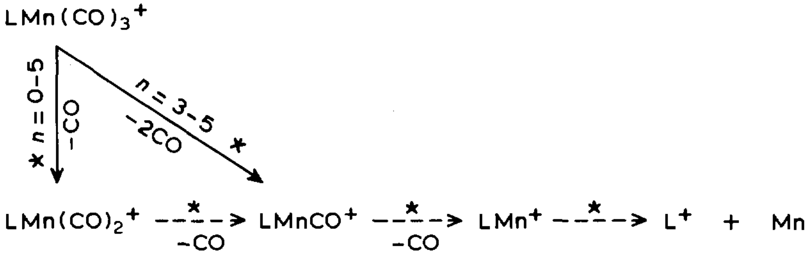
* Author to whom correspondence should be addressed.

** For part I see ref. 1



SCHEME 1. Primary fragmentation of molecular ions of $Me_nC_5H_{5-n}Mn(CO)_3$ (n = 0–5 (70 eV)).

Scheme 1 and Table 1 give (M^+) molecular ion fragmentations in Me_nCpMnT (n = 0–5), and their relative intensities (100% refers to the ion with maximum intensity), respectively. It follows from the data that Me_nCpMnT (M^+) molecular ions decompose by a much simpler scheme than those of Re analogues [1]. Mass spectra are characterized by successive elimination of three CO groups, which is confirmed by metastable peaks and further Mn–Cp bond breaking so that a small amount of Mn-containing ions is observed. Me_nCpMnT molecular ion intensities show these ions are stable to electron impact, their intensities being about a quarter (22–27%) of (M–3CO)$^+$, which is the highest intensity for the whole series. The Me_nCpReT series displayed molecular ion intensities which were 50 to 70% of the maximum [1]. This may be explained by the higher Re–CO bond strength as compared to Mn–CO bond [2–6]. No predicted Me_nCpMnT molecular ion stabilization occurs as a result of the electron-donor methyl group compensating for metal positive charge, with increase in n. On the other hand when the first methyl group appears, molecular ion intensity drops from 27% in CpMnT, to 22% in MeCpMnT. This trend in molecular ion intensity variations could be attributed to spatial methyl-carbonyl group interactions which increase with n in excited molecular ions. Molecular and (M–CO)$^+$ ion intensity considerations of the Me_nCpReT series also lead to this conclusion [1]. However, in the case of Me_nCpMnT we have one additional confirmation, i.e. the metastable peaks show the simultaneous elimination of two CO groups (Table 3) from molecular ions with n = 3–5, where spatial methyl-carbonyl interactions should be more distinct than for MeCpMnT and

TABLE 1

INTENSITIES (at 70 eV) OF Mn-CONTAINING IONS IN THE MASS SPECTRA OF $R_nC_5H_{5-n}Mn(CO)_3$ R = CH_3 n = 0–5, R = t-butyl n = 1

Ion	n						
	5	4	3	2	1	0	Bu^t
M^+	25	22.7	22.2	21	22.3	27.5	16
$(M-CO)^+$	–	1.4	1.6	1.3	1.7	2.3	0.5
$(M-2CO)^+$	16	20.5	22.2	20	22.5	24.1	20
$(M-3CO)^+$	100	100	100	100	100	100	100
$(M-CH_4)^+$	–	–	–	–	–	–	42
Mn^+	45	50	57	56	64	89.6	48
L^+	97	90.9	85.8	77	33	1.5	10

TABLE 2

INTENSITIES (at 70 eV) OF SOME Re-CONTAINING IONS IN THE MASS SPECTRA OF $R_nC_5H_{5-n}Re(CO)_3$) (R = CH_3, n = 0–5; R = t-butyl, n = 1)

Ion	n						
	5	4	3	2	1	0	Bu^t
M^+	50	55	54	52	69	56	100
$(M-CO)^+$	41	39	35	39	27	18	20
$(M-2CO)^+$	17	22	33	80	100	100	81
$(M-2CO-H_2)^+$	100	100	100	100	2	–	35
$(M-3CO)^+$	–	1.5	3	23	54	50	–
$(M-3CO-H_2)^+$	16	21	33	76	31	19	15
$(M-3CO-2H_2)^+$	12	14	26	26	15	6	31
M^{2+}	3	–	4	3	3	3	–
$(M-CO)^{2+}$	–	–	1.5	4	6	3	–
$(M-2CO-H)^{2+}$	–	11	9	–	7	–	–
$(M-3CO)^{2+}$	–	–	–	–	7	12.5	–
$(M-3CO-H_2)^{2+}$	8	5	5	–	7	–	–
$(M-CO-CH_3)^{2+}$	–	–	–	–	–	–	4.5
$(M-2CO-CH_4-H)^{2+}$	–	–	–	–	–	–	11

CpMnT. The spatial effect on molecular ion stability can also be seen from t-butyl cyclopentadienyl tricarbonylmanganese mass spectra where the M^+ molecular ion intensity amounts to 16% of that of $(M-3CO)^+$ (Table 1). In fact, more pronounced spatial interactions should be expected in the mass spectra of Mn complexes under study, since the Mn–CO bond is weaker than Re–CO bond [2–6] and, secondly, intramolecular non-bonding $CH_3 \cdots CO$ contacts in Mn complexes should be shorter (due to short Mn–Cp (1.766 Å) and Mn–CO (1.780 Å) bond lengths as compared with Re–Cp (1.955 Å) and Re–CO (1.903 Å)) bonds [4].

