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Mass Spectra of Organometallic Compounds. 6. Energetics of Fragmentations of Manganese-Containing Ions with Intact Ligands in the Series $CH_3C_5H_4Mn(CO)_2L$ and $CH_3C_5H_4Mn(CO)(CS)L$ [L = Ph_3As and Ph_3Sb] [1]

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The mass spectra of the related series $CH_3C_5H_4$-$Mn(CO)_2L$ and $CH_3C_5H_4Mn(CO)(CS)L$ (L = Ph_3P, Ph_3As, and Ph_3Sb) have been examined, and the appearance potentials of all manganese-containing ions with intact ligands determined. The primary fragmentation steps in the mass spectra of these series have been assigned and compared. A relative scale of manganese-to-ligand ionic bond dissociation energies has been established on the basis of the energetics of primary fragmentation steps and the relative currents of group ions. The relative bond strength of ligands in the fragment ions follows the order: CO < CS ≪ L(= Ph_3P, Ph_3As, Ph_3Sb) < Cp. The relative bond strength of individual members of L follows the order; Ph_3Sb < Ph_3As < Ph_3P. The conclusions reached in this study have been inferred from several independent sets of data, and this rules out coincidental agreements of results.

Introduction

In spite of the monumental volume of published mass spectral data on organometallic compounds [2], relatively little effort has been made to examine in detail fragmentation modes and their energetics [3]. Generally, metal-containing ions with intact ligands account for most of the ion current in the majority of the mass spectra of organometallic compounds. Moreover, most such ions exhibit one detectable appearance potential. The foregoing suggest, that metal-to-ligand bond breaking processes are favored, as well as the existence of a single primary precursor for each of these ions. Fragmentations which proceed *via* primary precursor ions will henceforth be referred to as primary fragmentation. Viable information concerning primary fragmentations should be available from appearance potential data, since subsequent ions in a sequence are normally expected to exhibit higher potentials due to the endothermicity of the bond breaking processes involved. Energetics of genuine fragmentations, determined from the appropriate appearance potential data, do provide a measure of ionic bond dissociation energies. Dissociation energies obtained by this technique have been viewed with considerable skepticism in light of their inherent errors. This view is partially justified since fragment ions formed under electron-impact conditions could be considered neither at their ground state nor under standard conditions. Admittedly, isolated values of mass spectrometrically determined dissociation energies are in most instances difficult to comprehend. Nevertheless, it is pertinent to ask whether complete sets of values – determined from the mass spectral data of structurally related series of complexes – could provide meaningful information concerning the relative scale of metal-to-ligand ionic bond dissociation energies. The investigation described in the current paper was undertaken in order to ascertain the above stated question.

Recently, we have reported comprehensive mass spectral studies on $CpMn(CO)_2(CX)$ and $Cp'Mn(CO)_2$-(CX) [where X = O, S; Cp = cyclopentadienyl, and Cp′ = methylcyclopentadienyl] [4], as well as on the binuclear complexes $[CpCr(CO)_2]_2$ [5], $[Me_5C_5Cr$-$(CO)_2]_2$ [5], $[CpFe(CO)_2]_2$ [5], $[CpNi(CO)]_2$ [5], $[CpMn(CS)(NO)]_2$ [1] $[Cp'Mn(CS)(NO)]_2$ [1], $[CpFe(CS)(CO)]_2$ [1] and $Cp_2Fe_2(CS)(CO)_3$ [1]. The current paper describes a detailed mass spectral study of the two interrelated series $Cp'Mn(CO)_2L$ (1) and $Cp'Mn(CS)(CO)L$(*2*); where L = Ph_3P, Ph_3As and Ph_3Sb. The primary objective of this study is to gain intimate knowledge concerning the relative behavior of metal-to-ligand bonds in fragment ions.

Experimental

Complexes in the series $Cp'Mn(CO)_2L$ (1) [6] and $Cp'Mn(CS)(CO)L$(2) [7] were prepared according to

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TABLE I. Relative Intensities (I) (at 80 eV) and Appearance Potentials (AP) of Metal-Containing Ions with Intact Ligands in the Mass Spectra of $Cp'Mn(CO)_2L$(*1*) and $Cp'Mn(CO)(CS)L$(*2*), where L = Ph_3P, Ph_3As and Ph_3Sb, and Cp' = $CH_3C_5H_4$.

