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THE FORMATION OF METAL—CARBON BONDS VIA INSERTION REACTIONS IN GASEOUS NEGATIVE ION/MOLECULE REACTIONS

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Summary

The negative ion mass spectra under chemical ionization conditions for a series of copper(II), nickel(II), and cobalt(II) Schiff base complexes have been measured. Reagent gases employed include methane, isobutane, and methane-d_4. For all complexes, molecular negative ions were produced with all three reagent gases via secondary electron capture processes. Ion/molecule reactions between the molecular negative ion and the neutral reactant gas appear to be the dominant processes for the formation of secondary ions. The secondary reactions lead to the incorporation of the CH_2 moiety into the nickel(II) complexes and the CH_3 group into the cobalt(II) compounds.

Introduction

Mass spectrometric studies of metal-containing compounds under electron impact conditions have been useful in providing details regarding the fragmentation reactions of molecular ions [1,2]. Ionization and appearance potential measurements have provided insight on the nature of the ionization and dissociation processes in metal coordination compounds [1,2]. More recently, investigations of the energetics of negative ion formation in metal compounds and examinations of the decomposition of molecular negative ions have been published [3—17]. The formation of molecular negative ions by capture of low energy electrons into empty metal orbitals appears to be the dominant reaction process [7,8,10,11] while electron capture into ligand orbitals is believed to be important for certain metal carbonyl compounds [13,17]. A common fragmentation process for metal complexes is the unimolecular loss of ligands from the

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molecular ion [3—8,12—14,17]. The formation of fragment ions via rearrangement processes has been noted in certain metal-containing compounds [9,12,14—16].

The study of metal ion and metal complex ion reactions in the gas phase has aided in elucidating the acid base properties of metal-containing species and in probing the mechanisms of nucleophilic and electrophilic substitution reactions of metal complex ions [18—27]. Among the reactions that have been investigated are the formation of bimetallic-containing ions from monometallic complex ions and substitution reactions by neutral ligands at metal ion centers in gaseous metal-containing positive and negative ions. Extensions of ion/molecule studies for the investigation of reactions under positive ion chemical ionization (CI) conditions [28,29] have been reported [30—35]. Protonated metal complex ions and fragment ions formed by loss of ligands from protonated molecular ions and from molecular ions are noted in the CI mass spectra [30—35]. The formation of MH^+ (protonated molecular ion) as the only significant ion in the CI mass spectra of metal acetylacetonates has been used to advantage in the analysis of lanthanide elements [34,35] and transition metals [33].

A recent study of negative ions at chemical ionization source pressures has shown that a large number of low energy secondary electrons is produced [36]. This large abundance of electrons promotes electron capture and for certain organic compounds yields negative ion currents two or three orders of magnitude higher than the corresponding positive ion currents [36]. In the past little attention has been given to negative ion chemical ionization studies with coordination compounds. The production of negative ions from volatile metal chelates under chemical ionization conditions has been described for metal β-diketonates [37] with methane as the reagent gas and for Schiff base complexes in methane gas mixtures [38]. The analysis of chromium hexafluoroacetylacetonate using negative ion chemical ionization conditions is 5000 times more sensitive than for positive ion chemical ionization techniques [37]. The negative ions formed in Schiff base complexes include the molecular negative ion and metal-containing species formed by the addition of simple gases, NO, CO, and O_2, to the molecular negative ions [38].

The present study was initiated to examine the reactivity of copper(II), nickel(II), and cobalt(II) Schiff base metal complex gaseous negative ions with methane and isobutane using chemical ionization conditions. Since it has been suggested [7,8,10,11] that in the electron capture process the electron is centered on the metal, the reactions of interest could be those for reduced metals, copper(I), nickel(I), and cobalt(I). Of particular interest in this paper is the inquiry into the formation of metal—carbon bonds via an ion/molecule process. For many transition metal compounds the tendency toward metal—carbon bond formation is enhanced for metals in lower oxidation states [39]. The production of the reduced metal ion by electron capture appears to facilitate metal—carbon bond formation in the gas phase ions. The influence of the ligand donor strength on the nature of the reaction processes and on the abundance of secondary ions is also probed in this study.

