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The generation and characterization of elusive metal complexes in the gas phase: neutralization–reionization mass spectrometry and related experiments

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Contents

Abstract

The results of neutralization–reionization mass spectrometry (NR MS) studies of metal-containing ions are presented and discussed. A unique application of NR MS is the generation of neutrals (in the gas phase) that cannot be easily produced and/or detected by other methods. A variety of elusive complexes having coordinatively saturated and unsaturated metal atom have been produced by collisional neutralization of their positively or negatively charged counterparts. Combined with other mass spectral techniques, the NR MS method is able to provide information about structure, stability, electronic properties, and reactivity of these neutrals. Neutralization–reionization is a powerful tandem mass spectrometry method of elucidating structures of metal-containing ions in the gas phase. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Mass spectrometry; Neutralization–reionization; Unstable metal complexes; Ion structures

Nomenclature

CC	collision cell; a cell located in a field-free region of a mass spectrometer for performing collision experiments with projectile ions and neutrals

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CI	chemical ionization
CID	collision-induced dissociation (also collisional activation); the dissociation induced by collisions (with a target gas)
CIDI	collision-induced dissociative ionization; a method for detection of neutral products of ion dissociation
CR	charge reversal (a single step transfer of two electrons to or from the projectile ion)
CS	charge stripping: a charge reversal process starting from negatively charged and resulting in a positively charged ion
EI	electron impact ionization
ESA	electrostatic analyzer
FAB	fast atom bombardment
Fc	ferrocenyl group, $C_5H_5FeC_5H_4^-$
FFR	field-free region; a region where no fields (magnetic, electric or RF) are affecting the ions on their flight between the ion source and analyzer, between analyzers, or between an analyzer and detector
FT-ICR	Fourier-transform ion-cyclotron resonance
IE	ionization energy; minimum energy required for the removal of an electron from a molecule or a radical
L	ligand at metal atom
M	metal atom
MI	metastable ion(s); ions unimolecularly dissociating in a FFR
N	neutral target (in collision experiments)
NIDD	neutral and ion decomposition difference; a technique involving a subtraction of CS mass spectrum from neutralization–reionization mass spectrum of an ion to obtain information about dissociations of neutrals
NR	neutralization–reionization (process) and also neutralization–reionization starting from and resulting in positively-charged species
$^-NR^+$	neutralization–reionization starting from anion and resulting in the formation of cation
NR/CID	collision-induced dissociation of survivor ions; CID following neutralization–reionization
NR MS	neutralization–reionization mass spectrometry (method)
T	(main ion beam) transmission

1. Introduction

The knowledge of intermediates formed on various stages of chemical reactions is one of the most important ways to understanding their mechanisms, and to control the products formed and their yields. One of the key questions about reaction mechanisms is whether or not a particular intermediate is formed or can possibly be produced in the course of the reaction. To answer this question methods allowing the detection of unstable, reactive, and usually short-lived species have to be applied.

A number of direct and indirect methods for observation and identification of reaction intermediates had been developed. A simple analysis of all products of the specific reaction may indicate that the sought (or suspected) intermediate indeed has been formed in the course of the experiment. Adding a reactant, which would react specifically with this intermediate, is one of the 'selective' methods for tracking its formation. A variety of spectroscopic techniques are able to monitor chemical reactions. The observation of new signals, disappearance of peaks, and other changes in spectra, may be useful in the identification of the (newly) formed and dissipating species.

One of the indirect methods of studying the reactivity of unstable molecules or radicals is to obtain their substituted (and less reactive) analogs. The introduction of substituents to specific sites is aimed at suppressing the reactivity of selected centers. For example, to obtain information about metal atom reactivity in complexes having other reactive centers, such as unstable metallocenes, carbon atoms of the cyclopentadienyl rings can be protected by methyl or carboxymethyl substitution and the reactivity of the metal center can be studied. The intrinsic properties of an unsubstituted derivative are supposedly reflected in the chemistry of the substituted analogs. It is understandable that this approach gives just an image of the original compound. However it provides useful information about its chemical properties.

A powerful method of identification of species formed in the course of reactions consists in their trapping in a low temperature (noble-gas) matrix. The matrix isolation usually follows flash vacuum photolysis or pyrolysis. After trapping a species in the matrix, the unstable molecule or radical can be further characterized spectroscopically. In particular, comparing UV or IR spectra of the matrix-isolated species with the theoretically predicted spectra of the sought products can be performed and aid their identification. The matrix-isolated species can also be released from the matrix to react with a specific reactant.

Theoretical calculations are frequently used for justifying proposed reaction mechanisms. They provide information on the possible stability of suspected intermediates and transition states, preferred or forbidden transformations, reaction energetics, etc. These calculations usually refer to the isolated systems, i.e. gas phase species having no solvent or other molecules surrounding them. Therefore, in many cases they may not be directly applied to a specific reaction, taking place in the condensed phase. However the calculated stabilities of selected molecules, ions, or radicals can be very helpful for picturing possible reaction pathways.

Another way of showing that a molecule or radical may exist as a stable species or as an intermediate, is to *generate* it in the gas phase, i.e. in the environment with no intramolecular interactions. This can be achieved by using the method of neutralization–reionization mass spectrometry (NR MS) [1]. The NR MS technique was developed about 25 years ago. Shortly after that it made a great impact on various fields of chemistry by providing *experimental* evidence for the intrinsic stability of a variety of molecules, radicals, and biradicals. A large number of previously unknown or believed to be unstable species were generated from their positively or negatively charged counterparts in the gas phase in the course of NR MS experiments. The results of these studies do not necessarily demonstrate that a certain intermediate has been a part of the particular reaction. However, they provide the *experimental* evidence for the intrinsic stability of such species and therefore for their *possible existence* in other experimental conditions.

The first step of each NR MS experiment is the production of ions that will be converted to neutrals. These ions should be structurally characterized, i.e. atom connectivity should be established by appropriate mass spectral methods. The next step is to separate the ions of interest from all other ionic species. Acceleration of these ions to translational energies of 4–10 kV will ensure effective neutralization which will take place upon collisions with a target gas. All remaining charged species are removed from the beam of fast moving neutrals, so that only the neutrals will be allowed to collide with another target gas. As a result of these collisions the ionization of some neutrals will take place allowing their detection as charged species.

The NR MS method has made significant contributions to organometallic and coordination chemistry [2]. The present review is aimed at presenting the results of these studies. The main purpose of the majority of NR MS experiments in this field was to test whether or not a particular neutral metal derivative was stable in the gas phase (in the microsecond time frame). Such observation is a good indication for the possible involvement of these species in the reactions taking place in the gas phase (such as interstellar processes) and their likely formation (and stability) in the condensed phase. The importance of the latter is indisputable because metal complexes are involved (as reactants or catalysts) in numerous chemical processes. As the reader will find, these studies have been performed on a variety of metal complexes, such as very simple two-atomic species, metal solvates, and poly-atomic transition metal derivatives. Some of these complexes were previously known while others had never been isolated or characterized. Among them are systems with coordinatively and electron unsaturated metal complexes, whereas others were electron-enriched (such as 19- and 20-electron) systems.

Other applications of the NR MS method will be discussed. One of them is the use of this technique for the investigation of structures of ions and mechanisms of their dissociation in the gas phase. This procedure is naturally incorporated in the process of any NR MS experiment aimed at the generation of the neutral of interest.

The present work is addressed to chemists, who are not necessarily specialists in mass spectrometry methods. The emphasis of the paper is to make them familiar with the *chemical* results generated by the NR MS method. However, for a better understanding of this information, the advantages and limitations of the method, and a brief discussion of its basics are a part of the review. NR MS of metal-containing species is still a relatively unexplored field of research as compared with neutralization–reionization of organic substances. For this reason some general problems of the NR MS method and experimental techniques and approaches will be illustrated with examples from non-metal-containing ions and neutrals.

We found it to be useful to provide a table of organometallics studied by the NR MS method even though the majority of them will be described in the text. Table 1 was arranged by the nature of the metal atom. As a result, the search can be performed on the metal atom and on its surrounding ligand, providing simple and comprehensive examination of the results performed by the NR MS method. The data included in the review cover the period from the first publication on the subject by Hudgins and Porter in 1987 [3] through most of 2000 as well as some unpublished results of the author.

Table 1
Metal derivatives studied by NR MS

Formula	Structure	Stability of the neutral[a]	Ref.
Alkali metal-containing			
$\mathrm{FLi_2}$	$\mathrm{Li_2F}$	Yes	[27a,27b]
$\mathrm{HK_2O}$	$\mathrm{K_2OH}$	Yes	[27b]
$\mathrm{HK_2S}$	$\mathrm{K_2SH}$	Yes	[27b]
$\mathrm{HLi_2O}$	$\mathrm{Li_2OH}$	Yes	[27b]
$\mathrm{HNa_2O}$	$\mathrm{Na_2OH}$	Yes	[27b]
$\mathrm{HNa_2S}$	$\mathrm{Na_2SH}$	Yes	[27b]
Aluminum-containing			
$\mathrm{CH_2Al}$	$\mathrm{AlCH_2}$	Yes	[39]
$\mathrm{CH_3Al}$	$\mathrm{AlCH_3}$	Yes	[39]
$\mathrm{C_2H_4Al}$	$\mathrm{Al(C_2H_4)/HCAlCH_3}$	Yes/No	[39]
$\mathrm{C_2H_6Al}$	$\mathrm{Al(CH_3)_2}$	Yes	[39]
Chromium-containing			
CCrO	$\mathrm{Cr(CO)}$	No	[23]
$\mathrm{C_2CrO_2}$	$\mathrm{Cr(CO)_2}$	No	[23]
$\mathrm{C_2H_6CrS_2}$	$\mathrm{Cr(CH_3SSCH_3)}$	No	[33]
$\mathrm{C_3CrO_3}$	$\mathrm{Cr(CO)_3}$	No	[23]
$\mathrm{C_4CrO_4}$	$\mathrm{Cr(CO)_4}$	No	[23]
$\mathrm{C_5CrO_5}$	$\mathrm{Cr(CO)_5}$	No	[23]
$\mathrm{C_6CrO_6}$	$\mathrm{Cr(CO)_6}$	Yes	[23]
$\mathrm{C_6H_6Cr}$	$\mathrm{CrC_6H_6}$	No	[33]
$\mathrm{C_6H_6CrS}$	$\mathrm{CrC_6H_5SH}$	No	[33]
$\mathrm{C_7H_8Cr}$	$\mathrm{CrC_6H_5CH_3}$	No	[33]
$\mathrm{C_9H_{12}Cr}$	$\mathrm{CrC_6H_5CH(CH_3)_2}$	No	[33]
$\mathrm{C_{10}H_{10}Cr}$	$\mathrm{Cr(C_5H_5)_2}$	Yes	[33]
$\mathrm{C_{12}H_{10}CrO}$	$\mathrm{Cr(C_6H_5OC_6H_5)}$	No	[46]
$\mathrm{C_{12}H_{10}CrS}$	$\mathrm{Cr(C_6H_5SC_6H_5)}$	No	[33]
$\mathrm{C_{12}H_{10}CrS_2}$	$\overline{\mathrm{SC_6H_5CrC_6H_5S}}\mathrm{/CrS_2(C_6H_5)_2}$	Yes	[33]
$\mathrm{C_{13}H_{12}CrO}$	$\overline{\mathrm{CH_2C_6H_5CrC_6H_5O}}$	Yes	[45]
$\mathrm{C_{14}H_{14}Cr}$	$\overline{\mathrm{CH_2C_6H_5CrC_6H_5C}}\mathrm{H_2}$	Yes	[45]
$\mathrm{C_{14}H_{14}Cr}$	$\overline{\mathrm{CH_2C_6H_5CrC_6H_5CH_2O}}$	Yes	[45]
$\mathrm{C_{15}H_{16}Cr}$	$\overline{\mathrm{CH_2C_6H_5CrC_6H_5CH_2C}}\mathrm{H_2}$	Yes	[45]
$\mathrm{C_{16}H_{18}Cr}$	$\overline{\mathrm{CH_2C_6H_5CrC_6H_5CH_2CH_2C}}\mathrm{H_2}$	Yes	[45]
$\mathrm{C_{17}H_{20}Cr}$	$\overline{\mathrm{CH_2C_6H_5CrC_6H_5CH_2CH_2CH_2C}}\mathrm{H_2}$	Yes	[45]
Cobalt-containing			
$\mathrm{C_2HCo}$	$\mathrm{CoC{\equiv}CH}$	Yes	[36]
$\mathrm{C_5H_5Co}$	$\mathrm{CoC_5H_5}$	Yes	[46]
$\mathrm{C_{10}H_{10}Co}$	$\mathrm{Co(C_5H_5)_2}$	Yes	[23]
Copper-containing			
CHCuN	$\mathrm{Cu(NCH)}$ and $\mathrm{Cu(CNH)}$	Yes	[35]
$\mathrm{CuH_3N}$	$\mathrm{Cu(NH_3)}$	Yes	[30]
$\mathrm{CuH_6N_2}$	$\mathrm{Cu(NH_3)_2}$	Yes	[30]
CuN	CuN	Yes	[38]
CuNO	CuNO or CuON	Yes	[38]
CuO	CuO	Yes	[38]
$\mathrm{CuO_2}$	OCuO	Yes	[38]
Gold-containing			
AuF	AuF	Yes	[32]
Iron-containing			
BrFe	FeBr	Yes	[7]
CFe	FeC	Yes	[25]
CFeN	FeCN	Yes	[7]
CFeO	FeCO	Yes	[11,41]
CHFe	FeCH or HFeC	Yes	[25]
$\mathrm{CHFeO_2}$	FeOOCH	Yes	[24]
$\mathrm{CH_2Fe}$	$\mathrm{FeCH_2}$	Yes	[25]
$\mathrm{CH_2FeO_2}$	$\mathrm{Fe(CO)H_2O}$	Yes	[41]

Table 1 (*Continued*)

Formula	Structure	Stability of the neutral[a]	Ref.
CH_3Fe	$FeCH_3$	Yes	[7,25]
CH_3FeNO	$Fe(CO)NH_3$	Yes	[41]
CH_3FeO	$FeOCH_3$ and $HFeOCH_2$	Yes	[37]
CH_5FeN	$CH_3FeNH_2/Fe(CH_3NH_2)$	Yes/No[b]	[42]
C_2HFe	$FeC{\equiv}CH$	Yes	[36]
C_2H_4Fe	$Fe(C_2H_4)$	No	[11]
C_2FeO_2	$Fe(CO)_2$	Yes	[41]
C_3H_4FeO	$Fe(CO)C_2H_4$	Yes	[41]
C_3H_6ClFeO	$ClFe(CH_3COCH_3)/CH_3Fe(Cl)COCH_3$	?/Yes	[40]
C_3H_6FeO	$(CH_2O)Fe(C_2H_4)$/Fe(acetone)/ Fe(propanal)/Fe(oxetane)/ Fe(methoxyethene)	No	[29]
	C_3H_5FeOH	Yes	[29]
C_4H_4Fe	$Fe(C_2H_2)_2$	No	[43]
C_4H_6Fe	Fe(butadiene)	No	[41]
C_4H_8Fe	$Fe(C_2H_4)_2$	No	[41]
C_5H_5Fe	FeC_5H_5	Yes	[46]
C_5H_5BrFe	$BrFeC_5H_5$	Yes	[16]
C_5H_5ClFe	$ClFeC_5H_5$	Yes	[16]
C_5H_5FFe	$FFeC_5H_5$	Yes	[16]
C_5H_5FeI	$IFeC_5H_5$	Yes	[16]
C_5H_5FeO	$OFeC_5H_5/Fe(C_5H_6O)$	Yes/No[b]	[16]
C_5H_5FeO	Fe(CO)butadiene	Yes	[41]
$C_5H_5Fe_2O$	$C_5H_5\overline{FeOFe}$	Yes	[34]
C_5H_6Fe	FeC_5H_6	No	[16]
C_5H_6FeO	$HOFeC_5H_5/Fe(C_5H_5O)$	Yes/No[b]	[16]
$C_5H_7FeO_2$	Fe(acac)	Yes	[7]
C_6H_5Fe	FeC_6H_5	Yes	[7]
C_6H_6Fe	FeC_6H_6 or $Fe(C_2H_2)_3$	No/No	[43]
C_6H_6FeO	FeC_6H_5OH, C_6H_5FeOH or C_6H_6FeO	[c]	[44]
C_7H_6FeO	$Fe(CO)C_6H_6$	Yes	[41]
C_8H_8Fe	$Fe(C_6H_6)(C_2H_2)$	No	[43]
$C_8H_{12}Fe$	$Fe(butadiene)_2$	No	[41]
$C_{10}H_9FeO$	$C_5H_5FeC_5H_4O$	Yes	[50]
$C_{10}H_{10}Fe$	$Fe(C_5H_5)_2$	Yes	[47]
$C_{10}H_{10}FeNO$	$C_5H_5\overline{FeOFe}(C_5H_5N)$ and $C_5H_5\overline{Fe(NO)Fe}(C_5H_5)$	?/Yes[b]	[34]
$C_{10}H_{11}Fe$	$[(C_5H_5)_2Fe]H$	No	[23]
$C_{11}H_9FeO$	$C_5H_5FeC_5H_4CO$	Yes	[50]
$C_{11}H_{10}Fe$	$C_5H_5FeC_6H_5$ and $FeC_{11}H_{10}$	Yes[b]/No	[16]
$C_{11}H_{10}FeN$	$C_5H_5FeC_5H_4CN$	Yes	[23]
$C_{11}H_{11}Fe$	$C_5H_5FeC_6H_6$ and $C_5H_5FeC_5H_4CH_2$	Yes	[50]
$C_{11}H_{11}FeN$	$[C_5H_5FeC_5H_4CN]H$	No	[23]
$C_{12}H_{13}FeO$	$[C_5H_5FeC_5H_4COCH_3]H$ and $[(C_5H_5)_2Fe]COCH_3$	No/No	[23]
$C_{12}H_{12}Fe$	$Fe(C_6H_6)_2$	No	[41]
$ClFe$	$FeCl$	Yes	[7,21]
Cl_2Fe	$Fe(Cl)_2$	Yes	[21]
Cl_3Fe	$Fe(Cl)_3$	Yes	[21]
Cl_4Fe	$Fe(Cl)_4$	No	[21]
FFe	FeF	Yes	[7]
FeH	FeH	Yes	[7]
$FeHO$	$FeOH$	Yes	[7]
FeH_2N	$FeNH_2$	Yes	[7]
FeH_2O	$Fe(H_2O)$	No	[41]
FeH_3N	$FeNH_3$	No	[41]
FeH_4O_2	$Fe(H_2O)_2$	No	[41]
FeH_6N_2	$Fe(NH_3)_2$	No	[41]
FeI	FeI	Yes	[7]
FeO	FeO	Yes	[31]
FeO_2	$OFeO$ and $Fe(O_2)$	Yes[c]	[28]
FeO_3	$Fe(O)_3$	Yes	[28]
FeO_4	$Fe(O)_2(O_2)$ or $Fe(O_2)_2$	Yes[c]	[28]
FeS	FeS	Yes	[31]
FeS_2	$\overline{FeSS}$ and $SFeS$	Yes	[19]

