

Evaluation of Organometallic Compounds using GC/Q-TOF with a Novel Soft Ionization Source

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Introduction

Organometallics synthesized from transition metals are a versatile class of compounds that are traditionally utilized as catalysts in organic synthesis. They are additionally finding new purpose in areas such as clinical biochemistry, being used as therapeutics to treat various ailments including carcinomas, lymphomas, and neurodegenerative diseases (Anilnert, B. Therapeutic Organometallic Compounds, Pharmacology, Dr. Luca Gallelli (Ed.), ISBN: 978-953-51-0222-9, InTech, DOI: 10.5772/33858).

Transition metals ligated with heteroatoms and hydrocarbons have high molecular weights and unique isotope patterns, so these compounds produce mass spectra rich with information. Soft ionization can be used to reduce low m/z ions and enhance higher m/z ions, including molecular ion in many cases. This study demonstrates mass accuracy, isotope distributions and soft electron ionization (EI) used in the evaluation of transition metal organometallic compounds.

Solids and liquid samples of complex matrix can be analyzed for GC amenable compounds via a Thermal Separation Probe (TSP), which fits into the inlet of a GC (Figures 1 and 2). Using an inlet that has rapid temperature and pressure ramps allows for volatilization of analytes, which are then transferred to the GC or directly to the MS.



Figure 1: The Thermal Separation Probe (TSP)



Figure 2: The TSP inserted into the GC Inlet

Experimental

Methods

The organometallic standards analyzed were transferred under dry conditions to 15 mm sample vials, and were then inserted in the TSP for analysis. Each standard was evaluated under optimized conditions which allowed volatilization without thermal decomposition so the compound could be evaluated without decomposition products being observed in the spectra. Under high flow of helium (5 mL/min), each standard was vaporized in the inlet, then transferred to an accurate mass high resolution GC/Q-TOF using He carrier gas at a flow of 1 mL/min via an uncoated 1.2 m x 0.1 mm capillary.

Instrumentation

Detection was done with an Agilent 7200 GC/Q-TOF accurate mass high resolution mass spectrometer system equipped with a prototype soft ionization EI source heated at 200°C. Operated in TOF-only (MS) mode, spectral data was collected at a mass range of 55 - 1150 m/z with an acquisition rate of 5 Hz. Data analysis was performed using Agilent MassHunter Software.



Figure 3: Agilent 7200 Series GC/Q-TOF mass spectrometer

The prototype EI source can be tuned and operated at different ionization energies to yield softer ionization. Increased molecular ion, reduced fragmentation and spectral tilt from lower mass fragments to higher mass fragments combined with the power of accurate mass allow for more enhanced selectivity and identification.

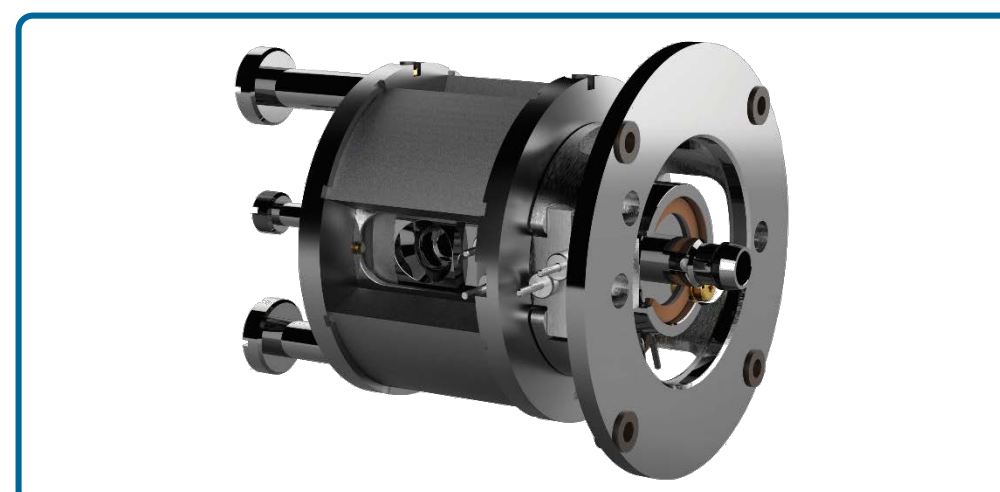


Figure 4: Agilent Prototype Source

Results and Discussion

Excellent Isotope Fidelity and Accurate Mass of a High Molecular Weight Organometallic

