STRUCTURAL ANALYSIS OF ORGANOMETALLIC COMPOUNDS WITH SOFT IONIZATION MASS SPECTROMETRY

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The analysis of organometallic compounds with mass spectrometry has some special features in comparison with organic and bioorganic compounds. The first step is the choice of a suitable ionization technique, where the electrospray ionization is certainly the best possibility for most classes of organometallic compounds and metal complexes. Some ionization mechanisms of organometallic compounds are comparable to organic molecules, such as protonation/deprotonation, and adduct formation with sodium or potassium ions; however, in many cases, different mechanisms and their combinations complicate the spectra interpretation. Organometallics frequently undergo various types of adduct and polymerization reactions that result in significantly higher masses observed in the spectra in comparison to molecular weights of studied compounds. Metal elements typically have more natural isotopes than common organic elements, which cause characteristic wide distributions of isotopic peaks; for example, tin has ten natural isotopes. The isotopic pattern can be used for the identification of the type and number of metal elements in particular ions. The ionization and fragmentation behavior also depend on the type of metal atom; therefore, our discussion of mass spectra interpretation is divided according to the different type of organometallic compounds. Among various types of mass spectrometers available on the market, trap-based analyzers (linear or spherical ion-traps, Orbitrap) are suitable to study complex fragmentation pathways of organometallic ions and their adducts, whereas high-resolution and high-mass accuracy analyzers (time-of-flight-based analyzers, or Fourier transform-based analyzers—Orbitrap or ion cyclotron resonance mass spectrometers) provide accurate masses applicable for the determination of the elemental composition of individual ions. © 2010 Wiley Periodicals, Inc., Mass Spec Rev 30:1013–1036, 2011

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I. INTRODUCTION

Organometallic compounds are defined as molecules that consist of an organic part, with one or more metal elements incorporated into their structure. In general, organometallic compounds consist of at least one covalent bond between carbon and metal atoms (Mehrotra & Singh, 2004). If the metallic character of nonmetallic elements, such as boron, silicon, arsenic, selenium, and tellurium, is also taken into consideration, then this definition might be extended to the statement that organometallic compounds contain a carbon atom bonded to elements that are more electropositive than carbon itself (Pruchnik, 1990). Moreover, so-called metal complexes that contain the central metal surrounded by ligands bounded to this metal ion by a coordination covalent bond (donor–acceptor) can be considered as well (Garnovskii, Vasilchenko, & Garnovskii, 2003). These complexes are often formed by the metal complexation with amino acids, sugars, and drugs (Alvarez, Vartanian, & Brodbelt, 1997; Vaisar et al., 2005; Fournier et al., 2008). Their gas-phase ion-molecule reactions are often studied (Gatlin & Tureček, 1997; Lemr, Holčapek, & Jandera, 2000; Asmis & Sauer, 2007; Di Marco et al., 2007; MacAleese & Maitre, 2007; Mo et al., 2007; Tureček, 2007; Burgert & Schnockel, 2008; Jirásko et al., 2008; Polfer & Oomens, 2009). The most famous metal complexes are even naturally occurring, such as chlorophyll (Mg), hemoglobin (Fe), and myoglobin (Fe), and their presence in living organisms is indispensable (Wöhrle & Pomogailo, 2003). Nevertheless, metal complexes or gas-phase reactions are not the main subject of this review, and will be not further discussed.

The first organometallic compound, tetramethyldiarsine (Cacodyl), was prepared by Louis Claude Cadet in 1760 (Mehrotra & Singh, 2004). Although many other compounds were synthesized later, the remarkable growth of organometallic chemistry was started during the second half of the 20th century. Due to many applications in the catalytical, agricultural, and pharmaceutical industries, organometallics have significantly contributed to the scientific progress (Halpern, 2001), as proved by four Nobel prizes for chemistry awarded in 1912 (Victor Grinard and Paul Sabatier), 1963 (K. Zieger and G. Natta), 1973 (G. Wilkinson and E. O. Fischer), and 2005 (Y. Chauvin, R. Grubbs, and R. Schrock) (http://nobelprize.org). The most important properties of these compounds become apparent, their participation in many stechiometric and catalytical reactions (e.g., cross-coupling reactions) are used to implement different chemical groups into the molecular structure. Mainly transition-metal complexes, but also organometallics with bismuth, antimony, tin, and other metals, are used for this purpose (Rao et al., 2002; Hocek, 2003; Netherton & Fu, 2004; Yasuike et al., 2005). Organotin compounds are also used as stabilizers of rigid polyvinyl chloride against photochemical and thermal transformations (Kizlink, 1996). It is also worth mentioning the applications in photocatalytical and asymmetrical reactions (Noyori, 2002; Yasuike et al., 2005).

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Concerning biological applications, early studies even reveal an anticancer activity of some organometallics. However, many of them are usually perceived as being too toxic, and their applications for medicinal purposes are accepted only in fields where no viable therapy is available, such as organotin and organoantimony compounds (Norman, 1997; Gielen, 2002). On the other hand, the relatively low toxicity of organogermanium (Kaplan et al., 2004), organoruthenium compounds (Allardyce et al., 2005; Jaouen, Beck, & McGlinchey, 2006), various metallocenes (Ti, Nb, Mo, V) (Allardyce et al., 2005; Vinklárek et al., 2006), and also organic complexes with important essential transition-metals (Cu, Co) suggests their suitability in a variety of medical applications (Osinsky et al., 2004; Wang & Guo, 2006).

In addition to antitumor properties, some organometallic compounds exhibit activity against various types of bacteria. The biological studies proved that organotin compounds inhibit the growth of Trypanosoma equiperdum, causes sleeping-sickness (Susperregui et al., 1999); organorhodium and organoruthenium compounds have been found active against the malaria (SanchezDelgado et al., 1996); and leishmania can be cured with organoantimony compounds (Norman, 1997). Most organometallic compounds have an artificial character; however, few natural occurring organometallics can be found, too. Most widely known is cobalamin and methyl cobalamin (Jaouen, Beck, & McGlinchey, 2006).

Nowadays, a huge number of new organometallic compounds is synthesized annually; their biological properties are studied and require reliable analytical techniques for structure verification of new compounds and to monitor the reaction course of synthetic reactions. Established spectroscopic techniques for this purpose are mainly X-ray crystallography, nuclear magnetic resonance, and mass spectrometry (MS), which is strongly dependent on the type of ionization technique. In older works, the use of conventional electron (EI) and chemical ionization (CI) coupled with double-focusing magnetic sector or quadrupole analyzers (Bruce & Thomas, 1968; Hunt, Torian, & Russell, 1972; Efraty, Huang, & Weston, 1975; Gielen & Jurkschat, 1983) was quite common; nowadays, EI is almost completely replaced by soft ionization techniques, such as fast atom bombardment (FAB), matrix-assisted laser/desorption ionization (MALDI), and atmospheric pressure ionization techniques, especially electrospray ionization (ESI) is suitable for most classes of organometallic compounds including polar and ionic compounds. A survey of published articles with soft-ionization techniques, together with mass analyzer, is listed in Table 1.

The growing interest in the use of ESI to characterize organometallic species has emerged from the possibility to analyze highly diluted solutions and soft conditions for the ionization process (Colton, Dagostino, & Traeger, 1995; Henderson et al., 1998; Henderson, Nicholson, & McCaffrey, 1998; Stewart, 1999; Traeger, 2000; Henderson & McIndoe, 2005). ESI-MS allows the acquisition of mass spectra directly from the sample solution due to transferring ions from the liquid-phase to the gas-phase; therefore, it enables an easy coupling with high-performance liquid chromatography (HPLC) (Rosenberg, 2003). ESI-MS is ideally suited for the analysis of polar and ionic organometallic compounds, the characterization of their hydrolysis mechanisms (Henderson & Taylor, 1996; Lintschinger, Schramel, & Kettrup, 1998; Wei & Miller, 2001), their biological studies (e.g., metal interactions with biomolecules) (Yan et al., 2005), and even to screen short-lived reactive intermediates involved in organometallic catalytic reactions (Plattner, 2001; Chen, 2003; Moreno-Manas et al., 2003; Guo et al., 2005; Pla-Quintana & Roglans, 2005; Chevrin et al., 2007; Santos, 2008). The soft character of ESI permits one to analyze organometallic complexes with weakly bound ligands (Bhaskar et al., 2005), and the possibility of cold-spray ionization techniques is offered for very labile compounds (Henderson & McIndoe, 2005). Mass spectra are relatively poor in fragment ions, which can be supported with in-source dissociation or tandem MS experiments (Traeger, 2000). Mass spectra of some non-polar organometallics can be measured with atmospheric pressure chemical ionization (APCI) or atmospheric pressure photoionization (APPI), as illustrated by several works (Ogo, Makihara, & Watanabe, 1999; Dorcier, Dyson, & McIndoe, 2003; Meurer et al., 2003; Rosenberg, 2003). MALDI is a method of choice to characterize polymeric species or dendrimers that contain metal elements because of the presence of mainly singly charged molecular adducts with a minimum fragmentation and the high-mass range accessible with a time-of-flight analyzer (Ferri et al., 1998; Xu et al., 2000; Arevalo et al., 2001; Royo & Brintzinger, 2002; Schumann et al., 2006). This technique is also suitable for mass spectrometric measurements of insoluble or low-soluble organometallic compounds (Wyatt, Stein, & Brenton, 2008).

II. INTERPRETATION OF MASS SPECTRA OF ORGANOMETALLIC COMPOUNDS

A. Basic Ionization Mechanisms of Organometallic Compounds

The character of organometallic ions observed in mass spectra depends on many factors, such as the type of ionization, polarity mode, values of applied voltages, solvents, and behavior of studied compounds.

The most important ionization mechanisms are summarized in the following text and in Table 2. One of the most common mechanisms of ion formation observed in the full-scan positive-ion mass spectra is the formation of sodium and potassium adducts ($[M+Na]^+$, $[M+K]^+$, $[2M+Na]^+$, $[2M+K]^+$), which are usually used to determine molecular weights (Henderson, Nicholson, & McCaffrey, 1998; Traeger, 2000; Kolářová et al., 2004). In general, the different metallation ($[M+Ag]^+$, $[M+Li]^+$, etc.) of organometallics can be observed, depending on particular ions present or added to the solution. Similarly, ammonium adducts $[M+NH_4]^+$ or $[2{*}M+NH_4]^+$ are described for some organometallics (Dinger & Henderson, 1998, 1999; Pla-Quintana & Roglans, 2005). When ionic contaminats such as trimethyl- or triethyl-amonium ions are present in the sample (from the synthesis) or mass spectrometer (from previous MS or HPLC/MS experiments), the ions $[M+(CH_3)_3NH]^+$ or $[M+(C_2H_5)_3NH]^+$ can be formed (Ang et al., 2006; Kilpin, Henderson, & Nicholson, 2007). Protonated molecules are also important for some organometallics that contain an appropriate ligand with a high proton affinity (Traeger, 2000), and even double-charged ions $[M+2H]^{2+}$ are observed in case of a compound with possible double-protonation.

On the other hand, the most important ions observed in full-scan negative-ion mass spectra are deprotonated molecules $[M-H]^-$. Compounds that contain an ionic bond provide relatively simple spectra (Traeger, 2000; Fridrichová et al., 2009) with two complementary ions, depend on the polarity mode,

TABLE 1. The type of soft-ionization techniques together with mass analyzers used in organometallic analysis

Ion source	Mass analyzer	Metal present in organometallic compounds (references)
APCI	Q	***Fe*** (Diehl & Karst, 2002) ***Pt*** (Mastrorilli et al., 2004)
APCI	QqQ	***Ge*** (Takeuchi et al., 2006) ***Si*** (Takeuchi et al., 2006)
APCI	3D ion-trap	***Sn*** (Bekri et al., 2006)
APCI	QqTOF	***Ti*** (Meurer et al., 2003; Meurer et al., 2006)
ESI	Q	***Ag*** (Rais et al., 2002) ***As*** (Pedersen & Francesconi, 2000) ***Au*** (Dinger & Henderson, 1998a, b; Dinger et al., 1998; Dinger & Henderson, 1999; Goss et al., 2003; Kilpin et al., 2007) ***Cu*** (Lipshutz et al., 1999) ***Fe*** (Alley & Henderson, 2001; Henderson & Alley, 2002) ***Hg*** (Nicholson & Whitley, 2004) ***Ir*** (Ozkar & Finke, 2004) ***Pb*** (Mester & Pawliszyn, 1999; Pham et al., 2007) ***Pd*** (Chevrin et al., 2007; Moreno-Manas et al., 2003; Pla-Quintana & Roglans, 2005) ***Pt*** (Mastrorilli et al., 2004) ***Re*** (Jiang et al., 2000) ***Ru*** (Wang et al., 2002; Yeo et al., 1999) ***Sb*** (Brown et al., 2006) ***Sn*** (Beckmann et al., 2002; Henderson & Taylor, 1996; Lawson et al., 1996; Yeo et al., 2001) ***Te*** (Beckmann et al., 2005)
ESI	QqQ	***As*** (Florencio et al., 1997) ***Co*** (Alsberg et al., 2001) ***Fe*** (Bakhtiar & Kaifer, 1998; KaneMaguire et al., 1996; Murao et al., 2005; Quirke & Van Berkel, 2001; Tharamani et al., 2008) ***Ge*** (Lamb & Sweetman, 1996) ***Ir*** (Ogo et al., 1999) ***Ge***, ***Ni*** (Goicoechea & Sevov, 2006b) ***Mo*** (Thompson et al., 2003) ***Os*** (Dyson et al., 2000) ***Pb*** (Aplin et al., 2002) ***Ru*** (Kriesel et al., 1998; Pelagatti et al., 2005) ***Sb*** (Lintschinger et al., 1998)

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TABLE 1. (*Continued*)

		W (Thompson et al., 2003) ***Zn*** (Goicoechea & Sevov, 2006a)
ESI	3D ion-trap	***As*** (Larsen et al., 2001) ***B*** (Dostál et al., 2007c) ***Bi*** (Dostál et al., 2006a; Dostál et al., 2007c; Dostál et al., 2009b; Fridrichová et al., 2009; Chovancová et al., 2009) ***Co*** (Arrais et al., 2006) ***Cr*** and ***Fe*** (Martinez-Alvarez et al., 2004) ***Cr*** and ***Ru*** (Moret et al., 2005) ***Fe*** and ***Ru*** (Paim et al., 2005) ***Ge*** (Jirásko et al., 2009; Wei et al., 2001) ***Mo*** (Gun et al., 2003) ***Os*** (Dorcier et al., 2005; Dorcier et al., 2008; Schmid et al., 2007) ***Pb*** (Casas et al., 2004) ***Pd*** (Macchioni et al., 2003) ***Rh*** (Dorcier et al., 2008) ***Ru*** (Ang et al., 2006; Dorcier et al., 2005; Dorcier et al., 2008; Schmid et al., 2007) ***Se*** (Zhou et al., 2007) ***Sb*** (Dostál et al., 2006a; Dostál et al., 2007a; Dostál et al., 2007c; Dostál et al., 2008; Dostál et al., 2009a; Dostál et al., 2009b; Fridrichová et al., 2009; Chovancová et al., 2009; Machuča et al., 2007) ***Sn*** (Baul et al., 2005a; Baul et al., 2005b; Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2006b; Baul et al., 2006c; Baul et al., 2006d; Baul et al., 2007a; Baul et al., 2007b; Baul et al., 2008; Bouška et al., 2009; Dostál et al., 2006b; Dostál et al., 2007b; Holčapek et al., 2006; Chalupa et al., 2006; Chalupa et al., 2008; Jirásko et al., 2007; Jones-Lepp et al., 1999; Jones-Lepp et al., 2001; Kašná et al., 2008; Kolářová et al., 2004; Wei & Miller, 2001) V (Palačková et al., 2007; Vinklárek et al., 2006)
ESI	Q-trap	***Fe*** (Seiwert & Karst, 2007) ***As*** (Schaeffer et al., 2006)
ESI	magnetic sector	***Bi*** (Mlýnek & Dahl, 1997) ***Si*** and ***Sn*** (Beckmann et al., 1998)
		heteromultimetallic (Packheiser & Lang, 2007; Packheiser et al., 2008a; Packheiser et al., 2008b)

TABLE 1. (*Continued*)

ESI	TOF	***Ge*** (Takeuchi et al., 2006) ***Ru*** (Mattsson et al., 2008) ***Sb*** (Zheng et al., 2001) ***Si*** (Takeuchi et al., 2006)
ESI	QqTOF	***Au*** (Kilpin et al., 2007) ***Co*** (Gentili et al., 2008) ***Fe*** (Ding et al., 2003; Wu et al., 2008) ***Ga*** (Young et al., 2007) ***Pd*** (Evans et al., 2002) ***Rh*** (Jimenez et al., 2008) ***Ru*** (Crawford et al., 2006; Chisholm et al., 2007) ***Te*** (Kandasamy et al., 2003)
ESI	FT-ICR	***Pd*** (Guo et al., 2005; Qian et al., 2006) ***Pt*** (Hartnell & Arnold, 2004) ***Ru*** (Mattsson et al., 2008) ***Ru*** and ***Si*** (Kriesel et al., 1998)
FAB	Q	***Ag*** (Rais et al., 2002) ***Au*** (Ferrer et al., 2005) ***Os*** and ***Si*** (Wong et al., 2003) ***Ru*** and ***Si*** (Wong et al., 2003)
FAB	magnetic sector	***Al*** (Majoumo-Mbe et al., 2005) ***Au*** (Lash et al., 2004) ***Fe*** (Osei-Twum et al., 2005) ***Ge*** (Lamb & Sweetman, 1996) ***Pd*** (Brady et al., 1995; Macchioni et al., 2003) ***Pt*** (Brady et al., 1995; Leininger et al., 1998) ***Te*** (Canseco-Melchor et al., 2001; Chauhan et al., 2002; Kandasamy et al., 2003)
FAB	TOF	***Fe*** (Manzur et al., 2003) ***Fe*** and ***Ru*** (Štěpnička et al., 1997)
MALDI	TOF	***Ag*** (Xu et al., 2000) ***B*** (Kappaun et al., 2006) ***Fe*** (Alonso et al., 2001; Wyatt et al., 2008) ***Fe*** and ***Si*** (Jain et al., 2005; Kohler et al., 2002; Ruiz et al., 1999) ***Ni*** and ***Si*** (Kohler et al., 2002) ***Pd*** (Sicard et al., 2004) ***Pt*** (Jang, 2005; Siemsen et al., 2001) ***Rh*** (Alvarez et al., 2007; Jimenez et al., 2008) ***Ru*** (Royo & Brintzinger, 2002; Salmain et al., 2004)

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TABLE 1. (*Continued*)

		Ru and ***Si*** (Kriesel et al., 1998) ***Sn*** (Carraher & Lanz, 2003; Carraher & Morie, 2004; Carraher et al., 2007) ***Sn*** and ***Si*** (Schumann et al., 2006) ***Ti*** and ***Si*** (Arevalo et al., 2001)
MALDI	QqTOF	***Fe*** (Osei-Twum et al., 2005)

$[\mathrm{Cat}]^+$ and $[\mathrm{An}]^-$, eventually doubly charged ions $[\mathrm{Cat}]^{2+}$ and $[\mathrm{An}]^{2-}$. This approach is common also for organometallic compounds with a labile covalent bond usually between metal–halogen (Kolářová et al., 2004) or metal–oxygen (Baul et al., 2005b, 2008) present in some ligands or substituents. The labile covalent bond is also cleaved to yield two complementary ions, where the cationic part of the molecule (e.g., $[\mathrm{LSnR_2}]^+$, $[\mathrm{SnR_3}]^+$, $[\mathrm{M}-\mathrm{X}]^+$) is detected in the positive-ion mode, and the anionic part ($[\mathrm{L}]^-$, $[\mathrm{X}]^-$) in the negative-ion mode (Holčapek et al., 2006). Among others, the formation of fragment ions is often observed according to the type of ionization and the values of applied voltages. Moreover, some adducts with these fragments are observed in the spectra, such as $[\mathrm{M}+\mathrm{SnR_3}]^+$, $[\mathrm{M}+\mathrm{SnR_3}\text{-}\mathrm{H}+\mathrm{Na(K)}]^+$, and $[\mathrm{M}+\mathrm{L}]^-$, $[\mathrm{M}+\mathrm{X}]^-$. Ions that undergo an oxidation-state change can be further observed in mass spectra of organometallics that contain an appropriate metal, for example; Fe (Ding et al., 2003). It is also noteworthy that some organometallics can undergo hydrolysis reactions because of the presence of polar bonds on the metal atom, and hydrolysis and solvent adducts might be observed in their mass spectra (Jirásko et al., 2007).

