charge-transfer bands at different wavelengths[13,14] means that the type of ligand can be deduced from the optical spectrum. Another aspect of the reagent that should increase its value is its ability to form stable complexes with purine and pyrimidine bases in DNA.[15] The chloropentaammineruthenium reagent may therefore prove to be of general utility in studies of the structural and dynamic properties of both amino and nucleic acid polymers.

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Selective Photoaggregation of Metal Atoms to Small Bimetallic Clusters of Known Size. The Chromium–Molybdenum System Cr$_n$Mo$_m$

Sir:

Cryophotoclustering of metal atoms,[1] a new technique whereby matrix entrapped transition metal atomic species are photomobilized and photoaggregated at low temperatures, shows great promise for achieving cluster size distributions not hitherto accessible by conventional metal deposition–bulk thermal annealing matrix procedures.[2] By selectively exciting metal atomic species isolated in low temperature weakly interacting solids, at energies corresponding to their atomic resonance transitions, one can observe (for example, by optical spectroscopy) a highly controlled photoclustering phenomenon,
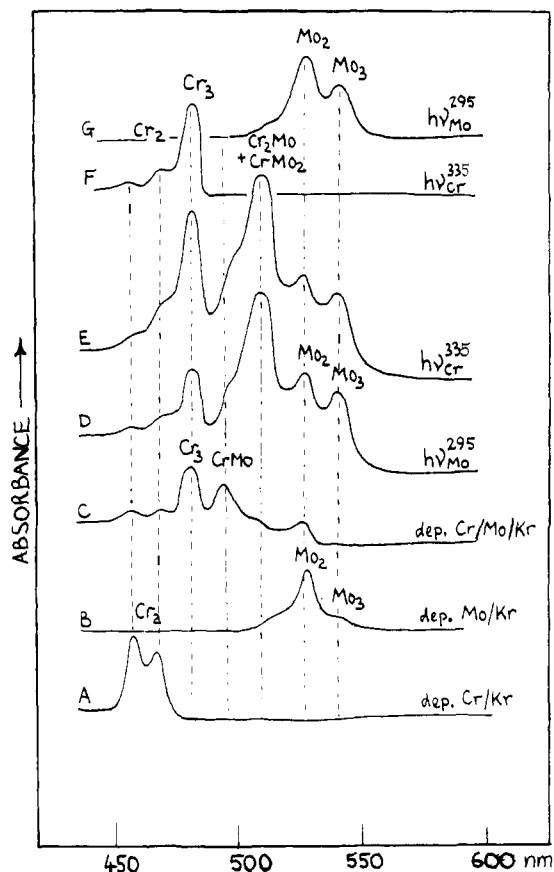

Figure 1. The low energy optical spectra of (A) Cr/Kr = 1/10^3, (B) Mo/Kr = 1/10^4, and (C) Cr/Mo/Kr = 1/1/10^3 mixtures all deposited at 12K showing the characteristic absorptions of Cr$_2$, Cr$_3$, CrMo, Cr$_2$Mo, CrMo$_2$, Mo$_2$, and Mo$_3$; (D) the result of 10 min $h\nu_{Mo}^{295}$ photolysis of sample C; (E) the result of 5 min $h\nu_{Cr}^{335}$ photolysis of sample D; (F) the result of 3 min $h\nu_{Cr}^{335}$ photolysis of sample A; (G) the result of 30-min $h\nu_{Mo}^{295}$ photolysis of sample B. (dep. ≡ deposition at 12K.)

whereby metal atom absorptions gradually decay and metal cluster absorptions concomitantly grow in.[1]

The process can be visualized as a reaction of a photomobilized metal atom with the substrate: M† + M → M$_2$; M† + M$_2$ → M$_3$; M† + M$_3$ → M$_4$ etc. In all of the above, M† represents the photomobilized metal atom which is assumed to diffuse in the system. Thus the photomobilization and the diffusion processes would control the rate of growth of metal clusters. In this communication we provide information on the question of selective photomobilization of metal atoms. The mixed metal cluster system Cr$_n$Mo$_m$ [1b,3] (where m = 3 to 0 and n = 0 to 3) was selected for study because details of the optical spectra of the various metal atom combinations in an argon matrix are known[1b,3] (see Figure 1). (Spectra in a krypton matrix are essentially the same except for a small frequency shift.)

