Mechanistic Investigations of the Photochemical Isomerizations of [(CO)₅MC(Me)(OMe)] (M = Cr, Mo, and W) Complexes

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**Supporting Information

ABSTRACT: The mechanisms for the photochemical isomerization reactions are determined theoretically using group 6 Fischer carbene complexes (CO)₅M=C(Me)(OMe) (M = Cr, Mo, and W) and the complete-active-space self-consistent field (CASSCF) (10-orbital/8-electron active space) and second-order Møller–Plesset perturbation (MP2-CAS) methods with the Def2-SVPD basis set. The structures and energies of the singlet/singlet conical intersections and the triplet/singlet intersystem crossings, which play a decisive role in these photoisomerizations, are determined. The former is applied to the chromium and molybdenum systems because their photoproducts are essentially from the singlet excited states. The latter is applied to the tungsten complex because its photoproducts are formed from a low-lying triplet excited state. Two reaction pathways are examined in this work: photocarbonylation (path I) and CO-photoextrusion (path II). The model studies strongly indicate that in the photochemistry of Cr and Mo Fischer carbene systems, the formation of metallaketene intermediates may occur at higher excitation wavenumbers, whereas the five-coordinated complexes that are attached by a solvent molecule are obtained at lower excitation wavenumbers. However, in the W analogue, because the activation barriers for path I are greater than that for path II and path I has more reaction steps than path II, the quantum yields for the metallaketene intermediate should be smaller than those for the five-coordinated species, which is also attached by a solvent molecule. These theoretical studies also suggest that the conical intersection and the spin crossover mechanisms that are identified in this work explain the process well and support the experimental observations.

1. INTRODUCTION

Fischer carbene complexes of the type (CO)₅M=C(R₁)(R₂) (R₁ and R₂ = alkyl, alkoxy, amino, etc.), which have a double bond between the transition metal (M) and the carbene carbon, have been extensively studied as reagents for use in various organic syntheses and in organometallic chemistry. Their vigorous reactivity means that many generations of chemists have searched for new chemical reactions and further synthetic applications in the fields of both thermal chemistry and photochemistry. However, many reaction mechanisms that involve these Fischer carbene complexes with different transition metal elements still remain undiscovered. The pioneering work of McGuire and Hegedus in 1982 demonstrated that chromium Fischer carbene complexes react with imines under visible light to yield β-lactams, which are at the origin of a famous reaction in organometallic chemistry. Hegedus and co-workers proposed that irradiation by sunlight facilitates the insertion of one of the five CO ligands into the metal–carbene–carbon double bond, which produces either a short-lived metallacyclopropanone (I) or a metallaketene (II) intermediate that, respectively, has one or no bridging carbonyl groups, as illustrated in Scheme 1. Although these two structures characterize various spectroscopic phenomena, they are not yet well understood. In this article, we report how the conical intersection and the spin crossover mechanisms that are identified in this work explain the process well and support the experimental observations.

Scheme 1. Two Intermediates Produced in a Photoinitiation Step

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scopic properties,35 the role that they play in these photochemical mechanisms of Fischer carbene complexes is uncertain because the existence of either (I) or (II) intermediate had not been experimentally confirmed by any laboratories for a very long time.24−34 However, until 2014, Harris and co-workers used ultrafast time-resolved infrared spectroscopy (TRIR) to study both photophysics and the photochemistry of (CO)5Cr−C(OMe)(Me) (Rea-Cr-S0) and (CO)5W−C(OMe)(Me) (Rea-W-S0) in cyclohexane.43 It was reported that the photoexcitation of Rea-Cr-S0 results in the rapid generation of both singlet and triplet "Cr−ketene" structures, whereas picosecond TRIR (psTRIR) of Rea-W-S0 gives no experimental evidence for the formation of the "W−ketene" intermediate.43 These experimental results seemed to support the earlier study of Sierra, Cossio, and co-workers.38−42 In 2015, Pryce and co-workers used psTRIR and low-temperature matrix isolation to study these molecules and detected no triplet states for the case of the Rea-Cr-S0 complex.44,45 That is to say, upon excitation of Rea-Cr-S0 at 400 nm, the Cr−ketene product (Pro1-Cr-S0), as shown in Scheme 2,44,45 In contrast to the Cr system, following both 400 and 320 nm excitation, the singlet ground state W−ketene product (Pro1-W-S0) is experimentally observed because of the intersystem crossing of the triplet state (Int1-W-T1 and Int2-W-T1) to the ground-state singlet hypersurface, which is shown in Scheme 3.39,44

