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Investigating reduced metal species via sequential ion/ion and ion/molecule reactions: The reactions of transition metal phenanthrolines with allyl iodide

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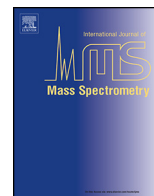*Department of Chemistry, Virginia Commonwealth University, 1001 W. Main St., Richmond, VA 23824 USA, USA*

A B S T R A C T

Sequential ion/ion and ion/molecule reactions are demonstrated in a linear ion trap mass spectrometer and are used to probe the reactivity of metal complexes in unusual ionization states. Taking advantage of the instrument's electron transfer dissociation (ETD) capabilities, the mono- and bis-phenanthroline complexes of Fe(I), Co(I), Ni(I), Cu(I), and Zn(I) were formed by reduction of the corresponding M(II) species in an ion/ion reaction with the fluoranthene radical anion. The chemistry of the M(I) species was probed in ion/molecule reactions with allyl iodide. The bis-phenanthroline complexes generally give slow reactions and the metals were oxidized to M(II) iodide complexes with presumably the release of allyl radicals. The mono-phenanthroline complexes are much more reactive and give M(II) iodide complexes, M(II) allyl complexes, and adducts. The overall reactivity is in accord with density functional theory calculations and mirrors that of proposed intermediates in condensed-phase catalytic cycles.

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1. Introduction

Ion/ion reactions have been widely studied in recent years because they offer novel ways to gain structural information about analytes, particularly complex biological molecules [1–4]. Although many approaches have been used, the one-electron reduction of analytes with the fluoranthene radical anion has been incorporated into commercial instrumentation and was been widely employed in peptide fragmentation schemes (commonly referred to as electron transfer dissociation, ETD) [3]. This methodology has much in common with electron-capture dissociation [5], but can be applied in situations where reactions with low-energy electrons are not practical. Although it is not as common, ion/ion reactions employing anions with weakly-bound electrons can also be used to generate species in novel oxidation states via the selective one-electron reduction of precursor ions. In ion-trap mass spectrometers, the trapping potentials make it feasible to conduct ion/ion or ion/molecule reactions. With appropriate reagent pressures and trapping sequences, it is possible to create hybrid experiments in these instruments that link together ion/ion, ion/molecule, and potentially collision-induced dissociation processes. In the current study, we demonstrate the ability to complete ion/ion followed by ion/molecule reactions in a modified, commercial linear ion trap mass spectrometer with ETD capabilities. The results suggest that this is a general way of studying the bimolecular chemistry of species in unusual oxidation states.

During a variety of reduction processes, metals pass through uncommon oxidation states. In many cases, it is difficult to isolate and study the metals in these oxidation states, but it is believed that they can engage in useful and interesting chemical reactivity. To establish a method for examining these types of systems, we have initially focused on phenanthroline complexes of transition metals in the +1 oxidation state (Scheme 1). Specifically, we have examined the mono- and bis-phenanthroline complexes of Fe(I), Co(I), Ni(I), Cu(I), and Zn(I). Aside from copper, each of these metals is typically not found in the +1 oxidation state. Mestdagh and Rolando have examined related bare metal cation species and their reactivity with allyl chloride [6]. Phenanthroline provides a rigid, bidentate ligand and the properties of phenanthroline metal complexes have been widely explored in the past in the condensed and gas phase [7–9]. In the present context, we view them as ideal models for testing our system for completing ion/ion followed by ion/molecule reactions. It should be noted that McLuckey [10,11] has used metal phenanthroline complexes in the past in ion/ion reactions. However in those studies, the metal phenanthrolines

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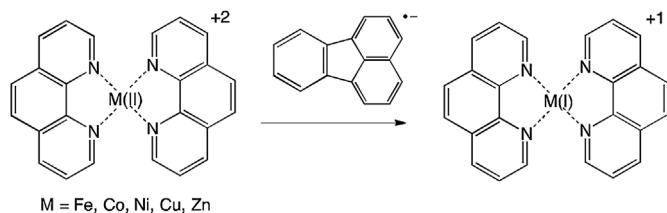
Scheme 1. Reactant ions.

were used to oxidize poly-anions of interest and the bimolecular chemistry of the reduced metal complex was not explored.

