

Analysis of Organometallic Compounds by Field Desorption (FD) and the AccuTOF™ GC-Alpha

Summary

Field Desorption (FD) is demonstrated as a useful way to obtain mass spectra for many organometallic complexes.

Introduction

FD is one of the softest ionization methods available for mass spectrometry, often producing a molecular ion for compounds that fragment readily when analyzed by other ionization methods. FD is well suited for the analysis of organometallic compounds.

Samples deposited onto the FD emitter, a wire with carbon microneedles, are desorbed by passing current through the wire. Electron tunneling occurs at the high electric field at the tip of the microneedles to produce molecular ions. Cation adducts such as $[M + Na]^+$ may also be observed. Fragmentation is less common with FD than for other ionization methods, but fragments may still be observed for certain compounds.

Experimental

The combination Electron ionization (EI)/Field ionization (FI)/Field desorption (FD) ion source was autotuned in FI mode using octamethyltetrasiloxane introduced through the reference sample inlet. A JEOL 10 μ m FI/FD emitter was used for all measurements. Three platinum complexes and one rhodium complex were selected for analysis. Approximately 1 mg of each sample was dissolved in 1 mL of dichloromethane. Samples were deposited onto JEOL FD emitters by using the Field Desorption Sampling Kit, which consists of an optical microscope, an FD probe holder, and an x,y,z-manipulator to facilitate sample application with a liquid junction from a 10 μ L- syringe.

The emitter current was increased from 0 to 50 mA at a rate of 51.2 mA min⁻¹ for a total analysis time of 0.98 minutes per sample. Reserpine was applied to the emitter as an internal mass reference standard. Mass spectra were acquired using the combination EI/FI/FD ion source for the range covering m/z 50 to m/z 1600 at a spectral acquisition rate of 1 spectrum per second.

JEOL msAxel software was used for instrument control, data acquisition, mass calibration, spectral averaging, and background subtraction. Elemental compositions were determined using the abundant isotope^[1] with Mass Mountaineer software (massmountaineer.com).

The four organometallic complexes analyzed are shown in Figure 1.

