Theoretical Mechanistic Studies on Methyltrioxorhenium-Catalyzed Olefin Cyclopropanation: Stepwise Transfer of a Terminal Methylene Group

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ⓢ Supporting Information

ABSTRACT: Methyltrioxorhenium (MTO)-catalyzed transfer of a methylene group to styrene has been computationally found to preferably follow a stepwise mechanism to give phenylcyclopropane via formation of a pseudo-metallacyclic intermediate and subsequent alkylative cyclization. The present result serves as the first theoretical evidence for d^0 transition metal mediated transfer of methylene as a terminal form rather than a metal carbene or carbenoid fashion, accompanied by the cleavage of a $H_2C=O$ double bond. The mechanism presented here is in contrast to the carbenoid or metal carbene promoted methylene transfer and to the MTO-catalyzed isoelectronic atom (group) transfer in $MeRe(O)_2(\eta^2\text{-O}-NH)$ or $MeRe(O)_2(\eta^2\text{-O}-O)$. This study not only enriches the chemistry of olefin cyclopropanation and the MTO-catalyzed group (atom) transfer event but also sheds new light on the reaction chemistry of formaldehyde.
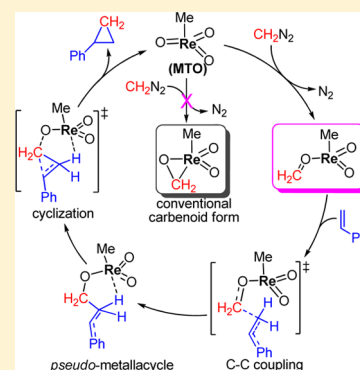
INTRODUCTION

The cyclopropane skeleton is an important unit because of its appearance in a wide variety of biologically active molecules, and studies on cyclopropanation reactions have therefore received intense attention.[1,2] Simmons–Smith-type cyclopropanation (Scheme 1a)[3−6] and transition metal catalyzed olefin cyclopropanation with diazo reagents[1a,c,e,f] (Scheme 1b) are two typical types of metal-mediated cyclopropanation reactions, which are highly useful synthetic strategies to construct cyclopropane-containing frameworks. An understanding of the exact reaction mechanism is an essential aspect of chemistry in general and of catalytic processes in particular. As to carbenoid-promoted cyclopropanation reaction by the Simmons–Smith-type reagents (**I**, $RMCH_2X$; M = Zn, Li, Al, Sm; X = halogen, OR), two types of mechanisms have long been discussed. One is direct methylene transfer, and the other is carbometalation (Scheme 1a).[3−6] The concerted methylene-transfer pathway is a $[1 + 2]$ addition through a butterfly-type transition state to give the cyclopropanation product, whereas the two-step carbometalation mechanism involves an intermediate followed by an intramolecular substitution to furnish the cyclopropanation. The mechanistic dichotomy for cyclopropanation reactions by Simmons–Smith-type reagents was suggested to be metal dependent. In light of previous studies, it is hereto accepted that transition-metal-catalyzed reactions of an olefin with diazo compounds occur via formation of a metal
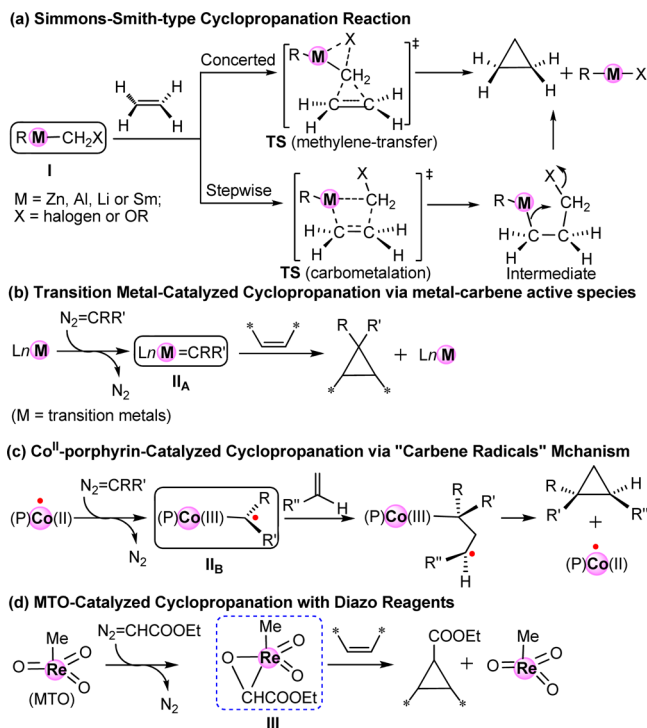
carbene active species (**II$_A$**, $L_nM=CRR'$; M = transition metal) and subsequent transfer of the carbene unit to the incoming olefin along with a concerted or stepwise pathway[1a,7] (Scheme 1b). Recently, the "carbene radical" mechanism in the Co^{II}(Pro)-catalyzed system was also proposed by Zhang and Bruin et al. on the basis of both theoretical and experimental studies (Scheme 1c).[8]