For these metals, complexes of the +1 oxidation state are expected to be active as reducing agents and can play roles in the reductive cleavage of carbon-halogen bonds. In addition, there has been recent interest in C—C coupling processes involving Ni(I), Co(I), and Fe(I) [12–16]. For example, Norrby has shown that it is an Fe(I) species that undergoes the rate-determining oxidative addition in an iron-catalyzed coupling reaction [12]. These species also are transients in the electrochemical reduction/oxidation of metals and can undergo unusual chemistry near electrodes [17–22]. Here we will focus on the reactions of M(I) phenanthroline species with allyl iodide.

2. Methods

All experiments were performed in a modified Thermo Electron LTQ XL^{TM} linear quadrupole ion trap mass spectrometer with an electrospray ionization source (ESI). The modifications allow for the introduction of reagent gases into the helium buffer gas and are similar to those we have made to Finnigan LCQ ion trap mass spectrometers in the past [23,24]. The metal complexes were generated via ESI from 10^{-5} M solutions of an appropriate metal salt and 1, 10-phenanthroline. Flow rates ranging from 5 to 10 μL/min were used with typically an ESI needle voltage of 5 kV.

The neutral reagents were introduced into the linear quadrupole as part of the helium buffer gas flow. A consistent and constant flow of the neutral reagent was added by a syringe pump (30–140 μL/h) to a measured flow of helium (1–1.5 L/min). Rapid vaporization of the liquid reagent at the needle tip allows for molar mixing ratios of ~10^3–10^5 He/reagent. The majority of the neutral reagent gas mixture exits the manifold through a flow meter; however a small amount is drawn into the mass analyzer cavity (~1 mL/min) through the "open split" restrictor capillary. The pressure created by the reagent can be calculated from helium pressure (~10^{-3} torr) and the mixing ratio (taking into account differential diffusion) [24]. The system is regularly calibrated using reactions with known rate constants [25].

In a typical experiment, the metal complex solution is introduced via the ESI interface. The system is tuned to the peak of interest and then this species is isolated in the ion trap. Electron transfer dissociation (ETD) is performed on the isolated dication, resulting in a reduced, singly charged complex. The newly reduced complex is then isolated again in the ion trap. Once a suitable, steady signal has been established, the neutral reagent mixture is introduced into the helium mixing manifold. The system is allowed to equilibrate for several minutes. The LTQ software is set for tandem mass spectrometry (MS/MS) scans of the singly-charged ion, but with an excitation energy of 0 V. The reactions were monitored and data was collected as a function of reaction time at various neutral reagent flow rates (reagent pressures). All kinetic measurements were performed under the assumption of pseudo first-order conditions. This assumption is made because the neutral reagent concentration is much greater than the ion concentration (reagent/cation = 10^5–10^6). The reagent flow rates are chosen to

produce kinetic runs that cover two to three half-lives. All reported rates are measured at three different flow rates and at least 10 kinetic runs were collected on two or more days. The kinetic plots showed linearity with correlation coefficients (r^2) greater than 0.95. No corrections are incorporated for possible mass discrimination in branching ratios. We have shown in the past that the ion trap provides a reaction environment at near thermal temperatures [23].

All reagents were purchased from commercial sources and were used with no further purification. The following salts were used in preparing the complexes: cobalt (II) chloride (Acros, Geel, Belgium), copper(II) acetate (Fisher, Pittsburgh, PA), iron(II) chloride (Mallinckrodt, St. Louis, MO), nickel (II) acetate tetrahydrate (Sigma, St. Louis, MO), and zinc (II) chloride (Sigma, St. Louis, MO). The ligand solution consisted of 1,10-phenanthroline (Sigma, St. Louis, MO). Density functional calculations were completed using the Gaussian03 and Gaussian09 suites of quantum mechanical programs [26,27].

