ences because the reactions for \( R = \text{t-Bu} \) and \( n-\text{Bu} \) differ by approximately 3 orders of magnitude in \( k_{\text{obsd}} \); yet the \( pK_a \) values for their corresponding parent amines are almost equivalent.\(^{(19)} \) Therefore, it is concluded that for \( L = \text{R-pyca} \) the pyridine nitrogen atom initially scavenges the \( \text{W(CO)}_5\text{S} \) photoproduct and that the slow chelation reaction occurs via the coordination of the aliphatic nitrogen atom. Contrastingly, when \( L = \text{R-pyca' the kinetic results imply that structure A is predominantly formed, presumably because the methyl group precludes initial coordination at the pyridine nitrogen atom.}

Figure 3 depicts the stereochemistries of two possible monodentate \( \text{W(CO)}_5\text{L} \) intermediates. The diimine ligands are shown in a trans configuration as both theoretical and experimental studies on related systems have concluded that the free ligands exist in this conformation as solids and in solution.\(^{(20)} \) Rotation about the \( \text{C}_3-\text{C}'_1 \) bond is needed to produce the cis chelation arrangement, although this energy barrier may be rather small as it has been calculated to be between 20 and 28 \( \text{kJ mol}^{-1} \) for other dimines.\(^{(20)} \) Structure A illustrates the monodentate \( \text{W(CO)}_5\text{L} \) intermediate that results when the aliphatic nitrogen atom of the ligand has scavenged the \( \text{W(CO)}_5\text{S} \) photoproduct. It is noted that this arrangement involves substantial steric hindrance and electronic repulsion by the interaction of the pyridine ring with the carbonyl ligands. Structure B depicts the monodentate \( \text{W(CO)}_5\text{L} \) intermediate that is formed when the initial scavenging takes place at the pyridine nitrogen atom, and it can be seen that this conformation involves much less steric hindrance. Hence, the observed kinetic data suggesting exclusive formation of structure B for the \( \text{W(CO)}_5\text{(R-pyca' \text{L})} \) intermediates may be rationalized on the basis of steric constraint. On the other hand, for \( L = \text{R-pyca' the kinetic results imply that structure A is predominantly formed, presumably because the methyl group precludes initial coordination at the pyridine nitrogen atom.}

The ligand scavenging observations are also in accordance with this reasoning. This is because when \( L = \text{R-pyca' the initial scavenging of \( \text{W(CO)}_5\text{S} \) by \( L \) was seen to be efficient and take place rapidly, and when \( L = \text{R-pyca' the scavenging was relatively slow and it suffered competition from solvent impurities. It is striking that the increased steric hindrance about the pyridine nitrogen atom in \( \text{R-pyca' has such a significant effect on the ability of this ligand (even at \( 10^{-2} \text{M} \)) to scavenge ~10^{-4} \text{M of the \( \text{W(CO)}_5\text{S} \) photoproduct, whereas extremely poor donor ligands such as \( \text{N}_3 \) or \( \text{Ar} \) can scavenge the unsaturated \( \text{W(CO)}_5\text{S} \) species at near diffusion-controlled rates.\(^{14,20} \) The results presented here clearly demonstrate that the steric properties of the entering ligand is a major factor in determining the scavenging mechanism of the \( \text{W(CO)}_5\text{L} \) primary photoproduct.}

**Acknowledgment.** We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for supporting this research and thank Dorene Price for assistance with the kinetic measurements.

### Laser–Ion Beam Photodissociation Studies of Ionic Cluster

#### Fragments of Iron Carbonyls: \( \text{Fe}_x(\text{CO})_y^+ (x = 1-3; y = 0-6) \)

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Ionic cluster fragments of the type \( \text{Fe}_x(\text{CO})_y^{+} (x = 1-3; y = 0-6) \) are mass resolved by high-resolution mass spectrometry (\( R = 7500 \)) and then photodissociated. The photofragment ions are mass analyzed by an electrostatic analyzer. The ions studied include \( \text{Fe}(\text{CO})_y^{+} (y = 1-5), \text{Fe}_2(\text{CO})_y^{+} (y = 0-6), \) and \( \text{Fe}_3(\text{CO})_y^{+} (y = 0-4) \) derived from \( \text{Fe}_x(\text{CO})_y^{+} \) neutral. Relative photofragment ion yields for each photodissociating ion and upper and lower limits to the average bond dissociation energies for both \( \text{Fe}^-\text{CO} \) and \( \text{Fe}^-\text{Fe} \) bonds are reported. Average metal–ligand binding energies in the range 19.5-58.6 kcal/mol are measured for the bond dissociation energy at <62.4 kcal/mol.

