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Mechanistic Studies on the Thermal and Photochemical Decomposition of Dimethyl(2,4-pentanedionato)gold(III) in Solution

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Mechanisms of the thermal and photochemical decomposition of dimethyl(2,4-pentanedionato)gold were examined by UV-visible and ^1H NMR spectroscopies in solution. The formation of gold mirrors results from both the thermal and photochemical decomposition reactions. The thermal decomposition reaction is extremely solvent dependent and is not observed in non-coordinating, non-polar solvents (i.e. cyclohexane). The kinetics for thermal decomposition are observed to be first-order in gold complex disappearance although the solvent plays a critical role in the decomposition process. Decomposition by reductive elimination of ethane and protonation of the 2,4-pentandionate ligand are major reaction modes. The mechanism for reductive elimination is examined by deuterium labeling with the perdeuteriodimethylgold compound. The formation of ethane-d_3 and traces of methane by reaction from the 50:50 mixture of (dimethyl-d_0)- and (dimethyl-d_6)(2,4-pentanedionato)gold indicates that free radicals are formed from the homolysis of gold-methyl bonds. On the basis of the ratio of ethane-d_0 to ethane-d_3, however, the reaction is believed to proceed predominantly via a concerted reductive elimination and, to a lesser extent, a free-radical mechanism simultaneously. On the other hand, the photochemical decomposition produces more 3-methyl-2,4-pentanedione and less ethane. In labeling studies, the ratio of ethane-d_0 to ethane-d_3 is also decreased and is indicative of the greater radical nature of the photolytic mechanism. The UV photolysis does not show the same solvent dependence to reaction as the pyrolysis does, although the observed product ratios do vary with solvent. Thus, solvent-cage effects may be important to the decomposition process.

Introduction

2,4-Pentanedione, or acetylacetone as it is more commonly known, has been extensively used to synthesize various metal complexes.[1] The strong chelating ability of this ligand is excellent for forming stable coordination complexes in which the metal center is O,O bonded to the ligand. Metal β-diketone complexes are soluble in a wide variety of organic solvents and quite often are volatile at room temperature.[2] These physical properties allow both solution and vapor-phase chemical reactions to be studied.

Dimethyl(2,4-pentanedionato)gold was first synthesized in 1939[3] and is a slightly volatile, crystalline solid. Several substituted analogues were later synthesized by Komiya and Kochi.[4] The ability of the acetylacetonate ligand to isomerize from O,O-bonded to stable C-bonded dimethylgold complexes has been reported upon the addition of trisubstituted phosphines.[4] Stable gold(I) complexes with C-bonded acetylacetonate have been synthesized[5] by conventional methods as well. Most recently, dimethyl(2,4-pentanedionato)gold and its fluorinated analogues have received considerable attention for use in laser-directed metal deposition of high-purity gold.[6a] The motivation for laser-induced processes is geared toward producing high-quality, thin metallic films in a selective manner. Laser processing offers several advantages over conventional techniques, including greater simplicity and the ability to produce metal features selectively without lithographic techniques.[6b] Thus, understanding the mechanism for the thermal and photochemical decomposition of dimethyl(2,4-pentanedionato)gold is of scientific and practical interest.

Reductive elimination and cis-trans isomerization reactions were found to be the major reaction pathways for trialkylgold(III) phosphine complexes. In general, both the cis-trans isomerization and reductive elimination of neighboring cis groups are observed after dissociation of the stabilizing phosphine ligand.[7] Molecular orbital calculations for C_{3h} symmetry of trimethylgold(III) have demonstrated that both T- and Y-shaped configurations are likely following the dissociation of the coordinated phosphine. The cis-trans isomerization, resulting in T-shaped minima on the potential energy surface, pass through Y-shaped saddle points during isomerization. The Y-shaped configurations are believed to be exit channels for reductive elimination of neighboring alkyl groups.[8]

Decomposition of alkyl transition-metal compounds often results in the reductive elimination[9-14] of the organic species, as mentioned for the trialkylgold phosphine complexes. The decomposition of dimethyl(2,4-pentanedionato)gold was also believed to occur via reductive elimination of the two cis methyl groups. The general concept of reductive elimination requires only that the formal oxidation state and coordination number of the metal center by reduced by two. During this process, the breaking of M-C bonds is followed by the formation of C-C bonds. Thus, the mechanism of reductive elimination can often be elucidated by the type of products formed

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from coupling of alkyl moieties as a result of reductive elimination. In this study, the mechanism for reductive elimination and decomposition of the title compound was examined by deuterium labeling and identification of the coupled reaction products. The reductive elimination in solution was found to occur by both concerted and free-radical recombination and was dependent upon the mode of decomposition. The solution decomposition studies of dimethyl(2,4-pentanedionato)gold are described in this paper.

