A model study on the photodecarbonyl reaction of \((\eta^5\text{-C}_5\text{H}_5)M(\text{CO})_2\) (M = Co, Rh, Ir)†

Zheng-Feng Zhang and Ming-Der Su *ab

The group 9 organometallic complexes \(\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\) (M = Co, Rh and Ir) and Si(CH\(_3\))\(_2\)(H) have been considered as a model system to study their photochemical decarbonylation reactions as well as the Si–H bond activation reactions using the CASSCF and MP2-CAS computational methods. For the cobalt complex, three kinds of reaction pathways, which result in the same oxidative addition product, are investigated. Our theoretical findings demonstrated that after the photoirradiation, \(\eta^5\text{-C}_5\text{M}(\text{CO})_2\) loses one CO ligand without any difficulty to form either the triplet (\(\eta^5\text{-C}_5\text{M}(\text{CO})_2\)) or singlet (\(\eta^5\text{-C}_5\text{M}(\text{CO})_2\)) species. The former plays a decisive role in the formation of the final oxidative addition product. On the other hand, the latter plays no role in the production of the final product molecule, but its singlet cobalt center interacts weakly with solvent molecules (\(\text{Me}_2\text{SiH}\)) to produce an alkyl-solvated organometallic complex, which is experimentally detectable. The present works reveal that both \(\eta^5\text{-C}_5\text{Rh}(\text{CO})_2\) and \(\eta^5\text{-C}_5\text{Ir}(\text{CO})_2\) should adopt the conical intersection mechanism after they are irradiated by light. Moreover, our theoretical examinations strongly suggest that for the 16-electron monocarbonyl \(\eta^5\text{-C}_5\text{M}(\text{CO})_2\) (M = Rh and Ir) species, the insertion into a Si–H bond by the Ir system is much more facile and more exothermic than that for the Rh counterpart.

I. Introduction

The photochemical oxidative addition reaction of one E–H (E = H or group 14 elements) bonding to the transition metal complex is of essential interest in different fields of chemical research, such as inorganic chemistry, organometallic chemistry, biochemistry, and most importantly, catalytic experimentation, even since the groundbreaking discovery by Schuster-Woldan and Basolo.7 The basic approach is to break a metal–ligand bond upon cooperation by using light to enable subsequent oxidative addition reactions. In this process, one particularly exciting reaction is the photochemical activation of an E–H bond by one unsaturated intermediate CpML (Cp = \(\eta^5\text{-C}_5\text{H}_5\)) with a 16 valence electron count, which is formed by the two-legged piano stool (half-sandwich) complex CpML2 upon light irradiation.8–11 Since the CpML complexes can be easily prepared for experiments,11–14 it is thus not surprising that many experimental and theoretical chemists have investigated either the chemical synthesis or the energy sequences of these intermolecular E–H bond activation reactions.8–14 Nevertheless, most of the E–H bond insertion reactions by CpML2 organometallic compounds are heavily focused on their thermodynamical aspects, with a few discussions of their initially photochemical aspects. Indeed, to our knowledge, there has been little mechanistic study regarding the photolysis of the CpML2 complex,14–16 much less related theoretical research. In addition to the limitations of the spectroscopic instruments, there are many fundamental questions about the photolysis of CpML2 in hydrosilane solution that need to be answered. For instance, how does a photo-excited CpML2 molecule go from the excited state to the ground singlet state? And, how does a spin state of the CpML intermediate play a role in its photochemical oxidative addition reactions?

Theoretical considerations should thus help experimental chemists to gain a better understanding for the mechanisms of the photochemical decarbonylation reactions of the CpML2 complexes. Until now, however, there have been no publications on theoretical interpretations for such photochemical mechanisms.8–14 The lack of theoretical investigations could be because the sophisticated computational methods for such photochemical reactions studies have not been suitable until recently. In particular, the photochemical activated systems involve transition metal atoms (concerning the spin–orbit coupling). The current work thus undertakes an examination of the mechanisms for the photochemical CO-extrusion reaction of the group 9 \(\text{d}^8\) transition metal complex, \(\eta^5\text{-C}_5\text{M}(\text{CO})_2\) (M = Co, Rh, and Ir) as well as its oxidative addition of a Si–H bond in trimethylsilane, eqn (1).
II. Methodology

