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CHEMICAL IONIZATION MASS SPECTROMETRY STUDIES

V*. SOME TRANSITION METAL ORGANOMETALLIC COMPOUNDS

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SUMMARY

Methane chemical ionization mass spectra are discussed for a series of diene–$Fe(CO)_3$ complexes, the iron group metallocenes, nickelocene, cobaltocene, dicyclopentadienyltitanium, -zirconium, and -hafnium dichlorides, and the Group VIB metal hexacarbonyls.

INTRODUCTION

In recent years mass spectrometry has become an important tool for elucidating the structure of organometallic compounds. Only μg quantities of sample are required to obtain a mass spectrum and the molecular weights and elemental compositions of most organometallic compounds can be easily determined from the data produced. In addition structural information about organometallic samples can be obtained from their mass spectral fragmentation patterns and an upper limit on organometallic bond dissociation energies can be calculated from appearance potential measurements.

Several excellent reviews on applications of mass spectrometry in the field of organometallic chemistry have appeared[2-4].

Recently a new procedure for ionizing sample molecules has been developed which dramatically enhances the utility of mass spectrometry in structural studies. In this technique, called chemical ionization (CI)[5,6], sample molecules are ionized by ion-molecule reactions in the gas phase rather than by the conventional electron impact (EI) process. A set of reagent ions is generated in the mass spectrometer by bombarding a suitable gas at a pressure of ca. 1 mmHg with high energy electrons (70–500 eV). Sample molecules are introduced in the usual manner and are ionized on collision with reagent ions in the ion source.

To date most CI spectra have been recorded using methane as the reagent gas. When subjected to electron bombardment at 1 mmHg, methane affords CH_5^+ and $C_2H_5^+$ ions in high abundance (eqns. 1–3)[5,6]. These ions in turn function primarily

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* For previous papers in this series see ref. 1.

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as either proton donors or hydride abstractors toward sample molecules.

$$CH_4 \xrightarrow{e^-} CH_4^{+}\cdot + CH_3^{+} \qquad (1)$$

$$CH_4^{+}\cdot + CH_4 \rightarrow CH_5^{+} + CH_3 \qquad (2)$$

$$CH_3^{+} + CH_4 \rightarrow C_2H_5^{+} + H_2 \qquad (3)$$

In contrast to conventional electron impact (EI) spectra, methane CI spectra generally exhibit abundant ions at high mass and a smaller number of fragment ions. Proton transfer from CH_5^+ to the sample is usually exothermic by less than 100 kcal. As a consequence the resulting $M+1$ ions derived from the sample are relatively stable toward fragmentation. Unlike the conventional EI method, which produces odd-electron ions initially, CI with methane as the reagent gas affords even electron cations and these frequently undergo fragmentation by different mechanisms than their odd-electron counterparts. Thus the structural information available from CI spectra often complements that obtained from EI data.

Of additional interest is the finding that the nature of the CI spectrum is dependent on the type of ion-molecule reaction employed to ionize the sample[5,6]. As a consequence, it is possible to obtain different structural information about a given sample by recording several CI spectra using different reagent gases.

As part of a continuing research effort in CI mass spectrometry, we have recently examined methane CI spectra of a number of diene–Fe(CO)$_3$ complexes, metallocenes, and metal carbonyls. Our results are summarized in this report.

DISCUSSION AND RESULTS

Diene–Fe(CO)$_3$ complexes

EI mass spectra of diene–Fe(CO)$_3$ complexes closely resemble that shown for cyclooctatetraene–Fe(CO)$_3$ (I) in Fig. 1. The presence of abundant ions corresponding to the loss of one, two and three carbon monoxide ligands from the parent ion is characteristic of this class of compounds. Ions derived from the organic ligand are also observed but most of the ion current is carried by metal containing fragments. One problem associated with the use of mass spectrometry to identify diene–Fe(CO)$_3$ complexes is that many derivatives do not form stable molecular ions under electron bombardment conditions. EI spectra of heptafulvene– (II)[7], cycloheptatrienone– (III)[8], and cycloheptatriene-carboxaldehyde–Fe(CO)$_3$ (IV)[9], for example, do not