**Introduction**

The chemical and physical properties of ionic transition-metal species, e.g., monatomic bare and ligated metals, as well as dimer, trimer, and small metal clusters, have been the subject of intense research over the past decade.\(^{(1-6)} \) There have been numerous recent studies that demonstrate the change in chemical reactivities as a function of...
For example, Mn\(^+\)–CO bond energies range from <10 kcal/mol to ca. 20 kcal/mol for ions having large metal-to-ligand ratios (e.g. Mn\(_2\)(CO)\(_5\)). In the cobalt system metal–ligand bond energies averaged 23 kcal/mol and the deviation from this value was small, ca. 0.5 kcal/mol. In the case of Fe\(_2\)(CO)\(_5\), the metal–ligand bond energies were ca. 20–23 kcal/mol except for Fe\(_3\)(CO)\(_5\) which has a Fe\(^+\)-CO bond energy of 45 kcal/mol. The photodissociation studies of Fe\(_2\)(CO)\(_5\) (\(x = 1–3; y = 0–4\)) is complicated by the overlap in masses for Fe\(^+\) and CO\(^+\). For example, the signal at nominal mass 196 is composed of a triplet of ions which corresponds to Fe\(_2\)(CO)\(_5\), Fe\(_3\)(CO)\(_5\), and Fe\(_4\)(CO)\(_5\). This problem prohibited us from studying the photochemistry of Fe\(_2\)(CO)\(_5\) (i.e. \(x = 1–3; y = 0–6\)) species with large metal-to-ligand ratios in our earlier publication.

In this paper, the photochemistry of the Fe(CO)\(_5\)\(^+\) (\(y = 1–4\)), Fe\(_2\)(CO)\(_5\)\(^+\) (\(y = 0–6\)), and Fe\(_3\)(CO)\(_5\)\(^+\) (\(y = 0–4\)) ions mass-selected by high-resolution mass spectrometry is reported. Branching ratios for photochemical reaction channels are reported as well as upper limits for metal–metal and metal–ligand bond energies. In general, the metal–ligand bond energies for the Fe\(_2\)(CO)\(_5\)\(^+\) species follow the same general trend as observed for Mn\(_2\)(CO)\(_5\) and Co\(_2\)(CO)\(_5\) systems. That is, low metal–ligand bond energies of ca. 20 kcal/mol for small \(x/y\) ratios and metal–ligand bond energies which increase to as much as 8 kcal/mol for \(x/y \geq 1\). Upper limits to the metal–metal bond energies for Fe\(^+\) ion and lower limits to the metal–metal bond energy for the Fe\(_2\)\(^+\) ion are determined (<28 and >62 kcal/mol, respectively). These metal–metal bond energies determined are in agreement with those reported by Smalley.

Experimental Section

All laser–ion beam photodissociation experiments were performed on a triple analyzer Kratos MS-50 TA mass spectrometer (see Figure 1). The instrument and the experimental procedures were described in detail in an earlier paper. For the purposes of this paper the important details are associated with MS-I. That is, the first electrostatic analyzer (ESA) and the magnet comprise a high-resolution (maximum resolving power ca. 150 000) instrument. The practicability of an instrument with high-resolution capabilities is that high sensitivities can be maintained at moderate resolutions, e.g., 8000–20 000 resolving power. The second electrostatic analyzer is then used for kinetic energy analysis of the photofragment ions. The kinetic energy of the photofragment ions can be related to the \(m/z\) ratio by the relationship; 

\[
m_z^2 = m_z(E_z/E) ,
\]

where \(m_z^2\) is the \(m/z\) value of the photofragment ion, \(m_z\) is the \(m/z\) value for the incident ion, \(E_z\) is the electrostatic analyzer voltage necessary to pass \(m_z^+\), and \(E\) is the electrostatic analyzer voltage necessary to pass \(m_z^+\). Ions are produced by electron-impact (EI) ionization using an ionizing energy of 70 eV.

The visible lines (514.5–458 nm) of an argon ion laser (Coherent Model CR-18) are used for all photodissociation experiments described herein. Mirrors M1, M2, and M5 (see Figure 1) are used to direct the laser beam through a sapphire window in the third field-free region where the laser beam and the ion beam are crossed in an orthogonal fashion. A 300-mm focal length sapphire lens is used to focus the laser beam to a small point (0.1–0.3 mm in diameter) just at the laser–ion beam intersection. Photodissociation is performed within 1 cm of the focal point of MS-I, where the dimensions of the ion beam are small (<0.25 mm). Therefore, focusing the laser beam to dimensions that are equal to or slightly less than the dimensions of the ion beam give marked enhancements in the photofragment ion yields. Photofragment ions formed between the magnetic analyzer and second electrostatic analyzer are energy analyzed by using standard MIKE scans. The laser beam is mechanically
chopped at a frequency of 400 Hz, and the photoinduced signal is separated from metastable and collision-induced products by using a lock-in amplifier (Princeton Applied Research Model 124A) which measures the laser "on"/laser "off" difference signal. The difference signal is accumulated and signal-averaged by using noise ratios are obtained.

