Production of Gas-Phase Bare Transition-Metal Clusters by Laser Photodissociation of Organometallic Cluster Compounds

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The characterization of the structure and reactivity of bare transition-metal clusters is currently an area of intense research. Information concerning the electronic and vibrational spectra of these highly reactive species has been successfully obtained in low-temperature matrix isolation experiments. However, the feasibility of perturbing effects of lattice interactions on the spectra and structure of the sample and the difficulty of extracting information concerning a particular cluster size in a sample of mixed composition complicate the interpretation of matrix results. Bare metal clusters have been produced in the gas phase by aggregation of metal atoms vaporized by resistance or laser heating, but limited cluster size specificity may render these techniques inappropriate to the study of large clusters by non-mass-selective spectroscopic methods.

In the present communication, we propose laser photodissociation of organometallic cluster compounds as an alternative method for producing bare transition-metal clusters in the gas phase. The great variety of metal cluster sizes and geometries available in polynuclear organometallic compounds, combined with the remarkable efficiency of multiphoton dissociation for producing neutral bare metal fragments from organometallic precursors, suggests the potential of this technique for preparing well-defined bare metal clusters in sufficient concentrations for spectroscopic characterization. A further advantage of this preparative scheme is that it is applicable to highly refractory metals without the use of high temperature sources. The feasibility of the proposed technique is illustrated below by the results of its application to Co(CO)₅.

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Figure 1. Mass spectrum of photoproducts following multiphoton dissociation and ionization of Co₂(CO)₈. The laser was tuned to 406 nm and focused onto the molecular jet by a 7-cm focal length lens mounted inside the vacuum chamber. The apparatus is described in the text and ref 7. Scans up to the parent mass at 342 amu detected no additional ionic species. Peak positions of the spectral features shown were measured to ±1.0 amu using several ions of known mass as calibration points. This precision is sufficient to positively assign the higher mass peak to Co²⁺ (117.9 amu) rather than the closest likely ion, Co(CO)₅⁺ (115.0 amu).

Figure 2. Wavelength dependence of Co⁺ and Co²⁺ signal intensities. The Co⁺ ion yield is enhanced when the laser wavelength is tuned to an allowed transition of Co(I). The assignments indicated in the figure were made by using the atomic energy level data of ref 8b. The Co²⁺ spectrum is expanded fivefold with respect to the Co⁺ spectrum. The spectra were taken with a resolution of 0.2 nm and were not corrected for the laser intensity, which maximizes at 407 nm.
As shown in Figure 1, irradiation at 406 nm yielded Co+ and Co2+ in a ratio of approximately 10:1. No other molecular ions were detected under these conditions, indicating maximum possible abundances of 0.3% relative to that of Co+. Observed signal levels suggest that the yield of Co2+ from Co2(CO)8 in the laser focal volume exceeded 1% under the experimental conditions employed.

In light of the work on other organometallic systems, the most likely mechanisms for the formation of Co+ and Co2+ from Co2(CO)8 are as follows:

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\text{Co}_2(\text{CO})_8 \rightarrow 2\text{Co} + 8\text{CO}
\]

Several experiments indicated that the Co2+ was not formed primarily via reaction of the abundant Co+ ion with the parent or other molecular species. Figure 2 shows the wavelength dependences between 400 and 410 nm of Co+ and Co2+ signal intensities. The Co+ spectrum contains a prominent band which can be assigned to atomic transitions of Co. These peaks are not observed in the Co2+ spectrum, indicating that the Co2+ ion yield is independent of Co+ production. A second argument against an ion-molecule recombination mechanism for Co2+ production is provided by studies of the pressure dependence of Co2+ signal strength, the results of which are shown in Figure 3. Variation of the Co2(CO)8 pressure in the photolysis region produced an approximately linear change in Co2+ signal strength, rather than the quadratic change which would be expected if a binary reaction were involved in Co2+ production. This pressure dependence also argues against a formation path in which neutral atomic and/or molecular recombinations are followed by ionization, which is in any case unlikely at the pressures employed in these experiments. In conclusion, the Co2+ detected upon irradiation of Co2(CO)8 appears to be formed directly by de-carbonylation of the parent compound and photoionization of the metal fragment rather than by combination reactions involving mononuclear species.

Cobalt(III)-Mediated Peptide Synthesis. 1. Cobalt(III)-Activated Amino Acid Methyl Esters and the Synthesis of Dipeptides

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Previously we described the rapid amidolysis of Co(III)-chelated glycine esters (I) in aprotic solvents1-3 [N4 = (en)2 or trien; R = (N4)C'NHR'] and suggested that reaction 1 might well provide a useful alternative to the active ester method for the synthesis of peptides. We have now extended this aspect to include coordinated amino acids other than glycine and herein report on a simple preparation for the Co(III) active ester, the coupling reaction and recovery of the dipeptide, and the degree of racemization at each stage. In the following communication3 the preparation of two tetrapeptides and the synthesis of [Leu]enkephalin is described.

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\text{CH}_3, \text{C}_2\text{H}_5; R' = \text{H}, \text{CHR'/CO/ET}] \text{ and suggested that reaction 1 might well provide a useful alternative to the active ester method for the synthesis of peptides. We have now extended this aspect to include coordinated amino acids other than glycine and herein report on a simple preparation for the Co(III) active ester, the coupling reaction and recovery of the dipeptide, and the degree of racemization at each stage. In the following communication3 the preparation of two tetrapeptides and the synthesis of [Leu]enkephalin is described.}

\[
\text{Treatment of [Co(N_4)(AA)]_2}^+ \text{ (7.5 mmol; N}_4\text{ = (en)_2 or trien;}
\]

\[
\begin{align*}
\text{C}r\text{C}_2\text{O}_8^+ + \text{C}_2\text{H}_5 & \rightarrow \text{Cr}^+ + \text{C}_2\text{H}_5\text{CO}_2^+ + \text{e}^- \\
\text{Cr}^+ + \text{C}r\text{C}_2\text{O}_8^+ & \rightarrow \text{C}r_2\text{C}_2\text{O}_8^+ + (6-n)\text{CO}
\end{align*}
\]