Experimental section

Instrumentation

A Hitachi Perkin—Elmer RMU-6 mass spectrometer modified for chemical ionization investigations was used to obtain negative ion chemical ionization mass spectra. An ion source block constructed of stainless steel was used with an ion volume measuring 15 × 14 × 11 mm. The electrons, produced from a rhenium filament, enter the ionization chamber through a 4.0 × 0.25 mm slit. The path length of the ions is 1.5 mm. A repeller potential of 0—5 V with respect to the chamber was used to expel ions through the ion exit slit. The exit slit (8.0 × 0.5 mm) was covered with 80—90% transmittance stainless steel mesh. The ion source temperature was maintained between 220 and 240°C, depending on the compound investigated.

Reagent gases were introduced via an all glass vacuum system. The gas entered the ionization chamber opposite the ion exit slit through a pinhole in the glass tubing. A model 144 MKS Baratron capacitance manometer was used to measure pressure in the ionization chamber. Gas flow was controlled by stainless steel metering valves. The ion source pressure was maintained between 0.15 and 0.30 Torr for these studies. The differential pumping system consisted of a 6 in. Varian-NRC diffusion pump (2400 l/sec) positioned on the ion source housing and a smaller diffusion pump (360 l/s) on the analyzer region.

Procedure

The metal complex sample was placed in a glass capilary and introduced into the ion source using the direct insertion probe. Sample heater temperatures were measured by means of a thermocouple mounted on the solid heater block. The following temperatures were used to sublime the compounds into the ion source:

M(OABEN) *, M(SALEN):	175—180°C	M = Cu, Co, Ni
M(SALOPHEN):	185—190°C	M = Cu, Co, Ni

Mass marking was performed using low boiling perfluorokerosene (PFK). Since the coordination compounds caused contamination of the ion source, the reproducibility of the spectra was affected by the ion source conditions. For these studies the ion source was cleaned about every 2—3 weeks. Comparable ion source conditions lead to a reproducibility of about ±20%.

Reagent gases

Methane (99.97%) and isobutane (99.0%) were purchased from Matheson Gas Products, East Rutherford, New Jersey. Methane-d_4 (99% isotopic purity) was obtained from Merck Sharp & Dohme of Canada, Ltd., Isotope Division.

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* OABEN = bis(*o*-aminobenzylidene)ethylenediamine; SALEN = bis(salicylidene)ethylenediamine; SALOPHEN = bis(salicylidene)-*o*-phenylenediamine.

Metal complexes

All the compounds were prepared using conventional methods described earlier [10,40,41]. The materials include tetradentate ligands with nitrogen and oxygen donor atoms. Low pressure positive ion mass spectra were measured for each compound to check the purity and the results were found to be similar to those discussed elsewhere [10]. For CuSALEN and CuSALOPHEN the minor contributions of $(FeSALEN)^-$ and $(FeSALOPHEN)^-$ were detected via an "exchange" reaction between the copper complex and iron from the stainless steel in the ion source. A similar observation was reported earlier [42]. All other compounds were found to be pure and no "exchange" reactions were noted at either low or high pressure source conditions.

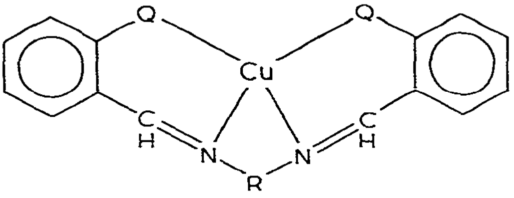
Results and discussion

General

The negative ion chemical ionization (NICI) data for MOABEN, MSALEN and MSALOPHEN ($M = Co^{II}$, Ni^{II}, and Cu^{II}) using CH_4, CD_4 and i-C_4H_{10} as reagent gases are summarized in Tables 1—3. The monoisotopic abundances calculated as described earlier [10], including metal and carbon-13 isotope

