



Cite this: *Dalton Trans.*, 2016, **45**, 15552

Electron ionization mass spectrometric analysis of air- and moisture-sensitive organometallic compounds†

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Electron ionization (EI) is a reliable mass spectrometric method for the analysis of the vast majority of thermally stable and volatile compounds. In direct EI-MS, the sample is placed into the probe and introduced to the source. For air- and moisture-sensitive organometallic complexes, the sample introduction step is critical. A small quantity must be briefly exposed to the atmosphere, during which time decomposition can occur. Here we present a simple tool that allows convenient analysis of air- and moisture-sensitive organometallic species by direct probe methods: a small purge-able glove chamber affixed to the front end of the mass spectrometer. Using the upgraded mass spectrometer, we successfully characterized a series of air- and moisture-sensitive organometallic complexes, ranging from mildly to very air-sensitive.

Received 29th July 2016,
Accepted 2nd September 2016

DOI: 10.1039/c6dt03020c

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Introduction

Electron ionization is a long-standing, reliable method for the analysis of volatile, non-polar compounds, including organometallics.¹ Samples are typically introduced either as effluent from a GC column, or for compounds that are insufficiently volatile or too reactive to survive passage through the column, placed on a sample holder or transferred directly into the source. For reactive organometallics, the sample introduction step is deeply problematic: a small quantity must be briefly exposed to the atmosphere, during which time (sometimes catastrophic) decomposition can occur.

Solutions to this problem include simply performing the necessary actions at speed, thus limiting exposure, performing the transfer under an open flow of inert gas, or attaching a flexible glovebag to the front end of the instrument.² For analysis by liquid secondary ion (LSIMS), organic solvents have been used as matrices under a low-temperature stream of nitrogen gas.³ Similar approaches have been taken for MALDI analysis.⁴ Integrating a fully-functional glovebox with the mass spectrometer has proved a successful approach for both MALDI⁵ and ESI⁶ mass spectrometry (ESI-MS has the methodological advantage that samples can be introduced in solution anaerobically *via* gas-tight syringe⁷ or pressurized sample introduction⁸ from a reaction flask). We report here a simple, reliable

design that is more permanent than a glovebag but requires much less investment than a full glovebox – a small purge-able glove chamber affixed to the front end of the mass spectrometer that allows convenient analysis of reactive organometallic species by direct probe methods. A 3D model and a photograph of the experimental setup appear in Fig. 1.

Results and discussion

Instrumental setup

The glove chamber is fabricated out of plexiglass, assembled with M2 SS Hex screws and sealed without adhesive or sealant. The dimensions of the chamber are 165 × 165 × 152 mm and the glove ports have a diameter of 89 mm. The gloves are disposable, flock lined, 0.02 mm thick nitrile (Dura Flock, Microflex Corporation NV). They are attached to the glove ports with electrical tape. Prior to the analysis, the chamber is flushed with a supply of dry nitrogen for 10 to 15 minutes with a constant flow of 20 L min⁻¹. The gas flow is reduced to half its value for the sample introduction and severely lowered after insertion of the probe into the mass spectrometer, at which point only a positive pressure needs to be maintained.

Mass spectrometric study

A variety of organometallic compounds were investigated using this modified instrument, ranging from relatively robust, briefly air-stable compounds such as cobalt carbonyl and zirconocene dichloride, to more sensitive compounds such as reduced titanocene dichloride (used as an indicator for O₂ in the atmosphere of gloveboxes)⁹ and pyrophoric compounds such as triisobutylaluminium.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6dt03020c

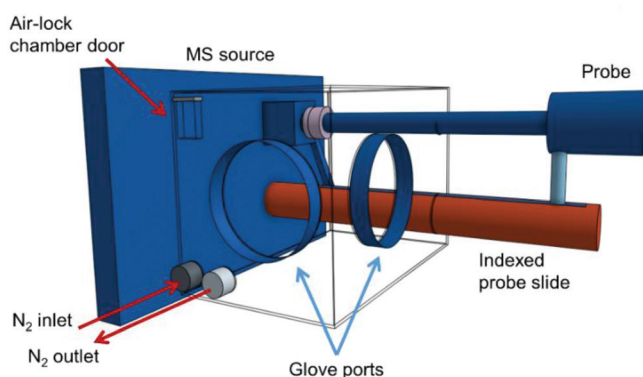


Fig. 1 Left: Schematic of the glove chamber. Right: Glove chamber in place on direct probe EI-MS.

