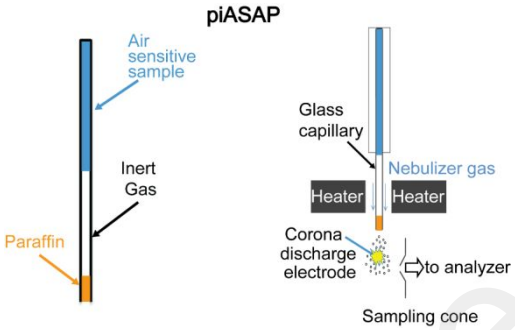
Paraffin-Inert Atmospheric Solid Analysis probe (piASAP): A Fast and Easy Approach to Characterize Extremely Air-Sensitive Organometallic Complexes by Mass Spectrometry

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ABSTRACT: Rational characterization of most organometallic compounds is hampered by their high reactivity in particular toward oxygen and water. Mass spectrometry experiments require to physically introduce the sample in the ionization source. So, the main challenge is to transfer air-sensitive organometallic compounds from inert atmosphere to the ionization source. In this aim, we have developed an easy technique that allows the analysis of air-sensitive compounds using the atmospheric solid analysis probe (ASAP). This method consists of a glass capillary filled with the sample (solid or liquid) and sealed by a paraffin plug to maintain the sample inert until the ionization process. It is illustrated through the structural characterization of a new highly air-sensitive dinuclear zirconium complex supported by an original switchable stilbene platform.

Early transition metallocene complexes have attracted a huge interest both in academy and industry as highly efficient α-olefin polymerization (pre)catalysts. Some of these complexes are nowadays commonly employed to obtain a specific stereochemistry, high molecular weight, narrow molecular weight distribution polymers and/or incorporation of comonomers,[1] thus ensuring the fabrication of polyolefin materials with controlled microstructure, crystallization behavior, rheological and mechanical properties.[2] And, all these peculiar properties of the polyolefin are largely correlated to the structure of the metallocene.[3–5] However, these complexes are not easy to handle since they are quite sensitive to moisture and oxygen and are therefore difficult to characterize.[6] NMR spectroscopy is often used, but this technique requires to be insightful, samples already purified to a significant extent and is limited to paramagnetic metal complexes[7] Conversely, mass spectrometry (MS) techniques can be used to identify and separate complex mixtures of metallic complexes with no limitation in their electronic configuration states, in particular owing to their characteristic isotopic patterns.[8–15] However, MS requires that the sample is introduced into the ionization source without being altered, that is without contact with air.[16–18] The main challenge is therefore to transfer the sensitive compounds from the inert atmosphere where they are stored (*e.g.* a glovebox) to the mass spectrometer ionization source. Many developments have been made to allow the analysis of sensitive early transition organometallic compounds by MS.[19–22] For instance, olefin polymerization reactions mediated by group 4 metal complexes have been monitored using electrospray

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ionization (ESI) tandem MS.[8] Also, MS was proved to be efficient for the analysis of highly air-sensitive organolanthanides by Evans *et al.* in 2000.[23] The authors succeeded to transfer a syringe filled with sample to the mass spectrometer in a rubber-septum-capped Schlenk flask under nitrogen atmosphere. However, the ESI source was not efficient to ionize so-called "ESMS silent ligands" such as allyl $[C_3H_5]^-$ and cyclooctatetraenide $[C_8H_8]^{2-}$ groups. To overcome this problem, Fogg *et al.* developed a MALDI target plate in the glove box directly connected to the ionization source to analyze air-sensitive compounds by coupling a MALDI-TOF mass spectrometer to an inert atmosphere glovebox through an open loading chamber.[24] Similarly, Lubben *et al.* have also coupled ESI to a glovebox.[16] The sample infusion was realized using a syringe pump inside a glovebox connected to a ESI source through a capillary tube passing through a feedthrough of glovebox. Other atmospheric pressure ionization techniques have also been applied such as photoionization[25] and chemical ionization[26] to either characterize air-sensitive complexes, or to monitor reaction mechanisms.[9,17,27–32] Recently, a modified mass spectrometer has been developed by McIndoe and coworkers to characterize metallocene complexes using electron ionization MS.[33] Hence, all direct analysis are based on the close proximity or coupling of a glove box to the mass spectrometer or modification of mass spectrometers.

