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# MASS SPECTROMETRY OF ORGANOALUMINUM DERIVATIVES

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## ABSTRACT

[to be written last]

## Keywords

### 1. Introduction

This review examines the use of mass spectrometric methods for the characterization of organoaluminum species. Fundamentally, there is no reason why mass spectra of organoaluminums should be significantly different to the mass spectra of any other organometallic complex, but the high reactivity of the Al-C bond towards hydrolysis coupled with the microscopic amounts of material required for mass spectrometric analysis means that obtaining good data without decomposition can be a significant challenge.

Mass spectrometry of organometallic compounds grew alongside the field of organometallic chemistry itself - the many and varied new compounds that were being made needed characterization by the full suite of analytical methods, mass spectrometry included. Litzow and Spalding published "Mass Spectrometry of Inorganic and Organometallic Compounds" in 1973, a fairly comprehensive overview of the field to that date.<sup>1</sup> Organoaluminum compounds feature in this tract briefly. A lot has changed in the 40 years since then in the field of mass

spectrometry, and a wide array of alternative ionization, separation and mass analysis methods have been developed.<sup>2</sup>

The chapter deals first with practical considerations involving the analysis of air- and moisture-sensitive materials, before delving into the specifics of the various ionization techniques available and closing with a section providing a quick way of assessing what sort of method should be used given some basic knowledge of the sample of interest.

## **2. Practical Considerations**

A principal concern of the organoaluminum chemist should be the manner in which the sample is handled prior to analysis. Few organoaluminum compounds will survive even brief exposure to the air when in quantities suitable for mass spectrometric analysis. How the sample should be treated is a function of the phase it is in.

Gases and volatile liquids can be sealed in a septum-capped vial and retrieved from the headspace with a narrow bore, gas-tight syringe and injected directly into the source of the mass spectrometer (typically EI or related). Provided the source is under high vacuum, exposure to oxygen and moisture will be minimal.

Solutions intended for analysis must use solvents that have been scrupulously dried and are free of oxygen. The spectrometer needs to be clean and exhaustively rinsed with the purified solvent of choice prior to analysis. If the solvent is compatible with a glovebox, the sample can be made up inside using a gas-tight syringe. While still in the glovebox, connect whatever tubing and fittings are required to connect the syringe to the mass spectrometer. If the solvent is

incompatible with the glovebox (or one is not available), make the solution up in a Schlenk flask, withdraw with the syringe and immediately connect to solvent-filled tubing and fittings. In either instance, the apparatus should be taken immediately to the MS and analyzed.

Solids are hardest to handle because transfer to the spectrometer nearly always requires brief exposure to the atmosphere. Practical solutions to this problem all involve increasingly stringent means of providing an inert atmosphere around the entry port. The sealed sample can be put inside a flexible plastic glove bag, which is then taped to the front end of the instrument and purged with nitrogen. The sample can then be broken open inside the bag and transferred to the source (Figure 1a). Semi-permanent solutions for regular analyses might involve the construction of a small purge-able glovebox to the front of the instrument. The best possible solution is to co-locate a fully-featured glovebox alongside the mass spectrometer, an approach that is relatively straightforward for solutions (the two simply need to be close to one another and a feedthrough available in the glovebox, Figure 1b)<sup>3</sup> but somewhat more involved for solids (the two need to be fully integrated).<sup>4</sup>

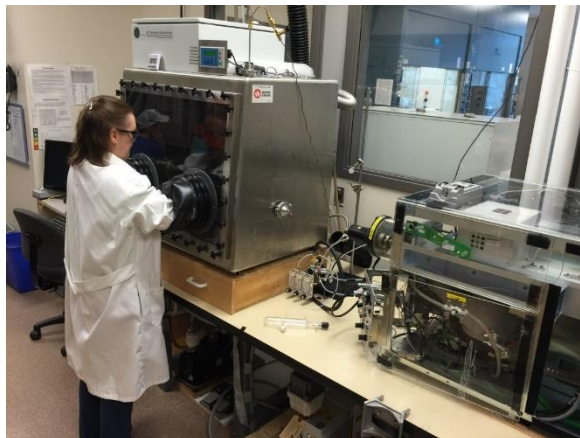


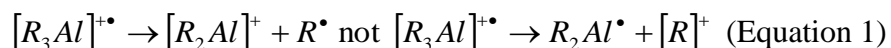
Figure 1. (a, left) MALDI mass spectrometer with glovebag attached for the analysis of air- and moisture-sensitive solids; (b, right) ESI mass spectrometer adjacent to an inert-atmosphere glovebox for the analysis of air- and moisture-sensitive solutions.

The fact that aluminum is a monoisotopic compound can make spectral assignment spectra slightly problematic, as there are no characteristic patterns that jump out at the analyst. However, there are many good tools available for assistance, and [www.chemcalc.org](http://www.chemcalc.org) is highly recommended as a powerful and freely available option.<sup>5</sup> Clever use of search strings in the molecular formula finder coupled with accurate mass calibration will allow speedy interpretation of mystery peaks.

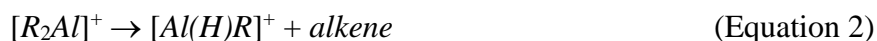
### **3. Ionization techniques**

The remainder of this chapter has been divided into sections based on the type of ionization method used. This factor is more important than the type of mass analyzer used, because the analyzer simply separates and measures the ions once they are safely formed in the gas phase, and all of the different types will provide essentially the same information ( $m/z$  ratio and isotope pattern) with differing degrees of resolution and mass accuracy. We will take an essentially historical approach, wherein we present the most long-standing methods first before moving on to more modern developments. Note that the non-appearance of a particular technique may very well be because no one has actually tried the method rather than it being inherently unsuitable, and a section will be devoted to casting an eye over potentially useful methods that appear to have been as yet underutilized in this field.

The longest established of the ionization techniques in common use,<sup>6</sup> **electron ionization** (EI; sometimes known as electron impact) involves delivering a volatile neutral molecule to the high vacuum source and passing them through a beam of energetic (70 eV) electrons. When these electrons encounter a molecule, they interact and result in the ejection of an electron to make a radical cation,  $[M]^{+\bullet}$ . Excess internal energy in this ion often results in bond-breaking to form fragments  $[M-R]^+$  and  $R^\bullet$ .<sup>7</sup> Because Al is electropositive, EI-MS of organoaluminum species generates charged fragments that nearly always retain Al,<sup>8</sup> i.e.



Further fragmentation of the charged fragment ion can occur through loss of a neutral molecule to generate further fragment ions e.g. through beta-elimination (Equation 2) or reductive elimination (Equation 3).



Provided the organoaluminum species can be transported into the source without decomposition, heat and exposure to high vacuum is enough to drive organoaluminum species with any sort of volatility into the gas phase for subsequent analysis.

A wide variety of organoaluminums have accordingly been characterized by EI-MS, especially those of low molecular weight. An illustrative example is that of  $AlEt_3$ , which exhibits a molecular ion as well as extensive fragmentation (Figure 2). The related compound  $Et_2AlCl$

exhibits a mass spectrum with the characteristic chlorine isotope pattern (75%  $^{35}\text{Cl}$ , 25%  $^{37}\text{Cl}$ ), and its fragmentation is more complicated than  $\text{AlEt}_3$  by virtue of competing pathways such as loss of  $\text{Cl}$ , rather than  $\text{Et}$  (Figure 3).