Fig. 2 shows the mass spectrum of $\text{Co}_2(\text{CO})_8$, a metal carbonyl complex representative of this class of compound: it is relatively robust and volatile. It provides high quality EI mass spectra¹⁰ involving fragments that arise from CO loss and/or metal–metal bond cleavage; this behavior is typical of metal carbonyl clusters in general.¹¹

Metallocene complexes are also often volatile and thermally stable. Ferrocene derivatives in particular provide excellent EI mass spectra with strong molecular ions, because loss of a single electron to form ferrocenium ions results in a complex that overall is still strongly bound.¹² Ferrocene is not air- or moisture-sensitive so we tried instead ZrCp_2Cl_2 , ZrCp_2Me_2 , TiCp_2Cl_2 , and TiCp_2Cl . ZrCp_2X_2 ($\text{X} = \text{Cl}, \text{Me}$) both provided spectra with molecular ions and fragments consistent with their known structures (Fig. 3).¹³ For ZrCp_2Me_2 the base peak in the spectrum was $[\text{Cp}_2\text{Zr}]^+$ whereas for ZrCp_2Cl_2 it was $[\text{CpZrCl}]^+$. Me^+ was more promptly lost from $[\text{Cp}_2\text{ZrMe}_2]^+$ than Cl^+ was lost from $[\text{Cp}_2\text{ZrCl}_2]^+$, and the dimethyl compound also readily eliminated ethane whereas Cl_2 loss was entirely absent from the spectrum of Cp_2ZrCl_2 . Dimethyl compounds are of course much more prone to reductive elimination than

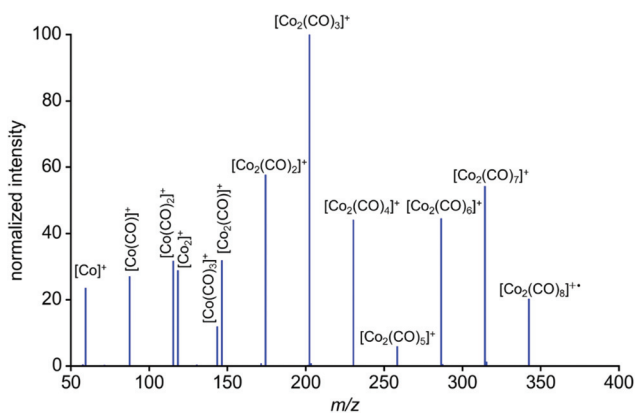


Fig. 2 EI-MS of $\text{Co}_2(\text{CO})_8$. Cobalt is monoisotopic so the mass spectra are comparatively simple. All ions can be assigned as $[\text{Co}_x(\text{CO})_y]^+$ ($x = 1$ or $2, y = 0-8$).

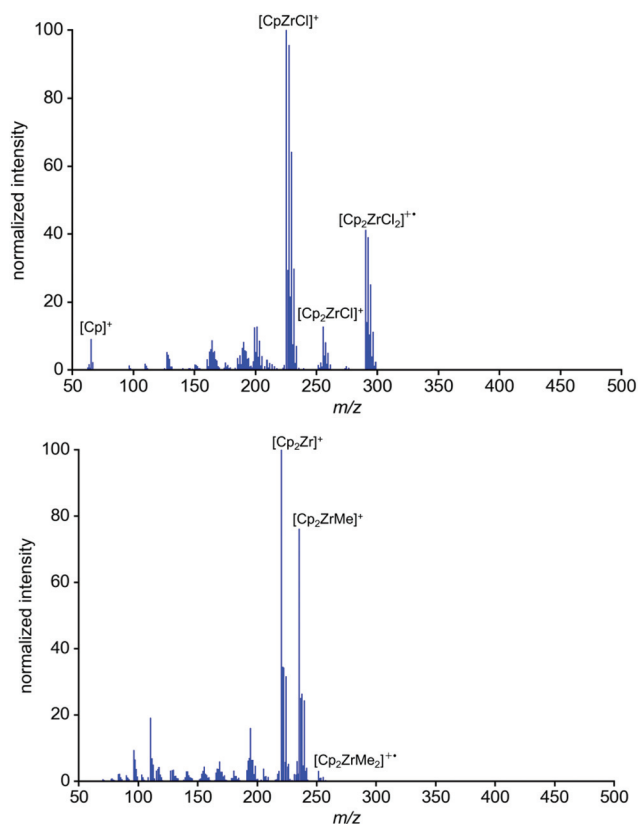


Fig. 3 Mass spectra of Cp_2ZrCl_2 (top) and Cp_2ZrMe_2 (bottom) obtained using the glove chamber.