Ion	L = Ph_3P		L = Ph_3As		L = Ph_3Sb	
	I	AP, eV	I	AP, eV	I	AP, eV
$Cp'Mn(CO)_2L$[a]						
$Cp'Mn(CO)_2L^+$	7	6.55(3)	3	6.38(3)	11	6.37(3)
$Cp'Mn(CO)L^+$	>1	8.95(2)	>1	8.53(4)	2	8.46(4)
$Cp'MnL^+$	100	8.54(3)	100	8.44(3)	100	8.38(3)
$Cp'Mn^+$	18	15.97(9)	9	14.73(2)	14	14.51(4)
Mn^+	15	–	11	–	30	–
$Cp'Mn(CO)(CS)L$[a]						
$Cp'Mn(CO)(CS)L^+$	31	6.58(2)	9	6.71(2)	8	6.61(3)
$Cp'Mn(CS)L^+$	10	7.37(2)	2	7.57(2)	1	7.30(4)
$Cp'MnL^+$	100	9.19(3)	100	9.01(2)	100	8.83(3)
$Cp'Mn(CS)^+$	3	12.54(50)[b]	3	11.78(30)	15	10.78(8)
$Cp'Mn^+$	65	16.23(2)	21	15.68(6)	34	14.95(10)
Mn^+	51	–	30	–	46	–

[a] Conditions: ICT, 200 ± 2 °C; SHT, 150–200 °C (The upper range was used primarily for the arsine and stibine analogs). [b] This AP was determined using nitrogen (i = 15.60 eV) as calibrant.

TABLE II. Metastable Transitions (M*) of Fragmentations Involving the Rupture of Intact Ligands in the Mass Spectra of $Cp'Mn(CO)_2L$(*1*) and $Cp'Mn(CO)(CS)L$(*2*), where L = Ph_3P, Ph_3As and Ph_3Sb, and Cp' = $CH_3C_5H_4$.

Process	M* (Found)[a]		
	L = Ph_3P	L = Ph_3As	L = Ph_3Sb
$Cp'Mn(CO)_2L$(1)			
$Cp'Mn(CO)_2L^+ \longrightarrow Cp'MnL^+ + 2CO$	346.9(m)	390.3(s)	435.8(s)
$Cp'MnL^+ \longrightarrow Cp'Mn^+ + L$	–	40.8(m)	–
$Cp'Mn^+ \longrightarrow Cp'^+ + Mn$	46.6(vw)	46.6(m)	46.6(m)
$Cp'Mn^+ \longrightarrow Mn^+ + Cp'$	–	22.6(w)	22.6(w)
$Cp'Mn(CO)(CS)L$ (2)			
$Cp'Mn(CO)(CS)L^+ \longrightarrow Cp'Mn(CS)L^+ + CO$	413.7(m)	457.5(w)	503.4(m)
$Cp'Mn(CS)L^+ \longrightarrow Cp'MnL^+ + CS$	356.4(m)	400.0(w)	445.6(m)
$Cp'MnL^+ \longrightarrow MnL^+ + Cp'$	253.8(w)	296.2(m)	340.8(s)
$Cp'Mn^+ \longrightarrow Cp^+ + Mn$	–	46.6(w)	–

[a] Relative intensities are given in parentheses: m, medium; s, strong; vw, very weak; w, weak.

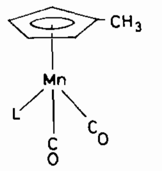
known procedures. The mass spectra of the complexes under consideration were measured at 80 eV on a Hitachi RMU-7E mass spectrometer which has been modified with a Keithley 427 current amplifier and a ITT model F 4074, 16-stage electron multiplier. The samples were introduced directly into the ionization chamber of the mass spectrometer under a low pressure of $\sim 10^{-6}$ Torr. The conditions [sample heater temperature (SHT) and ionization chamber temperature (ICT)] utilized in obtaining the spectra are specified in Table I. Intensities (I) of ions (Table I), those containing the most abundant isotopes of the element involved, are given relative to an arbitrary value 100 chosen for the base peak in each spectrum. Ions having high m/z values were determined with the aid of perfluorokerosene (PFK) standard. Metastable transitions (M*) of fragmentations involving the rupture of intact ligands are furnished in Table II. Experimental terms of M* correlate to theoretical terms which are based on the appropriate ions having the most abundant isotopes of the element involved. Relative currents of group ions with intact ligands were computed according to the procedure outlined in Table III.