These interesting experimental results prompt this investigation of mechanisms for the photoisomerization reactions of Fischer carbenes of the type ((CO)5M−C(OMe)(Me)), which feature group 6 transition metal elements (M = Cr, Mo, and W). There have been few theoretical investigations of the photochemical carbonylation of group 6 Fischer carbene complexes. To the best of the author’s knowledge, only three papers have reported photochemical mechanisms for group 6 Fischer carbene compounds using experimental procedures and computational methods.38,43,44 Sierra, Cossio, and co-workers studied the photocarbonylation of Cr- and W-Fischer carbene molecules and proposed that the photoreactivity of group 6 Fischer carbene compounds is strongly related to the coordinating ability of the solvent.38 Harris and co-workers proved the presence of Cr−ketene intermediates using psTRIR spectroscopy and density functional theory, but no W−ketene analogue was experimentally observed during any part of photochemical carbonylation reaction and no theoretical studies have been performed for the tungsten-Fischer carbene counterparts.43 Pryce and co-workers used time-dependent density functional calculations to determine the possible photochemical mechanisms for the Cr- and W-Fischer carbene complexes.44,45 However, none of these theoretical studies fully consider the

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Scheme 2. Photocarboxylation Processes of Rea-Cr-S0 Leading to the Formation of Metallaketene (Pro1-Cr-S0) via Singlet Excited States and the CO-Loss Molecule by Using 320 nm Irradiations.a

Scheme 3. Photocarboxylation Processes of Rea-W-S0 Leading to the Formation of Metallaketene (Pro1-W-S0) via Triplet Excited States.a

See experimental works reported in refs 44 and 45.
reaction pathways from the excited state to the ground state when the Fischer carbenes are irradiated by visible light. In particular, as already mentioned in Scheme 2, Pryce et al. proved that for the Cr Fischer carbene complex, the metallaketene (II) species originates from a singlet excited state. Pryce et al. also found that the lowest energy triplet state plays a decisive role in the photochemistry of the W-Fischer carbene compound. The reason for this could be due to the fact that the large spin–orbit coupling (SOC) for tungsten compared to chromium and molybdenum can assist the direct population of triplet states.

Therefore, scrutiny of the mechanisms of such photoisomerization reactions requires a more sophisticated quantum chemical theory.

To gain a better understanding of the energy hypersurfaces of the excited states of group 6 Fischer carbene complexes, this study performs a theoretical investigation of the photoisomerizations of (CO)₅M≡C(Me)(OMe) (Rea-Cr-S₀), (CO)₅Mo≡C(OMe)(Me) (Rea-Mo-S₀), and (CO)₅W≡C(OMe)(Me) (Rea-W-S₀). Information about the photochemical reaction behavior of group 6 Fischer carbene molecules allows better control of the results of these photo reactions and allows further organic as well as organometallic syntheses.

2. GENERAL CONSIDERATIONS

As mentioned in the Introduction, there are two possible reaction pathways for the photoisomerization reactions of group 6 Fischer carbenes (CO)₅M≡C(Me)(OMe) (M = Cr, Mo and W): path I (photocarbonylation) and path II (CO-photoextrusion), which, respectively, lead to the metallaketene intermediate (II, Pro1) and the five-coordinated square pyramid species (Pro2), as schematically illustrated in Scheme 4. The channel from the excited-state surface to the ground-state surface, which corresponds to either a conical intersection (S₁ → S₀) or an intersystem crossing (T₁ → S₀), is described in terms of these reaction routes in the following section.

3. RESULTS AND DISCUSSION

3.1. Singlet Photochemical Reaction Mechanisms of (CO)₅Cr≡C(OMe)(Me). The photoisomerizations of the Cr
Fischer carbene complex, \((\text{CO})_5\text{Cr} = \text{C(OMe)(Me)}\) \((\text{Rea-Cr-S}_0)\), are first considered. Figure 1 shows the reaction profiles that are calculated for both of the reaction pathways in Scheme 4 and the relative energies of the various points with respect to the energy of the corresponding reactant \((\text{Rea-Cr-S}_0)\). Selected geometrical parameters for all of the stationary points on the photoreaction pathways of \(\text{Rea-Cr-S}_0\), using CAS(8,10)/Def2-SVPD calculations, are given in Figure 2.

When the reactant \((\text{Rea-Cr-S}_0)\) is irradiated, it is initially promoted to its excited state by a vertical excitation. The CAS(8,10)/Def2-SVPD calculation for \(\text{Rea-Cr-S}_0\) predicts that the first excited state for this Cr species is the lowest-lying singlet state \((S_1)\), as shown on the left-hand side of Figure 1. This point on the excited singlet surface is shown as \(\text{FC-Cr-S}_1\) \((S_1 (\text{S}_0 \text{ geom}))\) and its vertical excitation energy is estimated to be 70 kcal/mol \((S_0 \rightarrow S_1 (\text{S}_0 \text{ geom}))\). The available experimental data give a value of 400 nm \((=72 \text{ kcal/mol in energy})\);\(^{18-45}\) so, it is theoretically predicted that the \(\text{Rea-Cr-S}_0\) reactant is situated on the singlet surface, after the vertical