Since the photochemical reaction paths involve the singlet ground state as well as the exited singlet and triplet states, the *ab initio* CASSCF (the complete-active-space SCF) program released in GAUSSIAN 09 is utilized in the presence of this study. That is, the stationary point structures on the S₀ and S₁ (for Rea-Rh-S₀ and Rea-Ir-S₀ molecules) and the S₀ and T₁ (for Rea-Co-S₀ molecule) potential energy surfaces are investigated at the CASSCF/Def2-SVPD level of computation.¹¹

The electronic structure of an organometallic “half-sandwich” complex of the type CpML₂ having only 18 electrons in their valence shell has already been discussed elsewhere,²²-³⁴ and is shown in detail in Fig. 1. The active space that needed to properly represent the ground and the lowest excited states of Rea-Co-S₀, Rea-Rh-S₀, and Rea-Ir-S₀ contains twelve electrons in eleven (bonding and antibonding metal d) orbitals. That is to say, according to the valence orbitals given in Fig. 1, the active space for the whole molecular system (one antibonding state-averaged CAS(12,11) mode for the active space for the half-sandwich two-legged-piano-stool 5-CpM(CO)₂ molecule is is carried out. As a result, the relative energies mentioned in this paper are those calculated at the MP2-CAS/Def2-TZVPPD level, using the CAS/Def2-SVPD geometry. The active space for each point used in this study is stated above. In consequence, they are abbreviated as MP2-CAS and CAS, respectively. The Cartesian coordinates (CAS) as well as the CAS and MP2-CAS energetics are given in ESL.†

In order to compare the MP2-CAS MP2-CAS singlet-triplet energy difference for the η⁵-CpCo(CO)₂ complex at different levels of theory, two kinds of density functional theory (DFT) and basis sets are used in this work. That is, B3PW91/Def2-TZVPPD,⁶⁶,⁶⁷ and B3LYP/DZP-DKH.⁶⁸,⁶⁹ The reason for choosing them is because they have been proved to be reliable for examining the relative energetics.⁷⁰ Their Cartesian coordinates and energetics are also collected in ESL.†

III. Results and discussion

(1) Mechanism for the photoactivation reaction of η⁵-CpCo(CO)₂ in the triplet state channel

We first study the photodecarbonyl reaction and the Si–H bond activation reaction of the half-sandwich two-legged-piano-stool CpCo(CO)₂ complex with trimethylsilane. When the CpCo(CO)₂ molecule absorbs light, it may jump directly from the singlet ground state to the excited states, which is called the Frank-Condon (FC) region and still has the geometry of its singlet ground state. The MP2-CAS computations are thus used in this work to compute its vertical excitation energies. As shown in the left-hand side of Fig. 2, the MP2-CAS results display eight electronic states that are achievable around the energies of a 325 nm photon: four triplet states (kcal mol⁻¹); Co-T₁-FC (42.8), Co-T₂-FC (47.1), Co-T₃-FC (69.4), and Co-T₄-FC (122.7), and four singlet states (kcal mol⁻¹); Co-S₁-FC (74.5), Co-S₂-FC (84.4), Co-S₃-FC (93.4), and Co-S₄-FC (95.5). Since the spin-allowed absorption cross-sections are well accepted to be larger than those for spin-forbidden excitations, photolysis thus advances CpCo(CO)₂ from the singlet ground state to an excited singlet state (S₁). Then, this dicarbonyl complex relaxes to the T₁ state (Co-T₁-Min). Our calculations estimate the energy of Co-T₁-Min is about 2.6 kcal mol⁻¹ above the ground-state minimum (Co-S₀-Rea). Also, we have used density functional theory to test the energy difference between the singlet and triplet η⁵-CpCo(CO)₂ species, *i.e.*, B3PW91/Def2-TZVPPD, and B3LYP/DZP-DKH. On the basis of these

![Image](https://example.com/image1.png)
computations (ESI†), the free energy of the singlet \( \eta^5\)-CpCo(CO)\(_2\) compound is computed to be lower than that of the triplet \( \eta^5\)-CpCo(CO)\(_2\) species by about 15 (B3PW91/Def2-TZVPPD)\(^{66,67}\) and 8.6 (B3LYP/DZP-DKH)\(^{68,69}\) kcal mol\(^{-1}\), respectively. Again, this reveals that its CO-photoextrusion reaction starts on the triplet state energy surface. Indeed, according to the available experiments,\(^{24–28}\) it was found that excitation of this molecule at 325 nm (\(78.0\) kcal mol\(^{-1}\)) leads to the generation of a \( \eta^5\)-CpCo(CO) intermediate in the triplet electronic state.