Table 1 (*Continued*)

Formula	Structure	Stability of the neutral[a]	Ref.
Manganese-containing			
CH_3Mn	$MnCH_3$	Yes	[17]
C_5H_5Mn	MnC_5H_5	Yes	[17]
C_6H_5Mn	MnC_6H_5	Yes	[17]
C_6H_5MnO	MnC_5H_4CHO	Yes	[17]
$C_6H_5MnO_2$	MnC_5H_4COOH or $HOMnC_5H_4CO$	Yes[b]/No	[17]
C_6H_7MnO	$MnC_5H_4CH_2OH$ or $HOMnC_5H_4CH_2$	Yes[b]/No	[17]
C_7H_7MnO	$MnC_5H_4COCH_3$	Yes	[17]
$C_{12}H_9MnO$	$MnC_5H_4COC_6H_5$	Yes	[17]
HMn	MnH	Yes	[17]
HMnO	MnOH	Yes	[17]
Nickel-containing			
CNiO	NiCO	Yes	[3]
C_2NiO_2	$Ni(CO)_2$	Yes	[3]
C_2HNi	$NiC\equiv CH$	Yes	[36]
C_5H_5Ni	NiC_5H_5	Yes	[46]
D_2NiO	NiD_2O	Yes	[3]
D_4NiO_2	$Ni(D_2O)_2$	Yes	[3]
D_3NNi	$NiND_3$	Yes	[3]
D_6N_2Ni	$Ni(ND_3)_2$	Yes	[3]
Praseodimium-containing			
FPr	PrF	Yes	[26]
F_2Pr	PrF_2	Yes	[26]
Rhodium-containing			
C_5H_5Rh	RhC_5H_5	Yes	[49]
$C_{10}H_{10}Rh$	$Rh(C_5H_5)_2$	Yes	[49]
$C_{11}H_{10}O_2Rh$	$Rh(C_5H_5)(C_5H_4COOH)$	Yes	[49]
$C_{11}H_{12}ORh$	$Rh(C_5H_5)(C_5H_4CH_2OH)$	Yes	[49]
$C_{11}H_{12}O_2Rh$	$Rh(C_5H_5)(C_5H_4COOCH_3)$	Yes	[23]
$C_{12}H_{12}O_2Rh$	$Rh(C_5H_5)$acac	Yes	[51
Titanium-containing			
C_5H_5Ti	TiC_5H_5	Yes	[47]
$C_{10}H_{10}Ti$	$Ti(C_5H_5)_2$ or $(C_5H_4)_2TiH_2$	Yes	[47]
Tungsten-containing			
C_6O_6W	$W(CO)_6$	Yes	[14]
Vanadium-containing			
$C_{10}H_{10}V$	$V(C_5H_5)_2$	Yes	[2]
Zirconium-containing			
$C_{10}H_{10}Zr$	$Zr(C_5H_5)_2$	Yes	[6]

[a] The stability refers to the particular experimental conditions and was indicated by the observation of a recovery signal.

[b] The most likely isomer surviving neutralization–reionization.

[c] Please see original data for details.

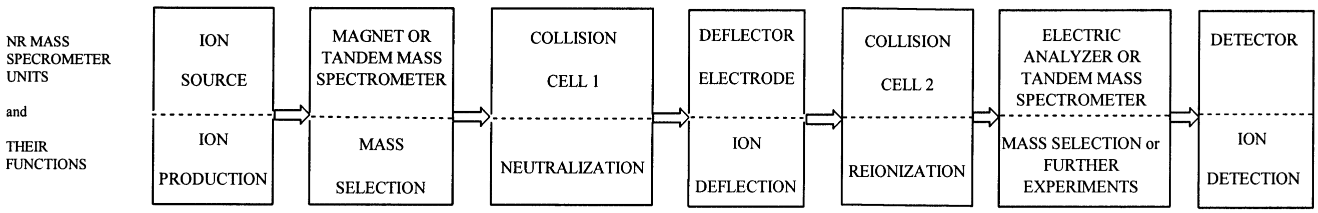

Fig. 1. Block-diagram of a typical mass spectrometer for NR MS studies.

2. Neutralization–reionization mass spectrometry; its principles and instrumentation

The principles of and instrumental arrangement for NR MS have been reported in a large number of reviews [1,2] and in original papers cited in the present article. Fig. 1 shows the instrumental and functional arrangement of NR MS experiments that include the following most common steps.

1. The generation of positively or negatively charged ions whose neutral counterparts are intended to be produced.
2. Structural characterization of the ions to ensure that they possess the desired atom connectivity.
3. Mass-separation of the ions from all other ions and acceleration to kV translational energies.
4. Neutralization by collisions with a target gas.
5. Removal of all remaining charged species from the beam of neutrals.
6. (Collisional) ionization of neutrals.
7. Detection of the reionized species and their dissociation products.
8. Further mass spectrometry experiments with (mass selected) reionized species to obtain information about their structure.

A variety of instruments have been used for conducting NR studies. In pioneer studies of neutralization of metal-containing ions [3], a single-sector mass spectrometer was used for mass separation of the ion of interest [4]. After collision of the ions with metal vapors, the remaining ions were removed from the beam by electrostatic deflection. The information on the extent of fragmentation and stability of neutrals was obtained from the analysis of the neutral beam-scattering profiles acquired with a translatable detector. From the beam scattering data for Ni–L molecules the maximum kinetic energy releases were estimated. These data were used to calculate Ni–L bond dissociation energies for L = CO (~ 1.2 eV), D_2O (~ 0.9 eV) and ND_3 (~ 0.7 eV) [3]. In parallel experiments, the neutrals were collisionally reionized. The reionized portion of the beam was deflected off-axis and detected. The extent of ion fragmentation was proportional to masses of ions, allowing the assignment of peaks to the ions.

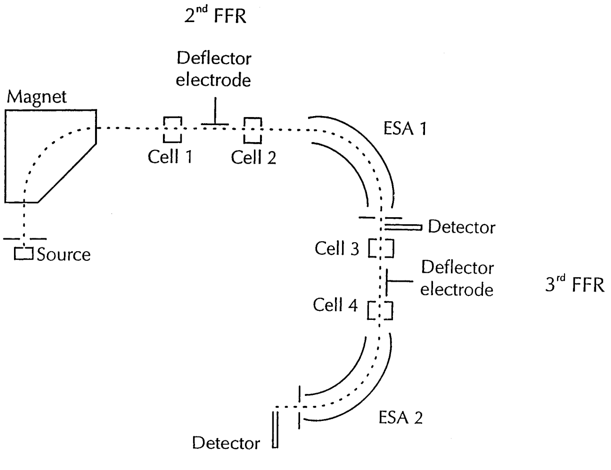

Fig. 2. A modified triple-sector (BEE) VG Analytical ZAB-2F mass spectrometer for neutralization–reionization studies from the University of Ottawa, Canada.

Mass spectrometers with different sets of magnet (B), electric (E), and quadrupole (Q) analyzers, have been used for neutralization–reionization studies. Among them are machines with EBEB (Cornell University, NY; University of Maryland Baltimore County, MD), BEE (University of Ottawa, Ontario), BEQQ (University of Toronto, Ontario), EBE (University of Akron, OH), BEBE (Technical University of Berlin, Germany) and EBEQEBE (University of Mons-Hanaut, Belgium) configurations. Some of these instruments were modified to improve their abilities to perform NR experiments.

All studies by the author have been performed on a modified triple-sector VG Analytical ZAB-2F mass spectrometer with a layout as shown in Fig. 2. On this instrument, CID and NR MS experiments can be carried out in the second and third field-free regions providing rare opportunities for conducting multi-stage tandem mass spectrometry experiments. One of the typical experiments that can be performed on this machine is when mass selected metastable or collisionally excited ions are allowed to dissociate in the 2-FFR. Any of the dissociation products can be mass (energy) selected by the second ESA and transmitted into the 3-FFR where their neutralization–reionization can be performed. A common goal of these experiments is to study ions originating from a single precursor and possibly possessing a single isomer structure. In some cases ions having different internal energies may produce products of different structures. For example, fast dissociation ('high' energy process in the ion source of the mass spectrometer) of the ionized silacyclobutane resulted in $CH_2SiH_2^{\bullet+}$ ions, whereas 'slow' ('low' energy) dissociation of metastable ions resulted in the $CH_3SiH^{\bullet+}$ isomer [5]. Neutralization–reionization experiments with these 'structure' selected ions have been performed in the 3-FFR to assign their structures and to produce the corresponding neutral counterparts.

The second set of experiments utilizing two field-free regions of the ZAB-2F mass spectrometer involved neutralization–reionization in the 2-FFR. Ions formed as a result of the neutralization–reionization process can be mass-selected and transmitted into the 3-FFR to obtain their CID mass spectra. These experiments are specifically useful to determine whether or not the ions formed by reionization of neutrals possess the atom connectivity of the ions *prior* to neutralization. If CID mass spectra of the ions before neutralization are similar to CID mass spectra of the ions surviving NR, it is

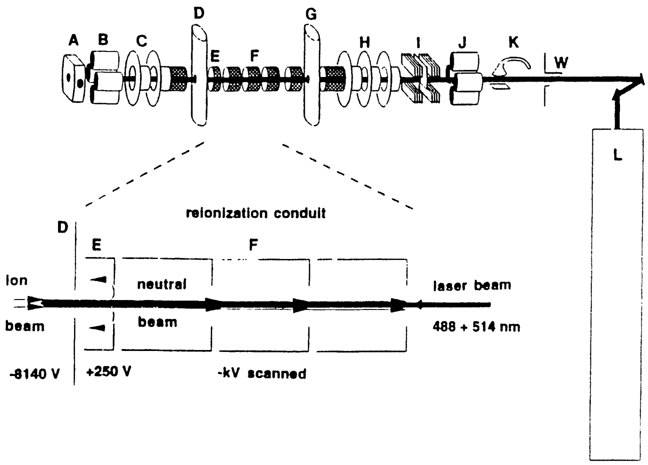

Fig. 3. University of Washington quadrupole acceleration–deceleration tandem mass spectrometer for variable time neutralization–reionization and photodissociation/photoionization studies, consisting of: ion source, quadrupole filter, acceleration lens, neutralization cell, ion reflector, reionization conduit, reionization cell, deceleration lens, energy filter, quadrupole mass analyzer, off-axis detector, Brewster-angle window, Ar-ion laser (provided by F. Turecek et al.).

very likely that the ions had the same atom connectivity. The case of the ionized silaethene [5] provides a good illustration. The CID mass spectra of ion source generated $CH_2SiH_2^{\bullet +}$ ions and of the ions surviving the NR event were indistinguishable indicating that the neutrals retained the original atom connectivity.

A general limitation of the experiments described above is that fluxes of ions produced in the 2-FFR are usually low compared to the intensity of the ion beam of the ion source generated ions entering the 2-FFR. In many cases the fluxes of ‘secondary’ ions (generated in the 2-FFR) are too low for obtaining a CID or NR mass spectrum with a sufficient signal-to-noise ratio. For example, it was impossible to obtain a satisfactory CID mass spectrum of zirconocenium ions surviving neutralization–reionization [6]. Also, a flux of FeH^+ ions generated from mass selected $FeC_6H_7^+$ ions was too low to obtain their neutralization–reionization mass spectrum [7]. However, when MS/MS/MS experiments are successful they provide unique information about ion/neutral structures and mechanisms of dissociation.

The group from the University of Washington has designed a quadrupole acceleration–deceleration mass spectrometer (QADQ; Fig. 3) for neutralization–reionization studies [8]. Quadrupole filters are used to select ions of a specific mass (mass-to-charge ratio) and to mass separate the reionized species. This instrument overcame the general inability of quadrupole mass spectrometers to conduct NR experiments because charge-transfer efficiencies are very small at low ion kinetic energies. In order to provide a high cross-section for electron transfer between the projectile ion or the corresponding neutral and a neutral target, the authors built a ‘ladder’ of lenses to accelerate ‘slow’ ions (leaving a quadrupole) up to 10 kV before they enter the first CC for neutralization. Ions formed by reionization in the second CC are decelerated and mass-analyzed by the second quadrupole. The drift region between the two collision cells is long and contains several collision cells. The design of the instrument provided ion transmission, resolution, and NR efficiency comparable with that of sector instruments. A recent modification of the instrument includes the ability to reionize neutrals by a laser beam [9]. Although the authors’ interests lie out of the field of chemistry of metal derivatives, their instrument could be used in future studies of metal-containing species.

3. Experimental NR MS studies of metal-containing ions

3.1. Evidence for stabilities of neutrals generated in NR MS experiments

One of the most common goals for conducting NR MS experiments is to generate a neutral molecule or a radical. The experimental evidence for the stability of a neutral formed in the course of a neutralization–reionization experiment is the observation of a so-called ‘recovery’ signal or ‘survivor ions’ in NR mass spectra. These ions usually have the same atom connectivity as the ions prior to neutralization. The recovery signal appears at the same mass (or energy)[1] as the original ions passing through the corresponding FFR without been neutralized–reionized. The observation of the recovery signal indicates that the neutrals’ lifetime exceeded the time between neutralization and reionization events. Depending on the mass of the ion and the experimental setting, this time varies from less than 1 μs to a few μs.

The observation or non-observation of a recovery signal depends on several factors. Firstly, collisional neutralization of ions may produce neutrals in their dissociative state(s). Electron transfer from the ion and the target is considered as a vertical Franck–Condon process. No (or very little) change in geometry takes place upon the electron transfer when a relatively small fast moving projectile ion collides with a mono-atomic target. If the geometry of the ion is close to that of the

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[1] A shift to lower translational energies is observed for recovery ions. This shift is roughly equal to the ionization energy of the target that is used for reionization.

neutral, the latter has a good chance of being formed as a stable species. When the geometry of the ion and the neutral are significantly different then the neutral is likely to be unstable. The energy diagram (Fig. 4) illustrates these possibilities. There is also a relatively unexplored case of the generation of stable neutrals from (vibrationally or electronically) excited states of the ions. A study of $(CH_3)_2SiOH^+$ showed that low energy ions generated from the metastable dissociation of $(CH_3)_2SiOR^+$ (R = ethyl, hexyl) did not produce a stable neutral whereas their higher energy analogs (generated by a loss of a methyl radical from the ionized $(CH_3)_3SiOH$ in the ion source of the mass spectrometer) survived the NR event [10]. Similar situations are possible for transition metal containing ions, where electronically excited states are easily available.

The non-observation of the recovery signal does not necessarily testify that the particular neutral cannot be produced. A low dissociation barrier for neutrals is a common rationale for their instability. This factor can be illustrated by the results for $FeC_2H_4^{+/0}$ system [11]. The calculated optimized geometry for the ion was not much different from the geometry of neutral FeC_2H_4, but the recovery signal was not detected in the NR mass spectrum. A very low yield of recovered $FeC_2H_4^+$ ions can be explained by the shallowness (only ~6 kcal mol^{-1}) of the potential well for FeC_2H_4 ($^5B_2$) neutrals. The vibrational excitation of the neutrals generated by collisional neutralization of the corresponding ions most likely exceeded that low dissociation barrier.

In many cases, a possible reason for non-observation of survivor ions is unfavorable experimental conditions; changing the conditions may result in detection of survivor ions. One of the most critical factors determining the stability or instability of neutrals is the nature of the target gas used for neutralization. The effect of the target gas was studied on many occasions [1,12]. The results of these studies can be summarized as follows. The closer the ionization energy (IE) of the target to the IE of the sought neutral the better are the chances for this neutral to survive in the experimental time frame. Also, charge transfer is the most efficient when the IE of the target is close to the IE of the projectile ion. If the IE of the target is lower than that of the neutral to be formed, then the neutral will be formed with an excess of internal energy. The latter will be roughly equal to the difference in the IEs of the target and the neutral. The internal energy of neutrals formed by exothermic electron transfer may be well above their (lowest) dissociation limit, resulting in complete dissociation of the neutrals before they are subjected to reionization.