In experiments described here a dilute mixed metal/krypton matrix of atom ratio Cr/Mo/Kr ≃ 1/1/10^4 and a more concentrated atom matrix of composition Cr/Mo/Kr ≃ 1/1/10^3 were irradiated with light of 335 nm. Such radiation should selectively photomobilize Cr atoms. Radiation at 295 nm used in a separate experiment should selectively photomobilize Mo atoms. In Kr the Cr(3d^{5}4s^1) → Cr(3d^{4}4s^{1}4p^1) band maximum lies at roughly 341 nm while the Mo(4d^{5}5s^1) → Mo(4d^{4}4s^{1}5p$'$)

Table I. Low Energy Optical Absorptions of Cr$_n$Mo$_m$ in Solid Argon and Krypton Matrices

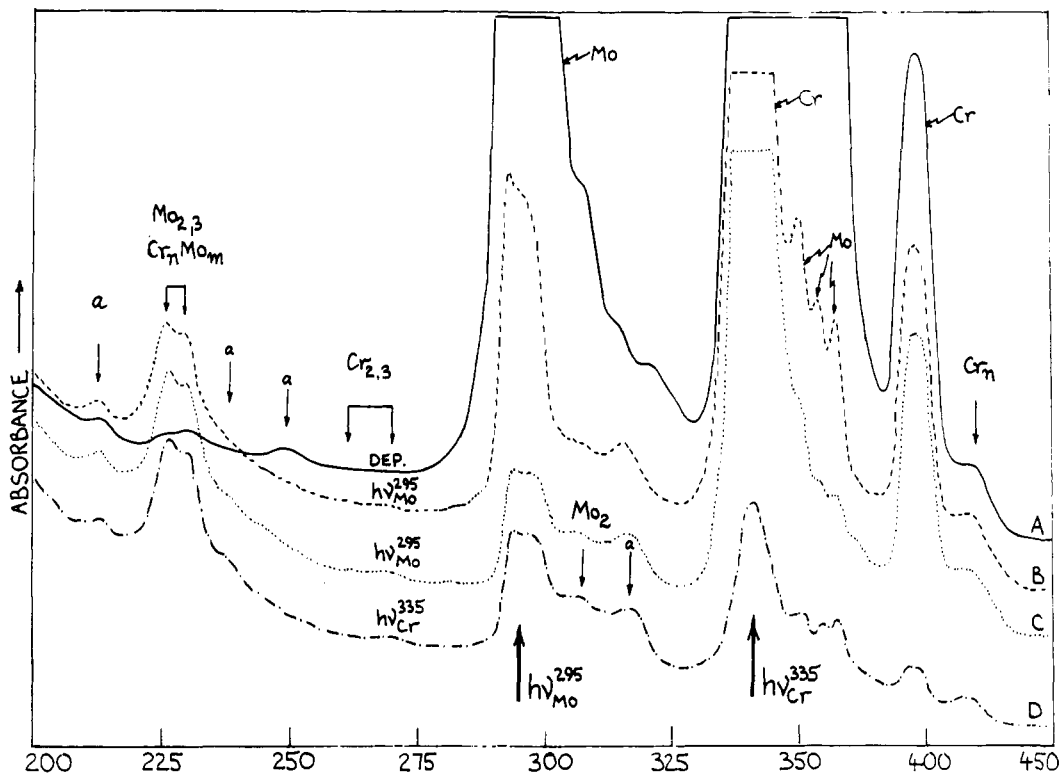|	Cr$_2$	CrMo	Mo$_2$	Cr$_3$	Cr$_2$Mo	CrMo$_2$	Mo$_3$
Ar	460/469	486/489	418/524	477	494	498	534
Kr	457/468	496	510/526	479	496	496	538