As seen in Fig. 2, the Co-T\(_1\)-Min complex then undergoes a Co–CO bond cleavage (2.066 Å) via a transition state (Co-T\(_1\)-TS1). From this transition state point, the intermediate complex may go forward three possible reaction pathways (i.e., path I, path II, and path III in Fig. 2) in order to undergo an oxidative addition reaction with trimethylsilane to produce the final insertion product (Co-S\(_0\)-Pro).

In path I, as seen in Fig. 2, the triplet Co-T\(_1\)-Min molecule can dissociate one CO ligand to produce two products: one triplet CO molecule and one singlet \( \eta^5\)-CpCo(CO) intermediate (Co-S\(_0\)-Int). The relative energy of the final products \([\text{CO}^3 + \text{Co-S}_0\text{-Int}]\) is, however, estimated to be 87 kcal mol\(^{-1}\) above the irradiated energy (325 nm = 88 kcal mol\(^{-1}\)).\(^{24–28}\) As a result, the present computational evidence reveals that the photo-excited energy of Co-S\(_0\)-Rea at 325 nm is unable to generate one triplet CO and one singlet Co-S\(_0\)-Int. Therefore, our theoretical finding anticipates that no such photoproducts can be detected in the photochemical activation reactions for \( \eta^5\)-CpCo(CO)\(_2\), which has been confirmed by the available experimental reports.\(^{24–28}\)

For convenience, the mechanism for path I of the Co-S\(_0\)-Rea complex can be expressed as follows:

Co system-path I: Co-S\(_0\)-Rea + [Si]\(^1\) + hv → Co-T\(_1\)-FC + [Si]\(^1\) → Co-T\(_1\)-Min + [Si]\(^1\) → Co-T\(_1\)-TS1 + [Si]\(^1\) → Co-S\(_0\)-Int + [CO]\(^3\) + [Si]\(^1\)
In the second pathway, path II, the triplet Co-T1-Min complex can undergo one CO ligand cleavage to produce one singlet CO and one triplet Co-T1-Int intermediate through the transition state [Co-T1-TS1]. The MP2-CAS data indicate that the Co-T1-Int + [CO] point is computed to be about 10 kcal mol\(^{-1}\) higher than that of Co-S0-Rea. Then, the triplet Co-T1-Int interacts with (CH\(_3\))\(_3\)Si–H to generate the precursor complex.
(Co-T1-Cpx) in the triplet state. Subsequently, this triplet complex encounters a triplet transition state (Co-T1-TS1) through the Co-T1/S0-1 intersystem crossing to form the final singlet photoproduct (Co-S0-Pro). On the basis of the MP2-CAS computations, path II is anticipated to be energetically accessible. The reason for this is once the initial reactants (Co-S0-Rea + [Si]) absorb light of 325 nm (= 88 kcal mol⁻¹) wavelength, they can obtain enough energy to overcome the barrier height (5.7 kcal mol⁻¹) from Co-T1-Cpx to Co-T1-TS2 in path II. In consequence, the mechanism for path II for both photochemical decarbonyl reaction and the Si-H bond activation reaction of η⁵-CpCo(CO)₂ is given as follows:
Co system-path II: Co-S0-Rea + [Si]1 + hν → Co-T1-FC + [Si]1 → Co-T1-Min + [Si]1 → Co-T1-TS1 + [Si]1 → Co-T1-Int + [CO]1