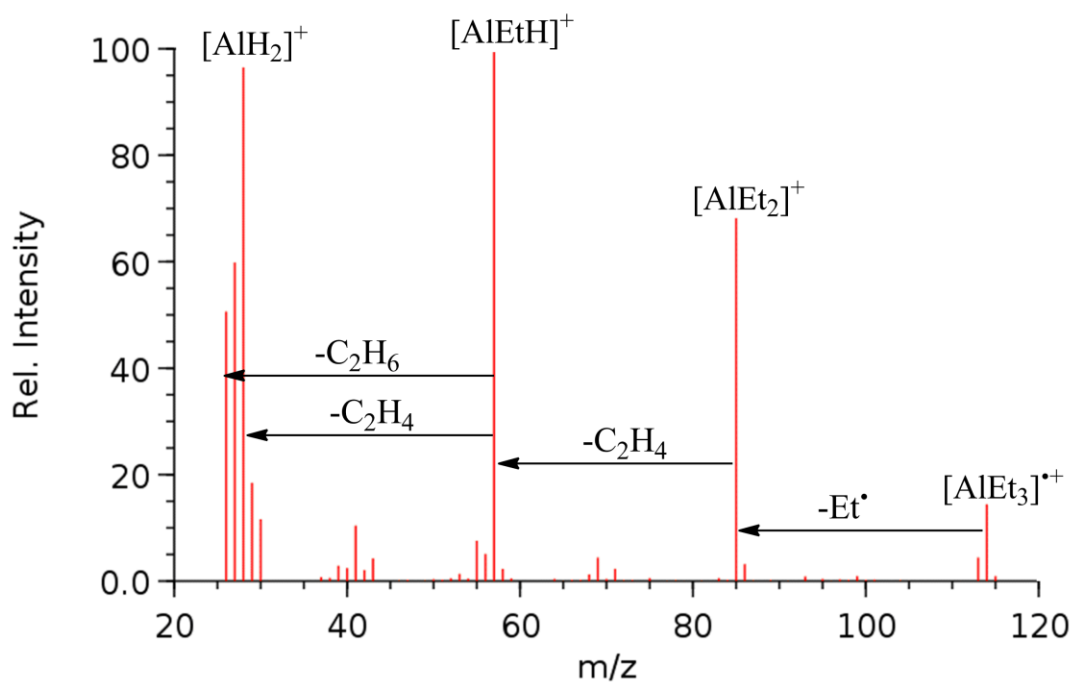


Figure 2. EI mass spectrum of  $\text{AlEt}_3$  (MS data from the NIST Chemistry WebBook). Reproduced with permission from NIST.

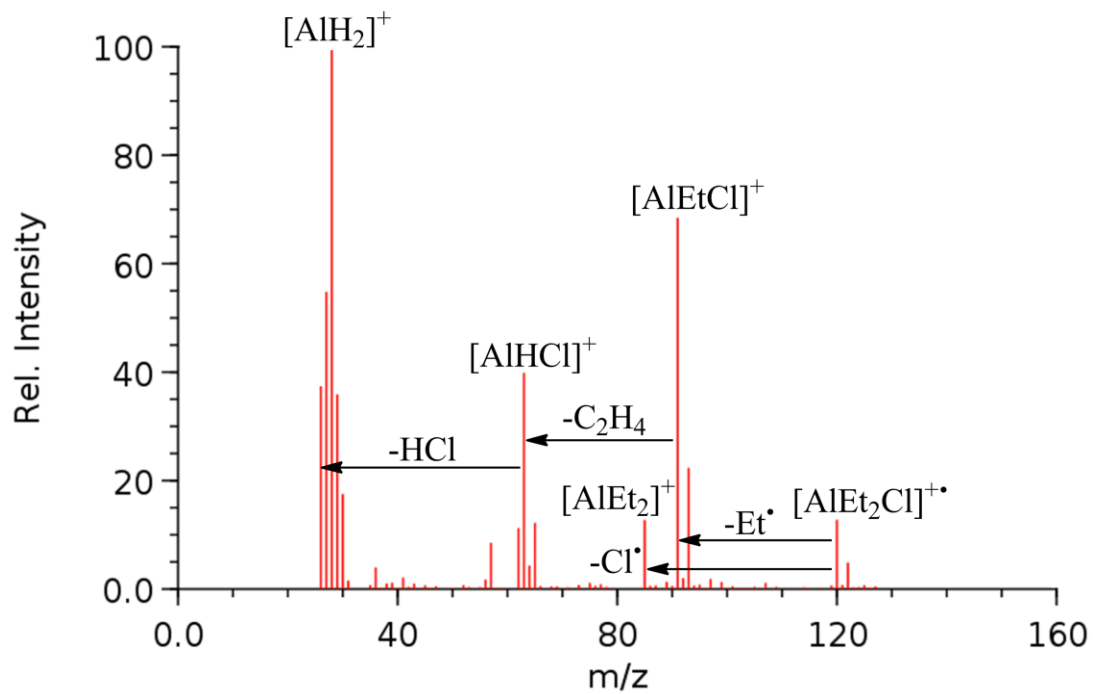


Figure 3. EI mass spectrum of AlEt<sub>2</sub>Cl (MS data from the NIST Chemistry WebBook). Reproduced with permission from NIST.

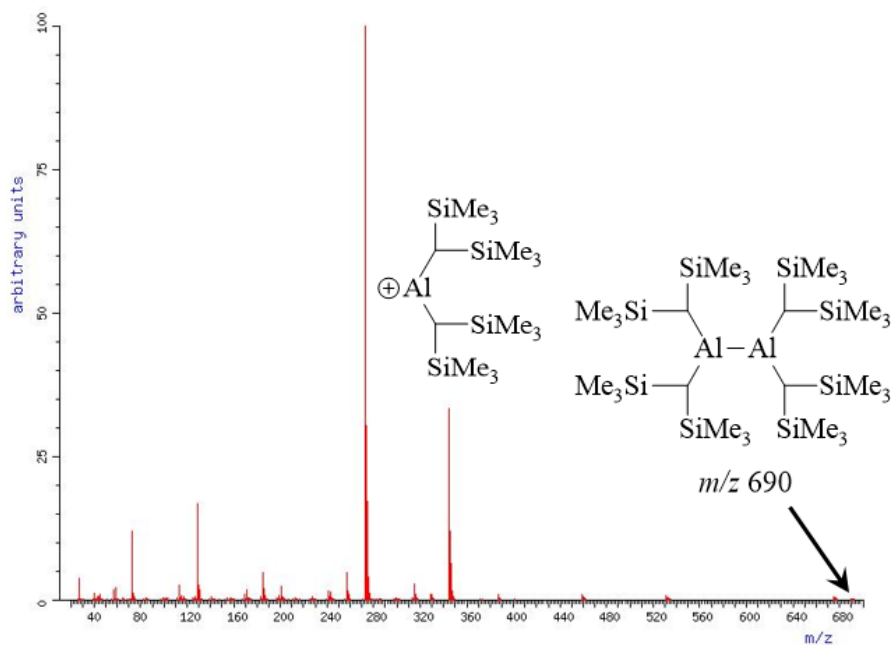


Figure 4. EI-MS of  $(\text{Al}(\text{CH}(\text{SiMe}_3)_2)_2)_2$ .<sup>9</sup> Spectral data were obtained from Wiley Subscription Services, Inc. (US). Note the low abundance of the molecular ion, typical of the EI-MS of high molecular weight analytes. Reproduced by permission of ©DeGruyter Publishing.

EI has seen steady use over the years, and any compound that has a sufficiently high thermal stability to endure its transfer (even in miniscule quantities) to the gas phase under high vacuum is fair game for the technique (Figure 4). Additional representative examples are collected in Figure 5, to give readers an appreciation of the scope of the technique.