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**Figure 2.** CAS(8,10)/Def2-SVPD geometries (in Å and deg) for path I and path II for the chromium Fischer carbene complex, that is, the reactant (Rea), FC, CI, Int, TS, and Pro. The derivative coupling and the gradient difference vectors for the conical intersections, which are calculated using the CAS method, are shown in square brackets. The bold arrows indicate the principal atomic motions in the transition-state eigenvector. For clarity, hydrogen atoms are omitted. For more details, see the Supporting Information.
photoexcitation, which has been confirmed by the recent experimental work.\textsuperscript{44,45}

For path I (photocarbonylation), Figure 1 shows that from the FC point (FC-Cr-S\textsubscript{1}), the Cr Fischer carbene relaxes to a local minimum (Int\textsubscript{1}-Cr-S\textsubscript{1}) at the singlet first excited state. Int\textsubscript{1}-Cr-S\textsubscript{1} then goes to a transition state, TS\textsubscript{1}-Cr-S\textsubscript{1}, in which one carbonyl group bends toward the carbene ligand, followed by the formation of a three-membered-ring intermediate, Int\textsubscript{2}-Cr-S\textsubscript{1}. The fully optimized structures for Int\textsubscript{1}-Cr-S\textsubscript{1} and Int\textsubscript{2}-Cr-S\textsubscript{1} are given in Figure 2. It is seen that the molecule in Int\textsubscript{1}-Cr-S\textsubscript{1} has an octahedral structure, whereas the pattern of Int\textsubscript{2}-Cr-S\textsubscript{1} is quite similar to the metallocyclopropanone (I), as already shown in Scheme 1. The absorptions that are the result of CO ligands in the two intermediates (Int\textsubscript{1}-Cr-S\textsubscript{1} and Int\textsubscript{2}-Cr-S\textsubscript{1}) are detailed in Table S1 (Supporting Information). The calculated frequencies at the complete-active-space self-consistent field (CASSCF) level of theory for Int\textsubscript{1}-Cr-S\textsubscript{1} and Int\textsubscript{2}-Cr-S\textsubscript{1} are 1966 and 1764 cm\textsuperscript{-1}, respectively. These values are in reasonable agreement with the experimentally reported absorptions at 1970 and 1770 cm\textsuperscript{-1}. The agreement between these theoretical findings and the available experimental observations\textsuperscript{46} of the Cr species is the convincing proof that the computational method that is used in this study provides a reliable basis for any discussion of the photochemical reaction mechanisms for the Fischer carbene complexes, for which the experimental data are still either scarce or non-existent.

Figure 1 shows that the Int\textsubscript{2}-Cr-S\textsubscript{1} intermediate subsequently undergoes a Cr–carbene bond breaking via a transition state TS\textsubscript{2}-Cr-S\textsubscript{1}. Figure 2 shows that TS\textsubscript{2}-Cr-S\textsubscript{1} connects the singlet local minimum Int\textsubscript{2}-Cr-S\textsubscript{1} and the corresponding conical intersection point, CI-Cr-1. The orientation of the two vectors (i.e., the gradient difference and the derivative coupling vectors), computed at CAS(8,10), is also shown schematically in Figure 2. The gradient difference vector for CI-Cr-1 corresponds to a Cr–C=O bending motion, which can result in a vibrationally hot species at the singlet ground state configuration. However, by following the derivative coupling vector for CI-Cr-1 and increasing the Cr–C(Me)(OMe) bond distance, the system can arrive at a final product, Pro\textsubscript{1}-Cr-S\textsubscript{0} whose geometrical structure is shown in Figure 2 and which is analogous to the metallaketene (II) (Scheme 1). The second-order Møller–Plesset perturbation theory (MP2-CAS) results show that the relative energy differences for Int\textsubscript{1}-Cr-S\textsubscript{1}, TS\textsubscript{1}-Cr-S\textsubscript{1}, Int\textsubscript{2}-Cr-S\textsubscript{1}, TS\textsubscript{2}-Cr-S\textsubscript{1}, CI-Cr-1, and Pro\textsubscript{1}-Cr-S\textsubscript{0} with respect to that of Rea-Cr-S\textsubscript{0} are 45, 56, 39, 51, 47, and 21 kcal/mol, respectively. This computational data strongly imply that when Rea-Cr-S\textsubscript{0} is photoirradiated at 400 nm, both singlet-excited intermediates (Int\textsubscript{1}-Cr-S\textsubscript{1} and Int\textsubscript{2}-Cr-S\textsubscript{1}) are kinetically unstable and rearrange spontaneously to give the more stable product, Pro\textsubscript{1}-Cr-S\textsubscript{0}, and the initial reactant, Rea-Cr-S\textsubscript{0}. These predictions are in good agreement with the experimental observations, as illustrated in Scheme 2.\textsuperscript{44} The theoretical evidence for path I that is shown in Figure 1 means that the photocarbonylation reaction mechanisms for the Cr Fischer carbene can be represented as follows:

Path I: \textbf{Rea-Cr-S}\textsubscript{0} + h\nu \rightarrow\textbf{FC-Cr-S}\textsubscript{1} \rightarrow\textbf{Int1-Cr-S}\textsubscript{1} \rightarrow\textbf{TS1-Cr-S}\textsubscript{1} \rightarrow\textbf{Int2-Cr-S}\textsubscript{1} \rightarrow\textbf{TS2-Cr-S}\textsubscript{1} \rightarrow\textbf{CI-Cr-1} \rightarrow\textbf{Pro1-Cr-S}\textsubscript{0}