In path III, on the other hand, after the Co–CO bond breaking (Co-T1-TS1), the intersystem crossing from the triplet state to the singlet state occurs in the region of the T1/S0 intersection (Co-T1/S0-2), as depicted in Fig. 2. By way of this crossing point, the triplet η5-CpCo(CO)2 complex separates into one singlet η5-CpCo(CO) (Co-S0-Int) intermediate and one singlet CO molecule. Trimethylsilane is subsequently coordinated to the central cobalt atom of the Co-S0-Int species in the pattern of an η2 to generate a singlet precursor complex (Co-S0-Cpx). As a result, the Si–H bond of (CH₃)₃Si(H) is broken through a singlet transition state (Co-S0-TS1) to produce the final oxidative addition product (Co-S0-Pro). The MP2-CAS data reveal that the energies of intermediates (Co-S0-Int + CO + (CH₃)₃Si(H)), the precursor complex (Co-S0-Cpx + CO), the transition state (Co-S0-TS1 + CO) and the final insertion product (Co-S0-Pro + CO) relative to that of the starting materials (Co-S0-Rea + (CH₃)₃Si(H)) are computed to be 37, 18, 122, and 1.4 kcal mol⁻¹, respectively. That is to say, the theoretical
calculations indicate that the energy of Co-S0-Cpx (19 kcal mol\(^{-1}\)) is much lower than that of its further activation barrier (105 kcal mol\(^{-1}\)) from Co-S0-Cpx to Co-S0-TS1 in path III. Our computational evidence, therefore, predicts that this singlet cobalt precursor complex (Co-S0-Cpx) should be easily located, which has already been verified by the available experimental observations.\(^{24-28}\) Furthermore, the theoretical data given in Fig. 2 show that the activation energy of Co-S0-TS1 is 105 kcal mol\(^{-1}\) much higher than the irradiation energy (325 nm = 88 kcal mol\(^{-1}\)) of the corresponding reactants (Co-S0-\textit{Rea} + (\textit{CH}3)\textit{Si(H)}). That is to say, compared to the excited promotion energy, the barrier height from Co-S0-Cpx to Co-S0-TS1 represented in path III cannot be surmounted. Accordingly, path III is energetically unfavorable for such photochemical oxidative additions of the \(\eta^5\text{-Cp}Co(CO)\) compound. Thus, the present theoretical investigations suggest that the mechanism of path III should proceed as follows:

Co system-path III: Co-S0-\textit{Rea} + [\textit{Si}]\textit{I} + \textit{hv} \rightarrow Co-T1-FC + [\textit{Si}]\textit{I} \rightarrow Co-T1-Min + [\textit{Si}]\textit{I} \rightarrow Co-T1-TS1 + [\textit{Si}]\textit{I} \rightarrow Co-T1/\textit{S0-2} + [\textit{CO}]\textit{I} + [\textit{Si}]\textit{I} \rightarrow Co-S0-\textit{Int} + [\textit{CO}]\textit{I} + [\textit{Si}]\textit{I} \rightarrow Co-S0-Cpx + [\textit{CO}]\textit{I} \rightarrow Co-S0-TS1 + [\textit{CO}]\textit{I} \rightarrow Co-S0-\textit{Pro} + [\textit{CO}]\textit{I}

In brief, the above computations reveal that once the \(\eta^5\text{-CpCo(CO)}\) \(\text{(Co-S0-\textit{Rea})}\) molecule absorbs light, it can easily generate a coordinatively unsaturated 16-electron \(\eta^5\text{-CpCo(CO)}\) fragment in either the triplet or the singlet excited state, \(\text{via the loss of a CO molecule upon photolysis. In a similar way, this dynamic half-sandwich intermediate can easily undergo oxidative addition to the Si–H bond of H–Si(\text{Me})_3. Three reaction routes (paths I, II, and III) can be used for interpreting the mechanisms of such CO-photoextrusion reaction as well as the Si–H bond activation reaction. The present theoretical evidence demonstrate that only path II, which can form the triplet Co-T1-\textit{Int} fragment, is the most energetically favorable reaction path for the photochemical reactions. On the other hand, both path I and path III, which can produce the singlet Co-S0-\textit{Int} species, are energetically unfeasible for the generation of Co-S0-\textit{Pro}. In other words, our theoretical investigations strongly indicate that it is only the triplet species, \(\eta^5\text{-CpCo(CO)}\) \(\text{(Co-T1-\textit{Int})}\), that play a decisive role in the photochemical Si–H bond activation reaction by the organometallic compound, \(\eta^5\text{-CpCo(CO)}\). These theoretical findings are in excellent agreement with the experimental observations reported by the team led by Harris.\(^{24-28}\)
(2) Mechanism for the photoactivation reaction of \( \eta^5\)-CpRh(CO)\(_2\) in the singlet state channel