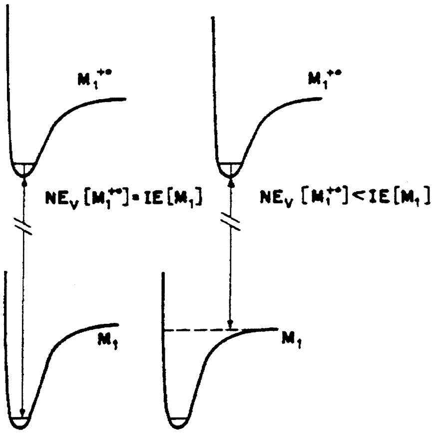

Fig. 4. Energy diagrams for vertical neutralization of an ion $M^{+\bullet}$.

For targets whose IEs are higher than the IE of the neutral, the resulting NR mass spectra are usually similar [12]. This observation was made for mono- and diatomic target molecules. When polyatomic targets are used for neutralization of polyatomic ions, the situation may be different and the effect of the target can be more prominent. As an example, the results for neutralization–reionization of vanadocenium ions (IE of neutral vanadocene is close to 7 eV) are shown in Fig. 5. When vanadocenium ions were neutralized with Xe (IE = 12.1 eV[2]), ethylamine (IE = 9.2 eV) and dimethylamine (IE = 8.9 eV), significant changes in the contribution of survivor and other metal-containing ions to the NR mass spectrum were observed. This effect might originate from non-vertical electron transfer between the projectile ion and the target. In any case, if no (or very weak) recovery signal is present in a NR mass spectrum it is worth trying a different neutralization target. The best results are expected when the IE of the target is close to that of the neutral. From this point of view, a rough estimation (by calculations, by analogy) of the IE of the neutral should be useful in choosing an appropriate target molecule. IEs of many transition metal complexes are relatively low (< 8 eV) and molecules like amines and methyl disulfide are the preferable targets for their neutralization. At the same time, there are many examples when using xenon (IE = 12.13 eV) and oxygen (IE = 12.07 eV) resulting in the observation of strong recovery signals.

When negatively charged ions, having a metal atom, were subjected to collisional neutralization, oxygen was the most commonly used target gas.

$$M + N \rightarrow M^{(+/-)} + N^{(-/+)} \tag{1}$$

$$M + N \rightarrow M^+ + \bar{e} + N^* \tag{2}$$

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[2] Here and below (unless specified otherwise) all thermochemical data are taken from Ref. [13].

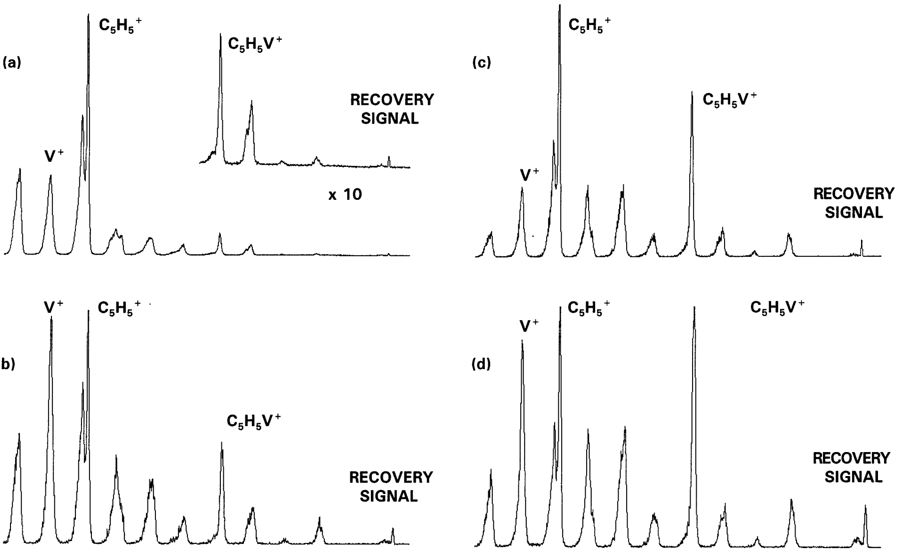


Fig. 5. NR mass spectra of vanadocenium ions at different experimental conditions. Oxygen (80% T) was used for reionization. (a) Neutralization with Xe (80% T) with 10 cm distance between collision cells; (b) neutralization with Xe (80% T) with 2 cm distance between collision cells; (c) neutralization with $C_2H_5NH_2$ (80% T) with 10 cm distance between collision cells; and (d) neutralization with $(CH_3)_2NH$ (80% T) with 2 cm distance between collision cells (reproduced from Ref. [2]).

Reionization is another important and critical stage of NR MS experiments. Two types of processes can contribute to the collisional ionization of neutrals (Reactions (1) and (2)). One of them is an electron transfer between the fast moving neutral and a target molecule. In Reaction (2), collision between the neutral and the target results in ejection of the electron from the projectile neutral. Reaction (1) is generally a softer process compared to Reaction (2), producing ions with lower internal energies. For this reason, molecules with high electron affinities are preferred targets in the reionization stage. Oxygen has been most frequently used for reionization of metal-containing neutrals. Another promising target, NO_2, was employed for reionization of weakly bound nickel solvates [3]. Both these molecules possess high electron affinities allowing them to easily 'strip' an electron from neutrals.

A study of tungsten hexacarbonyl ions [14] demonstrated that reionization may be the principal factor affecting yield and stability of survivor ions. The authors showed that neutral $W(CO)_6$ molecules generated by neutralization of the corresponding ions were likely to be stable. It was reionization that produced molecular ions in their dissociative states. The energy content of survivor ions was higher than the internal energy transferred upon electron impact ionization and in collision induced dissociation conditions. It was also demonstrated that the relative intensity of recovery peak depended upon translational energy of the ions. Lowering the acceleration voltage from 8 to 3 kV resulted in a significant increase of the contribution of $W(CO)_6^+$ ions to the NR mass spectrum.

3.2. Structures of neutralized species

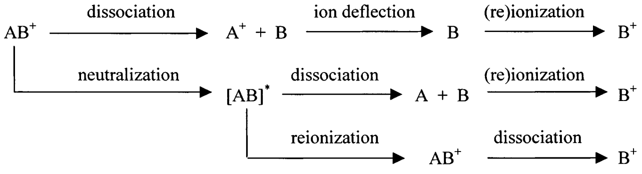
The identification of ion structure is a necessary step in any experiment aimed at the generation of a specific neutral using the NR MS method. Considering that the neutralization is a vertical Franck–Condon process, it is expected that the neutrals will retain the 'structure' of the ion. It should be noted that the term 'structure' in mass spectrometry usually refers to atom connectivity rather than to geometry and bond distances. In some cases, geometrical and stereochemical information can be extracted from the reactivity of ions in the gas phase [15].

A variety of tandem mass spectrometry methods can be employed to determine the atom connectivity in ions and to make sure that the sought neutral will possess this connectivity. Among the experimental techniques for the elucidation of ion structures are metastable and collision induced dissociation, ion–molecule reactions, and thermochemical measurements. These studies may require carrying out experiments on various types of mass spectrometers with differing experimental conditions. It is important that ions, whose structures are to be tested, be generated from the same precursors, in the same time frames and with similar internal energies as they were generated for NR MS experiments. Varying these conditions may result in ions whose structures (and properties) are not the same.

NR MS itself is a powerful method for the assignment of structures to ions and for the study of ion and neutral dissociation mechanisms. There are two distinct advantages of this method as compared with, for example, CID mass spectra. First, the amount of internal energy that is transferred to the ion and the neutral during the NR process usually exceeds the amount of energy transferred in collisional activation. This observation has been made for the dissociation of the ionized tungsten hexacarbonyl [14]. The NR mass spectra of mass selected $W(CO)_6^+$ ions displayed greater dissociation compared with the CID mass spectra and with the EI ionization of the neutral molecule. As a result of high internal energy transfer during NR, reactions having high activation energies can be readily accessed in the NR event. Some of these reactions may be very important for characterization of the atom connectivity in the ion. For example, the CID mass spectrum of $[C_5H_5,Fe,O]^+$ ions[3] [16] was consistent with $Fe^+(C_5H_5O)$ structure. A peak due to the FeO^+ ion, which is characteristic for the $(C_5H_5)FeO^+$ structure, was a minor product of collision-induced dissociation. The NR mass spectrum displayed a strong signal of FeO^+ ions. The observation of these ions was consistent with the presence of two ligands, C_5H_5 and O, at the metal atom; this structure could not be identified from the CID (or MI) experiment.

Neutralization–reionization mass spectra also contain peaks corresponding to neutral products from fragmentation of the ion. For example, the fragmentation of $Mn^+C_5H_4COOH$ ions to Mn^+OH might involve a loss of C_5H_4CO (an energetically favored process) or $C_5H_4 + CO$ (energetically unfavorable reaction). The NR mass spectrum [17] showed a strong peak for $C_5H_4CO^+$ ions, which confirmed the likely formation of the neutral 6-oxafulvalene.

In addition to the charged and neutral products of *ion fragmentation*, NR mass spectra may have a contribution from dissociation products of the *neutrals* generated by neutralization of the ion of interest (Scheme 1 represents possible sources for B^+ ions in NR MS experiments for a simple AB di-atomic system). These neutrals may decompose differently than their ionic counterparts. Collisional ionization of the dissociation products of these neutrals will produce fragments that may not be accessed by the dissociation of the ion. As a result, NR mass spectra usually contain a larger variety of peaks than CID mass spectra of the same ions, providing complementary information about ions and neutrals involved in the dissociation and neutralization–reionization processes.



Scheme 1. Possible origins of B^+ ions in a NR mass spectrum of AB^+ ions.

Structures of neutrals generated in NR MS experiments can be elucidated by comparison of CID mass spectra of the ions *prior* to their neutralization with CID mass spectra of the ions surviving neutralization–reionization. If the CID mass spectra are close to each other then it is very probable that structures of the ions before and after the NR event are the same. In such a case, it is highly likely that the intermediate neutrals possessed the same atom connectivity as their precursor ions and the ions formed upon their (re)ionization. This conclusion is based on the assumption that it is almost impossible to have two subsequent rearrangements (upon neutralization and after reionization) resulting in the initial ion structure. Quantitative differences in the CID mass spectra of the original and the reionized species may not be considered as an indication for different structures. These ions possess different internal energies, which will affect the contribution of various dissociation channels to and the extent of the total fragmentation.

The observation of significant differences between the CID mass spectra of the ions before neutralization and after reionization usually points out that the intermediate neutrals did not retain the atom connectivity of the precursor ions. The isomerization of neutrals may be very fast, e.g. it may be completed in a few μs before the reionization event will take place. As an example, the NR mass spectrum of RPS_2^+ was consistent with the RSPS connectivity of the atoms in the neutrals; the RPS_2 to RSPS isomerization took place within the microsecond time-frame [18]. A fast isomerization of acyclic SFeS to cyclic FeS_2 structure was observed when negatively charged $SFeS^-$ ions were neutralized [19].

A procedure for tracing the dissociation of neutrals was developed by Shalley et al. [20]. In this technique, called neutral and ion decomposition difference (NIDD) mass spectrometry, the NR mass spectra are compared with the charge-stripping spectra recorded in similar conditions. The CS involves a one-step two-electron transfer from the projectile, a negatively charged ion. The resulting mass spectrum is a fingerprint of the ions formed after the charge reversal because the corresponding neutrals are not formed in the process. In the NR process, the removal of electrons from the ion is separated in time. A part of the NR mass spectrum originates from the collisional ionization of neutrals formed in the period of time between neutralization and reionization. By subtracting the CS mass spectrum from the NR mass spectrum of the same ions recorded with the 'same' experimental conditions, the products

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[3] Here and below, square brackets are used for ions of (initially) unknown atom connectivity or as a general formula for several isomers.

of the dissociation of neutrals (arising in the NR conditions) can be retrieved. In order for the NIDD method to be successful, a number of specific conditions must be met; for example, structural identity of the ions formed, similarity in their internal energies, etc. [20]. It is not easy to achieve all these conditions; thus, this method may be unsuitable for many systems. However, when the most important conditions are met, extremely useful information about the properties of elusive neutrals can be disclosed. The NIDD procedure has been applied to a few metal-containing ions [19,21]. The $^{-}$NIDD^{+} spectrum of $FeCl_3^-$ ions did not display a signal due to Cl_2 disfavoring the formation of molecular chlorine from neutral $FeCl_3$ [21]. For the FeS_2 system, a great difference between the $^{-}$NR^{+} and $^{-}$CR^{+} mass spectra accounted for a high reactivity of the neutral species formed, i.e. to the isomerization of SFeS structure to a (cyclic) FeSS molecule.

A positive impact on the studies of neutral metal-containing ions originating in NR MS experiments may be achieved by using other techniques probing the reactivity of neutral molecules in the gas phase. After being formed from the corresponding ions, the neutrals can be collided with a target gas to induce their dissociation. The difference between NR mass spectra recorded using collisional excitation of neutrals and 'regular' NR mass spectra will reflect the contribution from dissociations of collisionally activated neutrals. A similar effect can be achieved by using laser activation. The latter method has been used to probe very unstable neutrals [22].

In any case, collision induced dissociation experiments with survivor (or other ions present in the NR mass spectrum) are very useful and important in revealing atom connectivity in the neutrals and for studying neutral transformations.

3.3. *Overcoming isotopic overlapping of ions*

One of the most prominent requirements for a successful NR MS experiment is the absence of ions having a different elemental composition but the same (nominal) mass as the ion of interest. Such interferences may lead to an inaccurate or even false interpretation of the experimental data. It is especially important to recognize ion overlapping in studies directed to the production of the neutral species of unknown stability. The 'contaminant' ion may produce survivor ions that can be wrongfully assigned to the sought neutral of the same mass, which is eventually unstable in the given experimental conditions.

Various sources can contribute to ion overlapping. Ions of the *same* elemental composition, but represented by different isotopes of the elements, often overlap with each other. This kind of overlapping may not create any problems for the interpretation of the results. On the contrary, the presence of different isotopes of the same element(s) can be helpful. As an example, a peak at the nominal mass 155 in the electron impact mass spectrum of $(CH_3)_3SnCl$ consists of $^{120}Sn^{35}Cl^+$ and $^{118}Sn^{37}Cl^+$ ions. The NR mass spectrum of mass selected m/z 155 showed a recovery signal and peaks at m/z 118 and m/z 120 [23]. Their ratio closely matched the natural abundance of ^{118}Sn and ^{120}Sn isotopes (19:81). Two other peaks in the NR mass spectrum corresponded to $^{35}Cl^+$ and $^{37}Cl^+$ ions with their natural abundance of ca. 3:1. All these data showed that $SnCl^+$ ions were free of contamination.

Isotope overlapping of ions having *different* elemental composition may create serious difficulties. This overlapping may originate from various sources. Ions from the background of the instrument and contaminants to the substance(s) that are used to generate the ion of interest may have the same nominal mass as the ion of interest. One of the most common sources for ion interference is the polyisotopic character of the elements. Very often an overlapping of ions having (slightly) different numbers of hydrogen atoms takes place. The best way of dealing with ion interference is to find experimental conditions at which no undesirable overlapping takes place. Among these approaches are changing the ionization technique, finding a different precursor or reaction for the ion of interest, and varying internal energy of the precursor ion.

Isotope labeling is a powerful tool to overcome various types of ion interference. Isotopic species naturally present in the ion of interest can be useful in some cases. As an example, we tested a large number of organometallic complexes to generate FeH^+ ions for performing NR MS experiments [7]. Fe^+ ions were co-produced in all cases and a peak corresponding to ^{57}Fe had the same nominal mass as the most abundant isotopic composition of FeH^+ ions ($^{56}Fe^1H^+$). No such overlapping occurred when ^{54}Fe-containing ions were investigated because of the absence of natural ^{55}Fe isotope. As a result, $^{54}FeH^+$ ions did not interfere with any isotope species of Fe^+ ions and their NR mass spectrum represented pure FeH^+ ions.

Intentional isotope labeling has a widespread use in mass spectrometry and can be specifically applied for separation of metal-containing ions of interest from any other species of the same mass. In addition to mass shifting, isotope labeling is a common approach for studies of mechanisms of ion dissociation indicating the involvement (or non-participation) of the labeled group to a particular process. Isotope labeling has one specific application for neutralization–reionization experiments. It can be illustrated by the case of $HC^{16}O^{18}OFe^+$ ions [24]. The observation of equal amounts of both oxygen isotopes in reaction products indicated the symmetrical structure of the ion, i.e. that of the metal ion connected to a formate ligand. In some cases the introduction of deuterium atom(s) in the ion increased the stability of the corresponding neutrals. For example, the NR mass spectrum of $FeCD_3^+$ ions showed a stronger recovery signal than the NR mass spectrum of its unlabelled analog, $FeCH_3^+$ [25].

Sometimes a single isotope label does not guarantee a successful separation of ions. For example, in CID and NR MS experiments with $[C, H_3, Si, O]^+$ ions, only using doubly labeled compounds (^2H and ^{18}O) would secure the separation of SiH and CHO ions and neutrals [26]. Similar situations may be applied to many organometallic systems containing poly-isotopic atoms.