Experimental Section

C_6D_{12} and CD_3OD were purchased from Aldrich Chemical Co. All other solvents were dried by standard procedures and stored over activated 1A sieves. Pyrolytic decomposition reactions were carried out in sealed quartz NMR tubes after the deuterated solvents (CD_3OD and C_6D_{12}) were degassed by freeze–pump–thaw cycles. Solutions of gold complex (0.02 M) were heated to 60 °C; spectra were taken as a function of time and referenced to the residual proton resonances of the deuterated solvents. The product resonance peaks were integrated and normalized to the residual protons of the deuterated solvent, as well. An IBM/Brucker 500 MHz NMR spectrometer equipped with a variable-temperature probe was used for the pyrolysis studies. The photoreactions were carried out in quartz NMR tubes that were sealed after the deuterated solvent was degassed by several freeze–pump–thaw cycles. The NMR tubes were irradiated in a Rayonet reactor equipped with low-pressure Hg lamps. After examination of the $t = 0$ sample, the photolysis was followed by ^1H NMR as a function of irradiation time. The NMR tubes were inverted during the irradiation to minimize the effects of the gold mirror formation on subsequent irradiations and spectra analyses. Since the photoreaction was fast, spectra were taken every 30 or 60 s. The photolytic decomposition takes place in both CD_3OD and C_6D_{12}, in contrast to the pyrolytic reaction. All ^1H NMR shifts are reported in parts per million relative to the residual protons in the deuterated solvent being used: 3.350 ppm for CD_3OD and 1.400 for C_6D_{12}. UV-visible spectra were obtained on a Hewlett-Packard diode-array spectrometer (Model 8451A) with a thermostatable cell. The cell was externally controlled to ± 1 °C with a Brinkmann Lauda RC-6 circulator. The spectrometer was programmed to obtain spectra every 5 min, and the spectra were stored for later manipulation. In a typical UV–vis experiment, a 10^{-4} M solution was placed in a 1-cm quartz cuvette. The sample was degassed and placed into the thermostatable cell at the desired temperature, and the experiment was started. It was observed that the t_0 absorbance spectrum is greater than the subsequent absorbance spectra due to the thermal expansion of the solvent, which effectively lowers the concentration of gold complex in solution. The thermal equilibration of the solution was found to take 15–20 min by monitoring the absorbance of Rhodamine B, of known concentration, in 2-propanol. Infrared (IR) spectra of the starting materials were obtained on a Perkin-Elmer double-beam spectrometer in KBr (Aldrich). Mass spectral data was obtained by direct inlet probe on a Hewlett-Packard mass spectrometer (Model 5995). Gas chromatography was carried out on a Hewlett-Packard gas chromatograph (Model 5750B) with $^1/_4$ in. columns. In most of the experiments described in this paper a mirrorlike gold film was formed from the decomposition reaction, but no attempts were made to analyze these films.

Dimethyl(2,4-pentanedionato)gold (1a). The synthesis of dimethyl(2,4-pentanedionato)gold was achieved by literature procedures. The pyridino tribromogold was reacted with a 6-fold excess of freshly prepared CH_3MgI in ether[15] to afford an 18% yield of dimethylgold iodide dimer, which was isolated by chelation with ethylenediamine. The dried gold dimer was reacted with thallous acetylacetonate (Alfa) in hexane/alcohol solvent to produce the desired dimethyl(2,4-pentanedionato)gold complex. For reasons of safety, the potassium salt can be substituted for the thallium salt of acetylacetonate with comparable yields. The isolated product was purified by sequential sublimations to yield long, white needles of pure material. Thermal analysis of the neat material by differential scanning calorimetry (DSC) shows a sharp melting endotherm at 82 °C and a decomposition exotherm beginning at 160 °C (T_{dec}(max) = 187 °C). IR (KBr): 2992, 2920 (s), 1592, 1517, 1391, 1353, 1263 (sh), 1235 (sh), 1196, 1023, 929, 778 (s), 687, 610 cm^{-1}. MS: 326 (M^+), 296, 281, 254, 239, 238, 227, 225, 211, 197, 100, 99, 85, 71, 55, 43 (base), 29, 27. NMR: (C_6D_{12}) δ 1.104 (6 H, s), 1.904 (6 H, s), 5.217 (1 H, s); (CD_3OD) δ 1.140 (6 H, s), 2.028 (6 H, s), 5.471 (1 H, s). The methine proton of the 2,4-pentanedionate ligand rapidly exchanges in deuterated methanol as was confirmed by mass spectral analysis. UV absorbance in hexane: $\lambda_{max} = 206$ ($\epsilon = 1.8 \times 10^4$) and 304 nm ($8.6 \times 10^3$).