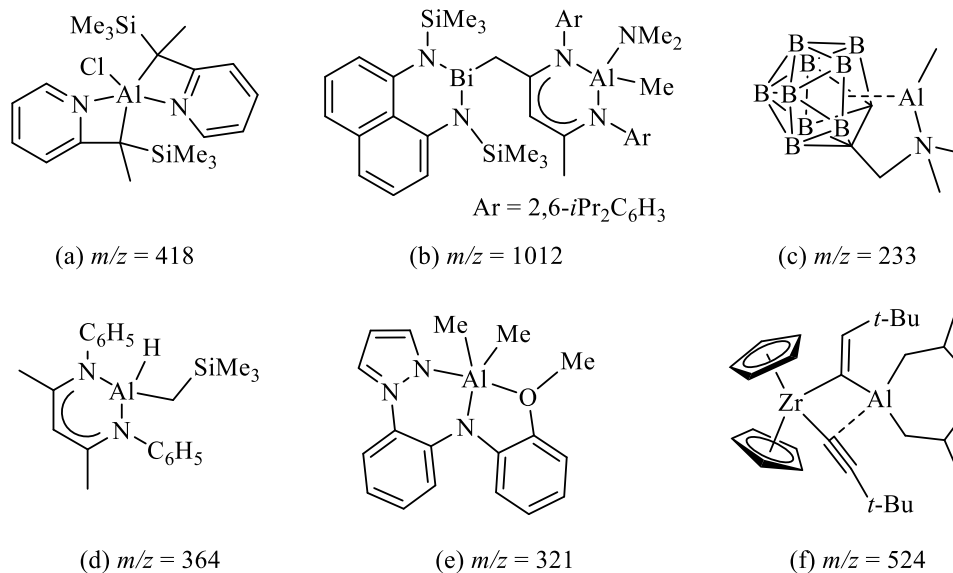


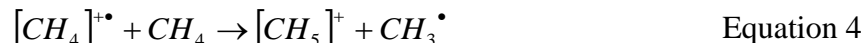
Figure 5. Structures and  $m/z$  values of some organoaluminums characterized by EI MS. The molecular ion was observed for each compound (a),<sup>10</sup> (b),<sup>11</sup> (c),<sup>12</sup> (d),<sup>13</sup> (e),<sup>14</sup> and (f).<sup>15</sup> Reproduced with permission from

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A modern variant of EI that better preserves the molecular ion is **Cold-EI**.<sup>16</sup> In this method, ions are supersonically cooled immediately after production in order to shed their internal energy and make fragmentation less probable. It would seem an attractive choice when attempting analyses of higher molecular weight organoaluminums.

Plenty of compounds studied by EI-MS provide only small or non-existent molecular ions due to the high energy of the process. Because the molecular weight is the critical parameter for a successful identification, early efforts were made to provide softer forms of ionization.<sup>17</sup>

Chemical ionization is a relatively simple modification of EI-MS wherein an excess of a so-called reagent gas is introduced into the source along with the analyte.<sup>18</sup> Due to its abundance, it is preferentially ionized and then undergoes a reaction with residual molecules of the reagent gas to provide new, highly acidic species<sup>19</sup> e.g. for methane:



If the  $[CH_5]^+$  encounters any gas-phase analyte, it will efficiently protonate it provided it is more basic than methane<sup>20</sup> (a very low hurdle to cross!) and generate a protonated pseudomolecular ion with a minimum of internal energy and hence not prone to fragmentation:



Chemical ionization has been most frequently applied to organoaluminum species that contain at least one heteroatom (a good target for protonation).<sup>21, 22</sup> Because many mass spectrometers with an EI source are capable of performing CI (modifications are essentially supplying reagent gas to the source chamber), CI is usually run in instances where EI has produced ions but there is reasonable apprehension that the molecular ion may be missing. Representative examples of CI-characterized organoaluminum compounds appear in Figure 6.

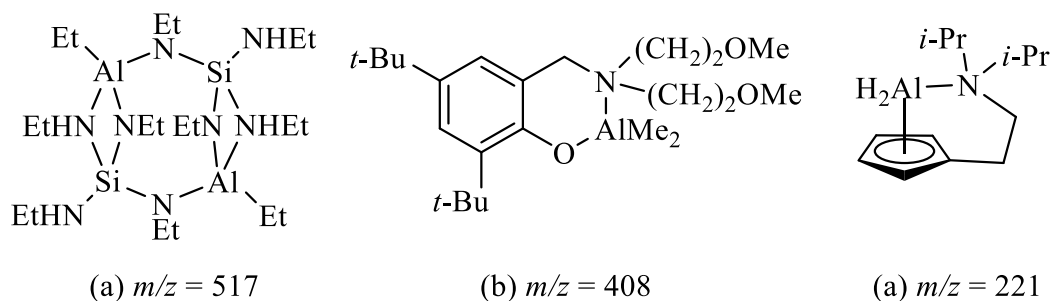


Figure 6. Structures and  $m/z$  values of some CI MS-characterized organoaluminums. (a) isobutane reagent gas  $[M+H]^+$ ;<sup>23</sup> (b)  $[M+H]^+$ ;<sup>21</sup> (c)  $CH_4$  reagent gas  $[M+H]^+$ .<sup>24</sup> Reproduced with permission from ©RSC Publishing, ©ACS Publishing and ©Wiley-VCH Verlag.

**Field ionization (FI) and field desorption (FD)** use high surface area carbon whiskers on an emitter to induce the high field gradients necessary to induce tunneling of an electron from an adsorbed (or nearby) molecule to the emitter.<sup>25</sup> The low internal energy so introduced greatly reduces fragmentation, thus better preserving the molecular ion. The principal limitation of the technique involves the relatively slow experiment (the emitter needs to be slowly increased in temperature) and the tedious preparation of the fragile emitters.<sup>26</sup> The latter limitation has been somewhat ameliorated with the development of **liquid introduction field desorption ionization (LIFDI)**,<sup>27</sup> which has rekindled interest in the essentially moribund FD technique with a simple but elegant methodological improvement. LIFDI allows introduction of the sample via siphoning a solution from a nearby vial or Schlenk flask, which can be deposited and evaporated on the emitter. It is a promising approach for organoaluminum species, because not only is fragmentation reduced compared to EI, it can handle air-sensitive samples routinely. An example is shown in Figure 8 for  $Cp^*_2AlH$ ,<sup>28</sup> showing a molecular ion  $[Cp^*_2AlH]^+$  at  $m/z$  298, along with  $[Al]^+$  at  $m/z$  27 and a signal for toluene at  $m/z$  92 (the solvent used for analysis).

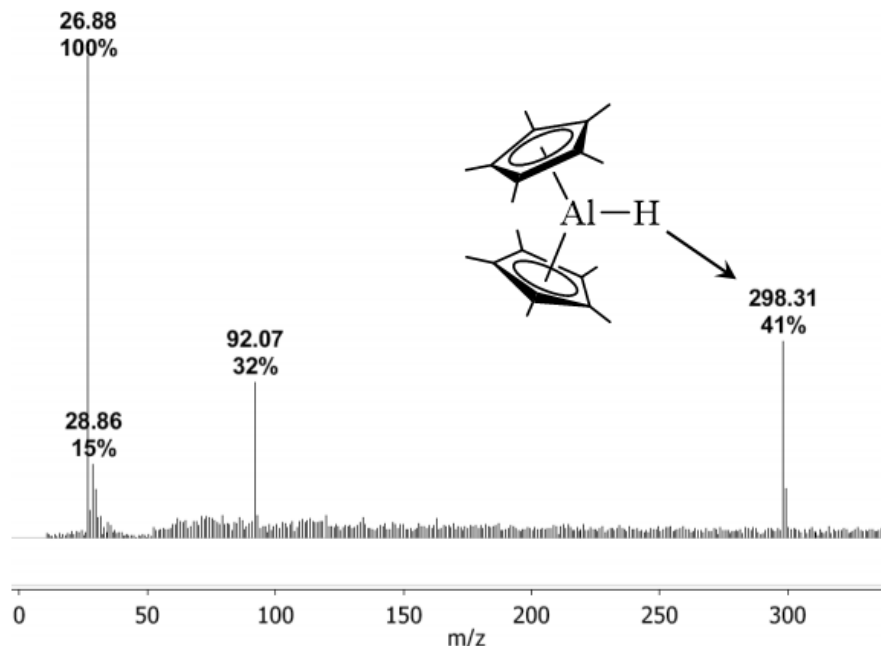


Figure 7. LIFDI-MS of  $(C_5Me_5)_2AlH$  from a toluene solution. Reproduced with permission from ©RSC Publishing.