3. Results and discussion

3.1. Formation of M(I) complexes by ion/ion reactions

The solutions of the metal salts and phenanthroline generally favor production of doubly-charged ions during ESI with two phenanthrolines bound to the M(II) metal center, M(II)Phen$_2$$^{+2}$ (throughout the manuscript, we will show the structures with neutral phenanthrolines – it is possible that in some species, charge transfer to the phenanthroline could occur to some extent). It is possible to prepare the mono-phenanthroline complexes, M(II)Phen^{+2}, by subjecting the bis-phenanthroline complexes to collision-induced dissociation (CID). The added steps in producing these ions led to somewhat lower signal intensities. Once isolated, the metal phenanthroline dication complexes can be subjected to ion/ion reactions with the fluoranthene radical anion using the ETD feature of the Thermo LTQ mass spectrometer. In typical experiments, an ion/ion reaction time of 200 ms was used to complete the reduction of the metal (the subsequent ion/molecule reaction times were 1000–9999 ms). In Fig. 1, spectra are given for the entire reaction sequence for the cobalt bis-phenanthroline system. Using this approach, it was possible to generate M(I)Phen^{+1} and M(I)Phen$_2$$^{+1}$ ions for iron, cobalt, nickel, copper, and zinc from their dication precursors. It appears that the M(I) species are very reactive with molecular oxygen and reactions with adventitious oxygen in the ion trap lead to addition products. The vacuum system of LTQ does not allow us to eliminate the background oxygen, but it is possible to study bimolecular chemistry despite the unwanted side reactions. Finally, it should be noted that in some cases, signals for M(I) species were observed in the ESI spectra of the starting solutions – reductions of this type during ESI have been observed previously [28]. These complexes produce the same products as the ETD-produced complexes.

3.2. Ion/molecule reactions of M(I) complexes

In our design, the neutral reagent enters the ion trap as part of the helium buffer gas and is held at a constant pressure throughout each stage of the experiment. An advantage of this approach is that the neutral gas reaches an equilibrium pressure and it is possible to conduct accurate kinetic measurements. A possible disadvantage is that the neutral reagent can react with precursor ions, including the fluoranthene radical anion. However, it has been proven that this interaction does not occur. As a result, the pressure of the neutral reagent must be carefully controlled so that the ion/ion reaction of the precursor dication is much faster than the reactions of the neutral reagent with the dication or with the fluoranthene radi-
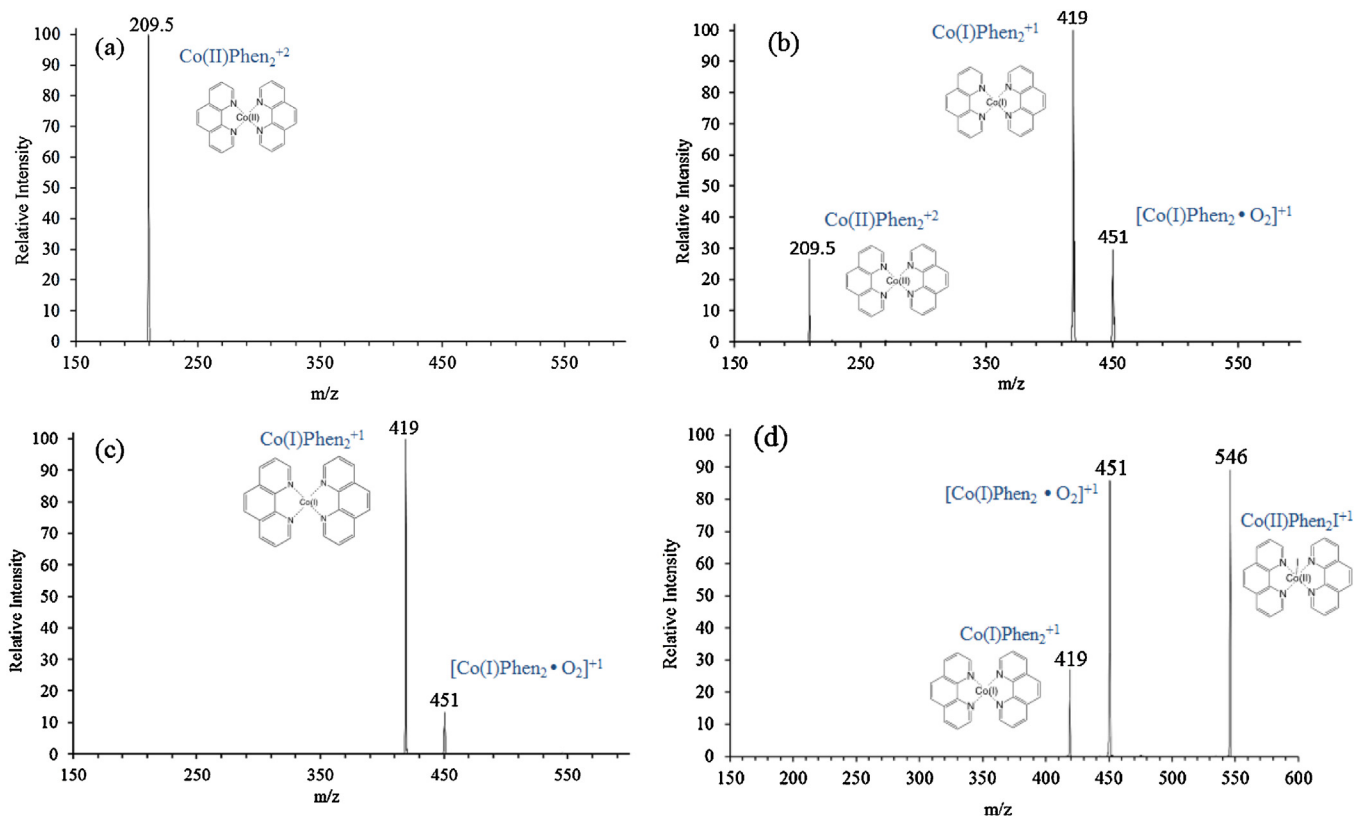
Fig. 1. Preparation and reactions of Co(I)Phen$_2^{+1}$: (a) isolation of Co(II)Phen$_2^{+2}$ at m/z 209.5, (b) reduction with fluoranthene radical anion to give Co(I)Phen$_2^{+1}$ at m/z 419, (c) isolation of Co(I)Phen$_2^{+1}$, and (d) reaction of Co(I)Phen$_2^{+1}$ with allyl iodide. Oxygen adducts of Co(I)Phen$_2^{+1}$ at m/z 451 are seen in panels (b)–(d).