TABLE 1

NEGATIVE ION SPECTRA FOR COPPER COMPOUNDS WITH DIFFERENT REAGENT GASES



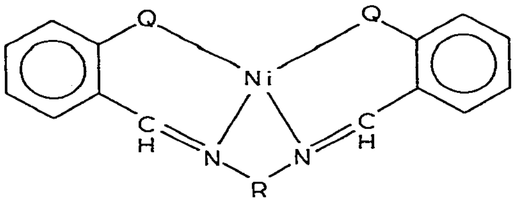
OABEN $Q = NH ; R = C_2H_4$
SALEN $Q = O ; R = C_2H_4$
SALOPHEN $Q = O ; R = C_6H_4$

m/z	Ion [a]	CH_4 [b]	i-C_4H_{10}
CuOABEN			
264	L^-	2	1
266	$(L + 2)^-$	4	2
327	M^-	100	100
CuSALEN			
266	L^-	13	57
268	$(L + 2)^-$	100	94
329	M^-	36	100
CuSALOPHEN			
312	L^-	5	13
316	$(L + 2)^-$	100	100
377	M^-	51	47

[a] L^- = deprotonated ligand ion. [b] CD_4 not measured since no secondary ion products were detected with CH_4.

TABLE 2

NEGATIVE ION SPECTRA FOR NICKEL COMPOUNDS WITH DIFFERENT REAGENT GASES



OABEN Q = NH ; R = C_2H_4
SALEN Q = O ; R = C_2H_4
SALOPHEN Q = O ; R = C_6H_4

M/z	Ion	CH_4	CD_4	i-C_4H_{10}
NiOABEN				
320	$(M-2)^-$	100	100	100
322	M^-	58	70	10
334	$(M+12)^-$	4	—	3
336	$(M+14)^-$	12	2	4
338	$(M+16)^-$	—	7	—
NiSALEN				
324	M^-	100	100	100
338	$(M+14)^-$	4	—	2
340	$(M+16)^-$	—	2	—
NiSALOPHEN				
314	L^-	6	—	18
316	$(L+2)^-$	61	—	43
372	M^-	100	100	100
386	$(M+14)^-$	3	—	2
388	$(M+16)^-$	2	4	1
392	$(M+20)^-$	—	3	—

contributions, are given as a percentage of the base peak in the table.

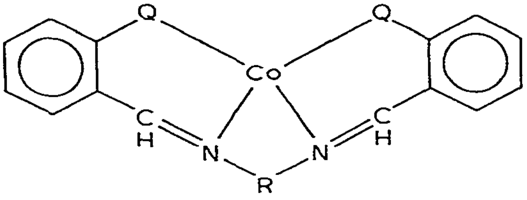
Under NICI conditions no reagent gas negative ions were detected. Although the O_2^- ion has been reported in methane NICI spectra due to trace amounts of water [37], this conditions was avoided by using ultra high purity (99.97%) methane, dry compounds, and a dry gas inlet system. The spectra of the compounds were found to be very simple, consisting of only a few metal-containing ions and in some cases ligand negative ions. That different results were obtained for each metal is supportive of the notion [38] that the reaction center is at the metal in the gaseous negative ion and as such may be representative of metal—carbon bonds in the gas phase.

Copper compounds

For each reagent gas for all three Cu complexes the molecular parent ion, M^-, is an intense peak in the spectrum. Intense ligand peaks were also detected for the copper complexes. Dakternieks et al. [16] studied copper β-diketonate complexes at ion source pressures of about 10^{-5} Torr and found that the molecular negative ion was the most abundant ion in the spectrum. Under such