It has been proven for many years that transition metal catalyzed reactions of olefins with diazo compounds could produce cyclopropanation products via transfer of the CRR' group (R, R' = H, alkyl). Such cyclopropanation reactions catalyzed by many transition metals, such as copper,[9] rhodium,[10] ruthenium,[11] and cobalt,[8,12] have been well documented via both experimental and theoretical studies. On the other hand, in rhenium chemistry, although methyltrioxorhenium (MeReO$_3$, MTO)-catalyzed atom (group) transfer, such as oxygen transfer, has been extensively studied,[13] the rhenium-promoted CRR' group transfer to achieve olefin cyclopropanation has remained relatively less explored[14,15] and MTO-catalyzed cyclopropanation has been hitherto proposed to occur via formation of $MeRe(O)_2(\eta^2\text{-CHR}-O)$ (**III**) species and subsequent transfer of the CHR group (Scheme 1d).[13a−c,14] The reaction mechanism of MTO-

Scheme 1. Metal-Mediated Cyclopropanation of Olefins

(a) Simmons-Smith-type Cyclopropanation Reaction

M = Zn, Al, Li or Sm;
X = halogen or OR

(b) Transition Metal-Catalyzed Cyclopropanation via metal-carbene active species

(M = transition metals)

(c) Co^{II}-porphyrin-Catalyzed Cyclopropanation via "Carbene Radicals" Mchanism

(d) MTO-Catalyzed Cyclopropanation with Diazo Reagents

catalyzed atom (group) transfer is diverse and fascinating. For example, DFT calculations revealed a concerted mechanism for the transfer of an oxygen atom from $[MeRe(O)_2(\eta^2\text{-}O\text{-}O)]$ (III_O) to ethylene and ended a longstanding argument on the concerted or stepwise issue.[13d,16] However, a detailed mechanism of the MTO-catalyzed transfer of the CHR group to olefin has remained unclear to date, possibly due to the difficulty in exploration of the reaction potential energy surface (PES), as far as we are aware.

Intrigued by the diverse and fascinating mechanism of MTO-catalyzed atom (group) transfer and the importance of cyclopropanation reactions, we focused on the rhenium chemistry involved in the MTO-catalyzed olefin cyclization using diazomethane to generate the III-like $MeRe(O)_2(\eta^2\text{-}CH_2\text{-}O)$ ($IIIa$) species, which is isoelectronic with III_O and suitable for investigation of the transfer mechanism of the methylene. In this study, having achieved a good agreement with the experimental product allowed us to rationalize the MTO-catalyzed cyclopropanation mechanism, which stands in sharp contrast to previously reported mechanisms operating by the transition metal mediated olefin cyclopropanation reaction.