The various ionization mechanisms described above concern mainly ESI and APCI; only few mechanisms are found in articles that deal with FAB or MALDI of organometallics; for example, $[\mathrm{M}+\mathrm{Na}]^+$, $[\mathrm{M}+\mathrm{H}]^+$ for MALDI or $[\mathrm{M}]^{+\cdot}$, $[\mathrm{M}+\mathrm{H}]^+$, $[\mathrm{M}-\mathrm{Cl}]^+$, $[\mathrm{M}-\mathrm{Br}]^+$, and various fragment and dissociation adducts for FAB.

B. Importance of Isotopic Distribution of Polyisotopic Elements

The wide distribution of isotopic peaks for most compounds is often observed in the spectra because of the greater number of isotopes of some elements (Sn, Ge, Se, Ni, Te, and others), which contributes to total isotopic distributions of studied ions (Goraczko & Szymura, 1999; Jirásko et al., 2007, 2008; Jirásko, Holčapek, & Rosenberg, 2009). Theoretical isotopic distributions for selected polyisotopic **p** and **d** elements that contain at least three isotopic peaks are shown in Figure 1. The complex isotopic distribution can sometimes complicate the spectra interpretation due to the presence of a high number of isotopic peaks. However, the main advantage of a complex isotopic distribution is the possibility to identify the presence and exact number of polyisotopic metals in individual ions by the comparison of experimental isotopic distributions with theoretical ones (Fig. 2). The complexity of isotopic pattern is enhanced with the increased number of polyisotopic elements, and the isotopic envelope can convert even to the Gaussian character; for example, in case of a high number of tin atoms (Fig. 2D). Compounds that contain a high number of metals with two isotopes also markedly extend the isotopic pattern; for example, a multisilver complex (Rais et al., 2002). Other non-metal elements that affect the isotopic distribution are bromine, chlorine, sulfur, or a high number of carbons.

The determination of the number and type of polyisotopic elements can be done with low- and high-resolution mass analyzers. However, properly calibrated high-resolution mass analyzers offer accurate *m/z* values of all isotopic peaks, and can be subsequently used for elemental composition verification based on the calculation of mean mass-accuracy parameters. The ion overlaps that occur due to the wide isotopic distribution of polyisotopic complexes can be detected as well (Jirásko, Holčapek, & Rosenberg, 2009).

C. Tandem Mass Spectra of Organometallic Compounds

Proposed structures of important ions can be confirmed with the additional fragmentation that is usually realized with collision-induced dissociation (CID). Tandem MS is divided into two groups according to the mechanism of the dissociation process (Henderson & McIndoe, 2005). When the selection of the precursor ion and the observation of product ions are carried out in different parts of the instrument, the technique is termed tandem MS in space (e.g., QqQ, QqTOF). The alternative approach is tandem MS in time (e.g., spherical and linear ion-traps, FT-ICR). Due to the possibility of a multistage mass spectra measurement, ion-trap analyzers are useful to characterize fragmentation paths (Larsen et al., 2001; Holčapek et al., 2006; Jirásko et al., 2007). The neutral losses typical for functional groups present in the organometallic compounds are summarized in Table 3. The presence of particular groups can be associated with the typical neutral losses, such as hydrogen halide for the presence of halogen, the loss of carbon dioxide for organometallic carboxylates, the loss of alkene or alkane in the presence of alkyl substituents on the metal atom or other ring structures, the loss of 28 ($\mathrm{N_2}$) confirms the presence of an azo group in the molecule, etc. For organometallic compounds that contain two or more alkyl/aryl substituents, cleavages of these bonds that result in subsequent neutral losses of alkene and alkane for the alkyl substitution (Baul et al., 2005a, 2006a, 2008; Chalupa et al., 2006, 2008; Jirásko et al., 2007),

TABLE 2. Mechanisms of ion formation of organometallic compounds

Type of ion	**Metal present in organometallic compounds (references)**
$[\mathrm{Cat}]^{+}$	***Ag*** (Rais et al., 2002); ***As*** (Larsen et al., 2001); ***Au*** (Dinger et al., 1998); ***Bi*** (Dostál et al., 2007c; Fridrichová et al., 2009); ***Cr*** (Moret et al., 2005); ***Ga*** (Young et al., 2007); **Ir** (Ogo et al., 1999); ***Pb*** (Mester & Pawliszyn, 1999; Pham et al., 2007); **Pd** (Macchioni et al., 2003); ***Pt*** (Hartnell & Arnold, 2004; Mastrorilli et al., 2004); ***Rh*** (Dorcier et al., 2008; Jimenez et al., 2008); ***Rh*** and ***Sb*** (Brown et al., 2006); ***Ru*** (Dorcier et al., 2005; Dorcier et al., 2008; Yeo et al., 1999); ***Ru*** and ***Fe*** (Paim et al., 2005); ***Os*** (Dorcier et al., 2005; Dorcier et al., 2008); ***Sb*** (Dostál et al., 2007c; Fridrichová et al., 2009); ***Sn*** (Holčapek et al., 2006; Kašná et al., 2008); ***V*** (Palačková et al., 2007; Vinklárek et al., 2006); ***heteromultimetallic*** (Packheiser & Lang, 2007; Packheiser et al., 2008a; Packheiser et al., 2008b)
$[\mathrm{M+H}]^{+}$	***As*** (Florencio et al., 1997; Pedersen & Francesconi, 2000); ***Au*** (Dinger & Henderson, 1998a, b; Goss et al., 2003; Kilpin et al., 2007); ***Bi*** (Dostál et al., 2009b; Chovancová et al., 2009); ***Co*** (Alsberg et al., 2001); ***Fe*** (Henderson & Alley, 2002; KaneMaguire et al., 1996; Seiwert & Karst, 2007; Wu et al., 2008); ***Ge*** (Jirásko et al., 2009; Takeuchi et al., 2006; Wei et al., 2001); ***Hg*** (Nicholson & Whitley, 2004); ***Pb*** (Casas et al., 2004); ***Pd*** (Chevrin et al., 2007); ***Ru*** (Ang et al., 2006; Pelagatti et al., 2005; Yeo et al., 1999); ***Sb*** (Dostál et al., 2009a; Dostál et al., 2009b); ***Se*** (Zhou et al., 2007); ***Si*** (Takeuchi et al., 2006); ***Sn*** (Baul et al., 2005a; Baul et al., 2005b; Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2006b; Baul et al., 2008; Chalupa et al., 2006; Wei & Miller, 2001); ***Sn*** and ***Si*** (Beckmann et al., 1998); ***Ti*** (Meurer et al., 2003; Meurer et al., 2006); ***heteromultimetallic*** (Packheiser & Lang, 2007; Packheiser et al., 2008a; Packheiser et al., 2008b)
$[\mathrm{M+Z}]^{+}$ Z=Na, K, Li, Ag	***As*** (Florencio et al., 1997); ***Au*** (Goss et al., 2003; Kilpin et al., 2007); ***Bi*** (Dostál et al., 2009b; Chovancová et al., 2009); ***Fe*** (Alley & Henderson, 2001; Henderson & Alley, 2002; Pla-Quintana & Roglans, 2005); ***Ge*** (Jirásko et al., 2009); ***Hg*** (Nicholson & Whitley, 2004); ***Pb*** (Aplin et al., 2002; Casas et al., 2004); ***Pd*** (Chevrin et al., 2007; Pla-Quintana & Roglans, 2005); ***Pt*** (Hartnell & Arnold, 2004); ***Ru*** (Ang et al., 2006; Pelagatti et al., 2005); ***Sb*** (Dostál et al., 2008; Dostál et al., 2009b; Chovancová et al., 2009); ***Se*** (Zhou et al., 2007); ***Sn*** (Baul et al., 2005a; Baul et al., 2005b; Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2006b; Baul et al., 2006c; Baul et al., 2007a; Baul et al., 2008; Dostál et al., 2006b; Dostál et al., 2007b; Chalupa et al., 2006; Jirásko et al., 2007; Kolářová et al., 2004); ***Sn*** and ***Si*** (Beckmann et al., 1998)
$[\mathrm{2M+H}]^{+}$	***As*** (Florencio et al., 1997); ***Au*** (Dinger & Henderson, 1998a, b; Goss et al., 2003; Kilpin et al., 2007); ***Fe*** (Henderson & Alley, 2002); ***Ru*** (Pelagatti et al., 2005)
$[\mathrm{2M+Na}]^{+}$ or $[\mathrm{2M+K}]^{+}$	***As*** (Florencio et al., 1997); ***Au*** (Goss et al., 2003; Kilpin et al., 2007); ***Fe*** (Henderson & Alley, 2002); ***Ru*** (Pelagatti et al., 2005); ***Sn*** (Baul et al., 2005b; Baul et al., 2005c; Chalupa et al., 2006)
$[\mathrm{M+R_3NH}]^{+}$ R=CH_3, Et	***Au*** (Kilpin et al., 2007); ***Ru*** (Ang et al., 2006)
$[\mathrm{M+NH_4}]^{+}$	***Au*** (Dinger & Henderson, 1998b, 1999); ***Fe*** and ***Pd*** (Pla-Quintana & Roglans, 2005)
$[\mathrm{2M+NH_4}]^{+}$	***Au*** (Dinger & Henderson, 1999)
$[\mathrm{M-X}]^{+}$, X=halide, CF_3COO, CF_3SO_3 or complex ligands	***Bi*** (Dostál et al., 2006a); ***Fe*** (Henderson & Alley, 2002); ***Os*** (Dorcier et al., 2005; Dorcier et al., 2008); ***Pb*** (Aplin et al., 2002; Casas et al., 2004); ***Rh*** (Dorcier et al., 2005; Dorcier et al., 2008; Jimenez et al., 2008); ***Ru*** (Moret et al., 2005; Pelagatti et al., 2005); ***Sb*** (Dostál et al., 2006a; Dostál et al., 2007c; Dostál et al., 2008; Machuča et al., 2007); ***Sn*** (Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2006b; Baul et al., 2006c; Baul et al., 2008; Bekri et al., 2006; Henderson & Taylor, 1996; Chalupa et al., 2006; Jirásko et al., 2007; Kašná et al., 2008; Kolářová et al., 2004; Lawson et al., 1996; Wei & Miller, 2001)
$[\mathrm{2M-X}]^{+}$, X=halide	***Ru*** (Pelagatti et al., 2005)
$[\mathrm{M+SnR_3}]^{+}$, R=CH_3, Et, Bu, Bz, Ph, C_6H_7	***Sn*** (Baul et al., 2005b; Baul et al., 2005c; Baul et al., 2007a; Chalupa et al., 2006; Wei & Miller, 2001)
$[\mathrm{M+SnR_2R'}]^{+}$, R=CH_3, Bu, Ph; R'=$C_9H_{12}N$	***Sn*** (Chalupa et al., 2008)
$[\mathrm{M+Na-H+SnR_3}]^{+}$ and $[\mathrm{M+K-H+SnR_3}]^{+}$	***Sn*** (Baul et al., 2005b; Baul et al., 2005c)
$[\mathrm{M}]^{+\cdot}$ or metal oxidation	***As*** (Florencio et al., 1997); ***Au*** (Kilpin et al., 2007); ***Fe*** (Alley & Henderson, 2001; Diehl & Karst, 2002; Ding et al., 2003; KaneMaguire et al., 1996; Murao et al., 2005; Pla-Quintana & Roglans, 2005; Quirke & Van Berkel, 2001; Tharamani et al., 2008); ***Te*** (Kandasamy et al., 2003)
$[\mathrm{M+2H}]^{2+}$	***Co*** (Alsberg et al., 2001; Gentili et al., 2008)
$[\mathrm{Cat}]^{2+}$	***Pt*** (Hartnell & Arnold, 2004); ***heteromultimetallic*** (Packheiser et al., 2008a; Packheiser et al., 2008b)
$[\mathrm{Cat}]^{n+}$, n=2 to 28	***Ru*** and ***Si*** (Kriesel et al., 1998)
$[\mathrm{An}]^{-}$	***B*** (Dostál et al., 2007c; Kašná et al., 2008); ***Mo*** (Thompson et al., 2003); ***Ni*** (Goicoechea & Sevov, 2006b); ***Re*** (Jiang et al., 2000); ***Ru*** (Crawford et al., 2006); ***W*** (Thompson et al., 2003); ***Zn*** (Goicoechea & Sevov, 2006a)
$[\mathrm{M+L}]^{-}$, X=halide, CF_3SO_3, complex ligand	***Bi*** (Dostál et al., 2006a); ***Fe*** (Henderson & Alley, 2002); ***Sb*** (Dostál et al., 2006a; Dostál et al., 2007a; Chovancová et al., 2009; Machuča et al., 2007); ***Sn*** (Baul et al., 2006a; Baul et al., 2007a; Wei & Miller, 2001)
$[\mathrm{M-SnR_2R'}]^{-}$, R=CH_3, Bu, Ph; R'=$C_9H_{12}N$	***Sn*** (Chalupa et al., 2008)
$[\mathrm{M-SnR_3}]^{-}$, R=CH_3, Et, Bu, Bz, Ph, C_6H_7	***Sn*** (Chalupa et al., 2006)
$[\mathrm{M-H}]^{-}$	***As*** (Florencio et al., 1997); ***Cr*** and ***Fe*** (Martinez-Alvarez et al., 2004); ***Fe*** (Alley & Henderson, 2001; Tharamani et al., 2008); ***Ge*** (Jirásko et al., 2009; Lamb & Sweetman, 1996; Wei et al., 2001) ***Pt*** (Mastrorilli et al., 2004); ***Ru*** (Pelagatti et al., 2005); ***Sn*** (Baul et al., 2005a; Baul et al., 2005b; Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2006d; Baul et al., 2007a; Baul et al., 2007b; Jirásko et al., 2007)
$[\mathrm{M+Na-2H}]^{-}$	***Sn*** (Jirásko et al., 2007)
$[\mathrm{2M+X}]^{-}$	***Fe*** (Henderson & Alley, 2002); ***Ru*** (Pelagatti et al., 2005); ***Sn*** (Baul et al., 2006d)
$[\mathrm{An}]^{2-}$	***Bi*** (Mlýnek & Dahl, 1997); ***Os*** (Dyson et al., 2000); ***Ru*** (Crawford et al., 2006)
$[\mathrm{M}]^{-\cdot}$	***As*** (Florencio et al., 1997)
solvent adducts	***Fe*** (Ding et al., 2003; KaneMaguire et al., 1996); ***Fe*** and ***Ru*** (Paim et al., 2005); ***Ga*** (Young et al., 2007); ***Hg*** (Nicholson & Whitley, 2004); ***Mo*** (Gun et al., 2003); ***Pb*** (Aplin et al., 2002); ***Pd*** (Guo et al., 2005); ***Pt*** (Mastrorilli et al., 2004); ***Re*** (Jiang et al., 2000); ***Sb*** (Lintschinger et al., 1998; Zheng et al., 2001); ***Sn*** (Henderson & Taylor, 1996; Jirásko et al., 2007; Jones-Lepp et al., 1999; Jones-Lepp et al., 2001; Lawson et al., 1996)
adducts with water, hydrolysis products	***Bi*** (Dostál et al., 2006a); ***Fe*** (Ding et al., 2003); ***Sb*** (Dostál et al., 2006a; Dostál et al., 2007a; Dostál et al., 2008; Lintschinger et al., 1998; Machuča et al., 2007; Zheng et al., 2001); ***Sn*** (Baul et al., 2006d; Beckmann et al., 2002; Henderson & Taylor, 1996; Chalupa et al., 2006; Jirásko et al., 2007; Lawson et al., 1996; Wei & Miller, 2001)
$[\mathrm{M-2H}]^{2-}$	***Fe*** (Alley & Henderson, 2001)

Bu, butyl; Ph, phenyl; Bz, benzyl; Et, ethyl; L, ligand; Cat, cationic part; An, anionic part.