TABLE 3

NEGATIVE ION SPECTRA FOR COBALT COMPOUNDS WITH DIFFERENT REAGENT GASES



OABEN Q = NH ; R = C_2H_4
SALEN Q = O ; R = C_2H_4
SALOPHEN Q = O; R = C_6H_4

M/z	Ion	CH_4	CD_4	i-C_4H_{10}
CoOABEN				
321	$(M-2)^-$	2	4	6
323	M^-	100	100	100
337	$(M+14)^-$	3	—	1
340	$(M+17)^-$	—	4	—
CoSALEN				
325	M^-	100	100	100
338	$(M+13)^-$	6	—	6
340	$(M+15)^-$	12	—	9
341	$(M+16)^-$	—	2	—
343	$(M+18)^-$	—	4	—
CoSALOPHEN				
314	L^-	3	[a]	2
316	$(L+2)^-$	11	[a]	7
373	M^-	100	100	100
388	$(M+15)^-$	13	—	8
391	$(M+18)^-$	—	19	—

[a] Not measured.

conditions the ligand negative ion abundance was not greater than 25%. Similar results were obtained in low pressure studies [10]. The formation of the M^- ions is due to secondary electron capture. Besides the copper-containing negative molecular ion, ions at m/z, 322, $(\text{FeSALEN})^-$ and at m/z, 370, $(\text{FeSALOPHEN})^-$, characteristic of iron complexes were detected for the N_2O_2 donors. The iron-containing ions are formed in a metal exchange reaction where iron from the source block replaces copper.

The most striking difference for copper compounds compared to cobalt and nickel compounds was the absence of ion/molecular reactions. It is likely that the stability and non-reactivity of the metal Schiff base complex negative ion may be related to reduction of copper(II) to copper(I) in the electron capture process. As copper(I) it is reasonable that the d^{10} electron configuration for copper renders the metal "inert" toward the formation of metal—carbon bonds. It has been reported [38] that copper complex negative ions are also "inert" in the reactions with simple gases.

Nickel compounds

For N_2O_2 donors (SALEN and SALOPHEN) the capture of a secondary electron producing the molecular ion is the primary ion-producing reaction. In the spectrum of NiOABEN the major negative ion is $(M - 2)^-$, an observation similar to the low pressure results [10]. In the case of the N_4 donor, NiOABEN, electron capture is followed by the loss of two hydrogens to produce the $(M - 2)^-$ negative ion. Loss of hydrogen to produce $(M - 2)^-$ could occur from the imine nitrogens or from the C_2H_4 bridging group. It is not possible to distinguish the site of hydrogen loss in the present experiments. Compared with the methane spectrum, the isobutane spectrum showed a greater abundance of the $(M - 2)^-$ ion. Since the methane and isobutane spectra were measured under identical conditions (pressure, temperature, etc.), it is not apparent what factors contribute to differences in the $(M - 2)^-$ ion abundances.

In CH_4 and in i-C_4H_{10} spectra, metal-containing secondary ions, produced via ion/molecule reactions, were noted for all three nickel compounds. The intensity of the product ion was less when using isobutane as the reagent gas compared to methane. The principal secondary negative ion detected for NiSALEN and NiSALOPHEN with CH_4 and i-C_4H_{10} reagent gases appeared at $(M + 14)^-$. For NiOABEN the abundant secondary ions produced via reaction in CH_4 and i-C_4H_{10} were recorded at $(M + 12)^-$ and $(M + 14)^-$.

Since no reagent gas negative ions were detected in this study, it is reasonable that the reactions noted occur between the reagent gas and metal complex negative ions. The most important ion/molecule process yields $(M + 14)^-$ in a reaction involving the expulsion of H_2 and of C_3H_8 as shown in reaction (1) for the methane and in reaction (2) for i-C_4H_{10}. Loss of H_2 rather than 2 H is suggested for thermodynamic reasons.

$$M^- + CH_4 \rightarrow (M + CH_2)^- + H_2 \tag{1}$$

$$M^- + i\text{-}C_4H_{10} \rightarrow (M + CH_2)^- + C_3H_8 \tag{2}$$

For NiSALEN and NiSALOPHEN the M^- ion in eqs. 1 and 2 would be the molecular ion. For NiOABEN it is probable that two ions, $(\text{NiOABEN-}H_2)^-$ and $(\text{NiOABEN})^-$, participate as M^- in reactions 1 and 2, to yield the $(M + 12)^-$ and $(M + 14)^-$ ions, respectively. To explore the details of the reaction processes with methane, NICI spectra were measured using CD_4 as the reagent gas.

