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Gas phase reactivity of iron pentacarbonyl with anionic metal clusters

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ABSTRACT

The anionic transition metal carbonyl cluster $[H_3Ru_4(CO)_{12}]^-$ may be energized in the gas phase through collision-induced dissociation (CID), which results in sequential loss of hydrogen and carbon monoxide from the cluster. If this experiment is performed in the presence of iron pentacarbonyl gas, up to three equivalents of the iron complex add to the tetranuclear ruthenium complex to give nearly-saturated product clusters with cores containing five, six and seven metal atoms. Further CID reveals that the iron atoms become intimately incorporated into the cluster core, and thus this process represents a method for the gas-phase synthesis of mixed-metal clusters.

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1. Introduction

A classic example of a hard-to-study reaction is the build-up of transition metal carbonyl cluster compounds, a process which typically occurs at elevated temperature in solution between ligated metal clusters and/or with mononuclear feedstocks [1]. A wide variety of different types of high nuclearity clusters can result [2], and such clusters have a possible role in nanoscience and nanotechnologies [3] as well as in catalysis [4]. However, the complexity of the reacting mixtures mean that few techniques are equipped to study the intermediate species formed on the way to the final product. Capturing the build-up process spectroscopically is a real challenge: the complex mixture, combined with a lack of truly diagnostic spectroscopic handles (^{13}C is not sensitive enough and copes poorly with a mixture of similar compounds; νCO peaks are broad and not discriminatory enough), means that the final products are usually the most thermodynamically stable species under the given conditions used and are usually isolated by crystallization and characterized by single-crystal X-ray diffraction [5]. Mass spectrometry has been sporadically used to examine these mixtures, but not in any systematic way, rather just as a collection of snapshots of solution speciation [6].

Gas-phase ion-molecule reactions provide insight into chemistry that is not easily studied in solution [7]. The gas phase has the

virtue of being free from solvent and hence ions are much more reactive as the solvent does not have to be displaced as a prerequisite initiation step for subsequent reactions to occur. Ions can be activated through collision-induced dissociation (and/or other activation methods that deposit energy using photons or electrons), which can be carried out in the same chambers in which reactive molecules are introduced. Ion-ion reactions can be excluded from consideration (these repel each other in the gas phase) as can molecule–molecule reactions (whose products are neutral and hence invisible to mass spectrometry), so the type of reactivity can be tightly controlled.

Others have looked at the reactivity of volatile transition metal organometallic molecules with ions in the gas phase [8], but the field is dominated by self-clustering reactions between ions generated using electron ionization between metal carbonyls in the gas phase and the residual metal carbonyl itself, using ion cyclotron resonance 'trapped-ion' techniques [9]. In the negative ion mode, Ridge showed that $[Fe(CO)_4]^-$ reacts with $Fe(CO)_5$ in the gas phase to form $[Fe_2(CO)_8]^-$ with an efficiency of about 0.01 [10]. Fackler illustrated that $[Fe(CO)_3]^-$ reacted with $Fe(CO)_5$ to generate $[Fe_2(CO)_6]^-$ [11]. The reactions of mononuclear $[Fe(CO)_n]^+$ ions with $Fe(CO)_5$ harvesting a variety of higher nuclearity $[Fe_x(CO)_y]^+$ clusters up to $x = 4$ and $y = 12$ [12]. Other self-clustering studies have included those with $Ni(CO)_4$, [13] $Co(NO)(CO)_3$, [14] $Cr(CO)_6$, [15] $Re_2(CO)_{10}$, [16] $ReMn(CO)_{10}$ [17] and $H_2Os_3(CO)_{10}$ [18]. Squires detailed the reactivity of an extensive series of anions with $Fe(CO)_5$ [19]. Freiser used the reaction between laser desorbed M^+ ions and the volatile organometallic molecules $Fe(CO)_5$ and $Co_2(CO)_8$ to

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generate clusters such as $[FeCo_2(CO)_6]^+$ and $[CoFe(CO)_4]^+$ [20]. Self-clustering of metal carbonyls is also observed in laser desorption ionization (LDI) experiments, with large aggregate ions forming from gas-phase reactions in the laser plume generated during analyses of a wide variety of neutral $M_n(CO)_m$ clusters [21]. Mononuclear precursors under LDI conditions can behave similarly [22], as can clusters under plasma desorption conditions [23].