(Dimethyl-d_6)(2,4-pentanedionato)gold (1b). The perdeuteriodimethyl (2,4-pentanedionato)gold complex was synthesized by an analogous route to the parent material by utilizing CD_3MgI in place of CH_3MgI. The subsequent reactions and purification were identical. IR (KBr): 2260, 2139, 2060, 1593, 1517, 1384, 1352, 1262, 1203, 1024, 927, 781, 651, 604 cm^{-1}. MS: 332 (M^+), 281, 254, 239, 233, 229, 215, 197, 100, 99, 73, 69, 55, 43 (base), 34, 27. NMR: (C_6D_{12}) δ 1.904 (6 H, s), and 5.217 (1 H, s); (CD_3OD) δ 2.028 (6 H, s), and 5.471 (1 H, s).

^{1}H NMR of Reaction Products. ^1H NMR spectra of gaseous products were compared to authentic samples when possible. The gas was bubbled into the deuterated solvents, the NMR tube was sealed, and NMR spectra were obtained. Methane was commerically available from Matheson Gas and used without further purification: δ 0.185 (s) in C_6D_{12} and δ 0.245 (s) in CD_3OD. CH_3D is a reaction product with a chemical shift centered at δ 0.188 (triplet with $J = 1.94$ Hz) in C_6D_{12}. Ethane was commercially available from Matheson Gas and used without further purification: δ 0.869 (s) in C_6D_{12} and δ 0.908 (s) in CD_3OD. Ethane-d_3 is a reaction product with a chemical shift centered at δ 0.844 (septet, $J = 1.21$ Hz) in C_6D_{12} and δ 0.882 in CD_3OD.

2,4-Pentanedione was purchased from Aldrich Chemical Co. and distilled prior to its used: δ 1.925 (6 H, s), 5.355 (1 H, s), and 15.59 (1 H, s) for enol form and δ 2.081 (6 H, s) and 3.364 (2 H, s) for keto form in C_6D_{12}; δ 2.069 (6 H, s) and 5.622 (1 H, s) and no OH proton for enol form and δ 2.232 (6 H, s) and no methine protons for keto form in CD_3OD.

3-Methyl-2,4-pentanedione was commercially available from Aldrich and was purified and collected by preparative gas chromatography on an SE-30 column. ^1H NMR spectra showed chemical shifts of δ 2.008 (6 H, s), 1.796 (3 H, s), and 16.500 (1 H, s) for enol form and δ 2.034 (6 H, s), 1.241 (3 H, d, $J = 7.1$ Hz), and 3.498 (1 H, quartet) for keto form in C_6D_{12} and δ 2.148 (6 H, s) and 1.899 (3 H, s) and no OH proton for enol form and δ 2.228 (6 H, s), 1.303 (3 H, d), and 3.903 (1 H, quartet) for keto form in CD_3OD. Both 2,4-pentanedione and 3-methyl-2,4-pentanedione exhibit a UV absorption centered at 276 nm and obey Beer's law.

2-Methoxy-2-penten-4-one was synthesized by the procedure of Hammond[16a] by reacting diazomethane with freshly distilled 2,4-pentanedione and was purified by preparative gas chromatography on an SE-30 column. ^1H NMR spectra[16b] showed chemical shifts of δ 2.014 (3 H, s), 2.235 (3 H, s), 3.534 (3 H, s), and 5.342 (1 H, s) in C_6D_{12} and 2.198 (3 H, s), 2.280 (3 H, s), 3.729 (3 H, s), and 5.699 (1 H, s) in CD_3OD.

Results and Discussion

Both thermal and photochemical decomposition of the title compound have found utility for the selective formation of thin gold films from the gas phase.[6] However, the quality of the deposited gold film is directly dependent upon the method used for decomposition; thermal decomposition produces high-quality gold metal while photochemical decomposition leads to carbon contaminated films. To better understand these results, solution studies were undertaken to determine the mechanism for decomposition. In this study, no attempts to analyze the gold films were made, but the reaction products and major reaction pathways for reductive elimination were determined. In the first part of this paper, the thermal de-

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Figure 1. Chemical structures of the dimethyl(2,4-pentanedionato)gold (**1a**) and the (dimethyl-d_6)(2,4-pentanedionato)gold, (**1b**) used in these studies.

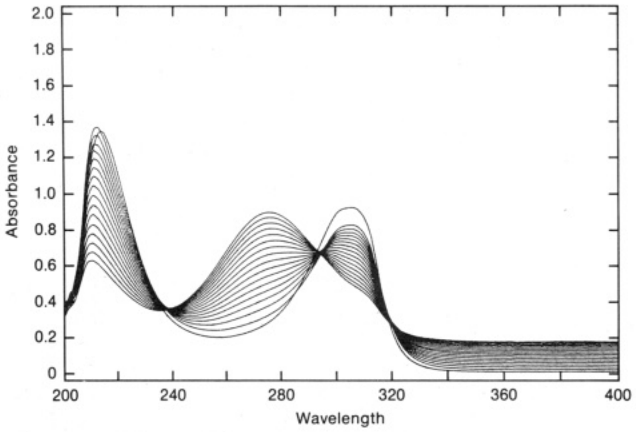

Figure 2. Thermal decomposition of **1a** in dried, degassed 2-propanol at 70 °C as monitored by UV-visible spectroscopy.

composition of dimethyl(2,4-pentanedionato)gold is discussed while the photochemical reaction is discussed in the second part.