cal anion. Of course, this competition is aided by the electrostatic attraction in the ion/ion reactions, which leads to very high reaction rates.

3.2.1. Reactions of M(I)Phen$_2^+$ with allyl iodide

Allyl iodide is an attractive reagent for probing the reduced metal complexes because it has an exceptionally weak carbon-halogen bond and can produce a relatively stable hydrocarbon radical (i.e., allyl) during one-electron reduction processes. With Fe(I)Phen$_2^{+1}$, Co(I)Phen$_2^{+1}$, Ni(I)Phen$_2^{+1}$, and Zn(I)Phen$_2^{+1}$, the sole reaction product with allyl iodide is iodine addition to the complex, presumably with the release of an allyl radical. (Eq. (1)). The iodine addition can be viewed as a metal oxidation process and the products are best described as M(II)Phen$_2$I^{+1} species with the metal returned to the +2 oxidation state. As noted above, there is competition from reactions with adventitious oxygen in the ion trap, and in some cases, is the major process (spectra in Supporting information). The copper complex, Cu(I)Phen$_2^{+1}$, does not give any products with allyl iodide.

$$M(I)Phen_2^{+1} + CH_2 = CHCH_2 - I \rightarrow I - M(II)Phen_2^{+1} + CH_2$$
$$= CHCH_2^\bullet \qquad (1)$$
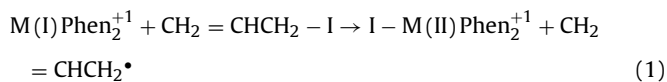
The rate constants of the reactions are listed in Table 1. With the bis-phenanthroline complexes, the reactions tend to be relatively slow (estimated efficiencies of less than 5%) and there is a clear dependence on the metal center. Fe(I)Phen$_2^{+1}$, Co(I)Phen$_2^{+1}$, and Zn(I)Phen$_2^{+1}$ give roughly similar rates (vary by a factor of 3) with cobalt being the most reactive. Calculations at the B3LYP/6–311 + G** level (see below) indicate that the iron and cobalt systems prefer high-spin ground states (quartet and triplet, respectively) with substantial unpaired spin at the metal center.

Table 1
Rate Constants for Reactions of M(I)Phen$_2^{+1}$ with Allyl Iodide.[a]

Metal	k
Fe	1.1 ± 0.1 (0.011)
Co	2.4 ± 0.5 (0.024)
Ni	0.059 ± 0.005 (0.0006)
Cu	NR[b]
Zn	0.8 ± 0.2 (0.0082)

[a] Rate constants in units of 10^{-11} cm^3 molecule^{-1} s^{-1}. Standard deviations from multiple runs are shown as uncertainties and reflect the precision of the experiments. We estimate absolute uncertainties of ± 30%. Efficiencies (k/k_{ADO}) are given parenthetically [32].
[b] No products observed, which suggests a rate constant $<10^{-14}$ cm^3 molecule^{-1} s^{-1}.