High-resolution experiments may be used to separate ions having different element compositions but the same nominal mass. At the resolution of ca. 4000, isobaric $FeCO^+$ and $FeC_2H_4^+$ ions were successfully resolved [11]. The ion beam of the latter (generated by substitution of the CO ligand in $FeCO^+$ by ethylene) was abundant enough to produce a distinctive NR mass spectrum. At this resolution, however, it was impossible to separate $FeC_2H_4^+$ from the corresponding isotopomers of $FeC_2H_3^+$ and $FeC_2H_2^+$ ions. The NR mass spectrum was corrected to the contribution of the latter two ions. In the corrected mass spectrum, a peak due to survivor $FeC_2H_4^+$ ions was negligible.

It should be noted that increasing the resolution on sector instruments usually results in a considerable reduction of fluxes of ions reaching a detector. A significant loss of the ion beam intensity may be crucial for NR experiments because ion fluxes produced after neutralization–reionization rarely exceed 1% of the ion fluxes present *prior* to neutralization. As a result, the NR mass spectrum of mass-selected ions at (relatively) high resolution may contain important peaks (such as recovery signal) whose intensities would barely exceed the detection limit.

A common procedure for separation of NR signals corresponding to overlapping ions involves subtraction of the NR mass spectrum of the contaminant from the NR mass spectrum of the mixture. To do this, all ions contributing to the main ion beam must be well identified. Their NR mass spectra should be recorded under the *same* conditions as the NR mass spectrum of the mixture. Even in this case, the procedure may not provide good results simply because it involves a subtraction of a small signal from a weak signal or a big signal from a large signal.

In a short summary, it is very important for ions selected for neutralization–reionization to be pure from other species having a similar mass-to-charge ratio. This can be achieved by one or more methods described above. Experiments with ions generated by a selected process appeared to be the best sources for ions free of interferences. Tandem mass spectrometry experiments with survivor ions may be conclusive in the determination of whether or not the ions of interest were subjected to neutralization–reionization.

3.4. Generation of metal-containing ions for NR MS studies

A variety of methods have been used to generate metal-containing ions for a study by NR MS. Electron impact and chemical ionization are the most frequently used methods to produce positively and negatively charged precursors. Fast atom bombardment (FAB) is also a useful method for making ions of interest. For example, FAB of praseodymium trifluoride, PrF_3, was employed to generate the PrF^+ ions that were studied by NR MS [26]. High yields of M_2F^+ ions were observed by FAB of alkali metal fluorides [27].

A valuable addition to the above methods has been the use of multi-sector tandem mass spectrometers for the generation of ions from mass-selected precursors. The importance of these studies results from the fact that the structure of an ion may depend on its precursor and internal energy. Ions generated from a mass selected metastably decomposing parent ion are usually those that are formed by the lowest energy reaction resulting (in many cases) in the most stable structure. In the case of $[C, Si, H_2, D_2]^{+\bullet}$ ions, MS/MS/MS experiments showed a distinct difference between the species generated from ionized 1,1-D_2-silacyclobutane, which dissociated in the ion source and metastably in the field-free region [5]. The use of instruments having at least three sectors is required to record CID mass spectra of survivor ions; that requirement makes these studies relatively infrequent. Also yields of survivor ions may be too small to permit recording a reasonably intense CID mass spectrum, even with extensive signal accumulation. For the latter reason, the structure of the $C_{10}H_{10}Zr^+$ ions formed after NR could not be compared with the structure of the ions prior to neutralization [6].

Ion–molecule reactions have been widely used to produce silicon- and transition metal-containing ions for NR experiments. In general, ions generated by electron impact, chemical ionization or generated in FAB conditions can be reacted with neutral molecules to yield the desired ion–molecule reaction products. Two types of ion–molecule reactions can be carried out to form ions of interest. The first reaction involves the interaction of a metal-containing ion with a neutral, non-metal containing molecule. This type of process can be illustrated by the production of FeO_2^+ ions by an exchange of CO ligand in $Fe(CO)_n^+$ ions by O_2 [27]. A similar reaction, involving the substitution of a CO ligand at the metal atom, was used to generate $FeC_2H_4^+$ ions [11]. Various ligand substitution reactions were employed to produce $[Fe, C_3, H_6, O]^+$ isomers [29].

FAB of CuCl mixed with aqueous NH_4OH gave rise to $Cu(NH_3)^+$ and $Cu(NH_3)_2^+$ ions subjected to neutralization–reionization [30].

The second type of ion–molecule reactions employs positively (or negatively) charged reactant ions and *neutral* metal complexes. 'Traditional' chemical ionization is a common way to protonate organometallic molecules, using a variety of protonating reactants. Chemical ionization with N_2O as the reagent gas was used for the generation of negatively charged transition metal derivatives [27,31,32]. Ethyl iodide and its deuterated analog, C_2D_5I, were used to generate protonated and deuteronated ferrocene derivatives [23].

Note that it is usually difficult to produce ions of interest in a sector instrument by a *selective* ion–molecule reaction. In most cases, more than one reaction can result in the same ionic product, and the different reactions may produce different ion structures. For example, ion–molecule reactions in mixtures of C_2D_5I with ferrocene and its derivatives resulted in the formation of $[C_5H_5FeC_5H_4R]D^+$ ions [23]. The 'high pressure' EI mass spectrum of C_2D_5I contains several ions that can transfer a deuteron to the organometallic molecule; namely, $C_2D_5^+$, $C_2D_5ID^+$, and D_2I^+. Generally, these reactants might protonate a substituted ferrocene at different sites; e.g. in the cyclopentadienyl ring, on the substituent and at the metal atom. For the protonated (deuteronated) ferrocene, it would not affect the most important result: $[C_5H_5FeC_5H_4R]D^+$ ions did not survive NR under any applied experimental conditions. In many other cases, however, the possibility of forming isomeric structures by different ion–molecule reactions in the ion source should be investigated. A study of ion–molecule reactions that involved *isolated* ionic reactants (using FTICR, ion trap and other methods) may provide insight into reaction mechanisms and structures of the reaction products.

Positive and negative ions that have the same elemental composition have been subjected to a NR study in order to elucidate ion/neutral structures. Experiments with AuF^+ and AuF^- ions are an example [32]. The NR mass spectra of both species were quite similar, and showed a peak due to Au^+ ions as well as a recovery signal. The latter demonstrated that neutral AuF resided in a potential minimum, and that the elusiveness of this molecule in the condensed phase was caused by intermolecular reactions rather than by intrinsic instability.

Negative ions are seldom used in NR MS experiments compared to positively charged species. There are several reasons for relatively infrequent use of negatively charged ions. One of them is that the ionization techniques (EI, CI, FAB) that are most commonly employed for NR MS studies do not always produce high fluxes of negatively charged ions of interest. From this point of view, electrospray ionization can be extremely advantageous in the future for the generation of negatively charged ions with high yields.

Another reason for utilizing negatively charged ions is that they have a lower tendency for rearrangements than their positively charged analogs. As a result, it is generally more difficult to produce negatively charged ions with 'unusual' atom connectivity, i.e. those that are often sought as precursors for the corresponding neutrals.

There is an obvious rationale for generating negatively and positively charged ions as precursors for neutrals in NR MS experiments. Atom connectivity in ions having opposite charges may be different. It gives a rare opportunity to generate and to study isomeric species. For example, a combined NR MS and ion–molecule reaction study of FeO_2^+ and FeO_2^- ions generated in the positive and negative chemical ionization modes clearly demonstrated that differently charged FeO_2 species possessed different structures [28].

Concluding this section, a variety of ionization methods, reactions and precursor molecules or ions can be employed to generate metal-containing ions for NR experiments. One of the requirements of these reactions is that they should yield enough ions for recording an acceptable NR mass spectrum. Because different methods may produce ions of different internal energies and structures, it is important to compare properties of all possible isomers before conducting NR MS experiments. Especially valuable are methods allowing the generation of ions having a proven single structure (atom connectivity).

3.5. Specifics of NR MS studies of metal-containing species

Studies of metal complexes sometimes require an approach which is different from that in the studies of organic systems. One of the most common goals of NR studies is the generation of elusive neutral species. The observation of a recovery signal indicates the intrinsic stability of the neutral in the gas phase. These observations may be used to support (indirectly) reaction mechanisms that supposedly involve the neutral as an intermediate. A variety of metal complexes were generated by the NR MS method. Among them are coordinatively unsaturated metal species, hypervalent (for example, 19-electron) complexes, molecules that are unstable in the condensed phase, and species possibly arising in interstellar chemistry.

One of the most common goals of all tandem mass spectrometry studies of metal complexes is to determine the ligand arrangement around the metal atom. From this point of view, mass spectrometry of organometallics is comparable with studies of proton-bound dimers, ion-neutral complexes and similar organic ions, in which the ionic center is well defined. Efforts, therefore, are mainly focused on the identification of the parts (ligands) surrounding the charged center (metal atom). The information about the ligands that can be obtained from mass spectrometry experiments may involve their elemental composition, atom connectivity, and, in some cases, stereochemistry. NR mass spectra may provide more thorough information about the ligands compared with CID and EI mass spectra because of higher internal energies of the species and due to the ability to detect neutral dissociation products. As an example, the NR mass spectrum of $Cr^+(CH_3SSCH_3)$ ions displayed a peak for $CH_3SSCH_3^{+\bullet}$ ions, in keeping with the presence of the intact dimethyldisulfide ligand [33]. This information could not be obtained from the CID experiments. A rearrangement of $(C_5H_5)_2Fe_2NO^+$ ions to the structure containing C_5H_5N as an entire unit was identified by the NR mass spectrum [34]. The latter displayed a strong signal at *m/z* 79, which was attributed to the loss of neutral pyridine.

The information about atom connectivity *in a ligand* at the metal atom may be obtained from dissociations involving bond ruptures within the ligand. Ions surviving neutralization–reionization usually possess higher internal energy compared with the ions in collision-induced dissociation experiments. Common consequences of a higher internal energy content are a relatively high yield of simple bond cleavage reactions and the observation of processes having high activation energies. As an example, the distinction between two [Cu, C, N, H] isomers has been made using CID and NR MS experiments. The cleavage of the (triple) C–N bond in neutralized–reionized CuCNH and CuNCH resulted in the formation of structure-specific fragments, CuC^+ and CuN^+, respectively [35]. A dissociation of the C–C bond in M^+CCH ions (M = Fe, Ni, Co) produced a structure-characteristic MC^+ fragment in the NR mass spectra [36]. The loss of CH was not observed in CID mass spectra of M^+CCH ions.

4. Metal complexes studied by the NR MS method

In this Section, the results of NR MS studies of metal-containing ions will be described in some detail. The data are organized according to the type of ligand(s) at the metal atom. In many cases the type of metal–ligand bond could be easily recognized, whereas in others the assignment of the complex to one or another type of metal–ligand bonding was not so straightforward. For the latter, we assigned ions to one or another group based on their properties in NR MS experiments. The same principle was applied to the systems containing two different types of ligands. As a cross-reference, all metal-containing ions that have been studied by the NR MS and related methods are listed in Table 1.

4.1. σ-Complexes with no metal–carbon bond

Simple two and three atomic metal-containing molecules and radicals have been characterized by NR MS. Most of these studies were directed to the generation of complexes that are unstable in the condensed phase, but their intrinsic stability was indicated by theoretical methods. Among the species studied are metal halides.

The stability of neutral AuF was predicted by the theory, but this molecule had never been isolated in its monomeric form. Neutral gold(I) fluoride was formed as a product of ion–molecule reactions between Au^+ ions and fluorine-containing organic molecules (C_2H_5F, CH_3COF, CH_3OCFO), but no experiments have been carried out to detect this species. NR mass spectrometry was employed to find experimental evidence for the stability of neutral AuF in the gas phase. AuF^+ ions were produced by electron impact induced dissociation of AuF_3. Subsequently, negatively charged AuF^- ions were generated by ion–molecule reactions in AuF_3–N_2O mixture. The NR mass spectra of both species were similar and displayed a recovery signal corresponding to the formation of a stable neutral gold(I) fluoride species within the experimental time frame [32].

Praseodymium mono- and difluorides were generated by neutralization of the positively charged ions, PrF^+ and PrF_2^+, respectively [26]. These ions were produced by FAB of PrF_3. The NR mass spectra of PrF^+ and PrF_2^+ ions displayed strong recovery signals providing clear evidence for the stability of their neutral counterparts, at least in the gas phase in the microsecond time frame.

Low-valence iron(I) halides have been generated by the NR MS method from their positively charged counterparts [7]. FeX^+ (X = F, Cl, Br, I) ions were produced by electron impact ionization of various π-cyclopentadienyliron complexes. Recovery signals were observed for all four species, indicating the intrinsic stability of neutral Fe(I) halides. Neutral FeF and FeCl have been characterized by experimental and theoretical methods before the NR MS experiments. The formation of stable in the gas phase FeBr was consistent with the theoretical predictions, whereas neutral FeI has not been a subject of theoretical or experimental studies (selected thermochemical parameters for FeI were estimated indirectly). Thus, the NR MS experiments provided the first experimental evidence for the stability of neutral iron(I) bromide and iodide.

The NR MS study of iron halides required special efforts to make sure that the survivor ions were indeed those of FeX [7]. Hydrocarbon ions, $C_6H_3^+$ and $C_7H_7^+$, might interfere with FeF^+ and $FeCl^+$, respectively. Two types of MS/MS/MS experiments were carried out to confirm the identity of these metal-containing ions. In a first set of experiments, FeF^+ and $FeCl^+$ ions were generated in the second FFR of the mass spectrometer from the collisionally excited *mass-selected* $C_5H_5FeX^+$ ions, energy selected and transmitted into the third FFR, where they were subjected to neutralization–reionization. The resulting NR mass spectra contained weak, but well recognizable signals of survivor ions. In the second type of experiments, ions surviving neutralization–reionization in the second FFR were transmitted to the third FFR and collisionally excited. The CID mass spectra displayed a peak corresponding to Fe^+ ions. This result confirmed that at least a part of survivor ions were those of FeF^+ and $FeCl^+$.

A combination of tandem mass spectrometry methods (CID, CR, CS and NR) was used to characterize electron transfer processes in gaseous positively charged, negatively charged and neutral iron chlorides [21]. The NR mass spectra of all positively charged ions, $FeCl_n^+$ ($n = 1-3$), displayed recovery signals indicating that successful one-electron reduction of the ions followed by one-electron oxidation of the neutrals have taken place. The NR mass spectrum of $FeCl_3^-$ ions also showed survivor ions corresponding to the formation of stable iron trichloride, whereas the highest mass peak in the NR mass spectrum of $FeCl_4^-$ ions corresponded to a loss of a Cl-atom. The positive-to-positive ion NR mass spectrum of $FeCl_3^+$ ions was characterized by a higher degree of fragmentation as compared to the negative-to-positive ion NR event. This result reflected the great changes in geometry between positively charged and neutral $FeCl_3$ than between $FeCl_3^-$ and $FeCl_3$. Based on the data obtained by the NIDD method, which allows estimation of the contribution from neutral dissociations, it was concluded that the neutral $FeCl_3$ originating from the corresponding ions was dissociated by a consecutive loss of chlorine atoms rather than by a loss of Cl_2. Signals for Cl_2^+ ions in the CR, CS and NR mass spectra were attributed to the dissociation of electronically excited $FeCl_3^+$ ions [21].

Few metal hydrides have been studied by the NR MS method. The NR mass spectrum of MnH^+ ions was very simple, displaying signals for MnH^+ and Mn^+ ions [23].

A study of FeH^+ ions [7] required more efforts than that of MnH^+. Unlike the monoisotopic manganese, iron has four stable isotopes, ^{54}Fe, ^{56}Fe, ^{57}Fe, and ^{58}Fe. When FeH^+ ions were generated from the electron impact induced dissociation of a variety of iron complexes, Fe^+ ions were *always* co-produced. As a result, the most abundant isotopic species of FeH^+ ions, $^{56}FeH^+$, were overlapping with $^{57}Fe^+$ ions. All attempts to generate FeH^+ ions from mass-selected precursors did not result in sufficient (for further NR MS experiments) fluxes of these ions. To avoid the interference between FeH^+ and Fe^+, the ions at m/z 55, $^{54}FeH^+$, were mass selected and subjected to neutralization–reionization. The NR mass spectrum of $^{54}FeH^+$ ions was dominated by Fe^+ ions, with the recovery signal accounting for only 2–3% of the total ion current. These results however, indicated that stable neutral FeH molecules had been generated in the course of the experiments. They also demonstrated a low stability of this species, which might arise from a (relatively) weak Fe–H bond.

Further NR MS studies of metal hydrides seem to be a very important issue in the elucidation of structures of ions and neutrals by this method. A point of interest is the ability to recognize isomers with the MXH and HMX connectivity of atoms (groups). The observation of a signal due to $MH^{(+-)}$ ions would be a good indication for the presence of the metal–hydrogen bond. This bond, however, is usually weak and may not survive the NR conditions. The absence of MH ions in the NR mass spectrum does not rule out the presence of a M–H bond in the original ion or in the corresponding neutral. However, it does not provide direct evidence for the existence of this bond. Therefore the experiment should be optimized to provide conditions for survival of the M–H bond. Otherwise any conclusions about possible isomerization of MXH to HMX in ions or neutrals based on the absence of the signal become controversial.