For path II (CO-photoextrusion), Figure 1 shows that after the reactant, Rea-Cr-S\textsubscript{0} is irradiated to the singlet FC point (FC-Cr-S\textsubscript{1}), this molecule relaxes to a conical intersection (CI-Cr-2), from which the photoexcited compound decays nonradiatively to S\textsubscript{0}. Again, funneling through CI-Cr-2 can lead to two different reaction paths on the ground-state surface, via either the gradient difference vector or the derivative coupling vector, as shown in Figure 2. The former results in a vibrationally hot molecule at the singlet ground state, and the latter corresponds to an extrusion of one carbonyl group in the \((\text{CO})\text{Cr} \equiv \text{C(OMe)(Me)}\) system, which leads to the CO-loss product, Pro\textsubscript{2}-Cr-S\textsubscript{0}.

The MP2-CAS calculations show that the CI-Cr-2 is higher in energy than the corresponding Rea-Cr-S\textsubscript{0} by about 82 kcal/mol. According to the recent experimental work by Pryce and co-workers,\textsuperscript{44,45} following 320 nm (89 kcal/mol) excitation of \((\text{CO})\text{Cr} \equiv \text{C(OMe)(Me)}\), a singlet-ground-state CO-loss product (Pro\textsubscript{2}-Cr-S\textsubscript{0}) is obtained. The IR frequencies for this CO-loss product are at 2043 and 1896 cm\textsuperscript{-1}, which is in line with the CAS(8,10) computational results of 2048 and 1901 cm\textsuperscript{-1}, as shown in Table S1 (Supporting Information). This theoretical finding strongly suggests that when the reactant Rea-Cr-S\textsubscript{0} is irradiated at 320 nm, the system proceeds to one-CO-extrusion reaction without any difficulty, as shown in Figure 1. The photochemical CO-extrusion mechanism for Rea-Cr-S\textsubscript{0} is described as follows:

Path II: \textbf{Rea-Cr-S}\textsubscript{0} + h\nu \rightarrow\textbf{FC-Cr-S}\textsubscript{1} \rightarrow\textbf{CI-Cr-2} \rightarrow\textbf{Pro2-Cr-S}\textsubscript{0}

In brief, this theoretical study readily shows that an understanding of the conical intersection of the chromium Fischer carbene complexes is necessary to interpret its reaction mechanism because it is the driving force for its photochemistry. That is to say, when a Cr Fischer carbene (Rea-Cr-S\textsubscript{0}) is vertically excited to the S\textsubscript{1} state, it can proceed along two types of reaction pathways. On path I, this singlet excited species encounters two local intermediates, one of which (Int\textsubscript{2}-Cr-S\textsubscript{1}) is the three-membered-ring metallocyclopropanone (I) species. Following a conical intersection, the system then reaches the final photoproduct (Pro\textsubscript{1}-Cr-S\textsubscript{0}) with the metallaketene (II) pattern. On path II, radiation-less decay from S\textsubscript{1} to S\textsubscript{0} of a Cr Fischer carbene (Rea-Cr-S\textsubscript{0}) occurs via a conical intersection (CI-Cr-2), which results in a CO-loss product (Pro\textsubscript{2}-Cr-S\textsubscript{0}). More importantly, starting from these conical intersections, the products of the photoisomerization (path I) and the photoextrusion (path II), as well as the initial reactant, are reached along a barrierless ground-state relaxation path. All of these theoretical observations for the photochemical reactions of a Cr Fischer carbene complex agree satisfactorily with the recent experimental results.\textsuperscript{44,45}

3.2. Singlet Photochemical Reaction Mechanisms of \((\text{CO})\text{Mo} \equiv \text{C(OMe)(Me)}\). The photochemical reactions of the molybdenum Fischer carbene complex, \((\text{CO})\text{Mo} \equiv \text{C(OMe)(Me)}\) (Rea-Mo-S\textsubscript{0}), are studied. To the author’s best knowledge, no detailed photoinduced reactions for the transition-metal complexes of Mo have been experimentally studied.\textsuperscript{36,37} To comprehend the SOC between the ground state and the first excited state for the complexes studied in this work, the CAS(8,10)/Def2-SVPD method is utilized to investigate the SOC of \((\text{CO})\text{Cr} \equiv \text{C(OMe)(Me)}\) (Rea-Cr-S\textsubscript{0}), \((\text{CO})\text{Mo} \equiv \text{C(OMe)(Me)}\) (Rea-Mo-S\textsubscript{0}), and \((\text{CO})\text{W} \equiv \text{C(OMe)(Me)}\) (Rea-Mo-S\textsubscript{0}). The computational results
The reaction pathways for the Mo Fischer carbene complex proceed starting from the Mo reactant and going to the Franck-Condon points on both pathways as shown in Figure 4. The main geometrical parameters for the critical points are schematically shown in Figure 3. That is, the theoretical lines of evidence reveal that the SOC values increase in the order: Cr < Mo < W. As a result, it is reasonable to directly populate singlet excited states from the singlet ground state for the Mo complexes. The singlet surfaces for the Mo Fischer carbene complex are the focus of this study hereafter.