Other successes in the organoaluminum field include tungsten complexes with Al-carbenoid ligands; *trans,cis,cis*-  $[W(AlCp^*)_2(PMe_3)_2(C_2H_4)_2]$  and  $[W(AlCp^*)_6(C_2H_4)_2]$ , both molecules being characterized as their  $[M]^{++}$  ions.<sup>29</sup> Earlier examples of organoaluminum compounds that were characterized employing FI or FD MS techniques can also be found in the literature.<sup>30</sup>

**Fast atom bombardment (FAB)**<sup>31</sup> and the closely related technique of **liquid secondary ion mass spectrometry (LSIMS)**<sup>32</sup> both involve the energetic collision of fast-moving particles (atoms for FAB, ions for LSIMS) with samples in a low volatility liquid matrix, such as triethanolamine or 3-nitrobenzyl alcohol. Protic matrices are incompatible with most organoaluminums, and even though it is possible to observe the  $[M+H]$  ion under such conditions, better results might be obtained using e.g. 2-nitrophenyloctylether. In the absence of

a source of protons for ionization, adventitious oxidation or cationization with alkali metal ions is necessary for neutral compounds. A recent review<sup>33</sup> outlined successes in the application of soft ionization methods to organometallic compounds, and the only examples of an organoaluminum compound listed, or cited in this review involved analysis by FAB<sup>34</sup> or ESI DART (*vide infra*). This and some other examples are shown in Figure 8 while additional examples are reported in the recent literature.<sup>35</sup>

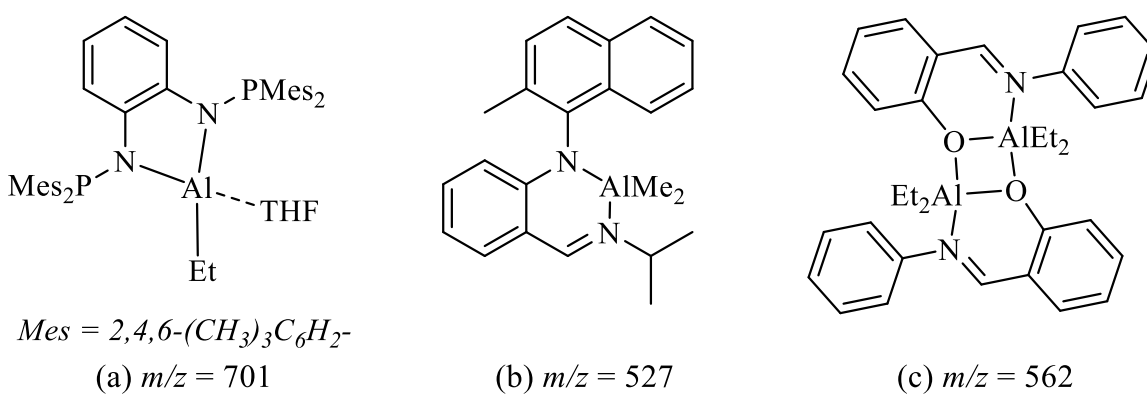


Figure 8. Representative examples of organoaluminum compounds characterized by FAB. Highest mass ion observed was (a) [M-THF]<sup>++</sup>,<sup>34</sup> (b) [M+Na]<sup>+</sup>,<sup>36</sup> (c) [M]<sup>++</sup>.<sup>37</sup> Reproduced with permission from

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There is a single example of the application of LSIMS to an organoaluminum compound (Me<sub>2</sub>AlNEt<sub>2</sub>)<sub>2</sub>; in this case, the compound was dissolved in a volatile (dry) solvent, and syringed onto the insertion probe, cooled to low temperature under a stream of N<sub>2</sub> and located within a specially modified, N<sub>2</sub>-blanketed inlet to the mass spectrometer.<sup>38</sup> The highest mass ion observed in these spectra was [M-Me]<sup>+</sup>, though the fragmentation patterns appear independent of solvent to a first approximation.

While FAB/LSIMS have been largely superseded by other methods, and the same issues of exposure to the atmosphere are experienced as in MALDI,<sup>4</sup> they have a reputation of being all-around techniques, i.e. capable of getting data from a wide range of different types of sample. This property is of course a valuable one, and the extension in mass range is in itself helpful in accessing different types of compounds, especially those containing multiple metals and/or complex structures.

**Electrospray ionization mass spectrometry (ESI-MS)** was developed in the late 1980s,<sup>39</sup> and along with MALDI (vide supra) was responsible for a massive expansion in the field of mass spectrometry.<sup>40</sup> No longer were MS analyses restricted to volatile, thermally robust materials - now, anything that was soluble in polar solvents such as methanol seemed to be fair game. This included previously unheard of substrates such as high molecular weight proteins, small molecules, and ionic compounds of all sorts.<sup>41</sup> However, it failed to have much of an impact in the field of organoaluminum compounds, because (a) it was already reasonably well-served by traditional methods and (b) running air-sensitive materials through an instrument whose normal operation involves the use of protic solvents can be an unrewarding exercise. Nonetheless, there remained organoaluminum compounds for which EI or CI was not a good choice, and methodological problems can always be solved if the motivation is there, so there do exist some nice examples of ESI-MS being applied to such systems,<sup>42</sup> with some representative structures shown in Figure 9.

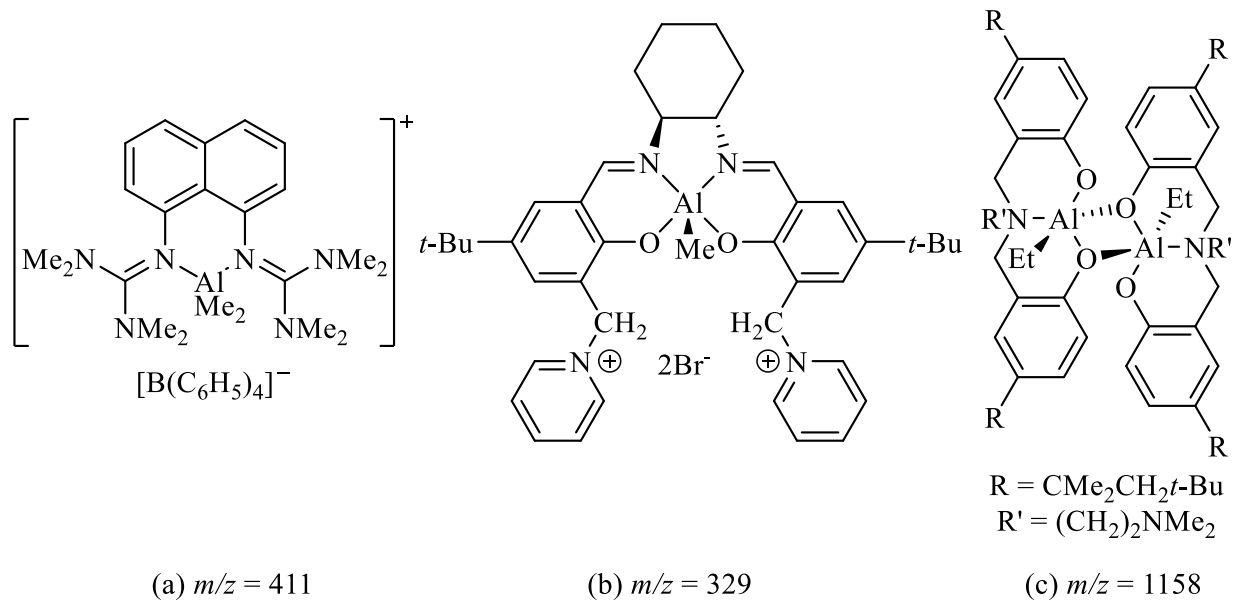


Figure 9. Structures of some organoaluminum compounds characterized by ESI-MS (a)  $[M]^+$ ,<sup>43</sup> (b)  $[M-2Br]^{2+44}$  (c)  $[M+H]^+$ .<sup>45</sup> Reproduced with permission from ©Wiley-VCH Verlag, and ©RSC Publishing.