Solution-Phase Pyrolytic Studies. The solution-phase thermal decomposition of **1a** was examined by UV–visible and ^{1}H NMR spectroscopies. For the UV–visible work separate studies had shown that both **1a** and 2,4-pentanedione followed Beer's law of absorbance; thus, absorbance data can be converted into concentrations. A typical plot of absorbance vs wavelength is given in Figure 2 as a function of the time of thermal reaction for **1a**. The kinetics of thermal decomposition for **1a** were first-order (Figure 3) with a rate (k) of 0.007 min^{-1} in 2-propanol at 70 °C. The production of 2,4-pentanedione and related products was observed by the formation of an absorbing species with a $\lambda_{max} = 276$ nm. The product formation is also consistent with a first-order reaction. It should be noted that the baseline of the spectra from 400 to 800 nm is increasing due to the formation of gold particulates that scatter the incident light. Interestingly, the thermal decomposition reaction does not occur in noncoordinating, aprotic solvents (i.e. cyclohexane), under similar conditions and prolonged reaction times. The strong solvent dependence on the thermal decomposition of **1a** was also noted by comparing the reaction in several alcohols (1,1,1,3,3,3-hexafluoro-2-propanol $\gg$ 2-propanol > ethanol > methanol) and by the lack of reaction in several nonpolar solvents. A similar solvent trend has been observed for the solution photochemical decomposition of copper bis(β-diketonate)[17a] and iron tris(β-diketonate)[17b] in alcohols. This solvent trend was attributed to the ease of hydrogen abstraction by the pentanedione radical and the resulting stability of the solvent radical. In the present study, the formation of protonated ligand as a reaction product would implicate hydrogen abstraction from the solvent, as well. Although no oxidized solvent species have been identified, the solvent effect is similar to that found in the previous studies. Also, the addition of acetic acid to a solution of **1a** in 2-propanol was found to accelerate the thermal reaction. Acid attack on the β-diketone results in protonation of the ligand and formation of dimethylgold complexes with the anionic species.[7] Thus, the rate-limiting step appears to be protonation of the pentanedione ligand during pyrolytic decomposition of the molecule in solution.

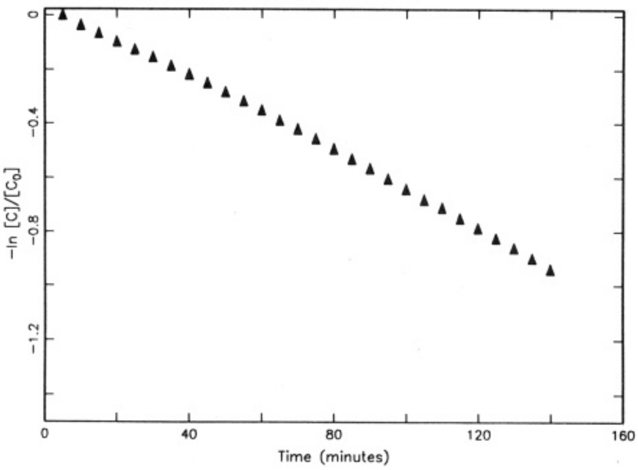

Figure 3. First-order kinetic plot of the disappearance of **1a** in 2-propanol versus the time of thermal reaction at 70 °C.

Although the UV–visible spectral method allows a rapid determination of the decomposition kinetics of **1a** in various solvents, the actual products cannot be readily determined. Thus, ^{1}H nuclear magnetic resonance (NMR) spectroscopy was used to monitor the reaction, identify the products of decomposition, and elucidate a probable mechanism for decomposition. Also, the formation of 2,4-pentanedione and related products can be closely monitored by NMR. The keto–enol tautomerization is easily observed by NMR, and several studies on keto–enol equilibration of 2,4-pentanedione exist in the literature.[18] The keto–enol equilibrium is known to be solvent dependent; in CD_3OD, the keto form represents 28% of the total protons while the enol form represents 72%. After several weeks at room temperature, some deuterium scrambling in the terminal methyl groups is observed by NMR. In C_6D_{12}, however, the keto form is 3% and the enol form is 97% of the total protons. These equilibria are consistent with the literature reported values.[19] 3-Methyl-2,4-pentanedione exists in a keto–enol equilibrium as well. In a freshly prepared sample in CD_3OD, the keto form is 41% with the enol form being 59% of the total protons. In C_6D_{12}, however, the keto form is 19% while the enol form is 81%. These keto–enol equilibria become quite important for monitoring the decomposition reaction of **1a** by ^{1}H NMR in terms of the quantitative analysis of products and their ratios. It was also found that the equilibrium of 3-methyl-2,4-pentanedione shifted after several weeks in CD_3OD; the keto form became dominant (85%) when compared to the enol form (15%). Deuterium incorporation at the methine position (keto form) can hinder the keto–enol tautomerism as a result of isotope effects.[20] Thus, the keto form would become the predominant species. Deuterium incorporation was confirmed by the disappearance of the quartet peak at 3.903 ppm and splitting of the methyl group into a triplet centered at 1.299 ppm with a coupling constant (J) of 1.91 Hz.

