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### Selective, Naked Cluster Cryophotochemistry: Trisilver, $\text{Ag}_3$

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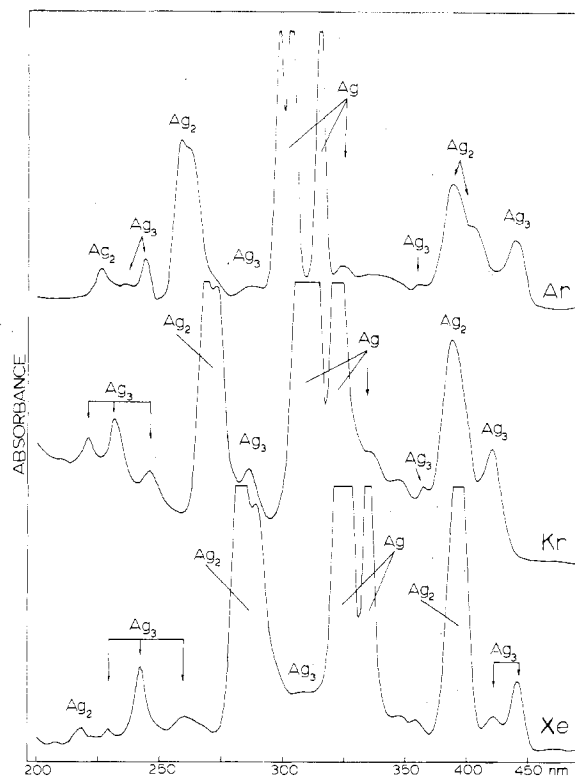
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A number of interesting observations have been made concerning the photoinduced diffusion/aggregation behavior of silver atoms isolated in cryogenic rare-gas supports.<sup>1</sup> The silver atomic diffusion process can be initiated and controlled by means of narrow-band UV photolysis centered at the atomic resonance absorption lines, and the aggregation processes can be followed by monitoring the optical spectra of the matrix deposits. These silver atom aggregation reactions provide a convenient and controlled route to matrix-isolated silver molecules, suitable for subsequent spectroscopic and cryochemical studies.<sup>2</sup> Similar photoaggregation processes have been reported for several other metal atomic species, including a number of the transition metals, in both uni- and bimetallic situations.<sup>2,3</sup>

A valuable insight into the mechanism of silver atom photomobility has been obtained through fluorescence spectroscopic studies of matrix-isolated silver atoms.<sup>4</sup> Furthermore, it has become apparent from preliminary investigations that fluorescence studies have the potential for revealing a richly detailed picture of the photophysical behavior of matrix-isolated silver molecules. A combination of fluorescence spectroscopy and selective, narrow-band photolysis coupled with UV-visible spectral monitoring has now been used to explore the concept of silver cluster photochemistry. In this note we report UV-visible absorption results relating to trisilver visible photochemistry, a system which we believe to be somewhat unique in a number of respects. A more detailed account of the photophysical aspects of this work will appear in a subsequent publication.<sup>4b</sup> Selective  $\text{Cu}_2$  and  $\text{Ag}_2$  cryophotochemistry, emission spectroscopy, and SCF-X $\alpha$ -SW molecular orbital calculations for  $\text{Cu}_2$  and  $\text{Ag}_2$  will also appear in a separate publication.<sup>1c,4b</sup>

The optical absorption bands attributed to  $\text{Ag}_{1-3}$  isolated in Ar, Kr, and Xe matrices<sup>1,5</sup> are illustrated in Figure 1. Because of the difficulties involved in arriving at an unambiguous correlation of absorption bands with specific cluster species, the assignments for some of the weaker features of the absorption spectra must be regarded as tentative. However, it is our contention that the results of the present study provide support for these assignments.

A detailed analysis of the trisilver absorption spectrum is subject to a number of complications. The  $\text{Ag}_3$  band assignments, for example, must be based on a molecular orbital