For comparison with the case of \( \eta^5\)-CpCo(CO)\(_2\), we next examine the mechanism of the photoactivation reaction of \( \eta^5\)-CpRh(CO)\(_2\) (Rh-S\(_0\)-REA) towards trimethylsilane. The same theoretical method (MP2-CAS) is utilized to explore the potential energy surfaces of Rh-S\(_0\)-REA for its Si–H bond activation reactions, which are all shown in Fig. 4. The selected geometrical parameters for the photochemical activation reaction of Rh-S\(_0\)-REA with trimethylsilane are given in Fig. 5. According to some available experimental observations, Harris and coworkers reported that the irradiation of light to Rh-S\(_0\)-REA is 295 nm (= 96.9 kcal mol\(^{-1}\)).

As seen in the left-hand side of Fig. 4, the MP2-CAS computational data indicates that the relative FC energies (kcal mol\(^{-1}\)) of the electronic states increase in the order: Rh-S\(_1\)-FC (73.0) < Rh-S\(_2\)-FC (78.0) < Rh-S\(_3\)-FC (87.6) < Rh-S\(_4\)-FC (94.7) < Rh-T\(_3\)-FC (104.0) < Rh-T\(_2\)-FC (104.5) < Rh-S\(_5\)-FC (105.6). The MP2-CAS results reveal that only the energy of the first excited triplet state (i.e., Rh-T\(_1\)-FC) is lower than that of its photoirradiated light (295 nm). In addition, we did not calculate the triplet energy surface for the photodecarbonylation reaction of the \( \eta^5\)-CpRh(CO)\(_2\) (Rh-S\(_0\)-REA) complex in the present work. First, on the basis of the available experimental results, Harris and coworkers reported that the irradiation of light to Rh-S\(_0\)-REA is 295 nm (= 96.9 kcal mol\(^{-1}\)).

As seen in the left-hand side of Fig. 4, the MP2-CAS computational data indicates that the relative FC energies (kcal mol\(^{-1}\)) of the electronic states increase in the order: Rh-S\(_1\)-FC (57.8) < Rh-S\(_2\)-FC (73.0) < Rh-T\(_1\)-FC (78.0) < Rh-S\(_3\)-FC (87.6) < Rh-S\(_4\)-FC (94.7) < Rh-T\(_3\)-FC (104.0) < Rh-T\(_2\)-FC (104.5) < Rh-S\(_5\)-FC (105.6). The MP2-CAS results reveal that only the energy of the first excited triplet state (i.e., Rh-T\(_1\)-FC) is lower than that of its photoirradiated light (295 nm). In addition, we did not calculate the triplet energy surface for the photodecarbonylation reaction of the \( \eta^5\)-CpRh(CO)\(_2\) (Rh-S\(_0\)-REA) complex in the present work. First, on the basis of the available experimental results, Harris and coworkers reported that the irradiation of light to Rh-S\(_0\)-REA is 295 nm (= 96.9 kcal mol\(^{-1}\)).

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predicted to be 7.6 kcal mol\(^{-1}\) above the energy of the corresponding reactants (\(\text{Rh-S}_0\text{-Rea} + (\text{CH}_3)_3\text{Si(H)}\)). Then, \(\text{Rh-S}_0\text{-Cpx}\) undergoes the oxidative addition into the Si–H bond of trimethylsilane via the transition state, \(\text{Rh-S}_0\text{-TS}\). Our computational findings suggest that the relative energies (kcal mol\(^{-1}\)) of \(\text{Rh-S}_0\text{-Cpx}\), \(\text{Rh-S}_0\text{-TS}\) and \(\text{Rh-S}_0\text{-Pro}\) with respect to the corresponding reactants are 7.6, 67.2, and –5.4, respectively. As a result, from the reaction profiles given in Fig. 4, it is clear that the photoexcitation energy at 295 nm of the \(\eta^5\)-CpRh(CO)\(_2\) reactant has sufficient internal energy to overcome the energy barrier from \(\text{Rh-S}_0\text{-Cpx}\) to \(\text{Rh-S}_0\text{-TS}\). In brief, the theoretical observations demonstrate that the conical intersection mechanism plays a decisive role in the mechanism of the Si–H bond-activation reaction of photogenerated singlet \(\eta^5\)-CpRh(CO)\(_2\) with trimethylsilane. Therefore, the mechanism of singlet photochemical oxidative addition reaction of \(\eta^5\)-CpRh(CO)\(_2\) can be represented as follows:

