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Supporting Information

Comparative Assessment of ESI-MS Softness for Inorganic Complexes: How Soft Is Your ESI-MS?

Ian C. Chagunda,* Peter J. H. Williams, Tiago Fisher, Naomi L. Stock, Daniel G. Beach,
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SUPPORTING INFORMATION

for

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Ian C. Chagunda,^{*a} Peter J. H. Williams,^a Tiago Fisher,^a Naomi L. Stock,^b Daniel G. Beach,^c Gilian T. Thomas,^d Jane Zhu,^e J. Scott McIndoe^{*a}

^a Department of Chemistry, University of Victoria, PO Box 1700 STN CSC, Victoria, BC V8W 2Y2, Canada.

* Tel: +1 (250) 721-7181; E-mail: chagunda@uvic.ca, mcindoe@uvic.ca; Website: <http://web.uvic.ca/~mcindoe/>

^b Water Quality Centre, Trent University, 1600 West Bank Drive, Peterborough, ON K9L 0G2, Canada.

^c Biotoxin Metrology, National Research Council Canada, 1411 Oxford St., Halifax, NS B3H 3Z1, Canada.

^d Centre for Catalysis Research and Innovation, Department of Chemistry and Biomolecular Sciences, University of Ottawa, 10 Marie Curie, Ottawa, ON K1N 6N5, Canada.

^e Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada.

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Materials and chemicals

Triphenylphosphine oxide, 98%, NaCl, 99%, and tetrakis(triphenylphosphine)palladium(0), 99%, and were purchased from Sigma-Aldrich and used as received. Bis(triphenylphosphine)iminium triphenylphosphine monosulfonate $[\text{PPN}]^+[\text{P}(\text{Ph})_2(m\text{-C}_6\text{H}_4\text{SO}_3)]^-$ or $[\text{PPN}][\mathbf{1}]$, was synthesized as reported previously and consistent characterization data obtained.^[42,56] Methanol (HPLC grade) and tetrahydrofuran (HPLC grade) were purchased from Fisher Scientific and degassed using the freeze-pump-thaw method and kept under inert atmosphere before use. N_2 (HP300 4.8) was purchased from Airgas (Calgary, Canada) and used without further purification. All chemicals were shared with collaborators at the University of British Columbia, Trent University – Water Quality Centre, Biotoxin Metrology – National Research Council Canada, and the University of Ottawa, and used without further processing unless otherwise specified. Experiments were set-up and performed under ambient conditions for $[\text{Na}(\text{OPPh}_3)_n]^+$ tests, or under inert (N_2) atmosphere using standard glovebox and Schlenk line techniques^[57] for $[\text{Pd}(\text{PPh}_3)_n(\mathbf{1})]^-$ tests, where available.

ESI-MS instruments operating parameters

Tables 1-8 show the operating parameters for ESI-MS Systems 1-8. For Systems 1 and 2, the non-optimized parameters refer to the “default” conditions used for spectra shown in Figure 1. Then, using OptiMS,^[34] parameters were optimised for “softness” until a set of parameters that maximized the signal intensity of the $[\text{Na}(\text{OPPh}_3)_4]^+$ ($m/z \sim 1135.33$) and $[\text{Pd}(\mathbf{1})(\text{PPh}_3)_2]^-$ ($m/z \sim 971.13$) corresponding peaks was reached. Optimizing instrument parameters led to notable improvements in softness, exemplified by the enhanced relative intensity of all peaks in System 1, and enhanced signal intensity with reducing baseline noise in System 2 shown in Figure 2. For Systems 3-8, ESI source parameters were chosen through manual user-driven optimization in each lab aimed at maximizing the signal intensity of higher n species.

Table S1: Waters TQD instrument parameters.