■ COMPUTATIONAL DETAILS

The scaled hypersphere search (SHS) method enables one to globally explore reaction pathways on the potential energy surface (PES) by detecting anharmonic downward distortions (ADD) as a symptom of the chemical reaction.[17] For its application to larger systems, the large-ADD-following (LADD) technique has been introduced to the SHS method and the search for a reaction route can be executed at the low-energy region of the PES.[18] Such a technique has been applied to molecular clusters.[19] The combination of the ONIOM approach[20] and the LADD technique in the SHS method has been also achieved and applied to the BINAP system.[21] In this work, the LADD technique in the SHS method has been utilized to study the reaction of MTO with CH_2N_2. Some transition states involved in the reaction of styrene with $IIIa$ or $IIIb$ were found by a double-ended saddle-point search option, which is available in the SHS method. The geometry optimizations

were performed at the B3LYP[22]/BSI level. The B3LYP functional has showed good performance for Re(VII) systems[23] and has been widely utilized to investigate MTO-related reaction mechanisms.[24] In the BSI, the LanL2DZ basis set plus outer p function and one f function (exponent of 0.869), viz., (9s9p3d1f)/[3s3p2d1f], and the associated pseudopotential were used for the Re atom.[25] The 6-31G(d) basis set was used for the nonmetal atoms in the BSI. The subsequent analytic frequency calculations were performed for each stationary point to verify the minima and transition states and to get the thermodynamic data. To obtain more accurate energy, single-point calculations were carried out at the B3LYP/BSII level for optimized geometries. In the BSII, the basis set and associated pseudopotential for the Re atom is same as that in the BSI, whereas the larger basis set 6-311+G(d,p) was used for nonmetal atoms. Since activation free energies were computationally overestimated due to entropy contribution when we dealt with 2:1 (bimolecular) transformations, the reaction enthalpies were utilized to describe the energy profiles in the text. However, the free energies of the optimized stationary points involved in Scheme 2 and Figure 1 are also given in Tables S1 and S2 in Supporting Information for the estimation of entropy contributions in the current system. The enthalpies reported were computed at the B3LYP/BSII// B3LYP/BSI level, including enthalpy corrections from the B3LYP/BSI calculations. To consider the solvation effect, similar single-point calculations were carried out with the SMD model[26] (toluene solution, commonly used in transition metal catalyzed cyclopropanations of olefin) for some stationary points involved in important pathways. The results (see Figure S4 in the Supporting Information) indicate that the solvation by toluene has no significant effect on the energy profile. In an experimental work,[14] neat styrene was used as the solvent, which is similar to toluene with respect to their dielectronic constants ($\varepsilon = 2.47$ vs 2.38).[27] In view of this and an agreement between computation and experiment (vide infra), the effect of various solvents was not investigated further. The stabilities of wave functions were tested. Except for the SHS procedures, all of the calculations were carried out utilizing the Gaussian 09 program.[28]

■ RESULTS AND DISCUSSION

During our studies on PES, we found that the scaled hypersphere search (SHS) method is very efficient for automatic exploration of PES. To access the formation of III, the SHS method was utilized to model the reaction of MTO with CH_2N_2. As shown in Scheme 2, it was successfully found that a concerted pathway going through $TS[IIIa]$ (23.3 kcal/ mol) leads to the conventional carbenoid species $MeRe\text{-}(O)_2(\eta^2\text{-}CH_2\text{-}O)$ ($IIIa$), which is structurally similar to $IIIo$, having a three-membered metallacycle. This process is significantly exergonic by 41.9 kcal/mol. Unexpectedly, a stepwise pathway giving $MeRe(O)_2(\eta^1\text{-}O=CH_2)$ ($IIIb$) with