The zinc system is a d^{10} doublet with the unpaired electron in a 4s orbital, but presumably well delocalized into the ligands as well. The situation with nickel is more complicated. The Ni(I)Phen$_2^{+1}$ ion is a d^9 system with a doublet ground state, but our calculations (see below) indicate that the halogen transfer product is strongly disfavored in its low-spin singlet state and as a result, the reaction effectively involves an energetically unfavorable electron-promotion component (production of the triplet halide complex) that could retard the reaction. The copper complex is a closed-shell, coordinatively-saturated d^{10} system, so the absence of reactivity is not surprising.

In the bis-phenanthroline complexes, the preference for forming a metal-halide bond drives the systems to release allyl radicals (see computational results below). The production of radicals with the ligated M(I) species is consistent with recent condensed-phase studies focused on their roles as reactive intermediates in catalytic cycles [29–31]. For example, divalent Ni(I) species can convert alkyl halides to dimeric alkane products (i.e., 2 R-X ≧ R-R) [30].
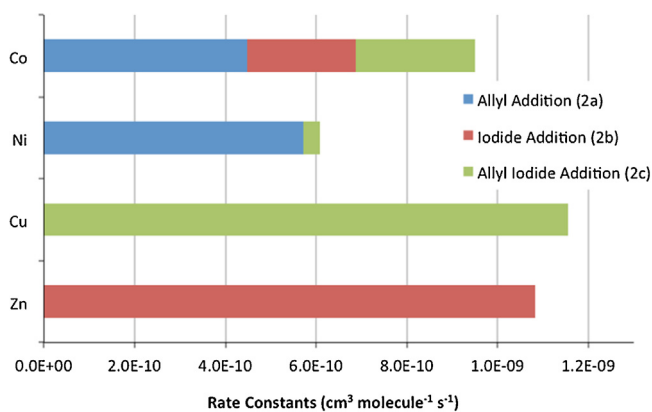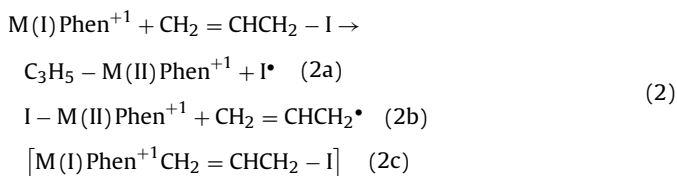
Fig. 2. Partial bimolecular rate constants are shown for each product channel. Contributions from background reactions have been subtracted from the observed pseudo first-order rates. Estimated absolute uncertainties are ± 40%. No rate data could be obtained for Fe(I)Phen$^+$. For all complexes, the collision rate is estimated as 1.08×10^{-9} cm^3 molecule^{-1} s^{-1}.

Table 2
Computed Data for M(I)Phen$_n$$^{+1}$ Species[a]

| Metal | M(I)Phen$_2$$^+$ | | M(I)Phen$^+$ | |
	low spin	high spin	low spin	high spin
Fe	5.3 (d)	0.0 (q)	11.0 (d)	0.0 (q)
Co	2.0 (s)	0.0 (t)	25.4 (s)	0.0 (t)
Ni	0.0 (d)	28.1 (q)	0.0 (d)	39.2 (q)
Cu	0.0 (s)	37.8 (t)	0.0 (s)	55.2 (t)

[a] Values are differences in electronic energies in kcal/mol. Spin states are given parenthetically.

3.2.2. Reactions of M(I)Phen^{+1} with allyl iodide

The reactions with the mono-phenanthroline complexes of the M(I) species are much faster and the rates approach the collision-controlled limit. It was more difficult to obtain accurate rate constants with these species because of their rapid reactions with oxygen and allyl iodide (as well as the reactions of precursor ions). This caused problems in creating a kinetic separation with the reduction process. However, it was possible in all cases to obtain clean spectra for the reactions with allyl iodide (kinetic data is available for all but the iron system). With the mono-phenanthroline complexes, three product channels are observed: iodine transfer, allyl transfer, and addition (Eq. (2)). Peaks were also observed for adducts with adventitious oxygen and water in the trap. The distributions are highly dependent on the identity of the metal (Fig. 2). With allyl iodide, the iron complex exclusively leads to iodine transfer – there is no adduct formation in this case. The cobalt complex reacts at near the collision-controlled limit and gives the most varied reactivity – it produces a relatively even mix of the three reaction channels. The nickel complex is somewhat less reactive (about 50% efficiency) and is the only one that exhibits a strong preference for allyl transfer (with a small amount of adduct formation). As was seen with the bis-phenanthroline complexes, the copper system does not produce transfer products and an adduct is rapidly produced in this case. Finally, the zinc complex exclusively undergoes a rapid iodine transfer with allyl iodide. These reactivity patterns can be rationalized with the results of computational modeling (see below).