A number of alkali metal derivatives, M_2X, were generated by NR MS experiments from their positively and negatively charged analogs [27]. This study can be considered as a continuation for a search of neutral hypervalent radicals, such as halonium, oxonium, ammonium, and others [1,9]. The presence of the metal atom made the neutrals more stable than their hydrogen analogs. Survivor ions were present in the NR mass spectra demonstrating the stability of $Li_2F^\bullet$, $Li_2OH^\bullet$, $Na_2OH^\bullet$, $K_2OH^\bullet$, $Na_2SH^\bullet$, and $K_2SH^\bullet$ radicals in the gas phase. These experimental observations were consistent with the theoretical calculations that predicted their stability. The calculations anticipated the involvement of the additional electron in metal–metal bonding. Charge reversal, positive-to-negative, experiments were performed with Li_2F^+ ions [27a] with trimethylamine as a target gas. The mass spectrum showed a strong signal due to Li_2F^- ions, which was considered as additional (to the $^+NR^+$ mass spectrum) evidence for the intermediate formation and intrinsic stability of the neutral $Li_2F^\bullet$.

The NR mass spectrum of FeO^+ ions was recorded [7,31]. Neutral FeO is a well-known stable species so that the observation of a strong recovery signal was not unexpected.

Positively and negatively charged FeO_2 ions were investigated by tandem mass spectrometry methods to determine the atom connectivity and to prove the stability of the corresponding neutrals [28]. These ions were generated by ion–molecule reactions in mixtures of ionized $Fe(CO)_5$ and O_2. Linear or bent *η^1-end-on* complex, symmetrical *η²-side-on* FeOO, or iron dioxide with the metal atom inserted in the O_2 molecule, OFeO, were considered as possible structures for these species.

The CID mass spectrum of FeO_2^+ ions was similar to the charge-stripping mass spectrum of their negatively charged counterparts. FeO^+ and Fe^+ ions were dominant species, with weak signals due to FeO^{2+}, Fe^{2+} and $O_2^{+\bullet}$ ions; the latter was very weak. The observation of O_2^+ ions was ascribed to the dissociation of iron dioxide. The major difference between the two mass spectra was due to a higher FeO^+/Fe^+ ion abundance ratio for FeO_2^- [28].

Differences in the reactivity of FeO_2^+ and FeO_2^- ions were more profound in oxygen isotope exchange reactions of $Fe^{18}O_2^{(+-)}$ with $^{16}O_2$. This study was performed in a FT-ICR spectrometer [28]. $Fe^{18}O_2^+$ ions underwent the substitution of the oxygen molecule by another to yield products that have two ^{16}O or two ^{18}O atoms only, whereas $Fe^{18}O_2^-$ also formed mixed oxygen isotope species, $Fe^{18}O^{16}O^-$. These results were consistent with OFeO and FeO_2 atom connectivity in anions and cations, respectively.

The NR mass spectra of both ions were recorded to prove the stability of the corresponding neutrals [28]. They showed the same ion peaks. The NR mass spectrum of FeO_2^+ ions displayed more abundant O_2^- ions compared to the NR mass spectrum of FeO_2^-. $O_2^{+\bullet}$ ions resulted from the collisional ionization of neutral O_2. The charge-stripping mass spectrum of FeO_2^- ions was essentially identical to the NR mass spectrum. A very weak signal due to $O_2^{+\bullet}$ ions was found; that result was consistent with an OFeO rather than an FeOO atom connectivity.

The observation of recovery signals in the NR mass spectra of FeO_2^- and FeO_2^+ ions [28] indicated that vertical neutralization of both species resulted in neutral counterparts, OFeO and FeO_2, respectively, which were stable within the mass spectral time frame.

Recovery signals were also found in the $^-NR^+$ mass spectra of FeO_3^- and FeO_4^- ions [28]. With respect to the O_2^+ signal intensities, the structure of the first corresponded to an iron(V) trioxide structure for FeO_3^-, whereas FeO_4 contained at least one O_2 ligand. Both ions formed neutrals that survived the NR conditions. It is worth noting, however, that the observation of a recovery signal in the NR mass spectra of metal-containing ions with an even-electron ligand(s) is rather uncommon. There is a reason, therefore, to believe that the oxygen ligand in FeO_4 ions formed a cyclic Fe–O–O fragment rather than existed as an oxygen molecule coordinated to the metal atom.

The NR mass spectrum of $FeOH^+$ ions [7] displayed a strong recovery signal along with other structure-specific ions (Fe^+, OH^+). No FeH^+ ions were present in the NR mass spectrum, giving no indication for the formation of the $HFeO^+$ isomer. It should be noted, again, that the *non*-observation of a signal in a NR mass spectrum does not necessarily rule out the absence of the corresponding species. Therefore, even though the $HFeO^+$ structure seems to be extremely unlikely, there were no *direct* experimental data that refuted its formation from the $FeOH^+$ isomer.

Similar results were obtained for $MnOH^+$ ions [17], being consistent with the MnOH atom connectivity in the ions and in the corresponding (stable) neutrals.

The case of $[Fe, C, O, H_3]^+$ ions [37] demonstrated the importance of an ion structure's dependence on its origin. $FeOCD_3^+$ ions generated by the reaction of FeR^+ ($R = F$, OH) with CD_3OH did not show H/D-atom exchange with H_2O in FT-ICR conditions; that lack of exchange indicated the exclusive formation of the isomer with the methoxy group. In contrast, a reaction of Fe^+ with CD_3NO_2 (in the presence of excess of Ar) resulted in ions that underwent H/D exchange with H_2O, C_2H_4 and CH_2O. The latter results were consistent with the formation of a mixture of $FeOCD_3^+$ and $DFeOCD_2^+$ ions.

Unfortunately, tandem mass spectrometry, CID and NR, experiments on a sector mass spectrometer could only be performed on ions generated from ion–molecule reactions with CH_3OX derivatives, and, therefore, were related to a mixture of isomers. The CID and NR mass spectra of these species showed structure-characteristic peaks for both isomers. The presence of the iron–methoxide structure was indicated by FeO^+ ions. The observation of FeH^+ ions was consistent with the $HFe(OCH_2)$ connectivity of atoms. Survivor ions showed a strong signal in the NR mass spectrum of $[Fe, O, C, H_3]^+$ ions. It is unclear, however, if they corresponded to the formation of stable $FeOCH_3$, to its isomer $HFe(OCH_2)$, or to both species.

The NR and CR mass spectral experiments were an essential contribution to the understanding of the redox chemistry of the FeS system [31]. The energy-resolved charge reversal of FeS^- ions resulted in the loss of energy of $\Delta E = 10.0 \pm 0.5$ eV. Subtracting the electron affinity of FeS from ΔE, the ionization energy of FeS was calculated as 8.3 ± 0.6 eV. In CR experiments, two electrons can be 'stripped' simultaneously from the ions. As a result, the observation of the 'recovery' signal in CR mass spectra cannot be considered as convincing proof for the formation of the corresponding neutral. To prove the existence of the neutral FeS, the NR experiment was carried out with FeS^+ ions. In this case, the observation of the recovery signal provided direct evidence for the formation of the (previously known) FeS molecule.

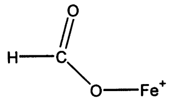
A transition from di-atomic FeS to tri-atomic FeS_2 posed a question about the connectivity of atoms in the latter [19]. The CID mass spectra of FeS_2^- and FeS_2^+ ions were dominated by structurally unspecific signals due to FeS^+ and Fe^+ ions. When neutralization–reionization of FeS_2^+ ions was performed, a strong peak due to S_2^+ ions was detected. It indicated the presence of a S–S bond in the positively charged ions. The $^-NR^+$ and $^-CR^+$ mass spectra of FeS_2^- ions, on the contrary, showed only weak signals of S_2^+ ions being consistent with the SFeS connectivity of atoms. The comparison of the latter two mass spectra (NIDD method) revealed that the S_2^+ ions greatly originated from neutrals formed upon neutralization, i.e. as a result of the SFeS to FeS_2 rearrangement. Another indication for the isomerization was provided by a very close similarity of CID mass spectra of FeS_2^+ ions before neutralization to the CID mass spectrum of FeS_2^+ ions originating from charge inversion of FeS_2^-. The experimental observations and the results of theoretical calculations were consistent with the cyclic structure of FeS_2^+ ions, SFeS connectivity of the atoms in FeS_2^- ions, and with dichotomy between the two structures in neutral FeS_2.

Two neutral copper-containing oxides, CuO and CuO_2, were successfully generated from the corresponding ions by the NR MS technique [38]. The dissociation characteristics of the latter were consistent with the OCuO atom connectivity. This was indicated by a strong signal due to CuO^+ ions in the CID and NR mass spectra.

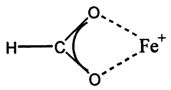
Cu^+N and Cu^+NO ions also displayed recovery signals in their NR mass spectra [38]. Structural assignment for Cu^+NO ions was based on the collision-induced dissociation, neutralization–reionization and it was supported by theoretical calculations. The CID and NR mass spectra were dominated by Cu^+ ions, the CuN^+ and CuO^+ ions being of only minor abundance. This observation was consistent with a “side-on” $Cu^+(NO)$ or with a mixture of two interconverting “end-on” structures, Cu^+–NO and Cu^+–ON, rather than with an insertion type structure $OCuN^+$.

The NR mass spectrum of iron(I) amide, $FeNH_2^+$ [7], showed characteristics that were similar to those of $FeOH^+$. The presence of the recovery signal confirmed the intrinsic stability of the neutral $FeNH_2$. The amido structure of the complex was established by the presence of NH_2^+ ions. No indications were found for the HFeNH structure of ions or neutrals involved in the neutralization–reionization process.

Two iron chelates, $HCOOFe^+$ [24] and $acacFe^+$ [7], were characterized by the NR MS method. The NR mass spectrum of the latter ion indicated the stability of the iron(I) acetylacetonate complex in the gas phase. The dissociation characteristics of the survivor ions were similar to those of the collisionally activated ions prior to their neutralization.



A



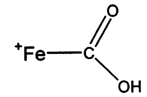
A'

$H-Fe^+-CO_2$

B

$HO-Fe^+-CO$

C



D

A study of $[Fe, C, H, O_2]^+$ ions was a good example of how a combination of various tandem mass spectrometry methods can be used to reveal the connectivity of the atoms [24]. The ions were produced by ion–molecule reactions in a $Fe(CO)_5/HCOOCH_3$ mixture and might possess structures **A**–**D**. Ion–molecule reactions of thermalized $[Fe, C, H, O_2]^+$ ions were performed in a FT-ICR spectrometer. The dominant reaction was a loss of CO_2, which might correspond to structures **A**, **B** or **D**. The absence of ligand exchange with $^{13}CO_2$ ruled out the structure **B**.

CID and NR mass spectra of $[Fe, C, H, O_2]^+$ ions and their partially ^{18}O-labeled analogs were studied to ascertain the positional identity of the oxygen atoms. A signal due to CO_2H^+ was expected for isomer **D**, but no peak at m/z 45 was found in either the CID or NR mass spectra thus leaving only two possible structures: **A** and/or **A′**. The CID mass spectrum of the $Fe^{18}O^{16}OCH^+$ product exhibited both $Fe^{18}O^+$ and $Fe^{16}O^+$ ions, favoring the former by a factor of 1.2. This value was too high to be explained by a heavy-atom isotope effect in the symmetrical structure **A′**. The connectivity of **A**, which underwent partial oxygen equilibration via a symmetrical carboxylate structure, was suggested as an explanation. In the NR mass spectrum of the labeled species, the $Fe^{18}O^+$ and $Fe^{16}O^+$ ions were of equal intensity. This fact as well as the presence of a strong recovery signal were rationalized by a bidentate structure for the neutral iron formate, $\mathbf{A}'^{(0)}$. The minimum estimated life-time of the latter was 0.8 μs [24].

In a short summary, all metal complexes with a bond with a non-carbon atom that were studied by the NR MS method had shown recovery signals. These results were consistent with the stability of neutrals that have been known before. Other low-valence derivatives of transition and alkali metals were generated for the first time. The stability of these species most likely originated from favorable Franck-Condon factors (closeness of the geometry of ions and neutrals) and from a relatively high stability of metal–heteroatom bonds. The NR mass spectra however, do not provide a quantitative relationship between the M–X bond strength and the intensity (abundance) of the recovery signal.

4.2. σ-Complexes having metal–carbon bond

NR MS has been used for the study of various σ-hydrocarbon derivatives of transition metals, $MC_nH_m^+$, where M = Mn, Co, Ni, Fe, Cr, Ti, Rh, and for the generation of their neutral counterparts. Among them were simple di-atomic metal carbides, FeC^+ [25] and RhC^+ [23]. Their NR mass spectra displayed very strong signals of recovery ions as expected for the systems with a multiple metal–carbon bond.

For the species having three or more atoms, the determination of hydrogen distribution between the metal and carbon atoms becomes essential. CID experiments are a common first step in elucidation of the atom connectivity. NR mass spectra can provide additional data about "structures" of the ions as well as information on whether the corresponding neutral is stable in the gas phase.

$FeCH_3^+$, $FeCH_2^+$, and $FeCH^+$ ions were generated by ion–molecule reactions in mixtures of $Fe(CO)_5$ with either CH_3I, CH_2Br_2, or $CHBr_3$, respectively [24]. The NR mass spectra of $FeCH_3^+$ and $FeCH_2^+$ were dominated by the Fe^+ ion and also showed peaks due to CH_3^+ and $CH_2^{+\bullet}$ ions, respectively. No FeH^+ ions were found. These data demonstrated that $FeCH_3^+$ and $FeCH_2^+$ ions and their neutral counterparts existed largely, if not exclusively, as metal–methyl and metal–methylene and not as the hydrido-metal structures, $HFeCH_2$ and HFeCH, consistent with the ion–molecule chemistry of the $FeCH_3^+$ and $FeCH_2^+$ ions reported elsewhere. The NR mass spectrum of $FeCD_3^+$ ions displayed a larger recovery signal compared to that for $FeCH_3^+$ ions. This result could be attributed to a kinetic isotope effect for C–H versus C–D bond fission or to a simple mass effect [24].

The NR mass spectrum of $FeCH_3^+$ ions generated by EI induced dissociation of acetylferrocene [7] was very close to that observed by ion–molecule reactions [24], even though different targets (dimethyl amine and xenon, respectively) were used for neutralization. Similar results were obtained for $MnCH_3^+$ [23] and $AlCH_3^+$ [39] ions; both of them showing recovery signals and other ions corresponding to MCH_3 connectivity of the atoms.

In contrast to $FeCH_3^+$ and $FeCH_2^+$, the CID and NR mass spectra of $FeCH^+$ displayed Fe^+ and FeH^+ ion peaks, indicating that part of the FeCH species may possess HFeC connectivity of the atoms [24].

The results of the $AlCH_2^+$ ions' investigation [39] were closely similar to those for the corresponding iron-containing species. The NR mass spectrum of $AlCH_2^+$ displayed an intense recovery signal and the Al^+ ion as a major dissociation product. The other peaks corresponded to AlC^+, $CH_2^{+\bullet}$, and CH^+ ions. Formation of hydrocarbon ions was considered to result from the (dissociative) reionization of the neutral CH_2 species arising from collision-induced dissociation of $AlCH_2^+$. No $H^\bullet$ or $CH^\bullet$ losses were found; these reactions would be indicative for $AlCH_2$ to HAlCH isomerization.

The NR mass spectra of MC_2H^+ ions, originating from ionized $(C_5H_5)_2M$ (M = Ni, Co, Fe), showed survivor ions whose abundances followed the order M = Fe < Co < Ni [36]. The decomposition characteristics of MC_2H^+ species corresponded to an acetylide, $MCCH^+$, and not to the $CC(H)M^+$ structure. This conclusion was indicated by the presence of MC^+ ions and by the total absence of MCH^+ ions. The formation of the third isomer, HMCC, was ruled out because of the absence of any significant peaks due to MH^+ ions.

Two aluminum-containing $C_2H_4M^+$ isomers, $Al(C_2H_4)^+$ and $HCAlCH_3$, generated from $Al(C_2H_5)_3$ and $Al(CH_3)_3$, respectively, have been identified by their CID and NR mass spectra [39]. For both $[Al, C_2, H_4]^+$ species, losses of H_2 and C_2H_4 were observed. In addition, the isomer of $HCAlCH_3$ connectivity showed $AlCH^{+\bullet}$ and $AlCH_3^{+\bullet}$ ion peaks. These peaks were not present in the CID or NR mass spectra of $Al(C_2H_4)^+$ ions, ruling out their communication with the $HCAlCH_3^+$ form, although the reverse isomerization could not be excluded. The NR mass spectrum of $HCAlCH_3^+$ did not give rise to detectable survivor ions, whereas a weak recovery signal was found in the NR mass spectrum of the aluminum–ethene complex. The weakness of survivor ions for $Al(C_2H_4)^+$ ions might be due to a low Al–ethene bond dissociation energy in the neutral species or to significant differences in the geometries of the ions and their neutral counterparts. The latter argument was used to explain the absence of a recovery signal in the NR mass spectrum of $HCAlCH_3^+$, and thus it does not necessarily follow that the neutral species having this connectivity is not a minimum on the $[Al, C_2, H_4]$ potential energy surface.

Electron impact induced dissociation of $(CH_3)_3Al$ and $(C_2H_5)_3Al$ also resulted in two $[Al,C_2,H_6]^+$ isomers [39]. The $(CH_3)_2Al$ connectivity of the atoms in the ions originating from trimethyl aluminum was clearly indicated by consecutive methyl radical losses and by the presence of CH_3^+ ions. In the NR mass spectrum of $(CH_3)_2Al^+$ ions, peaks due to $C_2H_n^+$ ions were not found, ruling out the formation of a C–C bond in the ions or in the corresponding neutrals.

