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Electrospray mass spectrometry of organometallic compounds

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Abstract

The development of electrospray mass spectrometry (ESMS) for the characterization of organometallic compounds is discussed. The diverse range of both ionic and neutral species amenable to investigation, together with the ability to detect in situ reaction intermediates, is evidence that ESMS should be regarded as one of the major techniques available for organometallic solution studies. (Int J Mass Spectrom 200 (2000) 387–401) © 2000 Elsevier Science B.V.

Keywords: Electrospray; Ionization; Metallation; Protonation; Quaternization; Organometallic; Reaction intermediate

1. Introduction

Organometallic compounds, which may be simply defined as substances containing at least one direct carbon–metal bond, have a wide range of applications. For example, they often play an important catalytic role in synthetic processes and are involved in numerous other diverse areas as a result of their biological activity. The use of mass spectrometry to study the chemistry of such compounds has been significantly extended by the advent of the electrospray ionization (ESI) technique in the mid 1980s [1–3]. Two major reviews of the application of electrospray mass spectrometry (ESMS) to organometallic chemistry have appeared in the literature [4,5].

Although electron ionization (EI) can be used to characterize organometallics [6,7], many systems are not amenable to such studies because of the need to prepare the sample in the gas phase before ionization. The high temperatures required to vaporize involatile compounds, especially ionic ones, frequently result in their decomposition. This invariably creates additional problems, such as ion-source contamination. Furthermore, EI often generates extensive fragmentation, even at relatively low ionizing electron energies. In many cases, no intact molecular ion is observed in the mass spectrum.

The field desorption (FD) ionization technique, largely developed in the 1970s, was the first alternative means of producing mass spectra of involatile molecules [8–11]. However, the experimental conditions required for its successful implementation are often difficult to achieve in practice. In the 1980s, the fast atom bombardment (FAB) method of ionization provided for the first time a reliable means of introducing organometallic ions into a mass spectrometer [12,13]. More recently, the soft ionization method of matrix assisted laser desorption ionization (MALDI) has been used to generate gas-phase ions, although few organometallic compounds have been studied by this method [14–17]. In a comparative investigation

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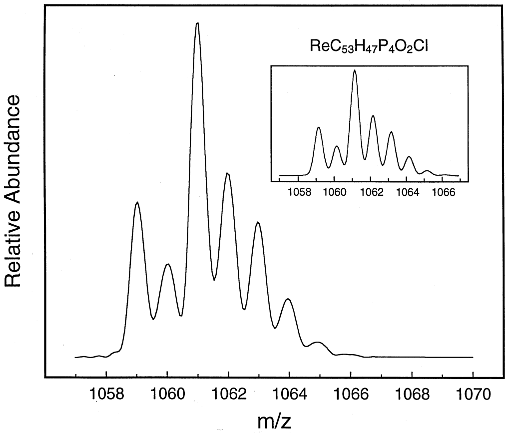
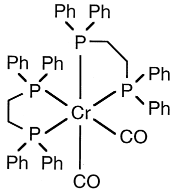


Fig. 1. Calculated and observed isotope patterns for the metal carbonyl cation $[Re(CO)_2(\eta^1\text{-dpmMe})(\eta^2\text{-dpm})Cl]^+$ (dpm = $Ph_2PCH_2PPh_2$).

of FD, FAB, and ESI for a range of organometallic π-hydrocarbon complex salts, Kane-Maguire et al. [18] found that the extent of fragmentation varied in the order FAB $>$ ESI $>$ FD. Because of the poor reproducibility and difficulty in producing effective emitter wires, they concluded that ESI provided the most convenient means of obtaining mass spectra for organometallic compounds.

Since its development, ESMS has been used largely as a biochemical tool [19–22], particularly as it allows the direct detection and accurate mass determination of large biomolecules, such as proteins, with just a modest mass analyzer [23]. However, it is the ability to gently transfer a preformed ion from the liquid phase into the gas phase [24] that has seen it being used increasingly for the study of inorganic and organometallic chemistry in solution [4,5,25–28]. Elemental speciation [29–31] and metallated biomolecules have also been investigated by ESMS [32,33], but these particular applications will not be discussed here.

Unlike the highly charged bipolymers often studied by ESMS, the charges on most organometallic ions are usually small. Consequently, the characteristic isotope patterns of many commonly encountered metals (Fig. 1) can be readily resolved with typical low-resolution mass analyzers and used to provide a positive identification, even in the presence of other ions with the same nominal *m/z* [34]. In addition, because the ion abundance is distributed among just one or two charge states, the detection sensitivity for a given ion will usually be enhanced.



Structure 1. *cis*-$Cr(CO)_2(dpe)_2$ (dpe = $Ph_2PCH_2CH_2PPh_2$)

The two major techniques used to study organometallic chemistry in solution are electrochemistry and NMR spectroscopy. ESMS provides complementary information and, in some cases, can be used to observe ionic species that are difficult or impossible to detect by these techniques. For example, many compounds are paramagnetic or may not have a suitable nucleus for multi-NMR spectroscopy. Because ESMS is capable of detecting all ionic components of a rapidly exchanging labile system [35–38], it also provides a good alternative to low-temperature NMR studies.

In most cases where inorganic and organometallic ions have been characterized in solution by a combination of other analytical techniques, the ESI mass spectra have been found to be in good agreement [4]. The series of laser photofragmentation experiments by Posey and coworkers [39,40] provide additional evidence that the gas-phase ions formed by ESI are analogous to those found in solution.