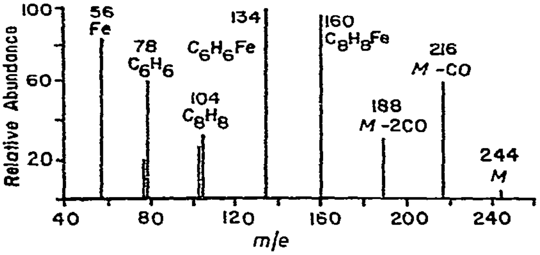
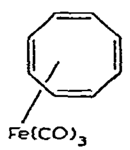
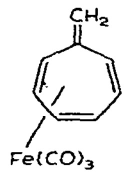


Fig. 1. Electron impact mass spectrum of cyclooctatetraene–Fe(CO)$_3$. Only metal ions containing the ^{56}Fe isotope are shown.

show M^+ ions and the abundance of the M^+ ions in the spectra of cyclobutadiene–Fe(CO)$_3$ (V)[10] and cyclooctatetraene–Fe(CO)$_3$ (I)[11] is less than 5% that of the base peak.



(I)



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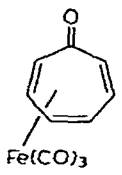

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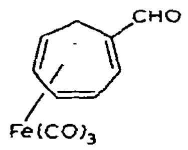

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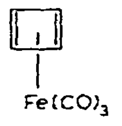


(V)

In contrast, determination of molecular weight is easily accomplished from CI (CH_4) spectra since each of the above compounds readily accepts a proton from CH_5^+ and forms an abundant $M+1$ ion. As shown in Fig. 2, the $M+1$ ion is the base peak in the CI (CH_4) spectra of (I) and (V). Data on other diene–Fe(CO)$_3$ complexes are summarized in Table 1.

In addition to abundant $M+1$ ions, CI (CH_4) spectra of diene–Fe(CO)$_3$ complexes also exhibit peaks at *m/e* values corresponding to the stepwise loss of one, two and three carbon monoxide ligands from the protonated parent molecule. Elimination of an Fe(CO)$_3$ moiety from the $M+1$ ion to give a protonated organic ligand is also observed in most cases. This latter result suggests, but does not require, that proton transfer from CH_5^+ in the gas phase occurs preferentially to the organic ligand rather than to the metal. Behavior of this type is consistent with the solution chemistry of (I), (III), and (V) but inconsistent with that of norbornadiene–Fe(CO)$_3$ (VI). In solution, (III) is protonated at C-2 to form the pentadienyl–Fe(CO)$_3$ cation

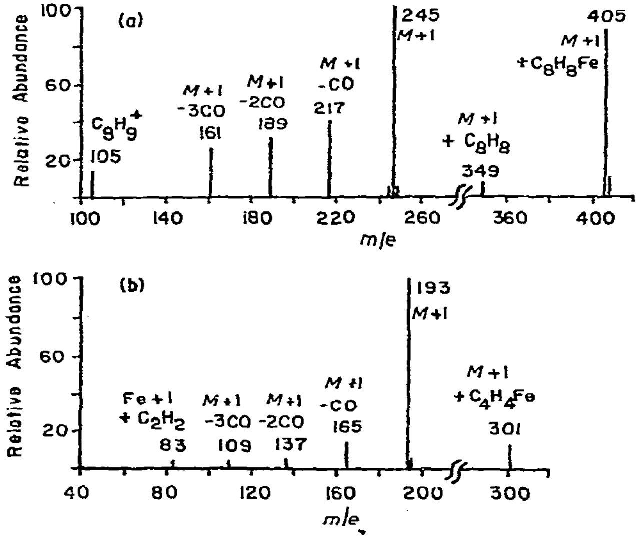


Fig. 2. (*a*) Methane chemical ionization mass spectrum of cyclooctatetraene–Fe(CO)$_3$; (*b*) methane chemical ionization mass spectrum of cyclobutadiene–Fe(CO)$_3$. Only metal ions containing the ^{56}Fe isotope are shown.