Aluminoxanes are a class of poorly-defined, oligomeric materials formed by partial hydrolysis of  $AlR_3$  precursors, many of which are effective activators of olefin polymerization catalysts.<sup>46</sup>

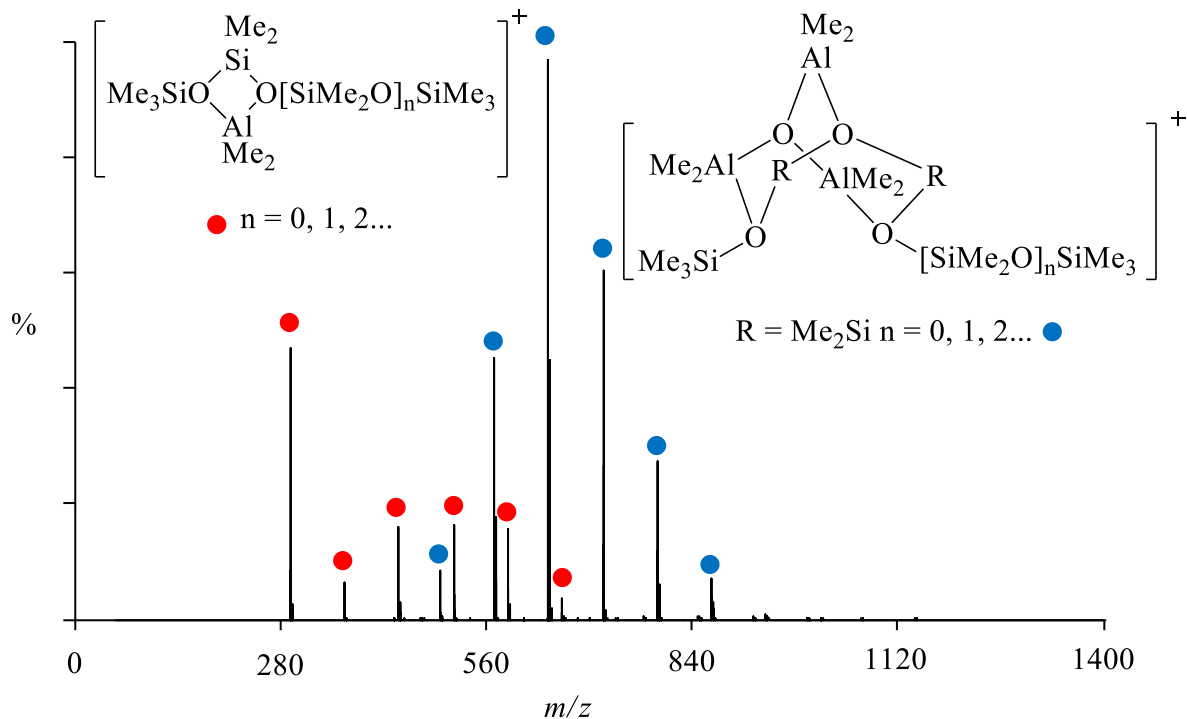


Figure 10. Positive ion ESI MS of a mixture of methylaluminoxane (MAO) and trace levels of silicone grease in fluorobenzene solution with proposed structures of the major ions depicted. Reproduced with permission from ©ACS Publishing.

Higher molecular weight involatile materials predictably have resisted characterization by most mass spectrometric approaches, but ESI-MS is capable of providing insights into the structure of the charged components of these mixtures.<sup>47</sup> In the case of methylaluminoxane, ESI-MS experiments in the presence of suitable donors show that the cations present are derived by coordination of  $[\text{Me}_2\text{Al}]^+$  and other Lewis acidic homologs to the donors (see e.g. Figure 10).<sup>48</sup> The corresponding negative ion spectra of these mixtures are largely independent of the donor additive (see Figure 11) and evidently the anions present are weakly coordinating in that they are paired with metallocenium ions, active in polymerization catalysis.<sup>49</sup>

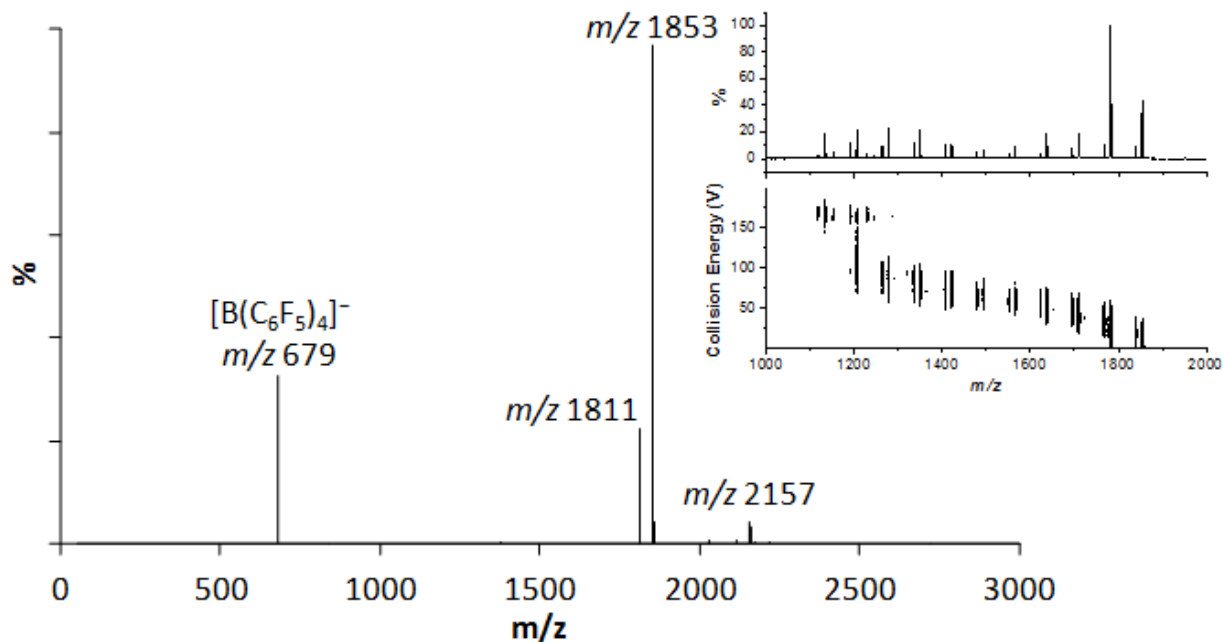


Figure 11. Corresponding negative ion spectrum of MAO + silicone grease in the presence of  $[(^{13}C_{18}H_{37})_4N][B(C_6F_5)_4]^-$  standard; inset - Tandem MS/MS spectrum and energy dependent (ED) ESI MS of the anion with  $m/z$  1853 showing 10 consecutive losses of  $AlMe_3$  as the collision energy is increased.

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Variants on ESI-MS have been developed that have increased the scope of the technique.

**Atmospheric pressure chemical ionization** (APCI) involves the addition of a sharp pin with a high charge to generate a corona discharge;<sup>50</sup> this effectively generates high concentrations of charged solvent molecules in the gas phase that are capable of protonating relatively low basicity substrates. **Atmospheric pressure photoionization** (APPI) uses UV light to ionize solvents such as acetone or toluene (these may be added as dopants), and the resulting radical cations are capable of oxidizing electron-rich metal-containing species in the gas phase.<sup>51</sup> While neither have been used widely for organoaluminums,<sup>52</sup> an illustrative and useful paper compared ESI, APCI and APPI performance on the complex (R,R)-[Salen-tBu]AlMe.<sup>53</sup> ESI-MS was found to be the most sensitive by a factor of 2 over APCI. An **atmospheric solids analysis probe** (ASAP)

uses the heated nitrogen desolvation gas to vaporize solid samples and a corona discharge for sample ionization, allowing low polarity compounds not amenable to ESI, APCI and APPI to be ionized with a high degree of sensitivity.<sup>54</sup> It has not been widely applied to organoaluminum compounds, but one example - albeit with a fair degree of fragmentation - has been reported recently (Figure 12).<sup>55</sup>