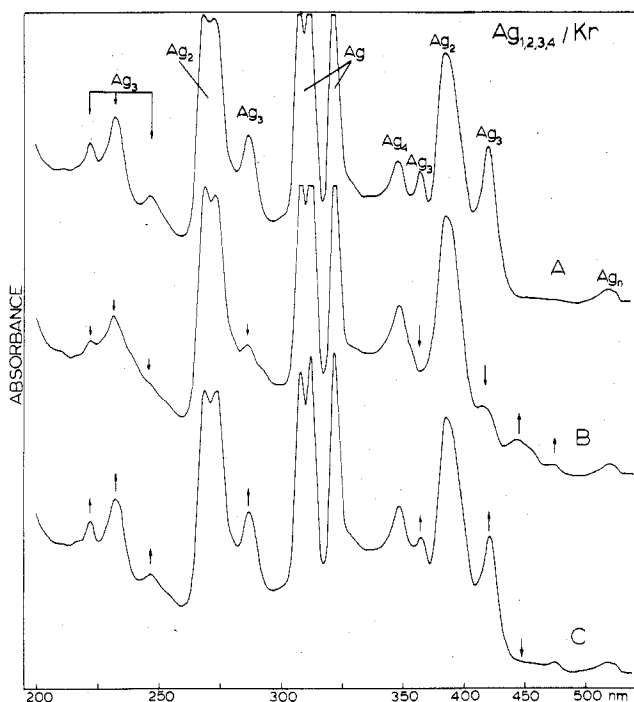


**Figure 1.** UV-visible spectra of  $\text{Ag}_{1-3}/(\text{Ar}, \text{Kr}, \text{and Xe})$  mixtures generated by condensing silver atoms with the rare gases ( $\text{Ag}/\text{matrix} \approx 1/10^3$ ) at 12 K and irradiating the deposits at the frequencies of silver atomic resonance absorption lines.

model together with an assumed or predicted geometry,<sup>6</sup> since no gas-phase spectroscopic data are presently available for  $\text{Ag}_3$ . Additional complications arise from the possible coexistence of geometrical isomers or spectroscopically distinct matrix trapping sites.<sup>7</sup> In this connection, we believe that the photochemical studies described below show potential for elucidating the optical spectroscopic consequences of structural rearrangements of matrix-entrapped trisilver molecules.

The outcome of photoexcitation centered at the visible band of entrapped  $\text{Ag}_3$  in  $\text{Ag}_{1-4}/\text{Kr}$  mixtures ( $\text{Ag}/\text{Kr} = 1/10^2$ ) at 12 K is illustrated in Figure 2. A comparison of spectrum B with spectrum A shows that major spectral changes result from the photolysis and that these alterations are restricted to the set of absorption bands believed to be associated with  $\text{Ag}_3$ . Thus, while the bands labeled  $\text{Ag}$ ,  $\text{Ag}_2$ , and  $\text{Ag}_4$  remain essentially invariant, each of the original  $\text{Ag}_3$  bands undergoes a substantial decrease in intensity, and a number of new features appear, the most prominent of which is centered near 445 nm. Spectrum C in Figure 2 illustrates the interesting result that the effects of the visible trisilver photolysis can be essentially exactly reversed by a brief, 25 K thermal annealing period. Thus, the photoinduced transformation is thermally reversible and can be recycled many times without major modifications to the optical spectrum. Notable also is the observation that the original  $\text{Ag}_3$  absorption spectrum can be similarly regenerated by irradiating the new band at 445 nm.

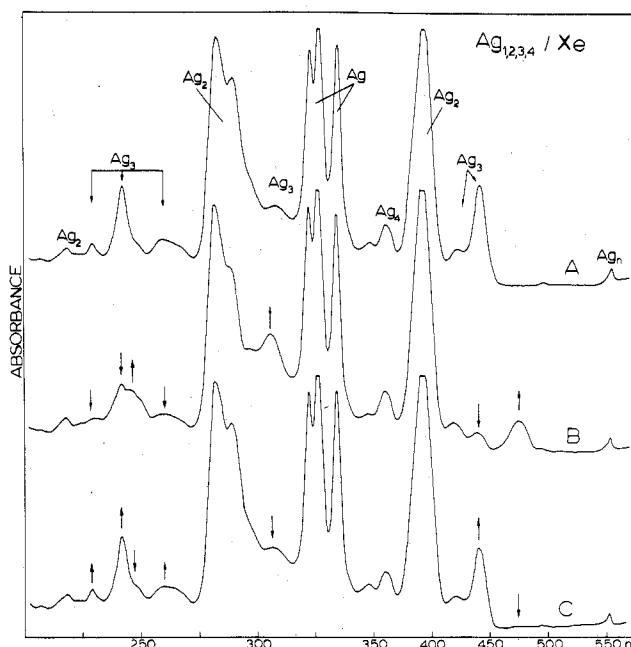
Figure 3 shows results for Xe matrices closely analogous to the Kr results illustrated in Figure 2, indicating a similar photochemical behavior of Xe- and Kr-entrapped trisilver. The results shown in Figures 2 and 3 indicate that visible  $\text{Ag}_3$  photoexcitation in Kr and Xe matrices results in a highly selective, thermally and photolytically reversible trisilver phototransformation. These results for Kr and Xe supports are in distinct contrast to the results for Ar supports, where prolonged trisilver visible photoexcitation produces no observable changes in the optical spectrum. Recent fluorescence