TABLE 1

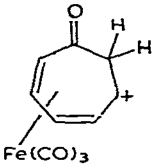
METHANE CHEMICAL IONIZATION MASS SPECTRA OF DIENE–Fe(CO)$_3$ COMPLEXES

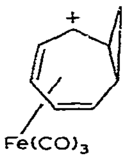
Compound	*Relative abundance (%)*[a]						
	M+1	*M*+1 −*CO*	*M*+1 −2*CO*	*M*+1 −3*CO*	*L*+1[b]	*M*+1[b] +*LFe*	*M*+1[b] +*LFeCO*
Cycloheptatrienone–Fe(CO)$_3$	30	10	100	20	15	30	13
Cycloheptatrienecarboxaldehyde–Fe(CO)$_3$	45	75	100	4.5	15	30	5
Butadiene–Fe(CO)$_3$	100	50	15	3	20		
Norbornadiene–Fe(CO)$_3$[c]	100	25	30	4	10		

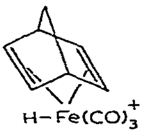
[a] Based on ^{56}Fe. [b] L = organic ligand. [c] Also M^+ = 45% and M^+ − CO = 20%

(VII)[8], (I) forms the homotropylium cation (VIII)[12] and (V) is converted to a perdeuterio derivative in trifluoroacetic acid-*d*[13]. In contrast, protonation of (VI) in sulfuric acid affords the metal-protonated cation (IX)[14].

Experiments to obtain evidence in support of gas-phase protonation on the organic ligand have so far met with failure. D_3O^+ and $MeOD_2^+$, generated by electron bombardment of D_2O and MeOD at 0.5 mmHg, were allowed to react with (V) in the ion source in an effort to effect deuterium exchange on the C_4H_4 ligand.


(VII)


(VIII)


(IX)

Abundant *M*+2 ions were produced under these conditions but further incorporation of deuterium was not observed.

As shown in Table 1, norbornadiene–Fe(CO)$_3$ (VI) forms a rather abundant M^+ ion and a fragment ion corresponding to M^+ −CO. These ions probably result from an electron transfer reaction between (VI) and the $C_2H_5^+$ cation [eqn. (4)]. If this is true, the formation of an M^+ ion indicates that electron transfer from (VI) to $C_2H_5^+$ is competitive with proton transfer from $C_2H_5^+$ to (VI). This, in turn, is consistent with the relatively low basicity and unique site of protonation observed for (VI) in solution[14].

(VI) (4)

Of additional interest in the CI (CH$_4$) spectra of diene–Fe(CO)$_3$ complexes is the presence of peaks at *m/e* values higher than the *M*+1 ion. Particularly prominent in the spectra of (I), (III), (IV), and (V) are ions corresponding to the composition

$(M+1)+\text{FeL}$ where L stands for the neutral organic ligand. As shown in Fig. 2, the spectrum of (I) also exhibits an ion at m/e 349 which presumably results from attachment of the protonated organic ligand, $C_8H_9^+$, to the neutral $C_8H_8Fe(CO)_3$ complex.

As might be expected, formation of these dimeric ions is quite sensitive to the ratio of CH_4 to sample in the ion source. Under normal CI conditions the sample concentration is maintained at less than 1 % that of the reagent gas and the abundance of adducts between fragment ions and neutral sample molecules is relatively low. At higher sample concentrations (CH_4/sample = 10) ion-molecule adducts often become the most abundant ions in the spectra.

Whether production of these dimeric species involves expansion of the coordination sphere of the metal, metal–metal bond formation, or coordination of an electron-deficient metal-containing fragment ion to the uncomplexed side of the π-bonded organic ligand to give sandwich-type structures is an open question at present. To clarify this issue, further experiments are planned to investigate the effect of ligand structure, the electronic environment of the metal, and the experimental conditions on the above reactions.

Metallocenes

Only three ions appear in the CI(CH_4) spectra of cobaltocene (X) and the iron group metallocenes (XI)–(XIII). (Table 2) These occur at m/e values corresponding to M^+, $M+1$, and $M+29$. As shown in Fig. 3, nickelocene (XIV) affords the same

TABLE 2

METHANE CHEMICAL IONIZATION MASS SPECTRA OF METALLOCENES

Compound	*Additive ionization* (%)			
	$M^{+\,a}$	$M+1^a$	$M+29^a$	*IP* (*eV*)[b]
Ferrocene	37	62	1.0	7.15[c]
Ruthenocene	43	52	4.2	7.81[c]
Osmocene	48	47	5.0	7.59[c]
Cobaltocene	94	5.8	0.2	6.2 [c]
Nickelocene[d]	62	32	0.3	7.16[c]

[a] Based on ^{56}Fe, ^{99}Ru, ^{188}Os, ^{59}Co, and ^{58}Ni. [b] Ionization potential. [c] See ref. 16. [d] For complete spectrum see Fig. 3.