**Rh system:**
\[
\text{Rh-S}_0\text{-Rea} + [\text{Si}]^1 + \text{hv} \rightarrow \text{Rh-S}_1\text{-FC} + [\text{Si}]^1 \\
\text{Rh-S}_1\text{/S}_0\text{-CT} + [\text{Si}]^1 \rightarrow \text{Rh-S}_0\text{-Int} + [\text{CO}]^1 + [\text{Si}]^1 \rightarrow \text{Rh-S}_0\text{-Cpx} + [\text{CO}]^1 \rightarrow \text{Rh-S}_0\text{-TS} + [\text{CO}]^1 \rightarrow \text{Rh-S}_0\text{-Pro} + [\text{CO}]^1
\]

### 3(3) Mechanism for the photoactivation reaction of \(\eta^5\)-CpIr(CO)\(_2\) in the singlet state channel

In spite of the fact that the photochemical behavior of \(\eta^5\)-CpIr(CO)\(_2\) (Ir-S\(_0\)-Rea) has been experimentally reported elsewhere, unlike its cobalt and rhodium counterparts, the photodecarbonyl mechanism of Ir-S\(_0\)-Rea has not been investigated neither experimentally nor theoretically.

In this work, the same computational method (MP2-CAS) is used to theoretically investigate the potential energy surfaces of \(\eta^5\)-CpIr(CO)\(_2\) for its photochemical oxidative reaction. The computational reaction routes and the related geometrical
parameters for the photoactivation reaction of Ir-S0-Rea with trimethylsilane are schematically represented in Fig. 6 and 7, respectively. To enable comparisons with the previous η⁵-CpCo(CO)₂ (Co-S0-Rea) and η⁵-CpRh(CO)₂ (Rh-S0-Rea) model systems, the irradiation of light to Ir-S0-Rea is assumed to be 295 nm (= 96.9 kcal mol⁻¹), as shown on the left-hand side of Fig. 6.

On the basis of the MP2-CAS computational data, Fig. 6 demonstrates that the lowest vertically excited energy state in the FC region is Ir-S1-FC (91.8 kcal mol⁻¹), whose energy is notably lower than that of its irradiation of light (96.9 kcal mol⁻¹). That is to say, the present theoretical observations indicate that the half-sandwich reactant complex (Ir-S0-Rea) is initially irradiated to its lowest lying singlet excited state (Ir-S1-FC). In the current work, we thus concentrate below on the singlet channel for the photochemical activation reaction of Ir-S0-Rea with Si(CH₃)₃(H) from now on.

