arachidonic acid in micelles by the O_2^{-}-H_2O_2 system.[25] Our preliminary studies of arachidonic acid indicate that it too reacts with the HO_2 radical.

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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.[1] Information concerning the electronic and vibrational spectra of these highly reactive species has been successfully obtained in low-temperature matrix isolation experiments.[2] However, the possibility 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[3] or laser[4] heating, but limited cluster size specificity may render these techniques inapplicable 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,[5] combined with the remarkable efficiency of multiphoton dissociation for producing neutral bare metal fragments from organometallic precursors,[6] 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 $Co_2(CO)_8$.

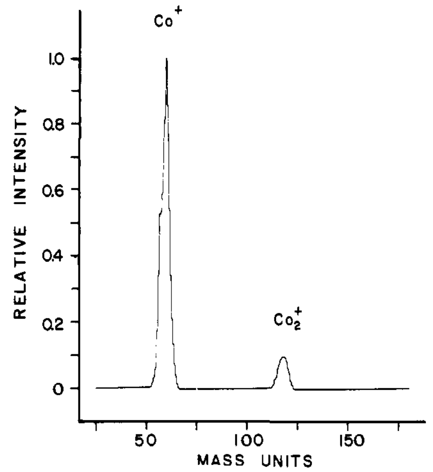

Figure 1. Mass spectrum of photoproducts following multiphoton dissociation and ionization of $Co_2(CO)_8$. The laser was tuned to 406 nm and focused onto the molecular jet by a 7-cm focal length lens mounted inside the vacuum chamber. The apparatus is described in the text and ref 7. Scans up to the 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 masses as calibration points. This precision is sufficient to positively assign the higher mass peak to Co_2^+ (117.9 amu) rather than the closest likely ion, $Co(CO)_2^+$ (115.0 amu).

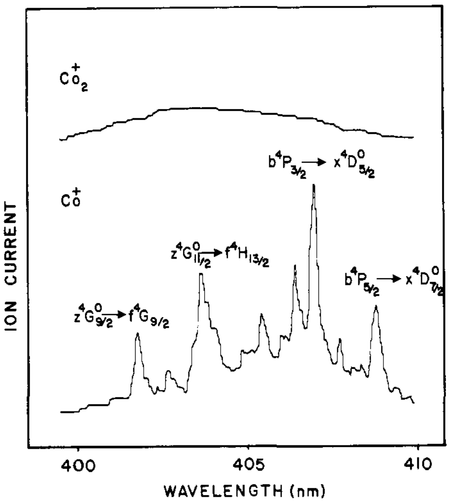

Figure 2. Wavelength dependence of Co^+ and Co_2^+ signal intensities. The Co^+ ion yield is enhanced when the laser wavelength is tuned to an allowed transition of Co(I). The assignments indicated in the figure were made by using the atomic energy level data of ref 8b. The Co_2^+ spectrum is expanded 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.

In the present experiment, gas-phase $Co_2(CO)_8$ was photodissociated, and the metal fragments were detected by mass-selective multiphoton ionization. $Co_2(CO)_8$ was evaporated under its room temperature vapor pressure into a chamber with a background pressure of less than 1×10^{-5} torr, where it was irradiated with pulses of 10-ns duration from a Lambda Physics excimer-pumped tunable dye laser system. The sample number density was approximately 10^{12} molecule mL^{-1} and the photon flux approximately 10^8 W cm^{-2} in the region of intersection of the sample jet with the laser beam. Multiphoton absorption processes resulted in dissociation and ionization of the $Co_2(CO)_8$ during a single laser pulse. The cations produced were collected, then mass selected by a quadrupole mass analyzer whose axis was perpendicular to both the molecular jet and the laser beam. The ion signal was detected by a channeltron electron multiplier and a boxcar averager.

[†] Alfred P. Sloan Fellow.

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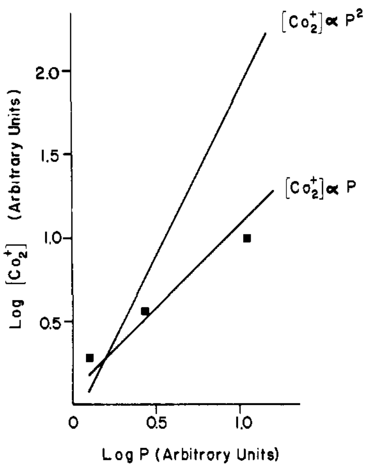

Figure 3. Dependence of Co_2^+ signal intensity on the sample number density in the photolysis region. Lines show the expected pressure dependences of products of direct unimolecular dissociation and ionization ($[Co_2^+] \propto P$) and of binary reaction ($[Co_2^+] \propto P^2$).

As shown in Figure 1, irradiation at 406 nm yielded Co^+ and Co_2^+ 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 Co_2^+ from $Co_2(CO)_8$ in the laser focal volume exceeded 1% under the experimental conditions employed.