Figure 3 shows the relative energies on the singlet potential energy surface along the presumed photoisomerization pathways from Rea-Mo-S0 to different photoproducts (path I and path II). The main geometrical parameters for the critical points on both pathways are shown in Figure 4.

The reaction profiles that are calculated for Rea-Mo-S0 resemble that of Rea-Cr-S0 as shown in Figure 3. That is, starting from the Mo reactant and going to the Franck-Condon point FC-Mo-S0, the photoisomerization reactions on the singlet excited-state energy surface can take two different reaction routes (Scheme 4): path I (photocarbonylation) and path II (CO-photoextrusion). The computational results that are schematically shown in Figure 3 indicate that these two reaction pathways for the Mo Fischer carbene complex proceed as follows:

Path I: Rea-Mo-S0 + hν → FC-Mo-S1 → Int1-Mo-S1 → TS1-Mo-S1 → Int2-Mo-S1 → TS2-Mo-S1 → Cl-Mo-1 → Pro1-Mo-S0

Path II: Rea-Mo-S0 + hν → FC-Mo-S1 → Cl-Mo-2 → Pro2-Mo-S0

For path I, the CAS-MP2 calculations show that the energies of Int1-Mo-S0, TS1-Mo-S1, Int2-Mo-S1, TS2-Mo-S1, Cl-Mo-1, and Pro1-Mo-S0 relative to the ground-state minimum (Rea-Mo-S0) are 42, 52, 38, 54, 43, and 23 kcal/mol and are lower than that of FC-Mo-S1 by 26, 16, 30, 14, 25, and 45 kcal/mol. Because of the additional energy (68 kcal/mol) generated by decay from Rea-Mo-S0 to FC-Mo-S1, it is anticipated that this relaxation energy is sufficient to induce an efficient photocarbonylation reaction (path I) for the Mo Fischer carbene complex. These theoretical lines of evidence are in good agreement with the available experimental reports.26,29,30 Additionally, the theoretical evidence demonstrates that when Rea-Mo-S0 is irradiated with visible light at 400 nm (=72 kcal/mol), one CO ligand is inserted into the Mo–C(Me)(OMe) bond to form a metallacyclopropanone (I; Int2-Mo-S1). This intermediate subsequently leads to a real conical intersection (Cl-Mo-1), at which the decay to either a metallaketene II (Pro1-Mo-S0) or an initial reactant on the ground-state surface occurs within a single vibrational period,49,50 so it follows a concerted pathway. The calculated CO stretching frequencies for the minima, Rea-Mo-S0, Int1-Mo-S1, Int2-Mo-S1, and Pro1-Mo-S0, are all listed in Table S1 (Supporting Information).

Unfortunately, as mentioned earlier, owing to a lack of experimental data for these Mo Fischer carbene complexes, the vibrational frequencies that are given in this study must be considered as predictions for future studies.

For path II, the theoretical results that are shown in Figure 3 suggest that Cl-Mo-2 is 11 kcal/mol higher in energy than FC-Mo-S1 and 79 kcal/mol higher in energy than the ground-state reactant Rea-Mo-S0, so it is expected that a CO-loss product, Pro2-Mo-S0, cannot be formed during the irradiation of Rea-Mo-S0 with 400 nm (=72 kcal/mol) light because the singlet excited energy of Rea-Mo-S0 (68 kcal/mol) is insufficient to yield it via radiation-less decay (i.e., the conical intersection channel). However, spectroscopic changes are observed following 320 nm (=89 kcal/mol) excitation of Rea-Mo-S0 as shown in Figure 3. The CO stretching frequencies for this CO-loss product (Pro2-Mo-S0) are listed in Table S1 (Supporting Information). However, the absence of related experimental and theoretical studies of the Mo Fischer carbene.
complexes means that these vibrational frequencies for the Pro2-Mo-S0 species are predictions. In this study of the chromium and molybdenum Fischer carbene systems, the CAS-MP2 computations demonstrate that if both Cr and Mo Fischer carbene complexes are irradiated, two types of photointermediates, Pro1-M-S0 (a metallaketene) and Pro2-M-S0 (a square pyramidal structure), are produced. Because path II undergoes the CO-photoextrusion process, the final intermediate, Pro2-M-S0, features a five-coordinated square-pyramidal geometry. This unstable intermediate must quickly attach to a solvent molecule to form a stable six-coordinated octahedral structure (Scheme 5). Therefore, it would be difficult to verify these five-coordinated species experimentally. Their further study is beyond the scope of this work.