The dissociation characteristics of $C_2H_6Al^+$ ions derived from $(C_2H_5)_3Al$ were different from those for ions of a $(CH_3)_2Al^+$ structure [39]. The major fragments in the CID mass spectrum corresponded to $C_2H_4Al^+$ and hydrocarbon ions, and no recovery signal was found in the NR mass spectrum. The connectivity in this second C_2H_6Al isomer was assigned to $HAlC_2H_5$.

The NR mass spectrum of $MnC_6H_5^+$ has been reported [17]. This ion originated from

$Mn^+C_5H_4COC_6H_5$ via a migration of the β-substituent in the π-cyclopentadienyl ligand to the central metal atom. The intensity of the recovery signal was very low, which can be (at least partially) accounted for by the use of a neutralization target with a high IE (Xe). The most intense peaks corresponded to Mn^+ and $C_6H_5^+$ ions. The latter was most likely due to the reionization of phenyl radicals produced from the metastable (or collision-induced) dissociation of $C_6H_5Mn^+$ ions or decomposition of their neutral counterparts.

The CID and NR mass spectra of $FeC_6H_5^+$ ions [7] were consistent with the presence of the phenyl group. The recovery signal was rather intense (Me_2NH was used for neutralization), and its observation undoubtedly indicated that a stable neutral phenyl derivative of Fe(I) has been formed. Other metal-containing ions were formed by losses of H, C_2H_n ($n = 2$–4), C_4H_n ($n = 4$, 5), and C_6H_5 from the reionized $Fe^+C_6H_5$. A peak at m/z 77 and other hydrocarbon fragments corresponded to the (reionized) phenyl group.

$FeCN^+$ ions were subjected to neutralization–reionization as a part of a search for (stable) low-valence iron derivatives [7]. The observation of the recovery signal proved the stability of neutral FeCN. The FeCN connectivity of the atoms was confirmed by the presence of FeC^+ and the absence of FeN^+ ions in the NR mass spectrum.

The NR mass spectrum of $[Fe, Cl, C_3, H_6, O]^+$ ions formed by ion–molecule reactions of $FeCl^+$ ions with acetone showed a weak recovery signal. This fact was assigned to the formation of $[CH_3Fe(Cl)COCH_3]^+$ rather than to the $FeCl^+$ cation solvated with an acetone molecule [40].

Only one of the $[Fe, C_3, H_6, O]^+$ isomers survived the NR event [29]. The ions formed by ion–molecule reactions in a mixture of ionized $Fe(CO)_5$ with CH_2=$CHCH_2OH$ were consistent with the structure having the metal atom inserted to the C–O bond, C_3H_5FeOH.

In summary, for almost all of the systems described in this section, recovery signals were present, which is associated with the presence of a strong σ-M–C bond and small geometry changes upon the electron transfer processes. The results for the $[Al, C_2, H_4]$ ion/neutral system were an exception. The non-observation of a recovery signal (for $HCAlCH_3$) may be explained by a weak metal–ligand bond in the species containing a non-transition metal atom and/or by significant geometry differences between the ion and the corresponding neutral.

4.3. Metal solvates

Several difficulties may accompany studies of metal complexes containing small, solvent-like molecules, L, as ligands by the NR MS method. A metal–ligand bond in these M^+L or M^+L_2 complexes is usually due to the electron pair of the heteroatom in L, but interaction with a π-system of the organic ligand is also possible (the results for the majority of π-complexes will be discussed in Section 4.5). In many cases it is difficult, if not impossible, to determine the type of coordination, and the appropriate models cannot be easily obtained. Also, M-solvent bonds in the neutral and ionic complexes are rather weak, so that even small differences in geometries of ion and neutrals may cause a facile dissociation of the latter. Thus very ‘soft’ NR MS conditions should be applied to produce stable metal–solvent systems by neutralization of the corresponding ions.

Some results of the Ni^+L and Ni^+L_2 ($L = CO$, H_2O, NH_3) ion study [3] have already been described in the present review. These ions were successfully neutralized by metal atom vapors, and the highest stability of their neutral counterparts was observed for targets whose IE was close to the IE of a metal complex. Neutralized beam scattering profile analysis was performed to estimate fragmentation energies. The values obtained for NiCO, $Ni(D_2O)$, and $Ni(ND_3)$ were 1.3, 0.9, and 0.25 eV, respectively, and were in agreement with theoretical predictions. It was not surprising that these species showed weak or no recovery signals when reionization was performed after neutralization. This result likely originated from a significant difference in the geometries of the ions and their neutral counterparts. For example, the calculated Ni^+–CO bond distance is about 0.4 Å greater than the Ni–C bond distance in NiCO. It should be noted again that the results of Hudgins and Porter [3] demonstrated the importance of varying the experimental conditions to assist the observation of elusive neutrals with binding energies as low as 0.2 eV.

The NR mass spectra of $Cu(NH_3)^+$ and $Cu(NH_3)_2^+$ ions showed that the corresponding neutrals were stable species in the gas phase [30], complementing the observation of these molecules in cryogenic matrixes. The mass spectra were dominated by Cu^+ ions. Low intensity of $CuNH_2^+$ ions relative to Cu^+ and NH_n^+ ions in the NR mass spectrum compared to the CID mass spectrum suggested that significant dissociation of neutral $CuNH_3$ had taken place. A comparison of NR mass spectra of $Cu(NH_3)^+$ and $Cu(NH_3)_2^+$ ions indicated an intensive dissociation of neutral $Cu(NH_3)_2$ by a loss of one ammonia. Neutral $Cu(NH_3)$ generated from $Cu(NH_3)_2$ was energetically less excited than the species formed by direct reduction $Cu(NH_3)^+$ ions. The absence of CuH^+ ions ruled out any significant isomerization to an isomer hiving a Cu–H bond.

A number of iron mono- and di-ligated ions were examined by the NR MS method [41]. LFe^+ ions ($L = H_2O$, NH_3, 1,3-butadiene, benzene) produced recovery signals of extremely low intensity (0.1–0.3% of the major peak); most of which was accounted for by isobaric interferences from other ions. The NR mass spectra were dominated by signals due to Fe^+ and L^+ ions; these ions were most likely produced by collisional ionization of the corresponding neutrals. Similar results were obtained for L_2Fe systems (H_2O, NH_3, C_2H_4, 1,3-butadiene, benzene). Recovery signals were barely (if any) observed and LFe^+ ions showed very low intensities (0.1–6% of the base peak). A significant stabilization of Fe-bond was provided by a CO ligand.

A number of $[C_3, H_6, O, Fe]^+$ isomers were studied using collision-induced dissociation, ion–molecule reactions, and NR MS [29]. Ligand exchange reactions in mixtures of ionized $Fe(CO)_5$ with C_2H_5CHO, $CH_2{=}CHOCH_3$, 1,2-propene oxide, acetone, oxetane, and CH_2O/C_2H_4 resulted in ions that did not survive NR. The NR mass spectra of all these species were dominated by Fe^+ ions. The presence of $C_3H_6O^+$ ions (except for $CH_2OFe^+C_2H_4$) indicated that C_3H_6O ligands were retained as an intact unit. This type of information could not be obtained from the CID mass spectra. Also the NR mass spectra provided evidence for rearrangement processes. For example, the NR mass spectrum of (oxetane)Fe^+ ions displayed ions indicative of the $CH_2OFe^+C_2H_4$ structure.

Ions of composition $(Cu, C, N, H)^+$ have been probed by the CID and NR techniques to establish atom connectivity within ligands and the metal atom coordination site [35]. The NR and CID mass spectra of the species generated from the $Cu^+(n\text{-}C_3H_7CN)$ complex displayed the CuC^+ ion; the latter was indicative of the 'end-on' Cu–CNH structure. All structures containing a Cu–H bond were ruled out because of the presence of ions corresponding to the intact HNC ligand and the absence of a CuH^+ ion. Complexes containing a Cu atom coordinated to the triple CN bond or the N atom of the HNC molecule were also excluded because the $CuNH^+$ signal expected for these structures was not observed. Similar arguments were used to select the Cu–NCH connectivity for the ions originating from the decomposition of $Cu^+(NCBu^t)$. The NR and CID mass spectra of this species showed CuN^+ and no $Cu(HC)^+$ or CuH^+ ions. Weak, but clearly recognizable, recovery signals were observed, providing evidence that stable (with lifetimes ≥ 0.8 μs), but probably weakly bound "end-on" complexes of HCN and HNC with Cu^+ and Cu^0 exist in the gas phase.

The NR behavior of $Cr^+(CH_3SSCH_3)$ ions [33], produced by ion–molecule reactions in arenetricarbonyl chromium/dimethyldisulfide mixtures, was similar to that of other species discussed in this section. No metal atom insertion into a ligand S–S bond was observed, and thus, the coordination of the ligand to the metal atom must be due to $Cr \leftarrow S$ bond(s). A possible participation of two sulfur atoms in coordination is indicated by the presence of CrS_2^+ ions in the NR mass spectrum. A weak metal–ligand bond and/or significant differences in geometry of the ion and the corresponding neutrals can explain the absence of a recovery signal; this change in geometry most likely relates to the Cr–S bond distance, but no theoretical calculations for such systems have been performed.

The NR MS technique was one of the methods for structural characterization of $[Fe, C, H_5, N]^+$ ions [42]. These ions were formed by ion–molecule reactions of $Fe(CO)_n^+$ ions with 2-amino-2-methylbutane (by a loss of C_4H_8 from the adduct) or with CH_3NH_2. None of these ions survived neutralization–reionization and their NR mass spectra were qualitatively similar. The presence of a strong signal due to $FeNH_2^+$ ions in the NR mass spectrum of the species originating from the unimolecular dissociation of $Fe^+(EtMe_2CNH_2)$ ions was consistent with the insertion of the metal atom to the C–N-bond. A peak for $CH_3NH_2^{+\bullet}$ ions was assigned to the reductive elimination process.

When $[Fe, C, H_5, N]^+$ ions were produced by ligand substitution reaction(s), their NR mass spectrum displayed a significantly lower signal of $FeNH_2^+$ ions [42]. This result was rationalized as supporting the formation of Fe^+ ions having methylamine as an intact ligand.

The vast majority of metal solvates studied by the NR MS method did not survive neutralization–reionization conditions. Only a few complexes produced very weak recovery signals. The most likely factor, which is responsible for the instability or a very low stability of these species in the NR MS conditions, is unfavorable Franck–Condon neutralization with low metal–ligand bond dissociation energies. The excess energy transfer to the neutral in the reionization act may also contribute to the low stability of survivor ions. The presence or the absence of a recovery signal may be used as a test for the structure of the ion and the corresponding neutral. This test should be especially helpful when two or more isomers are studied. The isomers having an even-electron molecule as a ligand are the least likely to survive neutralization–reionization.

4.4. Metal carbonyls

Some carbonyl complexes of transition metals have been subjected to neutralization–reionization. The results for $NiCO^+$ and $Ni(CO)_2^+$ ions [3] were described in previous sections. Recovery signals were observed in both cases, but only when IEs of targets were higher than (Zn; IE = 7.646 eV)) or similar (Mg; IE = 9.394 eV)) to EIs of neutral Ni(CO) (~ 7.6 eV) and $Ni(CO)_2$. Exothermic electron transfer from K (IE = 4.341 eV) and Na (IE = 5.139 eV) resulted in the disappearance of survivor ions. Low intensity or the absence of peaks of survivor ions in the NR mass spectra was explained by an unfavorable Franck–Condon factor; calculated Ni–

CO bond distances in Ni(CO) and $Ni(CO)^+$ differ by ~0.4 Å. Collisional ionization of the neutrals was performed using NO_2, which is considered as a very soft reionization target, but still might contribute to extensive fragmentation of newly formed $NiCO^+$ and $Ni(CO)_2^+$ ions.

Iron mono-carbonyl also showed a recovery signal in the NR (Xe/O_2) mass spectrum [11]. According to the quantum chemical calculations, the species surviving neutralization–reionization most likely were FeCO ($^5\Sigma^-$) neutrals generated from the $Fe(CO)^+$ ions in ($^5\Sigma^-$) electron configuration (in the following publication by the authors, however, the possibility of formation of neutral FeCO in the $^3\Sigma^-$ ground-state was not ruled out [41]). The calculated geometries of these two species were very close to each other as the calculated barrier for the dissociation of FeCO ($^5\Sigma^-$) was ~24 kcal mol^{-1}. Therefore, the internal energy of the neutrals (or at least of some of them) should have been lower than the dissociation limit. The NR mass spectrum of $FeCO^+$ ions was dominated by Fe^+ ions and also displayed peaks due to FeC^+, CO^+ and C^+. A significant signal was observed for FeO^+ ions. The latter indicated that a fraction of the precursor ions contained a metal coordinated to the oxygen atom of the CO ligand.

The stabilizing effect of the carbonyl ligand on neutralization–reionization of iron 'di-solvates' was found by a study of LFe^+, L_2Fe^+ and $LFe(CO)^+$ ions, where L = NH_3, H_2O, CO or a hydrocarbon ligand [41]. The NR mass spectra of all $LFe(CO)^+$ ions displayed distinctive recovery signals accompanied by LFe^+ and Fe^+CO ions. The observation of pronounced survivor ions for the LFeCO system was attributed to the formation of low-spin states of carbonyl-containing neutrals.

Unlike $Fe(CO)^+$, $Fe(CO)_2^+$ and $Ni(CO)^+$ ions, the NR mass spectrum of $Cr(CO)^+$ ions (dimethylamine/O_2) did not show a recovery signal [23]. Neutral CrCO is very weakly bound (calculated metal–ligand bond energy does not exceed 14 kcal mol^{-1}). According to some calculations it may have a bent geometry (unlike the ion), so that an unfavorable Franck–Condon factor may be another reason for the instability of CrCO. The only ion among chromium carbonyls, $Cr(CO)_n^+$ ($n = 1$–6), that produced a distinctive recovery signal was $Cr(CO)_6^+$. Although a participation of electronically excited states cannot be excluded in this case, it is likely that small geometry changes upon collisional neutralization and reionization in this coordinatively saturated system were the main reason for its stability in the experimental conditions. A similar argument can be applied to the $W(CO)_6^+/W(CO)_6$ system, which also produced a distinctive recovery signal [14]. In the latter case the formation of electronically excited states is rather unlikely because of the nature of the metal atom.

Although there have been just a few NR MS experiments with metal–carbonyl systems, the results show how many different factors may be involved in the processes and their output. A Metal–CO system looks very simple, but the CO ligand can be attached to the metal by C atom, O atom or by C=O (double) bond. The two first isomers, MCO and MOC can be easily identified by the presence of MC^+ and MO^+ (both of them were observed for the FeCO system [11]), whereas the detection of the *side-on* M–CO system is not that straightforward. It appears that the geometry of some $M(CO)_n$ complexes is very sensitive to the oxidation state of the metal atom. As a result, an unfavorable Franck–Condon factor may be significant in whether or not the recovery signal will be observed. The nature of targets that are used in the neutralization and reionization processes is also important. It is very unlikely that a recovery signal will be observed if the IE of the target for neutralization is lower than the IE of the neutral species to be produced from the projectile ion. Finally, electronic excited states are easily available for some transition metal derivatives, which should be taken into account in the interpretation of the experimental results.

4.5. Complexes with hydrocarbon π-ligands

A variety of transition metal complexes with a π-ligand or ligands have been studied by means of NR MS. Like many other cases, two general goals were pursued in these studies. One of them is the generation of unstable (in other experimental conditions) or unknown metal-containing derivatives. The success or failure of these experiments very much depended upon the nature of the ligand. In general, neutral (or reionized) species containing unsaturated even-electron hydrocarbons (acetylene, ethene, benzene, etc.) π-bonded to the central metal atom generated in the NR MS experiments easily dissociated. Most of the systems with an odd-electron (such as cyclopentadienyl) ligand produced neutrals that were stable in the experimental time frame. The other objective of NR MS studies was to elucidate structures of ions and mechanisms of their dissociations.

The results of a combined NR MS and theoretical study of the $Fe^+C_2H_4/FeC_2H_4$ system are described in the present review in several sections. This complex did not survive neutralization–reionization because of a low stability of the neutral and unfavorable Franck–Condon factor [11].