EXPERIMENTAL SECTION

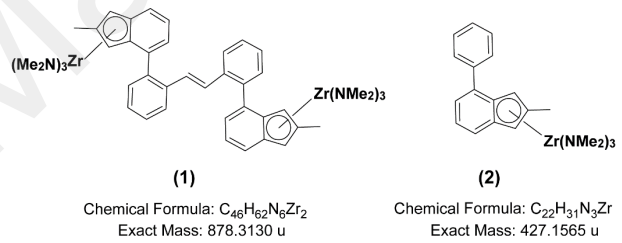
Materials. The melting point tubes (Length: 100 mm, Ø ext.: 1.55 mm, Ø int.: 1.15 mm) used in all experiments was provided from VWR supplier. The white paraffin pastilles that was used in the preparation experiments meets analytical specification of Ph. Eur. with mp 43-95 °C and it was ordered from Sigma-Aldrich.

Sample preparation. In glove box, a few tens to hundred milligrams of solid sample was dissolved in 2 mL of anhydrous toluene and the solution was transferred directly into a glass capillary sealed at one end. Then, the other end was closed by a paraffin plug. The sealed glass capillary was transported to the ASAP source. Anhydrous toluene was prepared through distillation over NaK Alloy under inert atmosphere and then was preserved over 1cm activated molecular sieves to ensure the dryness of the solvent. All preparations were performed under inert and controlled atmosphere ($[O_2] < 2$ppm and $[H_2O] < 2$ppm) in glovebox (GP Campus, JACOMEX). It is worthy to mention that no issues were encountered with solvents such as heptane, methanol and THF that have similar viscosity as toluene. The synthesis of complex E-(o)-{BisInd}$(Zr(NMe_2)_3)_2$ (1) and {Ind}$Zr(NMe_2)_3$ (2)) has previously been reported.[34]

Instrumentation. All data acquisitions were performed on hybrid quadripole time of flight mass spectrometer (Synapt G2, Waters Corp. Wilmslow, UK) in positive atmospheric solid analysis probe (ASAP) mode (Corona voltage 4.0 kV, probe temperature 650 °C, source temperature 140 °C, desolvatation gas flow 1200 L/hr). This instrument consists of a hybrid quadrupole/time-of-flight mass spectrometer, which incorporates a travelling wave (T-Wave)-based mobility separation device. Instrument control and data acquisition were carried out using MassLynx (version 4.1). The instrument is described in detail elsewhere.[35] The time of flight (TOF) mass spectrometer was externally *m/z* calibrated using sodium formate solution before sample analysis. The treatment of the data and preparation of figures was done using Waters MassLynx (version 4.1) and Waters DriftScope (version 2.8) softwares.

RESULTS AND DISCUSSION

In this work, we describe a simple technique for sample introduction that is based on the atmospheric solid analysis probe (ASAP) ionization source coupled to an ion-mobility-mass spectrometer (Waters, Synapt G2). This latter ionization mode has been established by McEwen in 2005 and allows analysis of pure or solution samples directly deposited on a glass tip, where the analyte is desorbed by a hot nitrogen flux and ionized by nitrogen plasma generated by corona discharge.[36] The ASAP source has been used in many applications for both targeted analysis[37–39] and untargeted analysis.[40–42] Unlike other techniques that require uncontrolled multi sophisticated preparation steps or modified setups,[43,44] in our new simple approach, referred to as paraffin-inert ASAP (piASAP),[45] a capillary tube containing air-sensitive compounds (liquid or solid) is sealed with paraffin plug under inert atmosphere condition. The sample is thus protected in a sealed glass capillary under inert atmosphere. And, it can be transported and carried away as long as the paraffin is intact. Herein, we describe the application of this new piASAP approach to the structural characterization of new highly air-sensitive dinuclear zirconium complex *E*-(o)-{BisInd}$(Zr(NMe_2)_3)_2$ (1) supported by an original switchable stilbene platform and analogous mononuclear zirconium complex {Ind}$Zr(NMe_2)_3$ (2) (Scheme 1).