The use of ESMS to study inorganic and organometallic compounds in our laboratory was not planned. During the commissioning of a BioQ triple quadrupole mass spectrometer at La Trobe University in 1991, one of my colleagues, Ray Colton, enquired whether this biomolecular instrument could produce a mass spectrum for a neutral metal carbonyl compound, *cis*-$Cr(CO)_2(dpe)_2$ (dpe = $Ph_2PCH_2CH_2PPh_2$; Structure 1), whose chemistry he had been studying. It was hoped that simple protonation in solution would provide the means of detection. However, the ESI mass spectrum (Fig. 2) showed a group of peaks at an

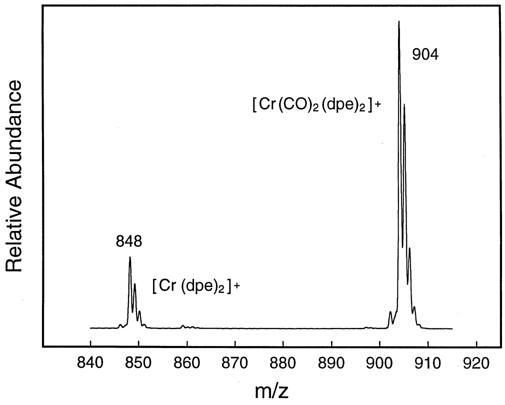
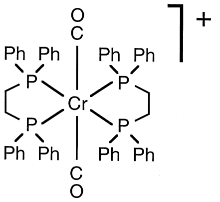


Fig. 2. Electrospray mass spectrum measured in 1991 for *trans*-$[Cr(CO)_2(dpe)_2]^+$ (dpe = $Ph_2PCH_2CH_2PPh_2$) at a cone voltage of 50 V.

m/z that was one less than that expected for the appropriate isotope pattern of an intact cation. After some discussion about the chemistry involved [41], it was considered that protonation might not be taking place and that the Cr(0) may have been adventitiously oxidized to Cr(I). This was subsequently confirmed by a significant increase in the ion abundance following deliberate addition of the chemical oxidant $NOBF_4$ to the sample solution. What we had observed in the mass spectrum for the first time was the intact, labile, and reactive 17-electron *trans*-$[Cr(CO)_2(dpe)_2]^+$ cation (Structure 2) [42,43]. This represented the start of a most rewarding collaboration over many years, the results of which form the basis of this paper.

2. Experimental procedures

The ESI process requires ions to be present in solution before desorption into the gas phase and subsequent mass analysis. Although this will be the situation for ionic compounds, neutral species need to be converted to a closely related ionic system for their characterization. The different techniques used to accomplish this are discussed in Section 4.



Structure 2. *trans*-$[Cr(CO)_2(dpe)_2]^+$ (dpe = $Ph_2PCH_2CH_2PPh_2$)

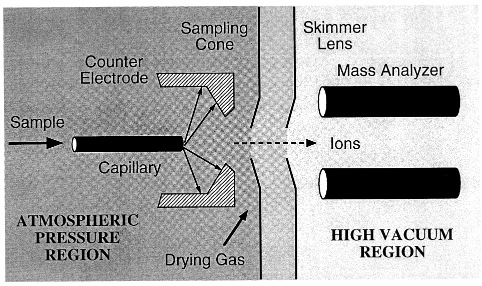


Fig. 3. Electrospray ion source schematic.

Various solvents are suitable for electrospray. These range from the highly polar water and dimethylformamide to the slightly polar dichloromethane and diethyl ether. Mixed organic-aqueous solvents, such as methanol–water or isopropanol–water, are also used for particular experiments. One of the most commonly used mobile phases is acetonitrile–water, as it provides good solubility for many polar and nonpolar compounds and can support both positive- and negative-ion formation.

Because of the soft nature of ESI, unlike EI, an intact molecular ion will usually be observed with very little accompanying fragmentation. In this case, it is necessary to use collisional activation to obtain useful structural information. This can be achieved in the ion source simply by increasing the cone voltage (Fig. 3). However, because the appearance of solvent adducts is cone-voltage dependent (Fig. 4), these ions will often complicate any fragment peak assignment. The use of a tandem (MS/MS) mass analyzer can overcome this interference problem and also provides more specific information about the fragmentation processes involved. However, for systems involving multiply charged ions or weakly bound aggregates, detection is often enhanced by decreasing the cone voltage.

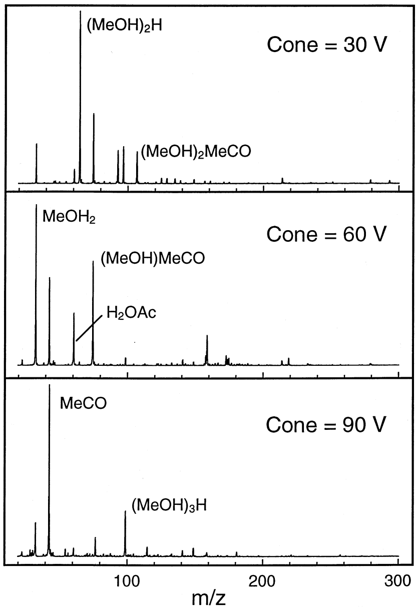


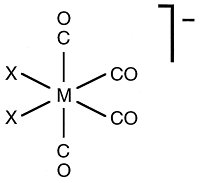
Fig. 4. Effect of cone voltage on the positive-ion mass spectra for a 50:50:1 MeOH:H_2O:HOAc solution.

3. Ionic compounds

The ability of ESI to gently transfer an ion from solution to the gas phase provides an ideal means for the study of ionic compounds. This was recognized at a very early stage in the development of ESMS, with numerous inorganic salts being characterized [1,44–47].

Organometallic carbonyl compounds have been studied widely by various mass spectrometric methods, although ionization techniques other than ESI have generally had difficulty in generating intact or molecular ions. The ease with which these compounds can be studied is demonstrated by the range of ionic metal carbonyl species that have been characterized in solution by ESMS. In most cases, the intact carbonyl complex cation is observed as the base peak, with facile loss of carbonyl ligands occurring at increased cone voltages.

Apart from the *trans*-$[Cr(CO)_2(dpe)_2]^+$ cation mentioned above [42,43], the ESI mass spectra of the seven-coordinate species $[M(CO)_2(P\text{–}P)_2X]^+$ (M = Mo, W; P–P = $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$; X = F, Cl, Br, I) all show a significant intact cation [48]. This is also found for the π-hydrocarbon metal carbonyl complexes of the type $[M(CO)_3(\eta\text{-}C_7H_7)]BF_4$ (M = Cr, Mo, W), $[Fe(CO)_2L(\eta^5\text{-dienyl})]BF_4$ (L = CO, PPh_3; dienyl = C_6H_7, 2-$MeOC_6H_6$, C_7H_9), $[CpFe(CO)_3]PF_6$ and $[CpFe(CO)_2(\eta\text{-}C_2H_4)]BF_4$ [18].