Figure 2. (A) The high energy optical spectra of Cr/Mo/Kr = $1/1/10^3$ mixtures deposited at 12K showing the known absorptions of Cr, Mo, Cr_2, Mo_2, and Mo_3. (B and C) the result of 50- and 130-min $h\nu_{Mo}^{295}$ photolysis of sample A and (D) the result of a further 22-min $h\nu_{Cr}^{335}$ photolysis of sample C. Note that the bands labeled "a" could be associated with mixed clusters Cr_nMo_m. (DEP ≡ deposition at 12K.)
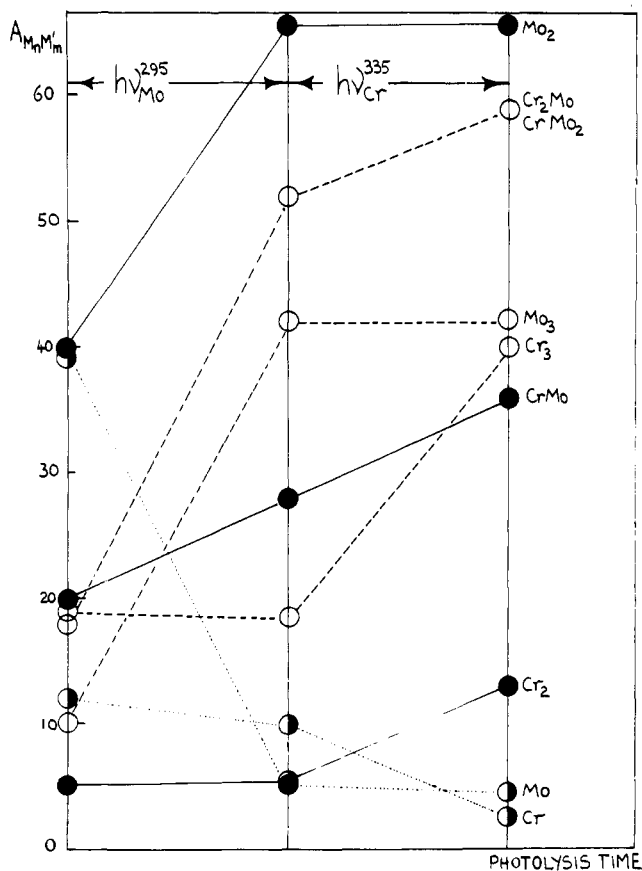

Figure 3. A schematic representation of the photoselectivity experiments involving Cr/Mo/Kr = $1/1/10^3$ mixtures deposited at 12K and then sequentially subjected to $h\nu_{Mo}^{295}$ and $h\nu_{Cr}^{335}$ photolyses. Note that the Cr and Mo atom absorbances are recorded on a scale *10× smaller* than that used for the Cr_nMo_m clusters.

band maximum lies at 295 nm. There is, however, some non-selective excitation with irradiation at 345 nm because other transitions of $Mo(4d^55s^1 \rightarrow 4d^55p^1)$ lie at 340, 358, and 364 nm. The starting matrix prepared in solid Kr at 12 K clearly displayed the characteristic absorptions of Cr, Mo, Cr_2, CrMo, Mo_2, Cr_3, Cr_2Mo, $CrMo_2$, and Mo_3. The spectrum of each species in a Kr matrix (apart from the $Cr_2Mo/CrMo_2$ combination) was reasonably well resolved. In a solid Ar matrix the $Cr_2Mo/CrMo_2$ combinations were also resolvable (Table I).

When a matrix of known composition was irradiated at 295 nm to excite Mo, major *decay* of molybdenum absorptions was observed (Figure 2B,C) and selective growth of CrMo, $CrMo_2$, Mo_2, and Mo_3 (Figure 1D)[4] was observed. Only slight *decay* of Cr (Figure 2B,C) was noted along with approximate *constancy* of Cr_2 and Cr_3. These observations argue strongly for *selective* photoexcitation and photomobilization of Mo atoms by radiation at 295 nm.