Although the mass resolution of MS-I is high (up to 150000), the mass resolution of MS-II is limited. The mass resolution is limited because the photofragment ions are energy analyzed and signal broadening can occur as a result of partitioning of internal energy as kinetic energy upon dissociation. Thus, it is not possible to distinguish loss of iron (m/z = 55.9349) from loss of two carbonyl ligands (m/z = 55.9368). To differentiate these two losses, photodissociation was performed on the iron isotope of a particular ion instead of the Fe isotope, e.g. FeFe2(CO)12+ (m/z = 222), instead of FeFe2(CO)12+ (m/z = 224). Assuming the ion at m/z = 222 loses iron and photodissociates in a statistical manner, then 33% of the ions will lose 54 mass units (56Fe), while 67% of the ions will photodissociate by loss of 56 mass units (56Fe).

The results of these studies indicate that in cases where the identity of the daughter ion was uncertain (e.g. Fe(CO)5 ions (x ≥ 2; y ≥ 2)), loss of two carbonyl ligands is the only photodissociation pathway observed (see Results and Discussion). FeFe2(CO)12 was purchased from Strem Chemical, Inc. (Newburyport, MA 01950). The sample was introduced into the mass spectrometer by a direct insertion solids probe. The direct insertion probe was heated to -85 °C. This temperature is rather critical, since higher temperatures cause the sample to decarboxylate, and at lower temperatures the rate of sample sublimation is low. Because no measurable impurities were observed in the mass spectra of FeFe2(CO)12, the sample was used without any purification.

**Results and Discussion**

This work investigates the single-photon photodissociation of FeFe2(CO)12+ ions (x = 1–3; y = 0–6) formed by electron-impact ionization of FeFe2(CO)12 and subsequent mass selection by high resolution. The 70-eV low-resolution electron-impact ionization mass spectra of FeFe2(CO)12 has previously been reported. The high-resolution mass spectrum reveals the presence of the FeFe2+(m/z = 168) indicating that rupture of all metal carbonyl bonds is possible. Fe-Fe bonds of FeFe2(CO)12 are also broken upon electron-impact ionization. That is, at m/z values ≤280, di- and monoiron carbonyl species are also observed in the mass spectrum. Mass doublets (m/z = 280, 252, 224, 140, 112) and triplets (m/z = 196, 168) are observed in the high-resolution mass spectrum of FeFe2(CO)12; e.g., m/z = 196 corresponds to Fe(CO)12+, Fe2(CO)12+, and Fe3(CO)12+. Figure 2 contains a portion of the high-resolution mass spectrum near mass 196 (MS-I mass resolution = 7500, 10% valley definition). These mass doublets and triplets require a minimum resolution of 4000–5000 for base-line separation of the individual ions. High resolution using ion-beam mass spectrometers is accomplished by narrowing mechanical slits, thereby attenuating the total ion current and instrument sensitivity. In the experiments described below the instrument resolution is set slightly above the minimum mass resolution required to completely separate the precursor ions.

Table I contains relative photodissociation cross sections for the cross-beam photodissociation of FeFe2(CO)12+ ions (x = 1–3; y = 0–5) as a function of laser wavelength. The...
Laser-Ion Beam Photodissociation Studies

Table I. Photodissociation Cross Sections Measured from the Cross-Beam Photodissociation of Fe$_x$(CO)$_y^+$ Ions over the Wavelength Range 458–514 nm

<table>
<thead>
<tr>
<th>Precursor ion</th>
<th>Photofragment Ion(s)</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>458</td>
</tr>
<tr>
<td>Fe$_6$(CO)$_4^+$</td>
<td>Fe$_6$(CO)$_3^+$</td>
<td>0.0074</td>
</tr>
<tr>
<td>Fe$_5$(CO)$_3^+$</td>
<td>Fe$_5$(CO)$_2^+$</td>
<td>0.17</td>
</tr>
<tr>
<td>Fe$_4$(CO)$_2^+$</td>
<td>Fe$_4$(CO)</td>
<td>0.097</td>
</tr>
<tr>
<td>Fe$_4$(CO)</td>
<td>Fe$_4^+$</td>
<td>0.0069</td>
</tr>
<tr>
<td>Fe$_3$(CO)</td>
<td>Fe$_3^+$</td>
<td>0.012</td>
</tr>
<tr>
<td>Fe$_2$(CO)</td>
<td>Fe$_2^+$</td>
<td>1.00</td>
</tr>
<tr>
<td>Fe$_2$(CO)</td>
<td>Fe$_2^+$</td>
<td>0.28</td>
</tr>
<tr>
<td>Fe$_2$(CO)</td>
<td>Fe$_2^+$</td>
<td>0.167</td>
</tr>
<tr>
<td>Fe$_2$(CO)</td>
<td>Fe$_2^+$</td>
<td>0.31</td>
</tr>
<tr>
<td>Fe$_2$(CO)</td>
<td>Fe$_2^+$</td>
<td>0.14</td>
</tr>
<tr>
<td>Fe$_2$(CO)</td>
<td>Fe$_2^+$</td>
<td>0.023</td>
</tr>
<tr>
<td>Fe$_2$(CO)</td>
<td>Fe$_2^+$</td>
<td>0.0098</td>
</tr>
</tbody>
</table>