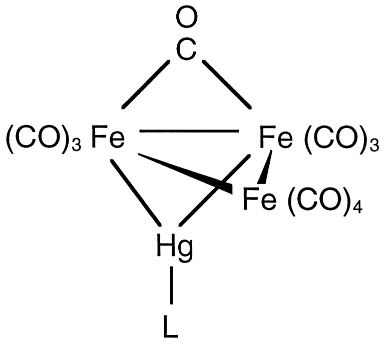
Structure 3. $[M(CO)_4X_2]^-$

In conjunction with electrochemistry, IR and NMR spectroscopy, and X-ray crystallography, ESMS has been used to study the $[M(CO)_2(P_2P')X]^{+/0}$ (M = Mn, Re; X = Cl, Br; P_2P' = η^3-$Ph_2P(CH_2)_2P(Ph)(CH_2)_2PPh_2$) system [49]. Systematic studies of several 17-electron Re(II) carbonyl phosphine complexes have also used ESMS to characterize the ionic species present in solution [50].

Metal alkene and arene complexes involving Ag(I) π-bonded to the ligand readily form in solution. However, they are very labile and difficult to isolate. A number of such complexes, formed by the reaction between $[Ag(cod)_2]^+$ (cod = 1,5-cyclooctadiene) and a variety of phosphine ligands, produced mixed-ligand cations that could be directly identified by ESMS [51].

Various anionic metal carbonyl complexes, such as the Group 6 and Group 7 halocarbonyl anions $[M(CO)_5X]^-$ (M = Cr, Mo, W; X = Cl, Br, I) and $[M(CO)_4X_2]^-$ (M = Mn, Re; X = Cl, Br, I) (Structure 3) [48], have been studied by ESMS. In all cases, the intact singly charged anion is observed.

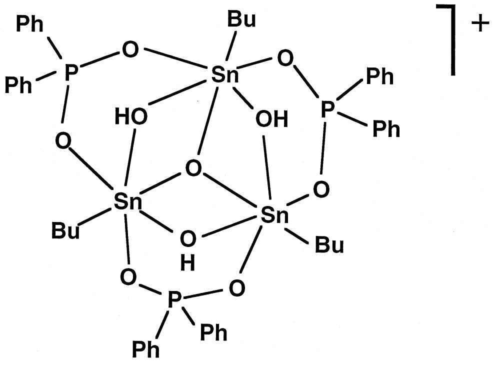
ESMS has also been able to provide useful mass spectra for a range of polynuclear metal anions. These include the singly charged cluster anions $[PtRh_5(CO)_{15}]^-$ [52] and $\{[PPh_4]^+[Pt_{12}(CO)_{24}]^{2-}\}^-$ [26], the heterometal anions $[Fe_3(CO)_{10}(\mu\text{-}CO)\{\mu\text{-}Hg(L)\}]^-$ (L = $Mo(CO)_3Cp$, $Co(CO)_4$, $Fe(CO)_2Cp$, $W(CO)_3Cp$, $Mn(CO)_5$; Structure 4) [53], the dianions $[Os_{10}C(CO)_{24}]^{2-}$ and $[Ru_6C(CO)_{16}]^{2-}$ [54], and the



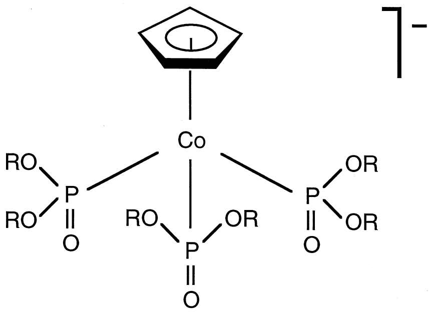
Structure 4. $[Fe_3(CO)_{10}(\mu\text{-}CO)\{\mu\text{-}Hg(L)\}]^-$

dianions $[Ni_{10}(SbR)_2(CO)_{18}]^{2-}$ (R = Me, Et, ^{i}Pr, ^{t}Bu, p-FC_6H_4) [55]. Cluster anions with up to five negative charges, formed from the reactions of $Ru_3(CO)_{12}$, $Ru_6C(CO)_{17}$, $H_4Ru_4(CO)_{12}$, and $H_2Os_3(CO)_{10}$ with the phosphine $P(m\text{-}C_6H_4SO_3Na)$, have been characterized by ESMS and shown to catalyze the conversion of H_2O and CO to CO_2 and H_2 (water–gas shift reaction) [56].

On the basis of its X-ray structure and ^{119}Sn NMR spectroscopy, the doubly charged cation of the organotin complex $[(BuSn)_{12}O_{14}(OH)_6]Cl_2$ has been shown to retain its structure in solution following ESI [57]. However, replacement of two hydroxo groups by methoxide from the CH_2Cl_2/MeOH solvent was observed after a 5-d period. A more rapid substitution reaction was observed via the changed ESI mass spectrum for a related $[\{BuSn(OH)(O_2PPh_2\}_3O]^+$ cation (Structure 5).



Structure 5. $[\{BuSn(OH)(O_2PPh_2\}_3O]^+$



Structure 6. $[CpCo\{P(O)(OR)_2\}_3]^-$ (R = Me, Et, ^{i}Pr)

ESI mass spectra have been obtained for several cationic methyl and dimethyl derivatives of gold(III), indium(III), and thallium(III), involving neutral bidentate or polydentate nitrogen donor ligands [58]. It was found that weak interactions between the metals and ligands observed in the solid state were often retained in the gas phase. Similar studies involving organo Pd(IV), Pt(IV), Pd(II), and $[MeHg]^+$ complexes with the same series of ligands demonstrated that ESMS analyses were in accord with the known chemical properties and behavior of the different compounds [59,60].