Similarly photoexcitation of Cr using radiation at 335 nm results in major *decrease* in the chromium absorptions (Figure 2D) and selective *growth* of Cr_3 and Cr_2Mo (Figure 1E)[5] was observed. Only slight *decay* of Mo (Figure 2D) was noted along with slight *growth* of Cr_2 and approximate *constancy* of Mo_2 and Mo_3 (Figure 1E). A schematic representation of these photoselectivity effects is illustrated in Figure 3. These observations provide a strong case for *selective* photoexcitation and photomobilization of Cr atoms by radiation at 335 nm.

Noteworthy support for these proposals can be considered to stem from the simultaneous Cr/Mo atomic excitation (350 nm) control experiments, which displayed the expected *growth* patterns for *all* cluster species concomitant with decay of both Cr and Mo atomic species, that is designed nonphotoselectivity. The corresponding high dilution Cr/Mo/Kr ≃ $1/1/10^4$ experiments also very effectively support our case for a highly selective photoaggregation process and will be reported in detail in a forthcoming publication.[6]

We feel that the experimental evidence that we have presented for selective photomobilization and photoaggregation of metal atomic species, as monitored by our mixed metal atomic–bimetallic cluster optical experiments, is overwhelmingly positive. Nevertheless further experimental probes of these new and interesting photophysical-photochemical phenomena, together with an intensive search for still higher clusters are planned for these as well as other metallic and bimetallic systems. The impetus for such "mini-alloy" cluster experiments, besides the intrinsic chemical novelty of "few-atom-bimetallics", is the long-range goal of probing the "molecular metal cluster-bulk metal particle interface",[2] the objective being a fundamental enquiry into bimetallic cluster electronic, geometric, chemisorptive, and catalytic properties as a function of the size and composition of the cluster.[9]

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(4) As Cr₂ remains essentially invariant under these circumstances we favor Mo↑ + CrMo → CrMo₂ rather than Mo↑ + Cr₂ → Cr₂Mo.
(5) As Mo₂ remains essentially invarlant under these circumstances we favor Cr↑ + CrMo → Cr₂Mo rather than Cr↑ + Mo₂ → CrMo₂.
(6) It is important to note here that, under a wide variety of concentration conditions in separate Cr/Kr(Ar), Mo/Kr(Ar), and Cr/Mo/Kr(Ar) experiments, bulk diffusion incurred by thermal annealing (12–40K for Ar, 12–60K for Kr) leads only to "catastrophic clustering" as seen by the general *decay* of all Crₙ, Moₘ, and CrₙMoₘ spectral absorbances (presumably arising from nonselective diffusion-aggregation processes, leading mainly to high clusters characterized by broad bulk metal-like, far-UV absorptions). This could imply "thermally activated clustering" for the lower diatomic, triatomic, etc. species which might well be kinetically impeded at the low temperatures employed in our matrix experiments. (Incidentally, this is not the case for silver, where at least Ag₂,₃,₄,₅ clusters can be generated by thermal-annealing techniques in Ar, Kr, Xe, and CH₄.[1,7,8]) It is therefore conceivable, that the *facile* photogeneration of CrMo, Mo₂, Cr₃, Cr₂Mo, CrMo₂, and Mo₃ is, in fact, the outcome of "photoactivated" nucleation events involving either electronically excited or "thermally hot" atomic/cluster moieties. Further research is required to establish this pertinent aspect of photoaggregation.
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Preparation and Isolation of Δ1,4-Bicyclo[2.2.0]hexene

Sir:

We wish to report details of the preparation and properties of the highly strained olefin, Δ1,4-bicyclo[2.2.0]hexene (1). Three previous papers have reported evidence for the presence of this compound, but none has described isolation of the pure

material.[1] Bromochloride **2** was prepared as previously described.[2] Compound **2** can be electrochemically reduced only with difficulty ($E_{1/2} = -2.50$ V vs. saturated calomel electrode in dimethylformamide),[1b] behavior not characteristic of 1,2-dihalides.[3] Dipole moment measurements of **2**[2b,4] suggest a large intervector angle between the carbon–halogen bonds. Since the molecule may also be twisted, these two effects could explain the observed electrochemical behavior.[5]