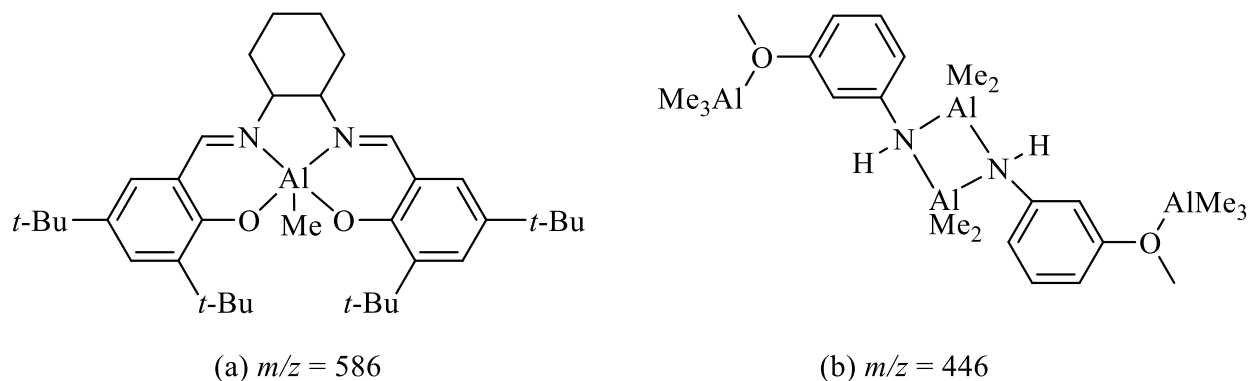


Figure 12. (a) Aluminum salen complex analyzed by ESI, APCI and APPI  $[M]^+$ ,<sup>53</sup> (b)  $[M + H - AlMe_2]^+$ .<sup>55</sup> Reproduced with permission from ©John Wiley & Sons Publishing and ©RSC Publishing.

Another modern variant on ESI is **cold spray**, essentially a cryogenically cooled ESI source capable of generating ions from solutions cooled to as low as  $-80^\circ\text{C}$ .<sup>56</sup> It makes the soft ionization of ESI even lower energy, and can preserve weak interactions present in solution into the gas phase. It does not yet appear to have been applied to organoaluminum chemistry, but may well prove to be a promising approach.

**Matrix assisted laser desorption ionization (MALDI)**<sup>57</sup> is probably the most prominent of the methods that has had minimal uptake in the field of organoaluminum compounds, despite success with other organometallic species.<sup>58</sup> There are two reasons why that may be the case: (1)

the analyte needs to be co-crystallized (or intimately mixed) with a large excess of a matrix with a UV chromophore, and given the tiny quantities involved in mass spectrometry the chances of hydrolysis through adventitious water are high and (2) few MALDI mass spectrometers have the facility to protect the sample from the atmosphere. Problem 1 can presumably be addressed through the use of scrupulously dried, neutral matrices such as 1,4-benzoquinone or polyaromatic matrices (pyrene, anthracene, etc.) may be good options, but problem 2 requires rather more effort in terms of preparation. One of the few examples characterized by this technique (though no matrix is specified) is the Al-Si cluster compound shown in Figure 13.<sup>59</sup>

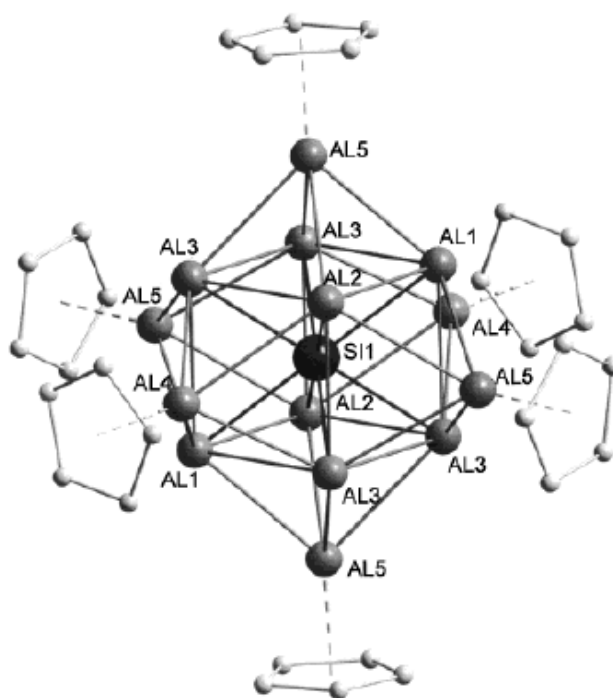


Figure 13. X-ray structure of a Cp\*Al-Si cluster (methyl groups omitted for clarity) analyzed by MALDI-TOF MS -  $m/z$  1217 ( $M^+$ ), 1081 ( $M^+ - Cp^*$ ).<sup>59</sup> Reproduced with permission from ©ACS Publishing.

**Direct analysis in real time (DART)** is an ionization technique that uses electronically excited helium atoms,  $He^*$ , to ionize samples of interest.<sup>60</sup> It is an appealing technique in that it requires a minimum of sample preparation: the analyte is simply held next to the source of the excited

atoms, and the newly-formed ions are drawn into the inlet to the mass spectrometer. The compound shown in Figure 14 was characterized using this method.

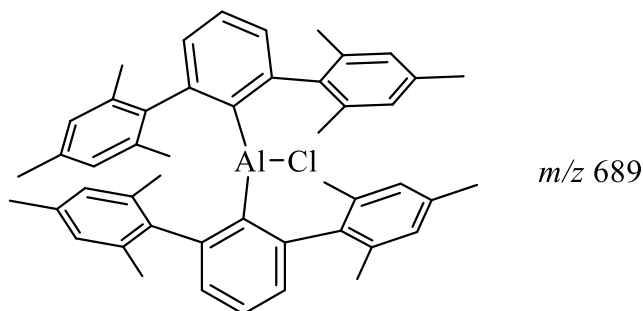


Figure 14. An organoaluminum compound characterized by DART as an  $[M + H]^+$  ion.<sup>61</sup> Reproduced with permission by ©Wiley-VCH Verlag.

#### 4. What ionization technique should I use for my sample?

Deciding on what MS technique to use for a particular sample can be complicated. Generally, the bigger and more expensive the instrument, the higher the resolution, and for the best possible data, higher resolution is better. However, more important than that is whether the information you collect is actually meaningful. In order to maximize the chances of a useful analysis, Figure 15 shows a decision-aiding flowchart that requires only that you know something about the physical properties of your sample. Of course, it is rare to have access to all of these, and the limits of any technique can always be pushed by a creative analyst, so don't be put off from trying your luck.