TABLE III. Relative Currents (RC) (at 80 eV) of Group Ions in the Mass Spectra of Cp'Mn(CO)$_2$L(*1*) and Cp'Mn(CS)(CO)L(*2*), where L = Ph$_3$P, Ph$_3$As and Ph$_3$Sb, and Cp' = CH$_3$C$_5$H$_4$.

Type of Group Ions	Relative Currents (RC, %)[a]							
	Cp'Mn(CO)$_2$L(*1*)				CpMn(CS)(CO)L(*2*)			
	L = Ph$_3$P	Ph$_3$As	Ph$_3$Sb	Av[b]	L = Ph$_3$P	Ph$_3$As	Ph$_3$Sb	Av[b]
Mn(CO)-containing	6	3	8	6	12	5	4	7
Mn(CS)-containing	–	–	–	–	17	9	12	13
Mn(L)-containing	76	84	72	77	54	67	53	58
Mn(Cp')-containing	90	91	81	87	88	82	78	83

[a] Computed from [$\Sigma I_i/I_t$] × 100; where ΣI_i is the sum of intensities of group ions type i, and ΣI_t is the sum of intensities of all manganese-containing ions with intact ligands, as well as bare manganese ions in the mass spectra of series *1* and *2*. [b] Average value for members of each series.

Ionization and appearance potentials, reported in Table I, were determined by a modified Honig method [8] according to the procedure [9] developed by Lossing, Tickner and Bryce, using either benzene (i = 9.44 eV) or nitrogen (i = 15.60 eV) as calibrant [10]. The appearance potential of each ion was measured at least three times independently, and the precision of the mean result is indicated by the quoted standard deviation. Energetics of fragmentations involving the rupture of intact ligands were determined from the appropriate AP data. The accuracy of the AP data and energetics of fragmentation could not be judged unambiguously; however, it is most probably an order of magnitude lower compared with the indicated precision terms.



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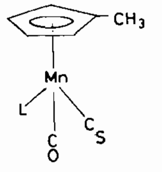

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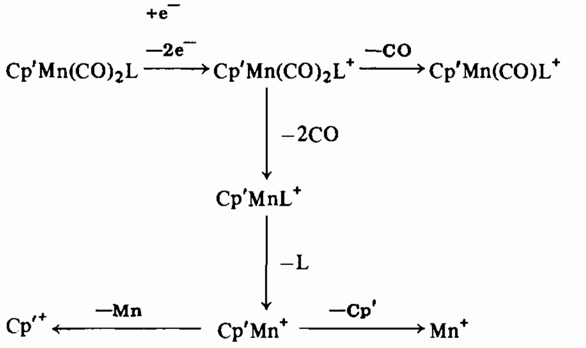
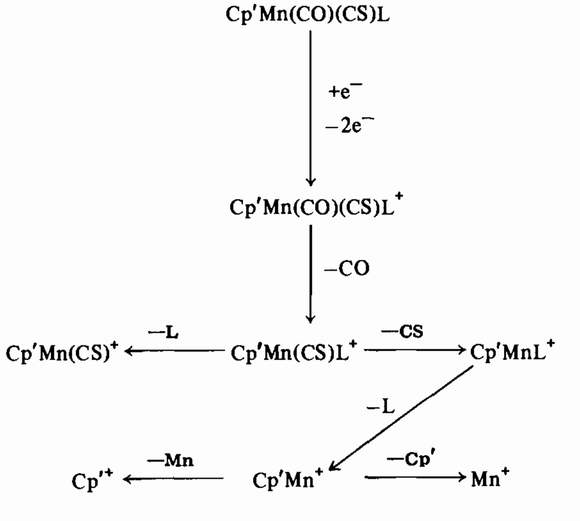
L = Ph$_3$P, Ph$_3$As, Ph$_3$Sb



Scheme I. Primary fragmentation steps proposed in the mass spectra of Cp'Mn(CO)$_2$L(*1*), where L = Ph$_3$P, Ph$_3$As, and Ph$_3$Sb.



Scheme II. Primary fragmentation steps proposed in the mass spectra of Cp'Mn(CO)(CS)L(*2*), where L = Ph$_3$P, Ph$_3$As and Ph$_3$Sb.