Subsequently, from the Ir-S1-FC point, this excited species relaxes to the conical intersection point (Ir-S1/S0-CI), whose energy is calculated to be about 52 kcal mol⁻¹ relative to that of its corresponding reactant. Funneling through the Ir-S1/S0-CI point, several reaction routes on the ground-state energy surface may be foreseen by following its derivative coupling and the gradient difference vectors, which are already collected in Fig. 7. It is apparent from Fig. 7 that the main contribution of the gradient difference vector is the bending motions of two C–O bonds that result in a vibrationally hot Ir-S0-Rea molecule, whereas the derivative coupling vector corresponds to an Ir–CO bond cleavage. Therefore, following the derivative coupling vector from Ir-S1/S0-CI (Fig. 7) can give rise to the generation of one singlet CO molecule and one singlet half-sandwich monocarbonyl η⁵-CpIr(CO) intermediate (Ir-S0-Int). The MP2-CAS computations, which are given in Fig. 6, reveal that this Ir-S0-Int + CO + Si(CH₃)₃(H) point is 32.0 kcal mol⁻¹ above the corresponding singlet reactants. Then the Ir-S0-Int species interacts with Si(CH₃)₃(H) to yield a precursor complex, Ir-S0-Cpx, whose energy is estimated to be about 18 kcal mol⁻¹ with respect to the corresponding singlet state species. Finally, this activated complex undergoes its oxidative addition reaction via a transition state (Ir-S0-TS) to lead to the formation of a photoproduct, Ir-S0-Pro, as demonstrated in Fig. 6. Our MP2-CAS data indicate that the energy barrier from Ir-S0-Cpx to Ir-S0-TS and the reaction enthalpy of Ir-S0-Pro are estimated to be about 26 and −12 kcal mol⁻¹, respectively. From the reaction profile given in Fig. 6, it is clear that the Ir-S0-Rea molecule has sufficient internal energy (38 kcal mol⁻¹) to overcome the energy barrier between Ir-S0-Cpx and Ir-S0-TS (26 kcal mol⁻¹) to reach the final insertion product (Ir-S0-Pro), after the photoexcited Ir-S0-Rea relaxes to the CI point (Ir-S1/S0-CI). Accordingly, the mechanism of the photoactivation reaction of η⁵-CpIr(CO)₂ with trimethylsilane can be described as follows: [Si]¹ stands for Si(CH₃)₃(H) at the singlet state.

IV. Conclusion

The photochemical Si–H bond activation reactions by the group 9, d⁶ organometallic molecules, η⁵-CpM(CO)₂ (M = Co, Rh, and Ir), have been studied by using the CAS as well as MP2-CAS computational methods. Taking all the model conclusions obtained in this work together yield the following summary:

1. Our model computations demonstrate that upon absorption of a photon of light, η⁵-CpCo(CO)₂ (Co-S0-Rea) is promoted vertically to one higher excited state and then relaxes to the triplet FC point, Co-T1-FC. From this point, this cobalt complex returns to the triplet minimum species, Co-T1-Min. After its photochemical decarbonylation, three important reaction pathways (paths I, II, and III) have been considered to examine its oxidative addition of a Si–H bond with Si(H)Me₅.

The theoretical observations indicate that Co-S0-Rea initiates from the excited triplet state surface and finally changes to the singlet ground-state pathway. In other words, the intersystem crossing between the triplet (T₁) and singlet (S₀) surfaces must play a vital role in describing the mechanisms for the photochemical CO-extrusion and oxidative addition reactions of the Co-S0-Rea complex. Our theoretical findings strongly suggest that path II is the most energetically favorable reaction route for such alkylsilane activation reactions. In particular, the computational examinations reveal that the triplet monocarbonyl species ([η⁵-CpCo(CO)]⁺) plays a dominant role, but the corresponding singlet intermediate ([η⁵-CpCo(CO)]⁻) plays no role, in the photochemical CO-extrusion reaction and its subsequent activation reaction for a Si–H bond in alkylsilane. The above theoretical conclusions have previously been verified by some experimental findings.²⁴-³⁶

2. On the other hand, after the CO-photoextrusions of η⁵-CpRh(CO)₂ (Rh-S0-Rea) and η⁵-CpIr(CO)₂ (Ir-S0-Rea), our theoretical findings demonstrate that their half-sandwich monocarbonyl intermediates (Rh-S0-Int and Ir-S0-Int) should still proceed on the singlet energy surfaces. In other words, the conical intersection plays a central role in determining the mechanisms of their photochemical oxidative addition reactions with alkylsilanes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are grateful to the National Center for High-Performance Computing of Taiwan for generous amounts of computing time, and the Ministry of Science and Technology of Taiwan for the financial support. One of the author (Ming-Der Su) also wishes to thank Professor Michael A. Robb, Dr Michael J. Bearpark, Dr S. Wilsey, (University of London, UK) and Professor Massimo Olivucci (Università degli Studi di Siena, Italy) for their encouragement and support during his stay in London. Special thanks are also due to reviewers 1 and 2 for very helpful suggestions and comments.
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