In light of the work on other organometallic systems,[6] the most likely mechanisms for the formation of Co^+ and Co_2^+ from $Co_2(CO)_8$ are as follows:[8]

$$Co_2(CO)_8 \rightarrow 2Co + 8CO$$

$$Co_2(CO)_8 \rightarrow Co_2 + 8CO$$

$$Co \rightarrow Co^+ + e^-$$

$$Co_2 \rightarrow Co_2^+ + e^-$$

Several experiments indicated that the Co_2^+ was not formed primarily via reaction of the abundant Co^+ ion with the parent or other molecular species.[9] Figure 2 shows the wavelength dependences between 400 and 410 nm of Co^+ and Co_2^+ signal intensities. The Co^+ spectrum contains a number of prominent peaks which can be assigned to atomic transitions of Co. These peaks are not observed in the Co_2^+ spectrum, indicating that the Co_2^+ ion yield is independent of Co^+ production. A second argument against an ion–molecule recombination mechanism for Co_2^+ production is provided by studies of the pressure dependence of Co_2^+ signal intensity, the results of which are shown in Figure 3. Variation of the $Co_2(CO)_8$ pressure in the photolysis region produced an approximately linear change in Co_2^+ signal strength, rather than the quadratic change which would be expected if a binary reaction were involved in Co_2^+ 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.[10] In conclusion, the Co_2^+ detected upon irradiation of $Co_2(CO)_8$ appears to be formed directly by decarbonylation of the parent compound and photoionization of the metal fragment rather than by combination reactions involving mononuclear species.

These results suggest that laser photodissociation of organometallic cluster compounds can provide an efficient method for producing ligand-free clusters in the gas phase. Given the diversity of known potential precursors,[5] this technique could provide specific access to a wide variety of bare transition-metal clusters.

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(8) The multiphoton dissociation steps require five 406 nm photons to produce the metal atom or the metal dimer. Depending on the amount of excess energy retained by the metal fragment, at least three additional photons are required to produce the atomic cation and at least one photon is needed to ionize the dimer. These figures were calculated from the mass spectrometric appearance potential data of ref 8a, the atomic data of ref 8b, and the metal dimer dissociation energy data of ref 8c. (a) Winters, R. E.; Kiser, R. W. *J. Phys. Chem.* **1965**, *69*, 1618–1622. (b) Moore, C. E. *Natl. Bur. Stand.* (*U.S.*) *Circ.* **1952**, *No. 467*. (c) Blackborow, J. R.; Young, D. "Metal Vapour Synthesis in Organometallic Chemistry"; Springer-Verlag: Berlin, 1979; p 53.

(9) The surprising efficiency of such processes was revealed by experiments in which products of the following reaction sequence were detected on microsecond timescales at sample pressures of 10^{-5} torr:

$$Cr(CO)_6 \rightarrow Cr^+ + 6CO + e^-$$

$$Cr^+ + Cr(CO)_6 \rightarrow Cr_2(CO)_n^+ + (6 - n)CO$$

(10) Such mechanisms have been employed to produce bare metal clusters under different experimental conditions. For example, see ref 3 and 4. Also see: Efremov, Yu. M.; Samoilova, A. N.; Kozhukhovsky, V. B.; Gurvich, L. V. *J. Mol. Spectrosc.* **1978**, *73*, 430–440.

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

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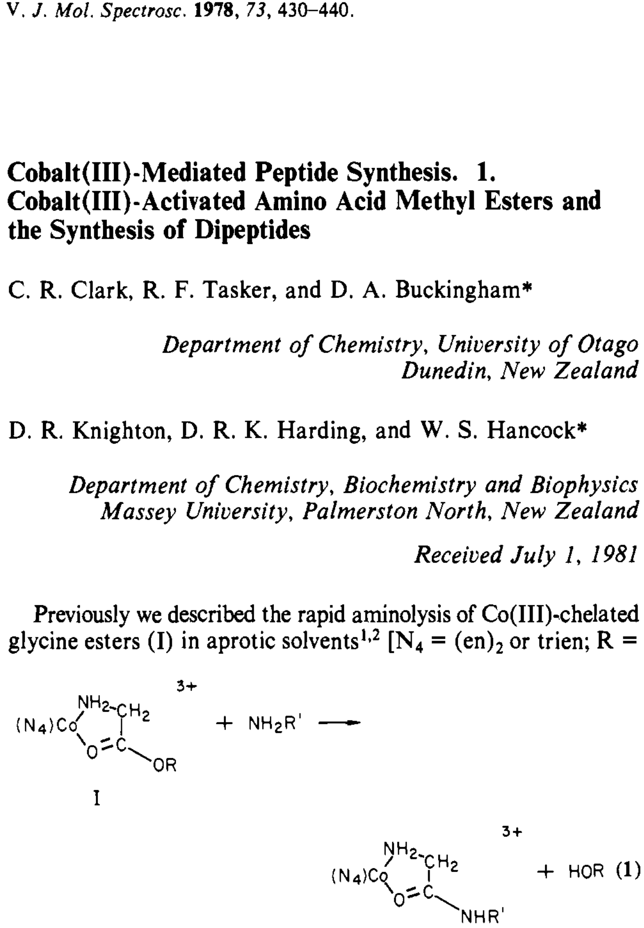
Previously we described the rapid aminolysis of Co(III)-chelated glycine esters (I) in aprotic solvents[1,2] [N_4 = $(en)_2$ or trien; R = CH_3, C_2H_5; R′ = H, $CHR''CO_2Et$] and suggested that reaction 1 might well provide a useful alternative to the active ester method for the synthesis of peptides. 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 communication[3] the preparation of two tetrapeptides and the synthesis of [Leu^5]enkephalin is described.



Treatment of $[Co(N_4)(AA)]I_2$[4] [7.5 mmol; N_4 = $(en)_2$ or trien;

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(3) See D. R. Knighton, D. R. K. Harding, M. J. Friar, W. S. Hancock, G. D. Reynolds, C. R. Clark, R. F. Tasker, and D. A. Buckingham, *J. Am. Chem. Soc.*, following paper in this issue.

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