Parameter	Non-optimized		OptiMS optimized	
	Positive Mode	Negative Mode	Positive Mode	Negative Mode
Flow rate (direct infusion)	20 $\mu\text{L min}^{-1}$	20 $\mu\text{L min}^{-1}$	20 $\mu\text{L min}^{-1}$	20 $\mu\text{L min}^{-1}$
Capillary voltage	4.0 kV	3.0 kV	2.0 kV	3.0 kV
Cone voltage	30 V	15 V	12 V	12 V
Extractor voltage	3.0 V	3.0 V	2.0 V	3.0 V
RF Lens voltage	0.5 V	0.3 V	0.3 V	0.3 V
Source temperature	120 °C	100 °C	80 °C	80 °C
Desolvation temperature	250 °C	180 °C	180 °C	180 °C
Cone gas flow	50 L hr^{-1}	100 L hr^{-1}	100 L hr^{-1}	100 L hr^{-1}
Desolvation gas flow	300 L hr^{-1}	200 L hr^{-1}	200 L hr^{-1}	200 L hr^{-1}

Table S2: Waters Synapt G2-Si instrument parameters.

Parameter	Non-optimized		OptiMS optimized	
	Positive Mode	Negative Mode	Positive Mode	Negative Mode
Flow rate (direct infusion)	20 $\mu\text{L min}^{-1}$	20 $\mu\text{L min}^{-1}$	20 $\mu\text{L min}^{-1}$	20 $\mu\text{L min}^{-1}$
Capillary voltage	3.0 kV	2.5 kV	1.5 kV	2.0 kV
Sampling cone voltage	40 V	40 V	0 V	0 V
Source offset	80 V	80 V	5 V	5 V
Source temperature	80 °C	100 °C	80 °C	80 °C
Desolvation temperature	200 °C	200 °C	200 °C	180 °C
Cone gas flow	50 L hr ⁻¹	50 L hr ⁻¹	50 L hr ⁻¹	100 L hr ⁻¹
Desolvation gas flow	600 L hr ⁻¹	600 L hr ⁻¹	200 L hr ⁻¹	200 L hr ⁻¹
Transfer collision energy	1.0 V	1.0 V	1.0 V	1.0 V

Table S3: Sciex QTRAP 5500 parameters. (NRC)

Parameter	Positive Mode	Negative Mode
Flow rate	5 $\mu\text{L min}^{-1}$	
IonSpray voltage	4.5 kV	
Declustering potential	120 V	
Spray temperature	200 °C	
Curtain gas	10 L min ⁻¹	
Ion Source gas 1	5 L min ⁻¹	
Ion Source gas 2	2 L min ⁻¹	

Table S4: Sciex QTRAP 5500 parameters. (Trent U.)

Parameter	Positive Mode	Negative Mode
Flow rate	7 $\mu\text{L min}^{-1}$	7 $\mu\text{L min}^{-1}$
IonSpray voltage	5.5 kV	4.5 kV
Entrance potential	10 V	10 V
Declustering potential	0 V	200 V
Spray temperature	43 °C	43 °C
Curtain gas	20 L min ⁻¹	20 L min ⁻¹
Ion Source gas 1	20 L min ⁻¹	20 L min ⁻¹

Table S5: Thermo Exactive Plus Orbitrap parameters.

Parameter	Positive Mode	Negative Mode
Flow rate	0.1 mL min ⁻¹	0.10 mL min ⁻¹
Spray voltage	3.5 kV	2.5 kV
Capillary temperature	250 °C	250 °C
Probe heater temperature	200 °C	200 °C
S-Lens RF level	50	50
Sheath gas	35	35
Aux gas	20	20

Table S6: Thermo QE HF Quad-Orbitrap parameters.

Parameter	Positive Mode	Negative Mode
Flow rate	3 $\mu\text{L min}^{-1}$	5 $\mu\text{L min}^{-1}$
Spray voltage	3.75 kV	3.75 kV
Capillary temperature	200 °C	250 °C
S-lens	70	70
Sheath gas	2	0
Aux gas	2	2
Sweep gas	0	0

Table S7: Bruker Solarix XR FT-ICR parameters.