$$M(I)\,Phen^{+1} + CH_2 = CHCH_2 - I \rightarrow$$
$$C_3H_5 - M(II)\,Phen^{+1} + I^\bullet \quad (2a)$$
$$I - M(II)\,Phen^{+1} + CH_2 = CHCH_2{}^\bullet \quad (2b) \qquad (2)$$
$$\left[M(I)\,Phen^{+1}CH_2 = CHCH_2 - I \right] \quad (2c)$$

3.3. Density functional theory (DFT) calculations

To gain better insight into the M(I) species and their reactions, DFT calculations were completed at the B3LYP/6–311+G** level. This methodology is not expected to provided highly accurate quantitative values, but can provide a reasonable overview of the energetics of competing processes. With iron, cobalt, nickel and copper, high and low-spin species were considered for each. Because of its d^{10} core, zinc was considered only in its lowest spin state. Relative energies are provided in Table 2 for the M(I)Phen$_n$$^{+1}$

species. In both ligation schemes, the iron and cobalt prefer high-spin ground states, whereas nickel and copper prefer low-spin ground states. The differences in energies are much larger in the mono-phenanthroline species, particularly for iron and cobalt.

To examine the reactions with allyl iodide, we have used allyl bromide as a model substrate because iodine is problematic for computational modeling [33]. Bromide is much more manageable computationally and should provide a reasonable qualitative picture of the reaction energetics. Allyl bromide was not used in the experimental work because the reactions were too slow to give accurate kinetics with all the complexes. We completed some preliminary survey work with allyl bromide and it produced similar products as allyl iodide (i.e., bromide transfer with the bis-phenanthroline complexes). The data is shown in Table 3 and all the values are referenced to the ground spin state of the metal complex. The energetics for the bis-phenanthroline species are in complete accord with the observed patterns in reactivity. With iron, cobalt, and zinc, pathways to the halide species are favorable, but formation of an allyl complex is not (in all cases, the allyl is a 2-electron, η^1 ligand). These reactions can be directly mediated via singly-occupied orbitals on the metal (i.e., q ≥ t for iron, t ≥ d for cobalt, and d ≥ s for zinc are possible). Both reaction pathways with copper are predicted to be highly unfavorable with allyl bromide and this is likely the case with allyl iodide. In these calculations, nickel offers no energetically favorable paths with allyl bromide, but a high-spin bromide complex is only 2 kcal/mol above the reactants, and therefore the reaction with allyl iodide is likely exothermic. However, this process involves conversion of the low-spin ground state to a high-spin product and consequently involves doubly occupied orbitals in the starting nickel complex. As a result, a slow reaction is expected.

The reactions with the mono-phenanthroline complexes are computed to be much more energetically favorable, including paths to allylic products. The computed structures of the M(I)Phen(C$_3$H$_5$)$^{+1}$ complexes exhibit varying coordination schemes. In their ground-states, iron and nickel prefer η^3-coordination, cobalt and zinc prefer η^1-coordination, and copper prefers an η^2 π-coordination scheme. In Table 3, energies are also given for the formation of oxidative addition products with allyl bromide, i.e., M(III)Br(C$_3$H$_5$)$^{+1}$. In these complexes, the allyl group has η^3-coordination with iron and cobalt, but adopts η^1-coordination with nickel, copper, and zinc (for the latter three metals η^3-coordination would exceed an 18-electron count). Fig. 3 demonstrates two possible products given by the cobalt and nickel complexes. The addition energies vary widely across this series, with d^{10} copper giving the least favorable addition product. In fact, the oxidative addition complex is 9 kcal/mol less stable than a non-covalent, ion-dipole complex with allyl bromide (in contrast, the nickel system prefers the covalent Ni(III) complex by about 4 kcal/mol).