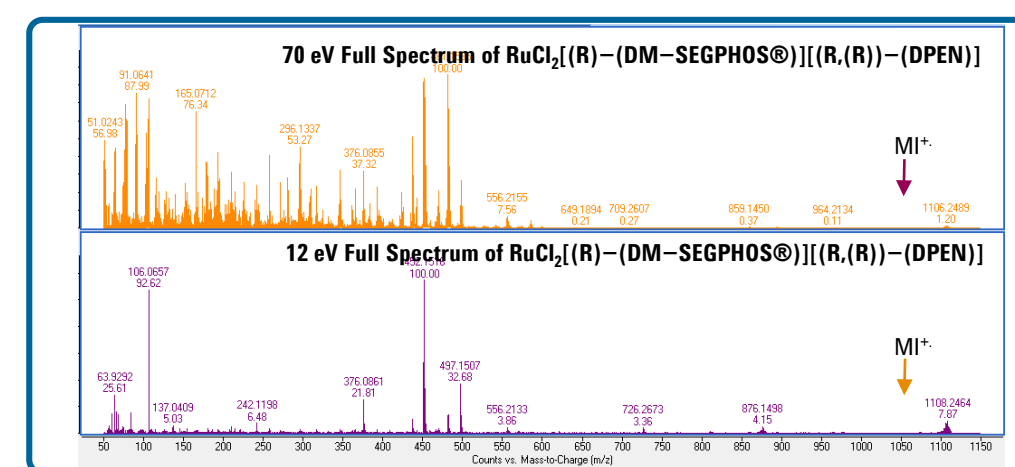


Figure 5: Mass Spectrum of Ru1107 at 70 eV and 12 eV

The spectrum obtained from Dichloro[(R)-5,5'-bis[di(3,5-xylyl)phosphino]-4,4'-bi-1,3-benzodioxole][(1R,2R)-1,2-diphenylethylenediamine]ruthenium(II) (Ru1107)-contained various low weight fragments that lacked signature isotope clusters derived from the ligands, specifically the phosphorous- hydrocarbon ligands, represented by ions m/z 481.1563, 452.1536 and 376.0859 (Figure 5). In the higher mass range for this compound, ruthenium clusters were observed between 800-1100 m/z , including the molecular ion cluster. The calculated mono mass of this compound is m/z 1106.2443 ($M+.$ +6) and contains 14 different ions over 1% abundance to the base peak (Figure 6).

m/z			Isotope Distribution		
Theoretical	Observed	Mass Error (ppm)	Theoretical	Observed	Difference (%)
1102.2466	1102.2484	1.6	11.01	13.51	2.5
1103.2466	1103.2461	-0.5	27.51	30.35	2.8
1104.2462	1104.2463	0.1	39.85	41.79	1.9
1105.2460	1105.2474	1.3	62.68	64.33	1.6
1106.2454	1106.2468	1.3	100	100.00	0.0
1107.2464	1107.2479	1.4	74.75	78.64	3.9
1108.2449	1108.2472	2.1	96.93	96.20	0.7
1109.2468	1109.2484	1.4	55.32	57.74	2.4
1110.2449	1110.2465	1.4	43.6	45.69	2.1
1111.2464	1111.2481	1.5	21.01	23.47	2.5
1112.2459	1112.2444	-1.3	9.59	12.24	2.7

Table 1: Mass errors and isotope ratios for the molecular ion cluster of Ru1107

Soft Ionization Decreases Low m/z Fragments and Enhances Ruthenium Clusters

Table 1 shows the excellent agreement observed between the measured mass assignment and isotope distribution from Ru1107. Also evident in contrasting the spectra obtained at 12 eV to the 70 eV is the reduction of ligand fragments and enhancement of high molecular weight ruthenium clusters, including the molecular ion cluster which went from 1.2% of the compound spectrum at 70 eV to nearly 8% at 12 eV.