Table II. Average Bond Dissociation Energies Measured from the Crossed Laser-Ion Beam Photodissociation Thresholds for Fe$_x$(CO)$_y^+$ Ions

<table>
<thead>
<tr>
<th>Transition</th>
<th>Threshold energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_6$(CO)$_4^+$ → Fe$_6$(CO)$_3^+$</td>
<td>502</td>
</tr>
<tr>
<td>Fe$_6^+$ → Fe$_5^+$</td>
<td>&gt;514.5</td>
</tr>
<tr>
<td>Fe$_5^+$ → Fe$_4^+$</td>
<td>&gt;514.5</td>
</tr>
<tr>
<td>Fe$_4$(CO)$_3^+$ → Fe$_4$(CO)</td>
<td>&lt;458</td>
</tr>
<tr>
<td>Fe$_4$(CO)$_2^+$ → Fe$_3^+$</td>
<td>488</td>
</tr>
<tr>
<td>Fe$_3$(CO)$_2^+$ → Fe$_2^+$</td>
<td>488</td>
</tr>
<tr>
<td>Fe$_3$(CO)$^+$ → Fe$_2^+$</td>
<td>488</td>
</tr>
</tbody>
</table>

*Triangular arrangement of three ion atoms assumed in the bond energy calculation. Linear arrangement of three ion atoms assumed in the bond energy calculation.

absorbed photon must be greater than the bond dissociation energy threshold(s). If an excited electronic state of A$^+$ lies close to the dissociation threshold, the measured bond dissociation energy is said to be thermodynamically controlled and will reflect the true bond dissociation energy. In most cases the fortuitous overlap between the energies of the excited state and dissociation thresholds does not exist. However, Freiser and co-workers have suggested that for metal containing ions, a high density of low-lying electronic states may often times result in an overlap between excited states and dissociation thresholds. Therefore, it should be emphasized that laser-ion beam photodissociation only provides estimates of the upper limits for bond dissociation energies.

The average bond dissociation energies reported in this paper are obtained by dividing the photodissociation threshold energy (disappearance of a photodissociation signal) by the number of ruptured metal–metal or metal–ligand bonds. Table II lists the average bond dissociation energies derived from the photodissociation thresholds for many of the Fe$_x$(CO)$_y^+$ ions, as well as the upper and lower limits to the bond dissociation energies for the Fe$_2^+$ and Fe$_3^+$ ions.

Figure 3 contains the photofragment ion spectrum for Fe$_4$(CO)$_4^+$ → Fe$_2$(CO)$_2^+$ over the visible wavelength range 458–514.5 nm. The Fe$_2$(CO)$_2^+$ ion shows an apparent photodissociation maximum between 458 and 476 nm. The Fe$_2$(CO)$_4^+$ ion shows an apparent photodissociation maximum between 458 and 476 nm. The Fe$_2$(CO)$_4^+$ ion shows an apparent photodissociation maximum between 458 and 476 nm.
photodissociation cross sections at high energies (458 nm) with smaller photodissociation cross sections at low energies (514.5 nm).17

It should be noted that the Fe(CO)₅⁺ ion is the only mononuclear carbonyl ion that photodissociates in the 458–514.5 nm range. There are three reasons why the Fe(CO)₅⁺ ions (y = 1–5) do not photodissociate in cross-beam experiments: (i) metal–ligand bond dissociation energies of Fe(CO)₅⁺ (y = 1–3, 5) are quite high, i.e., >2.7 eV (63 kcal/mol); (ii) the Fe(CO)₅⁺ ions (y = 1, 3–5) have low absorption cross sections in the blue-green wavelength region; (iii) the photoexcited Fe(CO)₅⁺ ions (y = 1–3, 5) may dissociate slowly.