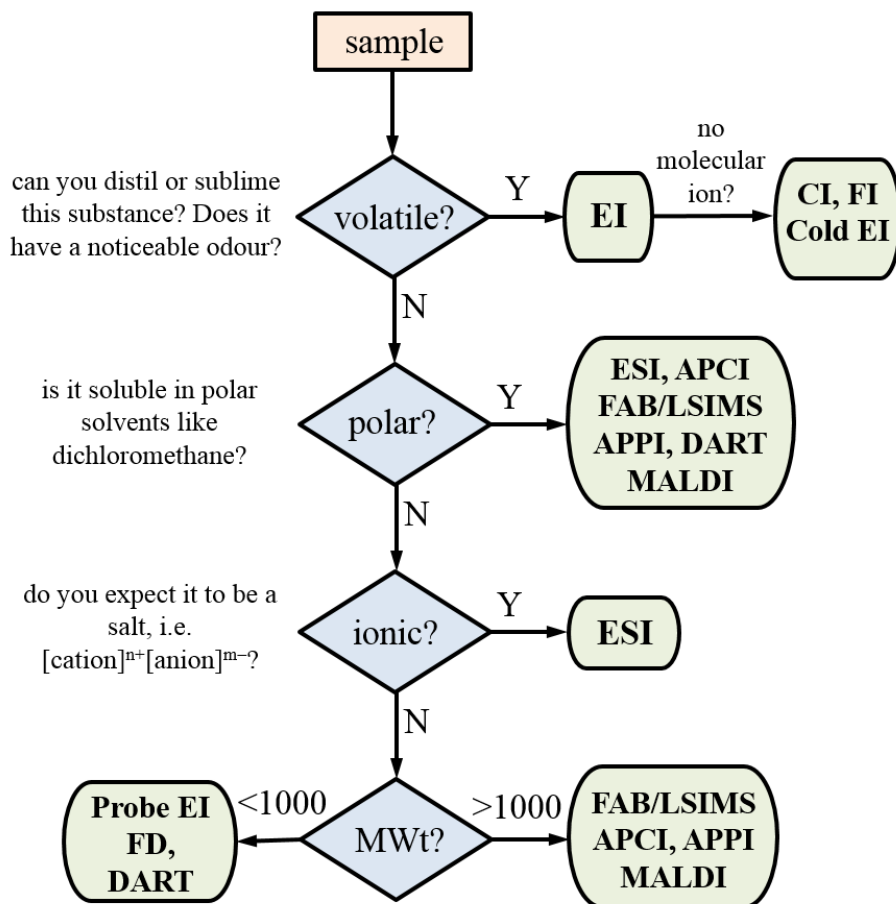


Figure 15. How to choose an ionization technique - a rough guide.

## 5. Conclusions

Organoaluminum compounds are among the most challenging of samples to analyze by mass spectrometry, but nearly every method has been attempted and there is precedent for the characterization of a wide range of different structures. Careful precautions to avoid sample decomposition are a critical part of any successful analysis.

## 6. Acknowledgements

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## 7. References

1. M. R. Litzow, T. R. Spalding, *Mass spectrometry of inorganic and organometallic compounds*, Elsevier Scientific Pub. Co., Amsterdam, New York, 1973.
2. W. Henderson, J. S. McIndoe, *Mass Spectrometry of Inorganic and Organometallic Compounds: Tools - Techniques - Tips*, John Wiley & Sons Publishers, Hoboken, NJ, 2005.
3. A. T. Lubben, J. S. McIndoe, A. S. Weller, *Organometallics*, **27**, 3303, (2008).
4. M. D. Eelman, J. M. Blacquiere, M. M. Moriarty, D. E. Fogg, *Angew. Chem.-Int. Ed.*, **47**, 303, (2008).
5. L. Patiny, A. Borel, *J. Chem. Inf. Model.*, **53**, 1223, (2013).
6. F. H. Field, J. L. Franklin, *Electron impact phenomena and the properties of gaseous ions*, Academic Press, NY, 1957.
7. J. H. Gross, *Gas Phase Ion Chemistry*, Springer-Verlag Publishers, NY, 2004.
8. (a) D. Stockigt, J. Schwarz, H. Schwarz, *J. Phys. Chem.*, **100**, 8786, (1996); (b) R. Srinivas, D. Sulzle, H. Schwarz, *J. Am. Chem. Soc.*, **112**, 8334, (1990).
9. W. Uhl, *Z. Naturforsch. B*, **43**, 1113, (1988).
10. N. C. Breit, T. Ancelet, J. W. Quail, G. Schatte, J. Müller, *Organometallics*, **30**, 6150, (2011).
11. S. P. Sarish, B. Nekoueshahraki, A. Jana, H. W. Roesky, T. Schulz, D. Stalke, *Chem. Eur. J.*, **17**, 890, (2011).
12. J. D. Lee, S. K. Kim, T. J. Kim, W. S. Han, Y. J. Lee, D. H. Yoo, M. Cheong, J. Ko, S. O. Kang, *J. Am. Chem. Soc.*, **130**, 9904, (2008).
13. W. Uhl, B. Jana, *J. Organomet. Chem.*, **694**, 1101, (2009).
14. K. F. Peng, C. T. Chen, *Dalton Trans.*, **44**, 9800, (2009).
15. V. V. Burlakov, K. Kaleta, T. Beweries, P. Arndt, W. Baumann, A. Spannenberg, V. B. Shur, U. Rosenthal, *Organometallics*, **30**, 1157, (2011).
16. A. Amirav, A. Gordin, M. Poliak, A. B. Fialkov, *J. Mass Spectrom.*, **43**, 141, (2008).
17. V. L. Tal'roze, A. K. Ljubimova, *J. Mass Spectrom.*, **33**, 502, (1998).
18. M. S. B. Munson, F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621, (1966).
19. A. J. R. Heck, L. J. Dekoning, N. M. M. Nibbering, *J. Am. Soc. Mass Spectrom.*, **2**, 453, (1991).
20. M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 2332, (1965).
21. A. R. F. Cox, V. C. Gibson, E. L. Marshall, A. J. P. White, D. Yeldon, *Dalton Trans.*, **42**, 5014, (2006).
22. (a) C. J. Carmalt, S. J. King, J. D. Mileham, E. Sabir, D. A. Tocher, *Organometallics*, **23**, 2939, (2004); (b) C. Krempner, H. Reinke, K. Weichert, *Organometallics*, **26**, 1386, (2007); (c) N. W. Mitzel, C. Lustig, M. Woski, *Z. Naturforschung B*, **58**, 363, (2003); (d) V. C. Gibson, D. Nienhuis, C. Redshaw, A. J. P. White, D. J. Williams, *Dalton Transactions*, **11**, 1761, (2004).