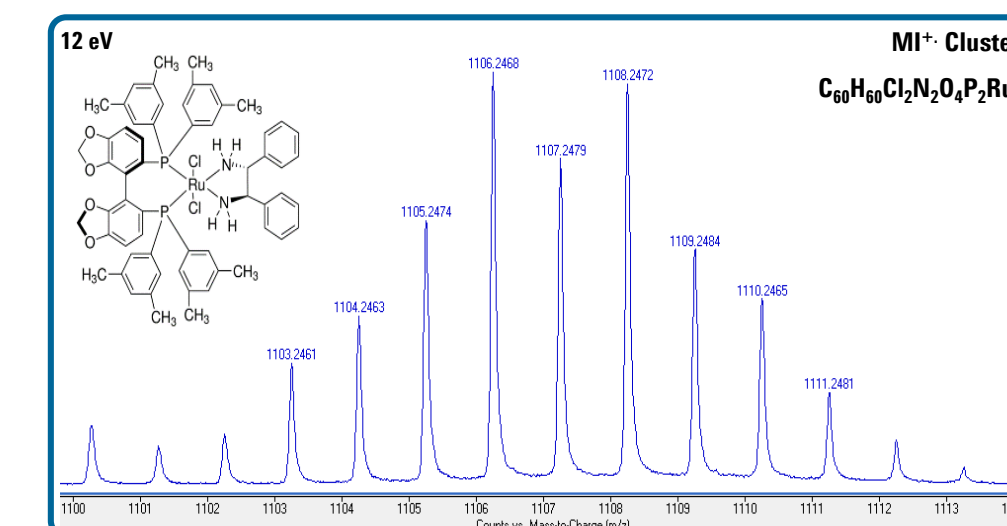


Figure 6: MI cluster for compound Ru1107 obtained at 12 eV

Results and Discussion

Soft Ionization Yields Molecular Ion as Predominant Ion for Transition Metals Sandwiched Between Cyclopentadienyl Ligands

Several transition metals that were "sandwiched" between cyclopentadienyl ligands feature some molecular ion at 70 eV as well as many low m/z fragments from the cyclopentadienyl ligands. At 10 eV, the molecular ion was the predominant ion and low m/z ions were reduced or eliminated. Figures 7-9 show the spectra of Cobalt, Niobium, Molybdenum, and Osmium with variants of the cyclopentadienyl "sandwiches" at 70 eV and 10 eV.

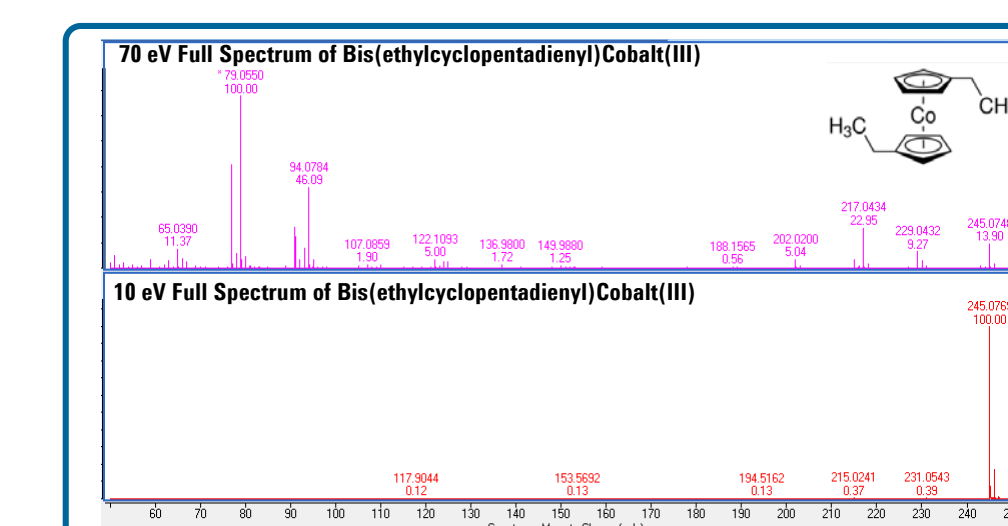


Figure 7: Mass spectrum of Bis(ethylcyclopentadienyl)Cobalt(III) at 70 eV and 12 eV