High metal–ligand bond energies for Fe(CO)₅⁺ (y = 1–3, 5) are contradictory to that observed for the neutral species. For example, the accepted value for the binding energy for Fe(CO)₅⁻→Fe(CO)₄ is ca. 2.4 eV, and the energy required for Fe(CO)₅⁺→Fe⁺+5(CO) is ca. 6.6 eV.28 Thus, the average metal–ligand binding energy for the Fe(CO)₅⁺ species is approximately 1 eV (23 kcal/mol).

Although the Fe(CO)₅⁺ (y = 1–3, 5) ions do not photodissociate between 514.5 and 458 nm, relatively strong photodissociation transitions are observed in the all-line UV mode of the argon ion laser (333–385 nm with a weighted average of 355 nm). For example, Fe(CO)₅⁺ photodissociates to Fe(CO)₄⁺ upon absorption of a UV photon. Thus, an upper limit for the average metal–ligand bond dissociation energy of Fe(CO)₅⁺→Fe(CO)₄⁺ is ca. 1.1 eV is indicated. The Fe(CO)₅⁺ ion photodissociates (UV lines) to Fe(CO)₄⁺ and Fe(CO)⁺ with branching ratios for the photofragment ions of ~1/1; metal–ligand bond dissociation energies of <3.4 and 1.7 eV, respectively. Fe(CO)₄⁺ gives exclusively Fe⁺ upon UV photodissociation yielding an upper limit for the bond energy of 1.7 eV/carbonyl ligand. The Fe(CO)⁺ ion photodissociates to Fe⁺ suggesting a metal–ligand bond dissociation energy of <3.4 eV. Although the photodissociation of Fe(CO)₄⁺ to yield Fe(CO)₃⁺ is strong in the visible region, no additional photofragments are observed upon UV photodissociation. The clear trend that emerges from this data is that the metal–ligand bond dissociation energies for Fe(CO)₅⁺ (y = 1–3, 5) do not exceed 1.7 eV and could be as low as 1.1 eV; Fe(CO)₃⁺ is the only possible exception. Our results for the Fe(CO)₅⁺ (y = 1–3, 5) are consistent with the photoionization mass spectrometry data reported by Distefano.29 Therefore, absorption of a visible photon should produce a photoexcited ion with sufficient internal energy to fragment.

Information on the absorption properties of the Fe(CO)₅⁺ (y = 1–5) ions can be extracted from coaxial laser–ion beam photodissociation experiments. Figure 4 shows the coaxial photofragment ion spectra for Fe⁺, Fe(CO)⁺, and Fe(CO)₂⁺ ions obtained at visible wavelengths. That is, these spectra all show the parent ions that upon photoexcitation yield Fe⁺, Fe(CO)⁺, and Fe(CO)₂⁺. There are several details to note in the spectra. (i) At 514.5 nm the yield for Fe⁺ from Fe(CO)⁺ is about three times that for Fe(CO)₂⁺, but as the photon energy is increased, the Fe(CO)₂⁺→Fe⁺ reaction becomes dominant. A similar trend is noted for Fe(CO)₃⁺→Fe(CO)⁺ compared to Fe(CO)₂⁺→Fe(CO)⁺. (ii) Figure 5 contains data for the photodissociation of Fe(CO)⁺→Fe⁺ (514.5 nm) as a function of laser power. Note the square root dependence of the photofragment ion yield on the laser power. Our interpretation of this result is that photodissociation of Fe(CO)⁺ to Fe⁺ in the visible region corresponds to a two-photon process. However, this interpretation of the data should be regarded as preliminary. In the coaxial photodissociation studies, the laser beam and ion beam overlap the entire length between the exit to the ion source and entrance to the first electrostatic analyzer (10–15 cm). Hence, the long laser–ion beam interaction distance may lead to sequential multiphoton process. The laser powers used in these studies are not sufficient for photodissociation by a ladder mechanism; thus any multiphoton processes observed must occur via long-lived excited states, i.e., a sequential photon absorption mechanism.30 Hence, the coaxial photodissociation experiments prove the Fe(CO)⁺ (y = 1, 3–5) ions do indeed absorb in the blue-green wavelengths.

Proposing that Fe(CO)⁺ (y = 1–3, 5) ions photodissociate via a sequential two–photon process has interesting implications. The question arises as to why the photoexcited Fe(CO)⁺ ions, formed by absorption of the first visible photon, do not dissociate. For instance, the UV photodissociation results yield estimated metal–ligand bond dissociation energies of between 1.1 and 1.7 eV, consistent with Distefano photoionization mass spectrometry data.29 The most logical explanation for the lack of photodissociation for the Fe(CO)⁺ ions in the cross-beam experiment is that the spin state of the precursor ion does not correlate with the spin state of the photofragment ion; thus the photoexcited ion must relax via slow spin-forbidden dissociation channel. On the other hand, if the photoexcited ion is long-lived (ca. 1–5 μs in our experiment), absorption of a second photon could produce a highly excited ion which dissociates. It is also reasonable to suspect that the photoexcited Fe(CO)⁺ ion (formed by absorption of one photon) decays by radiative processes which preempet dissociation. The details of photodissociation of Fe(CO)⁺ ions is being probed further with this.