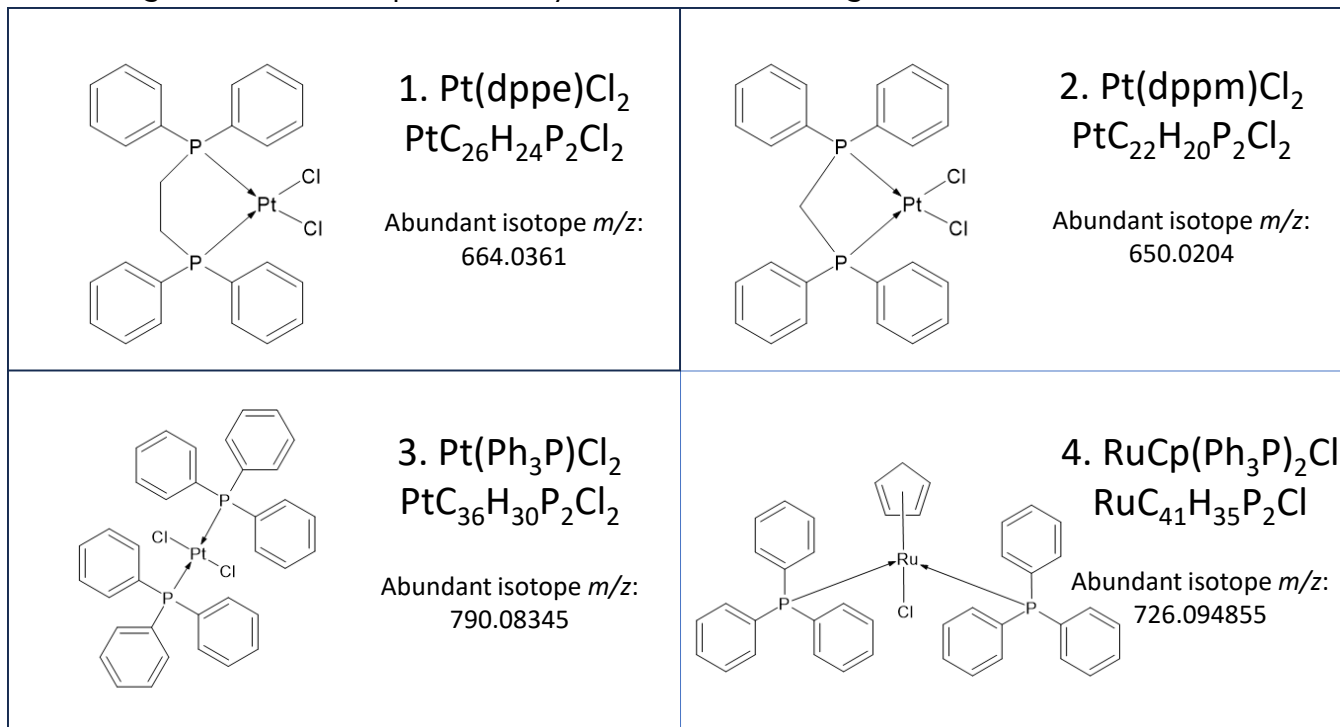


Figure 1. Organometallic complexes analyzed by FD.

Results

FD mass spectra for the four complexes are shown in Figures 2, 3, 4, and 5. The molecular ion was observed as the base peak for each complex, with good isotopic and mass accuracy (figure insets and Table 1). Minor peaks corresponding to the ligands, chloride loss, and adducts were also observed.

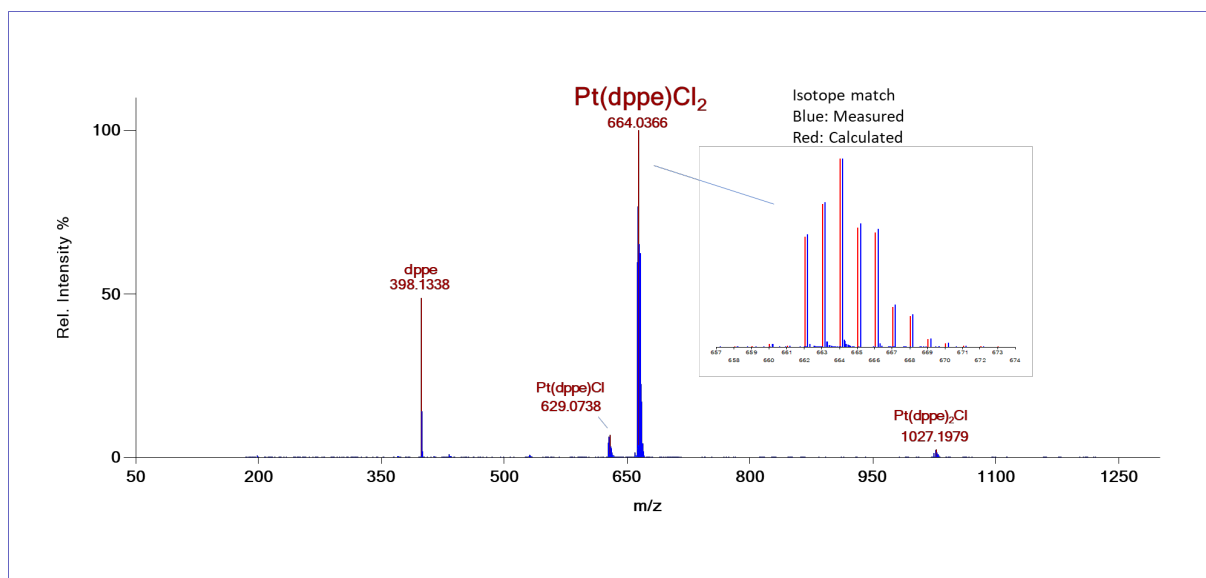


Figure 2. FD mass spectrum of compound 1: Pt(dppe)₂Cl₂.

