

Direct Analysis of Organometallic Compounds

Summary

Organometallic compounds play an important role in chemistry, as recently recognized by the awarding of the 2005 Nobel Prize in Chemistry to Chauvin, Schrock and Grubbs. Characterization of organometallic compounds by mass spectrometry can sometimes be complicated by problems with solubility and reactivity. Electron ionization can be used for some volatile organometallics. Fast atom bombardment (FAB) and electrospray ionization (ESI) are useful provided suitable solvents can be used. Field desorption (FD) is often effective, but FD emitters can be fragile and the analysis should be carried out by an experienced operator.

DART (Direct Analysis in Real Time) complements these methods and provides an alternative; it is fast and does not require solvents. The sampling area is purged

with an inert gas, reducing the likelihood of undesirable reactions. Further, AccuTOF-DART permits exact mass measurements without requiring the presence of a reference standard during the sample measurement. DART is extremely robust and does not require special operator training.

Mass spectra of several organometallic compounds were obtained by using DART. A few dry particles of each compound were placed in front of the DART source on a melting point tube and mass spectra were obtained within seconds. The best results were obtained by using small quantities of sample; very large quantities can result in ion-molecule reactions between sample ions and sample neutrals, resulting in isotopic patterns characterized by both M^+ and $[M+H]^+$. All labeled assignments were confirmed by exact mass measurements and isotope pattern matching.

Ferrocene: $Fe(C_5H_5)_2$

Ferrocene produces a molecular ion M^+ for low sample quantities (micrograms or less). If a larger quantity is analyzed, ion-molecule reactions result in protonation of the molecule to produce $[M+H]^+$.

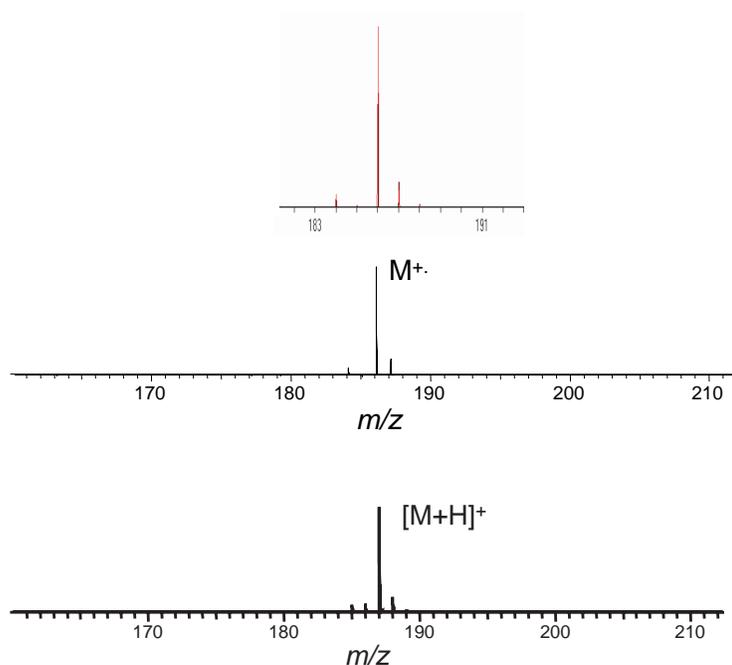


Figure 1. Top: Theoretical isotope pattern for $Fe(C_5H_5)_2^+$. Middle: Mass spectrum obtained by using a very small quantity of ferrocene. Bottom: Mass spectrum obtained by analyzing a large quantity of ferrocene on the melting point tube.

Tungsten hexacarbonyl: $W(CO)_6$

Like ferrocene, tungsten hexacarbonyl produces mass spectra characterized by a molecular ion for low sample concentrations. A protonated molecule is observed if large sample quantities are presented to the DART source.