3.3. Triplet Photochemical Reaction Mechanisms of (CO)5W≡C(OMe)(Me).

For the purpose of comparison, the triplet photoisomerization reactions of tungsten Fischer carbene complex, (CO)5W≡C(OMe)(Me) (Rea-W-S0), are studied.44 As demonstrated in the previous section, because the SOC data increase in the order: Cr < Mo ≪ W, one may consider the Rea-W-S0 complex to occupy triplet states directly from the singlet ground state, unlike the other two complexes (Rea-Cr-S0 and Rea-Mo-S0).55 In other words, the intersystem crossing pathways are used to examine both the singlet and triplet potential energy surfaces for (CO)5W≡C(OMe)(Me).

Figure 4. CAS(8,10)/Def2-SVPD geometries (in Å and deg) for path I and path II for the Mo Fischer carbene complex, that is, the reactant (Rea), FC, CI, Int, TS, and Pro. The derivative coupling and gradient difference vectors for conical intersections, which are calculated using the CAS method, are shown in square brackets. The bold arrows indicate the principal atomic motions in the transition-state eigenvector. For clarity, hydrogen atoms are omitted. For more details, see the Supporting Information.
The reason for this is simply because the present investigations want to resolve how this reactant initiates on an excited electronic potential surface and then crosses over to a lower surface somewhere along the reaction pathway. The photochemical reaction pathways that correspond to a photo-carbonylation mechanism (path I) and a CO-photoextrusion mechanism (path II) shown in Scheme 4 are studied. The discussion of these two reaction pathways is based on 10 fully optimized structures that correspond to minima, transition states, and intersystem crossing points on the S0 and T1 state energy surfaces. A schematic overview of the computed energy profile for the photochemical reaction routes for Rea-W-S0 is shown in Figure 5. The structures optimized at the CAS(8,10)/Def2-SVPD level of theory are outlined in Figure 6.

As mentioned briefly in Scheme 3, when the reactant, Rea-W-S0 absorbs light, most likely the excitation leads to a singlet excited state. That is to say, the present computational data at the MP2-CAS(8,10)/Def2-SVPD//CAS(8,10)/Def2-SVPD level of theory anticipate that the triplet excited-state energy (kcal/mol) at the Franck−Condon geometry for Rea-W-S0 is FC-W-T1 (61.0), FC-W-T2 (67.6), FC-W-T3 (98.1), and FC-W-T4 (100.4), while the singlet excited-state energy (kcal/mol) at the Franck−Condon geometry is FC-W-S1 (70.4), FC-W-S2 (87.4), and FC-W-S3 (99.5). In other words, the photoexcitation should promote Rea-W-S0 to a singlet excited state (S1 or S2). Then, this species decays to the triplet state, Int1-W-T1, and the W Fischer carbene complex relaxes to one intermediate at the lowest-lying triplet state (Figure 5), which has an octahedral geometrical structure, as shown in Figure 6, and is named Int1-W-T1. From this intermediate, the search for a transition state uses the model of its local minimum conformation at the triplet state. The photochemical isomerization reactions for the tungsten Fischer carbene complex originate from the excited triplet surface and eventually advance along the singlet ground-state path. Therefore, the spin intersystem crossing between the triplet (T3) and singlet (S1) surfaces must play a prominent role in characterizing the

Figure 5. Energy profiles for the photochemical reactions of (CO)5W≡C(Me)(OMe) (Rea-W-S0). The abbreviations, FC, Int, TS, CI, and Pro, respectively, stand for Franck−Condon, intermediate, transition state, conical intersection, and product. The relative energies are calculated at the MP2-CAS(8,10)/Def2-SVPD//CAS(8,10)/Def2-SVPD level of theory. All energies (in kcal/mol) are given with respect to the reactant, Rea-W-S0. Figure 6 shows the CAS-optimized structures for the crucial points. For more information, see the text.
mechanistic photoinduced reactions of Fischer carbene (CO)₅W=C(Me)(OMe) species.

On path I, similarly to the Cr and Mo cases, the W molecule may start from Int₁-W-T₁ and then undergo the insertion of one CO ligand into the W−C(Me)(OMe) bond to form a three-membered-ring intermediate, Int₂-W-T₁, via a transition state, TS₁-W-T₁. As shown in Figure 6, this intermediate is geometrically structurally analogous to metallacyclopropanone (I). Subsequently, a W−(MeO)(Me)C₁ bond breaking occurs via another transition state, TS₂-W-T₁, which adopts a metalketene-like conformation whereby two unpaired electrons are located on two different atoms (W and C₁), as shown in Figure 6. Following the intersystem crossing point (T₁/S₀-W-1), the W system finally produces a photoproduct, Pro₁-W-S₀, with a metalketene (II) geometrical structure, as shown in Scheme 1.