Parameter	Positive Mode	Negative Mode
Flow rate	180 $\mu\text{L hr}^{-1}$	180 $\mu\text{L hr}^{-1}$
Capillary voltage	5.5 kV	5.5 kV
Desolvation temp.	180 $^{\circ}\text{C}$	180 $^{\circ}\text{C}$
Desolvation gas flow	4 L min^{-1}	4 L min^{-1}
Nebulizer gas	1 bar	1 bar
Free ion decay (FID)	0.2621 s	0.2621 s
ICR cell accumulation	0.004 s	0.8 s

Table S8: Agilent 6545 LC/Q-ToF MS parameters.

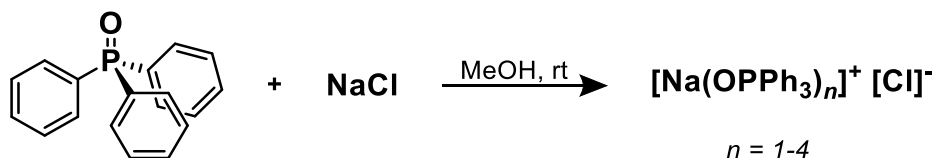
Parameter	Positive Mode	Negative Mode
Capillary voltage	4.0 kV	
Nozzle voltage	0 V	
Gas temperature	325 $^{\circ}\text{C}$	
Drying gas flow	10 L min^{-1}	
Sheath gas temp.	400 $^{\circ}\text{C}$	
Sheath gas flow	12 L min^{-1}	
Nebulizer gas	20 psi	

Table S9: Absolute ion intensities for the 100% relative intensity peaks.

ESI-MS Instrument	Ion mode	100% relative intensity peak	Absolute ion intensity / cps.
Waters TQD (non optimized)	+	n = 3	3.2×10^6
	-	n = 2	2.6×10^5
Waters Synapt G2-Si (non optimized)	+	n = 3	2.2×10^9
	-	n = 1	1.8×10^9
Waters TQD (optimized)	+	n = 3	5.4×10^7
Waters Synapt G2-Si (optimized)	+	n = 2	3.0×10^9
Sciex QTRAP 5500 (NRC)	+	n = 4	1.7×10^7
Sciex QTRAP 5500 (Trent U.)	+	n = 1	3.8×10^8
	-	n = 1	1.5×10^8
Thermo Exactive Plus Orbitrap	+	n = 3	1.6×10^8
	-	n = 2	3.3×10^5
Thermo QE HF Quad-Orbitrap	+	n = 3	1.2×10^9
	-	m/z 799	3.4×10^7
Bruker Solarix	+	n = 2	4.6×10^{10}
	-	n = 1	1.1×10^{11}
Agilent 6545	+	n = 2	1.0×10^6

General test procedures

Positive-mode ESI-MS of $[\text{Na}(\text{OPPh}_3)_n]^+$

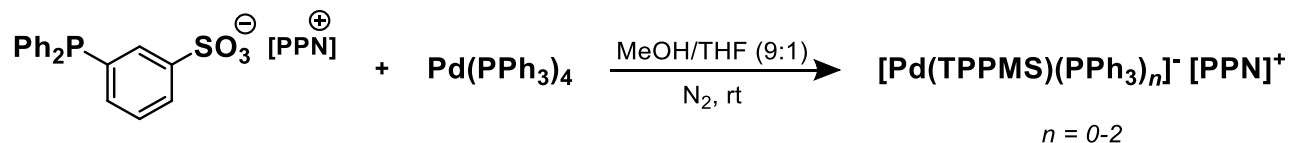


In a typical experiment, aliquots of the NaCl stock solution (1.0 mM in H₂O, 0.1 mL, 0.1 μmol) and the OPPh₃ stock solution (1.0 mM in MeOH, 0.1 mL, 0.1 μmol) were mixed, and the sample made up to 2 mL with methanol for a 1:4 equivalent sample (0.05 mM NaCl and 0.20 mM OPPh₃). Infusion of the sample to ESI-MS yielded a spectrum with $[\text{Na}(\text{OPPh}_3)_n]^+$ peaks where $n = 1-4$, with expected m/z values shown in Table S10.

Table S10: Expected spectral peaks for $[\text{Na}(\text{OPPh}_3)_n]^+$ test.

