Mechanistic Study for the Photochemical Reactions of d^6 M(CO)₅(CS) (M = Cr, Mo, and W) Complexes

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Supporting Information

ABSTRACT: The mechanisms of photoextrusion reactions are determined theoretically for the model system of six-coordinated M(CO)₅(CS) (M = Cr, Mo, and W), using both CASSCF and MP2-CAS methods and the Def2-SVPD basis set. Three types of elimination reaction pathways (i.e., path I, path II, and path III for axial CO extrusion, equatorial CO extrusion, and CS ligand extrusion, respectively) are considered in this study. Theoretical findings show that the photoextrusion mechanism for Cr and Mo complexes proceeds as follows: M-S₀-Rea + hν → M-S₁-FC → M-CI → M-Pro + CO. This study shows that when the reactant, M(CO)₅(CS) (M-S₀-Rea), is photoirradiated by UV light, it is excited to many low-lying singlet excited states. It may then relax to the first singlet excited state from the Franck-Condon point (M-S₁-FC). After passing through a conical intersection point (M-CI), this species eliminates a CO group to yield a five-coordinated product, M(CO)₄(CS) (M-S₀-Pro). However, for the W analogue, the photolysis mechanism is represented as W-S₀-Rea + hν → W-T₁-Min → W-T₁-TS → W-T₁/S₀ → W-S₀-Pro + CO. That is to say, when the reactant, W(CO)₅(CS) (W-S₀-Rea), absorbs UV light, it is excited to its several low-lying excited states by a vertical excitation. This species may then return to an intermediate at the first triplet excited state (W-T₁-Min) by means of intersystem crossings or conical intersections. After passing through a triplet transition state (W-T₁-TS) and a subsequent intersystem crossing (W-T₁/S₀), this molecule finally loses a CO ligand to produce a photoprodut at the ground singlet state (W-S₀-Pro). In other words, conical intersections and intersystem crossings play a decisive role in these photoextrusion reactions for M(CO)₅(CS). Theoretical evidence from a kinetic viewpoint strongly supports the theory that the photolysis of M(CO)₅(CS) only produces CO-loss photoproducts rather than the CS-loss photoproduct. Theoretical analysis using the results of this study allows a good interpretation of the available experimental observations.

I. INTRODUCTION

There has long been interest in the 18-electron metal hexacarbonyl complexes, M(CO)₆ (M = group 6 transition metal),¹⁻¹⁸ partly because they can be photoinduced as a five-coordinate intermediate, M(CO)₅, which plays an important role in many related photochemical reactions.¹⁹⁻³⁵ Turner, Poliakoff, and co-workers reported that irradiation with UV light causes the octahedral M(CO)₆ complex to separate, to produce one CO molecule and one M(CO)₅ fragment.³⁴⁻³⁸ Similar experimental phenomena are also observed in the photochemistry of pentacarbonyl thiocarbonyl complexes, M(CO)₅(CS) (M = Cr and W), which are summarized in a review.³⁹ This study initially postulated that if the CS group is a label, then the photochemistry of M(CO)₅(CS) must be closely analogous to that of M(CO)₅, which, in turn, clarifies the photochemical mechanisms for M(CO)₆. It has been experimentally reported that photolysis of these thiocarbonyl metal complexes in the inert matrices using UV light generates a mixture of the two isomers of M(CO)₄(CS) (M = Cr and W) that exhibit a square-pyramidal structure and one carbon monoxide molecule.³⁴⁻³⁹ See Scheme 1.

There have been no further experimental or theoretical studies of the photochemical reaction mechanisms for these six-coordinate M(CO)₅(CS) complexes, possibly because the experimental equipment is not sufficiently accurate to determine the spin state of the octahedral complexes from which these originate, and partly because theoretical methods

Scheme 1. Experimental Results

*See refs 34–39.

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and computers have not been sufficiently developed to allow the computations. This study undertakes a systematic investigation of the photoextrusion reactions for metal thiocarbonyls of chromium, molybdenum, and tungsten using sophisticated computational methods. See Scheme 2.