We previously studied the gas-phase reactivity of $[H_3Ru_4(CO)_n]^-$ ($n = 0$–12) with small molecules, including O_2, alkanes, silanes, alkenes and arenes [24]. Here, we extend those studies to the interaction of the cluster with the transition metal organometallic molecule $Fe(CO)_5$, which is a stable liquid at room temperature. The motivation for these experiments was to examine cluster build-up reactions to learn about their structure and reactivity through MS/MS studies [25]. This would give insight into the order of reactivity in cluster formation in a manner that might parallel condensed phase reactions, in which precursors have been activated following loss of CO ligands.

$Fe(CO)_5$ is a classic 18-electron organometallic complex with iron in an oxidation state of zero; the low oxidation state is stabilized by the strong synergistic bonding of the carbon monoxide ligands, which are weak σ-donors but strong π-acceptor ligands. It is highly fluxional thanks to the low energy of the Berry pseudo-rotation, and susceptible to a wide number of addition reactions following CO dissociation to generate reactive, unsaturated $Fe(CO)_4$. Similar organometallic compounds include $Ni(CO)_4$ and $Cr(CO)_6$, but the former is an extraordinarily toxic gas and correspondingly dangerous to handle while $Cr(CO)_6$ is a crystalline solid with a low vapor pressure. $Fe(CO)_5$ thus occupies a unique position among volatile organometallic compounds in being the only liquid known.

2. Materials and methods

The cluster salt $[PPN][H_3Ru_4(CO)_{12}]$ ($PPN = [Ph_3PNPPh_3]$, the bis(triphenylphosphine)iminium cation) was made by a published method [26]. Iron pentacarbonyl was purchased from Aldrich and used as supplied. Electrospray ionization mass spectra were collected using a Micromass QTof *micro* instrument. Capillary voltage was set at 2900 V, source and desolvation gas temperatures were at 50 and 100 °C, respectively. A minimum of the $[PPN][H_3Ru_4(CO)_{12}]$ salt was dissolved in dichloromethane and infused via syringe pump at 5–10 μL min⁻¹ in order to acquire a spectra consisting of about 500 ion counts per second. EDESI–MS(/MS) spectra were collected using published procedures and processed using the program EDit [27]. The reactive gas was introduced by passing a stream of nitrogen through liquid $Fe(CO)_5$ and directing the gas through the cone gas port. The flow rate was approximately 15 L h⁻¹, compared to a desolvation gas flow rate of 100 L h⁻¹. Incrementing the cone voltage or collision voltage (for MS/MS experiments) was automated using the program Autohotkey (freely available from http://www.autohotkey.com/).

3. Results and discussion

To conduct these reactions, we used a previously-reported home-built gas-phase reactivity apparatus in which we introduced the reactive gas into the cone region of the source of an electrospray ionization mass spectrometer (ESI-MS), as shown in Fig. 1 [24]. This set-up is similar to other modifications designed to produce highly solvated ions in ESI sources [28]. The voltages in the source region can be manipulated across a 200 V interval to influence the extent of in-source fragmentation (collision induced dissociation, CID) from practically none (0–15 V) to complete consumption of the precursor ion. For organometallic complexes, fragmentation in
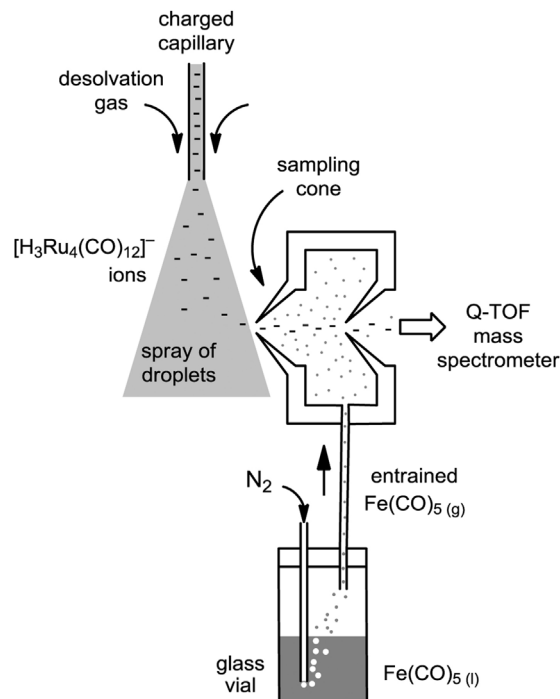