$[\text{Na}(\text{OPPh}_3)_n]^+$	$n = 1$	$n = 2$	$n = 3$	$n = 4$
m/z	301.0753	579.1613	857.2474	1135.3334

Negative-mode ESI-MS of $[\text{Pd}(\mathbf{1})(\text{PPh}_3)_n]^-$



An equimolar solution of 0.5 mM Bis(triphenylphosphine)iminium triphenylphosphine monosulfonate $[\text{PPN}]^+[\text{P}(\text{Ph})_2(m\text{-C}_6\text{H}_4\text{SO}_3)]^-$ or $[\text{PPN}][\mathbf{1}]$ and 0.5 mM $\text{Pd}(\text{PPh}_3)_4$ was prepared in 9:1 MeOH/THF and kept under inert atmosphere. A 1 mL sample of the solution was collected from the glovebox via a sealed syringe, with direct infusion into the ESI-MS inlet yielding a spectrum of $[\text{Pd}(\mathbf{1})(\text{PPh}_3)_n]^-$, where $n = 0-2$, with expected m/z values shown in Table S11.

Table S11: Expected spectral peaks for $[\text{Pd}(\mathbf{1})(\text{PPh}_3)_n]^-$ test.

$[\text{Pd}(\mathbf{1})(\text{PPh}_3)_n]^-$	$n = 0$	$n = 1$	$n = 2$
m/z	446.9442	709.0353	971.1264

$[\text{Pd}(\text{O}_2)(\mathbf{1})(\text{PPh}_3)_n]^-$	$n = 0$	$n = 1$	$n = 2$
m/z	478.9340	741.0251	1003.1163

Stoichiometric effects on $[\text{Na}(\text{OPPh}_3)_n]^+$ spectra

Exploring different molar ratios of Na^+ to OPPh_3 in our experiments revealed variations in the relative amounts of the produced ions in the mass spectra (Figure S1). As anticipated, a 1:4 $\text{NaCl}:\text{OPPh}_3$ molar ratio consistently yielded the highest relative intensity of the $n = 4$ peak, aligning with our expectations.