Scheme 2. Three Possible Photochemical Reaction Pathways

These photochemical reactions pertain to the excited potential energy surfaces. Therefore, the way in which these excited molecules from high-energy excited energy states undergo a radiation-less decay to the lowest-lying ground state has been of interest to both experimental and theoretical chemists for many years. Conical intersections, which correspond to crossings between states of the same multiplicity (generally singlet−singlet), and intersystem crossings, which are crossings between states of different multiplicity (most commonly triplet−singlet), provide very effective channels for the chemical deactivation of photoexcited molecules. This study locates either the conical intersection or the intersystem crossing regions on the potential surface, where decay to the ground-state surface can occur. Using this information, the photoextrusion reaction processes for M(CO)$_5$(CS) complexes are interpreted. It is worthy of note that this study focuses on the photochemical behavior for both chromium and molybdenum complexes, following excitation at 300 nm. It concentrates on the lowest accessible excited state for the tungsten complex because of its high spin-orbit coupling (SOC) effect. However, it has to be pointed out that even very small SOC effects are still enough for promoting efficient intersystem crossing. For instance, the kinetics of intersystem crossing in complexes containing Fe, or Ru, or Re elements are very similar, and that the heavy atom effect does not operate. This combination of available experimental results and theoretical study should increase understanding of the excited state behaviors of six-coordinate pentacarbonyl thiocarbonyl complexes, M(CO)$_5$(CS) (M = Cr, Mo, and W), which will provide a better understanding of the photolysis mechanisms for other photochemical carbonyl elimination reactions of transition metal complexes.

II. RESULTS AND DISCUSSION

II.I. Mechanisms for the Photolysis Reactions for Cr(CO)$_6$(CS). The photochemical reaction mechanisms for Cr(CO)$_6$(CS) (Cr-S$_0$-Rea) are initially studied. Several experimental studies have shown that only chromium or molybdenum undergo optical population of the singlet state in group 6 transition metal complexes because the effect of SOC is less than that for the tungsten complexes. Therefore, this study focuses on the singlet-excited states for both chromium and molybdenum complexes and conical intersections are used to interpret the mechanisms for photochemical isomerization.

It has to be mentioned here that this study states that the SOC is only significant for the tungsten system and not for the chromium or the molybdenum systems. However, it has to be noted that this is not universally accepted. The supporting evidence comes from an experimental study by Harris and co-workers that was published in 2014. However, in 2015, Pryce et al. failed to experimentally detect any triplet states for the chromium–Fischer carbene, but it was experimentally observed that the lowest energy triplet state plays a key role in the photochemistry of the tungsten–Fischer carbene. The results of these experiments show that both Cr and Mo complexes originate from a singlet-excited state, and the W complex starts from a triplet excited state.

As shown in Scheme 2, three types of reaction routes are possible on the singlet excited potential energy surface of Cr-S$_0$-Rea. Path I and path II lead to the final corresponding photoisomers (Cr-S$_x$-Pro-1 and Cr-S$_y$-Pro-2), whereby a CS group occupies the axial and equatorial positions. Path III only results in a CS-loss photoproduction (Cr-S$_z$-Pro-3). Figure 1 shows the computational results for these three reaction pathways and the relative energies for the various points with respect to the energy of the corresponding reactant, Cr-S$_0$-Rea. The geometrical structures of the various points on the three mechanistic pathways that are shown in Figure 1 are detailed in Figure 2.