Results and Discussion

Intensities, ionization and appearance potentials of the manganese-containing ions, those with intact ligands, found in the mass spectra of Cp'Mn(CO)$_2$L (*1*) and Cp'Mn(CO)(CS)L(*2*) [L = Ph$_3$P, Ph$_3$As, and Ph$_3$Sb] are given in Table I. Metastable transitions found in these spectra are shown in Table II. Based on the above furnished information, the primary fragmentation steps proposed in the mass spectra of the series *1* and *2* are illustrated in Schemes I and II, respectively. In the dicarbonylmanganese series *1*, the molecular ion undergoes the simultaneous elimination of two carbonyl groups to afford Cp'MnL$^+$. A second process involving a unimolecular carbonyl dissociation from the molecular ion , though possible

TABLE IV. Energetics of Fragmentations, and Bond Dissociation Energies of Ions in the Mass Spectra of $Cp'Mn(CO)_2L$(*1*) and $Cp'Mn(CO)(CS)L$(*2*), where L = Ph_3P, Ph_3As, Ph_3Sb, and Cp' = MeC_5H_4.

Fragmentation	Energetics of Primary Fragmentation			
	Energy, eV			Bond Dissociation[a] $D(Mn^+ - ligand)^n$
	L = Ph_3P	L = Ph_3As	L = Ph_3Sb	
$CpMn(CO)_2L$(1)				
$Cp'Mn(CO)_2L^+ \longrightarrow Cp'Mn(CO)L^+ + CO$	2.40(4)	2.15(5)	2.09(5)	–
$1/2\ Cp'Mn(CO)_2L^+ \longrightarrow 1/2\ Cp'MnL^+ + CO$	0.99(4)	1.03(4)	1.00(4)	$\bar{D}(Mn^+ - CO)^{1-2}$
$Cp'MnL^+ \longrightarrow Cp'Mn^+ + L$	7.43(10)	6.29(4)	6.13(5)	$D(Mn^+ - L)^3$
$CpMn(CO)(CS)L$(2)				
$Cp'Mn(CO)(CS)L^+ \longrightarrow Cp'Mn(CS)L^+ + CO$	0.79(3)	0.86(3)	0.69(5)	$D(Mn^+ - CO)^1$
$Cp'Mn(CS)L^+ \longrightarrow Cp'MnL^+ + CS$	1.82(4)	1.44(4)	1.53(5)	$D(Mn^+ - CS)^2$
$Cp'Mn(CS)L^+ \longrightarrow Cp'Mn(CS)^+ + L$	5.17(50)	4.21(30)	3.48(9)	$D(Mn^+ - L)^2$
$Cp'MnL^+ \longrightarrow Cp'Mn^+ + L$	7.04(4)	6.67(7)	7.12(10)	$D(Mn^+ - L)^3$

[a] The superscript n indicates the number of steps that a bond dissociation is removed from the molecular ion.

as evident by the presence of $Cp'Mn(CO)L^+$, is of a considerable lower probability compared with the former process. This conclusion is based on the much greater intensity and lower appearance potential of $Cp'MnL^+$ than that of $Cp'Mn(CO)L^+$. Dissociation of L from $Cp'MnL^+$ to afford $Cp'Mn^+$, and the subsequent decay of the latter by either manganese elimination or decyclopentadienylation (see Scheme I) are presumed to represent primary fragmentation steps. These assignments are consistent with the appropriate appearance potential data, and/or information concerning metastable transitions.

Fragmentation in the thiocarbonylmanganese series *2* is initiated by the decarbonylation of the molecular ion to give $Cp'Mn(CS)L^+$. The resulting ion degrades further by the dissociation of either L or CS to afford $Cp'Mn(CS)^+$ and $Cp'MnL^+$, respectively. Comparison between these two fragmentations reveals that the latter process involves a much lower energy pathway (Table IV), and therefore the dethiocarbonylation should be greatly favored. This conclusion is supported, in part, by the relative intensities of the ions under consideration. Subsequent steps in the dissociation of $Cp'MnL^+$, shown in Scheme II, are analogous to those described earlier for the same ion in the mass spectra of series *1*.

The main differences in the primary fragmentations of the related series *1* and *2* under electron impact conditions are consistent with the changing of a carbonyl group with a coordinated thiocarbonyl. In the systems under consideration, the dissociation of carbonyls invariably preceeds the rupture of the remaining CS, L (= Ph_3P, Ph_3As, and Ph_3Sb), and Cp ligands. The rupture of CS is greatly favored over that of L; the reverse process, though possible, is of a rather low probability. Rupture of the cyclopentadienyl ligand appears to be the least favored fragmentation step. The above stated observations have been reached solely on the basis of the proposed primary fragmentations of the complexes *1* and *2*. It should, however, be pointed out that these observations are in agreement with energetics of the proposed fragmentations (Table IV), as well as with the relative currents of group ions (Table III), aspects to be discussed next.