Scheme 1. Structures of dinuclear *E*-(o)-{BisInd}$(Zr(NMe_2)_3)_2$ isomer (1) and mononuclear {Ind}$Zr(NMe_2)_3$ (2) zirconium complexes used in this study.

An ASAP source was used to ionize the sample. The principle of the source and the capillary is shown in Figure 1. The glass capillary is directly introduced into the source thanks to the ASAP probe. Paraffin is a mixture of alkanes that do not ionize well in comparison to most analytes using ASAP conditions but melts quickly, releasing the samples in the source. And, the sample is released inside the source and ionized by a nitrogen plasma induced by hot nitrogen flow and corona discharge.[38] The sample can be introduced as pure (solid or liquid) or in solution, as the ASAP ionization allows to use any type of solvent. However, it is necessary to keep inert atmosphere between the solvent and the paraffin plug to not dissolve it and oxidize the sample before analysis.

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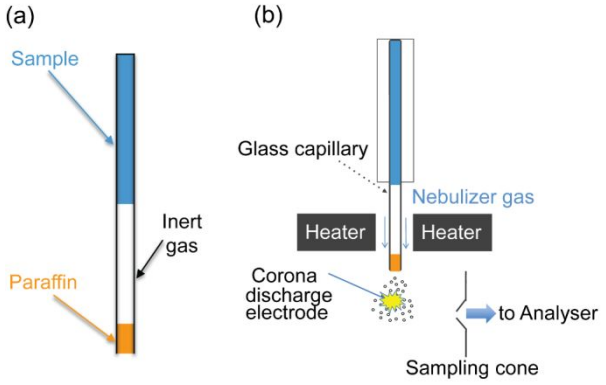


Figure 1. (a) paraffin-inert ASAP glass capillary. (b) paraffin-inert atmospheric solid analysis probe (piASAP) principle.

After analysis, the glass capillary can be removed slowly from the source to avoid contamination of the probe guide by the sample. If done properly, no carryover of the signal is observed. The total ion current obtained is relatively high and lasts for 2 minutes. This signal time allows to perform collision induce dissociation, ion mobility or any other post ionization experiments. Both metallocenes **1** and **2** were analyzed using piASAP technique. The piASAP spectra of **1** (Figure 2) and **2** (Figure S1) show the presence of protonated species of the molecular complex $[M+H]^+$ due to the presence of amine (-NMe_2) groups in both complexes. The accurate masses and isotopic distributions of complexes **1** and **2** (*m/z* 879.3233 and 428.1622, respectively) are in very good agreement (<5 ppm) with those expected theoretically based on the corresponding ions molecular formula (*m/z* 879.3208 and 428.1643, respectively). It is noteworthy to mention that even in case of low ionization efficiency analyte, the *m/z* values from the alkanes can be easily evidenced by their high mass defect by using high resolution mass spectrometry and also by using ion mobility, as alkanes appear at higher drift time. The control spectra and data extracted from drift time vs *m/z* plot where one can easily separate the paraffin and analyte ions (complex and its related ions) from the 2D map are shown in Figures S2, S3 and S4.