Earlier experimental studies have shown that the photolysis of Cr-S$_0$-Rea proceeds when there is irradiation with UV light with a wavelength of 300 nm (=95 kcal/mol). As shown on the left-hand side of Figure 1, the MP2-CAS results demonstrate that the singlet excited state energy in the Franck−Condon region (Cr-S$_1$-FC) is 89 kcal/mol, which is in reasonable agreement with the available experimental observations. The MP2-CAS data also shows that the triplet excited state energy for the Franck−Condon geometry for Cr-S$_z$-Rea is about 98 kcal/mol (≈291 nm). It is worthy of note that unlike most photochemical reactions for organic molecules, the differences between the energy levels are small for organometallic compounds because the energy splitting of the d orbitals of the central transition-metal atom that are involved is quite small. Therefore, for many photoextrusion reactions for organometallic molecules, when light is absorbed, the species can jump to the low-lying unoccupied orbitals, from which it may produce several nearly degenerate states (such as metal-to-ligand charge-transfer (MLCT) and metal-centered (MC) states), and then relax through the conical intersection in the proximity of the Franck−Condon region. The photochemical excited state electron configuration reactions for Cr(CO)$_6$ is an example. The experimental work on the photodynamics of Cr(CO)$_6$ can be found in references 3, 13, 33, 50, 51, 56, 61, and 64. It was found that after Cr(CO)$_6$ is irradiated by light, it can proceed to a $^3$T$_{1u}$ (MLCT) state, followed by ultrafast internal conversion to the nearly degenerate a $^3$T$_{1g}$ (MC) state because there is a conical intersection in the proximity of the Franck−Condon region. However, no MLCT states were computed in this study. For details, see references 18 and 50. Other papers concern vertical state assignments on binary metal carbonyls (see refs 52−56).

Considering these computational results and the nature of the photodissociative starting point, it is determined that the
photolysis of Cr-S0-Rea finally occurs from a singlet excited state in the FC region (Cr-S1-FC), which is in agreement with some experimental observations\textsuperscript{48−51} and supports the theory that the first excited state of the chromium complexes is a singlet, possibly because it exhibits weak SOC. It has to be mentioned here that our computations demonstrate that for the chromium system, the lowest triplet state (Cr-T1-Min) significantly lies above the lowest energy singlet state (Cr-S0-Rea) by about 59 kcal/mol, as shown in Figure 1. However, this triplet state (Cr-T1-Min) is not accessible from the singlet ground state following excitation due to the reason stated above.

When the reactant, Cr-S0-Rea, is photoirradiated by UV light, this species goes to the photoexcited Cr-S1-FC. Subsequently, this molecule undergoes a radiation-less decay to the singlet ground state by way of an S1/S0 conical intersection point. Beginning from the Cr-S1-FC excited state for Cr(CO)\textsubscript{5}(CS), the photochemically dynamic relaxation route can take one of three pathways: S1/S0 Cr-CI-1 (path I), S1/S0 Cr-CI-2 (path II), and S1/S0 CI-I-3 (path III), all of which are shown at the center of Figure 1. The MP2-CAS computations show that Cr-CI-1 and Cr-CI-2 are, respectively, lower in energy than Cr-S1-FC by 28 and 24 kcal/mol, but the other competing Cr-CI-3 is 2.3 kcal/mol higher in energy than its absorbing energy (300

