

Multiphoton Ionization Mass Spectrometric Studies of Transition Metal Carbonyl Complexes

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The multiphoton photochemistries of a variety of gas phase transition metal carbonyl complexes are investigated by MPI time-of-flight mass spectrometry, and results indicate that molecular fragment ionization can compete with atomization in these systems. Molecular ions detected include a variety of homonuclear and heteronuclear bare metal clusters, metal-sulfur clusters and metal monocarbonyls. Thus, multiphoton excitation of stable metal carbonyl compounds provides a versatile synthetic route to highly unsaturated neutral and ionic gas phase clusters which offers unique product cluster specificity and does not require the use of high temperature sources. The detection under collision-free conditions of bare metal dimers and trimers following MPI of several dinuclear and trinuclear metal cluster carbonyl compounds, respectively, indicates that dissociative CO loss can compete with metal-metal bond cleavage as a primary excited state reaction upon UV photolysis of these systems.

INTRODUCTION

We report here the production of highly unsaturated transition metal clusters by UV multiphoton dissociation (MPD) of volatile organometallic compounds.¹ Due to the difficulty of producing gaseous samples of bare metal clusters, metal sulfides, and other structurally simple transition metal systems, the spectroscopic data needed to test results of the current surge of theoretical efforts² are often not available. This is strikingly illustrated by a very recent report by Cotton and Shim of *ab initio* calculations on the Ru₂ molecule.² This

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was chosen as a particularly tractable theoretical subject in view of reduced electron correlation and relativistic effects as compared with molecules of the first and third transition series, respectively. Its experimental characterization, however, has not proved equally tractable: there are no spectroscopic studies of Ru_2 in the literature, and even rough dissociation energy measurements based on high temperature equilibria are unavailable. The difficulties encountered in producing gas phase samples of this highly refractory molecule by conventional methods are avoided by use of the metal carbonyl MPD technique. This is illustrated here by the production of dimers as well as trimers of ruthenium by photolysis of $\text{Ru}_3(\text{CO})_{12}$, a stable, commercially available compound.

MPD of transition metal carbonyls has several unique advantages over alternative³ metal cluster generation methods. For example, gas phase clusters of refractory metals can be prepared without the use of high temperature ovens. This is dramatically demonstrated by the production of gaseous dimers and trimers of osmium (m.p. $\sim 3000^\circ\text{C}$) by photodissociation of $\text{Os}_3(\text{CO})_{12}$ sublimed from a 120°C source (Figure 1). In addition, dissociation of photolabile ligands from a structurally well-defined precursor provides access to clusters of specific size and composition. We have been able to produce heteronuclear iron-ruthenium dimers without detectable homonuclear dimer production (Figure 2) by MPD of $\text{Fe}_2\text{Ru}(\text{CO})_{12}$, a difficult task for atom aggregation methods. Clearly, its ability to provide specific access to selected clusters renders the MPD technique of immense potential value for spectroscopic and chemical studies employing non-mass-selective detection methods.

Understanding of MPD mechanisms in metal carbonyl complexes is needed to guide the selection of precursors for specific target clusters. In addition, the multiphoton photochemistry of these complexes is itself of interest in view of its marked divergence from that encountered in other types of systems. The behaviour of most molecules struck by intense UV or visible laser pulses can be simply described as involving either (1) ionization followed by dissociation, as occurs in acetaldehyde, butadiene, benzene and many other multiply-bonded organic molecules excited into Rydberg states, or (2) dissociation followed by atomic ionization, a pattern observed in a variety of mono-metallic inorganic and organometallic systems such as chromium hexacarbonyl, the mercuric halides, and tetramethyl

tin.⁴ Results presented here, however, suggest that metal cluster carbonyl compounds may define a third, intermediate class of multiphoton photochemical behavior. Excitation mechanisms in many of these systems appear to involve dissociative loss of carbonyl ligands to produce relatively stable molecular fragments in which ionization to species such as M_m^+ and $M_mS_n^+$ can compete with atomization.

Diverse photochemical channels may be accessible to many stable metal-metal bonded carbonyl complexes as well. For example, results discussed below strongly suggest that ligand dissociation can compete with metal-metal bond homolysis⁵ as a primary photoreaction in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. In view of the significant roles that even relatively minor photochemical paths might play in catalytic cycles, a complete characterization of the photochemical behavior of metal cluster carbonyl systems is likely to prove of considerable practical value as the use of these compounds as photocatalysts⁶ is further exploited.

EXPERIMENTAL

Samples were sublimed at 25–125°C and photolyzed in the ionization region of a time-of-flight mass spectrometer by 20-nsec pulses from an excimer-pumped dye laser. Mass distributions of ionic photoproducts and mass-resolved multiphoton ionization (MPI) spectra of neutral photofragments were measured. Results reported here were obtained at 340–390 nm using laser energies of 0.2–2 mJ. In general, atomic ion signals increased quadratically with laser energy, and molecular ions showed a more linear I_0 dependence. Relative yields of molecular ions were independent of the number densities of precursor molecules in the excitation region, indicating that these fragments were direct photolysis products and not the results of ion-molecule or other bimolecular reactions.