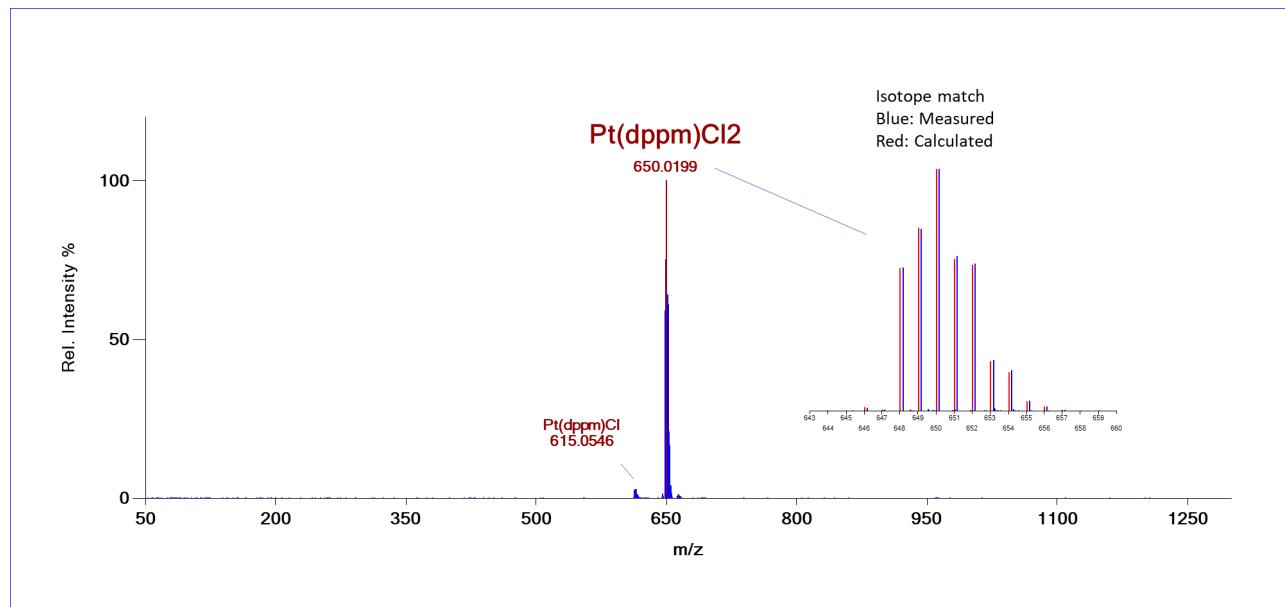


Figure 3. FD mass spectrum of compound 3: Pt(dppm)₂Cl₂.