The CAS-MP2 computations show that the energies of these stationary points, that is, Int₁-W-T₁, TS₁-W-T₁, Int₂-W-T₁, TS₂-W-T₁, T₁/S₀-W-1, and Pro₁-W-S₀, are all lower in energy than the FC point (FC-W-T₁) by 27, 8.4, 18, 4.3, 9.2, and 31 kcal/mol, respectively. This theoretical finding strongly suggests that when the W Fischer carbene complex absorbs visible light (400 nm), it can undergo the insertion of a CO ligand into the W−C(Me)(OMe) bond via an intersystem crossing process to produce a metalketene. The CAS(8,10) computations also predict the CO stretching frequencies for Int₁-W-T₁, Int₂-W-T₁, and Pro₁-W-S₀, and these are listed in Table S1. The recent experimental study by Pryce et al. found that the absorptions for these three species are Int₁-W-T₁ (1960 cm⁻¹), Int₂-W-T₁ (1920 cm⁻¹), and Pro₁-W-S₀ (1945 cm⁻¹). These experimentally detected values are in excellent agreement with the theoretical predictions.
agreement with the calculated frequencies: \(\text{Int}_1-T_1\) (1956 cm\(^{-1}\)), \(\text{Int}_2-T_1\) (1929 cm\(^{-1}\)), and \(\text{Pro}_1-W-S_0\) (1941 cm\(^{-1}\)). These are shown in Table S1 (Supporting Information).

On the basis of the reaction profiles that are shown in Figure 5, it is obvious that upon irradiation with visible light, the photoactivated \(\text{Rea}-W-S_0\) molecule has sufficient internal energy (400 nm = 72 kcal/mol) to overcome the energy barriers from \(\text{Int}_1-T_1\) to \(\text{Int}_2-T_1\) and from \(\text{Int}_2-T_1\) to the \(T_1/S_0-W-1\) crossover points. The mechanism for the triplet photocarbonylation of W Fischer carbene \((\text{Rea}-W-S_0)\) is represented below.

Path I: \(\text{Rea}-W-S_0 + h\nu \rightarrow \text{FC-W-S}_1 \rightarrow \text{Int}_1-W-T_1 \rightarrow \text{TS}_1-W-T_1 \rightarrow \text{Int}_2-W-T_1 \rightarrow \text{TS}_2-W-T_1 \rightarrow T_1/S_0-W-1 \rightarrow \text{Pro}_1-W-S_0\)

On path II, the reaction proceeds when a W–CO bond between the W and C atoms breaks via a transition state, \(\text{TS}_3-W-T_1\). Figure 5 shows that the W system undergoes a W–CO bond breaking to proceed to the \(T_1/S_0-W-2\) intersection point, which has a square-pyramidal structure wherein two unpaired electrons are located on the W and C atoms. These two unpaired electrons are apparently sufficiently distant that their singlet and triplet states are degenerate. The \(T_1\) and \(S_0\) surfaces can therefore cross. Both the optimized structure and the gradient difference vector for the \(T_1/S_0-W-2\) species at these points are shown in Figure 6. The CAS-MP2 computations demonstrate that the formation of \(T_1/S_0-W-2\) from \(\text{Int}_1-W-T_1\) proceeds via a transition state, \(\text{TS}_3-W-T_1\), with a barrier of 15 kcal/mol. In short, the mechanism for triplet photocarbonylation of \(\text{Rea}-W-S_0\) is described as follows:

Path II: \(\text{Rea}-W-S_0 + h\nu \rightarrow \text{FC-W-S}_1 \rightarrow \text{Int}_1-W-T_1 \rightarrow \text{TS}_3-W-T_1 \rightarrow T_1/S_0-W-2 \rightarrow \text{Pro}_2-W-S_0\)

The reaction profiles in Figure 5 clearly show that the W Fischer carbene complex has sufficient internal energy (72 kcal/mol) to overcome the barrier heights, after photoexcitation to the \(T_1\) state. However, because the activation barriers (19 and 14 kcal/mol) for path I are somewhat larger than that for path II (15 kcal/mol) and path I has more reaction steps than path II, the quantum yield of path I is anticipated to be smaller than that of path II. In other words, this theoretical study shows that path I is the unfavorable reaction route from a kinetic viewpoint. It has been experimentally confirmed that the W Fischer carbene complex usually does not exhibit any spectroscopic evidence for the existence of metal ketene intermediates, except for the works of Pryce et al. (Scheme 3) and Sierra, Cossio, and co-workers. In addition, the theoretical results of the CAS-MP2 calculations predict that a prototypical tungsten Fischer carbene complex generates a five-coordinated \(\text{Pro}_2-W-S_0\) species that is added to one solvent molecule to form a six-coordinated product (Scheme 5). However, this theoretical prediction requires experimental verification.

As already described in Scheme 3, Pryce et al. and Sierra, Cossio, and co-workers reported that the irradiation of the \(\text{Rea}-W-S_0\) reactant at 400 nm can lead to the formation of \(\text{Pro}_1-W-S_0\) \(\text{(I) (Scheme 1) type. Figure 5 shows that the appropriate photoexcitation of W Fischer carbene complexes results in both the photoinduced products: \(\text{Pro}_1-W-S_0\) and \(\text{Pro}_2-W-S_0\). Pryce et al. also reported that following excitation of \(\text{Rea}-W-S_0\) using 320 nm light, the spectral changes are essentially identical to those that occur following excitation at 400 nm, which are shown in Scheme 3. In other words, it was concluded that the photochemistry of \(\text{Rea}-W-S_0\) is essentially independent of the excitation wavelength. The theoretical evidence that is shown in Figure 5 confirms these experimental observations.