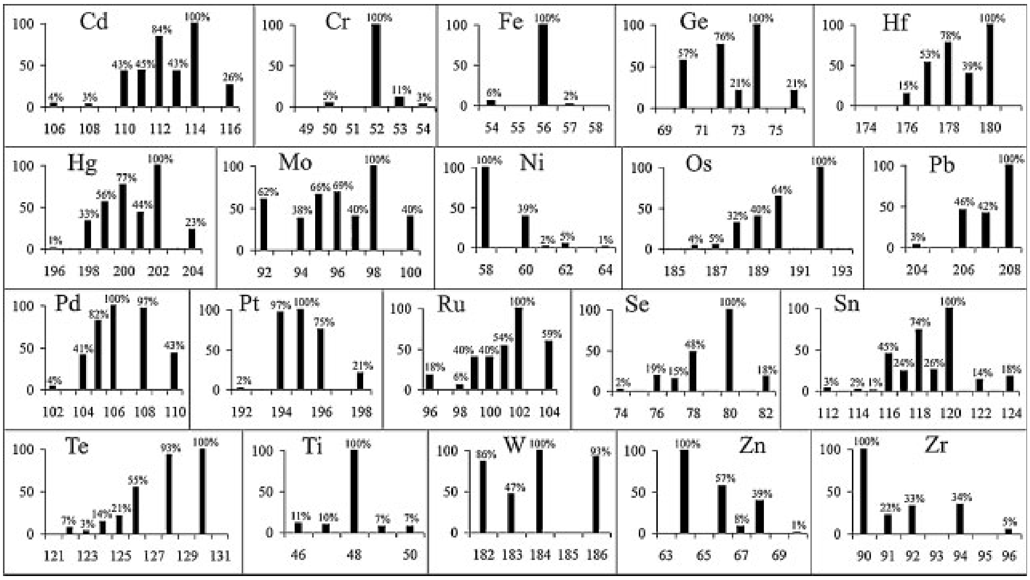

FIGURE 1. Isotopic distribution of polyisotopic **p** and **d** metal atoms.

cycloalkane and cykloalkene for cykloalkyl (Chalupa et al., 2006), C_6H_6 and C_6H_4 (Baul et al., 2006b; Chalupa et al., 2006, 2008) for the phenyl substitution or C_7H_8, and C_7H_6 for the benzyl substitution (Baul et al., 2006c; Chalupa et al., 2006, 2008; Jirásko et al., 2007) are typical. In the case of the presence of some complex ligand on the metal atom, the neutral losses depend on the structures of particular ligands. Moreover, the formation of adducts inside the ion-trap is relatively common for organometallics due to their reactivity, for example, an addition of water ($\Delta m/z$ 18) or solvent (CH_3CN, $\Delta m/z$ 41) observed in the multistage mass spectra (Baul et al., 2005a; Henderson & McIndoe, 2005; Jirásko et al., 2007).

III. MASS SPECTROMETRY OF INDIVIDUAL ORGANOMETALLIC CLASSES

This chapter that describes the MS of individual organometallic compounds is divided into two groups according to the position of the metal in the periodic table; that is, the main-group and transition-metals. Organometallics, for which no important article on soft-ionization techniques has been found (organolanthanides, organoaluminum, organogallium, and organoindium compounds), are not included. Although the main emphasis is given to the MS of complex organometallic compounds, simple organometallics are also mentioned in special cases, such as alkyl and aryl derivatives of organotin, organomercury, organoarsenic,

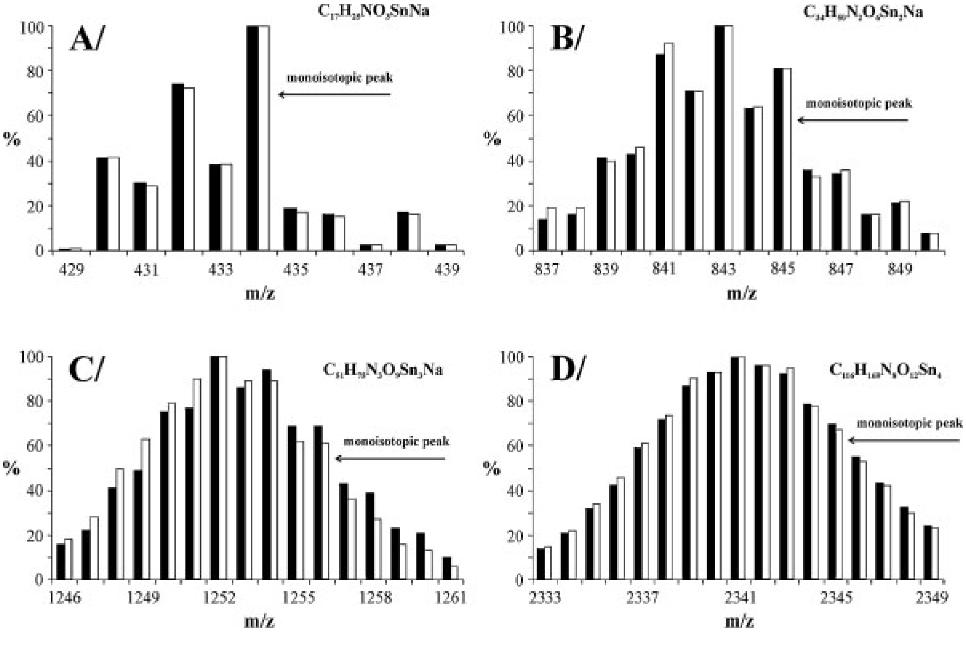

FIGURE 2. Comparison of experimental (white bars) and theoretical (black bars) isotopic abundances of ions with (**A**) one, (**B**) two, (**C**) three, and (**D**) four tin atoms (reproduced from Jirásko et al., 2007).

or organolead compounds. Metallocenes and their related compounds are also discussed.

A. Main-Group Organometallic Compounds

‘‘Poor metals’’ (Al, Ga, In, Tl, Ge, Sn, Pb, Bi) but also so-called metalloids (B, Si, As, Sb, Te) can be present in the structure of main-group organometallics.

1. Simple Main-Group Organometallic Compounds

Due to the wide range of applications of organometallics, their long-time persistence in the environment with respect to their water solubility, and the accumulation in the fat of living organisms is often observed. This serious problem is mainly related to organotin, organolead, organoarsenic, and organomercury compounds. These environmentally dangerous compounds are commonly observed at low concentration levels, so that the application of sensitive analytical technique is necessary to monitor their levels. The important point is the development of appropriate chromatographic methods. Gas chromatography combined with inductively coupled plasma time-of-flight mass spectrometry (ICP-MS) enables high sensitivity and resolution, but the time-consuming preparation of volatile derivates is inevitable, and can influence the reproducibility, especially for

TABLE 3. Common neutral losses observed in CID mass spectra of organometallic compounds

Nominal mass shift [ΔDa]	Neutral loss	Functional group or substituent	References
2	H_2	cyclization, oxidation	(Larsen et al., 2001)
15	$CH_3^{\cdot}$	methyl	(Larsen et al., 2001; Mester & Pawliszyn, 1999)
16	CH_4	methyl	(Chalupa et al., 2006; Larsen et al., 2001; Pham et al., 2007)
18	H_2O	hydroxyl, carboxylate	(Baul et al., 2006d; Baul et al., 2007b; Florencio et al., 1997; Chalupa et al., 2006; Chalupa et al., 2008; Jirásko et al., 2009; Kolářová et al., 2004; Larsen et al., 2001; Wei et al., 2001; Wei & Miller, 2001)
28	C_2H_4	ethyl	(Kolářová et al., 2004; Lamb & Sweetman, 1996)
	CO	carbonyl	(Baul et al., 2005a; Jirásko et al., 2007; Seiwert & Karst, 2007; Yeo et al., 1999)
	CO	carbene complexes	(Crawford et al., 2006; Jiang et al., 2000; KaneMaguire et al., 1996; Martinez-Alvarez et al., 2004; Mastrorilli et al., 2004; Mlýnek & Dahl, 1997; Moret et al., 2005; Thompson et al., 2003)
	N_2	azo group	(Baul et al., 2005b; Baul et al., 2006b)
29	$C_2H_5^{\cdot}$	ethyl	(Mester & Pawliszyn, 1999)
30	C_2H_6	ethyl	(Chalupa et al., 2006; Mester & Pawliszyn, 1999; Mlýnek & Dahl, 1997; Pham et al., 2007)

(*Continued*)

TABLE 3. (*Continued*)

	H_2CO	methoxy	(Dostál et al., 2006a; Dostál et al., 2007c; Henderson & Alley, 2002; Kolářová et al., 2004; Larsen et al., 2001)
32	CH_3OH	solvent adducts, methoxy	(Florencio et al., 1997; Kolářová et al., 2004; Larsen et al., 2001)
36	HCl	chloride	(Dostál et al., 2006a; Dostál et al., 2007c; Chovancová et al., 2009; Kolářová et al., 2004)
42	CH_2CO	-	(Kilpin et al., 2007; Larsen et al., 2001)
	C_3H_6	propyl	(Kolářová et al., 2004)
43	CH_3CN	solvent adducts	(Mastrorilli et al., 2004; Yeo et al., 1999)
44	CO_2	carboxylate	(Baul et al., 2005a; Baul et al., 2005b; Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2007a; Baul et al., 2007b; Dostál et al., 2007b; Dostál et al., 2009a; Florencio et al., 1997; Chalupa et al., 2006; Chalupa et al., 2008; Jirásko et al., 2007; Jirásko et al., 2009; Larsen et al., 2001; Wei et al., 2001)
	CH_2CHOH	ethoxy	(Kolářová et al., 2004; Larsen et al., 2001)
45	$(CH_3)_2NH$	dimethylamine	(Holčapek et al., 2006)
46	C_2H_5OH	ethoxy, solvent adducts	(Kolářová et al., 2004; Larsen et al., 2001)
	$H_2O + CO$	carboxylate	(Florencio et al., 1997)
56	C_4H_8	butyl	(Baul et al., 2005a; Baul et al., 2006a; Beckmann et al., 1998; Dostál et al., 2006a; Dostál et al., 2007b; Dostál et al., 2007c; Dostál et al., 2008; Jirásko et al., 2007; Kolářová et al., 2004)
58	C_4H_{10}	butyl	(Baul et al., 2006a; Baul et al., 2008; Beckmann et al., 2002; Chalupa et al., 2006)
60	CH_3COOH	-	(Baul et al., 2006a; Jirásko et al., 2007)
	C_3H_7OH	propyloxy	(Kolářová et al., 2004)
64	C_5H_4	cyclopentadienyl	(Paim et al., 2005)
65	$C_5H_5^{\cdot}$	cyclopentadienyl	(KaneMaguire et al., 1996; Paim et al., 2005)

TABLE 3. (*Continued*)

66	C_5H_6	cyclopentadienyl	(Alley & Henderson, 2001; Seiwert & Karst, 2007; Wu et al., 2008)
76	C_6H_4	phenyl	(Baul et al., 2006b; Chalupa et al., 2006; Chalupa et al., 2008)
77	C_6H_5	phenyl	(Casas et al., 2004; Paim et al., 2005)
78	C_6H_6	phenyl	(Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2006b; Holčapek et al., 2006; Chalupa et al., 2006; Jirásko et al., 2007; Kolářová et al., 2004)
80	HBr	bromide	(Baul et al., 2005b)
84	C_6H_{12}	cyclohexyl	(Chalupa et al., 2006)
90	C_7H_6	benzyl	(Baul et al., 2006c; Chalupa et al., 2006; Jirásko et al., 2007)
92	C_7H_8	benzyl	(Baul et al., 2006c; Chalupa et al., 2006; Jirásko et al., 2007)

natural samples (Prange & Jantzen, 1995; Jitaru, Infante, & Adams, 2004). Although the alternative approach for simple organometallic compounds separation is HPLC, where no derivatization is required, extraction and preconcentration steps are often necessary before the analysis (Harrington, Eigendorf, & Cullen, 1996; Ebdon, Hill, & Rivas, 1997; Mester & Pawliszyn, 1999; Gomez-Ariza et al., 2001; Forgacs & Cserhati, 2002). If no structural information is needed, then ICP-MS can be applied (Gonzalez-Toledo et al., 2003; Rosenberg, 2003). However, the most useful is ESI-MS (Jones-Lepp et al., 1999; Guo et al., 2005; Jones-Lepp & Momplaisir, 2005). The complicated situation is found for the HPLC of organotin compounds, and only few articles that deal with the HPLC separation of simple organotin compounds are found in the literature. Tin is very reactive to the oxygen, nitrogen, and sulfur present in analyzed matrices, stationary or mobile phases, which causes an irreversible adsorption and peak tailing of organotin compounds in normal- and reversed-phase systems.

Concerning simple organoarsenic compounds, ESI mass spectra (Florencio et al., 1997; Larsen et al., 2001; Schaeffer, Fodor, & Soeroes, 2006) are noted for several examples (e.g., arsenobetaine, tertramethylarsonium, dimethylarsenic acid). ESI yields a better specificity and sensitivity compared with preliminary experiments with APCI (Larsen et al., 2001). The presence of $[M+H]^+$, $[M+Na]^+$, and $[M]^{+\cdot}$ ions in the positive-ion mode, together with fragment and adduct ions, is observed, whereas $[M-H]^-$ and $[M]^{-\cdot}$ ions are typical for the negative-ion mode. Mass spectra of simple alkyl and aryl organotin derivatives as well as their organolead analogs depend on substituents. Usually, ESI is preferred for their ionization (Henderson, Nicholson, & McCaffrey, 1998; Jones-Lepp et al., 1999; Mester & Pawliszyn, 1999; Henderson & McIndoe, 2005), but the application of APCI (Bekri, Saint-Louis, & Pelletier, 2006) has been also published. When chlorine is bonded to the metal atom, the cleavage of this polar bond to yield $[M-Cl]^+$ ion is predominantly observed (e.g., for R_3SnCl, R_2SnCl_2, or R_3PbCl; $R = CH_3$, C_2H_5, C_4H_9, C_6H_5) (Henderson & Taylor, 1996; Mester & Pawliszyn, 1999). Further, fragment ions formed from the loss of an alkyl or aryl substituent are found in their mass spectra ($[RPb]^+$, $[Pb]^+$, $[RSnH_2]^+$, etc.). In the negative-ion mode, the presence of a stable ion $[Ph_3Sn]^-$ is described for triphenyltin compounds in contrast to spectra of trialkyl derivatives, where $[R_3SnX_2]^-$ ($X = Cl$, Br, I) are rather common (Henderson & Taylor, 1996), as illustrated in Figure 3.

Reactive organotin compounds are predisposed to hydrolysis and solvent-adduct formation. The hydrolysis aggregates of a polymeric character $[(R_3Sn)_n(OH)_{n-1}]^+$ ($R = CH_3$, Bu, Ph) and adducts $[(R_3Sn)(ACN)]^+$ were investigated (Fig. 4) for triorganotin halide ACN/H_2O (1:1) solution (Henderson & Taylor, 1996). A similar behavior was reported for a methanol solution (Lawson et al., 1996), and solvent-adduct ions were also observed for simple organoantimony compounds (Lintschinger, Schramel, & Kettrup, 1998; Zheng, Takeda, & Furuta, 2001).

2. *Organotin Compounds*

Numerous interesting articles have been published on the MS of complex organotin compounds. Organotin complexes that contain so-called pincer ligands were studied with ESI-MS (Kolářová et al., 2004; Dostál et al., 2006b, 2007b; Holčapek et al., 2006; Bouška et al., 2009) with an ion-trap analyzer. Their spectra are strongly dependent on the character of other substituents and ligands, which are directly bonded to the tin atom. The basic process of ion formation of mono-, di-, and triorganotin complexes that hold at least one polar substituent (small inorganic ions, halogen- and oxygen-containing anionic species) or a weakly bonded ligand (azo dyes sulfonate and benzoate complexes) on the tin atom is the cleavage of this polar

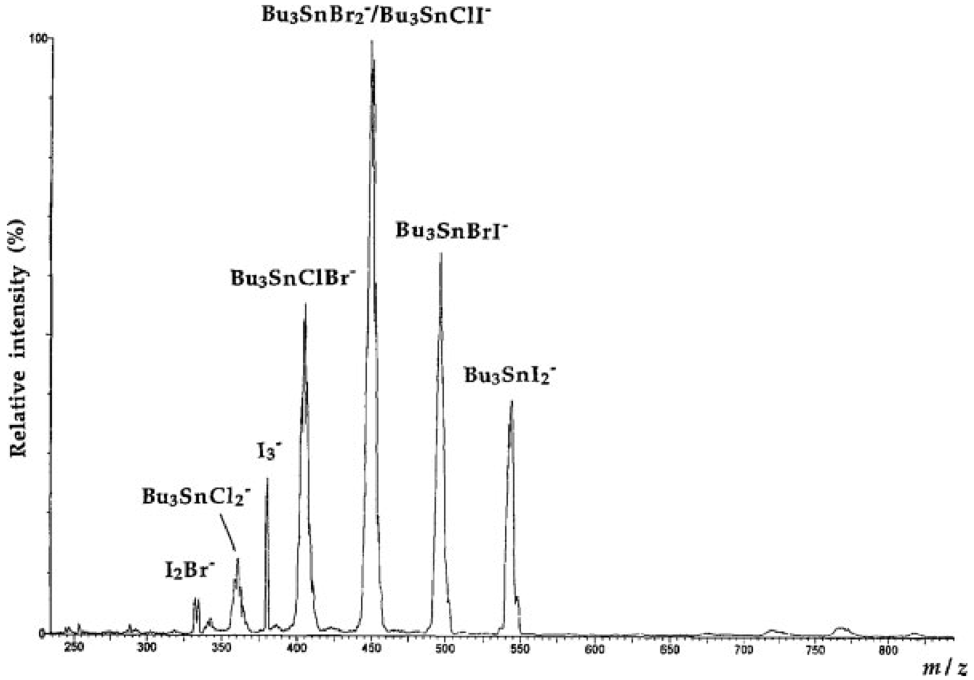

FIGURE 3. Negative-ion ESI mass spectrum of hydrolysis mixture of Bu_3SnCl in the solution with added NaCl, KBr, and KI (reproduced with permission from Henderson & Taylor, 1996).

bond to yield two complementary ions, positively charged and negatively charged parts, which are the base peaks in positive- or negative-ion ESI mass spectra for most compounds. The sum of the masses of those two parts corresponds to the MW. Negative-ion mass spectra of small inorganic ions are trivial (e.g., chloride, bromide, cyanide, etc.), but they provide valuable structure confirmation on the anionic parts of studied organotin compounds, which cannot be obtained from NMR spectra. The quadrupole analyzer is preferred for ions *m*/*z* lower than 100, because the sensitivity of an ion-trap is significantly decreased in the low-mass region because of the cut-off effect. The cationic part includes usually a tin atom; therefore, the isotopic pattern can be useful for the spectra interpretation. Moreover, the fragment ions of the cationic part and sodium or potassium molecular adducts are often observed in the positive-ion full-scan mass spectra. When the polar bond on the tin atom is missing (tetraorganotin compounds), then the formation of molecular adducts with alkali metal ions is the most important process of ion formation. Monoorganotin derivatives that contain three chlorine atoms show a quite unexpected behavior. They might react in the gas-phase according to the equation $M + M \rightarrow M_{dim} + SnCl_4$ with $[M_{dim} - Cl]^+$ observed in the positive-ion full-scan mass

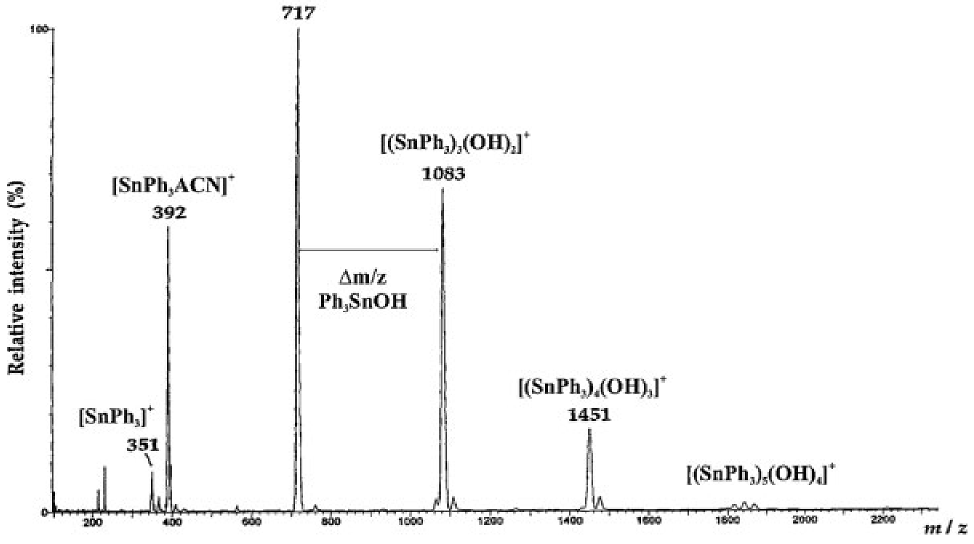

FIGURE 4. Positive-ion ESI mass spectrum of a hydrolysis mixture of Ph_3SnCl in 1:1 (v/v) H_2O/ACN solution (reproduced with permission from Henderson & Taylor, 1996).