Fig. 1. Schematic illustrating the introduction of reactive molecules to the instrument. The volatile liquid is entrained in a stream of nitrogen gas, and directed to the source region through a line intended for auxiliary desolvation.

ESI-MS consists primarily of loss of "L-type" two-electron donor ligands as stable molecules, but other low energy processes are also observed (for example, reductive elimination of two "X-type" formally anionic ligands) [29]. For carbonyl clusters, fragmentation is dominated by loss of carbonyl ligands as carbon monoxide, and the production of unsaturated and partially-ligated clusters. If these clusters begin as open frameworks, they can compensate for ligand loss by forming additional M–M bonds (e.g. trigonal prismatic to octahedral transitions), but clusters that are already structurally compact (e.g. tetrahedral) cannot and therefore have vacant coordination sites on their surfaces. This can lead to high degrees of reactivity in extreme cases, e.g. $[CoRu_3]^-$ reacts with methane to form a variety of $[CoRu_3C_xH_y]^-$ species, [30] in an example of Fischer–Tropsch chemistry [31] in the gas phase.

The extent to which cone voltage can be modulated enables hundreds of different experiments to be carried out at a given concentration of reactant gas. Presenting and interpreting these data is complicated, because every different cone voltage changes the distribution of fragment ions and the products of those fragment ions after gas-phase reactions. We have introduced tools to deal with this complication, namely energy-dependent electrospray ionization mass spectrometry (EDESI-MS) [32]. This technique involves mapping the data as a three dimensional surface of cone (or collision) voltage against m/z, where ion intensity is displayed by means of contour lines. This presentation enables the simultaneous interpretation of nearly 200 experiments and separates the product ions spatially in an intuitive format that is difficult to replicate by evaluating the 200 individual spectra. All spectra used to generate the contour map are summed and the resulting spectrum plotted above the map.

Before reacting $Fe(CO)_5$ with the anionic cluster, we initially ran a control experiment, whereby the $Fe(CO)_5$ vapor was introduced to the cone without any injected analyte. The capillary voltage was still on, as was the desolvation gas (nitrogen). This experiment gave only a very weak spectrum, and only under very high cone voltage settings. Intensities were approximately two orders of magnitude
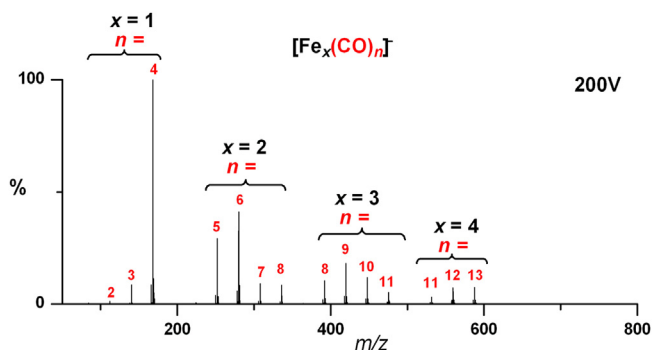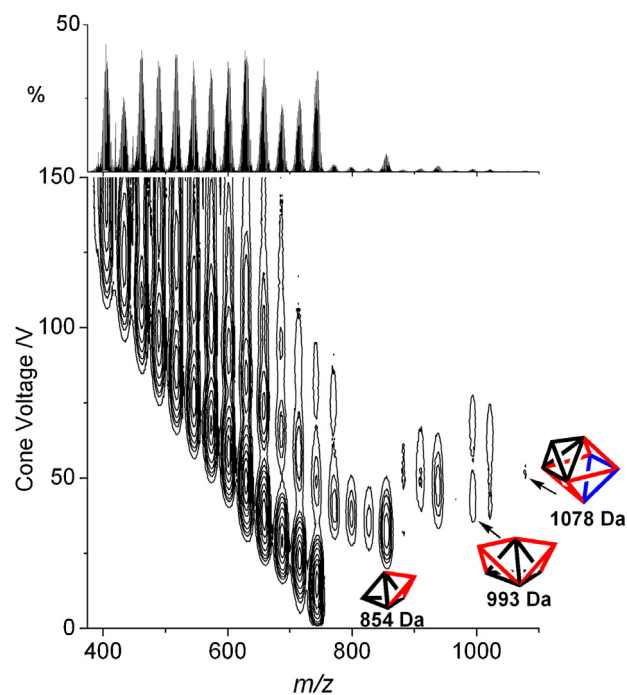
Fig. 2. ESI-MS of Fe(CO)$_5$ that has been vaporized and introduced to the cone. Cone voltage is set to 200 V. Ionization is expected to occur by reduction of a small amount of the monomer to generate [Fe(CO)$_4$]$^-$, which goes on to react with further Fe(CO)$_5$ vapor.