**Figure 2.** UV-visible spectra of  $\text{Ag}_{1-4}/\text{Kr}$  mixtures ( $\text{Ag}/\text{Kr} \approx 1/10^2$ ) at 12 K: (A) spectrum after a 30-min irradiation centered at the atomic resonance absorption lines; (B) outcome of a 10-min, 423-nm  $\text{Ag}_3$  irradiation, showing major decay of the bands associated with  $\text{Ag}_3$  (indicated by arrows) and the appearance of two new bands near 450 nm; (C) result of a 5-min, 25 K bulk thermal annealing period, showing regeneration of the original  $\text{Ag}_3$  spectrum and loss of the new band near 445 nm.

spectroscopic studies, to be described in detail in a separate publication,<sup>4b</sup> are similarly indicative of a different photochemical behavior of trisilver entrapped in Ar as compared with the behavior in Kr or Xe matrices. In the case of Ar matrices, excitation centered at the visible band of trisilver produces a very intense emission which corresponds exactly with the major emission band produced by atomic silver excitation.<sup>4</sup> No such emission is observed for the analogous trisilver excitations in Kr and Xe matrices. At present we wish only to point out that Ar-entrapped trisilver molecules behave differently from the Kr- and Xe-entrapped  $\text{Ag}_3$  species. Further discussion of this point must await the outcome of more detailed studies, including fluorescence lifetime and polarization measurements.

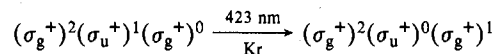
Apart from the possibility of a photoionization process, which we discount on the basis of estimated  $\text{Ag}_n$  cluster ionization potentials,<sup>8</sup> the occurrence of two different photolytic processes can be suggested to explain our observations: (1) a photodissociation process ( $\text{Ag}_3 \rightarrow \text{Ag}_2 + \text{Ag}$ ) and (2) "photoisomerization" of the trisilver/matrix cage unit, involving either different geometrical isomers of  $\text{Ag}_3$  or different orientations of a "rigid"  $\text{Ag}_3$  molecule within a deformable matrix cage. The invariance of the Ag and  $\text{Ag}_2$  absorption bands during the  $\text{Ag}_3$  visible photolysis/thermal (or photolytic) regeneration cycle provides a strong argument against the photodissociation proposal. On the basis of relative extinction coefficient measurements for matrix-isolated  $\text{Ag}_{1-3}$ ,<sup>1b</sup> we conclude that a photodissociation process could have been detected through substantial intensity variations of the Ag and  $\text{Ag}_2$  bands. Also inconsistent with the photodissociation proposal is the fact that visible  $\text{Ag}_3$  photolysis results in the appearance of *new* absorption bands. These bands seem to be associated with  $\text{Ag}_3$  rather than  $\text{Ag}_2$  or Ag. Similarly, the observation of thermal *and* photolytic reversibility would argue in favor of a nondissociative process.



**Figure 3.** UV-visible spectra of  $\text{Ag}_{1-4}/\text{Xe}$  mixtures ( $\text{Ag}/\text{Xe} \approx 1/10^2$ ) at 12 K: (A) spectrum after a 30-min irradiation centered at the atomic resonance absorption lines; (B) outcome of a 10-min, 440-nm irradiation, showing major decay of some of the bands associated with  $\text{Ag}_3$  and growth of other  $\text{Ag}_3$  bands (indicated by arrows) (note the appearance of the new band near 470 nm and the invariance of the Ag,  $\text{Ag}_2$ , and  $\text{Ag}_4$  bands); (C) result of a 5-min, 30 K bulk thermal annealing period, showing regeneration of the original  $\text{Ag}_3$  spectrum.

We conclude from these considerations that a "photoisomerization" process is responsible for the spectral changes illustrated in Figures 2 and 3.