dichloro compounds, so this observation is consistent with known chemistry.¹³

However, in crystalline form neither of these complexes are exceptionally air- and moisture-sensitive, and decent spectra were obtained even after direct exposure to the atmosphere (though considerable amounts of dimeric oxidized products were also observed, see ESI†). As such, we turned to TiCp_2Cl_2 , itself not especially air-sensitive (similar to Cp_2ZrCl_2) but it may be reduced using zinc to a Ti(III) compound that is air-

sensitive enough to be used as an indicator of the presence of trace levels of oxygen in gloveboxes. It changes colour from blue to yellow through green in the presence of O₂, so it also offered a visual clue to the degree to which the glove chamber was excluding air. Thanks to the glove chamber, the EI mass spectrometric analysis gave clean and distinct results for each of Cp₂TiCl₂ and Cp₂TiCl (Fig. 4). The spectrum of Cp₂TiCl₂ showed a relatively high intensity for the molecular ion [Cp₂TiCl₂]⁺⁺ and the base peak was [CpTiCl₂]⁺. Contrastingly, the two most intense peaks in the spectrum of Cp₂TiCl were [Cp₂TiCl]⁺ (the molecular ion) and [CpTiCl]⁺. In both cases, hydrolysis products were not detected, and only a small amount of oxidised Cp₂TiCl was observed in the form of a small signal for [Cp₂TiCl₂]⁺⁺.

Another class of organometallic compounds that are unusually air- and moisture-sensitive, and therefore challenging to analyze by MS, are trialkyl aluminums.¹⁴ The Al-R bond is highly susceptible to hydrolysis to form Al-OH and R-H, and the more volatile alkyl aluminums are pyrophoric as a result.¹⁵ The charged products of hydrolysis (aluminum oxanes) can be characterized by ESI-MS¹⁶ using an instrument with an attached full-size glovebox,^{6a} but neutral species are not detectable by ESI-MS. Electron ionization analysis of trialkylalumi-

num compounds is straightforward with the glove chamber: a toluene solution of Al*i*Bu₃ was exposed in the box and the toluene allowed to evaporate from a drop placed on the probe. The resulting analysis showed a mixture of toluene (with its characteristic intense peak at [M - 1]⁺ corresponding to the tropylium ion, [C₇H₇]⁺ at *m/z* 91) and ions attributable to Al*i*Bu₃. The molecular ion at *m/z* 198 was barely observable, and ready loss of butyl radical to generate [AlBu₂]⁺ at *m/z* 141 and further loss of butene to generate [AlBuH]⁺ (the base peak) at *m/z* 85 occurred (Fig. 5).

The products of decomposition of Al*i*Bu₃ through hydrolysis will mostly be less volatile than Al*i*Bu₃ itself (with the exception of isobutane, which will likely be lost even before transfer to vacuum). On the other hand, air- and moisture-sensitive organometallic complexes can sometimes decompose to generate lower molecular weight species, which by virtue of their greater volatility, end up dominating the mass spectrum. As such, analysis of lanthanide complexes Ln[N(SiMe₃)₂]_n (Ln = Dy, Sm, Nd; *n* = 2, 3) show small amounts of high molecular weight ions, and the most abundant fragments are those due to HN(SiMe₃)₂. This lower molecular weight species, with a boiling point of just 126 °C, is easily driven into the gas phase, ionized and becomes the most prominent species. For example, Sm[N(SiMe₃)₂]₂ provides mass spectra with low portions of the highest molecular weight ion and subsequent numerous fragments corresponding to the cleavage of methyl radicals from the trimethylsilylamido groups (Fig. 6) (see ESI† for Ln = Dy, Nd). In this case, the complex has partially oxidized to the tris-amido species, and subsequently eliminated HN(SiMe₃)₂. The specific fragmentation pattern of silane derivatives has already been studied and in the case of the bis(trimethylsilyl) amido ligand, it gives rise to the formation of HN(SiMe₃)₂, which overlaps with the hydrolysis product.¹⁷ Such behaviour is known and has previously been observed for bis(trimethylsilyl)amido alkaline earth metal complexes.¹⁸ In this case, ligand rearrangement is a limiting factor and does not allow for discrimination between hydrolysis and ligand rearrangement. Therefore, inert-