The pyrolytic decomposition of **1a**, in CD_3OD, was observed to follow first-order kinetics, after an initial induction period. This induction period is indicative of the

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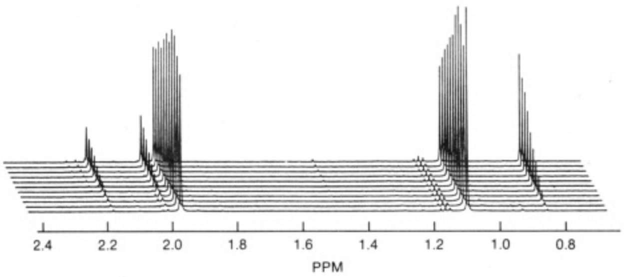

Figure 4. Thermal decomposition of **1a** in CD_3OD at 60 °C as a function of reaction time. The NMR spectra were taken each hour for 11 h.

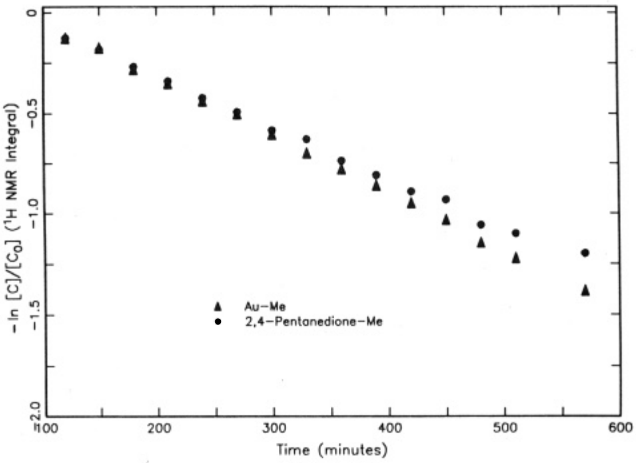

Figure 5. Disappearance of **1a** and **1b** in CD_3OD versus the reaction time at 60 °C. Plot shows a linear first-order dependence.

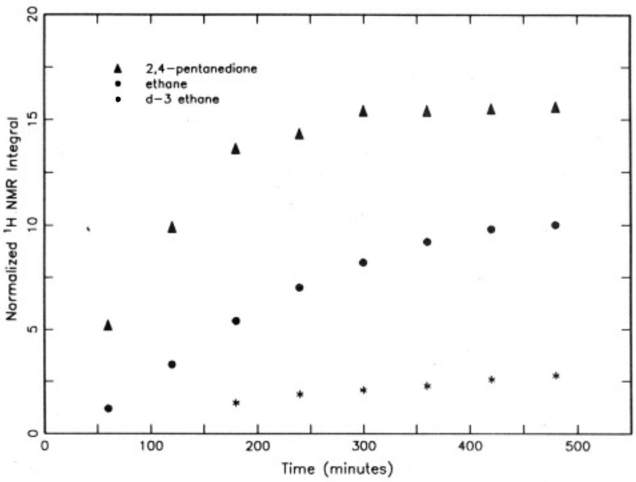

Figure 6. Reaction products formed from the thermal decomposition of **1a** and **1b** in CD_3OD versus the reaction time at 60 °C.

thermal equilibration between the probe temperature and the sample. However, it is possible that some solvent-coordinated species could also be formed during this induction period at the elevated temperature. Figure 4 depicts a typical time-dependent NMR spectral plot for the decomposition of **1a** in CD_3OD. As can be seen in Figure 4, the disappearance of the chemical shifts of **1a** (δ 1.140 and 2.028) coincide with the appearance of chemical shifts at δ 0.908, 2.069, and 2.232 and others. These chemical shifts correspond to ethane, the enol form of 2,4-pentanedione, and the keto form of 2,4-pentanedione, respectively. The formation of 3-methyl-2,4-pentanedione and trace quantities of methane (CH_3D only) are also observed. The reaction was first-order in the disappearance of **1a** and formation of products; at a conversion of 13%, ethane (50%), 2,4-pentanedione (43%), 3-methyl-2,4-pentanedione (4%), and methane (1%) were observed. The products account for 96% of the total protons from the disappearance of **1a**. Interestingly, the pyrolysis of **1a** does not proceed in C_6D_{12} under identical conditions and increased reaction times (20 h).

