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Gas phase reactivity of iron pentacarbonyl with anionic metal clusters

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This manuscript is dedicated to the memory of the energetic and inspirational Detlef Schröder.

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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.

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 $\mu L\,min^{-1}$ 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 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.

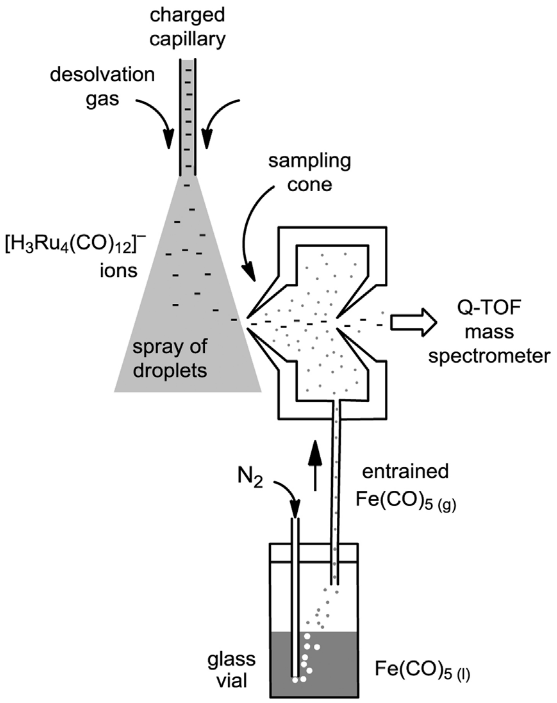

Fig. 1. Schematic illustrating the introduction of reactive molecules to the instrument. The volatile liquid is entrained in a stream of nitrogen gas, and directed to the source region through a line intended for auxiliary desolvation.

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