The uninegative tripodal oxygen ligand $[L]^- = [CpCo\{P(O)(OR)_2\}_3]^-$ (R = Me, Et, ^{i}Pr) (Structure 6) has been directly observed as the free anion by ESMS [61]. In addition to the $[L]^-$ ion, peaks caused by $[NaL_2]^-$ and $[Na_2L_3]^-$ appeared in the ESI mass spectrum of the sodium salts (Fig. 5). Monoanions incorporating replacement of L by an isopropoxide ligand, originating from the isopropanol–water mobile phase, were also observed. The presence of $[NaL_2]^-$ and $[Na_2L_3]^-$ anions confirmed that these complexes, which are trimeric or polymeric in the solid state, remained partially associated in solution.

Negative-ion ESMS has also been used to investigate some highly reactive Gilman reagents ($RR'Cu^-Li^+$) in solution. Using a low sample introduction temperature (78° C), Lipshutz and coworkers [62] found that a number of anionic aggregates formed in solution. As expected, the monomeric species predominated at higher cone voltages.

Several bimetallic ruthenocenyl ruthenium complexes $[RuX(\eta^5\text{-}C_5H_5)(dppr)]^+$ (X = CO, CH_3CN,

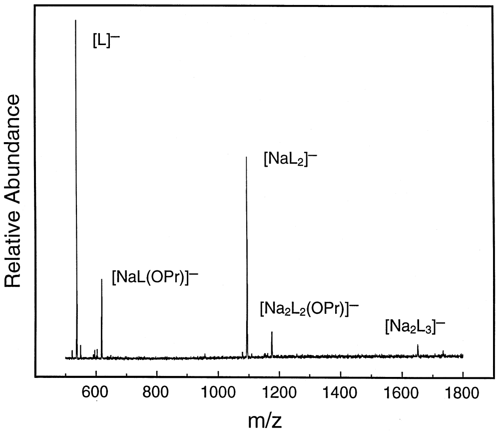
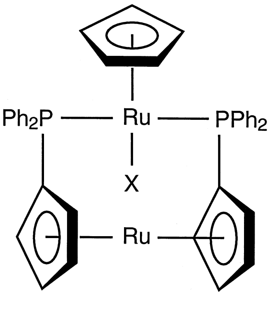


Fig. 5. Electrospray mass spectrum measured at a cone voltage of 50 V for the tripodal oxygen ligand $[CpCo\{P(O)(OEt)_2\}_3]^-$ in a 50:50 $^iPrOH:H_2O$ solution.

C=CHPh; dppr = $[Ru(\eta^5\text{-}C_5H_4PPh_2)_2]$; Structure 7) have been detected by positive-ion ESMS [63]. X-ray crystallography of the carbonyl complex indicated that there was no interaction between the two Ru(II) centers. In each case, intact cations were observed at low cone voltages, with the most labile ligand (X) being lost as the collision energy was increased. A higher cone voltage was required for CO loss relative to CH_3CN loss, indicating a stronger binding of the CO ligand to Ru(II). A doubly charged cation was also detected at low cone voltages for the complex incorporating a C=CHPh ligand. This was attributed to oxidation of the dppr-ruthenium, giving rise to a complex with Ru present in two different oxidation states (II and III).

More recently, Yamanari et al. [64] used positive-ion ESMS to provide complementary data to UV/vis, NMR spectroscopic, and X-ray crystallographic experiments involving self-assembling reactions between $[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$ and pyrimidine-2-thionate or related ligands. Dinuclear rhodium(III) complexes of structure $[\{Rh(\eta^5\text{-}C_5Me_5)(L)\}_2]^{n+}$ were shown to have formed.



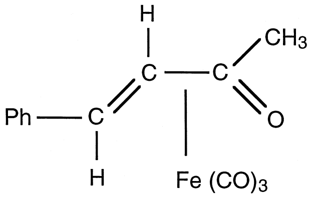
Structure 7. $[RuX(\eta^5\text{-}C_5H_5)(dppr)]^+$

4. Neutral compounds

Like conventional EI mass spectrometry, the direct analysis of neutral compounds by ESMS requires conversion of the precursor molecule to an ionic species. However, with ESI, this will not normally take place in the ion source, with ionization occurring instead in solution before sample introduction. It is by this means that large biomolecules can be analyzed, either as multiprotonated cations or as deprotonated anions. Because protonation of organometallic systems is generally limited to molecules containing a suitable oxygen or nitrogen atom, other in situ ionization techniques have needed to be devised. In addition to protonation, methods that have been successfully used with organometals include metallation, chemical reaction, quaternization, and oxidation. Some examples of each of these will be discussed in the following sections.

4.1. Protonation

If an organometallic complex has a ligand that can be protonated, it will usually be possible to observe an $[M+H]^+$ cation in its ESI mass spectrum. This was demonstrated for a range of neutral $[(\eta^4\text{-diene})Fe(CO)_3]$ and $[(\eta^6\text{-arene})Cr(CO)_3]$ species and related enone and enimine complexes with protonatable sites on their hydrocarbon ligands [65]. For example, $[(Ph(CH)_2C(O)Me)Fe(CO)_3]$ (Structure 8) formed a protonated cation that was the base peak in its mass spectrum at a cone voltage of 30 V, whereas $[(PhCN^tBu)Cr(CO)_3]$ (Structure 9) produced an $[M+H]^+$ ion that was 95% of the base peak at 47 V. In these experiments, protonation was not observed



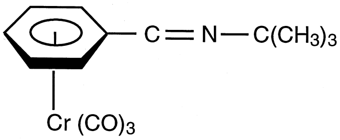
Structure 8. $[(Ph(CH)_2C(O)Me)Fe(CO)_3]$

for various neutral binary metal carbonyls and clusters unless a basic ligand, such as PPh_3, was present.