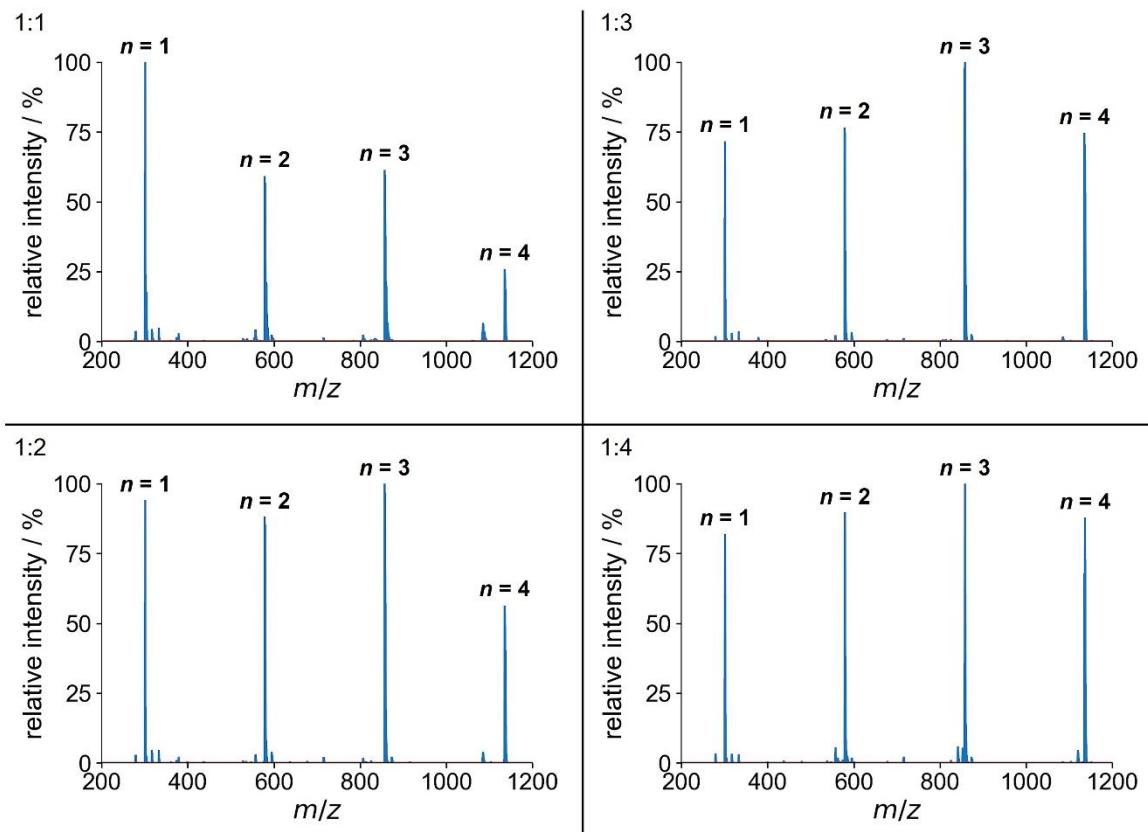


Figure S1: Effects of NaCl and OPPh_3 stoichiometry on positive-ion ESI mass spectra of $[\text{Na}(\text{OPPh}_3)_n]^+$ ions collected on System 1. Pane numbers represent the molar ratio of NaCl to OPPh_3 .

Fragmentation by ion trapping for System 3

The impact of ion trapping on ion fragmentation is illustrated in Figure S2, specifically evident in the Q3 ion trapping results. In this experiment, ion trapping, which imparts an additional minimum trapping energy of 5 V, resulted in a reduction in the relative signal intensity of the $n = 3$ peak, accompanied by an increase in the relative intensity of the $n = 2$ peak (Figure S2a). (The upper mass range limit (m/z 1000) hindered the detection of $n = 4$ ions). This observed shift in peak intensities is attributed to the additional ion fragmentation induced by the heightened internal energy caused by the ion trapping process, where additional energy is imparted to focus/trap ions in Q3. This shift is not attributed to in-source conditions, which were the same as in normal full scan mode (Figure S2b). The Q3 ion trapping results underscore the intricate interplay between ion trapping and fragmentation dynamics, emphasizing the need for a nuanced understanding of these processes to optimize experimental conditions and interpret mass spectra accurately.

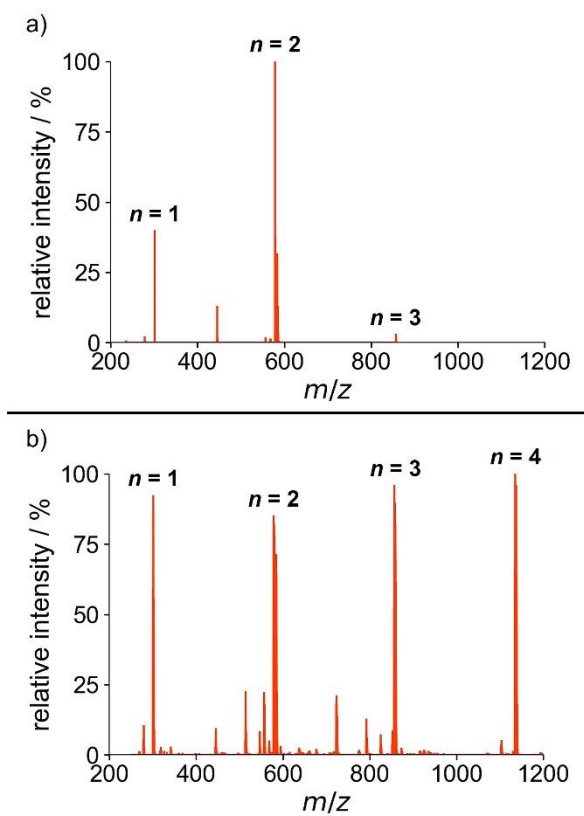


Figure S2: Full scan positive-ion ESI mass spectra of [Na(OPPh₃)_n]⁺ ions on System 3 (SCIEX QTrap 5500), obtained using a) Q3 as an ion trap and b) Q3 as a quadrupole filter.