Figure 1. Energy profiles for the photoextraction reactions for Cr(CO)\textsubscript{5}(CS) (Cr-S0-Rea). The abbreviations, FC and CI, respectively, represent Franck-Condon and conical intersection. The relative energies are given at the MP2-CAS-(12,10)/Def2-SVPD//CAS(12,10)/Def2-SVPD level of theory. All energies (in kcal/mol) are given with respect to the reactant (Cr-S0-Rea). For the crucial points of the CASSCF optimized structures, see Figure 2. For more information, see the text.
Figure 2. CAS(12,10)/Def2-SVPD geometries (in Å and deg) for path I, path II, and path III, for Cr(CO)$_5$(CS) (Cr-S$_0$-Rea), the conical intersection (CI), and the isomer products (Pro). The derivative coupling and the gradient difference vectors are computed using CASSCF at the conical intersections, Cr-CI-1, Cr-CI-2, and Cr-CI-3. The corresponding CASSCF vectors are shown in the inset.
The geometrical structures at these conical intersections are shown in Figure 2. Therefore, this theoretical study anticipates that the photoextrusion reactions for both path I (Cr-S₀-Rea + hν → Cr-S₀-Pro1 + CO) and path II (Cr-S₀-Rea + hν → Cr-S₀-Pro2 + CO) are barrier-less. Beginning from the Cr-S₁-FC point, the six-coordinated Cr(CO)₅(CS) complex enters two very efficient decay channels: Cr-CI-1 and Cr-CI-2. After decay at these conical intersection points, the final five-coordinated complexes, Cr-S₀-Pro1 and Cr-S₀-Pro2, and the initial reactant, Cr-S₀-Rea, are obtained via a ground-state barrier-less relaxation pathway. From an energetic viewpoint, it is unlikely that a pentacarbonyl chromium, Cr(CO)₅, and one CS molecule (i.e., path III) are formed after UV photolysis of Cr(CO)₅CS. That is to say, the Cr(CO)₅CS complex cannot lose a CS compound to yield a five-coordinate Cr(CO)₅ molecule via the S₀ → S₁ (300 nm) photoexcitation reaction, followed by the conical intersection channel. As mentioned previously, Turner, Poliakoff, and co-workers confirmed these theoretical observations but failed to experimentally generate the CS-loss product (Cr-Pro-3) by UV photolysis of Cr(CO)₅CS. The CAS-MP2 computational results that are shown in Figure 1 demonstrate that the photoextrusion reaction for the octahedral Cr(CO)₅(CS) complex progresses as follows.
Figure 4. CAS(12,10)/Def2-SVPD geometries (in Å and deg) for path I, path II, and path III for Mo(CO)₅(CS) (Mo-S₀-Rea), the conical intersection (CI) and the isomer products (Pro). The derivative coupling and gradient difference vectors are computed using CASSCF at the conical intersections, Mo-CI-1, Mo-CI-2, and Mo-CI-3. The corresponding CASSCF vectors are shown in the inset.
II.II. Mechanisms for the Photolysis Reactions for Mo(CO)$_5$(CS). The mechanisms for the photochemical reaction for the pentacarbonyl thiocarbonyl molybdenum complex, Mo(CO)$_5$(CS), Mo-S$_0$-Rea, are then studied. Similar to the case for Cr-S$_0$-Rea, the photoextrusion results for Mo-S$_0$-Rea, which are summarized in Figure 3, are almost the same as those that are shown in Figure 1. The geometrical structures of the various key points on the three possible mechanistic pathways in Figure 3 are shown in Figure 4.

The MP2-CAS calculations show that the vertical excitation energy for the promotion of Mo-S$_0$-Rea to its excited singlet state (Mo-S$_1$-FC) is 81 kcal/mol. The same level of calculation also predicts that the energy of its excited triplet state (Mo-T$_1$-FC) is 16 kcal/mol higher than that of Mo-S$_1$-FC, as shown on the left-hand side of Figure 3. This theoretical evidence confirms previous experimental results that the SOC is weak for the molybdenum system. To the best of the authors’ knowledge, there have been no experimental reports concerning the photolysis reactions of Mo(CO)$_5$(CS), so the value of this FC energy is a prediction. The wavenumber (300 nm) of the UV light of Cr(CO)$_5$(CS) is used as a reference line in the potential energy surfaces’ diagram of the Mo complex that is
Figure 6. CAS(12,10)/Def2-SVPD geometries (in Å and deg) for path I, path II, and path III for W(CO)₅(CS) (W-S₀-REA), the conical intersection (CI), the intermediate (Min), the transition state (TS), and the isomer products (Pro). The gradient difference vectors at the intersystem crossings (W-T₁/S₀-1, W-T₁/S₀-2, and W-T₁/S₀-3), which are computed using CASSCF, are shown in the inset.
shown in Figure 3. Similar to the Cr(CO)₅(CS) photolysis reactions, the photoexcitation promotes Mo(CO)₅(CS) to a series of low-lying excited states (e.g., MC and MLCT), from where it can undergo ultrafast internal conversion to the S₁ state from the FC point (Mo-S₀-FC). The photoelimination reactions for Mo(CO)₅(CS) then proceed on singlet surfaces. The computational data, however, indicate that for the Mo(CO)₅(CS) complex, the lowest triplet state (Mo-T₁-Min) lies apparently above the lowest energy singlet state (Mo-S₀-Rea) by about 54 kcal/mol, as shown in Figure 3. Again, due to the weak SOC for the molybdenum system mentioned above, it is foreseen that the triplet Mo-T₁-Min state is not accessible from the singlet Mo-S₀-Rea state following excitation.