Relative currents, (RC) of group ions in the mass spectra of *1* and *2*, reflect the tendency of the ligands to survive cleavage of the manganese atom under electron-impact conditions. It is to be expected that the probability of dissociation of a manganese-to-ligand bond should decrease with increased bond strength. Since the relative currents pertain to ions containing specific ligands, an increase in current should reflect moving from weaker to stronger bonds. Average values (AV) of relative currents of group ions in the mass spectra of series *1* (Table III), reveal the increasing order; CO[~6%] ≪ L(Ph_3P, Ph_3P, Ph_3A_s, Ph_3Sb)[~77%] < Cp[~87%]. Likewise, the AV values in the mass spectra of series *2* show the increasing order; CO[~7%] < CS[~13%] ≪ L(Ph_3P, Ph_3As, Ph_3Sb)[~58%] < Cp'[~83%]. This treatment, based on manipulating relative intensity data of fragment ions, appears to provide an independent support to the proposed primary fragmentations which have been described earlier. Energetics of primary fragmentation steps in the mass spectra of series *1* and *2*, determined from the appropriate appearance potential data, are furnished in Table IV. Ionic bond dissociation energies determined from energetics of fragmentations may not be accurate in an absolute sense because of indeterminate errors due to excess of excitation and/or kinetic energies of the participants in these processes. It should also be pointed out that energetics considered here pertain to relatively short-lived fragment ions whose gross properties (electronic structure, geometry, bonding, *etc.*) differ considerably from those of ground-state molecular complexes. Despite the apparent difficulties associated with the interpretation of mass spectrometrically determined ionic bond dissociation energies, it can be argued that such data might meaningfully reflect a relative scale of metal-to-ligand bond strengths in instances of analogous complexes which undergo similar fragmentation steps under electron-impact conditions. This argument is based on the assumption that the energetics of related fragmentation in analogous series should involve indeterminate errors similar in magnitude. Ionic bond dissociation energies determined by this technique depend, among others, on the nature of the metal-to-ligand bond and the mechanism by which this specific bond is influenced by the remaining ligands. The latter factor is greatly influenced by the degree to which the metal-containing fragment ion is stripped of its ligands; namely, the number of steps that a presumed bond dissociation is removed from the molecular ion. Therefore, a meaningful comparison between the energetics of appropriate fragmentations should always involve processes which are equally removed from the molecular ions. The foregoing considerations will now be viewed in light of the energetics of fragmentations data which has been generated during the course of the current study.