Fig. 3. EDESI-MS of the reaction of [H$_3$Ru$_4$(CO)$_n$]$^-$ (n = 0–12) with Fe(CO)$_{5(g)}$. Bonds in red are from ruthenium to iron, and bonds in blue are between iron atoms. Bonds in black are between ruthenium atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lower than needed for a high-quality EDESI-MS, so a single spectrum was accumulated for hundreds of scans at maximum cone voltage in order to gain insight into what was going on (Fig. 2).

In this experiment, ions of the type [Fe$_x$(CO)$_y$]$^-$ were observed. The mononuclear species [Fe(CO)$_x$]$^-$ (x = 2, 3 or 4) are presumably generated first by reduction at the charged capillary and concomitant CO loss, and these unsaturated, 'hot' ions react energetically with the cool Fe(CO)$_5$ vapor. Cluster buildup initially generates [Fe$_2$(CO)$_x$]$^-$ (x = 5–8), ions which are presumably related to the neutral dimeric cluster Fe$_2$(CO)$_9$. Eight CO ligands is the most an anionic dimer of this sort can contain without rendering the cluster susceptible to facile CO loss or cleavage of the Fe–Fe bond. Similarly, the trinuclear clusters [Fe$_3$(CO)$_n$]$^-$ have a maximum of n = 11, related to the neutral, saturated triangular cluster Fe$_3$(CO)$_{12}$. The absence of a peak with n = 12 suggests the triangular structure is preserved and that no linear clusters are present. The final set of peaks correspond to the tetranuclear clusters [Fe$_4$(CO)$_x$]$^-$ (x = 11–13), and again, a correspondence to the known solution chemistry of tetrahedral iron clusters is observed. The neutral tetrahedral Fe$_4$(CO)$_{14}$ cluster does not exist, but the [Fe$_4$(CO)$_{13}$]$^{2-}$ dianion does, so a tetrahedral core is capable of accommodating up to 13 CO ligands. The lack of clusters with n > 13 suggests that no open clusters (e.g. butterfly, square, linear) are produced (which could have n = 15, 16 and 17, respectively). Overall, the pattern of reactivity is remarkably similar to that observed by Ridge and others in the EI-FTICR-MS studies alluded to earlier [9–11]. A referee characterizes our experiment as "a negative ion chemical ionization experiment in which the electrons emitted from the capillary are "pseudo" thermalized with the nitrogen drying gas", and this seems to be a perfectly plausible interpretation.

While the peaks observed in this experiment were of low intensity, it was abundantly clear that plenty of Fe(CO)$_5$ was reaching the gas phase and ionizing, so the reaction of Fe(CO)$_5$ with [H$_3$Ru$_4$(CO)$_n$]$^-$ (n = 0–12) was examined. This cluster was chosen for a number of reasons: it has a mixture of hydride and carbonyl ligands, providing multiple pathways for reactivity; it is large enough that the degree of unsaturation can be carefully controlled but small enough that CID is an effective method for dissociation; and it is a known catalyst [33], implying a reasonably high level of reactivity, especially when unsaturated.