4. CONCLUSIONS

This study gives detail to the standard model for the photoexcitation reactions of group 6 Fischer carbene complexes and also provides theoretical explanations for the experimental results. Initially, \(\text{Rea}-M-S_0\) \((M = \text{Cr and Mo})\) and \(\text{Rea}-W-S_0\) complexes are vertically excited to the \(S_1\) and \(T_1\) states and then, respectively, decay to the singlet and triplet local minima, \(\text{Int}_1-M-S_1\) and \(\text{Int}_1-W-T_1\). Two types of radiation-less decay from either \(S_1\) to \(S_0\) or \(T_1\) to \(S_0\) then occur via either conical intersections \((\text{CI-M-1} \text{ and CI-M-2})\) or intersystem crossings \((T_1/S_0-W-1 \text{ and } T_1/S_0-W-2)\). Finally, these can result in either metal-ketene \((\text{Pro}_1-M-S_0)\) or CO-release \((\text{Pro}_2-M-S_0)\) intermediates. The two types of short-lived intermediates that are generated are grouped according to the 1,2-biradical intermediates \((\text{Int}_1-M-S_1 \text{ and } \text{Int}_2-M-S_1 \text{ or } \text{Int}_1-W-T_1 \text{ and } \text{Int}_2-W-T_1)\) that arise when the metal and carbon bonds are cleaved, as shown in Figures 2, 4, and 6.

In particular, this theoretical investigation shows that in both Cr and Mo Fischer carbene complexes, the relative energy for the CO-photoextrusion reaction (path II) is essentially greater than that for the photocarbonylation reaction (path I). Therefore, the metallaketene photoproduct should be observed at high excitation wavelengths, and the five-coordinated square pyramid species should be obtained at lower excitation wavelengths. However, for the W Fischer carbene complex, the theoretical computations demonstrate that the barrier heights for the photocarbonylation reaction (path I) are higher than that for the CO-photoextrusion reaction (path II) and the former has more reaction steps than the latter, so it is predicted that both reaction pathways compete and that the quantum yield for the former is smaller than that for the latter. These theoretical investigations from the point of view of conical intersections and spin crossover allow a better understanding of the photochemical reactions for group 6 Fischer carbene complexes and support the available experimental observations.

5. METHODOLOGY

All geometries reported herein are fully optimized, without imposing any symmetry constraints, using the ab initio CASSCF program released in Gaussian 09. In the study of the photochemical reaction routes, the stationary point structures on the \(S_0\) and \(S_1\) \((\text{for } \text{Rea-Cr-S}_0\text{ and } \text{Rea-Mo-S}_0)\) molecules and the \(S_0\) and \(T_1\) \((\text{for } \text{Rea-W-S}_0)\) surfaces are optimized at the CASSCF level of computation, using the Def2-SVPD basis set.

The active space that is required to describe the ground and the lowest excited states of \(\text{Rea-Cr-S}_0\text{, Rea-Mo-S}_0\text{, and Rea-W-S}_0\) contains 8 electrons in 10 metal d (bonding and antibonding) orbitals, which is referred to as CAS(8,10). Therefore, the state-averaged CAS(8,10) method is used in this work to determine the stationary points on the intersection space. Frequency calculations at the CAS(8,10)/Def2-SVPD level are used to compute all stationary points as either minima [the number of imaginary frequencies (NIMAG) = 0] or...
transition states (NIMAG = 1). Optimization occurs when the maximum force and its root mean square are, respectively, less than 0.00065 and 0.00005 hartree/bohr.

To reform the energies for dynamic electron correlation, the multireference Møller–Plesset (MP2-CAS) algorithm, which is implemented in the Gaussian 09 program package, is used. Unless otherwise indicated, the relative energies that are given in the text are computed at the MP2-CAS(8,10)/Def2-SVPD level, using the CAS(8,10)/Def2-SVPD (hereafter marked MP2-CAS and CASSCF, respectively) geometry. The Cartesian coordinates (CASSCF) and the energies (MP2-CAS and CASSCF) are given in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00766.

Optimized geometries and the absolute energies (in hartree) for all points on the potential energy surfaces of photochemical reactions of (CO)_xM=CM(Me)(OMe) (M = Cr, Mo, and W) at the CAS(8,10)/Def2-SVPD (geometries) and MP2-CAS(8,10)/Def2-SVPD//CAS-(8,10)/Def2-SVPD (energies) levels of theory (PDF).

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Author Contributions
The author conducted all of the theoretical computations and analyzed the results. The author also contributed to the manuscript preparation and then gave approval for the final version.

Notes
The author declares no competing financial interest.

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