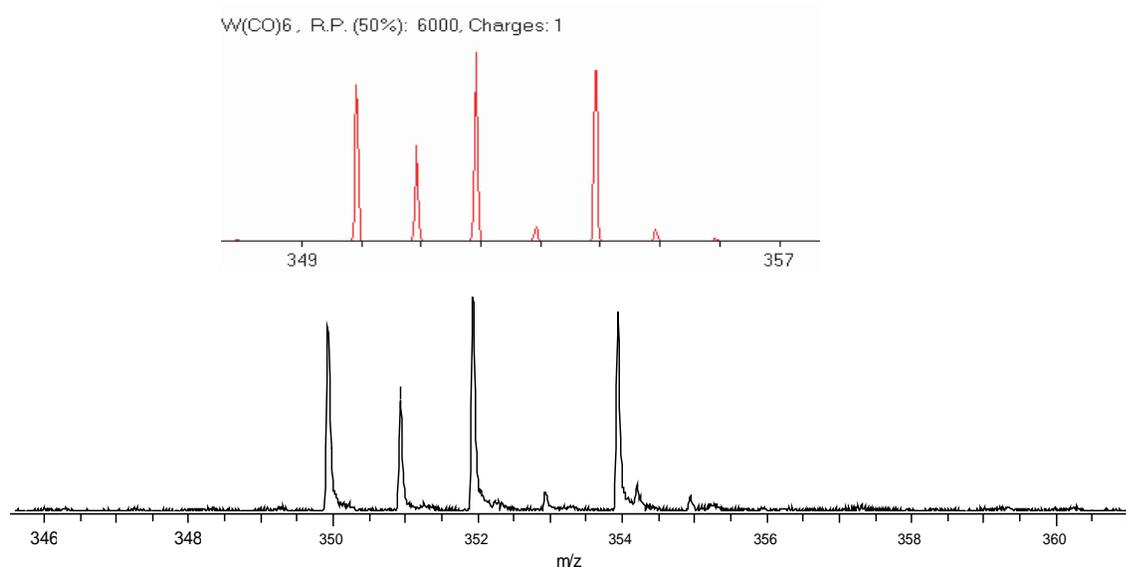


Figure 2. Top: theoretical isotope pattern for $W(CO)_6^+$. Bottom: measured mass spectrum for tungsten carbonyl.

Acetylacetonato rhodium dicarbonyl: $C_5H_8O_2Rh(CO)_2$

This compound readily produces a molecular ion.

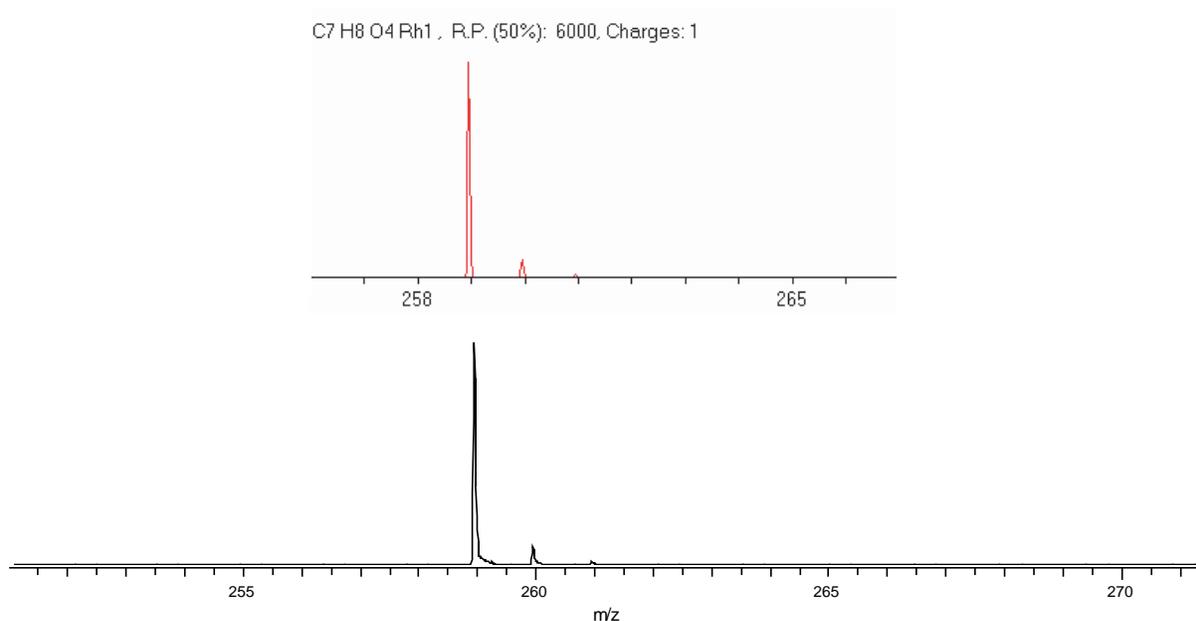


Figure 3. Top: theoretical isotope pattern for $C_5H_8O_2Rh(CO)_2^+$. Bottom: measured mass spectrum.