In the series *1*, L = Ph_3P, Ph_3As and Ph_3Sb, the unimolecular carbonyl dissociation process of the molecular ion to give $Cp'Mn(CO)L^+$ involves energetics in the range (2.09–2.40 eV) which is far too high to be attributed to $D(Mn^+ - CO)$. Furthermore, the resulting ion is clearly not the genuine precursor of $Cp'MnL^+$ whose formation proceeds *via* the simultaneous decarbonylation of the molecular ion by a process involving 1.98–2.06 eV. It is quite likely that the energetics of the unimolecular carbonyl dissociation in *1* reflect upon an unusual mechanism of excess energy release. This aspect, however, will not be explored further in the current paper. The presence of essentially σ-donor ligands(L) in the series *1* and *2* is expected to effect the strengthening of the manganese-to-carbonyl bonds as compared with those found in $Cp'Mn(CO)_3$ and $Cp'Mn(CO)_2CS$, respectively. For instance, in the ground state molecular complexes such a trend can be monitored from the infrared spectra by following changes in the ν(CO) frequencies of the respective derivatives. The findings of the current investigation reveal that presence of σ-donor ligands in fragment ions causes an increase in the $D(Mn^+ - CO)$ values. This conclusion is self-evident by comparing the $\bar{D}(Mn^+ - CO)^{1-2}$ values of series *1* [range: 0.99–1.03 eV] with that of $Cp'Mn(CO)_3$ [0.57 eV] or $CpMn(CO)_3$ [0.61 eV]. Similarly, the $D(Mn^+ - CO)^1$ values of *2* [range: 0.69–0.86 eV] are significantly greater than that of $Cp'Mn(CO)_2CS$ [0.23 eV] or $CpMn(CO)]_2CS$ [0.4 eV], as might be expected. These results demonstrate that coordinated carbonyl groups in metal-containing fragment ions with intact ligands are effected by the presence of σ-donor ligands in a manner similar to that found in ground state complexes. Another noteworthy comparison between $D(Mn^+ - L)^3$ in series *1* [range: 6.13–7.43 eV] and $D(Mn^+ - CO)^3$ in $Cp'Mn(CO)_3$ [2.20 eV] or $CpMn(CO)_3$ [2.39 eV] reveals the former type bond is considerably stronger. The same basic conclusion can also be reached by comparing the $D(Mn^+ - L)^2$ values in series *2* [range: 3.48–5.17 eV] with the values of $D(Mn^+ - CO)^2$ in $Cp'Mn(CO)_2CS$ [1.20 eV] and $CpMn(CO)_2CS$ [1.07 eV]. A similar comparison between $D(Mn^+ - L)^2$ (cited above) and $D(Mn^+ - CS)^2$ (range: 1.44–1.82 eV) in series *2* shows a significantly stronger bonding interaction for the former type ligands. In the same context, it should also be pointed out that an earlier study [4] on $Cp'Mn(CO)_3$, $CpMn(CO)_3$, $Cp'Mn(CO)_2CS$ and $CpMn(CO)_2CS$ revealed that $D(Mn^+ - CS)^3$ is some 25–39% larger than $D(Mn^+ - CO)^3$. Based on the above furnished comparative ionic bond dissociation energies, the relative scale of manganese-to-ligand bond strength in the fragment ions appears to follow the order: CO < CS ≪ L(= Ph_3P, Ph_3As, Ph_3Sb). Incidentally, this order is identical to that obtained from the relative currents of group ions. In the series *1* and *2*, we have not been able to generate reliable appearance potential data on Mn^+. The dissociation of the cyclopentadienyl ligand in the spectra of the complexes under consideration is a process removed by four steps from the molecular ion. Irrespective of its availability, the term $D(Mn^+ - Cp')^4$ could not have been used for comparison purposes, since none of the remaining ligands considered in this work dissociate that far in the fragmentation sequences.

Studies of the energetics of fragmentations of certain metal carbonyl derivatives of the type $QM(CO)_n$ [*e.g.*, $QMn(CO)_3$ (Q = indenyl [11], fluorenyl [11], pyrrolyl [11], cyclopentadienyl [4], methylcyclopentadienyl [4]); $R_4C_4Fe(CO)_3$ (R = H, CH_3, C_6H_5; R_4C_4 = benzocyclobutadiene [11, 12]); $C_5H_5V(CO)_4$ [13]; $C_5H_5Co(CO)_2$; *etc.*] have revealed that in a unimolecular carbonyl dissociation sequence, a subsequent decarbonylation step occurs with considerably greater energetics. Judging from the rather limited data available on the energetics of dethiocarbonylation processes, this ligand also appears to obey the same trend. The trend detected in such π-acidic ligands is not at all surprising, since the rupture of such a ligand is expected to enhance back-bonding interaction to remaining ligands, and this should account for the bond strengthening effect. Moving our attention to essentially σ-donor ligands, the terms $D(Mn^+ - L)^2$ in series *2* and the comparable terms $D(Mn^+ - L)^3$ in series *1* and *2*, suggest the existence of a similar trend to that found for π-acidic ligands. In the instance of σ-donor ligands, this trend most probably originates due to an entirely different bonding mechanism. A plausible mechanism could perhaps be associated with the effective positive charge of the metal center in the fragment ions. A decrease in the number of ligands around the metal during fragmentations should result in an increase of the effective positive charge on the metal center, since charge delocalization probability is reduced. The ultimate step in this process is the formation of bare metal ion at which point all of the positive charge resides on the metal itself. The strength of the bond between a σ-donor ligand and the metal is expected to increase parallel to that of the effective positive charge on the metal and this, in part, might account for the observed trend.

So far, little attention has been given to the analysis of the term $D(Mn^+ - L)^n$ with regards to its L constituant, and this aspect will be touched on next. In the systems under consideration, bond dissociation energies of the σ-donor ligands $D(Mn^+ - L)^n$, where n = 2 and 3 (Table IV), show a systematic decrease of strength in the order: $Ph_3P > Ph_3As > Ph_3Sb$. This order has been inferred from three independent sets of data, and thus, is unlikely to be coincidental. This order, which pertains to metal-containing fragment ions, is the same as that expected in L-containing complexes at their ground state.