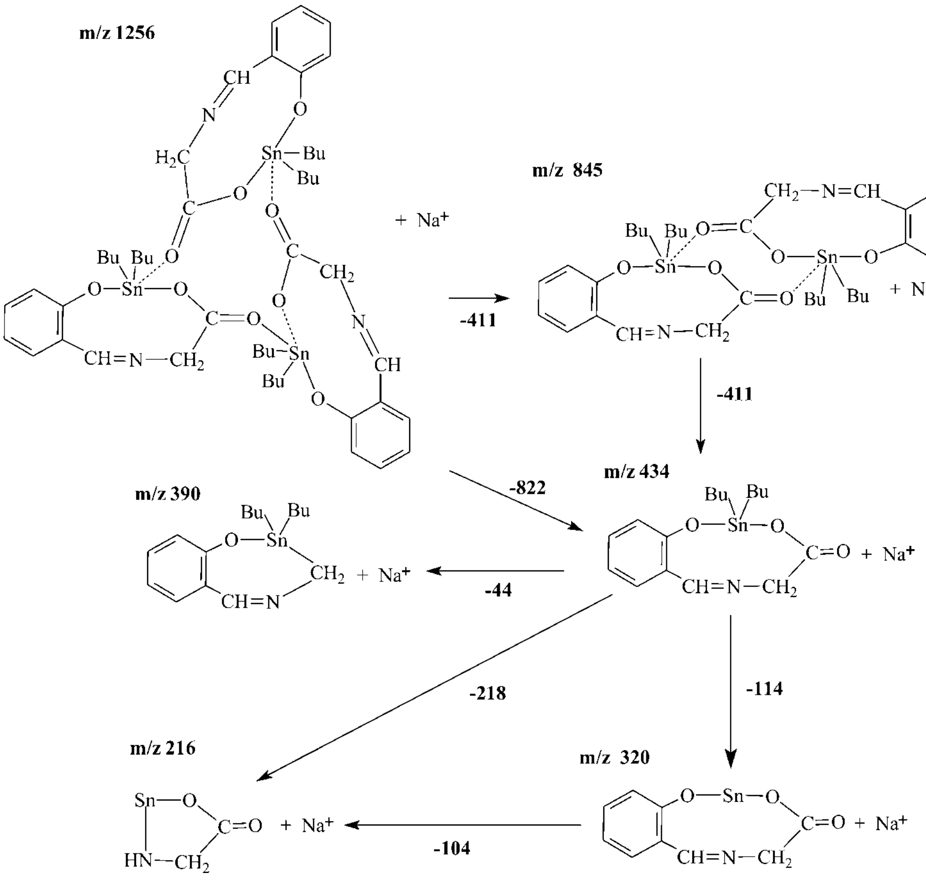

FIGURE 5. Suggested fragmentation pattern of the $[M+Na]^+$ ion at *m/z* 1,256 for trimeric organotin carboxylate (reproduced from Jirásko et al., 2007).

spectra (M_{dim} corresponds to the dimeric molecule $2M - SnCl_4$). Tandem mass spectra of organotin compounds with pincer ligands are related to substituents. Alkene losses are observed for *tert*-butyl and isopropyl substituents, whereas alcohol or aldehyde losses are preferred for methyl and ethyl substitution of a pincer ligand. Other neutral losses are Sn, C_6H_6, C_6H_4, etc. (Kolářová et al., 2004).

Similar ions are described also for other organotin compounds, such as trialkyl-, triphenyl-, dialkyl-, and diaryl-organotin complexes with carboxylated and hydroxylated ligands (Baul et al., 2005a,b,c, 2006a,b,c,d, 2007a,b, 2008; Beckmann et al., 2005; Jirásko et al., 2007). The formation of adduct ions $[M+SnR_3]^+$ and $[M+SnR_3-H+Na(K)]^+$ is sometimes observed in addition to previous mechanisms. The simplest spectra exhibit compounds with the ionic bond that typically contain only two important ions, depending on the polarity mode, $[Cat]^+$ and $[An]^-$.

On the other hand, ESI mass spectra of organometallic compounds that contain more tin atoms with non-covalent bonds are rather complex and difficult to interpret, because these bonds are cleaved easily during the ionization process, and hence the corresponding ions of non-covalently bonded complexes are missing completely or they have low relative abundances in the full-scan ESI mass spectra. Therefore, the applied voltages on ion optics have to be reduced to minimize any undesirable fragmentation. Proposed structures of important complex ions are confirmed with MS^n analysis. Non-covalent bonds are much weaker compared to covalent bonds; hence, the fragmentation of non-covalent bonds is strongly preferred. When all non-covalent bonds are broken, then the fragmentation continues with covalent bonds; for example, the fragmentation of a sodium adduct of trimeric organotin carboxylate at *m/z* 1,256 in Figure 5 (Jirásko et al., 2007). Unlike common organic molecules, multitin organometallic compounds have wide isotopic distributions, so that the isolation width for MS/MS experiments must be wider (8–12 *m/z*). The same situation applies to other polyisotopic metals (Goraczko & Szymura, 1999).

The formation of unusual solvent and hydrolysis adduct ions is also observed for more complex organotin compounds. The ESI-MS is often used for their mass spectrometric characterization (Beckmann et al., 2002; Jirásko et al., 2007). Various adduct ions with water are produced with ion-molecule reactions in an ion-trap analyzer. Unusual adduct ions with water can be confirmed with isotopically labeled standards (Fig. 6). This approach has been applied to study the hydrolysis of triorganotin chloride with a *C,N*-chelating ligand (Holčapek et al., 2006). Non-labeled, and three isotopically labeled, compounds (D6, D10, D16) have been treated with aqueous NaOH. Hydrolysis reaction products were the same for phenyl, methyl, and *n*-butyl substitution, but differ for a *tert*-butyl substituent probably because of steric reasons. Further, hydrolysis products of tribenzyltin substituted-phenoxyacetate compounds have been investigated in aqueous acetonitrile solution with the measurement of ESI-MS (MS^n) in both polarity modes (Wei & Miller,

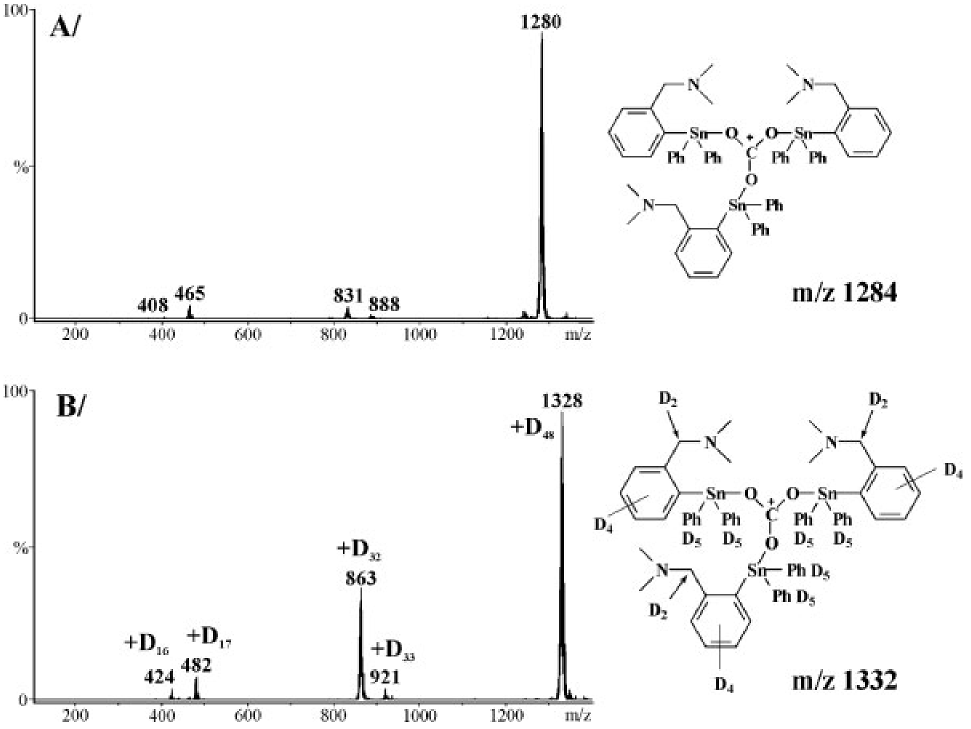

FIGURE 6. Positive-ion full-scan ESI mass spectra of the hydrolysis product of (**A**) [(2-dimethylaminomethyl)phenyl]diphenyltin(IV) chloride, and (**B**) its deuterated analog (reproduced with permission from Holčapek et al., 2006).

2001). No effect on the formation of hydrolysis products was observed for isomers that differ in the position of the substitution group on the phenyl group of tribenzyltin nitrophenoxyacetates, and similar spectra were observed for all compounds. In general, the hydrolysis and solvent-adduct formation is caused mainly by the presence of a polar bond, such as between metal and halogen, and it is no wonder that the hydrolysis of diorganotin (Beckmann et al., 2002; Jirásko et al., 2007) and monoorganotin (Kolářová et al., 2004; Bouška et al., 2009) compounds occurs. Hydrolysis adduct ions with a polymeric character of $OSnR_2$ (R = Bu or Oct) unit were observed for tetrameric diorganotin compounds (Jirásko et al., 2007) in positive-ion ESI-MS. To fully characterize these adducts, four solvents (acetonitrile, methanol, ethanol, and 2-propanol) were used for adduct characterization. In addition to the polymeric character, the spectra measured in alcoholic solvents contained solvent adducts. Similar types of ions were formed for all compounds and solvents, but with different masses due to the shifts of masses of individual solvents. In case of acetonitrile, only adducts with $OSnR_2$ were observed in the spectra contrary to alcoholic solvents. There is no doubt that ESI is the most suitable technique tor study hydrolysis and solvent organotin adducts.

On the other hand, MALDI provides better results for high-molecular weight organotin polymers and dendrimers. Oligomeric and polymeric products of the polycondensation reaction system formed from medically important drugs (norfloxacin, ticarcillin) with diorganotin dihalides were characterized with MALDI-MS, and their mass spectra revealed multiple units of higher masses (Carraher & Lanz, 2003; Carraher & Morie, 2004). MALDI-MS does not require the polymer to be in the solution, and poorly soluble tin-containing condensation polymers were characterized with a focus on fragment analysis (Carraher et al., 2007).

3. *Organolead Compounds*

Concerning organolead compounds, the generation of sodium and potassium molecular adducts was observed in ESI-MS of various organolead carboxylates. Due to the presence of carboxylic group bonded through oxygen to the lead atom, the ions $[M - RCOO]^+$ were observed in their spectra. The existence of facile ligand equilibration was deduced based on the formation of solvent (acetonitrile) and pyridine adducts for several different aryllead(IV) carboxylates (Aplin, Buston, & Moloney, 2002). Similar spectra were observed for other complexes formed by $Pb(C_6H_5)_2(OAc)_2$ with salicylaldehyde, 2-ketobutyric acid, pyridine-2-carbaldehyde, 2-acetylpyridine, and 2-benzoylpyridine thiosemicarbazones, which were studied in detail with CID, ESI, and an ion-trap analyzer. Sodium adducts $[M + Na]^+$ were observed for compounds that contain a carboxylic group, whereas the production of abundant protonated molecules was recorded when no carboxylic group was present (Casas et al., 2004). Recently, simple organolead compounds (Ph_3PbCl, Ph_2PbI_2, Ph_2PbBr_2, and Me_3PbOAc) were treated with $[Pt_2(l\text{-}S)_2(PPh_3)_4]$ to yield solutions that contain positive ions $[Pt_2(l\text{-}S)_2(PPh_3)_4PbR_3]^+$ ($R_3 = Ph_3$, Ph_2I, Ph_2Br, Me_3) in ESI mass spectra, and their fragmentation behavior was studied (Pham et al., 2007). The initial loss of PPh_3 was observed in all cases. Furthermore, the loss of $PbPh_2$ occurred for R = Ph compared with R = Me, for which the elimination of ethane followed by a loss of CH_4. The simplification of the isotope envelope can be also mentioned for the loss of isotopically rich Pb.

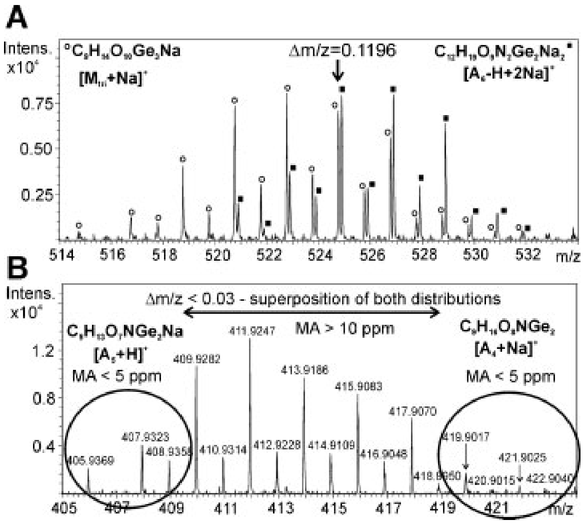

FIGURE 7. Details of full-scan positive-ion ESI mass spectra of a mixture of Ge-132 with alanine: (**A**) two resolved ions without the superposition of both isotopic distributions, and (**B**) two non-resolved ions with the superposition of both isotopic distributions (reproduced from Jirásko, Holčapek, & Rosenberg, 2009).

4. *Organogermanium Compounds*

Only a few articles of MS of organogermanium compounds can be found in the literature, and most of them are devoted to the analysis of so called Ge-132 (germanium sesquioxide) (Lamb & Sweetman, 1996; Wei, Chen, & Miller, 2001; Jirásko, Holčapek, & Rosenberg, 2009). ESI with an ion-trap analyzer was used for Ge-132 characterization. A wide range of complex polymeric ions were formed inside an ion-trap, and their fragmentation behavior was explained by MS^n measurements. Moreover, Ge-132 mixtures with different amino acids were measured, with an emphasis on the determination of the elemental composition and the theoretical isotopic pattern of product ions (Jirásko, Holčapek, & Rosenberg, 2009). The hybrid analyzer QqTOF was used, and information from both polarity modes was subsequently used to elucidate some structural aspects, and the proposal of reaction mechanisms that lead to the adduct formation. A new approach to identify potential overlap of ion signals with wide isotopic patterns was described based on the use of accurate masses of overlaid and non-overlaid isotopes at the borders of isotopic envelopes (7).

5. *Organoarsenic, Organoantimony, and Organobismuth Compounds*

MS of organoarsenic compounds is mostly concerned with the environmental analysis of simple arsenic species. Only arsenic-containing carbohydrates (arsenosugars) measured with ESI with a single quadrupole analyzer are more complex. The typical fragment ion at *m/z* 237 and protonated molecules were observed (Pedersen & Francesconi, 2000). ESI was also successfully applied to the analysis of rhodium and iridium distibine complexes (Brown et al., 2006) and homolog $[Ni_{10}(EMe)_2(CO)_{18}]^{2-}$ dianions (E = P, As, Sb, Bi) (Mlýnek & Dahl, 1997). It is noteworthy that complexes with pincer ligands, similar to above-mentioned organotin compounds, can be also found with antimony or bismuth. A similar mechanism of labile-bond cleavage to yield $[M - X]^+$ in positive-ion and $[X]^-$ in negative-ion spectra is observed (Dostál et al., 2006a, 2007b,c, 2008, 2009a,b; Machuča et al., 2007; Chovancová et al., 2009; Fridrichová et al., 2009). The main difference among the spectra of these three organometallics is the isotopic pattern that arises from the isotopic contribution of individual metals. The most important mechanism for ion formation in negative-ion mass spectra is an anion addition $[M + X]^-$ that confirm the molecular weight. Organoantimony compounds are prone to hydrolysis in contrast to organometallics with Bi—as evident from their positive-ion mass spectra (Dostál et al., 2006a, 2007c).