(1,5-cyclooctadiene) platinum (II) chloride ($C_8H_{12}PtCl_2$)

This compound does not readily protonate. However, it produces an ammonium adduct if vapor from a dilute solution of ammonium hydroxide is present. Chloride loss and a related water adduct are also observed. A dimer ($(C_8H_{12}Pt)_2Cl_3^+$) is also observed at higher mass (not shown).

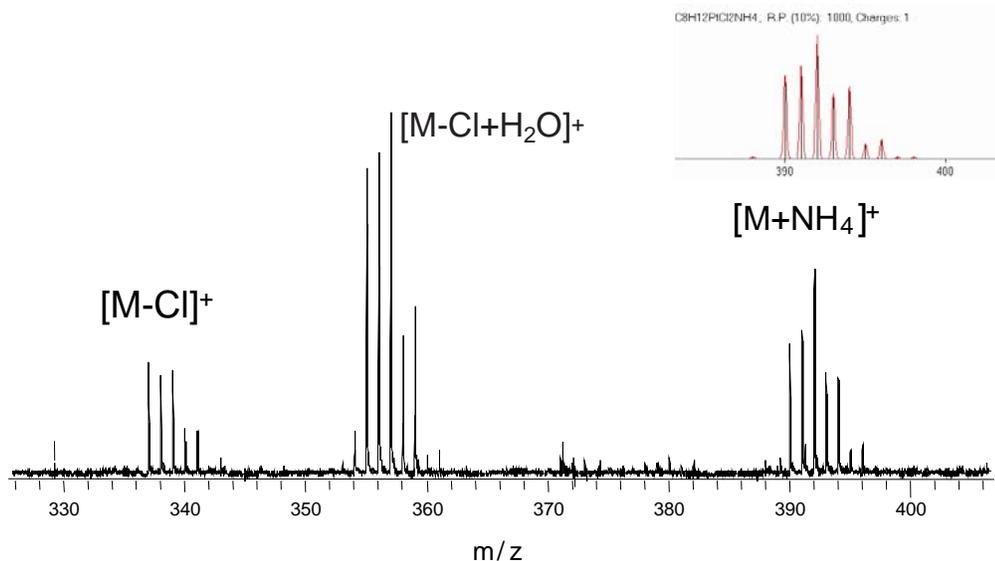


Figure 4. Top inset: theoretical isotope pattern for $[C_8H_{12}PtCl_2 + NH_4]^+$. Bottom: measured mass spectrum.

Bis(diphenylphosphoethane) platinum dichloride: $Pt(DPPE)Cl_2$

This compound behaves in a similar manner to (1,5-cyclooctadiene) platinum (II) chloride. An ammonium adduct can be observed, together with a chloride loss and a dimer $[2M-Cl]^+$.

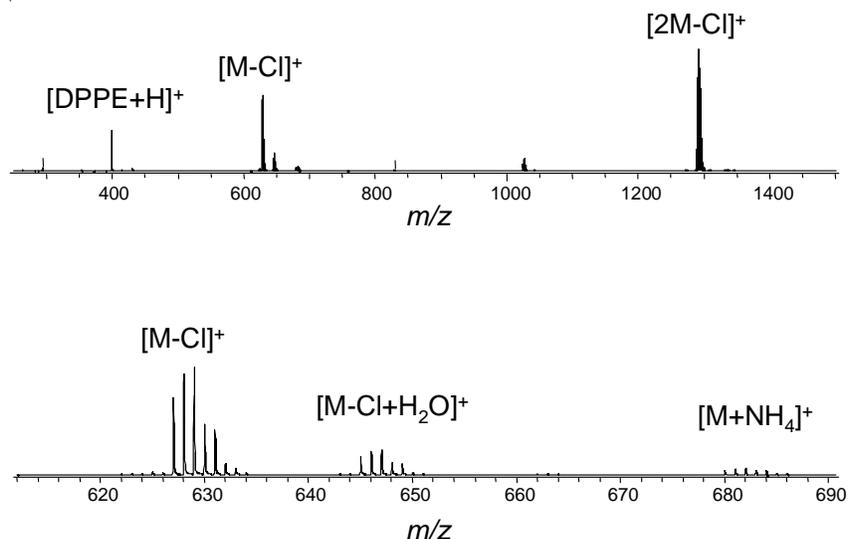


Figure 5. DART mass spectrum of $Pt(DPPE)Cl_2$. Top: mass spectrum for m/z 350 to m/z 1500. Bottom: enlarged view of region near $[M-Cl]^+$.

Conclusion

AccuTOF-DART provides a convenient means for characterizing many organometallic compounds. No solvents are required and excellent agreement between theoretical and observed masses and isotopic abundances are obtained.