In order to elucidate the mechanism for thermal decomposition of **1a**, the deuterium-labeled analogue (dimethyl-d_6)(2,4-pentanedionato)gold (**1b**) was synthesized. A 50:50 mixture of **1a** and **1b** was reacted in CD_3OD and monitored by ^1H NMR. At a conversion of 24%, ethane-d_0 (25%) and ethane-d_3 (7%) were evident as well as 2,4-pentanedione (61%), 3-methyl-2,4-pentanedione (2%), and trace amounts of methane (CH_3D) (3% at 50% conversion). The total identified products account for 95% of the protons with one unidentified product (5%). The reaction kinetics are first-order in the disappearance of starting material (Figure 5) ($k = 0.003$ min^{-1} at 60 °C) and in the formation of products (Figure 6). The rate constant found by NMR is consistent with that found by UV–vis spectroscopy. Also, no concentration effect in **1a** was observed that reduces the potential of a dinuclear gold intermediate to decomposition. However, the fact that the ethane-d_0 to ethane-d_3 ratio is 3.6:1 would indicate that two processes for reductive elimination may be occurring simultaneously. In the case of a completely free-radical mechanism, one would expect a statistical ratio of 1:2:1 for the formation of ethane-d_0 to ethane-d_3 to ethane-d_6. In the pyrolysis of **1a** and **1b** the ratio is clearly 3.6:1:3.6. The formation of methane and ethane-d_3 are indicative of free-radical reactions: radical abstraction of deuterium from the solvent to form CH_3D and radical–radical recombination to form ethane-d_3. However, both of these products are minor and indicate that less than 20% of the reaction proceeds via free radicals. The major reaction modes are protonation (or deuteration) of the 2,4-pentanedionate and concerted reductive elimination of two cis methyl groups to form ethane. For square-planar, four-coordinate d^8 metal complexes, orbital symmetry analyses predicted that thermal concerted reductive elimination is symmetry-allowed.[21] Thus, for the dimethyl(2,4-pentanedionato)gold, which is square-planar, four-coordinate by NMR, electron diffraction, and X-ray analysis,[22] the concerted, pyrolytic reductive elimination can proceed on the basis of symmetry arguments. However, the formation of methane and ethane-d_3 clearly demonstrate that a simultaneous free-radical pathway also exists, albeit small.

In an effort to explain the nonstatistical formation of ethane products, a 50:50 mixture of **1a** and **1b** was examined by mass spectral analysis. It was thought that some scrambling of the starting materials may have occurred, resultng in the formation of a (dimethyl-d_3)(2,4-pentanedionato)gold complex. A partially reacted sample was cooled while the solvent and reaction products were pumped away under vacuum. The recovered solid was introduced directly into the mass spectrometer; no scrambling of the starting materials was noted (no $M^+ = 329$ or 330). However, it was found that the two gold complexes **1a** and **1b** had a deuterium incorporated into the molecule and specifically in the pentanedionate ligand. This was evident by the M^+ peaks of 333 for **1b** and 327 for **1a**. Also, the ratio of abundances for M = 100 to M = 99 was greatly increased when compared to fresh, unreacted or nonsolvated starting materials. The rapid exchange between the

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OD in CD_3OD and the methine peak of the pentanedionate ligand of the gold complex had also been noted by NMR. The mass spectral data confirmed the NMR data. This deuterium exchange has been observed prior to hydrolysis of C-bonded dimethyl(2,4-pentanedionato)gold phosphine complexes in solution[12] and is believed to occur via prototropic keto-enol tautomerism of the C-bonded species. In the present case, however, the C-bonded species is not supported by the NMR data; rapid ring opening followed by keto-enol deuteration would seem more likely. The strong solvent dependence on deuterium incorporation was further noted by examining a 50:50 mixture of **1a** and **1b** that was placed in C_6D_{12} solvent. No deuterium incorporation was observed by mass spectral analysis, which is consistent with the presence of a methine proton (5.217 ppm) by NMR.

The formation of 3-methyl-2,4-pentanedione could result from either intramolecular reductive elimination of a C-bonded pentanedione cis to a methyl group or via radical–radical recombination. Thus far, no evidence for a C-bonded ligand has been substantiated. Intermolecular reaction to form this product seems unlikely on the basis of the first-order kinetics and the polarity of the solvent. The best explanation for the formation of this product is radical–radical recombination.

The strong solvent dependence of the thermal reaction is interesting. As was previously shown,[10] the solvent can profoundly alter the mechanism for reductive elimination of trialkylgold species, presumably by solvent coordination and/or solvent cage effects. Thus, the solvent dependence in the present study may result from the ability of the solvent to coordinate to the metal complex, as well as to protonate the β-diketonate ligand. Since the thermal reaction does not occur in nonpolar, noncoordinating solvents (i.e. cyclohexane), it appears that the ability of the solvent to coordinate to the gold complex may be a critical feature of the thermal decomposition process. It should also be noted that the strong solvent dependence on the pyrolysis of **1a** may result in solvent cage effects that can alter the observed product ratios. Further work is needed to examine the role of the solvent and possible solvent cage effects. Lastly, it has been found that the kinetics of thermal decomposition have been observed to be zero-order (spontaneous or catalytic) in wet alcohols.