6. *Organoboron Compounds*

Organoboron compounds often occur in the form of a polyhedral anion $[CB_{11}H_{12}]^-$ or its thiaborane analog $[SB_9H_{12}]^-$, which are usually counterparts of other organometallic cations (Alvarez et al., 2007; Dostál et al., 2007c; Kašná et al., 2008). Although the boron has only two isotopes ^{10}B (24%) and ^{11}B (100%), a wide isotopic distribution is observed in their ESI and FAB mass spectra due to the presence of a high number of boron atoms. Further, MALDI was used for accurate mass determination of organoboron quinolinolates (Kappaun et al., 2006). The fragment ions $[M - C_6H_5]^+$, together with molecular adducts $[M + Na]^+$, were observed in their mass spectra.

7. *Organoselenium and Organotellurium Compounds*

ESI product-ion mass spectra of mercaptoethanol pre-column derivatization of a novel antitumor organoselenium heterocycle (Zhou et al., 2007) showed $[M + H]^+$ and $[M + Na]^+$ ions. Diphenacyltellurium dibromide and some other tellurium complexes were characterized with FAB (Canseco-Melchor et al., 2001; Chauhan et al., 2002) ionization, where the most intense peaks corresponded to fragment ions that have the characteristic isotopic distribution pattern of tellurium. The reaction products of tetraorganoditelluroxanes with water traces were revealed with ESI because of the mononuclear cation $[(p\text{-}MeOC_6H_4)_2TeOH]^+$ observed in its solution spectra (Beckmann et al., 2005). In addition, cationic tellurium intermediates were monitored with ESI/MS/MS (Santos, 2008).

8. *Organosilicon Compounds*

The presence of other metalloid (Weinmann et al., 1999), main-group metal (Beckmann et al., 1998; Constantine, Cardin, & Bollen, 2000; Schumann et al., 2006), transition-metal (Ruiz et al., 1999; Arevalo et al., 2001; Wong, Wong, & Lu, 2003; Jain, Lalancette, & Sheridan, 2005), or lanthanoids (Al-Juaid et al., 1999) is typical for silicon organometallics. Complexes of low-molecular weights were mostly measured with EI MS (Al-Juaid et al., 1999; Weinmann et al., 1999; Constantine, Cardin, & Bollen, 2000), whereas the method of choice to measure polymers and dendrimers is MALDI-TOF. The observation of monocharged molecular adducts with a high-resolution isotopic pattern and a minimum of fragment ions establishes the chemical formula of different species, determines the abundance of all components, and the molecular weights and the mean ring size or chain length of samples (Kohler, Schell, & Weber, 2002) as for

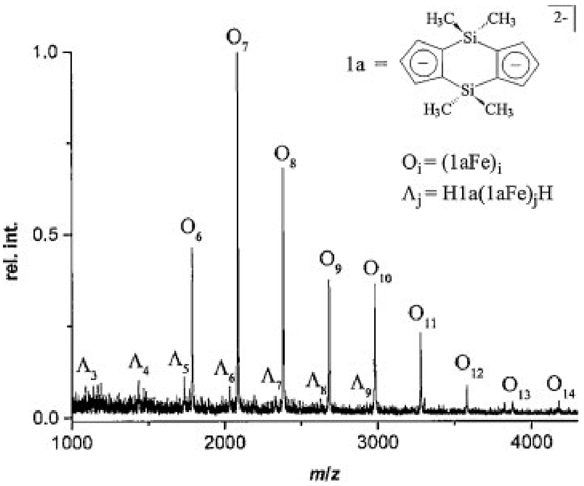

FIGURE 8. MALDI-TOF mass spectrum of products obtained from the reaction of 1aLi$_2$ with [FeCl$_2$(thf)$_{1.5}$] (reproduced with permission from Kohler, Schell, & Weber, 2002).

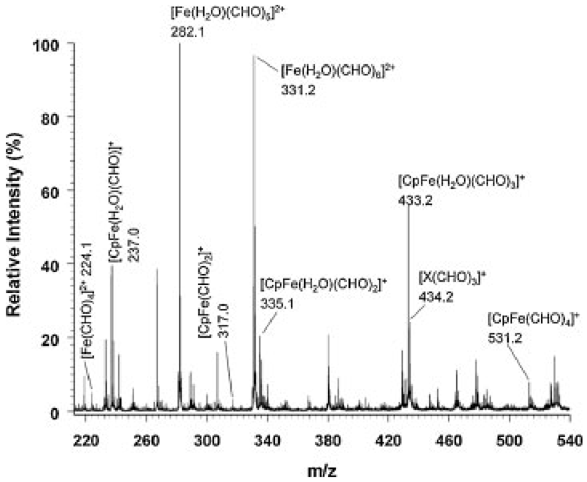

FIGURE 9. Full-scan positive-ion ESI mass spectrum obtained after the photolysis of [CpFebz]$^+$ and cyclohexene oxide (CHO) in 1,2-dichloroethane (reproduced with permission from Ding et al., 2003).

polymeric ion distribution of doubly silyl-bridged metallocenes in Figure 8. Concerning dendrimer characterization, the metallation (Na, K, Ag) of novel first-generation silicon-centered tin dendrimers was used in their MALDI spectra to verify no branching defect, and that all synthetic steps proceeded efficiently without the steric hindrance and competitive reactions (Schumann et al., 2006). Similarly, ESI spectra provided evidence for the first- and second-generation carbosilane dendrimers capped with C_5H_5Ru by a complete resolution of individual isotopic distributions of observed charge states (Kriesel et al., 1998). On the contrary, MALDI spectra of fourth-generation titanium–silicon-centered dendrimers contained no molecular ions, and only first- and second-generations were confirmed based on $[M+Na]^+$, $[M+K]^+$, and $[M+H]^+$ ions (Arevalo et al., 2001).

B. Transition-Metal Organometallic Compounds

In contrast to main-group metals, transition-metals are mostly in the form of metal complexes (Henderson & Evans, 1999; Di Marco et al., 2007) and metallocenes; not so many real organometallics that contain the covalent bond between carbon and metal is described.

1. Metallocenes and Related Compounds

Metallocenes can be defined as compounds in which two cyclopentadienyl ligands (Cp) are coordinationally bounded to the metal center with the oxidation state II in a so-called ‘‘sandwich’’ structure. Ferrocene (Cp_2Fe) and its related compounds are one of the most well-known metallocenes, and ESI is usually used for their mass spectrometric characterization. The easy oxidation of ferrocene results in a $[Cp_2Fe]^+$ positively charged ion in ESI-MS. This oxidation can be promoted by the reaction with the chemical oxidant followed by an increase of signal intensity (Henderson & McIndoe, 2005). The direct coupling of mass spectrometric techniques with electrochemical detectors is often used to monitor redox processes (Traeger, 2000; Henderson & McIndoe, 2005). No protonated molecules are generated for ferrocenes in contrast to ferrocene derivates that contain other elements (S, P, N, O), in which the formation of $[M+H]^+$, $[M+Na]^+$, and $[M+K]^+$ ions is common (Henderson & Alley, 2002). Redox properties of metallocenes often result in an interesting photochemical behavior, as illustrated in the study of [CpFebz]$^+$ with positive-ion ESI in a solution (Ding et al., 2003); Figure 9 represents the mass spectrum obtained after the photolysis of [CpFebz]$^+$ and cyclohexene oxide in 1,2-dichlorethane.

The negative-ion measurement can be useful for ferrocene-derived acids to provide deprotonated molecules (Alley & Henderson, 2001). Although typical fragment ions for the ferrocene skeleton correspond to the loss of one Cp ligand $[M-Cp]^+$, other fragments associated with the structure of ferrocene can be found as well (KaneMaguire, Kanitz, & Sheil, 1996). Recently, the monitoring of the metal-ion interaction with ferrocene derivates was performed with ESI (Tharamani et al., 2008). Ferrocenes can be used as derivatization agents (Seiwert & Karst, 2008), because the derivation improves the sensitivity of HPLC/MS determination. The simultaneous HPLC/ESI-MS/MS determination of free and disulfide-bound thiols in urine was developed with the sequential derivatization with two ferrocene-based maleimide reagents (Seiwert & Karst, 2007). The ferrocene derivatization was also used to determine of 1-hydroxyvitamin D_3 in rat plasma (Murao et al., 2005). ESI/MS/MS spectra of ferrocene carbamate esters of saturated alkyl primary, secondary, and tertiary alcohols distinguished straight-chain primary alcohol derivatives from tertiary alcohol derivatives (Quirke & Van Berkel, 2001). Ferrocenyl esters were also investigated based on the rapid HPLC separation coupled with APCI ionization (Diehl & Karst, 2002). The application of MALDI or FAB ionization was also reported (Savage et al., 2005, 2006).

In addition to iron, other central metals can be present in metallocenes. Polyisotopic titanocene intermediates of the Tebbe olefination reaction (Meurer et al., 2006) and Petasis olefination reaction (Meurer et al., 2003) were characterized with APCI-MS/MS. MALDI-TOF MS in combination with reversed-phase HPLC was used to screen the reaction between ruthenocene derivate with hen egg white lysozyme (Salmain et al., 2004), and the application of ESI was published for ruthenocenes

(Henderson & McIndoe, 2005; Yeo et al., 1999) and vanadocenes (Vinklárek et al., 2006; Palačková et al., 2007).

When only one cyclopentadienyl or arene planar ligand is coordinatively bonded to the metal center, the wide family of so-called ''half-sandwich'' compounds can be prepared. Due to the common presence of a polar bond on the metal atom, ESI is mostly used for their mass spectrometric analysis. The formation of an $[M-Cl]^+$ ion is typical for structures with chlorine bonded to the central metal (Pelagatti et al., 2005; Schmid et al., 2007). ESI-MS is applicable for the mass spectrometric analysis of ruthenium and osmium arene complexes (Wang et al., 2002; Dorcier et al., 2005; Ang et al., 2006; Schmid et al., 2007; Mattsson et al., 2008), the analysis of dinuclear iridium with a μ-hydride complex (Ogo, Makihara, & Watanabe, 1999), the study of Ru(II)-catalyzed asymmetric transfer hydrogenation of acetophenone (Pelagatti et al., 2005), and the characterization of products formed from the reaction of ''half-sandwich'' (Ru, Rh, Os) complexes with DNA bases (Dorcier et al., 2008). Moreover, the combination of ESI-MS with infrared spectroscopy monitored thermal and photochemical reactions of cyclopentadienyl compounds with molybdenum or tungsten (Thompson, Jones, & Baird, 2003), and the electrochemical reduction of the complex $[Cp_2Mo_2O_5]$ was studied with an on-line electrochemical flow cell followed by ESI-MS (Gun et al., 2003).

2. *Transition-Metal Organometallic Compounds That Contain a Covalent Carbon-Metal Bond*

The organometallics, including precious metals (Ag, Au, Ru, Rh, Pd, Os, Ir, Pt), represent this class of compounds, and their mass spectra can be found in the literature. ESI-MS is the dominant technique for their characterization. The suitability of ESI can be demonstrated with the example of low-resolution mass spectra of auracyclic complexes; their reaction products show a strong signal of $[M+H]^+$, $[M+Na]^+$, or $[M+NH_4]^+$ ions accompanied by their dimeric analogs which are usually resistent towards cone voltage-induced fragmentation (Dinger & Henderson, 1998a,b, 1999; Goss et al., 2003; Kilpin, Henderson, & Nicholson, 2007). Low-resolution ESI-MS was also used to analyze of rhombic dodecahedral silver-alkynyl cages $[Ag_{14}(C{=}C^tBu)_{12}X][BF_4]$ (X = Cl, Br, F), and to reveal that chloride and bromide complexes are very stable in solution contrary to fluoride analogs (Rais et al., 2002). Nevertheless, high-resolution ESI mass spectra offer the possibility of elemental composition determination—as illustrated with organopalladium (Evans et al., 2002) and organoplatinum compounds (Hartnell & Arnold, 2004). An appropriate mass analyzer can be useful to suggest a fragmentation mechanism as for ESI-FTICR-MS measurements of organopalladium ions with deuterium-labeling experiments (Qian et al., 2006). Concerning other ionization techniques, the solution aggregation of the dinuclear palladium(I) complex was observed in FAB mass spectra, and, together with ESI spectra, confirmed the stability of polynuclear aggregates (Macchioni et al., 2003). FAB-MS was further used for organoplatinum dendrimers (Leininger, Stang, & Huang, 1998); and σ-acetylide complexes of ruthenium- and osmium-containing alkynylsilane ligands (Wong, Wong, & Lu, 2003). MALDI ionization disclosed the presence of an oligomeric organometallic species that contained silver (Xu et al., 2000), palladium (Sicard et al., 2004), platinum (Siemsen et al., 2001), or rhodium (Hahn et al., 1999).

Some other transition-metal organometallic complexes were characterized with MS in addition to precious-metal complexes. An example is the HPLC/ESI-MS analysis of cobalamin or substituted derivatives performed either simultaneously with other water-soluble vitamins (Gentili et al., 2008) or independently (Alsberg et al., 2001). It was found that the intensity of the two most important ions $[M+H]^+$ and $[M+2H]^{2+}$ depends on the solvent composition.

3. *Heteropolymetallic Complexes*

Many heteropolymetallic compounds contain transition-metals. These complexes are often ionic or ionizable already in the solution, therefore ESI-MS is a valuable tool in their analysis, as illustrated on the following examples. The most abundant ion in the spectra of heterotrimetallic complexes $Ru(Cp)(dppf)SnX_3$ as well as their heterobimetallic precursors Ru(Cp)(dppf)X (dppf = diphenylphosphine ferrocene, X = Cl, Br) corresponds to the positively charged ion at *m/z* 721, $[Ru(Cp)(dppf)]^+$ (Paim et al., 2005). The formation of the characteristic isotopic

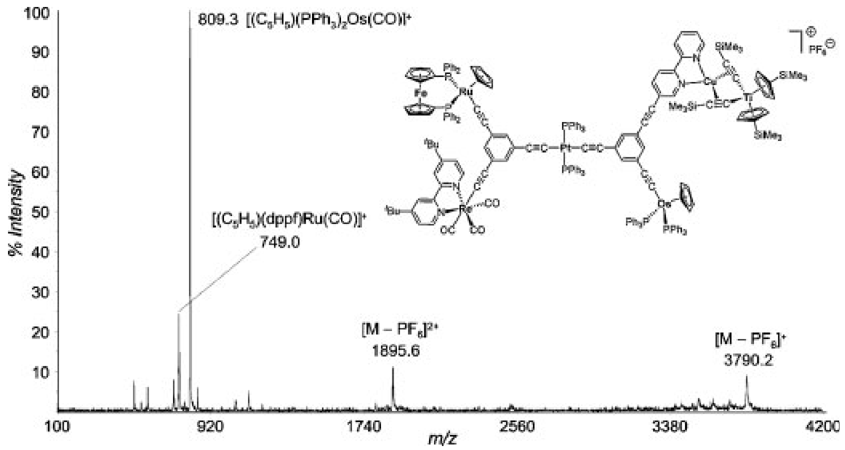

FIGURE 10. Full-scan positive-ion ESI mass spectrum of heteropentametallic complex shown in this figure (reproduced with permission from Packheiser et al., 2008b).

envelope from the superposition of all isotopes of particular metals plays an important role in the spectra interpretation. This fact is also evident for polymetallic carbene complexes (Martinez-Alvarez et al., 2004; Moret et al., 2005), nickel-centered clusters of nine germanium (Goicoechea & Sevov, 2006), or heteroatomic *closo*-clusters $[E_9Zn\text{-}Ph]^{3-}$ (E = Si, Ge, Sn, or Pb) (Goicoechea & Sevov, 2006). Furthermore, ESI-TOF MS of a unique series of heteromultinuclear transition-metal complexes with up to seven other different metal atoms (Ti, Fe, Ru, Os, Re, Pt, and Cu) and silicon was performed (Packheiser & Lang, 2007; Packheiser et al., 2008a,b), as illustrated in Figure 10. Ions that correspond to the loss of anionic part $[M - PF_6]^+$ were used for the molecular weight determination. These complexes that contain seven different metal atoms in their structures are probably the most complex organometallic species with reported ESI mass spectra in the literature.

IV. CONCLUSIONS

This review highlights the great potential of different mass spectrometric techniques in the structure characterization of complex organometallic compounds. The wide range of ionization techniques and mass analyzers have been developed and applied to organometallics. The most successful ionization technique in this field is electrospray ionization, which is applicable for organometallic compounds from medium polarity to ionic species that include non-covalent complexes and labile compounds. Conventional electron ionization might be a suitable alternative for certain types of organometallics with low polarity and good volatility. Although the use of other ionization techniques is less frequent that fact does not disqualify their use in particular applications. Typical ionization and fragmentation mechanisms are described for particular groups of organometallics with a discussion of some illustrative examples. Polyisotopic metal atoms offer an additional advantage for spectra interpretation, because their wide isotopic distributions can be theoretically calculated for individual ions and correlated with experimental results to confirm a proposed interpretation. Finally, the role of multistage tandem MS and accurate mass measurements performed with high-resolution mass analyzers is discussed.

V. NOMENCLATURE

An	anionic part
APCI	atmospheric pressure chemical ionization
APPI	atmospheric pressure photoionization
Bu	butyl
Bz	benzyl
Cat	cationic part
CI	chemical ionization
CID	collision-induced dissociation
Cp	cyklopentadienyl
EI	electron ionization
ESI	electrospray ionization
Et	ethyl
FAB	fast atom bombardment
FT-ICR	Fourier-transform ion cyclotron resonance
HPLC	high-performance liquid chromatography
HPLC/MS	high-performance liquid chromatography/mass spectrometry
L	ligand
MALDI	matrix-assisted laser desorption/ionization
Me	methyl
MS	mass spectrometry
MS/MS	tandem mass spectrometry
MS^n	multistage mass spectrometry
MW	molecular weight
Ph	phenyl
QqTOF	quadrupole–quadrupole-time-of-flight
R	alkyl or aryl
TOF	time-of-flight
X	halide or simple negatively charged ligands

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REFERENCES

Al-Juaid S, Gun'ko YK, Hitchcock PB, Lappert MF, Tian S. 1999. Organolanthanide chemistry with bis(trimethylsilyl)methyl- and tert-butyldimethylsilyl-substituted cyclopentadienyl ligands. Synthesis and characterisation of tris(cyclopentadienyl)lanthanide(III) complexes, including crystal structures of $[Ln\{\eta^5\text{-}C_5H_4CH(SiMe_3)_2\}_3]$ (Ln = Nd or Tm) and $[Ce\{\eta5\text{-}C_5H_3(SiMe_2Bu^t)_2\text{-}1,3\}_3]$. J Organomet Chem 582:143–152.