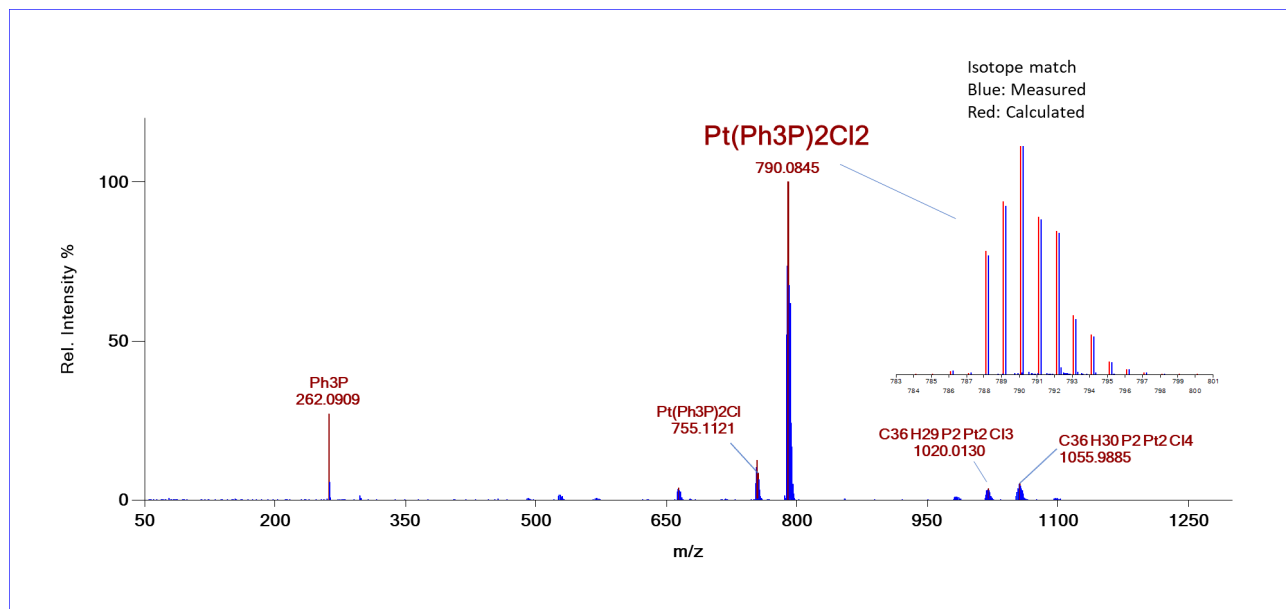


Figure 4. FD mass spectrum of compound 3: Pt(Ph₃P)₂Cl₂.

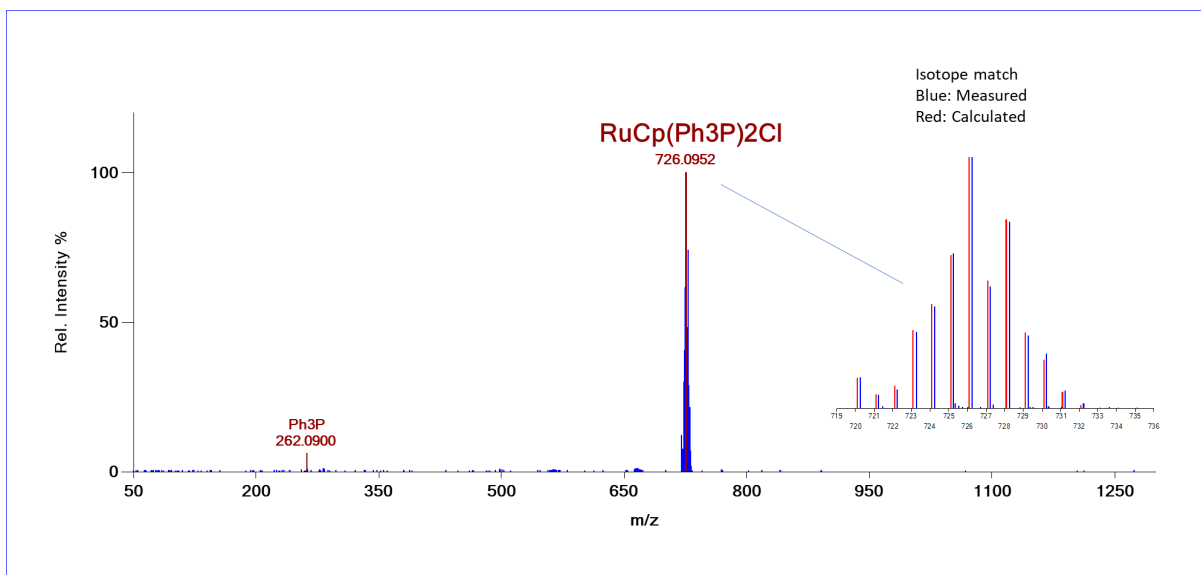


Figure 5. FD mass spectrum of compound 4: $\text{RuCp(Ph}_3\text{P)}_2\text{Cl}$.

<u>Sample</u>	<u>Calculated</u>	<u>Measured</u>	<u>Diff. (mmu)</u>	<u>Diff. (ppm)</u>
1	664.0361	664.0366	0.5	0.75
2	650.0204	650.0199	-0.5	-0.77
3	790.0834	790.0845	1.1	1.39
4	726.0949	726.0952	0.3	0.41

Table 1. Calculated and measured m/z for the abundant isotope for the molecular ion for each compound.

Conclusion

The FD option for the JEOL AccuTOF GC-Alpha mass spectrometer produced an abundant molecular ion with good mass and isotopic accuracy for each of the four complexes studied. FD analysis was easily and rapidly carried out with an analysis time of less than one minute per compound by using the combination EI/FI/FD ion source. An optional liquid introduction field ionization (LIFDI) source is also available for the analysis of air-sensitive organometallics.

References

1. R. B. Cody, T. Fouquet. Elemental Composition Determinations Using the Abundant Isotope. *Journal of the American Society for Mass Spectrometry*, 2019, 30, 1321.