NR MS was employed to study the mechanism of oligomerization of acetylene on metal centers [43]. $[(C_2H_2)_n]Fe^+$ ions ($n = 2$, 3, 4) were generated by ion–molecule reactions in mixtures of the ionized $Fe(CO)_5$ with acetylene and their structures tested by CID and NR mass spectra. A recovery signal was practically

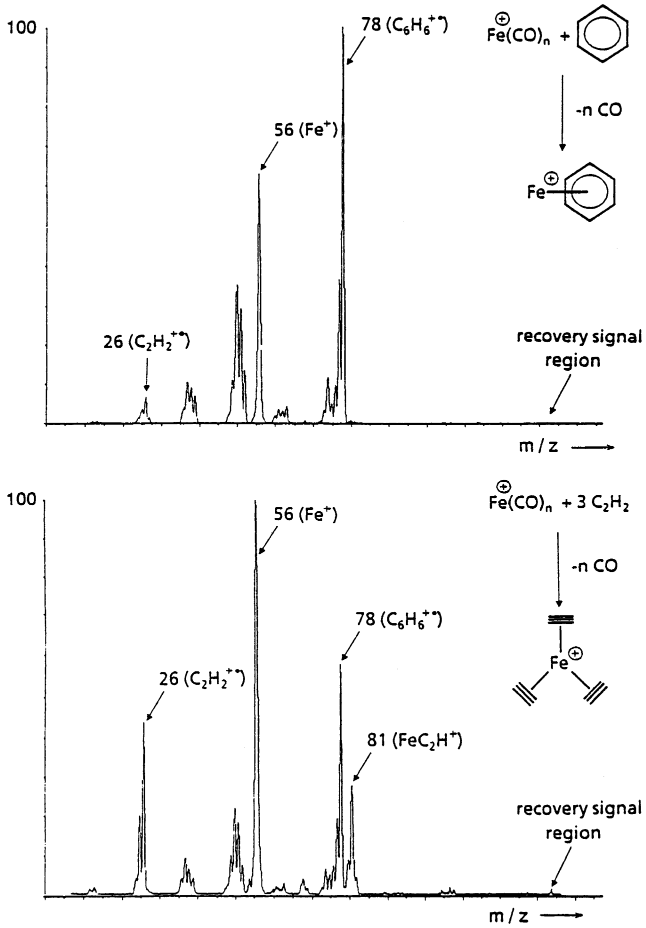


Fig. 6. NR mass spectra of (a) $[FeC_6H_6]^+$ and (b) $Fe[(C_2H_2)_3]^+$ ions (reproduced with permission from Ref. [43]).

absent for $[(C_2H_2)_2]Fe^+$ ions and signals for $C_4H_m^+$ ions were very weak. The dominant signals in the NR mass spectrum corresponded to Fe^+, $C_2H_2^+$, and $FeC_2H_m^+$ ($m = 0$–2) ions. These features were consistent with the formation of bis-acetylene structure $Fe^+(C_2H_2)_2$. Similar observations were made for $[(C_2H_2)_4]Fe^+$ ions. The NR mass spectrum of the latter ions showed no or very weak recovery signals and peaks due to $C_8H_m^+$ ions. The presence of a strong signal for $C_6H_6^+$ ions was consistent with the formation of a partially condensed structure, $C_6H_6Fe^+C_2H_2$.

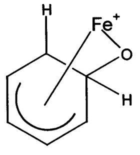
To evaluate a structure of $[(C_2H_2)_3]Fe^+$ ions, mass spectral characteristics of tri-acetylene adduct were compared with those for the ion having a benzene ring [43]. The latter was generated in a mixture of ionized $Fe(CO)_5$ with benzene. The NR mass spectrum of Fe^+(benzene) ions (Fig. 6) did not show a recovery signal, which could be explained by a low metal–ligand binding energy in the neutral. The most intense peaks corresponded $C_6H_6^+$ and Fe^+ ions, being consistent with the presence of the benzene moiety. The NR mass spectrum of $[(C_2H_2)_3]Fe^+$ ions that have been generated in a $Fe(CO)_5$–acetylene mixture is also shown in Fig. 6. In addition to expected signals for Fe^+, $Fe(C_nH_m)^+$ and $C_2H_2^+$ ions, it displayed intense signals for the ionized benzene and related hydrocarbon ions. These signals were accounted for by the presence of an intact C_6H_6 ligand in $[(C_2H_2)_3]Fe^+$ ions. The observation of strong signals corresponding to $C_2H_m^+$ and $FeC_2H_m^+$ ions was characteristic of the presence of acetylene ligands. The experimental results indicated that a *partial* trimerization of acetylene in the coordination sphere of the iron ion has taken place. Some of these ions, however, retained intact acetylene ligands. It should be noted that CID mass spectra of the two $[Fe, C_6, H_6]^+$ ions were less structure specific than their NR mass spectra, demonstrating that "NR MS may be superior to other mass spectrometric techniques to probe the structural features of the organic ligands attached to transition metal ions" [43].

The NR mass spectrometric study of $Fe[(C_2H_2)_4]^+$ ions was also consistent with the formation of the benzene ring. It was indicated by the presence of $FeC_6H_m^+$, $FeC_2H_m^+$ and $C_6H_m^+$ ions. These results together with the non-observation of $C_8H_m^+$ were consistent with the $Fe(C_2H_2)(C_6H_6)^+$ structure of the ions [43].

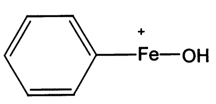
The results for LFe, LFeCO and L_2Fe complexes (L = ethane, 1,3-butadiene or benzene [41]) were presented in Section 4.4. Similar to LFe^+ ions, L_2Fe^+ ions did not survive neutralization–reionization. A characteristic feature of the latter type of ions was the observation of hydrocarbon ions having more carbon atoms than in one ligand. This was due to ligand coupling or as a result of C–C-bond formation on the metal cation "surface". The substitution of one L-ligand in L_2Fe^+ ions by a CO ligand resulted in a significant stabilization of the system and all studied $LFeCO^+$ systems produced stable neutral counterparts in the NR MS conditions.

Structures and reactivity of $[Fe, C_6, H_6, O]^+$ ions and corresponding neutrals were examined by the NR MS method [44]. The ions were generated by ion–molecule reactions in mixtures of ionized $Fe(CO)_5$ with phenol and with N_2O/benzene. The NR mass spectrum of the first ion (Fig. 7a) was consistent with the expected structure of a Fe^+–phenol complex. It displayed characteristic peaks of Fe^+ and $C_6H_5OH^+$ ions. Similar to Fe^+–benzene ions, the Fe^+–phenol complex did not survive neutralization–reionization (cyclopropane/O_2).

The NR mass spectrum of $[Fe, C_6, H_6, O]^+$ ions produced in the $Fe(CO)_5/N_2O/C_6H_6$ mixture (Fig. 7b) was significantly different from that of the phenol adduct [44]. Observation of FeO^+ and $C_6H_6^+$ ions was consistent with the initial formation of a complex between FeO^+ and benzene. The presence of $C_6H_6O^+$ ions indicated a transfer of the oxygen atom to the benzene ligand. (Note, that similar rearrangement was observed for $C_5H_5FeO^+$ ions [16].) The structure of these ions should have been different from the Fe–phenol structure, because a strong recovery signal was present in the NR mass spectrum. The latter indicated the formation of a strongly bonded complex, having a σ-ligand (or ligands) at the metal atom. Structures **E** and **F** were considered by the authors as those producing stable neutral counterparts in the NR MS experiment.



E



F

Similar to iron–benzene ions, simple arene–chromium derivatives $Cr^+C_6H_5R$, having only one aromatic ring in the ligand (structure **G**), did not survive neutralization–reionization conditions [33,45]. These results most likely originated from a weak arene–chromium bond in the neutral complexes (calculated bond energies for the Cr–benzene system did not exceed 14 kcal mol^{-1}). A different situation was observed for a majority of complexes having a ligand with two aromatic rings, $Cr^+(C_6H_5XC_6H_5)$. Especially abundant recovery signals were obtained when two or more atoms separated two phenyl rings. Among these systems were ω-diphenyl alkanes, dibenzyl ether, dibenzyl amine, etc. The results were rationalized by the formation of bis-arene structures of the type **H**, where both aromatic rings of the same ligand were coordinated to the central metal atom. The additional differentiation between **G** and **H** structures was provided by ion–molecule reaction experiments: ions having a coordinatively unsaturated metal atom (structure **G**) showed a significantly higher reactivity in addition reactions (with ammonia and other molecules). Also, the CID mass spectrum of $Cr^+[C_6H_5(CH_2)_4C_6H_5]$ ions surviving neutralization–reionization was indistinguishable from the CID mass spectrum of the ions *prior to* neutralization, confirming that the **H** structure is the one that produced stable neutrals. Some of the neutral complexes of the **H** type generated by the NR MS experiments [33,45] have been described before ($X = (CH_2)_4$, $(CH_2)_5$), whereas others were observed for the first time ($X = (CH_2)_2$, $(CH_2)_3$, CH_2OCH_2, CH_2NHCH_2, CH_2O, etc.).

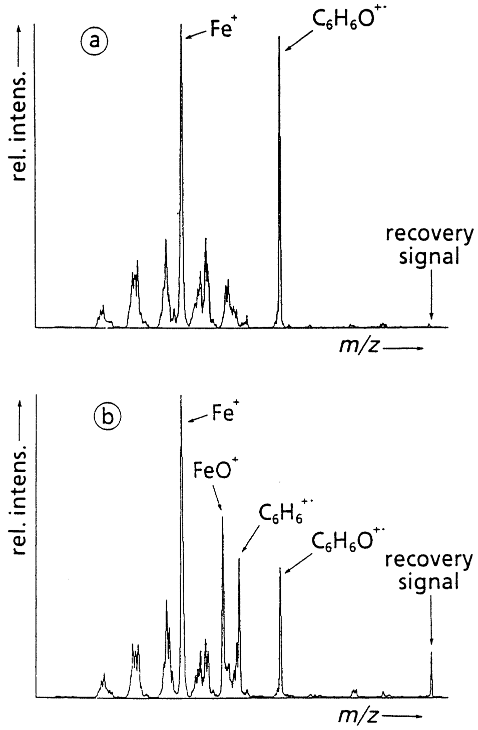
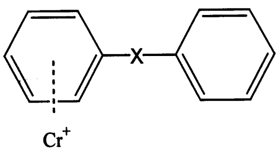
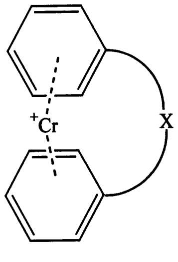


Fig. 7. NR mass spectra of $[Fe, C_6, H_6, O]^+$ isomers originating from electron impact ionization of (a) $Fe(CO)_5$/phenol and (b) $Fe(CO)_5$/N_2O/benzene mixtures (reproduced with permission from Ref. [44]).



G



H

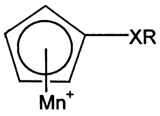
A number of mono- and bisarene chromium complexes have been studied, being model species for the elucidation of the $Cr^+(C_6H_5SSC_6H_5)$ ion structure [33,45]. The latter ions were produced by ion–molecule reactions in arenechromium tricarbonyl/diphenyl disulfide mixtures. None of the $RC_6H_5Cr^+$ or $(RC_6H_5)_2Cr^+$ (R = H, SH, alkyl) ions showed recovery signals, again indicating a lack of arene–metal bonded survivors under NR conditions. In contrast, survivor ions were detected for $Cr^+(C_6H_5SSC_6H_5)$, ruling out all structures with one arene–metal bond. Note also, that a thirty-fold increase in survivor ion abundance (relative to organic ions) was observed when dimethylamine was used for the neutralization compared to the experiments with Xe as a target. $(CH_3C_6H_5)_2Cr^+$ ions did not show a recovery signal under any conditions. The formation of isomers containing Cr–S bond(s) was indicated by the presence of CrS^+ and CrS_2^+ signals in the MI, CID, and NR mass spectra. However these isomers could not be responsible for stable $Cr(C_6H_5SSC_6H_5)$ neutrals, because the analogous complex with CH_3SSCH_3 failed to show a survivor ion [33]. To explain the presence of a recovery signal, formation of a cyclophane structure **H** (X = SS) was proposed.

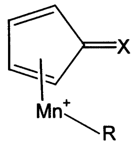
Monocyclopentadienyl derivatives of transition metals have been a subject of several NR MS studies. In one of the first papers on neutralization–reionization of transition metal π-complexes, $C_5H_5Fe^+$, $C_5H_5Ni^+$, and $C_5H_5Co^+$ ions were investigated [46]. All three complexes were dominated by $C_5H_5^+$ and M^+ ions and produced recovery signals of substantial intensity in the NR mass spectra (Xe/O_2), indicating that the corresponding stable neutral 'half-sandwich' complexes can be produced in the gas phase. The order of the relative abundance of survivor ions, similar to that for M^+ CCH [36], was $M = Fe < Co < Ni$ [46]. The trend in stabilities of neutral C_5H_5M however, can be different because various processes contribute to the formation of (fragment) ions observed in NR mass spectra. For example, $C_5H_5^+$ ions can be formed by collisional ionization of neutral cyclopentadienyl generated from metastable and collisionally excited $C_5H_5M^+$ ions, by the dissociation of neutral C_5H_5M, and, possibly, from the reionized $C_5H_5M^+$.

Recovery signals were observed for $C_5H_5Rh^+$ [23] and $C_5H_5Mn^+$ [17] ions, indicating the stability of their neutral counterparts.

A similar result was obtained for $C_5H_5Ti^+$ ions. The recovery signal was very strong and was accompanied by peaks due to the loss of up to five hydrogen atoms. The most intense peak in the NR mass spectrum corresponded to Ti^+, and only a weak $C_5H_5^+$ signal was detected. These observations might be indicative of facile migrations of H-atoms from the π-ligand to the metal atom, and the survivor C_5H_5Ti species could have possessed a metal–hydride rather than metal–cyclopentadienyl structure [47].

A series of substituted cyclopentadienyl–manganese ions was probed by the NR MS method [17] to study a substituent effect on the isomerization of $Mn^+C_5H_4XR$ ions (**I**) to the $RMn^+C_5H_4X$ (**J**) structure. The nonsubstituted derivative as well as $Mn^+C_5H_4CN$ ions could exist only as **I** structure, whereas **J** ions could be formed from $Mn^+C_5H_4XR$ ions ($X = CO$, $R = H$, OH, C_6H_5; $X = CH_2$, $R = H$, OH). The MI and CID mass spectra of $Mn^+C_5H_4COR$ and $Mn^+C_5H_4CH_2R$ ions were consistent with the formation of a mixture of isomers **I** and **J**. The presence of strong signals of Mn^+ ions was consistent with the intact structure **I**, whereas the presence of MnR^+ and $C_5H_4X^+$ ions in the MI and CID mass spectra indicated the migration of group R from the ligand to the metal atom (structure **J**). Recovery signals were present in the NR mass spectra of most of the studied derivatives (except for $Mn^+C_5H_4COOH$ ions). Their observation should be attributed to the survivor **I** structure. $C_5H_4X^+$ ions were also abundant in the NR mass spectra of $Mn^+C_5H_4COR$ ($X = CO$) and $Mn^+C_5H_4CH_2R$ ($X = CH_2$) complexes. However, they could not be considered as an indication of **J** isomers surviving neutralization–reionization and most likely originated from collisional ionization of neutral products of dissociation of metastable and collisionally activated $RMn^+C_5H_4X$ ions *prior* to the neutralization event. In general, NR mass spectra, being unable to give an estimate for the degree of the **I** to **J** isomerization, were less informative on the structure of Mn^+ C_5H_4XR ions compared with either MI and CID mass spectra [17], or ion–molecule reactions [48].

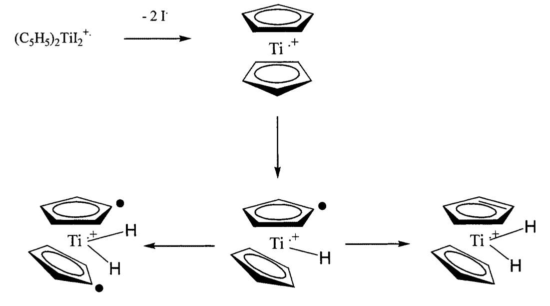




I **J**

Investigations of π-cyclopentadienyl complexes also included metallocenes. The majority of the first row transition metal metallocenes are stable compounds, and thus the observation of a recovery signal in their NR mass spectra was not a surprise. Examples include ferrocene [47], vanadocene [2], chromocene [33], and cobaltocene [23]. A more intriguing application of NR MS was to generate and investigate the structure of unknown metallocenes or those with lower stability. For this purpose, $C_{10}H_{10}Ti^+$ [47] and $C_{10}H_{10}Rh^+$ [49] ions were subjected to a combined study by MI, CID, and NR mass spectrometry methods. Rhodocenium was generated by the electron impact-induced dissociation of norbornadiene(cyclopentadienyl)rhodium derivatives and from the ionized $(C_5H_5)_4Rh_4(CO)_2$. The decomposition characteristics of $C_{10}H_{10}Rh^+$ ions originating from these sources were very similar and corresponded to a metallocenium structure. The observation of a recovery signal indicated that 19-electron transition metal complexes could successfully be generated (and characterized) by NR MS. The low stability of $(C_5H_5)_2Rh^\bullet$ in the condensed phase may, therefore, be accounted for by its high intermolecular reactivity rather than by its intrinsic instability. In addition, previously unknown neutral monosubstituted derivatives of rhodocene were generated in the NR experiments from their positively charged counterparts. The formation of stable rhodocene carboxylic acid and its methyl ester was indicated by the observation of survivor ions. The attempt to produce stable $C_5H_5RhC_5H_4CH_2OH$ failed by using xenon as neutralizing target most likely because of a large difference in IEs [49]. However, when dimethyl amine was employed for neutralization of the ions, a detectable recovery signal was recorded, indicating the formation of neutral hydroxymethylrhodocene stable in the experimental time-frame [23].

Another unstable biscyclopentadienyl complex, titanocene, has never been isolated as a stable monomeric complex, although its formation as an intermediate in various reactions has been proposed. To produce this complex, NR experiments were performed [47] with $C_{10}H_{10}Ti^+$ ions generated from the electron impact-induced dissociation of $(C_5H_5)_2TiI_2$. The MI and CID study of these ions preceded the NR experi-



Scheme 2.