Scheme 2. Formation of IIIa,b^a
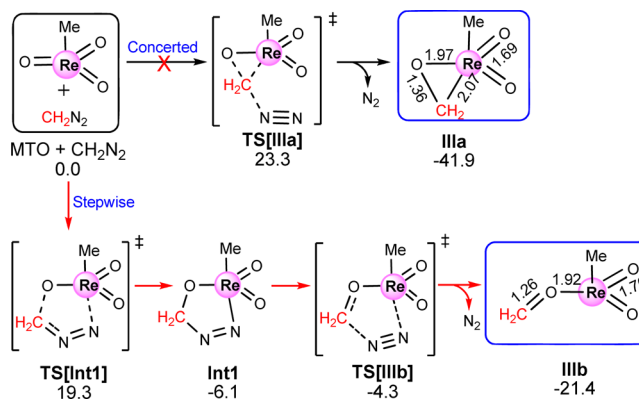
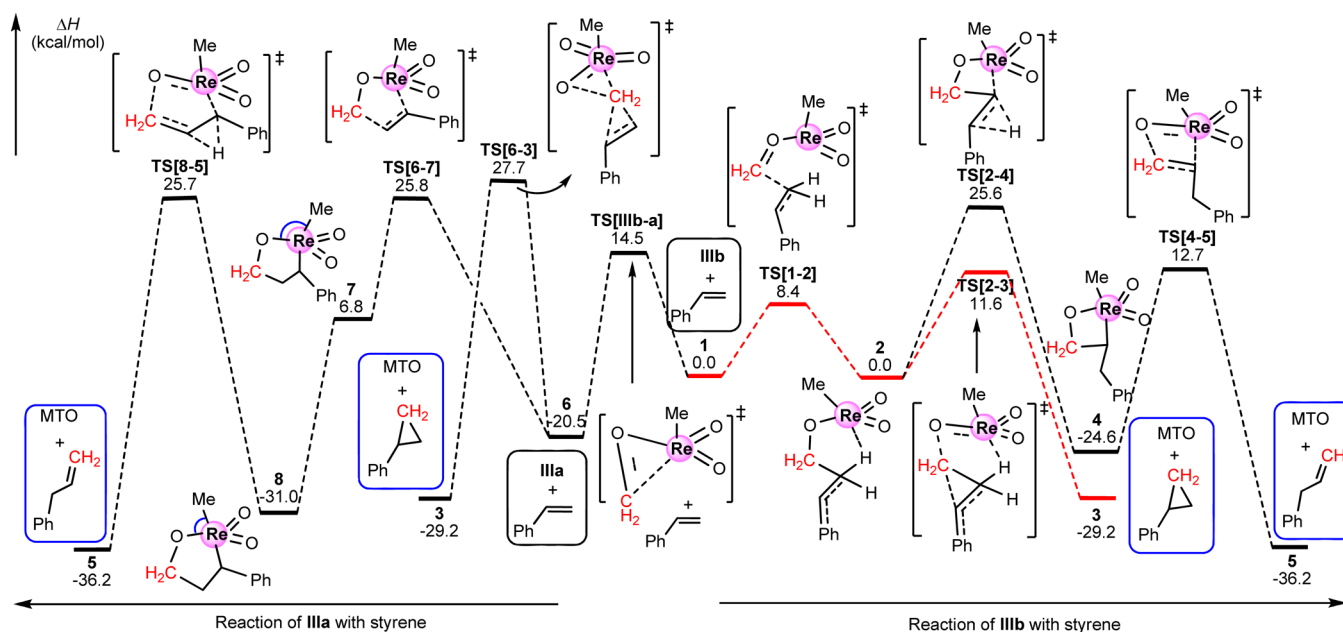^{a}Enthalpies are given in kcal/mol and distances in Å.