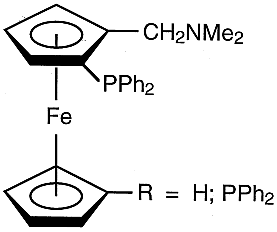
As will be discussed in Section 4.5, the metallocenes can be observed directly in solution by means of electrochemical oxidation. However, in addition to the expected M^+ cations, Cole and coworkers [66] also detected $[M+H]^+$ cations for $[CpFeC_5H_4C(O)CH_3]$, $[(CH_3C(O)C_5H_4)_2Fe]$, and $[Cp_2Os]$. These were found to be solvent dependent, with their formation being enhanced by the addition of up to 1% trifluoroacetic acid. Several aminoalkyl ferrocenyl phosphines (Structure 10) have been observed as the corresponding $[M+H]^+$ cation [67], presumably being protonated at the amino function.

ESMS has been used to characterize the cyclic tricubane metal cluster $[(\eta^5\text{-}C_5Me_5)_2Mo_2Fe_2S_4]_3(\mu\text{-}S_4)_3$ following its synthesis [68]. The complex was readily protonated in solution, where it formed both $[M+H]^+$ and the corresponding $[M+2H]^{2+}$ dication. Some gold(III)–salicylate and –thiosalicylate complexes (Structure 11), which have moderate to high antitumor, antibacterial, and antifungal activity, have also been observed as the protonated molecule. They all demonstrated a high stability toward cone voltage–induced fragmentation [69].

Many neutral organometallic complexes that contain a triphenylphosphine ligand are not readily protonatable. To facilitate their analysis via ESMS, Henderson and coworkers [70] have proposed that replacement of this group by an appropriately substituted triarylphosphine, containing, for example, a p-OCH_3 or p-NMe_2 group, can be used to produce $[M+H]^+$ ions in the ESI mass spectra. This has been successfully demonstrated for some Mo, Fe, and Ru triphenylphosphine carbonyl complexes. IR and NMR spectroscopy was used to confirm that the modified ligands behaved like their unsubstituted counterparts.



Structure 9. $[(PhCN^tBu)Cr(CO)_3]$

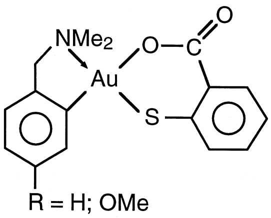


Structure 10. aminoalkyl ferrocenyl phosphine

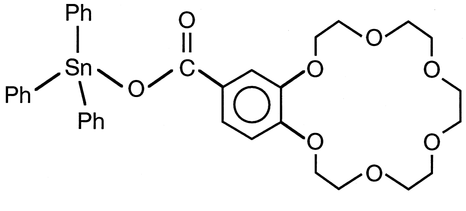
4.2. Metallation

If a neutral organometallic molecule contains an appropriate heteroatom, it will often form a metal ion adduct in solution. Because this carries one or more positive charges, it can thus be detected by ESMS. In many cases, these adducts are formed in preference to a protonated molecule. Alkali metal ions, such as Na^+ and K^+, are commonly found in the sample introduction system, and these will often form adducts in competition with protonation. This also facilitates studies in nonprotic solvents.

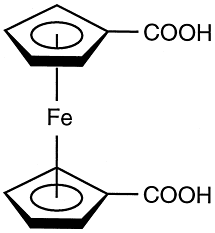
The intentional addition of Na^+ has been used to characterize a range of neutral rhenium bipyridine complexes [fac-$Re(X_2bpy)(CO)_3Y$] (X_2bpy = 4,4′-X_2-2,2′-bipyridine; X = H, Me, CF_3; Y=CN, Cl, Br, OCHO, OH) [71]. Like the metallocenes discussed



Structure 11. $[\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}R\text{-}5\}Au\ \{C_6H_4(CO_2)\text{-}2\text{-}S\}]$



Structure 12. [$Ph_3SnOC(O)R$]



Structure 13. [$Fe(Cp\text{-}COOH)_2$]

above, the ability of Na^+ to adduct with the complex depended on the nature of the solvent. Because complexes without any bipyridine ligand, such as $Re(CO)_5Cl$, did not form adducts, it was concluded that the Na^+ cation was interacting with the bpy ligand. This technique allowed the identification of the neutral metal bipyridine complex [$Re(bpy)(CO)_2\{P(OEt)_3\}Cl$] that was produced during a photochemical ligand substitution reaction [72].

Henderson et al. [54] have observed alkali metal cation (Li^+, Na^+, and K^+) adduction with the ruthenium carbonyl compounds [$Ru_3(CO)_9(PPh_3)_3$] and [$Ru_3(CO)_{10}(AsPh_3)_2$]. They suggested that such electron-rich compounds have sufficient charge residing on the CO ligands to enable attachment to the cation. The adduction of Na^+ was found to occur for a range of Fe, Co, Ru, and W carbonyls [54].

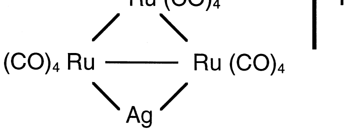
The interactions of crown ethers and their derivatives with alkali, alkali earth, and other metal ions have been investigated extensively by ESMS [73–78]. Recently, a number of novel di- and triorganotin derivatives of crown ethers, such as Structure 12, were able to be identified by ESMS via their corresponding Na^+ adduct [79].

Alkali metal cation adduction has also been used to detect some self-assembled structures of 1,1′-ferrocenedicarboxylic acid (Structure 13) formed in both acetonitrile and methanol [80]. The sodiated multimers dominated the positive-ion ESI mass spectrum when equimolar amounts of $XClO_4$ ($X = Li$, Na, K, Rb, Cs) salts were added to a methanol solution of the acid. At low cone voltages, the most stable complex was a tetramer, although a corresponding negative-ion mass spectrum only showed dimer formation, in agreement with X-ray crystallographic data. It was proposed that the tetramer has a cyclic structure that is stabilized by Na^+ through a pseudo–crown ether–type interaction.