At low cone voltages – below 25 V – no reaction was observed between the cluster and Fe(CO)$_5$, and the only process observed was sequential loss of CO ligands. As the CO ligands were stripped off at higher energies, the addition of one, two, and even three iron atoms was observed (Fig. 3). The difference between this reaction and those of the organic molecules previously studied [23] is that Fe(CO)$_5$ does not behave as a ligand, but rather it forms bonds with the metal core and shares its carbonyls about the [Ru$_4$Fe$_n$]$^-$ (n = 1, 2 or 3) framework.

An observation in Ridge's Fe(CO)$_5$ system was that more unsaturated metals were more reactive [10]. The more electron deficient a cluster is, the greater its propensity to add another metal or ligand. After loss of three CO ligands and one molecule of H$_2$ from [H$_3$Ru$_4$(CO)$_{12}$]$^-$, the cluster [HRu$_4$(CO)$_9$]$^-$ has eight electrons less than predicted by the effective atomic number (EAN) rule for electron counting in clusters [34], corresponding to a fully vacant coordination site per metal atom (Scheme 1).

This deficiency is sufficient to activate the cluster enough to allow addition of one equivalent of Fe(CO)$_5$, and with CO distribution about all of the metals, the product ion cluster [HRu$_4$Fe(CO)$_{14}$]$^-$ is observed at m/z 854. This product ion only has a 2e$^-$ deficiency compared to what we would expect for a capped tetrahedron, but there is a hint of a species at m/z 882, which would correspond to the