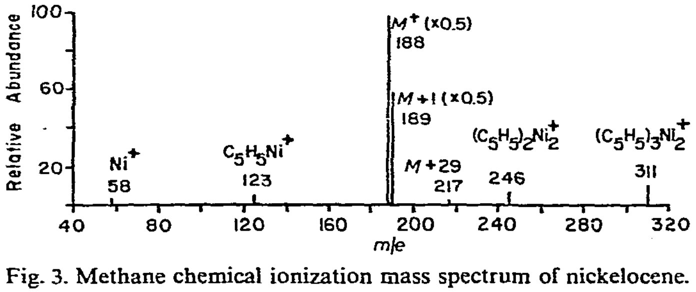
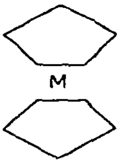


Fig. 3. Methane chemical ionization mass spectrum of nickelocene. Only metal ions containing the ^{58}Ni isotope are shown.



M=Co, (X); Fe, (XI); Ru, (XII); Os, (XIII); Ni, (XIV)

three ions but in addition also yields the fragments, Ni^+ and $C_5H_5Ni^+$, and the dimeric species, $(C_5H_5)_2Ni_2^+$ and $(C_5H_5)_3Ni_2^+$*.

Proton transfer to the metallocenes from CH_5^+ and $C_2H_5^+$ accounts for the formation of abundant $M+1$ ions [eqn. (5)] and electrophilic addition of $C_2H_5^+$ to the sandwich complexes affords the observed $M+29$ ions [eqn. (6)]. Generation of abundant M^+ ions probably occurs by an electron transfer reaction between the metallocene and the ethyl cation [eqn. (7)]. This type of process does not occur to a

$$(C_5H_5)M+CH_5^+(C_2H_5^+) \rightarrow (C_5H_5)_2MH^+ + CH_4(C_2H_4) \quad (5)$$

$$(C_5H_5)_2M+C_2H_5^+ \rightarrow (C_5H_5)_2MC_2H_5^+ \quad (6)$$

$$(C_5H_5)_2M+C_2H_5^+ \rightarrow (C_5H_5)_2M^+ + C_2H_5^{\bullet} \quad (7)$$

large extent in most organic molecules but is particularly favorable in the above examples since the ionization potentials of the metallocenes (Table 2) are all lower than that of the ethyl radical (8.3–8.8 eV)[17]. As a consequence the electron-transfer reaction, [eqn. (7)] is exothermic as written. In the case of cobaltocene, which has the lowest ionization potential of the molecules studied, 94% of the ion current is carried by the very stable cobalticinium ion which occurs at *m/e* 389 (M^+).

Of additional interest is the relative abundance of $M+1$ ions in the CI (CH_4) spectra of the iron triad metallocenes (Table 2). Because both CH_5^+ and $C_2H_5^+$ protonate the metallocenes and $C_2H_5^+$ also functions as an electrophile and an electron abstracting agent, it is difficult to assess the effect of metallocene structure on the relative rates of the electron transfer, electrophilic addition, and protonation reactions. To a first approximation, however, the abundance of $M+1$ ions (and, therefore, the ease of protonation) seems to decrease as one descends the family from ferrocene to osmocene. Protonation experiments conducted in solution also indicate that the basicity order is $(C_5H_5)_2Fe > (C_5H_5)_2Ru > (C_5H_5)_2Os$[18]. That similar trends are observed in the gas phase and in solution suggests that the results obtained in the latter medium do reflect properties inherent to sandwich complexes and are not a measure of stabilization associated with selective solvation of one or more of the metallocenium cations**.

As shown in Table 2 the relative abundance of M^+ ions increases as the transition metal in the sandwich complex is changed from Fe to Ru to Os. This

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* Similar types of dimeric ions are often encountered in conventional EI mass spectra when the energy of the ionizing electron beam is low (20 eV) and the pressure of the organometallic sample in the ion source is high (2×10^{-5})[15].

** Due to steric interactions, stabilization of protonated tertiary amines by solvation is greatly reduced and the following basicity order is observed in solution: sec > tert > pri. In the gas phase where solvent effects are absent, the order is that expected from consideration of the electronic properties and polarizability of the alkyl groups attached to the nitrogen atom: sec > tert > pri[19].