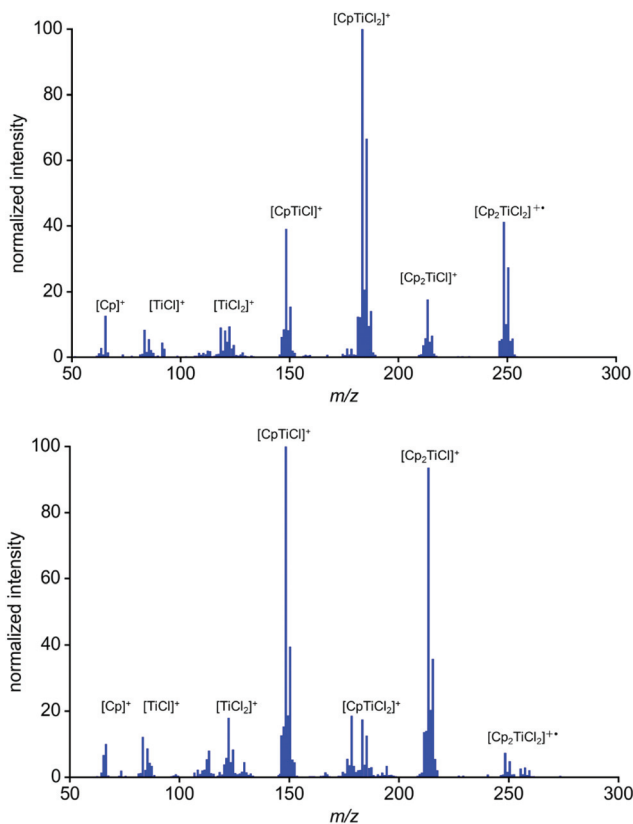


Fig. 4 Top: EI mass spectrum of Cp₂TiCl₂ obtained using the glove chamber. Bottom: EI mass spectrum of Cp₂TiCl generated *in situ* from Cp₂TiCl₂ and Zn using the glove chamber. Note the greatly increased abundance of [Cp₂TiCl]⁺ and the near-disappearance of [CpTiCl₂]⁺ (a fragment of Cp₂TiCl₂).

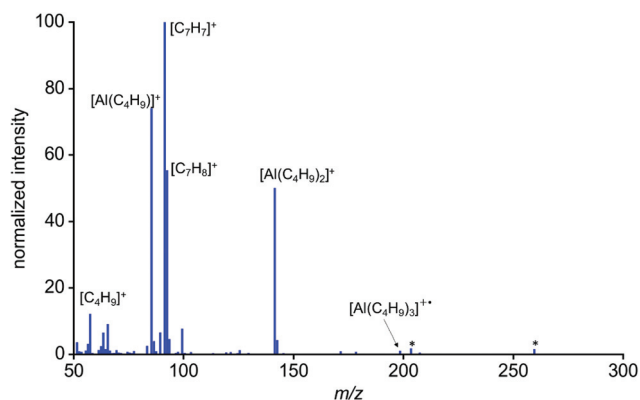


Fig. 5 Triisobutylaluminum in toluene. Low levels of molecular ion are observed at *m/z* 198. Prominent ions due to toluene are observed at *m/z* 92 and 91 (*m/z* 91 being the characteristically stable C₇H₇⁺ tropylium ion). Peaks marked * are unassigned decomposition products.

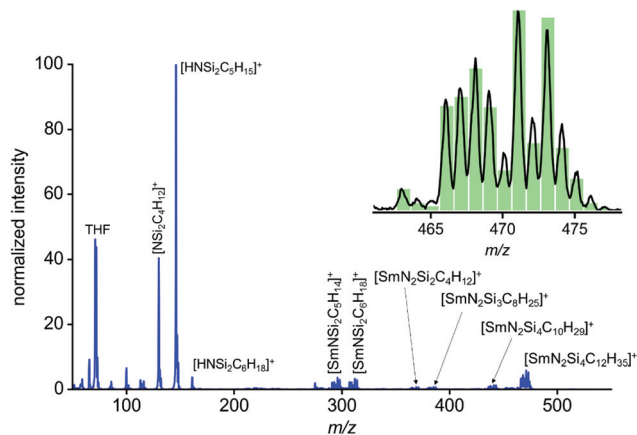


Fig. 6 Positive ion EI-MS spectrum of $\text{Sm}[\text{N}(\text{SiMe}_3)_2]_2$. Inset: Actual spectrum (black) and predicted isotope pattern (green bars).

atmosphere electron ionization mass spectrometry can be used as a complementary analysis technique as it provides insight into the composition and reactivity of air- and moisture-sensitive organolanthanide complexes.