Using the theoretical computations that are shown in Figure 3, the photoextrusion mechanisms for the reactant, Mo-S₀-Rea, for two reaction pathways (path I and path II), can be represented as

path I: Mo-S₀-Rea + hν → Mo-S₁-FC → Mo-CI
  -1 → Mo-Pro-1 + CO

path II: Mo-S₀-Rea + hν → Mo-S₁-FC → Mo-CI
  -2 → Mo-Pro-2 + CO

The MP2-CAS computational results show that the energies of Mo-CI-1 and Mo-CI-2 are 71 and 68 kcal/mol, relative to the corresponding reactant (Mo-S₀-Rea), but these are, respectively, 10 and 13 kcal/mol lower in energy than Mo-S₀-FC. These theoretical observations predict that the photoextrusion reactions for both path I and path II are barrier-less. From the initial FC point (Mo-S₀-FC), Mo-S₀-Rea enters a productive decay channel, either Mo-CI-1 or Mo-CI-2, and then decays from these conical intersection points. The CO-loss products (Mo-S₀-Pro1 and Mo-S₀-Pro2, respectively) and the reactant (Mo-S₀-Rea) are obtained via singlet barrier-less relaxations.

Similarly, the theoretical results in Figure 3 show that the photoextrusion reaction mechanism for path III proceeds as

path III: Mo-S₀-Rea + hν → Mo-S₁-FC → Mo-CI
  3 → Mo-S₀-Pro3 + CS

The CAS-MP2 computations in Figure 3 show that Mo-CI-3 is about 0.4 kcal/mol higher in energy than its absorbing energy (300 nm = 95.3 kcal/mol), which strongly implies that the singlet excited energy for Mo-S₀-Rea is insufficient to generate its photoproducts, a five-coordinated Mo(CO)₅ complex (Mo-Pro-3) and a CS molecule, via the conical intersection channel.

These model computations predict that both path I and path II are preferable to path III, from a kinetic viewpoint. In particular, the first two produce the CO-loss products, but the latter yields the CS-loss product.

II.III. Mechanisms for the Photolysis Reactions for W(CO)₅(CS)

Finally, the photoextrusion reaction mechanisms for the tungsten complex, W(CO)₅(CS), W-S₀-Rea, are considered. As previously mentioned because tungsten exhibits greater SOC, it is possible for the W(CO)₅(CS) complex to occupy triplet states directly from the singlet ground state, unlike the other two systems (Cr-S₀-Rea and Mo-S₀-Rea). The intersystem crossing mechanisms are used to determine both the singlet and triplet potential energy surfaces for W-S₀-Rea, to determine how the reactant (W-S₀-Rea) starts on an excited electronic potential surface and then crosses over to a lower surface somewhere along the reaction pathway. This tungsten complex finally arrives at the ground-state surface via a sequence of radiation-less transitions (e.g., intersystem crossings) and then moves on the ground-state surface toward the products. The three reaction profiles (path I, path II, and path III) are shown in Figure 5, which also shows the relative energies for the important points with respect to the ground-state minimum, W-S₀-Rea. Figure 6 shows selected optimized geometrical parameters for the critical points that are given in Figure 5.

The MP2-CAS calculations show that the energies of the first excited triplet and singlet states (in kcal/mol) are in the order: W-T₁-FC (58) < W-S₁-FC (96). Similar to Cr(CO)₅(CS) (Figure 1) and Mo(CO)₅(CS) (Figure 3), the six-coordinate W-S₀-Rea complex is initially promoted to its lowest-lying excited state via a vertical excitation. This W complex then proceeds through ultrafast conical intersections (or intersystem crossings) and finally decays to the minimum point at the triplet first excited state, W-T₁-Min. The agreement between the experimental and theoretical data means that the photo-induced W-S₀-Rea complex originates from the excited triplet surface, so the crossing between the triplet and singlet states is a focus. It has to be mentioned that in Figure 5, both W-T₁-TS1 and W-T₁-TS2 are on the triplet excited states, and they connect with W-T₁-Min, which are the results of IRC calculations for the reactant sides of these transition states. The MP2-CAS computations that are schematically illustrated in Figure 5 show that in contrast to the Cr-S₀-Rea and the Mo-S₀-Rea systems, the photoextrusion reaction mechanisms for W-S₀-Rea proceed as