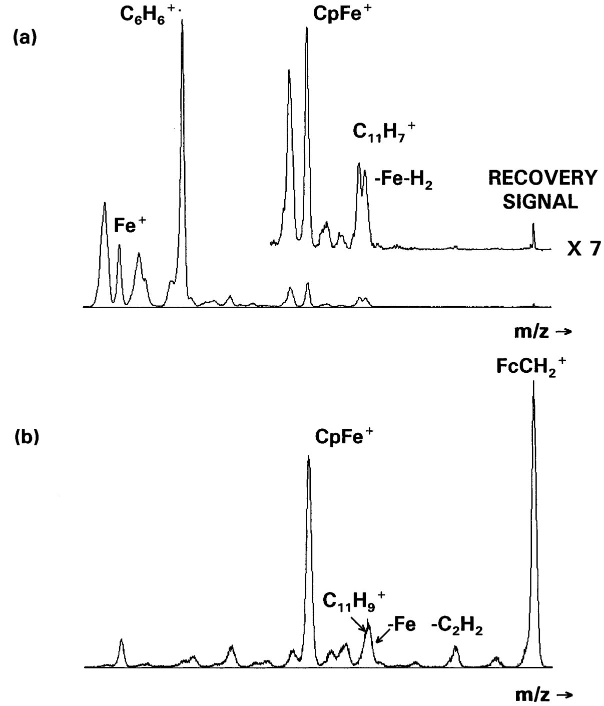


Fig. 8. Neutralization–reionization (dimethylamine–O_2; 50% T/70% T) mass spectrum of $C_5H_5Fe^+C_5H_4CH_2$ ions (a) and collision-induced dissociative ionization (O_2; 70% T) mass spectrum of $C_5H_5FeC_5H_4CH_2CH_2C_5H_4FeC_5H_5^+$ ions (b) (reproduced with permission from Ref. [50]).

ment, and showed that their structure corresponded to a hydride complex (or complexes) rather than to a metallocenium cation (Scheme 2). The NR mass spectrum was compatible with these results, showing quantitative and qualitative differences when compared with 'classical' biscyclopentadienyl metal complexes. First, survivor $C_{10}H_{10}Ti^+$ ions were of substantially higher abundance than, for example, their iron-containing analogs. Second, no significant $C_5H_5Ti^+$ peak was found; instead, an intense signal due to $C_5H_4Ti^+$ was present in the NR mass spectrum. Third, the highest mass hydrocarbon ion in the NR mass spectrum of $C_{10}H_{10}Ti^+$ corresponded to $C_{10}H_7^+$, whereas $C_{10}H_8^{+\bullet}$ ions were observed for ferrocene. Combining the experimental results, the facile isomerization of $(C_5H_5)_2Ti^+$ ions to hydride structures was proposed. The formation of neutral hydride(s), as well as fast interconversion of isomers, might provide the reason for the unique stability of the neutral gas-phase counterparts [47].

Zirconocene, as well as titanocene, is considered as a key intermediate in catalytic transformations of organic substrates on metal complexes. This molecule had never been isolated or characterized in its pure monomeric form. The observation of a recovery signal in the NR mass spectrum [5] proved the possible existence of neutral zirconocene, at least as an intermediate species. An important element in the study was to demonstrate the metallocene structure of $[C_{10}H_{10}Zr]^+$ ions. Unlike early transition metal metallocenium ions, the dissociation of late transition metal metallocene ions is favored by a loss of H-atoms and small hydrocarbon units. A simple metal–ligand bond cleavage usually results in a rather weak $C_5H_5M^+$ ion signal. The NR mass spectrum of $[C_{10}H_{10}Zr]^{+\bullet}$ ions exhibited intense peaks of $C_5H_5Zr^+$ and $C_5H_5^+$ ions; the latter corresponded to the (reionized) neutral cyclopentadienyl group.

A number of elusive ferrocenyl-related radicals ($FcX^\bullet$, $Fc = C_5H_5FeC_5H_4$, $X = CH_2$, O, CO) were generated by NR mass spectrometry [50]. Ferrocenylmethyl ions produced a strong recovery signal in their NR mass spectrum (Me_2NH/O_2). This result was not unexpected because the corresponding radical, $FcCH_2^\bullet$, was a well-known stable species in the condensed phase. Two different experiments were carried out to detect $FcCH_2^\bullet$. In one of them, $FcCH_2^+$ ions were neutralized by collisions with a target gas (dimethylamine). The NR mass spectrum is shown in Fig. 7. It exhibited a moderate recovery signal and characteristic fragments ($C_6H_6Fe^+$, $C_5H_5Fe^+$, $C_6H_6^{+\bullet}$). When $FcCH_2^+$ ions were generated from metastable $FcCH_2CH_2Fc^+$ ions, the only neutral product of the dissociation was the ferrocenylmethyl radical. Compared with the NR mass spectrum of $FcCH_2^+$ ions, the CIDI mass spectrum of $FcCH_2CH_2Fc^+$ displayed a significantly stronger signal of $FcCH_2^+$ ions, corresponding to collisionally ionized neutral $FcCH_2^\bullet$ radicals (Fig. 8). The result can be easily explained by the difference in the two techniques. In CIDI experiments, the neutralization step, which is associated with a great transfer of internal energy to the neutral, is excluded. As a result, the ions formed after the collisional ionization of the neutrals possess lower energy and, therefore, show a reduced fragmentation as compared with the ions surviving neutralization–reionization.

Protonated metallocenes have been investigated to determine the site of protonation and in an attempt to generate odd-electron (17- or 19-electron) organometallic complexes [23]. The protonation of ferrocene and its mono-substituted derivatives in the CI ion source of the mass spectrometer was performed, using C_2D_5I as a reactant gas. The resulting mass spectra showed $[FcR]D^+$ ions along with a substantial amount of the ionized ferrocenes, $FcR^{+\bullet}$. The NR mass spectra of deuteronated metal complexes showed 'recovery' peaks that might indicate the formation of the corresponding hyper-valent neutrals. Analysis of the isotopic contribution from $FcR^{+\bullet}$ ions showed, however, that survivor ions with a mass 2 Da higher than that of $FcR^{+\bullet}$ did *not* correspond to the reionized $[FcR]D^{\bullet}$. These ions appeared as a result of the neutralization–reionization of isotopomeric (due to ^{57}Fe, ^{58}Fe, ^{13}C, and other atoms) $[FcR]^{+\bullet}$ ions. This observation was confirmed by the NR study of $[FcCOCH_3]H^+$ ions generated by the acylation of ferrocene: $FcH + CH_3CO^+ \rightarrow [Fc(H)COCH_3]^+$. The NR mass spectrum of the product did not display a recovery signal, and that result indicated the instability of neutral analogs of protonated ferrocenes under the experimental conditions.

Some complexes containing metal–cyclopentadienyl and metal–heteroatom bonds at the same time have been investigated in NR experiments. A recovery signal was observed for the $C_5H_5Rh^+$(acac) ion, indicating the existence of the corresponding 17-electron neutral complex [51].

A combined study of $[C_5H_5, Fe, R]^+$ ions by different tandem mass spectrometry methods was used to elucidate their structure and the possibility of isomerization of $C_5H_5FeR^+$ ions (**K**) to a system with a single ligand at the metal atom, $(C_5H_5R)Fe^+$ (**L**) [16]. Two criteria were used to identify these structures. The observation of a recovery signal as well as the presence of FeR^+ and the absence of $C_5H_5R^+$ ions would be indicative for **K** structure. The **L** isomer is unlikely to survive neutralization–reionization and should show ions corresponding to migration of the R group to the cyclopentadienyl ring (such as $C_5H_5R^+$, and dissociation products involving a loss of molecules combined from R (or its parts) and of the atoms from the cyclopentadienyl ring).

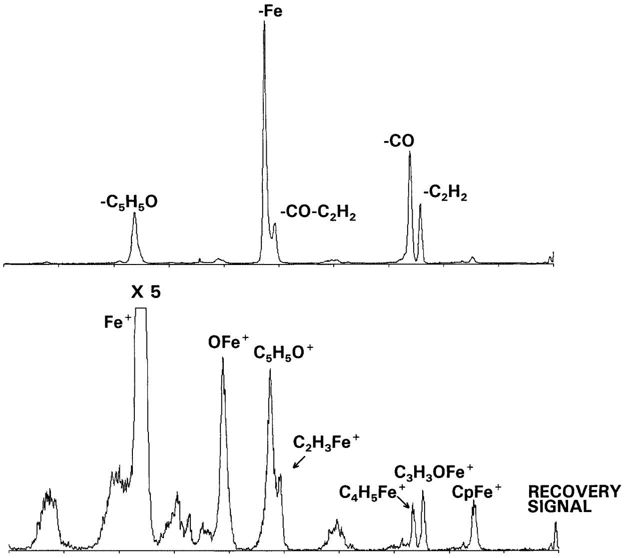
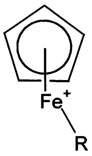
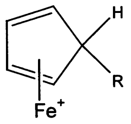


Fig. 9. CID (top) and NR (bottom) mass spectra of $[Fe, C_5, H_5, O]^+$ ions (reproduced with permission from Ref. [16]).

The NR mass spectra of $C_5H_5FeF^+$, $C_5H_5FeCl^+$, $C_5H_5FeBr^+$, and $C_5H_5FeI^+$ [16] were consistent with the structure **K**. All these ions showed strong recovery signals and abundant FeR^+ ions. No $C_5H_5R^+$ ions were found in their NR mass spectra that would be indicative of the isomer **L**.



K

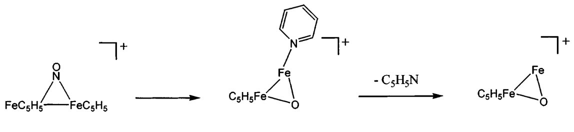


L

The NR mass spectrum of $C_5H_5FeOH^+$ [16] could also be rationalized in terms of the presence of the **K** structure. The MI and CID mass spectra of these ions showed a peak due to a loss of CO indicating the migration of the oxygen atom to the hydrocarbon ligand. These ions were not present in the NR mass spectrum but they were found in the CID mass spectrum of the ions surviving neutralization–reionization. These results clearly demonstrated that both **K** and **L** isomers were formed, but only ions of the **K** structure produced stable neutral counterparts.

The case of $C_5H_5Fe^+O$ ions is yet another example illustrating the capability of the NR MS method to identify structures of ions [16]. The CID mass spectrum of $[C_5, H_5, O, Fe]^+$ ions (Fig. 9) was dominated by the ions ($C_4H_5Fe^+$, $C_5H_5O^+$, Fe^+) that corresponded to **L** structure with a single C_5H_5O ligand with no or very little indication for the $C_5H_5Fe^+O$ structure (**K**). This result was explained by a low energy barrier for the isomerization of $C_5H_5Fe^+O$ to $C_5H_5OFe^+$ combined with high activation energies for the formation of fragment ions specific for the **K** structure. The latter isomer, having an Fe–O bond, was effectively identified by the NR mass spectrum (Fig. 9). The observation of strong signals for $C_5H_5Fe^+$ and FeO^+ ions was indicative of the presence of the structure having two ligands at the metal atom. The case of $C_5H_5OFe^+$ ions proved the NR MS method as a useful technique for probing ions that sit in a shallow potential well and that have high energy barriers for structure-specific dissociation.

The NR mass spectrum of $[C_5, H_6, Fe]^+$ ions [16], on the contrary, was consistent with a significant isomerization of **K** to **L**. Only a trace recovery signal was observed; it could be attributed to a small fraction of survivor $C_5H_5FeH^+$ ions or to an isotopic contribution from $C_5H_5Fe^+$ ions. The NR mass spectrum displayed a signal due to $C_5H_6^+$ ions, which is characteristic for the structure **L**. The experimental results were consistent with the formation of the cyclopentadiene–Fe^+ complex, but could not provide any direct evidence for or against the presence of **K** isomer.



M

Scheme 3.

A high degree of the **K** to **L** isomerization was observed for $C_5H_5FeC_6H_5^+$ ions [16]. The NR mass spectrum of these species was dominated by $C_5H_5C_6H_5^+$ and Fe^+ ions. Rather weak signals due to survivor and $FeC_6H_5^+$ ions were found, being indicative of the **K** structure of the ions and neutrals.

A combined study of $C_5H_5FeOCH_3^+$ ions by tandem mass spectrometry (MI, CID, CIDI, and NR) methods demonstrated that facile hydrogen migration(s) from the methoxy group to the metal atom have taken place [16]. The observation of a recovery signal in the NR mass spectrum indicated that a part of the ions retained **K** structure, which was indeed the one surviving neutralization–reionization.

The NR MS method was used to study a mechanism of a neutral loss of 79 Da from $(C_5H_5)_2Fe_2NO^+$ ions [34]. The NR mass spectrum showed an intense signal for reionized $C_5H_5N^{+\bullet}$, unambiguously confirming that this neutral (pyridine) molecule was formed intact upon fragmentation. Such a result could also be obtained by a CIDI experiment, but the NR mass spectrum provided additional information about the dissociation (and therefore the structure) of the ion and its neutral counterpart. In particular, a very weak recovery signal in the NR mass spectrum of the ions was taken to indicate the presence of a non-covalently-bound ligand. The $C_5H_5Fe_2O^+$ ion, originating from the loss of C_5H_5N from **M** ions, showed an abundant survivor signal, which could correspond to the metal atoms being covalently bonded together and to the ligands (Scheme 3). Intense signals due to Fe_2O^+, Fe_2^+, and FeO^+ ions indicated the presence of an oxidodiiron moiety, in which the oxygen atom was considered as a bridging ligand. The observation of ions corresponding to reionized $C_5H_5^\bullet$ was consistent with the presence of an intact cyclopentadienyl ring.

Summarizing this section, the majority of π-cyclopentadienyl complexes of transition metals investigated by the NR MS method have shown recovery signals, indicating the formation of the corresponding stable in the gas phase neutral counterparts. Of course, the presence of a η^5-C_5H_5–metal bond does not guarantee the stability of these species in the NR conditions. The presence of other, more weakly bonded ligands, such as CO, benzene, ethene, etc., will most likely result in the dissociative neutralization of the ions. However, the chances for the η^5-cyclopentadienyl–metal bond to survive are very high in any ligand arrangement, making the NR MS method a convenient technique for the generation of neutrals of the type $C_5H_5ML_n$. The latter involve a variety of complexes having electron and coordinatively deficient and electron enriched metal atom(s). This method is a powerful tool for the elucidation of structures of ions containing π-ligands. One of the most promising applications is a differentiation between isomers having even- and odd-electron ligands. Atom connectivity within ligands as well as rearrangements involving migration of atoms or groups to/from the metal atom may be gained from NR experiments.

5. Conclusions and future prospects

NR MS has made a significant impact on coordination and organometallic chemistry. The most prominent and exciting application of this method is the generation of metal-containing molecules and radicals that are unstable in other experimental conditions or as yet unknown to the chemists. One of the biggest advantages of the NR MS technique derives from the rich chemistry of ions in the gas phase. Because ions can be made using various ionization methods and reactions, it is possible to produce metal-containing ions having the metal atom in different oxidation and coordination states, surrounded by various types of ligands. These ions are convenient sources for the corresponding neutrals. A variety of metal compounds have been generated using the NR MS method by neutralization of the ionic counterparts. Among them are well-known stable molecules, unstable coordinatively unsaturated systems, and electron-enriched (for example, 19-electron) complexes. Attempts at the generation of other metal-containing systems, especially neutrals that have been proposed as transient species or intermediates, will be made in the future. Extension of ionization techniques that are used for generation of metal-containing precursor ions will allow production of a larger variety of ions. One of the methods that can make a positive impact on these studies is electrospray ionization, allowing the probing of ions from solutions.

The production of neutral molecules and radicals from the corresponding ions (cations or anions) and their stability in the mass spectral time frame (few µs or more) is justified by the presence of a recovery signal in the NR mass spectrum. The observation of the recovery signal is a big challenge in many cases. The non-observation of a recovery signal is not necessarily an indication that the particular neutral cannot exist as a stable species, it is rather an invitation for changing the experimental settings. A variety of experimental conditions can and should be 'tuned' in order to produce neutrals that live long enough to undergo (and to survive) collisional (re)ionization. A choice of targets for neutralization and reionization is very important for a successful experiment. Internal and translational energies of the projectile ion, as well as other factors may well affect the state and stability of the neutralized species.

Metal-containing ions are convenient models for understanding electron transfer processes. In positively charged ions, the metal atom is the most likely bearer of the charge. This fact aids the choice of a proper target for neutralization without knowing the IE of the desired neutral. Future efforts shall be made for detection of electronically excited states of metal containing ions and neutrals participating in the neutralization–reionization process. A promising approach to the generation of stable neutrals is by neutralization of ions in electronically excited states. Another point of interest is a possibility of formation of neutrals in Ridberg states.

A wider use of NR MS combined with other techniques is expected to make a pronounced impact on studies of neutrals generated in a course of NR experiments. At this point, only dissociation processes of neutralized species can be tested. For this purpose the neutrals can be activated by collisions or using a laser beam. Also a comparison of NR mass spectra (in the course of which neutrals are formed) with the corresponding charge-reversal mass spectra (one-step charge inversion without formation of intermediate neutral) allows detection of products originating from neutral dissociations.

NR MS is a valuable addition to other tandem mass spectrometry experiments in structural characterization of ions in the gas phase. It has been demonstrated that the NR MS method can serve as a major tool in determining ligands surrounding a metal atom and atom connectivity within the ligands. Therefore, this technique should be employed more frequently in studies aiming at elucidation of structures of ions in the gas phase.

Finally, the role of quantum chemical calculation should not be underestimated. Theoretical calculations are very useful for interpretation of the experimental observations. They are able to explain why some neutrals can and others cannot be produced in a NR MS experiment, what transformations are allowed and what reactions are forbidden. It is worth testing predictions of theory about possible stability of unknown molecules and radicals by conducting NR MS experiments with the corresponding ions.

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