RESULTS AND DISCUSSION

Table I is a comprehensive listing of the metal-containing molecular ions we have detected to date by MPI mass spectrometry of transition metal carbonyl complexes. A number of bare homonuclear metal

dimers and trimers have been observed, such as Fe_2^+ and Ru_3^+ , as well as some heteronuclear metal clusters, such as FeRu_2^+ . Several types of metal-nonmetal clusters have also been detected, including metal monocarbonyls (CrCO^+) and metal sulfides (Fe_2S_2^+). Figures 1-3 display representative MPI mass spectra.

Pronounced enhancements in atomic metal ion signals were observed when the laser was tuned into resonance with known atomic transitions, indicating that the atomic ions were largely produced by photoionization of the neutral atoms rather than by fragmentation of larger ions.^{1,7} Although the processes leading to the molecular ions listed in Table I could not be determined directly, the atomic MPI results suggest that these ions also derive, at least in part, from the corresponding neutral clusters produced by multiphoton dissociation of the indicated precursors.

Thus, UV multiphoton excitation of transition metal carbonyl compounds provides an effective means of producing a wide variety of highly unsaturated neutral and ionic metal-containing molecules in the gas phase. As noted in the Introduction, this metal cluster generation method has several potential advantages over alternative techniques with respect to source temperature requirements and product cluster specificity. The large number of metal carbonyl compounds reported in the literature (many of which are commercially available) suggests the applicability of this technique for preparing a diversity

TABLE I
Metal cluster ions detected by MPI-mass spectrometry of photodissociated organometallics

Homonuclear metal clusters		Heteronuclear metal clusters	
Ion	Precursors	Ion	Precursors
Mn_2^+	$\text{Mn}_2(\text{CO})_{10}$	FeRu^+	$\text{Fe}_2\text{Ru}(\text{CO})_{12}$, $\text{FeRu}_2(\text{CO})_{12}$
Fe_2^+	$\text{Fe}_2(\text{CO})_6\text{S}_2$, $\text{Fe}_3(\text{CO})_{12}$	FeRu_2^+	$\text{FeRu}_2(\text{CO})_{12}$
Co_2^+	$\text{Co}_2(\text{CO})_8$, $\text{Co}_4(\text{CO})_{12}$	Metal-nonmetal clusters	
Ru_2^+	$\text{FeRu}_2(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$	Ion	Precursors
Ru_3^+	$\text{Ru}_3(\text{CO})_{12}$	MCO^+	$\text{Cr}(\text{CO})_6$, $\text{Mn}_2(\text{CO})_{10}$
Re_2^+	$\text{Re}_2(\text{CO})_{10}$	$\text{C}_5\text{H}_5\text{Cr}^+$	$[(\pi\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$
Os_2^+	$\text{Os}_3(\text{CO})_{12}$	MnBr^+	$\text{Mn}(\text{CO})_5\text{Br}$
Os_3^+	$\text{Os}_3(\text{CO})_{12}$	$\text{Fe}_{1,2}\text{S}_{1,2}^+$	$\text{Fe}_2(\text{CO})_6\text{S}_2$

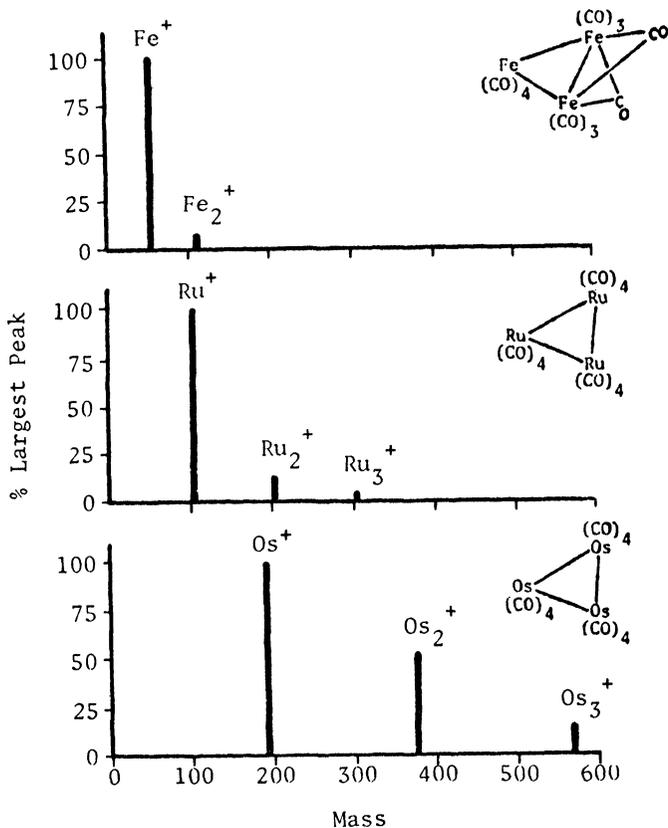


FIGURE 1 MPI mass spectra at 3853 \AA of $\text{Fe}_3(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$, and $\text{Os}_3(\text{CO})_{12}$ obtained at fluxes of 3×10^7 , 7×10^7 and $1 \times 10^8 \text{ W cm}^{-2}$, respectively. Intensity dependences noted in the text indicate that at constant laser flux, the trend of increased molecular vs. atomic ion signal for heavier members of the $\text{M}_3(\text{CO})_{12}$ series would be even more pronounced than is illustrated in this figure. Source temperatures were $100\text{--}120^\circ\text{C}$.

of well-defined gas phase metal clusters for spectroscopic and chemical studies.