path I: W-S₀-Rea + hν → W-T₁-Min → W-T₁-TS1 → W-T₁-TS2 → W-S₁-Pro1 + CO

path II: W-S₀-Rea + hν → W-T₁-Min → W-T₁-TS2 → W-S₁-Pro2 + CO

path III: W-S₀-Rea + hν → W-T₁-Min → W-T₁-TS3 → W-S₁-Pro3 + CS

The MP2-CAS results demonstrate that the photoirradiated W-S₀-Rea is promoted to its lowest-lying triplet excited state by a vertical excitation and then relaxes to the triplet minimum point, W-T₁-Min. The triplet W(CO)₅(CS) then undergoes either CO-extrusion or CS-extrusion via the transition state. The relative energies for these two processes with respect to the energy of the corresponding reactant complex (W-S₀-Rea) (in kcal/mol) are in the order: W-T₁-TS1 (53) < W-T₁-TS2 (57) < W-T₁-TS3 (73). Figure 5 also shows that these transition states (W-T₁-TS) connect the triplet local minimum, W-T₁-Min, to the corresponding intersystem crossing points (W-T₁/S₀).

It is worthy of note that the six-coordinate W(CO)₅(CS) complex originates from the excited triplet surface and finally moves to the singlet ground-state route, so the spin crossover between the triplet (T₁) and singlet (S₀) surfaces must play a fundamental role in characterizing its mechanistic photo-extrusion reaction. As shown in Figure 5, the intersystem crossing from the T₁ to the S₀ states occurs at the T₁/S₀ intersection, that is, W-T₁/S₀. The CASSCF optimized structures and the gradient difference vectors for the W-T₁/S₀-1 (path I), W-T₁/S₀-2 (path II), and W-T₁/S₀-3 (path III) points are given in Figure 6. Figure 6 shows that relaxation through the intersystem crossing point creates a reaction.
pathway to the final photoproducts, W-S0-Pro, on the singlet state surface, via the gradient difference vector. In Figure 5, the MP2-CAS computations also show that these intersystem crossing points lie about 49 (W-T1/S0-1), 49 (W-T1/S0-2), and 78 (W-T1/S0-3) kcal/mol above the energy of the corresponding reactant, W-S0-Rea. Therefore, after UV photo-irradiation, both path I and path II have sufficient internal energy to overcome the barrier heights between the W-T1-Min intermediate and the W-T1/S0-1 or W-T1/S0-2 intersection points. However, W-T1-TS3 and W-T1/S0-3 are, respectively, much higher in energy than the other points on the reaction pathways of path I and path II, which strongly supports the theory that pathways I and II are energetically feasible, and pathway III is energetically unfavorable, from a kinetic viewpoint. Therefore, UV photolysis of W(CO)5(CS) should produce a mixture of two isomeric forms of W(CO)4(CS) and molecular CO in large amounts, rather than the pentacarbonyl W(CO)5 complex and CS. This result is in good agreement with the experimental observations for the W(CO)5(CS) molecule.34−39

III. CONCLUSIONS

The results for the three six-coordinate pentacarbonyl thiocarbonyl d8 transition metal systems studied allow the following conclusions to be drawn:

1. It is theoretically demonstrated that the photolysis of M(CO)5(CS) (M = Cr, Mo, and W) proceeds along three reaction pathways: path I, path II, and path III (Scheme 2). The former two reaction routes produce one CO-loss photoproduct (M(CO)4(CS)) and the latter generates a CS-loss molecule (M(CO)5).