23. S. Kaskel, C. W. Lehmann, G. Chaplais, K. Schlichte, M. Khanna, *Eur. J. Inorg. Chem.*, **6**, 1193, (2003).
24. S. Bensiek, M. Bangel, B. Neumann, H. G. Stammer, P. Jutzi, *Organometallics*, **19**, 1292, (2000).
25. (a) H. D. Beckey, *Principles of Field Ionization and Field Desorption Mass Spectrometry: International Series in Analytical Chemistry*, Pergamon, Oxford, UK, 1977; (b) H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 500, (1969); (c) H. D. Beckey, A. Heindrichs, H. U. Winkler, *Int. J. Mass Spectrom. Ion Phys.*, **3**, A9, (1970).
26. R. P. Lattimer, H. R. Schulten, *Anal. Chem.*, **61**, 1201, (1989).
27. H. B. Linden, *Eur. J. Mass Spectrom.*, **10**, 459, (2004).
28. C. Ganesamoorthy, S. Loerke, C. Gemel, P. Jerabek, M. Winter, G. Frenking, R. A. Fischer, *Chem. Commun.*, **49**, 2858, (2013).
29. M. Molon, C. Gemel, R. A. Fischer, *J. Organomet. Chem.*, **751**, 573, (2014).
30. (a) J. Pinkas, D. Chakraborty, Y. Yang, R. Murugavel, M. Noltemeyer, H. W. Roesky, *Organometallics*, **18**, 523, (1999); (b) U. Dembowski, M. Noltemeyer, J. W. Gilje, H. W. Roesky, *Chem. Ber.*, **124**, 1917, (1991); (c) W. Uhl, I. Hahn, M. Koch, M. Layh, *Inorg. Chim. Acta*, **249**, 33, (1996).
31. (a) D. J. Surman, J. C. Vickerman, *J. Chem. Soc. Chem. Commun.*, 324, (1981); (b) M. Barber, R. S. Bordoli, R. D. Sedgwick, A. N. Tyler, *Nature*, **293**, 270, (1981); (c) M. Barber, R. S. Bordoli, R. D. Sedgwick, A. N. Tyler, *Biomed. Mass Spectrom.*, **8**, 492, (1981).
32. (a) J. Sunner, *Org. Mass Spectrom.*, **28**, 805, (1993); (b) W. Aberth, K. M. Straub, A. L. Burlingame, *Anal. Chem.*, **54**, 2029, (1982).
33. R. Jirásko, M. Holčápek, *Mass Spectrom. Rev.*, **30**, 1013, (2011).
34. F. Majoumo-Mbe, E. Smolensky, P. Lonneck, D. Shpasser, M. S. Eisen, E. Hey-Hawkins, *J. Mol. Catal. A Chem.*, **240**, 91, (2005).
35. (a) A. K. Jain, R. Bohra, R. C. Mehrotra, *Main Group Met. Chem.*, **27**, 113, (2004); (b) A. Schisler, P. Lonneck, T. Gelbrich, E. Hey-Hawkins, *Dalton Trans.*, 2895, (2004); (c) J. C. Cannadine, W. Errington, P. Moore, M. G. H. Wallbridge, E. Nield, D. Fenn, *J. Organomet. Chem.*, **486**, 237, (1995); (d) S. A. Ahmed, M. S. Hill, P. B. Hitchcock, S. M. Mansell, O. S. John, *Organometallics*, **26**, 538, (2007); (e) T. Iijima, T. Yamamoto, *J. Organomet. Chem.*, **691**, 5016, (2006).
36. K. Hayashi, Y. Nakajima, F. Ozawa, T. Kawabata, *Chem. Lett.*, **39**, 643, (2010).
37. A. K. Jain, A. Gupta, R. Bohra, I. P. Lorenz, P. Mayer, *Polyhedron*, **25**, 654, (2006).
38. M. W. Huang, H. L. Chei, J. P. Huang, J. Shiea, *Anal. Chem.*, **71**, 2901, (1999).
39. J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong, C. M. Whitehouse, *Science*, **246**, 64, (1989).
40. (a) C. A. Schalley, P. B. Armentrout, *Modern mass spectrometry*, Springer, NY, 2003; (b) D. T. Rossi, M. Sinz, *Mass spectrometry in drug discovery*, CRC Press, NY, 2002; (c) G. Siuzdak, *The Expanding Role of Mass Spectrometry in Biotechnology, 2nd Ed.*, MCC Press, San Diego, 2006.
41. (a) A. J. R. Heck, R. H. H. v. d. Heuvel, *Mass Spectrom. Rev.*, **23**, 368, (2004); (b) M. H. Amad, N. B. Cech, G. S. Jackson, C. G. Enke, *J. Mass Spectrom.*, **35**, 784, (2000); (c) S. Cristoni, L. R. Bernardi, *Mass Spectrom. Rev.*, **22**, 369, (2003); (d) C. A. Schalley, *Int. J. Mass Spectrom.*, **194**, 11, (2000).
42. (a) A. Lorbach, A. Nadj, S. Tüllmann, F. Dornhaus, F. Schodel, I. Sanger, G. Margraf, J. W. Bats, M. Bolte, M. C. Holthausen, M. Wagner, H. W. Lerner, *Inorg. Chem.*, **48**, 1005, (2009); (b) F. Qian, K. Y. Liu, H. Y. Ma, *Dalton Trans.*, **39**, 8071, (2010); (c) K. Albahily, E. Koc, D. Al-Baldawi, D. Savard, S. Gambarotta, T. J. Burchell, R. Duchateau, *Angew. Chem. Int. Ed.*, **47**, 5816, (2008); (d) P. M. Castro, P. Lahtinen, K. Axenov, J. Viidanoja, T. Kotiaho, M. Leskela, T. Repo, *Organometallics*, **24**, 3664, (2005); (e) S. Caille, S. Cui, T. L. Hwang, X. Wang, M. M. Faul, *J. Org. Chem.*, **74**, 3833, (2009); (f) S. L. Yao, Y. Xiong, M. Driess, *Chem. Eur. J.*, **18**,

- 11356, (2012); (g) Z. M. Dzhabieva, S. V. Topilin, T. S. Dzhabiev, *Russ. J. Phys. Chem. A*, **86**, 875, (2012).
43. M. Reinmuth, U. Wild, D. Rudolf, E. Kaifer, M. Enders, H. Wadepohl, H. J. Himmel, *Eur. J. Inorg. Chem.*, 4795, (2009).
44. T. Kull, J. Cabrera, R. Peters, *Chem. Eur. J.*, **16**, 9132, (2010).
45. E. Kober, Z. Janas, T. Nerkowski, L. B. Jerzykiewicz, *Dalton Trans.*, **42**, 10847, (2013).
46. W. Kaminsky, *Macromolecules*, **45**, 3289, (2012); W. Kaminsky, H. Sinn, *Adv. Organomet. Chem.*, **18**, 99, (1980).
47. M. A. Henderson, T. K. Trefz, S. Collins, M. Y. Wang, J. S. McIndoe, *Organometallics*, **32**, 2079, (2013).
48. T. K. Trefz, M. A. Henderson, M. Y. Wang, S. Collins, J. S. McIndoe, *Organometallics*, **32**, 3149, (2013).
49. T. K. Trefz, M. A. Henderson, M. Linnolahti, S. Collins, J. S. McIndoe, *Chem. Eur. J.*, **21**, 2980, (2015).
50. A. P. Bruins, *Mass Spectrom. Rev.*, **10**, 53, (1991); M. Tsuchiya, *Adv. Mass Spectrom.*, **13**, 333, (1995).
51. (a) A. Raffaelli, A. Saba, *Mass Spectrom. Rev.*, **22**, 318, (2003); (b) C. M. Yang, J. Henion, *J. Chromatogr. A*, **970**, 155, (2002); (c) D. B. Robb, T. R. Covey, A. P. Bruins, *Anal. Chem.*, **72**, 3653, (2000); (d) J. A. Syage, K. A. Hanold, T. C. Lynn, J. A. Horner, R. A. Thakur, *J. Chromatogr. A*, **1050**, 137, (2004); (e) T. J. Kauppila, T. Kuuranne, E. C. Meurer, M. N. Eberlin, T. Kotiaho, R. Kostianen, *Anal. Chem.*, **74**, 5470, (2002).
52. (a) E. C. Meurer, L. L. da Rocha, R. A. Pilli, M. N. Eberlin, L. S. Santos, *Rapid Commun. Mass Sp.*, **20**, 2626, (2006); (b) R. J. Baker, M. Brym, C. Jones, M. Waugh, *J. Organomet. Chem.*, **689**, 781, (2004).
53. B. Slominska, W. Chaladaj, W. Danikiewicz, *J. Mass Spectrom.*, **49**, 392, (2014).
54. (a) C. McEwen, S. Gutteridge, *J. Am. Soc. Mass Spectrom.*, **18**, 1274, (2007); (b) C. N. McEwen, R. G. McKay, B. S. Larsen, *Anal. Chem.*, **77**, 7826, (2005).
55. Y. Z. Li, K. Q. Zhao, M. R. J. Elsegood, T. J. Prior, X. S. Sun, S. Y. Mo, C. Redshaw, *Catal. Sci. Technol.*, **4**, 3025, (2014).
56. (a) K. Yamaguchi, *J. Mass Spectrom.*, **38**, 473, (2003); (b) I. Elguraish, K. L. Zhu, L. A. Hernandez, H. Amarne, J. W. Luo, V. N. Vukotic, S. J. Loeb, *Dalton Trans.*, **44**, 898, (2015).
57. (a) F. Hillenkamp, J. Peter-Katalinic, *MALDI-MS: A Practical Guide to Instrumentation, Methods and Applications*, John Wiley & Sons, Weinheim, 2007; (b) M. Karas, D. Bachmann, F. Hillenkamp, *Anal. Chem.*, **57**, 2935, (1985); (c) M. Karas, D. Bachmann, U. Bahr, F. Hillenkamp, *Int. Journal Mass Spectrom. Ion Proc.*, **78**, 53, (1987).
58. M. F. Wyatt, *J. Mass Spectrom.*, **46**, 712, (2011).
59. A. Purath, C. Dohmeier, A. Ecker, R. Koppe, H. Krautscheid, H. Schnockel, R. Ahlrichs, C. Stoermer, J. Friedrich, P. Jutzi, *J. Am. Chem. Soc.*, **122**, 6955, (2000).
60. R. B. Cody, J. A. Laramee, H. D. Durst, *Anal. Chem.*, **77**, 2297, (2005).
61. J. D. Young, M. A. Khan, D. R. Powell, R. J. Wehmschulte, *Eur. J. Inorg. Chem.*, **2007**, 1671, (2007).