Figure 1. Computed energy profile (energies in kcal/mol) for the reaction of styrene with **IIIa,b** via CH$_2$ group transfer, respectively. The enthalpies are relative to the energy sum of **IIIb** and styrene molecule.
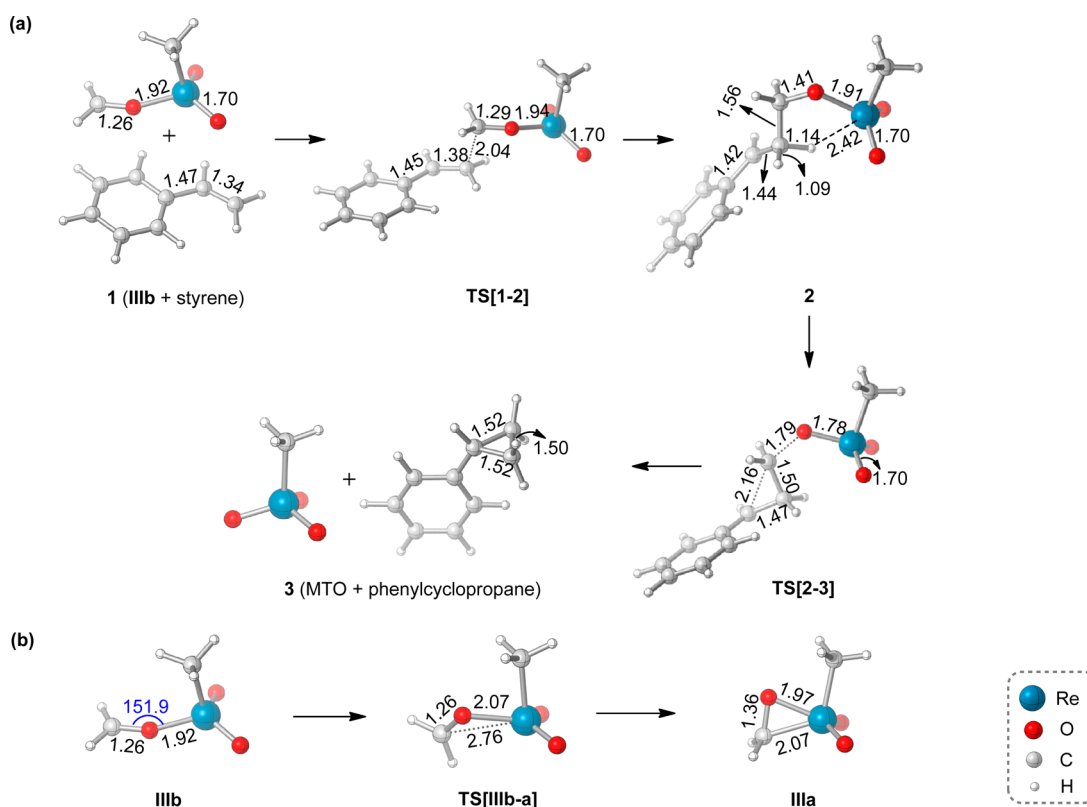

Figure 2. Computed structures for some key stationary points and transition states involved in Figure 1, with selected structural parameters given (distances in Å and angle in deg): (a) structures for the favorable pathway of the reaction of **IIIb** with styrene to give MTO and phenylcyclopane; (b) Structures for the conversion of **IIIb** to **IIIa**.

a terminal CH$_2$ group[29] has been also found for the reaction of MTO with CH$_2$N$_2$. It is notable that the formation of **IIIb** via **TS[Int1]** (19.3 kcal/mol) and **Int1** is kinetically more favorable than the concerted pathway via **TS[IIIa]** (23.3 kcal/mol) leading to **IIIa**. The results derived from pure M06L and hybrid M06 functionals having good performance in the treatment of