Allardyce CS, Dorcier A, Scolaro C, Dyson PJ. 2005. Development of organometallic (organo-transition metal) pharmaceuticals. Appl Organomet Chem 19:1–10.

Alley SR, Henderson W. 2001. Synthesis and characterisation of ferrocenyl-phosphonic and -arsonic acids. J Organomet Chem 637:216–229.

Alonso B, Astruc D, Blais JC, Nlate S, Rigaut S, Ruiz J, Sartor V, Valerio C. 2001. Metallodendrimers towards enzyme mimics and molecular electronics: New-generation catalysts, sensors and molecular batteries. CR Acad Sci Ser II C 4:173–180.

Alsberg T, Minten J, Haglund J, Tornqvist M. 2001. Determination of hydroxyalkyl derivatives of cobalamin (vitamin B_{12}) using reversed phase high performance liquid chromatography with electrospray tandem mass spectrometry and ultraviolet diode array detection. Rapid Commun Mass Sp 15:2438–2445.

Alvarez A, Macias R, Fabra MJ, Martin ML, Lahoz FJ, Oro LA. 2007. Square-planar Rhodium(I) complexes partnered with $[arachno\text{-}6\text{-}SB_9H_{12}]^-$: A route toward the synthesis of new rhodathiaboranes and organometallic/thiaborane salts. Inorg Chem 46:6811–6826.

Alvarez EJ, Vartanian VH, Brodbelt JS. 1997. Metal complexation reactions of quinolone antibiotics in a quadrupole ion trap. Anal Chem 69:1147–1155.

Ang WH, Daldini E, Scolaro C, Scopelliti R, Juillerat-Jeannerat L, Dyson PJ. 2006. Development of organometallic ruthenium-arene anticancer drugs that resist hydrolysis. Inorg Chem 45:9006–9013.

Aplin RT, Buston JEH, Moloney MG. 2002. Detection of aryllead(IV) carboxylates and their solvent adducts by ESI-mass spectrometry. J Organomet Chem 645:176–182.

Arevalo S, de Jesus E, de la Mata FJ, Flores JC, Gomez R. 2001. Synthesis of carbosilane dendrimers containing peripheral (cyclopentadienyl)(aryloxy)titanium(IV) units. Organometallics 20:2583–2592.

Arrais A, Boccaleri E, Sappa E, Secco A. 2006. Reactions of $Co_2(CO)_6$ (RCCR') (RC_2Rhydroxy- or alkoxysilyl-alkynes) with tetraethylorthosilicate. J Sol-Gel Sci Techn 38:283–292.

Asmis KR, Sauer J. 2007. Mass-selective vibrational spectroscopy of vanadium oxide cluster ions. Mass Spectrom Rev 26:542–562.

Bakhtiar R, Kaifer AE. 1998. Mass spectrometry studies on the complexation of several organometallic complexes by α- and β-cyclodextrins. Rapid Commun Mass Sp 12:111–114.

Baul TSB, Masharing C, Willem R, Biesemans M, Holčapek M, Jirásko R, Linden A. 2005a. Self-assembly of diorganotin(IV) 2-{[(E)-1-(2-oxyaryl)alkylidene]amino}acetates: An investigation of structures by X-ray diffraction, solution and solid-state tin NMR, and electrospray ionization mass spectrometry. J Organomet Chem 690:3080–3094.

Baul TSB, Singh KS, Holčapek M, Jirásko R, Linden A, Song XQ, Zapata A, Eng G. 2005b. Electrospray ionization mass spectrometry of tributyltin(IV) complexes and their larvicidal activity on mosquito larvae: Crystal and molecular structure of polymeric ($Bu_3Sn[O_2CC_6H_4$ {$N = N(C_6H_3$-4-OH ($C(H) = NC_6H_4OCH_3$-4))}-o])$_{(n)}$. Appl Organomet Chem 19:935–944.

Baul TSB, Singh KS, Holčapek M, Jirásko R, Rivarola E, Linden A. 2005c. Synthesis, characterization and crystal structures of polymeric and dimeric triphenyltin(IV) complexes of 4-[((E)-1-{2-hydroxy-5-[(E)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methyl idene)amino]aryls. J Organomet Chem 690:4232–4242.

Baul TSB, Masharing C, Basu S, Rivarola E, Holčapek M, Jirásko R, Lyčka A, de Vos D, Linden A. 2006a. Synthesis, characterization, cytotoxic activity and crystal structures of tri- and di-organotin(IV) complexes constructed from the beta-{[(E)-1-(2-hydroxyaryl)alkylidene]amino}-propionate and beta-{[(2Z)-(3-hydroxy-1-methyl-2-butenylidene)]-amino}propionate skeletons. J Organomet Chem 691:952–965.

Baul TSB, Mizar A, Lyčka A, Rivarola E, Jirásko R, Holčapek M, de Vos D, Englert U. 2006b. Diphenyltin(IV) complexes of the 5-[(E)-2-(aryl)-l-diazenyl]quinolin-8-olates: Synthesis and multinuclear NMR, Sn-119 Mossbauer, electrospray ionization MS, X-ray characterization and assessment of in vitro cytotoxicity. J Organomet Chem 691:3416–3425.

Baul TSB, Mizar A, Song XQ, Eng G, Jirásko R, Holčapek M, Willem R, Biesemans M, Verbruggen I, Butcher R. 2006c. Dibenzyltin(IV) complexes of 5-[(E)-2-(aryl)-1-diazenyl]quinolin-8-olates: Synthesis and an investigation of structures by X-ray diffraction, solution and solid-state tin NMR, Sn-119 Mossbauer and electrospray ionization MS. J Organomet Chem 691:2605–2613.

Baul TSB, Rynjah W, Rivarola E, Lyčka A, Holčapek M, Jirásko R, de Vos D, Butcher RJ, Linden A. 2006d. Synthesis and characterization of bis[dicarboxylatotetraorganodistannoxane] units involving 5-[(E)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acids: An investigation of structures by X-ray diffraction, NMR, electrospray ionisation MS and assessment of in vitro cytotoxicity. J Organomet Chem 691:4850–4862.

Baul TSB, Masharing C, Ruisi G, Jirásko R, Holčapek M, de Vos D, Wolstenholme D, Linden A. 2007a. Self-assembly of extended Schiff base amino acetate skeletons, 2-{[(2Z)-(3-hydroxy-1-methyl-2-butenylidene)]amino} phenylpropionate and 2-{[(E)-1-(2-hydroxyaryl)-alkylidene]amino} phenylpropionate skeletons incorporating organotin(IV) moieties: Synthesis, spectroscopic characterization crystal structures, and in vitro cytotoxic activity. J Organomet Chem 692:4849–4862.

Baul TSB, Rynjah W, Rivarola E, Pettinari C, Holčapek M, Jirásko R, Englert U, Linden A. 2007b. Di-n-octyltin(IV) complexes with 5-[(E)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acid: Syntheses and assessment of solid state structures by Sn-119 Mossbauer and X-ray diffraction and further insight into the solution structures using electrospray ionization MS, Sn-119 NMR and variable temperature NMR spectroscopy. J Organomet Chem 692:3625–3635.

Baul TSB, Mizar A, Chandra AK, Song XQ, Eng G, Jirásko R, Holčapek M, de Vos D, Linden A. 2008. Synthesis, crystal structures, cytotoxicity and qualitative structure-activity relationship (QSAR) of cis-bis{5-[(E)-2-(aryl)-1-diazenyl]quinolinolato} di-n-butyltin(IV) complexes, (Bu2Sn)-Bu-n(L)(2). J Inorg Biochem 102:1719–1730.

Beckmann J, Mahieu B, Nigge W, Schollmeyer D, Schurmann M, Jurkschat K. 1998. Reaction of $(^{t}Bu_2SnO)_3$ with organohalosilanes. Simple formation of open-chain and cyclic stannasiloxanes. Organometallics 17:5697–5712.

Beckmann J, Henn M, Jurkschat K, Schurmann M, Dakternieks D, Duthie A. 2002. Hydrolysis of bis((trimethylsilyl)methyl)tin dihalides. Crystallographic and Spectroscopic Study of the hydrolysis pathway. Organometallics 21:192–202.

Beckmann J, Dakternieks D, Duthie A, Lewcenko NA, Mitchell C, Schurmann M. 2005. The reactivity of bis(para-methoxyphenyl)telluroxide towards triflic acid and diphenylphosphinic acid. Theoretical considerations of the protonation and hydration process of diorganotelluroxanes. Z Anorg Allg Chem 631:1856–1862.

Bekri K, Saint-Louis R, Pelletier E. 2006. Determination of tributyltin and 4-hydroxybutyldibutyltin chlorides in seawater by liquid chromatography with atmospheric pressure chemical ionization-mass spectrometry. Anal Chim Acta 578:203–212.

Bhaskar G, Chary MA, Kumar MK, Syamasundar K, Vairamani M, Prabhakar S. 2005. Electrospray ionization studies of transition-metal complexes of 2-acetylbenzimidazolethiosemicarbazone using collision-induced dissociation and ion-molecule reactions. Rapid Commun Mass Sp 19:1536–1544.

Bouška M, Dostál L, Jirásko R, Růžička A, Jambor R. 2009. Synthesis of [{2,6-(Me2NCH2)(2)C6H3}Sn(OH)O](6): An N → Sn coordinated stannonic acid. Organometallics 28:4258–4261.

Brady FJ, Cardin DJ, Domin M. 1995. New organometallic complexes of buckminsterfullerene having π-bonded nickel, palladium, or platinum with triorganophosphite ligands, and their characterization. J Organomet Chem 491:169–172.

Brown MD, Levason W, Reid G, Webster M. 2006. Synthesis and properties of Rh(I) and Ir(I) distibine complexes with organometallic co-ligands. Dalton Trans 33:4039–4046.

Bruce MI, Thomas MA. 1968. Electron-impact studies of organometallic molecules. 8. Some transition metal derivatives of polyfluorobenzenes. Org Mass Spectrom 1:835.

Burgert R, Schnockel H. 2008. Monitoring the dissolution process of metals in the gas phase: Reactions of nanoscale Al and Ga metal atom clusters and their relationship to similar metalloid clusters. Chem Commun 18:2075–2089.

Canseco-Melchor G, Garcia-Montalvo V, Toscano RA, Cea-Olivares R. 2001. Synthesis and spectroscopic characterization of new mixed ligand organotellurium(IV) compounds employing dithiocarbamates and imidotetraphenyldithiodiphosphinates. Crystal structure of [C_4H_8Te (S_2CNEt_2){$(SPPh_2)_2N$}], [$C_4H_8Te(CNC_5H_{10})${$(SPPh_2)_2N$}] and [C_4H_8 $Te(S_2CNC_4H_8S)${$(SPPh_2)_2N$}]. J Organomet Chem 631:99–104.

Carraher CE, Lanz L. 2003. Synthesis and initial structural characterization of organotin polymers containing Norfloxacin (TM). J Polym Mater 20:91–99.

Carraher CE, Morie K. 2004. Synthesis of organotin polyesters containing ticarcillin. J Polym Mater 21:383–391.

Carraher CE, Battin A, Shahi KR, Roner MR. 2007. Synthesis, structural characterization, and initial evaluation as anticancer drugs of dibutyltin polyamines derived from various 4,6-diaminopyrimidines. J Inorg Organomet Polym 17:631–639.

Casas JS, Garcia-Tasende MS, Sordo J, Taboada C, Tubaro M, Traldi P, Vidarte MJ. 2004. Electrospray ionization mass spectrometry in the structural characterization of some diphenyllead(IV) thiosemicarbazonates. Rapid Commun Mass Sp 18:1856–1864.

Colton R, Dagostino A, Traeger JC. 1995. Electrospray mass spectrometry applied inorganic and organometallic chemistry. Mass Spectrom Rev 14:79–106.

Constantine SP, Cardin DJ, Bollen BG. 2000. Electron impact and chemical ionisation mass spectrometry in the characterisation of organometallic silicon, germanium, tin and lead compounds. Rapid Commun Mass Sp 14:329–334.

Crawford E, Dyson PJ, Forest O, Kwok S, McIndoe JS. 2006. Energy-dependent electrospray ionisation mass spectrometry of carbonyl clusters. J Clust Sci 17:47–63.

Di Marco VB, Bombi GG, Ranaldo M, Traldi P. 2007. Metal-ligand solution equilibria studied by electrospray ionization mass spectrometry: Correlation between ion intensity and acid-base equilibria in solution. Rapid Commun Mass Sp 21:3825–3832.

Diehl G, Karst U. 2002. Fast liquid chromatography-electrochemistry-mass spectrometry of ferrocenecarboxylic acid esters. J Chromatogr A 974:103–109.

Ding W, Johnson KA, Kutal C, Amster IJ. 2003. Mechanistic studies of photochemical reactions with millisecond time resolution by electrospray ionization mass spectrometry. Anal Chem 75:4624–4630.

Dinger MB, Henderson W. 1998a. Organogold(III) metallacyclic chemistry. Part 4. Synthesis, characterisation, and biological activity of gold(III)-thiosalicylate and -salicylate complexes. J Organomet Chem 560:233–243.

Dinger MB, Henderson W. 1998b. Organogold(III) metallacyclic chemistry. Part 2. Synthesis and characterisation of the first gold(III) ureylene complexes. Crystal structures of $[\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}\text{-}Au\{RNC(O)NR\}]$ (R = Ph and C(O)Me). J Organomet Chem 557: 231–241.

Dinger MB, Henderson W, Nicholson BK, Robinson WT. 1998. Organogold(III) metallacyclic chemistry. Part 3. Self-assembly of the nonametallic gold(III)-silver(I)-sulfido aggregates $[\{LAu(\mu\text{-}S)_2AuL\}_3 Ag_3X_2]^+$ (L = cycloaurated N,N-dimethylbenzylamine ligand; X = Cl, Br), by thiourea desulfurisation. J Organomet Chem 560:169–181.

Dinger MB, Henderson W. 1999. Synthesis and characterisation of the first auracyclobutane complex. J Organomet Chem 577:219–222.

Dorcier A, Dyson PJ, McIndoe JS. 2003. Analysis of coordination and organometallic compounds using photoionisation mass spectrometric techniques. Eur J Inorg Chem 24:4294–4297.

Dorcier A, Dyson PJ, Gossens C, Rothlisberger U, Scopelliti R, Tavernelli I. 2005. Binding of organometallic ruthenium(II) and osmium(II) complexes to an oligonucleotide: A Combined Mass Spectrometric and Theoretical Study. Organometallics 24:2114–2123.

Dorcier A, Hartinger CG, Scopelliti R, Fish RH, Keppler BK, Dyson PJ. 2008. Studies on the reactivity of organometallic Ru-, Rh- and Os-pta complexes with DNA model compounds. J Inorg Biochem 102:1066–1076.

Dostál L, Císařová I, Jambor R, Růžička A, Jirásko R, Holeček J. 2006a. Structural diversity of organoantimony(III) and organobismuth(III) dihalides containing O,C,O-chelating ligands. Organometallics 25: 4366–4373.

Dostál L, Jambor R, Růžička A, Jirásko R, Císařová I, Holeček J. 2006b. Reactivity of intramolecularly coordinated aluminum compounds to R_3EOH (E = Sn, Si). Remarkable migration of N,C,N and O,C,O pincer ligands. J Organomet Chem 691:35–44.

Dostál L, Jambor R, Císařová I, Beneš L, Růžička A, Jirásko R, Holeček J. 2007a. Unexpected product formed by the reaction of $[2,6\text{-}(MeOCH_2)_2\text{-}C_6H_3]Li$ with $SbCl_3$: Structure of Sb-O intramolecularly coordinated organoantimony cation. J Organomet Chem 692:2350–2353.

Dostál L, Jambor R, Růžička A, Jirásko R, Taraba J, Holeček J. 2007b. Intramolecularly coordinated organotin(IV) sulphides and their reactivity to iodine. J Organomet Chem 692:3750–3757.

Dostál L, Novák P, Jambor R, Růžička A, Císařová I, Jirásko R, Holeček J. 2007c. Synthesis and Structural Study of organoantimony(III) and organobismuth(III) triflates and cations containing O,C,O-pincer type ligands. Organometallics 26:2911–2917.

Dostál L, Jambor R, Růžička A, Jirásko R, Císařová I, Holeček J. 2008. The synthesis of organoantimony(III) difluorides containing Y,C,Y pincer type ligands using organotin(IV) fluorinating agents. J Fluorine Chem 129:167–172.

Dostál L, Jambor R, Růžička A, Erben M, Jirásko R, Černošková E, Holeček J. 2009a. Efficient and reversible fixation of carbon dioxide by NCN-chelated organoantimony(III) oxide. Organometallics 28:2633–2636.

Dostál L, Jambor R, Růžička A, Jirásko R, Lochař V, Beneš L, de Proft F. 2009b. Nonconventional behavior of NCN-chelated organoantimony(III) sulfide and isolation of cyclic organoantimony(III) bis(pentasulfide). Inorg Chem 48:10495–10497.

Dyson PJ, Johnson BFG, McIndoe JS, Langridge-Smith PRR. 2000. Applications of laser desorption and electrospray ionization mass spectrometry at the transition between clusters and colloids. Inorg Chem 39:2430–2431.

Ebdon L, Hill SJ, Rivas C. 1998. Organotin compounds in solid waste: a review of their properties and determination using high-performance liquid chromatogramy. Trac-Trends Anal Chem 17:277–288.

Efraty A, Huang MHA, Weston CA. 1975. Mass-spectra of organometallic compounds 5. Electron-Impact Study of cyclopentadienylmanganese thiocarbonyl and carbonyl-complexes $RC_5H_4Mn(Co)_2CX$ [R = H, Ch3 − X = S, O]. Inorg Chem 14:2796–2799.

Evans DR, Huang MS, Seganish WM, Fettinger JC, Williams TL. 2002. Synthesis, structures, and solution behavior of bis(sulfoxide)-pincer complexes of palladium(II). Organometallics 21:893–900.