At this stage it is possible only to speculate on whether the proposed structural interconversion can be described in terms of the geometry of  $\text{Ag}_3$  alone or whether it is necessary to consider also the geometry of the matrix cage. In view of the orbital symmetry and energy correlations which can be deduced for a  $\text{Ag}_3 D_{\infty h}$  linear to  $C_{2v}$  nonlinear to  $D_{3h}$  triangular structural interconversion, it is at least feasible that selective 423-nm  $\text{Ag}_3/\text{Kr}$  or 440-nm  $\text{Ag}_3/\text{Xe}$  HOMO-LUMO population of the strongly antibonding molecular orbital of a linear, three-level  $\text{Ag}_3$  cluster,<sup>9</sup> that is



could induce photoisomerization to a "matrix-stabilized" (at 12 K), triangular  $(a_1')^2(e')^1 D_{3h}$  or isosceles  $(a_1')^2(b_2)^1 C_{2v}$  form of  $\text{Ag}_3$ .<sup>10</sup> Of course, 25 K, Kr or Xe matrix annealing could provide just sufficient thermal energy to permit cage softening and back-conversion of "metastable"  $\text{Ag}_3$  to the ground-state, linear form of  $\text{Ag}_3$ . Further experimentation for example with combined FTIR, Raman, and ESR spectral monitoring will be required to clarify the intriguing visible phototransformations of  $\text{Ag}_3$ .

In the scientifically and technologically relevant field of very small metal particles, the discovery of new cluster phenomena, especially in the "few-atom regime" (below 10 Å), is the essence for stimulating new theories and experiments, so vital for developing our understanding of important cluster properties such as the electronic, magnetic, structural, thermodynamic, phase, chemisorptive, sintering, and catalytic behavior as a function of cluster size and composition. We feel reasonably confident that the fundamental photochemistry and photophysics of naked metal atoms and clusters in low-temperature (and hopefully high-temperature) supports can begin to fulfill some of these needs.

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Registry No. Ag<sub>3</sub>, 12595-26-5.

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### A Simple Photochemical Synthesis of Some Bis(bipyridyl)ruthenium(II) Complexes

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Existing methods for the synthesis of bis(2,2'-bipyridine) complexes of ruthenium(II) are often quite tedious. General methods for producing [Ru(bpy)<sub>2</sub>X<sub>2</sub>] or [Ru(bpy)<sub>2</sub>XY] complexes most commonly rely on chloride displacement from [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>].<sup>1-6</sup> This compound may be prepared through the pyrolysis or reduction of (bpyH)[Ru(bpy)Cl<sub>4</sub>],<sup>7</sup> which in turn may be prepared from K<sub>2</sub>[RuCl<sub>5</sub>(H<sub>2</sub>O)].<sup>7,8</sup> The latter compound is not generally available but may be prepared from RuO<sub>2</sub>.<sup>9</sup>

A second route to [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>] proceeds by heating [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> with powdered silica under vacuum.<sup>10</sup> We have found that this preparation leaves a variety of complexes on the silica, and separation is difficult.

More recently [Ru(bpy)<sub>2</sub>CO<sub>3</sub>] has been used as a general intermediate.<sup>6,11</sup> It too, however, is prepared from [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>].<sup>11</sup> The oxalato complex [Ru(bpy)<sub>2</sub>(ox)], which can be prepared directly from K[RuCl<sub>5</sub>(H<sub>2</sub>O)]<sup>10</sup> or K<sub>2</sub>RuCl<sub>6</sub>,<sup>12</sup> has also been used to synthesize [Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>].<sup>12</sup> This compound has also been produced directly from K<sub>2</sub>[Ru-

Cl<sub>5</sub>(H<sub>2</sub>O)] in aqueous solution.<sup>13</sup>

While studying the substitutional photochemistry of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, we reported a photochemical synthesis of [Ru(bpy)<sub>2</sub>(NCS)<sub>2</sub>]<sup>14</sup> and [Ru(bpy)<sub>2</sub>Br<sub>2</sub>].<sup>15</sup> The procedure can be extended to other complexes. It is simple and direct and makes use of the low solubility of some of the [Ru(bpy)<sub>2</sub>X<sub>2</sub>] complexes in ethanol or water.

Unfortunately, [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>] is not easily prepared this way. It is quite soluble in alcohols and is substitutionally labile in water. Still, it is possible that one or another of the complexes which can be produced photochemically may be usable as a general precursor to other complexes.

### Experimental Section

To prepare [Ru(bpy)<sub>2</sub>X<sub>2</sub>], we used [Ru(bpy)<sub>3</sub>]X<sub>2</sub> as starting material, although, in general, satisfactory results could be obtained with [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> and a stoichiometric excess of a salt of the anion X<sup>-</sup>. [Ru(bpy)<sub>3</sub>]X<sub>2</sub> was prepared from [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> by ion-exchange chromatography, utilizing 5% or less of the total resin capacity (Dowex 1-X8).