For NiSALEN the prominent secondary ion detected with CD_4 was $(M + 16)^-$. With NiSALOPHEN the abundant ions were recorded at $(M + 16)^-$ and $(M + 20)^-$, and for NiOABEN secondary ions were noted at $(M + 14)^-$ and $(M + 16)^-$. These results support the reaction proposed in eq. 1 and provide additional information regarding the mechanism of CH_2 incorporation. The reaction of NiSALEN and NiSALOPHEN with CD_4 reveals that the deuterium loss occurs from the reagent gas.

$$M^- + CD_4 \rightarrow (M + CD_2)^- + D_2 \tag{3}$$

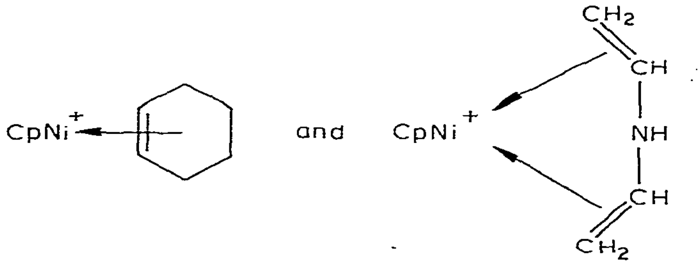
The formation of $(M + 14)^-$ and $(M + 16)^-$ in the reaction of CD_4 with NiOABEN ions supports the notion that both the $(M - 2)^-$ and M^- ions react with the reagent gas.

$$(\mathrm{NiOABEN})^- + \mathrm{CD_4} \rightarrow (\mathrm{NiOABEN} + \mathrm{CD_2})^- + \mathrm{D_2} \quad (4)$$

$$(\mathrm{NiOABEN} - 2\,\mathrm{H})^- + \mathrm{CD_4} \rightarrow (\mathrm{NiOABEN} - 2\,\mathrm{H} + \mathrm{CD_2})^- + \mathrm{D_2} \quad (5)$$

A significant difference is noted in the spectrum of NiSALOPHEN. The presence of $(M + 16)^-$ and $(M + 20)^-$ ions with CH_4 and CD_4, respectively, indicates that stable addition products $(M + CH_4)^-$ and $(M + CD_4)^-$ are formed in the ion/molecule reactions. The absence of these association ions in NiSALEN and in NiOABEN spectra may be related to the relative rates of reactions for NiSALEN and NiOABEN compared to NiSALOPHEN. At present it is not possible to speculate on the chemical nature of the $(M + CH_4)^-$ ion.

The nature of the $(M + CH_2)^-$ product ion deserves further comment. That the secondary ion products for copper, nickel and cobalt complex reactions with the reagent gas are different suggests that CH_2 is not associated with the ligand in the secondary ion. Thus, it is reasonable to suggest that a nickel—carbon bond may be present in $(M + CH_2)^-$. Other investigations have presented evidence for the formation of metal—carbon bonds in positive ion/molecule studies. The likely formation of the $Pb(C_2H_5)_3CH_2^+$ ions has been mentioned [24] in the study of ion/molecule reactions of tetraethyllead. No details regarding the reaction for the formation of this ion were presented. The interaction of positive gaseous transition metal ions with alkyl halides yields MX^+ and MCH_3^+ secondary ions through a metal ion insertion reaction [26]. For aryl halides the formation of $FeC_6H_5^+$ was noted [26] in the reaction of Fe^+ with iodobenzene, but not for other aryl halides. The formation of nickel—olefin bonds in the reactions of nickel organometallic positive ions with saturated hydrocarbons proceeds with ligand displacement from the organometallic ion and loss of H_2 from the saturated hydrocarbon [21]. The formation of the ions via H_2 loss from neutral hydrocarbon molecules has been described [21]. The reaction for $(M + CH_2)^-$ formation reported here is similar to those involved in the formation of nickel—carbon bonds in positive ion reactions. Because the loss of H_2 occurs from methane and not from the ligand or from the ligand and methane, it is reasonable to suggest that the CH_2 moiety is bonded to Ni in the $(M + 14)^-$ and in the $(M + 12)^-$ secondary ions. The square planar nature of the Schiff base complexes [43] would favor a process where the reagent gas molecule could interact with the filled d_{z^2} orbitals of nickel. A reaction mechanism involving oxidative addition of methane to M^-, followed by loss of H_2 may be a reasonable process for the formation of $(M + 14)^-$, a nickel carbene species.