The ASAP experiments that were performed under air for **1** and **2** show the absence of $[M+H]^+$ ion and its related isotopic fragments. This observation reflects fast oxidation/hydrolysis of complexes **1** and **2** in air. Since the sampling cone voltage could have an effect on the gas-phase fragmentations and transmission of ions inside the source, we performed piASAP analysis at different sampling cone voltages. As shown in Table S1, Figure S5 and Figure S6, the highest relative intensity of $[M+H]^+$ ion for **1** and **2** was achieved at 40 and 10 V, respectively. This indicates that **1** has an enhanced ion transmission at 40 V in comparison to 10 V. With **2**, we clearly noticed that the increase of sampling voltage leads to more fragmentations and disappearance of isotopic distribution of $[M+H]^+$ ion at higher voltage (Figure S6). Furthermore, both structures of **1** and **2** were validated by tandem mass spectrometry experiments (MS/MS) using the piASAP technique. The piASAP MS/MS spectra of **1** and **2** (Figure S9 and Figure S10) display similar mode of fragmentation with successive loss of dimethyl amine moieties for **1** leading to the ions observed at *m/z* 834.2622, 790.2046 and 525.117; the ion at *m/z*613.2177 corresponds to loss of a zirconium dimethyl amine group ($Zr(N_2C_4H_{11})$).

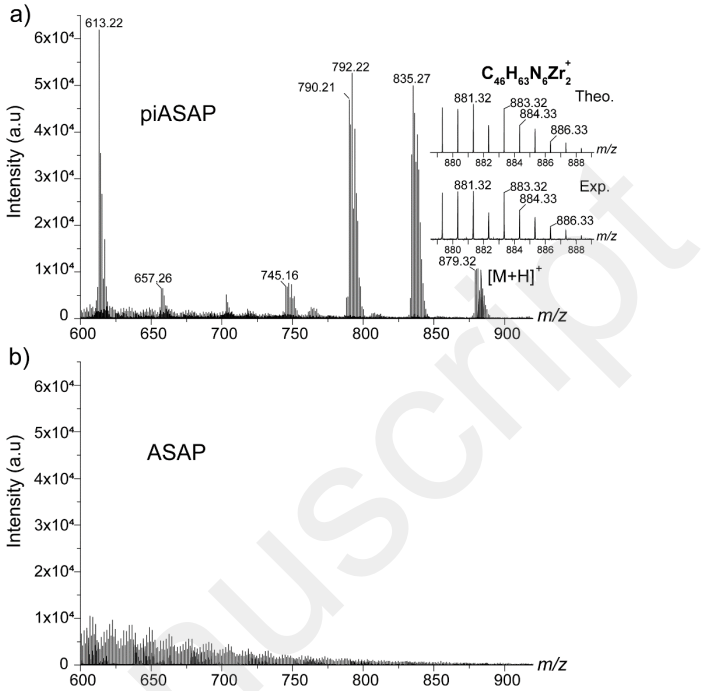


Figure 2. Analysis of *E*-Zr dimer (**1**) by piASAP and ASAP techniques. (a) and (b) are mass spectra of piASAP and ASAP conducted under inert and aerobic conditions, respectively. The zoomed areas showcase the theoretical and experimental isotopic patterns of complex **1**.

Similarly, complex **2** shows subsequent loss of dimethyl amine groups leading to the ions observed at *m/z* 401.1157, 357.0669, 330.0197 and with isotopic distributions related to the gain of water molecules. This did occur because of the presence of minute amounts of water in the instrument collision cell. It is noteworthy that the detection of free ligand in piASAP MS analysis and its absence in both MSMS spectra of **1** and **2** imply that the detected free ligand is linked to the degradation of the complexes inside the source and not to collisional activation during the ions transfer.[46,47]

CONCLUSIONS

In this study, we have described a technique referred as piASAP that allows the easy handling of extremely air sensitive solid or liquid complexes from a glove box to a mass spectrometer without modification of the instrument. We characterized effectively two metallocenes **1** and **2** using this technique by ASAP source. Both structures of **1** and **2** were confirmed by piASAP MSMS experiments and they display similar mode of fragmentation with the successive loss of amine groups. We believe that this technique will open the way for many researchers to characterize many highly air sensitive complexes in easy and fast way.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX

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Experimental details, supporting tables, and supporting figures (PDF)

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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