electron precise version of this cluster, [HRu$_4$Fe(CO)$_{15}$]$^-$. The fact that the electron deficient cluster is much more abundant in the EDESI map is likely a function of the greater reactivity of the more unsaturated [HRu$_4$(CO)$_9$]$^-$ cluster versus [HRu$_4$(CO)$_{10}$]$^-$, rather than an indication of the relative stabilities of the two product ions. Further reactivity with Fe(CO)$_5$ generates [HRu$_4$Fe$_2$(CO)$_{17}$]$^-$, which assuming a bicapped tetrahedral arrangement of metal atoms, is electron-precise: the electronic requirements of the metals are met with this collection of metals, ligands, charge and metal-metal bonding. A third addition of Fe(CO)$_5$ occurs at even higher cone voltages, but the gas-phase overall yield of these three additions is barely 1%. Two structures are feasible for a compact, seven-metal carbonyl cluster. The most common is the capped octahedron, which has an electron count of 98 [35]. The observed product ion, [HRu$_4$Fe$_3$(CO)$_{18}$]$^-$, has a total of 94 electrons, making it unsaturated by the equivalent of two CO ligands assuming a capped octahedral geometry. Note that such a structure would require significant rearrangement of Ru–Fe bonds, and such rearrangements are well-known to occur at high energies in the gas phase [36]. Another possibility is a tricapped tetrahedron,
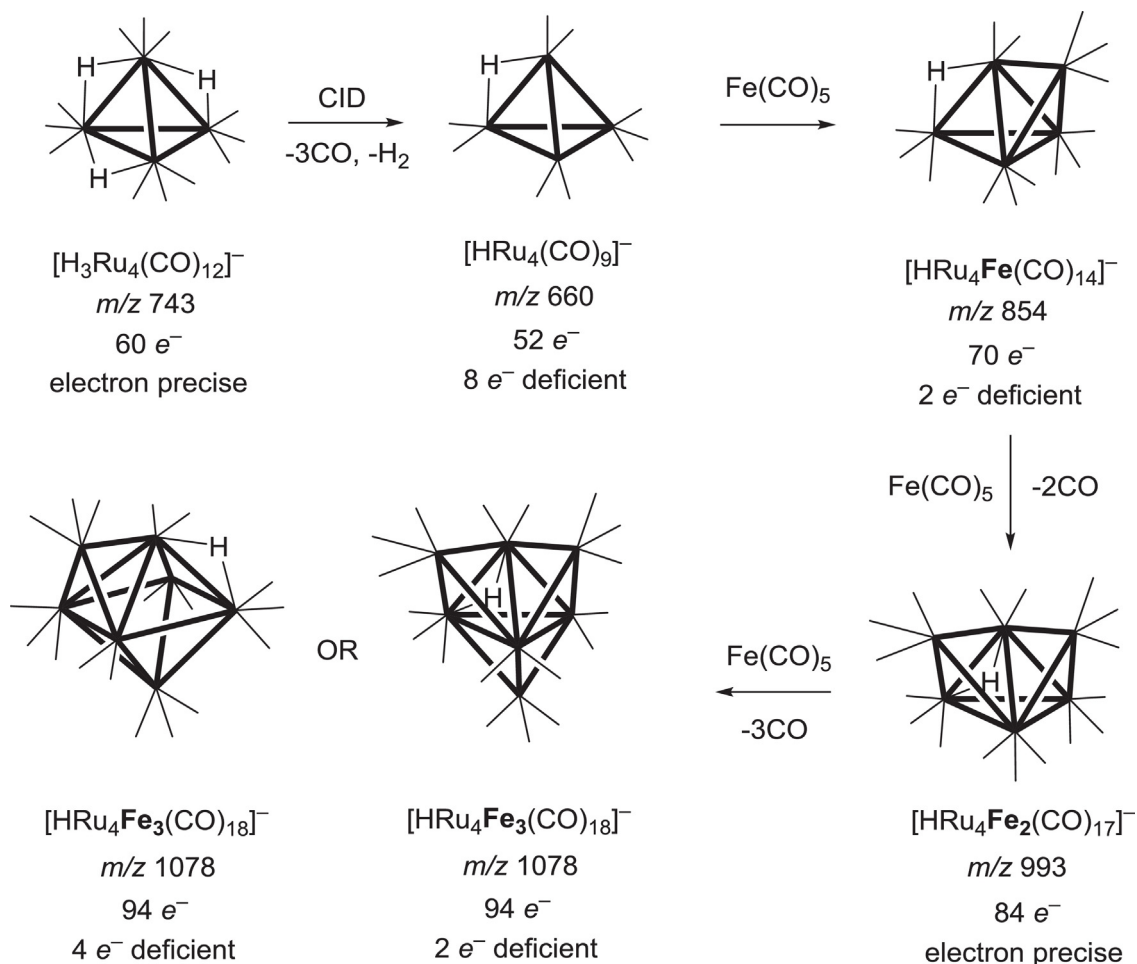
Scheme 1. Reactivity of $[H_3Ru_4(CO)_{12}]^-$ with $Fe(CO)_5$ in the gas phase to generate larger nuclearity clusters.