Ionization potentials in the series *1* and *2* as compared with those of the respective $Cp'Mn(CO)_3$ and $Cp'Mn(CO)_2CS$ complexes are of interest since their values depend to a large degree on the σ-basicity/π-acidity ratio of the ligands. Complexes in the series *1* and *2* are obtained by replacing a strongly π-acidic carbonyl group with an essentially σ-donor ligand (L). The net effect in such a process is a substantial increase in the σ-basicity:π-acidity ratio, and this is expected to result in the lowering of the ionization potential upon substitution. In fact, a substantial decrease, greater than one eV, was realized by comparing the ionization potentials of the respective complexes; $CpMn(CO)_3$ [8.06 eV], $Cp'Mn(CO)_3$ [7.86 eV], $Cp'Mn(CO)_2L$ [range, 6.37–6.55 eV], $CpMn(CO)_2CS$ [7.78 eV], $Cp'Mn(CO)_2CS$ [7.72 eV], and $Cp'Mn(CO)(CS)L$ [range, 6.58–6.71 eV].

Conclusion

The mass spectral data of two closely related series *1* and *2* was investigated in great detail in order to ascertain the relative behavior of the ligands CO, CS, L(= Ph_3P, Ph_3As, Ph_3Sb), and Cp′ in manganese-containing fragment ions under electron-inpact conditions. Primary fragmentation sequences in these systems have been determined on the basis of the presence of manganese-containing ions with intact ligands, their appearance potentials, and in light of the appropriate metastable transitions. Relative currents of group ions, and ionic bond dissociation energies (derived from energetics of fragmentations), have revealed a relative scale of manganese-ligand bond strength in the order: CO < CS ≪ L(= Ph_3P, Ph_3As, Ph_3Sb) < Cp′. Ionic Mn–L bond dissociation energies of individual members of L have revealed a relative scale of bond strength in the order: $Ph_3Sb < Ph_3As < Ph_3P$.

Relative currents of group ions and ionic bond dissociation energies of the ligands under consideration are in complete agreement with proposed primary fragmentation sequences. The conclusions reached in this work have been inferred from several independent sets of data, and thus, coincidental agreement of results can be ruled out. This study, to the best of our knowledge, represents the most consistent correlation between mass spectrometrically determined ionic bond dissociation energies in organometallic systems.

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References

1 Part 7: A. Efraty, D. Liebman, M. H. A. Huang, C. A. Weston and R. J. Angelici, *Inorg. Chem.*, *17*, 2831 (1978).

2 M. I. Bruce, *Adv. Organometal. Chem.*, *6*, 273 (1967); M. Cais and S. Lupin, *ibid.*, *8*, 211 (1970).

3 G. A. Junk and H. J. Svec, 'Recent Topics in Mass Spectrometry', R. I. Reed, Ed., Gordon and Breach, New York, N. Y. (1971) pp. 85–126 and pertinent references therein.

4 A. Efraty, M. H. A. Huang and C. A. Weston, *Inorg. Chem.*, *14*, 2796 (1975).

5 A. Efraty, M. H. A. Huang and C. A. Weston, *Inorg. Chem.*, *16*, 79 (1977).

6 Prepared according to the procedure of C. Carbeau, *Can. J. Chem.*, *45*, 161 (1967).

7 R. Arneri, *Ph. D. Dissertation*, Zagreb, May 1976. These derivatives were prepared according to the procedure developed by N. J. Coville and I. S. Butler, *J. Organometal. Chem.*, *64*, 101 (1974).

8 R. E. Honig, *J. Chem. Phys.*, *16*, 105 (1948).

9 F. P. Lossing, A. W. Tickner and W. A. Bryce, *J. Chem. Phys.*, *19*, 1254 (1951).

10 J. Roboz, 'Introduction to Mass Spectrometry, Instrumentation and Techniques', Interscience, New York, N. Y. (1968) Appendix II, p. 515.

11 A. Efraty and M. H. A. Huang, unpublished results.

12 A. Efraty, M. H. A. Huang and C. A. Weston, *J. Organometal. Chem.*, *91*, 327 (1975).

13 R. E. Winters and R. W. Kiser, *J. Organometal. Chem.*, *4*, 190 (1965).