Figure 4. Coaxial photofragment ion spectra for Fe+, Fe(CO)+, and Fe(CO)2+ ions.

Fe(CO)⁺ → Fe⁺

Figure 5. Coaxial photofragment ion yield for the photodissociation of Fe(CO)+ → Fe⁺ as a function of the square root of the laser power (W0.5). (λ = 514.5 nm).

Freiser et al. have reported photodissociation data for Fe(CO)⁺ → Fe⁺ + CO.57 The authors found that Fe(CO)+ photodissociates over the entire UV-visible wavelength range (225-700 nm). They observe large photodissociation intensities in the UV and a low intensity photodissociation tail at visible wavelengths (400-700 nm). This is contradictory with the results presented here. We find that the Fe(CO)+ ion does not photodissociate in the wavelength range 458-514.5 nm in a crossed laser-ion beam configuration. One possible explanation for the differences between the ICR and ion beam results could be due to a reduced dynamic range for the crossed laser-ion beam photodissociation technique. This may especially be true since high-resolution mass selection attenuates the number of photofragment ions transmitted through the second electrostatic analyzer. The dynamic range limitation was examined, however, by attempting to photodissociate the Fe(CO)+ ion derived from electron impact of Fe(CO)₉ neutral (instead of Fe₆(CO)₁₂ neutral) in a cross laser-ion beam configuration in the third field-free region of the mass spectrometer. Although collector signals for pro-

The photodissociation cross section of the Fe(CO)$_{12}^+$ ion is small at all wavelengths; e.g., relative photodissociation cross sections vary from 7.4 $\times$ 10$^{-4}$ at $\lambda = 458$ nm to 1.1 $\times$ 10$^{-4}$ at $\lambda = 496$ nm, and no photodissociation signal is detectable at 502 and 514.5 nm. We assign a threshold energy for photodissociation of Fe$_3$(CO)$_9^+$ at 502 nm yielding a bond dissociation energy of 57 kcal/mol. The assigned threshold for Fe$_3$(CO)$_9^+$ to Fe$_3$(CO)$_7^+$ implies that the Fe$_3$(CO)$_9^+$ ion is extremely stable with respect to the Fe$_3$(CO)$_7^+$ ion; i.e., the metal carbonyl bonds of the Fe$_3$(CO)$_9^+$ system are unusually strong.

The stability of the Fe$_3$(CO)$_9^+$ ion relative to other Fe$_n$(CO)$_{2n}^+$ ions is supported by complimentary information derived from the high-resolution, collision-induced dissociation (CID) data of various Fe$_n$(CO)$_{2n}^+$ ions. For example, Figure 8 contains the CID spectra for the Fe$_5$(CO)$_{15}^+$ ion. Note the unusually large CID signal corresponding to the production of the Fe$_3$(CO)$_4^+$ daughter ion. One feature common to all the CID spectra of iron cluster fragment ions is that loss of one carbonyl ligand is always the dominant reaction channel, and the relative abundances of the iron carbonyl ions, corresponding to successive carbonyl losses, decrease in a monotonic fashion (e.g., $-1$ CO > $-2$ CO > $-3$ CO etc.). The exception to this trend is the Fe$_5$(CO)$_{15}^+$ ion. Collision-induced dissociation of the Fe$_5$(CO)$_{15}^+$ ions (for $y = 5$–12) also reveal anomalously large Fe$_5$(CO)$_{15}^+$ ion intensities suggesting the Fe$_5$(CO)$_{15}^+$ ion has an uncommon stability. This stability may be rationalized in terms of a different type of iron metal center-to-ligand bonding. The carbonyl ligands in the Fe$_5$(CO)$_{15}^+$ ion may be bridging (two-electron or four-electron donors to the metal center) rather than terminal CO groups which have lower binding energies.