which can be considered in this context because of the unsaturation of the cluster. Assuming that electron counting based on the EAN rule can be applied, a tricapped tetrahedron should have 96 e (18e per metal atom made up of 96 e from charge,

ligands and metal electrons, and the rest from the 15 metal-metal bonds). The observed cluster would only be electron deficient by two electrons in this instance, or the equivalent of one CO ligand.
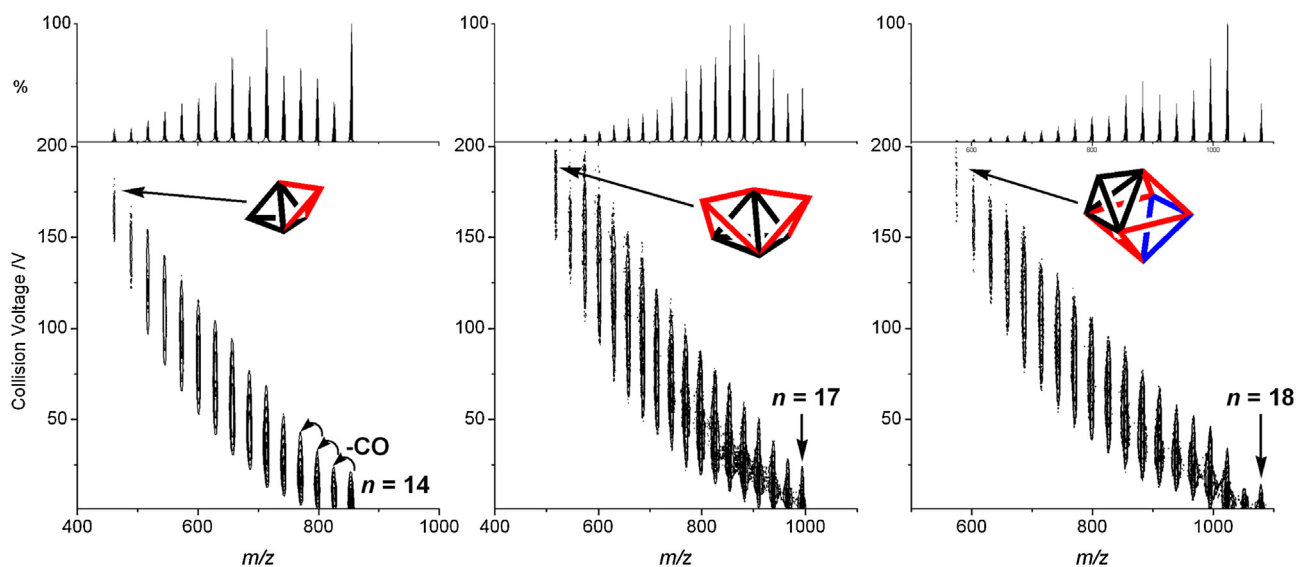
Fig. 4. EDESI-MS/MS spectra of the three base product clusters that form in the reaction with $[H_3Ru_4(CO)_n]^-$ ($n = 0–12$). Left: $[HRu_4Fe(CO)_n]^-$ ($n = 0–14$). Middle: $[HRu_4Fe_2(CO)_n]^-$ ($n = 0–17$). Right: $[HRu_4Fe_3(CO)_n]^-$ ($n = 0–18$). The ions $n = 14$, 17 and 18 were the precursor ions mass selected in each case.

Evidence for the newly bound iron atoms becoming part of the embedded cluster core can be seen from the MS/MS fragmentation patterns (Fig. 4). For each of the precursor ions selected ($[HRu_4Fe(CO)_{14}]^-$, $[HRu_4Fe_2(CO)_{17}]^-$ and $[HRu_4Fe_3(CO)_{18}]^-$) loss of CO is the only fragment that is observed. At very high collision voltages, where no further COs are observed to dissociate, peak assignment of the bare cluster corresponds to the tetraruthenium core plus the requisite number of iron atoms that were added as $Fe(CO)_5$. Had the iron been bound weakly to the cluster, and had the carbonyl ligands not redistributed themselves onto the tetraruthenium framework, then elimination of a neutral $Fe(CO)_5$ molecule would have been expected. This dissociation is not observed, and therefore we presume that the iron has become fully incorporated into the cluster with formation of new Ru–Fe and Fe–Fe bonds.

Build-up of iron clusters of the form $[Fe_x(CO)_n]^-$ can also be seen in this system, but only at very high cone voltages, where translational energies might be expected to parallel conditions of EI-MS. Notably, the relative abundance of $[Fe(CO)_3]^-$ and $[Fe(CO)_2]^-$ are quite low at all voltages where $[Fe(CO)_4]^-$ is observed. This low abundance is attributed to their unsaturation and increased reactivity with neutral $Fe(CO)_5$ to make the higher mass clusters. All of these ions have uneven electron counts attributed to an initial $1e^-$ reduction of $Fe(CO)_5$ vapor, with concomitant CO loss, that occurs at the capillary.

4. Conclusions

Clusters containing iron atoms may be readily synthesized in the gas phase by combination of the volatile molecule $Fe(CO)_5$ with an anionic metal carbonyl cluster. While the example described herein involves a ruthenium cluster, there seems no reason why this approach could not be extended to any other charged transition metal cluster. The ability to synthesize nearly saturated product clusters, and to strip these in turn of their ligands right down to the bare metal core, promises to open a rich field of experimentation of the gas-phase chemistry of ligated, mixed-metal clusters containing iron.

Acknowledgements

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