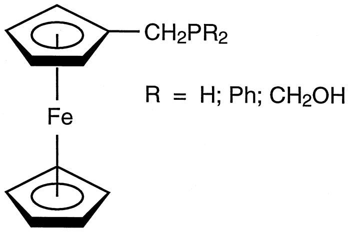
Many organometallic complexes do not form adducts with alkali metal cations. However, various transition metal ions can be used instead to promote ionization. Henderson and Nicholson [81] have shown that Ag(I) ions readily form adducts with a range of neutral metal carbonyl complexes, such as [$M_3(CO)_{12}$] ($M = Ru$, Os), [$SiFe_4(CO)_{16}$], and [$Re_2(CO)_{10}$], thereby enabling their analysis by ESMS. On the basis of related solid-state experiments, they proposed that the adduct formation occurred via an isocarbonyl $M–C{=}O\cdots Ag^+$ interaction.

In a subsequent, more detailed study, adduction to other metal carbonyls, including PPh_3 and $AsPH_3$ ligands, was observed [54]. The inability to produce adducts with mononuclear complexes was explained by a revised model involving an interaction between the Ag^+ cation and the energy-rich M–M bond (Structure 14). At low Ag(I) concentrations, ferrocenyl methyl phosphine complexes (Structure 15) were found to form $[3M + Ag]^+$ and $[2M + Ag]^+$ adducts in addition to $[M + Ag]^+$ [67].

Ionization via Ag^+ adduction has also been used to characterize the ruthenium carbonyl complex [$Ru_3H(CO)_9(C_{12}H_{17})$] (Structure 16) [82], although at low cone voltages, the additional adduction of a



Structure 14. $[Ru_3(CO)_{12}Ag]^+$

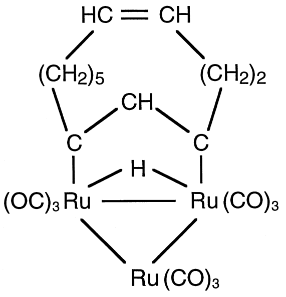


Structure 15. ferrocenyl methyl phosphine

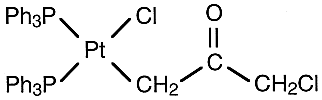
solvent CH_3CN molecule was observed. On the basis of ESI mass spectra, NMR spectra, and X-ray crystallographic data, an earlier identification of the involvement of a $(C_{12}H_{15})$ ligand was able to be revised.

4.3. Chemical reaction

A major limitation of the Ag^+ adduction method of derivatization for metal carbonyls is that it is not applicable to mononuclear compounds [83]. A more versatile in situ technique, which has been demonstrated for a range of mononuclear and polynuclear metal carbonyl compounds [54], is the reaction with alkoxide anions in an alcohol solvent, preferably methanol. This involves nucleophilic attack of one of the coordinated carbonyl groups to produce a coordinated $-C(O)OR$ group. The reaction, which is general for many metal carbonyls, is rapid with a favorably large equilibrium constant. Sodium methoxide, ethoxide, and isopropoxide have each been used. Examples of neutral metal carbonyl compounds that have been studied by this technique include $Cr(CO)_6$, $Re_2(CO)_{10}$, $[Os_3(CO)_{12}]$, $[Rh_4(CO)_{12}]$, $[Ru_6C(CO)_{17}]$, and the π-bonded complex $[Fe(CO)_2Cp]_2$ [54].



Structure 16. $[Ru_3H(CO)_9(C_{12}H_{17})]$



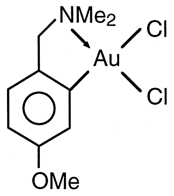
Structure 17. *cis*-$[PtCl\{CH_2C(O)CH_2Cl\}(PPh_3)]$

Because the alkoxide anions are strongly basic, it is possible to observe deprotonation when acidic hydrogens are present in the complex. For example, $Co_2(CO)_6(dppm)$, $Ru_3H(C_2{}^tBu)(CO)_9$, and $Os_4H_2(CO)_{10}(C_6H_6)$ all show a prominent $[M-H]^-$ anion in their mass spectra [54]. Sodium cation adduction may also occur, producing cationic derivatives. As a general observation for sodium methoxide reagent, unsubstituted metal carbonyls tend to add OMe^- but not Na^+, whereas highly substituted ones add Na^+ but not OMe^- [54].

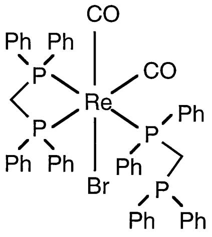
Displacement of an anionic ligand by a neutral ligand can be used to ionize a neutral complex. Although the resulting ion is different than the precursor, it will often be a predictable and closely related species. The replacement of a coordinated halide ligand by a CH_3CN solvent molecule has been observed at low cone voltages for the complexes *trans*-$[PtI(Me)(PPh_3)_2]$ and *cis*-$[PtCl\{CH_2C(O)CH_2Cl\}(PPh_3)_2]$ (Structure 17) [84]. Direct halide loss, which produced a singly charged cation, was used to characterize these neutral Pt(II) complexes. A similar displacement of chloride by pyridine to produce a monocation was found to occur with a cyclic gold(III) complex (Structure 18) [69].

4.4. Quaternization

A large number of neutral organometallic complexes contain a pendant phosphine or arsine ligand.



Structure 18. $[\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}R\text{-}5\}Au\,Cl_2]$



Structure 19. *cis/mer*-[Re$(CO)_2$Br(η^1-dpm)(η^2-dpm)]

In these cases, conversion to a phosphonium or arsonium salt is possible, resulting in a charged species that can be detected by ESMS. As an example, following the addition of a few drops of CH_3I to a solution of *cis/mer*-[Re$(CO)_2$Br(η^1-dpm)(η^2-dpm)] (dpm = $Ph_2PCH_2PPh_2$; Structure 19) converts the pendant phosphorus into the phosphonium salt [Re$(CO)_2$Br(η^1-dpmMe)(η^2-dpm)]I without oxidation of the rhenium [42]. The ESI mass spectrum is dominated by the characteristic group of isotopic peaks at *m/z* 1105 from the intact cation (Fig. 6). Apart from the pendant ligand, the rest of the molecule is shown by IR and ^{31}P NMR spectroscopy to be unaffected by the methylation. This quaternization technique has also been used to successfully characterize a range of Group 6 and Group 7 metal carbonyl complexes [48].