The only other iron carbonyl fragment ions examined that undergo photodissociation via loss of one carbonyl ligand are the Fe$_5$(CO)$_{15}^+$ and Fe$_3$(CO)$_{12}^+$ ions (see Tables I and II). For both of these ions the photodissociation threshold occurs at approximately 514.5 and 488 nm, respectively. The relatively large metal carbonyl binding energies in these ions may also imply that the carbonyl ligands are bonded in a bridging fashion. The electron deficiencies of the bare metal iron cluster ions (Fe$_5^+$ and Fe$_3^+$) are large with respect to more fully ligated systems. Hence, to reduce this electron deficiency, iron carbonyl ions with few ligands (e.g., Fe$_5$(CO)$_{12}^+$, Fe$_5$(CO)$_{10}^+$, and Fe(CO)$_{12}^+$) may form bridging ligand complexes with the metal center, or alternatively the metal center (or atom) may bond with both the carbon and oxygen atoms of the carbonyl ligands. This latter idea is supported by results from this laboratory which indicate that both iron carbide and iron oxide ions are produced by the collision-induced dissociation of singly ligated iron carbonyl ions. Thus, the idea of bridging carbonyl groups or unusual metal carbonyl bonding for certain iron carbonyl ions may explain why their photodissociation and CID spectra appear anomalous. This type of Fe--CO interaction may also explain why Fe(CO)$_{12}^+$ does not photodissociate to Fe$^+$ in the visible wavelengths.

Photodissociation of Fe$_3^+$ leads to the formation of the Fe$_3^+$ ion exclusively (see Figure 9). A photodissociation threshold for Fe$_3^+$ is not observed in the blue-green wavelength regions. Thus, the photodissociation reaction Fe$_3^+$ $\rightarrow$ Fe$_2^+$ + Fe has an energy requirement of less than 2.43 eV. If a linear structure for the Fe$_3^+$ ion is assumed, an upper limit to the iron–iron bond dissociation energy of <56 kcal/mol is obtained (see Table II). However, if the structure of the Fe$_3^+$ ion is triangular, an upper limit

Figure 7. Photodissociation cross section as a function of laser wavelength for Fe$_3$(CO)$_{15}^+$ $\rightarrow$ Fe$_3$(CO)$_{12}^+$. The stability of the Fe$_3$(CO)$_{15}^+$ ion relative to other Fe$_n$(CO)$_{2n}^+$ ions is supported by complimentary information derived from the high-resolution, collision-induced dissociation (CID) data of various Fe$_n$(CO)$_{2n}^+$ ions. For example, Figure 8 contains the CID spectra for the Fe$_5$(CO)$_{15}^+$ ion. Note the unusually large CID signal corresponding to the production of the Fe$_3$(CO)$_4^+$ daughter ion. One feature common to all the CID spectra of iron cluster fragment ions is that loss of one carbonyl ligand is always the dominant reaction channel, and the relative abundances of the iron carbonyl ions, corresponding to successive carbonyl losses, decrease in a monotonic fashion (e.g., $-1$ CO > $-2$ CO > $-3$ CO etc.). The exception to this trend is the Fe$_5$(CO)$_{15}^+$ ion. Collision-induced dissociation of the Fe$_5$(CO)$_{15}^+$ ions (for $y = 5$–12) also reveal anomalously large Fe$_5$(CO)$_{15}^+$ ion intensities suggesting the Fe$_5$(CO)$_{15}^+$ ion has an uncommon stability. This stability may be rationalized in terms of a different type of iron metal center-to-ligand bonding. The carbonyl ligands in the Fe$_5$(CO)$_{15}^+$ ion may be bridging (two-electron or four-electron donors to the metal center) rather than terminal CO groups which have lower binding energies.

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to the average iron–iron bond dissociation energy is 28 kcal/mol. This latter value for the iron–iron bond strength falls within the lower end of a range of energies Smalley et al. measured for the photodissociation threshold for Fe₃⁺ → Fe₂⁺ + Fe (26.9–50.3 kcal/mol). The Fe₂⁺ ion does not photodissociate even at the highest energy used (458 nm); therefore, we assign a lower limit of >62.4 kcal/mol to the iron–iron bond dissociation energy. This lower limit for the Fe²⁺-Fe bond strength in the Fe₂⁺ ion is in good agreement with measurements from complimentary techniques for determination of metal–metal bond strengths. For example, Freiser et al. reported a value for D(Fe-Fe)²⁺ between 58 (±5) and 69 (±5) kcal/mol obtained by CID bracketing techniques and a Fe²⁺-Fe bond dissociation energy of 62 (±5) kcal/mol by photodissociation. Smalley et al. estimated the bond strength of Fe₂⁺ (based on the photodissociation threshold for the Fe₂⁺ ion) to be in the range 56.0–67.3 kcal/mol.