It is sometimes the case that apparent decomposition is not due to exposure to oxygen or moisture but instead due to the lability of the compound under study and the inherent difficulty of transferring an involatile sample to the gas phase. For example, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (Wilkinson's catalyst)¹⁹ is not particularly air-sensitive in the crystalline form but analysis by anaerobic EI-MS resulted in a spectrum that matched exactly that of PPh_3 (see ESI[†]). Essentially, it is easier to dissociate and evaporate the ligand than it is to drive the intact complex from the surface.

Conclusions

The examples discussed above illustrate that inert-atmosphere electron ionization mass spectrometry can be a powerful tool for synthetic inorganic/organometallic chemists. Electron ionization mass spectrometry requires transfer of a (usually) solid sample to the mass spectrometer, and without suitable precautions, the small amounts of air- and moisture-sensitive compound involved can easily decompose by oxidation or hydrolysis. An inexpensive glove chamber enclosure attached to a commercial instrument prevents sample decomposition and enables routine characterization of highly reactive air- and moisture sensitive organometallic compounds safely and effectively. In some cases, *e.g.* $\text{Co}_2(\text{CO})_8$, ZrCp_2Cl_2 , ZrCp_2Me_2 , TiCp_2Cl_2 and $\text{Al}i\text{Bu}_3$, molecular ions are readily formed. In other cases, ligand redistribution can occur *e.g.* the lanthanide bis- and tri-(trimethylsilyl)amide complexes, or thermal stability can be the limiting factor, *e.g.* with $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ generating only PPh_3 in the analysis. For very labile complexes, the observed ions provide information only about the components in the system and cannot be relied upon for the overall composition.

With only a few micrograms and uncomplicated sample preparation, inert-atmosphere electron ionization mass spectrometry can be used to characterize highly air- and moisture sensitive organometallic complexes.

Experimental

General procedure

$\text{Co}_2(\text{CO})_8$, ZrCp_2Cl_2 , ZrCp_2Me_2 , TiCp_2Cl_2 , $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ and $\text{Al}i\text{Bu}_3$ were purchased from Sigma-Aldrich and used as received. TiCp_2Cl was prepared according to literature procedure.⁹ $\text{Dy}[\text{N}(\text{SiMe}_3)_2]_3$, $\text{Nd}[\text{N}(\text{SiMe}_3)_2]_3$ and $\text{Sm}[\text{N}(\text{SiMe}_3)_2]_2$ were provided by Professor David Berg's research group at the University of Victoria.²⁰ All sample preparations of air- and moisture-sensitive compounds were carried out in a glovebox. A few tens to hundreds micrograms of each compound were introduced into a direct insertion probe (DIP) sample cup. The sample cups were brought under inert atmosphere into the glove chamber affixed to mass spectrometer and directly deposited onto the probe tip. Samples were heated within the probe tip under a programmed heating cycle, and spectra were obtained on a Thermo Scientific Finnigan TRACE DSQ mass spectrometer. The positive ion EI/MS analyses were performed at 70 eV with a source temperature of 200 °C. The background pressure in the mass spectrometer was below 10^{-5} Torr.

Details on the EI-MS measurements

For $\text{Co}_2(\text{CO})_8$, ZrCp_2Cl_2 , ZrCp_2Me_2 , TiCp_2Cl_2 , and TiCp_2Cl , the DIP was temperature-programmed from 30 (for 0.5 min) to 350 °C (for 1 min) at a rate of 50 °C min^{-1} and with a scan range of 50 to 650 amu at a rate of 1.2 scan per s. For $\text{Al}i\text{Bu}_3$, the DIP was temperature-programmed from 30 (for 1.5 min) to 350 °C (for 0.5 min) at a rate of 10 °C min^{-1} and with a scan range of 50 to 650 amu at a rate of 1.2 scan per s. For the lanthanides complexes, the DIP was temperature-programmed from 30 (for 2 min) to 400 °C (for 0.5 min) at a rate of 10 °C min^{-1} and with a scan range of 50 to 700 amu at a rate of 1.3 scan per s. For $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, the DIP was temperature-programmed from 30 (for 0.5 min) to 400 °C (for 1 min) at a rate of 50 °C min^{-1} and with a scan range of 50 to 1000 amu at a rate of 1.9 scan per s.

Acknowledgements

JSM thanks NSERC (Discovery and Discovery Accelerator Supplements) for operational funding and CFI, BCKDF and the University of Victoria for infrastructural support. Professor David Berg is thanked for the lanthanide samples and Jeff Trafton for his contribution in the elaboration of the glove chamber.

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