2. These theoretical findings show that on irradiation with UV light, both Cr(CO)5(CS) and Mo(CO)5(CS) complexes are excited to their singlet excited states, and the W(CO)5(CS) compound is promoted to its triplet excited state. From these spin states, conical intersection (S1/S0) and intersystem crossing (T1/S0) concepts are respectively used to interpret the mechanisms for the photochemical reactions, which feature two different types of spin states.
instance, using the CS symmetry (Figure 7), the $a_1A^3d$ minima and transition state energies. The optimization of the $(12,10)$ active space has therefore been used to calculate the ground state CASSCF optimized geometry using the CASSCF 12 electrons in 10 orbitals, which is denoted as $(12,10)$. The same orbital active space so these active orbitals form a space of diagram for a d$_6$ transition-metal complex has been published octahedral geometry, whose traditional molecular orbital energy ground-state configuration. Low-lying virtual orbitals correspond to the ($\pi_{CS/zy}$)$^2$($\pi_{CS/yz}$)$^2$($\pi_{CS/zz}$)$^2$($\sigma_{CS/yz}$)$^2$($\sigma_{CS/zy}$)$^2$, which corresponds to the ($\sigma_{CS/zz}$)$^2$($\pi_{CS/zy}$)$^2$($\pi_{CS/yz}$)$^2$($\sigma_{CS/yy}$)$^2$, ($3d_{y^2}$)$^2$($3d_{x^2}$)$^2$ configuration. Low-lying virtual orbitals correspond to $\pi^*_{CS/3d_{yz}}$ ($59a^2$), $\pi^*_{CS/3d_{xz}}$ ($60a^2$), $3d_{xz}/\sigma_{CS/61a^1}$, and $3d_{yz}/\sigma_{CS/62a^1}$. This study considers the other two transition-metal complexes, Mo(CO)$_5$(CS) and W(CO)$_5$(CS), using the same orbital active space so these active orbitals form a space of 12 electrons in 10 orbitals, which is denoted as $(12,10)$. The ground state CASSCF optimized geometry using the CASSCF $(12,10)$ active space has therefore been used to calculate the minima and transition state energies. The optimization of conical intersections is achieved in the $(f - 2)$-dimensional intersection space, using the method of Bearpark et al.$^{63}$ that is implemented in the Gaussian 09 program.$^{60}$ The lowest energy points of $T_1$/S$_0$ surface crossing were optimized using the computational method previously mentioned with state-average orbitals.$^{65}$ For $T_1$/S$_0$ crossing, a weighting of 50/50% was chosen for the triplet and singlet states in the state-averaging procedure.$^{60}$

Geometry optimizations are initially performed using the CASSCF and the Def2-SVPD basis sets.$^{57}$ This basis set uses a split valence basis set, with one polarization function and diffuse functions on all atoms. This is an all-electron basis set for C, O, and Cr, Mo, and W are respectively treated as a 14- and 14-electron system, and the relativistic effective core potentials that are used are those that are published in the literature.$^{68,69}$

When the prevailing electronic configurations are considered for the CASSCF calculations, dynamic correlation contributions are evaluated using a second-order perturbation process (MP2-CAS)$^{70,71}$ for which the CASSCF wave function is the reference function. Therefore, all stationary points on the potential energy surfaces of either the singlet or the triplet excited and the singlet ground states are computed using the GAUSSIAN 09 package of programs$^{60}$ at the CAS(12,10)/Def2-SVPD (geometries) and MP2-CAS(12,10)/Def2-SVPD//CAS(12,10)/Def2-SVPD (energies) levels of theory. Cartesian coordinates that are computed for the critical points at the CASSCF level are available as Supporting Information.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00380.

Optimized geometries and the absolute energies (in hartree) for all of the points on the potential energy surfaces of photochemical reactions of Cr(CO)$_5$(CS), Mo(CO)$_5$(CS), and W(CO)$_5$(CS) at the CAS(12,10)/Def2-SVPD (geometries) and MP2-CAS(12,10)/Def2-SVPD//CAS(12,10)/Def2-SVPD (energies) levels of theory (PDF).

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#### Author Contributions

Zhang conducted all of the theoretical computations and analyzed the results. Su supervised the research activities and contributed to the manuscript preparation. The two authors regularly discussed the progress of the research, reviewed the manuscript, and gave approval for the final version.

#### Notes

The authors declare no competing financial interest.

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