TABLE 3

METASTABLE IONS ($m^\star$) IN THE MASS SPECTRA OF $Me_nC_5H_{5-n}Mn(CO)_3$ (n = 0–5)

Process	$m^\star$					
	$n=5$	4	3	2	1	0
$M^+ \rightarrow (M-CO)^+ + CO$	220.9	207	193.2	179.4	165.6	151.8
$(M-CO)^+ \rightarrow (M-2CO)^+ + CO$	193.2	179.4	165.4	151.8	138.1	–
$M^+ \rightarrow (M-2CO)^+ + 2CO$	173.5	160.1	146.7	133.8	–	–
$(M-2CO)^+ \rightarrow (M-3CO)^+ + CO$	165.6	151.8	138.1	124.4	110.8	97.3
$(M-3CO)^+ \rightarrow Mn + L^+$	95.9	83.2	70.7	58.3	46.6	–
$(M-3CO)^+ \rightarrow Mn^+ + L$	–	–	18.7	–	–	–
$L^+ \rightarrow (L-H_2)^+ + H_2$	–	–	103.	89	75.1	–
$(L-CH_4)^+ \rightarrow (L-CH_4-H_2)^+ + H_2$	–	101	–	–	–	–
$L^+ \rightarrow (L-CH_4)^+ + CH_4$	–	–	77.4	63.8	–	–
$(L-H_2)^+ \rightarrow (L-H_2-C_2H_2) + C_2H_2$	–	–	–	46.4	–	–
$L^+ \rightarrow (L-C_2H_4)^+ + C_2H_4$	84.8	71.5	58.3	–	–	–
$(L-CH_4)^+ \rightarrow (L-CH-C_2H_2)^+ + C_2H_2$	–	59.4	46.4	–	–	–
$L^+ \rightarrow (L-C_3H_6)^+ + C_3H_6$	64	–	–	–	–	–

When examining Me_nCpMnT and Me_nCpReT mass spectra, some differences in their molecular ion fragmentations can be seen. Thus in the earlier paper [1], a great number of Re-containing fragment ions (about 60) was found in Me_nCpReT mass spectra and attributed to the high Re–Cp bond strength and to direct Re atom contribution to Re-bonded polymethylcyclopentadienyl ring fragmentation. Me_nCpMnT mass spectra are their direct opposites, since there are very few (5–6) Mn-containing ions, the most typical fragmentation (beside decarbonylation), $Mn{-}CpMe_n$ bond breaking is confirmed by the metastable peaks (Table 3). The Me_nCpReT mass spectra did not actually show [1] such fragmentation, irrespective of n. Mn^+ and $(Me_nCp)^+$ intensity variations with differing degrees of methyl substitution were as predicted (Table 1); the intensity of the cyclopentadienyl-ligand ion increases with increase in methyl group number and, at the same time, Mn^+ intensity declines. This is as expected because the probability of positive charge localization on the (Me_nCp) ligand increases with the degree of Cp ring substitution, and $(Me_nCp)^+$ intensities increase. Since Mn^+ and $(Me_nCp)^+$ ions are primarily formed as a result of $Mn{-}CpMe_n$ bond breaking in $(M-3CO)^+$ ions, Mn^+ intensity should decrease with decrease in n, and this was found to be the case.

Another difference observed in Mn and Re complex mass spectra is total lack of dehydrogenation in Mn complexes, though it is very typical for Me_nCpReT (Table 2). Peculiar features of the dehydrogenation reaction in the Me_nCpReT mass spectra, when weakly bound CO groups are present in $(M-2CO)^+$ ($n \geqslant 2$), indicate an active Re contribution to coordinated polymethylcyclopentadienyl ligand fragmentation. It follows that the Mn atom, unlike Re, does not affect coordinated polymethylcyclopentadienyl ligand fragmentation during molecular ion fragmentations in Me_nCpMnT complexes. This dissimilar effect of the 1st and 3rd row transition-metal elements upon fragmentation emphasizes various features of Me_nCpMnT and Me_nCpReT molecular ion fragmentations, together with different $M{-}CpMe_n$ and M–CO bond strengths. The third and final difference, is the total lack of doubly-charged Mn-containing ion peaks in all of the Me_nCpMnT mass spectra.

Mass spectra were recorded on a CH-8 Varian MAT instrument with a 70 eV ionization potential and an ion source temperature of 150 °C. Me_nCpMnT $n = 0$–5 and t-butyl CpMnT were synthesized by a published procedure [7].

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