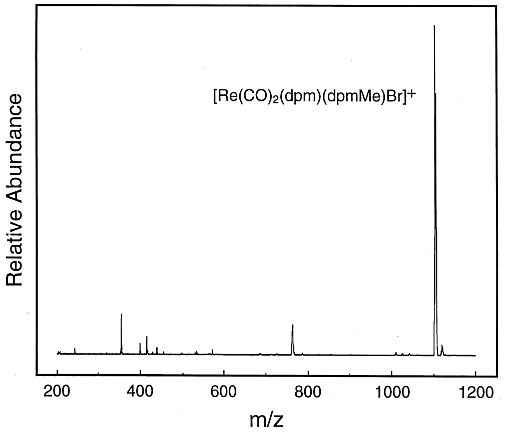
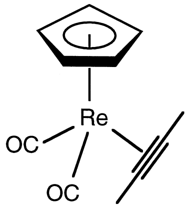


Fig. 6. Electrospray mass spectrum measured at a cone voltage of 50 V for a solution of *cis/mer*-[Re$(CO)_2$Br(η^1-dpm)(η^2-dpm)] (dpm = $Ph_2PCH_2PPh_2$) in CH_2Cl_2/MeOH following the addition of a few drops of CH_3I.



Structure 20. CpRe$(CO)_2(C_4H_6)$

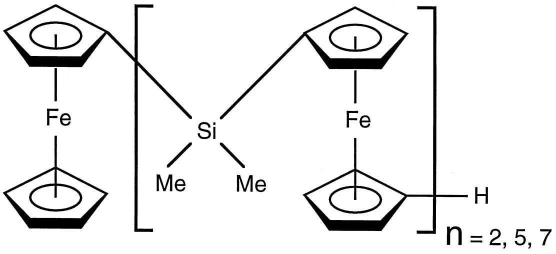
4.5. Oxidation or reduction

Neutral species may be converted to cations or anions by oxidation or reduction, respectively, thereby enabling mass spectrometric detection. This may be carried out either electrochemically or via a chemical process.

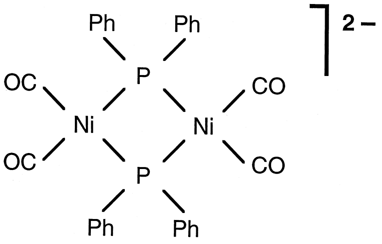
Under certain conditions, the metal electrospray capillary can act as an electrode for a redox reaction [85,86]. Van Berkel and Zhou [87] have shown that the electrospray ion source is a constant or controlled-current device in which electrolysis can occur in a similar way to that carried out in a flow cell. This technique was used to observe the mass spectra for a number of metallocenes and related cyclopentadienyl complexes of ruthenium [66] and some indenyl and cyclopentadienyl carbonyl complexes of rhenium (Structure 20) [88].

The constant-current electrolytic nature of the ESI process has also been used to study some polymeric metallocenes [89]. Oligo(ferrocenyldimethylsilanes) (Structure 21) were observed as multiply charged cations, with an M^{4+} species being detected for the octa(ferrocenyldimethylsilane).

The bimetallic Ni(0) phosphido carbonyl complex



Structure 21. [$(Cp_2Fe)\{(SiMe_2)(CpFeC_5H_4)\}_nH$]



Structure 22. $[Ni_2(CO)_4(PPh_2)_2]^{2-}$

$[Ni_2(CO)_4(\mu\text{-}PPh_2)_2]^{2-}$ (Structure 22) was recently characterized by IR and NMR spectroscopy, electrochemistry, and X-ray crystallography [90]. In agreement with these data, the negative-ion ESI mass spectrum of the complex in DMF solvent showed the one-electron oxidation product as a monoanion, presumably formed as a result of in-source oxidation. Successive decarbonylation products were also observed, although the cone voltage used for the mass spectrum was not reported.

The direct coupling of an external electrochemical cell to an ESI source has enabled in situ monitoring of redox processes [91,92]. A simple cell, constructed from two lengths of platinum microtubing (Fig. 7), has been shown to generate the same charged species produced as an off-line electrolysis experiment [91]. It was, however, necessary to modify the usual supporting electrolyte conditions to minimize signal suppression in the ESI mass spectrum.

The use of a chemical oxidant, such as NO^+ from the nitrosium salt $NOBF_4$, often provides a simple and convenient means of converting a neutral organometallic compound into a corresponding cation before introduction into the electrospray source. Examples of this method include the preparation of the intact ferrocenium and *trans*-$[Cr(CO)_2(dpe)_2]^+$ cations [42].

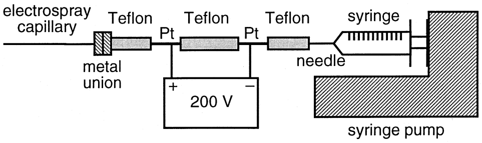


Fig. 7. On-line ESI electrochemical cell.

5. Detection of reaction intermediates

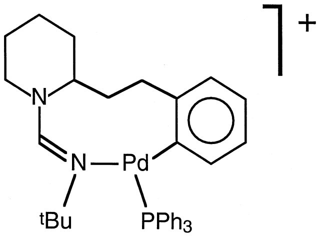
The ability to detect ionic species in solution provides a convenient technique for directly observing reaction intermediates in organic reactions. This is particularly helpful when the intermediates are transient and can enable the progress of reactions to be conveniently monitored, as well as acting as a useful mechanistic probe.

To demonstrate that ESMS could be used to successfully identify such intermediates, Wilson et al. [93] used a number of organophosphorus reactions (Wittig, Mitsunobou, and Staudinger) for which the intermediates had been identified previously by NMR spectroscopy. In each case, the ionic species were detected, together with protonated derivatives for most of the neutral intermediates. This work provided another example of the complementary nature of ESMS and NMR experiments.