With iron, formation of a triplet halide complex is preferred by 11 kcal/mol over formation of the triplet allyl complex. Apparently, this is sufficient to push the system to give only halide products experimentally. The high exothermicity of the halide transfer pro-

Table 3
Computed Reaction Energies of Ground-State M(I)Phen$_n^{+1}$ complexes with Allyl Bromide.[a]

Metal	M(II)Phen$_2$Br^{+1}		M(II)Phen$_2$(C$_3$H$_5$)$^{+1}$		M(II)PhenBr^{+1}		M(II)Phen(C$_3$H$_5$)$^{+1}$		Adduct[b]
	low spin	high spin	low spin	high spin	low spin	high spin	low spin	high spin	ground-state
Fe	−0.7 (s)	−9.6 (t)	47.2 (s)	35.9 (t)	4.3 (s)	−24.5 (t)	21.5 (s)	−13.2 (t)	−63.4 (q)
Co	−11.4 (d)	−15.0 (q)	30.9 (d)	35.0 (q)	−15.0 (d)	−29.1 (q)	−13.1 (d)	1.9 (q)	−53.4 (t)
Ni	15.4 (s)	2.0 (t)	50.7 (s)	50.7 (t)	6.4 (s)	−6.3 (t)	0.3 (s)	20.0 (t)	−25.0 (d)
Cu	20.7 (d)	84.4 (q)	59.6 (d)	90.7 (q)	4.0 (d)	73.2 (q)	22.4 (d)	96.1 (q)	−13.6 (s)
Zn	−20.3		27.0 (s)		−33.9 (s)		2.8 (s)		−41.8 (d)

[a] Values are differences in electronic energies in kcal/mol. Spin states are given parenthetically.
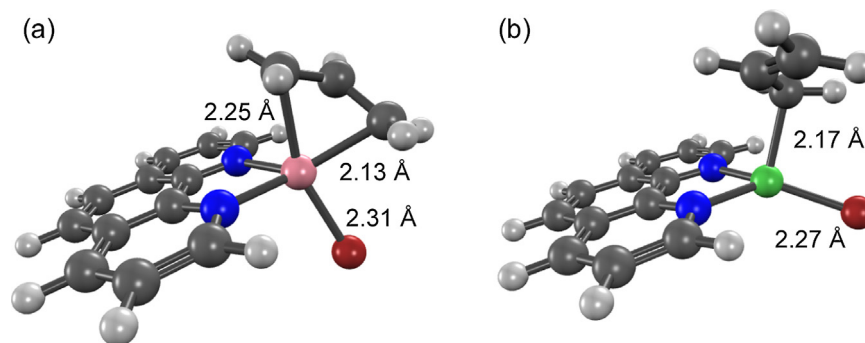[b] Oxidative addition complex, M(III)Br(C$_3$H$_5$)$^{+1}$.

Fig. 3. M06/6−311+G** computed structures of oxidative addition products from reactions of allyl bromide with (a) Co(I) phenanthroline and (b) Ni(I) phenanthroline complexes. Distances metal, and bromide and carbons are shown.

cess can also explain the lack of adduct formation. For cobalt, the paths to the doublet halide and allylic products are equally favorable, which is consistent with the observed product distribution. The cobalt reactions are less exothermic, which can be part of the reason that adduct formation also competes. With nickel, the allyl complex is the preferred singlet product. The reaction is computed to be slightly unfavorable with allyl bromide, but is likely favorable with allyl iodide. The most favorable product energetically is the high-spin, triplet halide, but it requires the participation of a filled orbital in the reactant ion. Experimentally, the allyl product is observed, which suggests a strong preference for a singlet product. Aside from adduct formation, none of the paths are favorable for Cu(I)Phen^{+1}. Zinc has a strong preference for halide transfer and this is the path observed experimentally.

4. Conclusions

We have demonstrated that a commercial ion trap mass spectrometer with ETD capabilities can be modified to give sequential ion/ion and ion/molecule reactions. To illustrate the capabilities of the instrument, a series of doubly-charged, mono- and bis-phenanthroline metal complexes were reduced with the flouranthene radical anion to give M(I)Phen$^+$ and M(I)Phen$_2^+$ complexes. These complexes could then be allowed to react with allyl iodide. The reactions led to iodine transfer, allyl transfer, and adduct formation, depending on the nature of the metal and the number of phenanthroline ligands. The experimental data are completely consistent with the results of computational modeling. These experiments suggest that the modified instrument can be useful in studying the chemistry of metal complexes in reduced oxidation states, a characteristic often found in the reactive intermediates of carbon–carbon coupling processes.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijms.2016.11.018.

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