Solution-Phase Photochemical Study. Metal β-diketonate complexes exhibit a number of electronic transitions that are ligand centered such as the n–π* and π–π* transitions and ligand–metal transitions such as ligand to metal (LMCT) and metal to ligand charge-transfer states.[23] Molecular orbital (MO) theory has predicted that an electronic transition at 250 nm is the LMCT state ($\sigma_L \rightarrow d_{xy}$) for a series of copper bis(β-diketonates). Thus, UV irradiation of this transition leads to reduction of the metal center. Other workers have also shown that UV irradiation of several metal β-diketonates complexes in solution results in the reduction of the metal center and liberation of the β-diketone ligand.[24] As can be seen in Figure 2, a relatively weak UV absorbance is observed for the gold complex in the 250-nm range. In the present study, UV irradiation results in reduction of the gold(III) center by reductive elimination and liberation of the β-diketone moiety. Orbital symmetry analysis of transition metal complexes has shown that charge-transfer reactions are increasingly important for metals in high, formal oxidation states.[21] UV excitation of **1a** is believed to result in the formation of a LMCT state as has been postulated for other β-diketonate complexes.

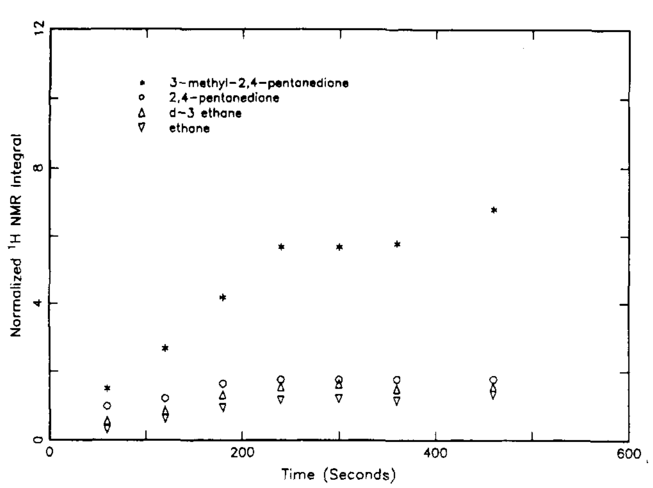

Figure 7. Reaction products formed from the UV photolysis of **1a** and **1b** versus the time of irradiation (254 nm) in C_6D_{12}.

UV irradiation of **1a** in CD_3OD was monitored by NMR, and the percent conversion was calculated on the basis of the disappearance of gold–methyl and 2,4-pentanedione–methyl absorptions. Since the photoreaction is rapid, conversions of 50% or more were observed within 10 min of irradiation. The primary photoproducts were determined at conversions of 10–30% to decrease the importance of secondary photoreactions. Ethane, 2,4-pentanedione, 3-methyl-2,4-pentanedione, and traces of methane were primary photoproducts. The mechanism for decomposition was examined by using a 50:50 mixture of **1a** and **1b**. The formation of deuterium-labeled products was evident by the formation of ethane-d_3. At a conversion of roughly 16%, 3-methyl-2,4-pentanedione (28%), 2,4-pentanedione (46%), ethane-d_0 (6%), and ethane-d_3 (5.5%) were formed and accounted for 86% of the total number of protons. At higher conversions, only trace quantities of methane were observed. The formation of ethane-d_3 could result either from free-radical recombination or by the decomposition of a binuclear complex in solution. Further concentration experiments are needed to rule out the latter. Nevertheless, the decreased production of ethane and the nearly 1:1 ratio of ethane-d_0 to ethane-d_3 clearly indicates that the percentage of concerted reductive elimination is decreased upon UV photolysis in contrast to the pyrolytic reaction. Also, the formation of 3-methyl-2,4-pentanedione as a major photoproduct is quite interesting, since this species was a minor product in the pyrolytic reaction. This product could be formed via methyl radical recombination with the liberated 2,4-pentanedione radical or by concerted formation in the excited state.

Photolysis of **1a** in C_6D_{12} has been observed to produce products similar to those found in CD_3OD. The photochemical decomposition of a 50:50 mixture of **1a** and **1b** at a conversion of 25% results in the formation of the following primary products with 77% of the total protons being accounted for: 2,4-pentanedione (22%), 3-methyl-2,4-pentanedione (35%), ethane-d_0 (7%), and ethane-d_3 (13%) (Figure 7). At higher conversions, CH_3D and CH_4 were formed in a 3:1 ratio. Several other products were present but could not be identified by their NMR spectra. These products represent 23% of the total protons and appear to be formed from the pentanedione ligand on the

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(23) Fackler, J. P; Cotton, F. A.; Barnum, D. W. *Inorg. Chem.* **1963**, *2*, 97. Fackler, J. P.; Cotton, F. A. *Inorg. Chem.* **1963**, *2*, 102. Johnson, P. R.; Thornton, D. A. *J. Mol. Struct.* **1975**, *29*, 97. Yokoi, H. *Inorg. Chem.* **1978**, *17*, 538. Ferraudi, G.; Muralidharan, S. *Coor. Chem. Rev.* **1981**, *36*, 45.