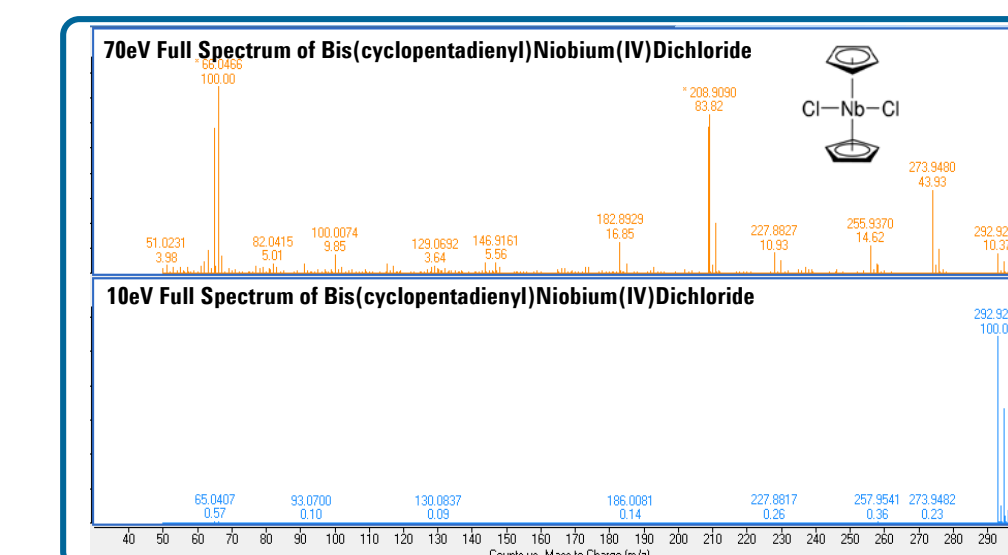


Figure 8: Mass spectrum of Bis(cyclopentadienyl)Niobium(IV) Dichloride at 70 eV and 12 eV

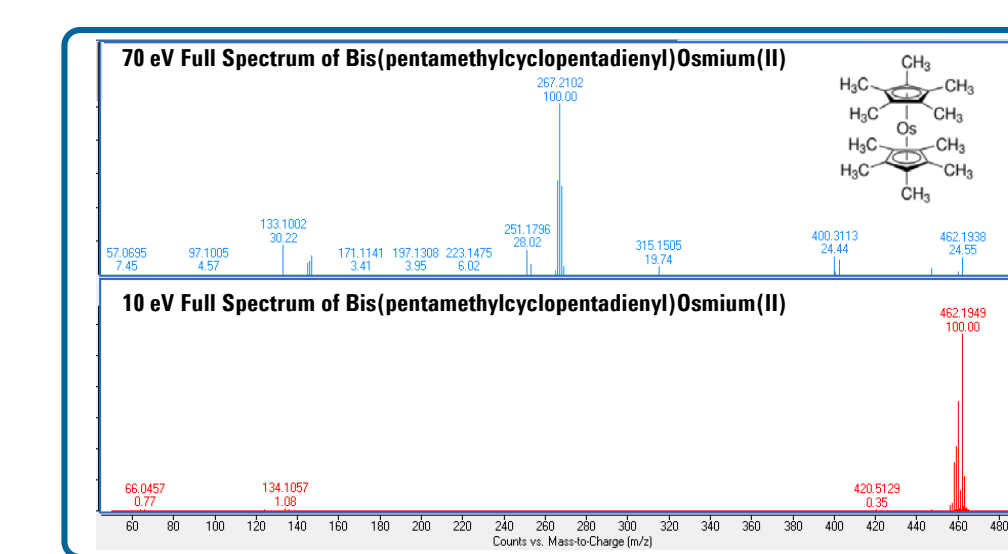


Figure 9: Mass spectrum of Bis(pentamethylcyclopentadienyl)Osmium(II) at 70 eV and 12 eV