Cobalt compounds

The base peak for all three Co complexes is the parent molecular ion which is formed via a secondary electron capture process. This result compares with previous low pressure results where abundant molecular ions were detected [10]. However, CoOABEN produced a $(M-2)^-$ ion of low abundance which was not detected in the low pressure spectrum. As noted earlier for NiOABEN, isobutane showed a greater tendency to form a $(M-2)^-$ with CoOABEN than CH_4. Secondary negative ions also appeared in the CH_4, CD_4 and i-C_4H_{10} spectra of the cobalt complexes. However, a significant difference was detected in the reactions of the reagent gas species with the N_2O_2 donor and the N_4 donor complex ions. In the CH_4 and i-C_4H_{10} spectra of the N_4 donor CoOABEN, $(M+14)^-$ is the principal secondary ion. For the N_2O_2 donor ligands, CoSALEN and CoSALOPHEN, the dominant ion recorded was $(M+15)^-$, while in the case of CoSALEN, a $(M+13)^-$ ion was also detected.

The mechanism of the ion/molecule reactions may be explained by examining the data obtained using CD_4 as reagent gas. A $(M+17)^-$ ion was found in the CD_4 spectrum of CoOABEN. A $(M+18)^-$ ion is formed in CoSALEN and CoSALOPHEN while CoSALEN showed an addition $(M+16)^-$ ion. The $(M+17)^-$ ion of CoOABEN is associated with the loss of HD. This feature indicates that the detachment of a hydrogen atom from the ligand is involved in stabilizing the product ion:

$$\mathrm{CoOABEN^- + CD_4 \rightarrow (CoOABEN - H + CD_3)^- + HD} \tag{6}$$

The strong donor property of OABEN with its labile hydrogen facilitates the reaction pathway in eq. 6. Lack of easily removable hydrogens from the ligands in CoSALEN and CoSALOPHEN yields a different reaction pathway. The $(M+15)^-$ ion in the spectra of both compounds indicates the incorporation of a reagent gas molecule with the loss of a hydrogen atom for CH_4 (reaction 7) or a C_3H_7 group for i-C_4H_{10}, respectively. Loss of a hydrogen atom from the reagent gas molecule is confirmed by the presence of the $(M+18)^-$ ion with CD_4 (reaction 8),

$$\mathrm{M^- + CH_4 \rightarrow (M + CH_3)^- + H} \tag{7}$$

$$\mathrm{M^- + CD_4 \rightarrow (M + CD_3)^- + D} \tag{8}$$

In the CoSALEN spectrum with CH_4 a secondary ion $(M+13)^-$, formed by the loss of H_2, is also detected. In the CD_4 spectrum, the appearance of a $(M+16)^-$ ion suggests that H_2 is lost from the ligand but that CD_3 is incorporated into the product ion according to reaction 9,

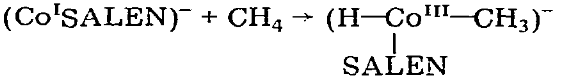
$$\mathrm{M^- + CD_4 \rightarrow (M - H_2 + CD_3)^- + H_2 + D} \tag{9}$$

At the present time it is not possible to suggest the ligand site from which hydrogen is lost.