(24) Lindvedt, R. L. *Concepts in Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; pp 299–332.

basis of their relative shifts. Comparison of the unknown product NMR signals to authentic 2-methoxy-3-penten-4-one ruled out the formation of this material as a photoproduct in both solvents. The formation of methane and the observed ethane-d_3 to ethane-d_0 ratio of 1.85:1 strongly suggest free methyl radical formation.[25] Also, the observed product ratios can be altered if the solution is not degassed prior to reaction, which further supports radical formation. As can be seen in Figure 7, the formation of products is consistent with a first-order kinetic process. However, the potential for dinuclear species in C_6D_{12} would be increased and cannot be excluded with the present data. Further concentration dependent studies are necessary to conclusively exclude this mechanism.

Interestingly, the photolysis in C_6D_{12} when compared with the photolysis in CD_3OD demonstrates the importance of the solvent. Although the major photoproducts are the same, the ratios of ethane-d_0 to ethane-d_3 are different. Also, methane is formed to a larger extent in C_6D_{12} when compared to CD_3OD. Both of these observations demonstrate that solvent coordination or cage effects are important to the observed products and their ratios. Clearly, however, the photolytic decomposition mechanism is quite different from the pyrolytic mechanism; greater radical character is clearly evident on the basis of the primary photoproducts via photochemical decomposition of **1a**.

The formation of 3-methyl-2,4-pentanedione in the photolyses of **1a** and **1b** in both CD_3OD and C_6D_{12} has been noted. This product clearly results from the combination of methyl and β-diketonate ligand during photolysis. The actual percentages of this product are underestimated due to the incorporation of CD_3 into the ligand as well. This could increase the actual reaction percentage by 6% over the reported product percentages. Also, the formation of this product could occur via radical–radical recombination, via radical pair formation in the excited state, or by intermolecular (dinuclear) excited-state recombination.

Lastly, the formation of a peak at 1.102 ppm was noted during the photolysis of **1a** and **1b** in C_6D_{12}. This product increases with the time of irradiation; the position and resonance of the peak would seem to indicate that it is very similar to the Au–CH_3 signal observed in the starting complex. Several reasonable explanations for the formation of this signal, upon photolysis, can be postulated: (a) a long-lived dimethylgold intermediate is formed, (b) a dimethylgold dimer is formed, and (c) the starting gold complex becomes scrambled via a dinuclear species or Au–CH_3 and Au–CD_3 homolysis. The formation of dinuclear species in C_6D_{12} is certainly possible, but the production of methyl radicals could explain partial scrambling of **1a** and **1b** with time. Interestingly, this peak is not present in the photolysis of **1a** and **1b** in CD_3OD and may explain the difference in product ratios with varying solvent. Further studies are necessary to provide a definite explanation.

Summary and Conclusions

Solution studies on the pyrolytic decomposition of **1a** have shown that reductive elimination of ethane is observed in CD_3OD and crossover products (ethane-d_3) are observed when a 50:50 mixture of **1a** and **1b** are used as starting materials. The predominate mode of reaction appears to be concerted reductive elimination of ethane and protonation of the 2,4-pentanedionate ligand, while a small percentage of the reaction proceeds via free-radical formation. The concerted reductive elimination of the cis methyl groups is symmetry-allowed for d^8 square-planar complexes. The strong solvent dependence may be indicative of coordination of the solvent to the metal center prior to reductive elimination. Thus, solvents that cannot coordinate and/or protonate the pentanedionate ligand do not encourage pyrolytic decomposition. For the photochemical decomposition of **1a**, no solvent dependence is observed for the photolysis rate, although a strong solvent dependence on the reaction product ratios is observed. The UV photolysis of **1a** and **1b** proceeds via formation of free radicals from a charge-transfer excited state. The decreased production of ethane, the increased ethane-d_3 to ethane-d_0 ratio, and the formation of 3-methyl-2,4-pentanedione as a major photoproduct exemplify the greater radical nature of the photochemical decomposition mechanism.

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Registry No. **1a**, 14951-50-9; **1b**, 122520-27-8; CD_3MgI, 41251-37-0.

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(25) The reaction products of methyl radicals in solution has been shown to result in dimerization (radical–radical recombination) or H abstraction. For examples, see: Volman, D. H.; Swanson, L. W. *J. Am. Chem. Soc.* **1960**; *82*, 4141. Mickewich, D.; Turkevich, J. *J. Phys. Chem.* **1968**, *72*, 2703. Son, T. D.; Sutton, J. *J. Phys. Chem.* **1971**, 851. Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 1285.