Molybdenum Compound Evaluated with Soft Ionization

Dichlorobis[(2,6-diisopropylphenyl)imido](1,2-dimethoxyethane)Molybdenum(VI) (Mo607) was analyzed at 70 eV and 12 eV (Figure 10). While a small spectral tilt is seen in low m/z ions, a large enhancement of higher m/z molybdenum clusters are observed. The most abundant cluster at 12 eV is the m/z 511.1631 (base peak of cluster: +7, m/z 518.1138, -0.6 ppm mass error) elimination of the 1,2-dimethoxy ethyl ligand. The cluster at m/z 554.1631 (base peak of cluster: +7, m/z 560.1596, -2.7 ppm mass error) is the loss of CH_2O_2 .

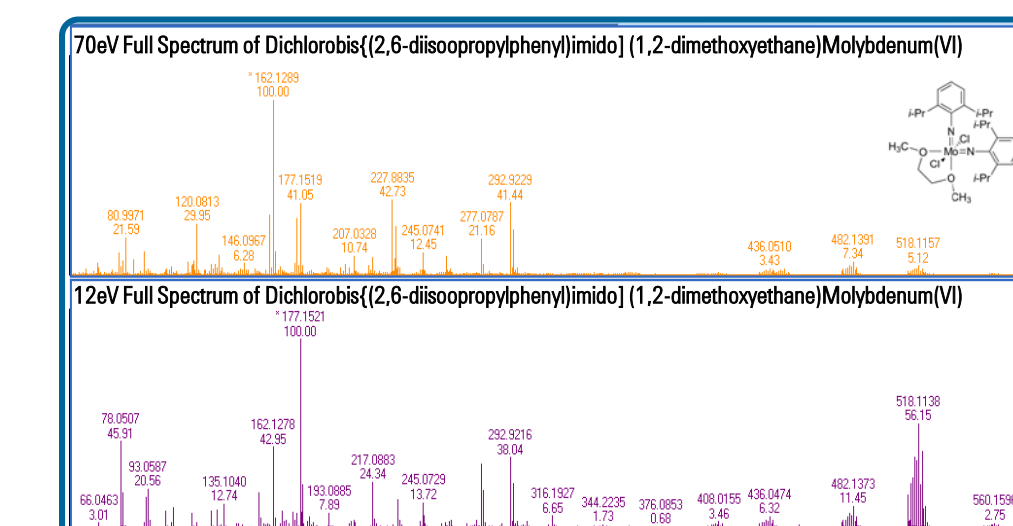


Figure 10: Mass Spectrum of Mo607 at 70 eV and 12 eV

Isotope Distribution for m/z 554.1631 cluster (Mo607)

Theoretical	Observed	Difference (%)
34.39	33.89	0.5
10.45	11.27	0.8
45.03	44.77	0.3
50.38	49.92	0.5
69.3	68.86	0.4
64.83	64.34	0.5
100	100.00	0.0
45.67	44.55	1.1
71.93	70.87	1.1
22.45	22.18	0.3
23.75	23.19	0.6
6.5	7.00	0.5
3.23	3.79	0.6

Table 2: Isotope ratios for ion m/z 554.1631 cluster of Mo607

Conclusions

- Under optimized conditions, high molecular weight transition metal organometallics can be evaluated using accurate mass high resolution GC/Q-TOF
- Soft ionization enhances high m/z ions and molecular ion for transition metal organometallics
- Unique isotope patterns and accurate mass can be used to identify specific compounds and yield information about the structure.

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