[Ru(bpy)<sub>2</sub>I<sub>2</sub>] and [Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>], which are only very slightly soluble in ethanol, were prepared by dissolving the corresponding [Ru(bpy)<sub>3</sub>]<sup>2+</sup> salt in ethanol (15 mL), placing the solution in a 5-cm quartz spectrophotometer cell, deoxygenating by bubbling N<sub>2</sub> through the cell for 15 min, and irradiating the cell for 4 h with a 500-W mercury lamp. The black (iodo) or golden (nitro) crystals which formed were filtered, washed with boiling ethanol, and dried in vacuo. Anal. Calcd for [Ru(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>I<sub>2</sub>]-C<sub>2</sub>H<sub>5</sub>OH: C, 37.04; H, 3.11; I, 35.58. Found: C, 37.04, 37.79; H, 2.35, 2.78; I, 34.71. Calcd for [Ru(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]-1.5H<sub>2</sub>O: C, 45.11; H, 3.60; N, 15.79. Found: C, 44.89, 45.40; H, 3.66, 3.73; N, 15.49, 15.94.

A number of anions yielded complexes which are soluble in ethanol and methanol but insoluble in water. [Ru(bpy)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>], [Ru(bpy)<sub>2</sub>(mal)], where mal = malonate, and [Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>] fall into this category. The procedure followed was to photolyze the corresponding [Ru(bpy)<sub>3</sub>]X<sub>2</sub> salt in ethanol for 4 h as before and then dilute the resulting photolysate with an equal volume of H<sub>2</sub>O. Black (malonato and azido) or red (cyano) crystals formed upon cooling overnight, which were washed with water and dried in vacuo. Anal. Calcd for [Ru(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]-1.5H<sub>2</sub>O: C, 45.79; H, 3.65; N, 26.71. Found: C, 45.84; H, 3.45; N, 25.91. Calcd for [Ru(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)]-2.5H<sub>2</sub>O: C, 49.28; H, 4.14; N, 10.00. Found: C, 49.30; H, 4.18; N, 10.08. Calcd for [Ru(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(CN)<sub>2</sub>]-3.5H<sub>2</sub>O: C, 49.99; H, 4.39; N, 15.90. Found: C, 50.19; H, 4.36; N, 15.47. Our yields were generally in the range of 15–35% with 4-h irradiation times, but the unreacted starting material could be reused.

For those anions which form bis(bipyridine) complexes which do not crystallize from ethanol or water, the complexes may still be obtained photolytically by subjecting the photolysate (in ethanol) to Sephadex LH-20 chromatography, where the tris complex is generally eluted first. The eluant containing the bis complex may be evaporated to yield the solid product. This method may be more tedious, however, than standard synthetic procedures.

Unexpected products were obtained upon photolysis of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> salts with IO<sub>3</sub><sup>-</sup> and SeCN<sup>-</sup> as counterions, indicating that the substitution reaction may not be as straightforward as it appears to be. In both cases a product crystallized directly from ethanol solution.

The product from photolysis of [Ru(bpy)<sub>3</sub>](IO<sub>3</sub>)<sub>2</sub> in ethanol was [Ru(bpy)<sub>2</sub>I<sub>2</sub>]. This is at least reasonable, since the excited-state [Ru(bpy)<sub>3</sub>]<sup>2+</sup> complex is thermodynamically capable of reducing IO<sub>3</sub><sup>-</sup>,<sup>16</sup> while the resulting [Ru(bpy)<sub>3</sub>]<sup>2+</sup> could oxidize the solvent. How the iodate reduction and the bipyridine substitution are related is not yet clear.

The selenocyanate case is more baffling. Because of the chemical similarity to thiocyanate, it was assumed that an analogous product would be formed, [Ru(bpy)<sub>2</sub>(NCSe)<sub>2</sub>]. Analysis revealed, however, that the black crystalline product obtained contained no selenium and was consistent with its formulation as [Ru(bpy)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]. Anal. Calcd for [Ru(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]: C, 48.28; H, 3.24; N, 28.16. Found: C, 48.01; H, 3.45; N, 27.58.

Among the unusual features associated with this reaction is the direct crystallization of the product from ethanol, with no solvent of crystallization. With azide present from the outset, water had to be added to induce crystallization, which occurred with 1.5 water molecules per complex.