The Suzuki coupling reaction provides an excellent synthetic tool for C–C bond formation. ESMS has been used to identify transient catalytic intermediates in this Pd(0)-catalyzed coupling reaction of arylboronic acids with aryl halides [94]. Bromopyridine was used as the aryl halide for these experiments so that the proposed $[(pyr)Pd(PPh_3)_2Br]$ neutral intermediate could be detected as a protonated species. A second diaryl Pd(II) intermediate was also observed as an $[M+H]^+$ cation. In a related study, Pd-containing intermediates in the Pd(0)-catalyzed self-coupling of the arylboronic acids $[R(C_6H_4)B(OH)_2]$ ($R = 3\text{-}NH_2$; $4\text{-}CF_3$) were characterized by ESMS as either M^+, $[M+H]^+$, or $[M+Na]^+$ [95]. This provided useful information about the steps occurring after biaryl formation and leading to recovery of the catalytic species.

A series of experiments to control the double-bond migration process in the Pd-catalyzed intramolecular arylation of enamidines has used ESMS to follow the reaction pathway [96]. On the basis of the appearance of Pd-containing peaks in the ESI mass spectra, a number of organopalladium intermediates, such as Structure 23, were able to be proposed.

A mechanistic study of C–H bond activation involving the cationic iridium(III) complexes

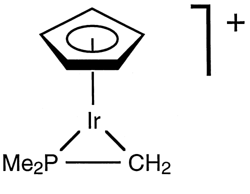


Structure 23. organo-Pd intermediate

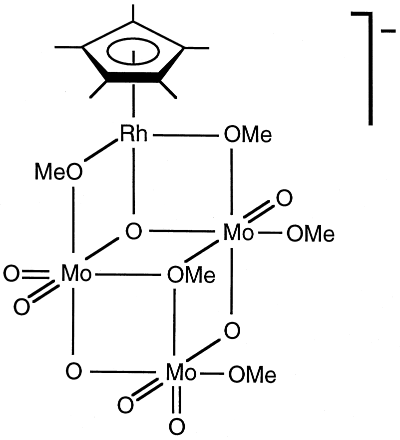
$[CpIr(PMe_3)Me]^+$ and $[Cp^*Ir(PMe_3)Me]^+$ ($Cp^* = \eta^5$-C_5Me_5) has been conducted in the gas phase by ESI MS/MS [97,98]. With the support of isotopic labeling experiments, an elimination-addition mechanism involving a Cp* or $[CpIr(\eta^2$-$CH_2PMe_2)]^+$ intermediate (Structure 24) was observed for pentane, cyclohexane, and benzene.

ESMS was used to directly observe the singly charged organometallic anion $[Cp^*RhMo_3O_8(OMe)_5]^-$ (Structure 25) [99]. This is a key intermediate generated in solution during formation of the $[(Cp^*Rh)_2Mo_6O_{20}(OMe)_2]^{2-}$ double-bookshelf-type oxide cluster.

The platinum(II)-amidate complex, *cis*-$[PtCl\{N(CO_2Et)C(O)CH_2CH\}(PPh_3)_2]$ (Structure 26), which is an intermediate in the silver(I) oxide-mediated synthesis of the platinalactam $[Pt\{N(CO_2Et)C(O)CHCN\}(PPh_3)_2]$, has been characterized in solution by both ESMS and multinuclear NMR spectroscopy [100]. In the ESI experiments, the neutral complex was detected as the corresponding monocation, with the Cl being selectively displaced by a CH_3CN solvent molecule, as discussed in Section 4.3. A single-crystal X-ray study was also carried out on the isolated intermediate.



Structure 24. $[CpIr(\eta^2$-$CH_2PMe_2)]^+$



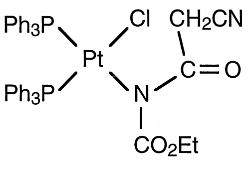
Structure 25. $[Cp^*RhMo_3O_8(OMe)_5]^-$

In a recent study of the ruthenium(II) catalyzed asymmetric reduction of ketones to alcohols, Wills et al. [101] used ESMS to detect intermediate species likely to be involved in the process. The speculated precatalyst (Structure 27), formed by the combination of aminoindanol with the Ru(II) dimeric complex $[RuCl(\eta^6$-cymene$)]_2$, was identified in isopropanol as the $[M + H]^+$ cation on the basis of its mass spectral isotope pattern. From subsequent changes in the mass spectra following the addition of KOH, which acts as the hydrogen source for the reduction reaction, it was proposed that a six-center transition state is probably involved in the H-transfer mechanism.

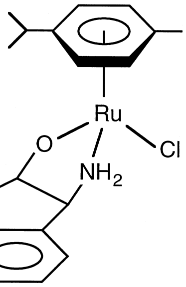
6. Conclusions

Over the past decade, the routine use of ESMS for the characterization of organometallic compounds has expanded considerably, although there are still many compounds, such as organolithium derivatives and metal fullerenes, for which there are little or no experimental data available.

The range of examples described here illustrates



Structure 26. *cis*-$[PtCl\{N(CO_2Et)C(O)CH_2CN\}(PPh_3)_2]$



Structure 27. ruthenium precatalyst

that the ESI technique is not just well suited to ionic compounds in solution but also to neutral compounds that may be detected following their conversion to closely related ionic species. Some of the successful ionization techniques used include protonation, metallation, chemical reaction, quaternization, and oxidation or reduction. These are generally carried out in solution before sample introduction, although in situ electrochemical conversion processes can also be used.

Many investigations of organometallic systems have involved other complementary techniques, including X-ray crystallography, NMR spectroscopy, and electrochemistry. In most cases, there is an excellent correlation between the observed mass spectra and the species known to be present in solution. This illustrates the soft nature of the electrospray process and indicates that ESMS can provide an additional useful analytical tool for the organometallic chemist, particularly when the more traditional methods are either inappropriate or unable to be used.

The ability of ESMS to detect reaction intermediates in solution, often at very low concentrations, also provides a convenient means of following the pathways of many reactions. In particular, the role played by many industrially important organometallic catalysts can be probed in this way and may help to open up new and previously unexplored areas of chemistry.

Uncited references

*M.A. Aramendia, F. Lafont, M. Moreno-Manas, R. Pleixats, A. Roglans, J. Org. Chem. 64 (1999) 3592.

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