TABLE 3

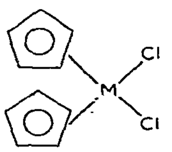
METHANE CHEMICAL IONIZATION MASS SPECTRA OF GROUP IVB DICYCLOPENTADIENYL METAL DICHLORIDES

Compound	*Relative abundance (%)*[a]				
	M^+	$M+1$	M^+-Cl	$M^+-C_5H_5$	$M^++(C_5H_5)_2MCl$
$(C_5H_5)_2TiCl_2$	6.5	1.0	100	10	5
$(C_5H_5)_2ZrCl_2$	15	1.5	100		40
$(C_5H_5)_2HfCl_2$	9	3	100		9

[a] Based on ^{48}Ti, ^{90}Zr, ^{176}Hf.

order does not parallel the order of decreasing ionization potentials but can be understood in terms of relative rates of competing reactions. To explain the data it is only necessary to assume that the rate of proton transfer from $C_2H_5^+$ decreases faster than the rate of electron transfer to $C_2H_5^+$ as one proceeds down the iron triad.

In contrast to the simple sandwich complexes discussed above, dicyclopentadienyl–titanium (XV), –zirconium (XVI), and –hafnium dichloride (XVII) do not form abundant $M+1$ ions on treatment with CH_5^+ and $C_2H_5^+$ (Table 3). Instead, protonation occurs at the metal–halogen bond to form $(C_5H_5)_2MCl^+$ and a molecule of HCl. Molecular ions formed by electron transfer to $C_2H_5^+$ are also observed for (XV), (XVI), and (XVII) but their abundance is relatively low. Protonation on the C_5H_5 ring with subsequent loss of C_5H_6 to form an ion of the type $(C_5H_5)MCl^+$, occurs in the case of (XV) but is not an energetically favored process for (XVI) and (XVII). Unlike the iron group metallocenes, titanocene, zirconocene, and hafnocene dichlorides all form dimeric ions readily. These occur at *m/e* values corresponding to $(C_5H_5)_3M_2Cl_3^+$ and probably result from collisions between the major fragment ion, $(C_5H_5)_2MCl^+$, and neutral sample molecules in the ion source. Changing the CH_4/sample ratio from > 100 to 10 increases the abundance of the $(C_5H_5)_3M_2Cl_3^+$ species markedly.



M = Ti,(XV); Zr,(XVI); Hf,(XVII)

Metal carbonyls

EI mass spectra of the Group VIb metal hexacarbonyls exhibit abundant ions corresponding to M^+ and fragments derived from the molecular ion by stepwise loss of six carbon monoxide ligands[20].

In comparison the $CI(CH_4)$ spectra (Table 4) of chromium, molybdenum, and tungsten hexacarbonyls are relatively uninformative. The $M+1$ ion is the base peak

TABLE 4

METHANE CHEMICAL IONIZATION MASS SPECTRA OF METAL CARBONYLS

Compound	*Relative abundance* (%)[a]				
	M^+	$M+1$	$(M+1)-CO$	$2M+1$	$(2M+1)-CO$
$Cr(CO)_6$	40	100	4		
$Mo(CO)_6$	20	100	20	0.5	3
$W(CO)_6$	10	100	10	0.05	0.3

[a] Based on ^{52}Cr, ^{92}Mo, and ^{182}W.

in each case and this is accompanied by a relatively low abundance of M^+ (10–40%) and $M+1-CO$ (4–20%) ions. Dimeric ions corresponding to $M_2(CO)_{12}H^+$ and $M_2(CO)_{11}H^+$ are also observed but these carry less than 2% of the total additive ion current.

EXPERIMENTAL

EI spectra were recorded on a Hitachi–Perkin–Elmer RMU-6E mass spectrometer using an electron energy of 70 eV and an ion-source temperature of 250°. CI spectra were recorded on an Associated Electronics Industries MS-902 mass spectrometer equipped with a dual EI/CI source manufactured by Scientific Research Instruments Corporation, Baltimore, Md[21]. Operating conditions were as follows: electron energy, 500 eV; accelerating potential, 8 kV; ion-source temperature, 80–150°; resolution, 3000; and reagent gas pressure ca. 1 mmHg.

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