Ferrer M, Mounir M, Rodriguez L, Rossell O, Coco S, Gomez-Sal P, Martin A. 2005. Effect of the organic fragment on the mesogenic properties of a series of organogold(I) isocyanide complexes. X-ray crystal structure of $[Au(C$ equivalent to $CC_5H_4N)(CNC_6H_4O(O)CC_6H_4OC_{10}H_{21})]$. J Organomet Chem 690:2200–2208.

Ferri A, Polzonetti G, Licoccia S, Paolesse R, Favretto D, Traldi P, Russo MV. 1998. Ethynyl porphyrins bridging bis(phosphine)platinum(II) centers: Molecular models for conjugated organometallic porphyrin polymers. J Chem Soc Dalton 23:4063–4069.

Florencio MH, Duarte MF, deBettencourt AMM, Gomes ML, Boas LFV. 1997. Electrospray mass spectra of arsenic compounds. Rapid Commun Mass Sp 11:469–473.

Forgacs E, Cserhati T. 2002. Liquid chromatography of organometallic compounds. J Liq Chromatogr R T 25:2023–2038.

Fournier F, Afonso C, Menand M, Hamon L, Xie J, Tabet JC. 2008. Investigation by mass spectrometry of metal complexes of new molecular hosts: Cyclic oligomer of sugar amino acid and sugar-aza-crown ethers. Eur J Mass Spectrom 14:61–69.

Fridrichová A, Svoboda T, Jambor R, Padělková Z, Růžička A, Erben M, Jirásko R, Dostál L. 2009. Synthesis and structural study on organoantimony(III) and organobismuth(III) hydroxides containing an NCN pincer type ligand. Organometallics 28:5522–5528.

Garnovskii AD, Vasilchenko IS, Garnovskii DA. 2003. Fundamental concepts of coordination chemistry. In: Garnovskii AD, Kharisov BI, editors. Synthetic coordination and organometallic chemistry. New York: Marcel Dekker. pp. 1–22.

Gatlin CL, Tureček F. 1997. Electrospray ionization of inorganic and organometallic complexes. In: Cole RB, editor. Electrospray ionization mass spectrometry, fundamentals, techniques, applications; Chapter 15. New York: Wiley-Interscience. pp. 527–570.

Gentili A, Caretti F, D'Ascenzo G, Marchese S, Perret D, Di Corcia D, Rocca LM. 2008. Simultaneous determination of water-soluble vitamins in selected food matrices by liquid chromatography/electrospray ionization tandem mass spectrometry. Rapid Commun Mass Sp 22:2029–2043.

Gielen M, Jurkschat K. 1983. Organometallic compounds 80. Electron-impact fragmentation of selected organotriphenyltin compounds. Org Mass Spectrom 18:224–225.

Gielen M. 2002. Organotin compounds and their therapeutic potential: A report from the organometallic chemistry department of the free university of Brussels. Appl Organomet Chem 16:481–494.

Goicoechea JM, Sevov SC. 2006a. Organozinc derivatives of deltahedral zintl ions: Synthesis and characterization of closo-$[E_9Zn(C_6H_5)]^{3-}$ (E = Si, Ge, Sn, Pb). Organometallics 25:4530–4536.

Goicoechea JM, Sevov SC. 2006b. Deltahedral germanium clusters: Insertion of transition-metal atoms and addition of organometallic fragments. J Am Chem Soc 128:4155–4161.

Gomez-Ariza JL, Morales E, Giraldez I, Sanchez-Rodas D, Velasco A. 2001. Sample treatment in chromatography-based speciation of organometallic pollutants. J Chromatogr A 938:211–224.

Gonzalez-Toledo E, Compano R, Granados M, Prat MD. 2003. Detection techniques in speciation analysis of organotin compounds by liquid chromatography. Trac-Trend Anal Chem 22:26–33.

Goraczko AJ, Szymura JA. 1999. The prediction of relative abundance of isotopic clusters in mass spectrometry of coordination and organometallic compounds. Comput Chem 23:135–142.

Goss CHA, Henderson W, Wilkins AL, Evans C. 2003. Synthesis, characterisation and biological activity of gold(III) catecholate and related complexes. J Organomet Chem 679:194–201.

Gun J, Modestov A, Lev O, Saurenz D, Vorotyntsev MA, Poli R. 2003. Studies on the reduction of $[(C_5Me_5)_2Mo_2O_5]$ in methanol/water/acetate solutions by on-line electrochemical flowcell and electrospray mass spectrometry. Eur J Inorg Chem 3:482–492.

Guo H, Qian R, Liao YX, Ma SM, Guo YL. 2005. ESI-MS studies on the mechanism of Pd(0)-catalyzed three-component tandem double addition-cyclization reaction. J Am Chem Soc 127:13060–13064.

Hahn C, Spiegler M, Herdtweck E, Taube R. 1999. Complex catalysis 55—Oxidative addition reactions of organorhodium(I) complexes containing the tridentate ligand 2,6-bis(diphenylphosphanylmethyl)pyridine [Rh(PNP)R] ($R = CH_3$, C_6H_5) with iodine and methyl iodide and investigation of the reductive elimination. Eur J Inorg Chem 3:435–440.

Halpern J. 2001. Organometallic chemistry at the threshold of a new millennium. Retrospect and prospect. Pure Appl Chem 73:209–220.

Harrington CF, Eigendorf GK, Cullen WR. 1996. The use of high-performance liquid chromatography for the speciation of organotin compounds. Appl Organomet Chem 10:339–362.

Hartnell RD, Arnold DP. 2004. Peripherally η^1-platinated organometallic porphyrins as building blocks for multiporphyrin arrays. Organometallics 23:391–399.

Henderson W, Taylor MJ. 1996. Organotin halides and their hydrolysed species studied in solution by positive and negative ion electrospray mass spectrometry. Polyhedron 15:1957–1964.

Henderson W, McIndoe JS, Nicholson BK, Dyson PJ. 1998a. Electrospray mass spectrometry of metal carbonyl complexes. J Chem Soc Dalton 4:519–525.

Henderson W, Nicholson BK, McCaffrey LJ. 1998b. Applications of electrospray mass spectrometry in organometallic chemistry. Polyhedron 17:4291–4313.

Henderson W, Evans C. 1999. Electrospray mass spectrometric analysis of transition-metal halide complexes. Inorg Chim Acta 294:183–192.

Henderson W, Alley SR. 2002. Ferrocenyl hydroxymethylphosphines $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4P(CH_2OH)_2]$ and 1,1'-$[Fe\{\eta^5\text{-}C_5H_4P(CH_2OH)_2\}_2]$ and their chalcogenide derivatives. J Organomet Chem 658:181–190.

Henderson W, McIndoe JS. 2005. Mass spectrometry of inorganic and organometallic compounds. Chichester: Wiley.

Hocek M. 2003. Syntheses of purines bearing carbon substituents in positions 2, 6 or 8 by metal- or organometal-mediated C-C bond-forming reactions. Eur J Org Chem 2:245–254.

Holčapek M, Kolářova L, Růžička A, Jambor R, Jandera P. 2006. Structural analysis of ionic organotin(IV) compounds using electrospray tandem mass spectrometry. Anal Chem 78:4210–4218.

Hunt DF, Torian RL, Russell JW. 1972. Chemical ionization mass-spectrometry studies. 5. Some transition-metal organometallic compounds. J Organomet Chem 43:175.

Chalupa J, Handlíř K, Císařová I, Jirásko R, Brus J, Lyčka A, Růžička A, Holeček J. 2006. Structural study of bis(triorganotin(IV)) esters of 4-ketopimelic acid. J Organomet Chem 691:2631–2640.

Chalupa J, Hanlíř K, Paděková Z, Vejsová M, Buchta V, Jirásko R, Růžička A. 2008. C,N-chelated triorganotin(IV) diesters of 4-ketopimelic acid and their fungicidal activity. Appl Organomet Chem 22:308–313.

Chauhan AKS, Kumar A, Srivastava RC, Butcher RJ. 2002. Synthesis and characterization of monomeric diorganotellurium dihalides: Crystal and molecular structures of diphenacyltellurium dibromide and -diiodide. J Organomet Chem 658:169–175.

Chen P. 2003. Electrospray ionization tandem mass spectrometry in high-throughput screening of homogeneous catalysts. Ange Chem Int Edit 42:2832–2847.

Chevrin C, Le Bras J, Roglans A, Harakat D, Muzart J. 2007. Substitution of allylic acetates with sodium para-toluenesulfinate in aqueous media using allylpalladium chloride dimer and a water-soluble ligand as the catalytic system; electrospray ionisation mass spectrometry analysis. New J Chem 31:121–126.

Chisholm DM, McIndoe JS, Bodizs G, Ang WH, Scopelliti R, Dyson PJ. 2007. Investigation into the formation of heteronuclear clusters of formula $[\{Ru_6C(CO)_{16}Ag_2X\}_2]^{2-}$ ($X = Cl$, Br or I). J Clust Sci 18:303–318.

Chovancová M, Jambor R, Růžička A, Jirásko R, Císařová I, Dostál L. 2009. Synthesis, structure, and reactivity of intramolecularly coordinated organoantimony and organobismuth sulfides. Organometallics 28: 1934–1941.

Jain R, Lalancette RA, Sheridan JB. 2005. Poly{ferrocene(phenylene)bis(silylenevinyleine)}s via platinum- and rhodium-catalyzed hydrosilylation of diethynylbenzenes with 1,1 '-bis(dimethylsilyl)ferrocene. Organometallics 24:1458–1467.

Jang WD. 2005. Synthesis of dendrimer based polymeric and macrocyclic complexes with a platinum-acetylide π-conjugated organometallic core. Macromol Res 13:334–338.

Jaouen G, Beck W, McGlinchey MJ. 2006. A novel field of research: Bioorganometallic chemistry, origins, and founding principles. In: Jaouen G, editor. Bioorganometallics: Biomolecules, labelling, medicine. Weinheim: Wiley-VCH. pp. 1–38.

Jiang CH, Hor TSA, Yan YK, Henderson W, McCaffrey LJ. 2000. Fragmentation pathways of $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ ($R = H$, Me) and ligand exchange reactions with oxygen donor ligands, investigated by electrospray mass spectrometry. J Chem Soc Dalton 18:3197–3203.

Jimenez MV, Perez-Torrente JJ, Bartolome MI, Gierz V, Lahoz FJ, Oro LA. 2008. Rhodium(I) complexes with hemilabile N-heterocyclic carbenes: Efficient alkyne hydrosilylation catalysts. Organometallics 27:224–234.

Jirásko R, Holčapek M, Kolářová L, Baul TSB. 2007. Electrospray ionization-multistage tandem mass spectrometry of complex multitin organometallic compounds. J Mass Spectrom 42:918–928.

Jirásko R, Holčapek M, Kolářova L, Nádvorník M, Popkov A. 2008. Characterization of Ni(II) complexes of Schiff bases of amino acids and (S)-N-(2-benzoylphenyl)-1-benzylpyrrolidine-2-carboxamide using ion trap and QqTOF electrospray ionization tandem mass spectrometry. J Mass Spectrom 43:1274–1284.

Jirásko R, Holčapek M, Rosenberg E. 2009. Characterization of bis-carboxyethyl germanium sesquioxide and its complexes with amino acids using electrospray QqTOF mass spectrometry. Int J Mass Spectrom 280:198–203.

Jitaru P, Infante HG, Adams FC. 2004. Simultaneous multi-elemental speciation analysis of organometallic compounds by solid-phase microextraction and multicapillary gas chromatography hyphenated to inductively coupled plasma-time-of-flight-mass spectrometry. J Anal Atom Spectrom 19:867–875.

Jones-Lepp TL, Varner KE, McDaniel M, Riddick L. 1999. Determination of organotins in water by micro liquid chromatography-electrospray/ion trap mass spectrometry. Appl Organomet Chem 13:881–889.

Jones-Lepp TL, Varner KE, Hilton BA. 2001. Speciation and detection of organotins from PVC pipe by micro-liquid chromatography-electrospray-ion trap mass spectrometry. Appl Organomet Chem 15:933–938.

Jones-Lepp TL, Momplaisir GM. 2005. New applications of LC-MS and LC-MS^2 toward understanding the environmental fate of organometallics. Trac-Trend Anal Chem 24:590–595.

Kandasamy K, Kumar S, Singh HB, Wolmershauser G. 2003. Influence of both steric effects and Te center dot center dot center dot N intramolecular nonbonded interactions on the stabilization of organotellurium compounds incorporating [2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole]. Organometallics 22:5069–5078.

KaneMaguire LAP, Kanitz R, Sheil MM. 1996. Electrospray mass spectrometry of neutral π-hydrocarbon organometallic complexes. Inorg Chim Acta 245:209–214.

Kaplan BJ, Parish WW, Andrus GM, Simpson JSA, Field CJ. 2004. Germane facts about germanium sesquioxide: I. Chemistry and anticancer properties. J Altern Complement Med 10:337–344.

Kappaun S, Rentenberger S, Pogantsch A, Zojer E, Mereiter K, Trimmel G, Saf R, Moller KC, Stelzer F, Slugovc C. 2006. Organoboron quinolinolates with extended conjugated chromophores: Synthesis, structure, and electronic and electroluminescent properties. Chem Mater 18:3539–3547.

Kašná B, Dostál L, Jirásko R, Císařová I, Jambor R. 2008. Role of Y,C,Y-chelating ligands in control hydrolysis of diorganotin compounds. Organometallics 27:3743–3747.

Kilpin KJ, Henderson W, Nicholson BK. 2007. Organogold(III) complexes containing chelating bis(amidate) ligands: Synthesis, characterisation and biological activity. Polyhedron 26:434–447.

Kizlink J. 1996. Stabilization of poly(vinyl chloride) with organotin compounds. Chem Listy 90:147–154.

Kohler FH, Schell A, Weber B. 2002. Polymer rings and chains consisting of doubly silyl-bridged metallocenes. Chem Eur J 8:5219–5227.

Kolářová L, Holčapek M, Jambor R, Dostál L, Nádvorník M, Růžička A. 2004. Structural analysis of 2,6-[bis(alkyloxy)methyl]phenyltin derivatives using electrospray ionization mass spectrometry. J Mass Spectrom 39:621–629.

Kriesel JW, Konig S, Freitas MA, Marshall AG, Leary JA, Tilley TD. 1998. Synthesis of highly charged organometallic dendrimers and their characterization by electrospray mass spectrometry and single-crystal X-ray diffraction. J Am Chem Soc 120:12207–12215.

Lamb JH, Sweetman GMA. 1996. Structural identification of an organogermanium compound by electrospray tandem mass spectrometry. Rapid Commun Mass Sp 10:594–595.

Larsen BR, Astorga-Llorens C, Florencio MH, Bettencourt AM. 2001. Fragmentation pathways of organoarsenical compounds by electrospray ion trap multiple mass spectrometry (MS^6). J Chromatogr A 926:167–174.

Lash TD, Colby DA, Szczepura LF. 2004. New riches in carbaporphyrin chemistry: Silver and gold organometallic complexes of benzocarbaporphyrins. Inorg Chem 43:5258–5267.

Lawson G, Dahm RH, Ostah N, Woodland ED. 1996. Electrospray mass spectrometry: An alternative method for the identification of organotin compounds. Appl Organomet Chem 10:125–133.

Leininger S, Stang PJ, Huang SP. 1998. Synthesis and characterization of organoplatinum dendrimers with 1,3,5-triethynylbenzene building blocks. Organometallics 17:3981–3987.

Lemr K, Holčapek M, Jandera P. 2000. Oxygen attachment to metal complex ions during their collision induced dissociation in ion trap. Rapid Commun Mass Sp 14:1878–1879.

Lintschinger J, Schramel O, Kettrup A. 1998. The analysis of antimony species by using ESI-MS and HPLC-ICP-MS. Fresen J Anal Chem 361:96–102.

Lipshutz BH, Keith J, Buzard DJ. 1999. An electrospray ionization mass spectrometry study of the aggregation states of organocopper complexes in solution. Organometallics 18:1571–1574.

MacAleese L, Maitre P. 2007. Infrared spectroscopy of organometallic ions in the gas phase: From model to real world complexes. Mass Spectrom Rev 26:583–605.

Macchioni A, Romani A, Zuccaccia C, Guglielmetti G, Querci C. 2003. Experimental evidence for the aggregation of $[(Phen)_2Pd_2(\mu\text{-}H)(\mu\text{-}CO)]^+$ in solution. Organometallics 22:1526–1533.

Machuča L, Dostál L, Jambor R, Handlíř K, Jirásko R, Růžicka A, Císařová I, Holeček J. 2007. Intramolecularly coordinated organoantimony(III) carboxylates. J Organomet Chem 692:3969–3975.

Majoumo-Mbe F, Smolensky E, Lonnecke P, Shpasser D, Eisen MS, Hey-Hawkins E. 2005. Polymerisations of epsilon-caprolactone and beta-butyrolactone with Zn-, Al- and Mg-based organometallic complexes. J Mol Catal A Chem 240:91–98.

Manzur C, Millan L, Figueroa W, Boys D, Hamon JR, Carrillo D. 2003. Organo-iron benzaldehyde-hydrazone complexes. Synthesis, characterization, electrochemical, and structural studies. Organometallics 22:153–161.

Martinez-Alvarez R, Gomez-Gallego M, Fernandez I, Mancheno MJ, Sierra MA. 2004. ESI mass spectrometry as a tool for the study of electron transfer in nonconventional media: The case of bi- and polymetallic carbene complexes. Organometallics 23:4647–4654.

Mastrorilli P, Nobile CF, Suranna GP, Fanizzi FP, Ciccarella G, Englert U, Li Q. 2004. Synthesis and carbonylation of platinum(II) organometallic complexes with bis(phosphanyl) monosulfides—Crystal structures of $[\kappa P^2,S\text{-}\{Ph_2CH_2P(S)Ph_2\}Pt(CH_3)(Cl)]$ and $[\kappa P,\mu\text{-}\kappa\ S\text{-}\{Ph_2CH_2CH_2P(S)Ph_2\}Pt(CH_3)]_2[BF_4]_2$. Eur J Inorg Chem 6:1234–1242.

Mattsson J, Govindaswamy P, Furrer J, Sei Y, Yamaguchi K, Suess-Fink G, Therrien B. 2008. Encapsulation of aromatic molecules in hexanuclear arene ruthenium cages: A strategy to build up organometallic carceplex prisms with a dangling arm standing out. Organometallics 27:4346–4356.

Mehrotra RC, Singh A. 2004. Organometallic chemistry: A unified approach. New Delhi: New Age International.