It is interesting to compare the bond dissociation energy for the Fe₂⁺ ion and Fe₂ neutral. Bond dissociation energies reported for Fe₂ neutral are, in general, much smaller than the iron–iron bond strength in the Fe₂⁺ ion determined by ICR and ion beam photodissociation methods. For example, D(D(Fe-Fe))²⁺ has been reported to be 19 ± 7 kcal/mol by Lin and Kant²⁶ and 18 ± 4 kcal/mol by Shim and Gingerich.³⁶ The much larger bond dissociation energy of Fe₂⁺ as compared to Fe₂ neutral may arise from the fact that ionization of Fe₂ neutral involves removal of an electron from a strongly antibonding orbital. This explanation, however, is contradictory to negative ion photoelectron studies of Fe₂⁻ which have demonstrated that the Fe₂⁻ anion has slightly larger bond lengths and lower vibrational frequencies than Fe₂ neutral.³⁷ These results suggest that detachment of the electron in Fe₂⁻ must arise from slightly antibonding molecular orbitals. Hence, ionization of Fe₂ neutral is not expected to occur by removing a strongly antibonding electron. Thus, one would not expect the bond dissociation energy of Fe₂⁺ to be substantially larger than that of Fe₂.

The differences in bond strengths between Fe₂ and Fe₂⁺ raises important questions concerning the bonding in the two species. Bond energies based upon photodissociation are subject to inherent limitations. That is, in order to accurately measure the bond strength for Fe₂⁺, an excited electronic state (S₂) must lie close to the dissociation threshold. If S₂ lies above the dissociation threshold, the measured bond dissociation energy will be high. Another potential problem with the photodissociation technique stems from the fact that other energy loss mechanisms can compete with the dissociation process, e.g., radiative decay. If at low photon energies the rate for radiative decay is much greater than the rate for cleavage of the iron–iron

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Conclusions

The high-resolution and large dynamic range capabilities of the laser-ion beam mass apparatus allow the electronic and thermodynamic properties of novel ionic transition-metal cluster fragments to be studied without complicating solvation effects. Although much higher mass resolutions \( R = 100 000 - 150 000 \) are obtainable by using a double-focusing mass spectrometer of the sort described herein, these resolutions result in poor ion transmission efficiencies. As a result, laser-ion beam photodissociation methods may be limited to moderate resolutions \( (5000 - 50 000) \) since data acquisition times become prohibitively long at higher mass resolutions.

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Registry No. Fe(CO)$_3^+$, 73145-64-9; Fe$_2^+$, 61674-88-8; Fe(CO)$_2^+$, 35038-16-5; Fe(CO)$_3^+$, 35038-15-4; Fe(CO), 35038-14-3.

Mono(cyclooctatetraenyl) Actinide Complexes. 1. Preparation of the Diamides (C$_8$H$_8$)An[N(SiMe$_3$)$_2$]$_2$ (An = Th, U) and the Structure of (C$_8$H$_8$)Th[N(SiMe$_3$)$_2$]$_2$

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An improved synthesis of the mono(cyclooctatetraenyl)thorium ("half-sandwich") complex (C$_8$H$_8$)ThCl$_2$(THF)$_2$ (1a) is reported. Although treatment of 1a or the uranium analogue (C$_8$H$_8$)UCl$_2$(THF)$_2$ (1b) with alkyllithium or Grignard reagents leads to intractable products, metathesis of the chloride ligands of 1a or 1b with 2 equiv of Na[N(SiMe$_3$)$_2$] cleanly gives the pseudo-seven-coordinate diamide complexes (C$_8$H$_8$)An[N(SiMe$_3$)$_2$]$_2$ (An = Th, 2a, An = U, 2b). A single-crystal X-ray diffraction study of (C$_8$H$_8$)Th[N(SiMe$_3$)$_2$]$_2$ \( (T = 298 \text{ K}, \text{ monoclinic, } P2_1/n, a = 12.071 \text{ (2) Å, } b = 13.160 \text{ Å, } c = 18.113 \text{ Å, } \beta = 90.96^\circ, V = 2876.9 \text{ Å}^3, Z = 4) \) revealed that one carbon of each silyl amide ligand is directed toward the thorium in such a way as to mimic a four-legged piano stool with trans nitrogen atoms and trans carbon atoms. This result is ascribed to the coordination number deficiency at the metal center. The amide complex 2a does not react with H$_2$ even at elevated temperatures.

Introduction

In 1980, the first mono(cyclooctatetraenyl)thorium ("half-sandwich") complexes were reported. The parent compound (C$_8$H$_8$)ThCl$_2$(THF)$_2$ (1a) was prepared by prolonged (ca. 1 week) reaction of thorocene with thorium tetrachloride in refluxing THF (eq 1) and its structure

\[
(C_8H_8)_2\text{Th} + \text{ThCl}_4 \xrightarrow{\text{THF}} 2(C_8H_8)\text{ThCl}_2(\text{THF})_2 \quad (1)
\]

was determined by single-crystal X-ray diffraction.$^{1,2}$ In the