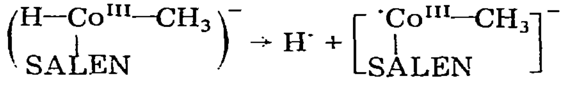
The incorporation of the CH_3 groups into the gaseous cobalt complex ions is similar to the reactions reported for the formation of cobalt—carbon bonds [44—46]. Nucleophilic reactions of the $(CoSALEN)^-$ anion with various alkyl halides have been reported [44,45]. The gas phase reactions reported here are similar to the processes carried out in solution in that $(CoSALEN)^-$ is the nucleophilic reagent. However, the production of neutral species $H^{\cdot}$ and $C_3H_7^{\cdot}$ in the gas phase reactions differs from the generation of halide ions formed in the solution processes.

For the $(\mathrm{CoSALEN})^-$ anion in solution, cobalt is considered to be present as cobalt(I) [45]. However, from magnetic susceptibility measurements and other considerations [44], it is reasoned that the added electron in $(\mathrm{CoSALEN})^-$ is delocalized on the organic ligand and that any attempt to view the electron as localized on the metal is an oversimplification. The magnetic properties and NMR spectra for $\mathrm{CH_3CoSALEN}$ [44] are consistent with the notion that cobalt(III) is present. Thus the reaction of $(\mathrm{CoSALEN})^-$ with alkyl halides involves the oxidative addition process where cobalt is oxidized according to the process $\mathrm{Co^I} \rightarrow \mathrm{Co^{III}}$ [44]. In previous negative ion mass spectrometric studies [10], the results were interpreted to suggest electron capture into predominantly metal orbitals. This result appears to be supported in this study since the reactions noted for copper, nickel and cobalt are dissimilar. It is likely that the reactions reported here involve nucleophilic reactions of cobalt(I) species with the neutral reagent gases. The reaction could be viewed as an oxidative addition reaction in which $\mathrm{Co^IL^-}$ reacts to produce $\left[\mathrm{H{-}\underset{\substack{|\\ L}}{Co^{III}}{-}CH_3}\right]$ where the cobalt is present as cobalt(III). Subsequent loss of atomic hydrogen would yield $\left(\mathrm{{}^{\cdot}\underset{\substack{|\\ L}}{Co^{III}}{-}CH_3}\right)^-$. Stabilization of the cobalt-containing ion, $(\mathrm{L{-}\dot{Co}^{III}{-}CH_3})^-$, could occur via reduction of cobalt(III) to cobalt(II) to yield $(\mathrm{L{-}Co^{II}{-}CH_3})^-$. These postulated reactions are summarized as shown in reactions 10—13 for CoSALEN.

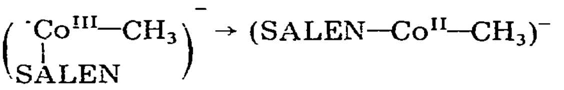
$$\mathrm{Co^{II}SALEN} + e^- \rightarrow (\mathrm{Co^ISALEN})^- \qquad (10)$$



$$(\mathrm{Co^ISALEN})^- + \mathrm{CH_4} \rightarrow \left(\mathrm{H{-}\underset{\substack{|\\ SALEN}}{Co^{III}}{-}CH_3}\right)^- \qquad (11)$$



$$\left(\mathrm{H{-}\underset{\substack{|\\ SALEN}}{Co^{III}}{-}CH_3}\right)^- \rightarrow H^{\cdot} + \left[\mathrm{{}^{\cdot}\underset{\substack{|\\ SALEN}}{Co^{III}}{-}CH_3}\right]^- \qquad (12)$$



$$\left(\mathrm{{}^{\cdot}\underset{\substack{|\\ SALEN}}{Co^{III}}{-}CH_3}\right)^- \rightarrow (\mathrm{SALEN{-}Co^{II}{-}CH_3})^- \qquad (13)$$

From the data reported in this study, negative ion studies at CI conditions applied to organometallic compounds provide complementary information to positive and negative EI results. The results indicate the occurrence of ion/molecule reactions at chemical ionization source pressures. Different results have been found for the Co compounds compared to the Ni compounds, whereas the copper complexes did not show evidence of ion/molecule reactions. The occurrence and pathway of these reactions is influenced mainly by the electronic nature of the central metal ion.

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