Mester Z, Pawliszyn J. 1999. Electrospray mass spectrometry of trimethyllead and triethyllead with in-tube solid phase microextraction sample introduction. Rapid Commun Mass Sp 13:1999–2003.

Meurer EC, Santos LS, Pilli RA, Eberlin MN. 2003. Probing the mechanism of the petasis olefination reaction by atmospheric pressure chemical ionization mass and tandem mass spectrometry. Org Lett 5:1391–1394.

Meurer EC, da Rocha LL, Pilli RA, Eberlin MN, Santos LS. 2006. Transient intermediates of the Tebbe reagent intercepted and characterized by atmospheric pressure chemical ionization mass spectrometry. Rapid Commun Mass Sp 20:2626–2629.

Mlýnek PD, Dahl LF. 1997. New noncentered icosahedral nickel-bismuth carbonyl clusters: Geometric analysis of the homologous $[Ni_{10}(EMe)_2(CO)_{18}]^{2-}$ dianions ($E = P$, As, Sb, Bi) containing noncentered 1,12-$Ni_{10}E_2$ icosahedral cages. Organometallics 16:1655–1667.

Mo O, Yanez M, Salpin JY, Tortajada J. 2007. Thermochemistry, bonding, and reactivity of Ni^+ and Ni^{2+} in the gas phase. Mass Spectrom Rev 26:474–516.

Moreno-Manas M, Pleixats R, Spengler J, Chevrin C, Estrine B, Bouquillon S, Henin F, Muzart J, Pla-Quintana A, Roglans A. 2003. 15-Membered triolefinic macrocycles—Catalytic role of (E,E,E)-1,6,11-tris(arenesulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-tr iene complexes of palladium(0) in the presence of phosphanes. Eur J Org Chem 2:274–283.

Moret ME, Chaplin AB, Lawrence AK, Scopelliti R, Dyson PJ. 2005. Synthesis and characterization of organometallic ionic liquids and a heterometallic carbene complex containing the chromium tricarbonyl fragment. Organometallics 24:4039–4048.

Murao N, Ishiga M, Sekiguchi N, Takahashi T, Aso Y. 2005. Ferrocene-based Diels-Alder derivatization for the determination of 1α-hydroxyvitamin D_3 in rat plasma by high-performance liquid chromatography-electrospray tandem mass spectrometry. Anal Biochem 346:158–166.

Netherton MR, Fu GC. 2004. Nickel-catalyzed cross-couplings of unactivated alkyl halides and pseudohalides with organometallic compounds. Adv Synth Catal 346:1525–1532.

Nicholson BK, Whitley SK. 2004. Characterisation of the first authenticated organomercury hydroxide, $4\text{-}Me_2NC_6H_4HgOH$. J Organomet Chem 689:515–521.

Norman NC. 1997. Chemistry of arsenic, antimony, and bismuth. New York, USA: Springer.

Noyori R. 2002. Asymmetric catalysis: Science and opportunities (Nobel lecture). Ange Chem Int Edit 41:2008–2022.

Ogo S, Makihara N, Watanabe Y. 1999. pH-dependent transfer hydrogenation of water-soluble carbonyl compounds with $[Cp^*Ir\text{-}III(H_2O)_3]^{2+}$

($Cp^* = \eta5\text{-}C^5Me^5$) as a catalyst precursor and HCOONa as a hydrogen donor in water. Organometallics 18:5470–5474.

Osei-Twum EY, Litorja LA, Darkwa J, Maisela LL, Lesimple A, Mamer O. 2005. Mass spectral behavior of some homoleptic and mixed aryldichalcogenide bis(diphenylphosphino)ferrocenenickel(II), palladium(II), and platinum(II), and bis(diisopropylphosphino)ferrocene-palladium(II) complexes. J Am Soc Mass Spectrom 16:94–99.

Osinsky S, Levitin I, Bubnovskaya L, Sigan A, Ganusevich I, Kovelskaya A, Valkovskaya N, Campanella L, Wardman P. 2004. Selectivity of effects of redox-active cobalt(III) complexes on tumor tissue. Exp Oncol 26:140–144.

Ozkar S, Finke RG. 2004. The hydrogenphosphate complex of (1,5-cyclooctadiene)iridium(I), $\{[Bu_4N][(1,5\text{-COD})Ir \text{ center dot } HPO_4]\}_n$: Synthesis, spectroscopic characterization, and ES-MS of a new, preferred precursor to HPO_4^{2-} and Bu_4N^+ stabilized $Ir(0)_n$ nanoclusters. J Organomet Chem 689:493–501.

Packheiser R, Lang H. 2007. The first heterohexametallic transition-metal complex. Eur J Inorg Chem 24:3786–3788.

Packheiser R, Ecorchard P, Rueffer T, Lang H. 2008a. Mixed-transition-metal acetylides: Synthesis and characterization of complexes with up to six different transition metals connected by carbon-rich bridging units. Chem Eur J 14:4948–4960.

Packheiser R, Ecorchard P, Ruffer T, Lang H. 2008b. Heteromultimetallic transition metal complexes based on unsymmetrical platinum(II) bis-acetylides. Organometallics 27:3534–3546.

Paim LA, Augusti DV, Dalmazio I, Alves TMA, Augusti R, Siebald HGL. 2005. Electrospray ionization and tandem mass spectrometry characterization of novel heterotrimetallic $Ru(\eta^5\text{-}C_5H_5)(dppf)SnX_3$ complexes and their heterobimetallic $Ru(\eta^5\text{-}C_5H_5)(dppf)X$ precursors. Polyhedron 24:1153–1159.

Palačková H, Vinklárek J, Holubová J, Císařová I, Erben M. 2007. The interaction of antitumor active vanadocene dichloride with sulfur-containing amino acids. J Organomet Chem 692:3758–3764.

Pedersen SN, Francesconi KA. 2000. Liquid chromatography electrospray mass spectrometry with variable fragmentor voltages gives simultaneous elemental and molecular detection of arsenic compounds. Rapid Commun Mass Sp 14:641–645.

Pelagatti P, Carcelli M, Calbiani F, Cassi C, Elviri L, Pelizzi C, Rizzotti U, Rogolino D. 2005. Transfer hydrogenation of acetophenone catalyzed by half-sandwich ruthenium(II) complexes containing amino amide ligands. Detection of the catalytic intermediates by electrospray ionization mass spectrometry. Organometallics 24:5836–5844.

Pham K, Henderson W, Nicholson BK, Hor TSA. 2007. Tuning the sulfur-heterometal interaction in organolead(IV) complexes of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$. J Organomet Chem 692:4933–4942.

Pla-Quintana AP, Roglans A. 2005. ESI-mass spectrometry as a tool for investigating the mechanistic role of a 15-membered triolefinic macrocyclic palladium(0) complex in the Heck reaction. Arkivoc 51–62.

Plattner DA. 2001. Electrospray mass spectrometry beyond analytical chemistry: Studies of organometallic catalysis in the gas phase. Int J Mass Spectrom 207:125–144.

Polfer NC, Oomens J. 2009. Vibrational spectroscopy of bare and solvated ionic complexes of biological relevance. Mass Spectrom Rev 28:468–494.

Prange A, Jantzen E. 1995. Determination of organometallic species by gas-chromatography inductively-coupled plasma-mass spectrometry. J Anal Atom Spectrom 10:105–109.

Pruchnik FP. 1990. Organometallic chemistry of the transition elements. New York: Springer.

Qian R, Liao YX, Guo YL, Guo H. 2006. ESI-FTICR-MS studies on gas phase fragmentation reactions of $ArPd(PPh_3)_2I$ complexes. J Am Soc Mass Spectrom 17:1582–1589.

Quirke JME, Van Berkel GJ. 2001. Electrospray tandem mass spectrometric study of ferrocene carbamate ester derivatives of saturated primary, secondary and tertiary alcohols. J Mass Spectrom 36:179–187.

Rais D, Mingos DMP, Vilar R, White AJP, Williams DJ. 2002. Directing role of anions in the syntheses of the silver-alkynyl cages $[Ag_{14}(C = (CBu)\text{-}Bu^t)_{12}X][BF_4]$ (X = FCl, Br) and silver-alkynyl polymers $[Ag_3(C = (CBu)\text{-}Bu^t)_2(X)]_n$ (X = Tos, NO_3). J Organomet Chem 652:87–93.

Rao MLN, Shimada S, Yamazaki O, Tanaka M. 2002. Cross-coupling reaction of organobismuth dialkoxides with aryl bromides and iodides catalyzed by $Pd(PPh_3)_4$. J Organomet Chem 659:117–120.

Rosenberg E. 2003. The potential of organic (electrospray- and atmospheric pressure chemical ionisation) mass spectrometric techniques coupled to liquid-phase separation for speciation analysis. J Chromatogr A 1000:841–889.

Royo E, Brintzinger HH. 2002. Mass spectrometry of polystyrene and polypropene ruthenium complexes. A new tool for polymer characterization. J Organomet Chem 663:213–220.

Ruiz J, Alonso E, Blais JC, Astruc D. 1999. Hydrosilylation of an hexa-olefin star with organometallic hydrogenosilanes: Ferrocenylsilylation and desilylenation. J Organomet Chem 582:139–141.

Salmain M, Caro B, Le Guen-Robin F, Blais JC, Jaouen G. 2004. Solution- and crystal-phase covalent modification of lysozyme by a purpose-designed organoruthenium complex. A MALDI-TOF MS study of its metal binding sites. Chembiochem 5:99–109.

SanchezDelgado RA, Navarro M, Perez H, Urbina JA. 1996. Toward a novel metal-based chemotherapy against tropical diseases .2. Synthesis and antimalarial activity in vitro and in vivo of new ruthienium- and rhodium-chloroquine complexes. J Med Chem 39:1095–1099.

Santos LS. 2008. Online mechanistic investigations of catalyzed reactions by electrospray ionization mass spectrometry: A tool to intercept transient species in solution. Eur J Org Chem 2:235–253.

Savage D, Neary N, Malone G, Alley SR, Gallagher JF, Kenny PTM. 2005. The synthesis and structural characterization of novel N-meta-ferrocenyl benzoyl amino acid esters. Inorg Chem Commun 8:429–432.

Savage D, Alley SR, Goel A, Hogan T, Ida Y, Kelly PN, Lehmann L, Kenny PTM. 2006. Synthesis and characterization of novel N-para-ferrocenyl benzoyl dipeptide esters. Inorg Chem Commun 9:1267–1270.

Seiwert B, Karst U. 2007. Simultaneous LC/MS/MS determination of thiols and disulfides in urine samples based on differential labeling with ferrocene-based maleimides. Anal Chem 79:7131–7138.

Seiwert B, Karst U. 2008. Ferrocene-based derivatization in analytical chemistry. Anal Bioanal Chem 390:181–200.

Schaeffer R, Fodor P, Soeroes C. 2006. Development of a liquid chromatography/electrospray selected reaction monitoring method for the determination of organoarsenic species in marine and freshwater samples. Rapid Commun Mass Sp 20:2979–2989.

Schmid WF, John RO, Arion VB, Jakupec MA, Keppler BK. 2007. Highly antiproliferative ruthenium(II) and osmium(II) arene complexes with paullone-derived ligands. Organometallics 26:6643–6652.

Schumann H, Aksu Y, Schutte S, Wassermann BC, Muhle SH. 2006. Synthesis and characterization of new silicon-centered tin-dendrimers $Si[CH_2CH_2SnR_3]_4$. Single-crystal X-ray structure of the tetrahydrofuran adduct of tetrakis [2-(tribromostannyl)ethyl]silane. J Organomet Chem 691:4717–4724.

Sicard S, Berube JF, Samar D, Messaoudi A, Fortin D, Lebrun F, Fortin JF, Decken A, Harvey PD. 2004. Mixed-ligand organometallic polymers containing the "$Pd_2(dmb)_2^{2+}$" fragment: Properties of the $\{Pd_2(dmb)_2(diphos)^{2+}\}_n$ polymers/oligomers in solution and in the solid state. Inorg Chem 43:5321–5334.

Siemsen P, Gubler U, Bosshard C, Gunter P, Diederich F. 2001. Pt-tetraethynylethene molecular scaffolding: Synthesis and characterization of a novel class of organometallic molecular rods. Chem Eur J 7:1333–1341.

Stewart II. 1999. Electrospray mass spectrometry: A tool for elemental speciation. Spectrochimica Acta Part B-Atomic Spectroscopy. 54: 1649–1695.

Susperregui J, Bayle M, Lain G, Giroud C, Baltz T, Deleris G. 1999. Synthesis and evaluation of the in vivo trypanocidal activity of water soluble organotin compounds. Eur J Med Chem 34:617–623.

Štěpnička P, Gyepes R, Lavastre O, Dixneuf PH. 1997. Ferrocene-containing (η^6-hexamethylbenzene)ruthenium(II) methoxycarbenes: Synthesis, structure, and electrochemistry. Organometallics 16:5089–5095.

Takeuchi T, Shirai Y, Matsumura Y, Iwai K, Matsutani T, Oshita J, Naka A. 2006. Mass spectrometric and theoretical studies on the fragmentation mechanism of protonated molecules and molecular radical cations of organometallic compounds with Si-C, Si-Si, Ge-C and Ge-Ge bonds. Surf Interface Anal 38:1650–1653.

Tharamani CN, Song H, Ross ARS, Hughes R, Kraatz HB. 2008. Electrochemical investigation of metal ion interactions of a ferrocene deoxyuridine conjugate. Inorg Chim Acta 361:393–399.

Thompson DM, Jones M, Baird MC. 2003. Anionic cyclopentadienyl C_{60} complexes of molybdenum and tungsten: The strange case of iron. Eur J Inorg Chem 1:175–180.

Traeger JC. 2000. Electrospray mass spectrometry of organometallic compounds. Int J Mass Spectrom 200:387–401.

Tureček F. 2007. Copper-biomolecule complexes in the gas phase. The ternary way. Mass Spectrom Rev 26:563–582.

Vaisar T, Heinecke JW, Seymour JL, Tureček F. 2005. Copper-mediated intraligand oxygen transfer in gas-phase complexes with 3-nitrotyrosine. J Mass Spectrom 40:608–614.

Vinklárek J, Palačková H, Honzíček J, Holubová J, Holčapek M, Císařová I. 2006. Investigation of vanadocene(IV) α-amino acid complexes: Synthesis, structure, and behavior in physiological solutions, human plasma, and blood. Inorg Chem 45:2156–2162.

Wang FY, Chen HM, Parkinson JA, Murdoch PD, Sadler PJ. 2002. Reactions of a ruthenium(II) arene antitumor complex with cysteine and methionine. Inorg Chem 41:4509–4523.

Wang T, Guo ZJ. 2006. Copper in medicine: Homeostasis, chelation therapy and antitumor drug design. Curr Med Chem 13:525–537.

Wei JH, Chen J, Miller JM. 2001. Electrospray ionization mass spectrometry of organogermanium compounds. Rapid Commun Mass Sp 15:169–181.

Wei JH, Miller JM. 2001. Electrospray ionization mass spectrometry of tribenzyltin substituted-phenoxyacetate compounds. J Mass Spectrom 36:806–815.

Weinmann M, Kamphowe TW, Fischer P, Aldinger F. 1999. Tris(hydridosilylethyl)boranes: Highly reactive synthons for polymeric silicon compounds. J Organomet Chem 592:115–127.

Wöhrle D, Pomogailo AD. 2003. Metal complexes and metals in macromolecules. Weinheim: Wiley-VCH.

Wong WY, Wong CK, Lu GL. 2003. σ-Acetylide complexes of ruthenium and osmium containing alkynylsilane ligands. J Organomet Chem 671:27–34.

Wu LM, Hernandez-Soto H, Liu DQ, Vogt FG, O'Neill-Slawecki SA, Su QG. 2008. Tandem mass spectrometry and hydrogen/deuterium exchange studies of protonated species of 1,1 '-bis(diphenylphosphino)-ferrocene oxidative impurity generated during a Heck reaction. Rapid Commun Mass Sp 22:314–320.

Wyatt MF, Stein BK, Brenton AG. 2008. Characterisation of organometallic and coordination compounds by solvent-free matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry. Analyst 133: 47–48.

Xu YH, He XR, Hu CF, Teo BK, Chen HY. 2000. Characterization of organometallic coordinative cluster compounds of silver by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. Rapid Commun Mass Sp 14:298–303.

Yan YK, Melchart M, Habtemariam A, Sadler PJ. 2005. Organometallic chemistry, biology and medicine: Ruthenium arene anticancer complexes. Chem Commun 38:4764–4776.

Yasuike S, Kishi Y, Kawara SI, Kurita J. 2005. Catalytic action of triarylstibanes: Oxidation of benzoins into benzyls using triarylstibanes under an aerobic condition. Chem Pharm Bull 53:425–427.

Yeo JSL, Vittal JJ, Henderson W, Hor TSA. 2001. Probing the Lewis basicity of the metalloligand $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ on tin substrates by electrospray mass spectrometry. J Chem Soc Dalton 3:315–321.

Yeo SP, Henderson W, Mak TCW, Hor TSA. 1999. Ruthenocenyl ruthenium bimetallic complexes: electrospray mass spectrometric study of $[RuX(\eta^5\text{-}C_5H_5)(\eta^2\text{-dppr})]^{n+}$ (dppr = 1,1 '-bis(diphenylphosphino)ruthenocene) (X = Cl, n = 0; X = CO, CH_3CN, C = CHPh, n = 1) and the X-ray crystal and molecular structure of $[Ru(\eta^5\text{-}C_5H_5)(CO)(\eta^2\text{-dppr})]PF_6$. J Organomet Chem 575:171–181.

Young JD, Khan MA, Powell DR, Wehmschulte RJ. 2007. m-Terphenylaluminum and -gallium compounds: Synthesis and conversion into low-coordinate organogallium cations. Eur J Inorg Chem 12:1671–1681.

Zheng J, Takeda A, Furuta N. 2001. Investigating the electrospray mass spectra of inorganic and organic antimony compounds. J Anal Atom Spectrom 16:62–67.

Zhou HY, Dou GF, Meng ZY, Lou YQ, Zhang GL. 2007. High performance liquid chromatographic determination of 1.2-[bis(1,2-benzisoselenazolone-3(2H)-ketone)]-ethane (BBSKE), a novel organoselenium compound, in dog plasma using pre-column derivatization and its application in pharmacokinetic study. J Chromatogr B 852:617–624.

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