It is generally accepted, on the basis of results of a number of solution phase photochemical and spectroscopic studies, that metal-metal bond cleavage is the only primary excited state reaction induced by UV photolysis of the manganese and rhenium dinuclear decacarbonyls; ligand substitution products observed are believed to result

from coupling of thermally substituted photofragments.⁵ However, our observation of the ligand-free dimers of manganese and rhenium following UV multiphoton dissociation of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ under collision-free conditions⁸ demonstrates that ligand dissociation is an alternative primary photochemical channel in these systems. Results of flash photolysis experiments recently reported from this and other laboratories on $\text{Mn}_2(\text{CO})_{10}$ ⁹ and other dinuclear carbonyl complexes¹⁰ indicate that competitive metal-metal bond homolysis and dissociative CO loss occurs in solution phase as well. This may prove to be a general pattern of photochemical behavior under ultraviolet excitation for many metal-metal bonded systems containing carbonyl ligands.

Comparison of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ MPI mass spectra indicates a substantially higher ratio of dimeric to atomic ions for the third transition series complex than for the isostructural first transition series complex. A parallel trend is observed in the $\text{M}_3(\text{CO})_{12}$ systems ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$), whose MPI mass spectra, displayed in Figure 1, show an increased preservation of the metal cluster core as the series progresses to heavier members of the iron triad. Interestingly, this pattern is also evident in the electron impact (EI) mass spectra of the $\text{M}_2(\text{CO})_{10}$ and $\text{M}_3(\text{CO})_{12}$ series.¹¹ It has been observed¹² that similar trends obtain in bond energies of cationic transition metal species, whose fragmentation mechanisms determine EI results, and the corresponding neutral molecules, whose dissociation behavior is important in the MPI process. Such correlations have been reported for

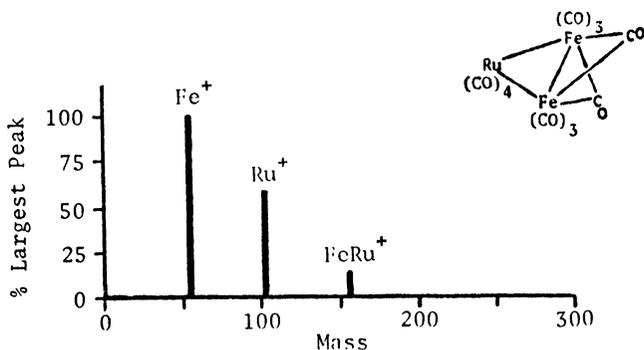


FIGURE 2 $\text{Fe}_2\text{Ru}(\text{CO})_{12}$ MPI mass spectrum at 3853 \AA , $2 \times 10^8 \text{ W cm}^{-2}$, 100°C .

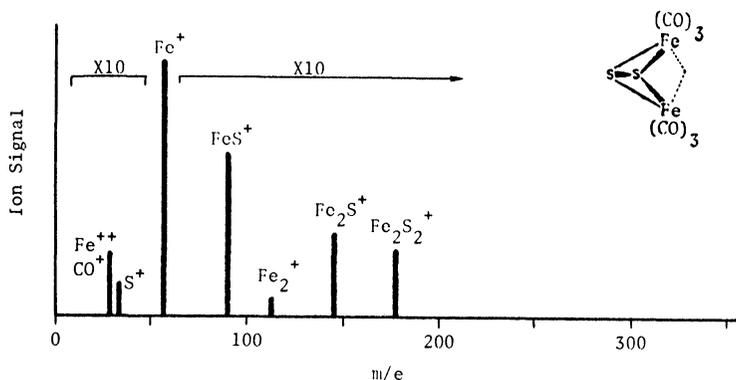


FIGURE 3 MPI mass spectrum of $\text{Fe}_2(\text{CO})_6\text{S}_2$ sublimed at room temperature and photolyzed at 3853 \AA , $1 \times 10^6 \text{ W cm}^{-2}$. FeS_2^+ was also observed in other runs employing higher laser fluxes.

both metal–metal and metal–ligand bonds in transition metal carbonyl complexes,¹² and may partially explain parallel trends in EI and MPI fragmentation patterns. The wealth of data available concerning the fragmentation behavior under electron impact of a wide variety of transition metal complexes¹¹ may prove a valuable resource in the selection of promising precursors for target clusters generated by multiphoton techniques.

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