Controlled current electroreduction of 400 mg of **2** in 40 mL of dimethylformamide[6] in a divided cell, with 0.18 M tetramethylammonium hexafluorophosphate[7] was conducted at -14 °C over a stirred mercury pool cathode[8] while the apparatus was maintained at 2×10^{-3} Torr pressure in a vacuum line. Volatile effluents were collected in cold traps maintained at -23, -45, and -95 °C, respectively, while 2.0 F of current were passed. The current was held at 100 mA, and resulted in an applied voltage of 10–14 V. The -95 °C trap contained 10–30 mg of a white crystalline solid, melting below -60 °C, which could be identified as Δ1,4-bicyclo[2.2.0]hexene (**1**) from the behavior and properties described below.

In contrast to its behavior in dilute hydrocarbon solution,[1c] the pure olefin **1** is extremely reactive. It can be transferred from a -45 °C bath to a -200 °C bath over a short path length with some loss to polymer, but at -23 °C the neat olefin polymerizes with a half-time of <10 s. Vapor pressures of >1 Torr have not been obtained, owing to polymerization. The polymer is a clear solid, insoluble in most solvents: IR (cm^{-1}) 3000, 2960, 2880, 1425, 1225, 1010.

The ^{1}H NMR (CD₂Cl₂) of **1** consisted of a sharp singlet at 3.24 ppm.[1a] In dilute solution ($\sim$1%) in C₆D₅CD₃, the olefin disappeared with a half-time of 420 s at 0 °C. The product was an insoluble polymer. The ^{13}C NMR of **1** at -50 °C showed peaks at 163.5 and 43.7 ppm (CD₂Cl₂) (relative to Me₄Si). The low field peak, assigned to the olefinic carbon, is significantly further downfield than any other simple olefinic resonance heretofore reported.[11] The mass spectrum, recorded at 2.1 kV, show m/e (percent of base peak) of 80 (49) (M$^+$), 79 (100), 77 (28), and 43 (26).

The Raman spectrum of **1** was recorded at -190 °C using a sample prepared by condensing vapor onto a copper plate. Spectra were recorded of unannealed and annealed (at -110 °C) films excited with $\sim$50 mW of 514.5-nm Ar$^+$ laser radiation. Both C=C and C—H bands were observed. The C=C band appeared at 1661 cm^{-1} in the solid and was shifted when measured in solution (1664 cm^{-1} in CD₂Cl₂ at -50 °C, 1673 cm^{-1} in cyclopropane at -56 °C). The C—H bands appeared at 2843, 2923, 2951, and 2961 cm^{-1} and were consistent with CH₂ modes in normal strained alicyclic hydrocarbons.[12a]

The infrared spectrum of a solid film of **1**, obtained by vapor deposition onto a cesium iodide plate at -196 °C, was recorded before and after annealing at -110 °C. The C—H bands appeared at 2832, 2930, and 2965 cm^{-1}; the latter two appear normal for aliphatic CH₂.[12b] Only five bands appear between 650 and 200 cm^{-1}. They were found at 424, 410, 400 (sh), 393, and 288 cm^{-1} and seem to account for the fundamental out-of-plane deformation modes. It was not possible to measure the gas phase infrared spectrum of **1**, even in a 10-m multipass cell, owing to decomposition of the olefin at room temperature. The appearance of strong, low frequency fundamental bands in the infrared and their complete absence in the Raman spectrum are consistent with D_{2h} symmetry, characteristic of a planar skeleton. The unusual downfield ^{13}C chemical shift of the olefinic carbon in **1** suggests a tendency toward allene-like sp character.

Although the olefin is reactive with cyclopentadiene,[1a,b] it failed to undergo cycloaddition with 2,3-dimethyl-1,3-butadiene in CD₂Cl₂ solution at temperatures below those necessary for polymerization.