the organometallic system[30] also indicate that **TS[Int1]** is lower in energy than **TS[IIIa]** by 5.4 and 3.8 kcal/mol, respectively, therefore further suggesting the kinetic priority for the stepwise pathway. The generation of **IIIb** is significantly exothermic by 21.4 kcal/mol, although **IIIb** is less stable than **IIIa**.[31]
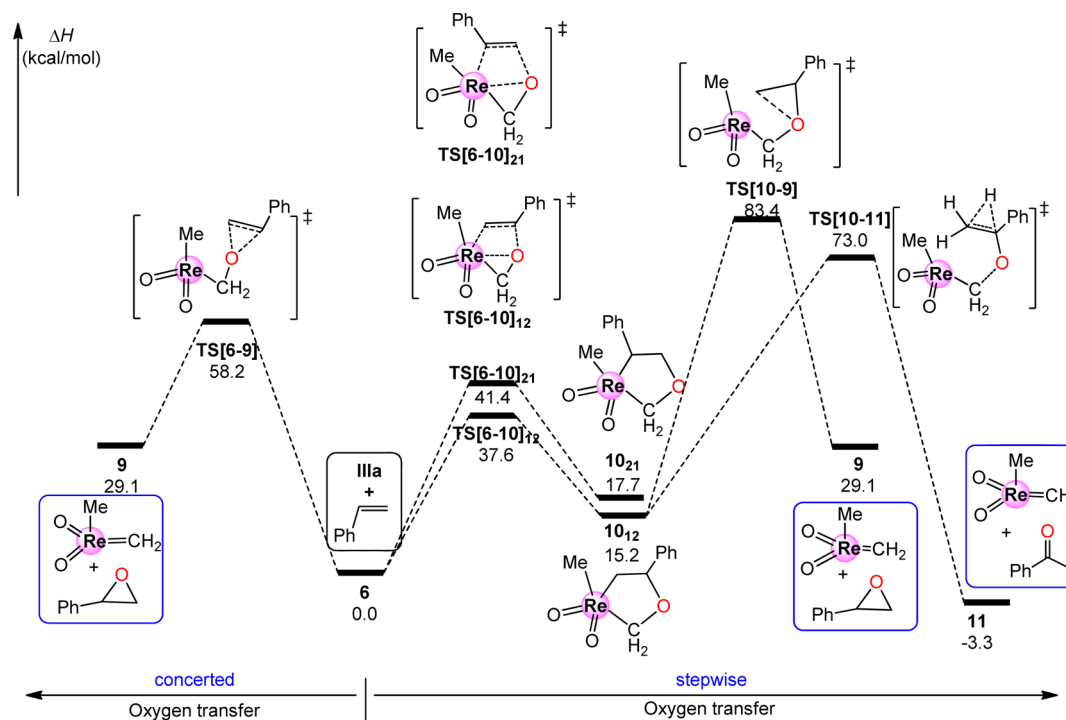
Figure 3. Computed energy profile (energies in kcal/mol) for the reaction of styrene with **IIIa** via oxygen transfer. The enthalpies are relative to the energy sum of **IIIa** and styrene molecule.

In view of the result that the reaction of MTO with CH_2N_2 yielded **IIIb** as a kinetically favorable product, the reaction of styrene with **IIIb** was computed. As shown in the right part of Figure 1, **1** (**IIIb** and styrene) directly goes through a $C(sp^2)-C(sp^2)$ coupling transition state (TS), **TS[1-2]** with an enthalpy barrier of 8.4 kcal/mol to give **2**. This step is almost an isoenergetic conversion. The intermediate **2** shows the agostic interaction Re⋯H−CHCHPh, which participates in the formation of a pseudo-metallacyclic moiety. A hydrogen transfer TS, **TS[2-4]** (with an enthalpy barrier of 25.6 kcal/mol), was located for the conversion of **2** to the intermediate **4** with a four-membered ring. Then, **4** might be converted to **5** via **TS[4-5]** through concerted cleavage of the Re−C and O−C bonds. Unexpectedly, it has been found that **2** preferably encounters a direct ring closure leading to **3**. The ring closure transition state, **TS[2-3]**, has a significantly lower enthalpy barrier (11.6 kcal/mol) in comparison to that (25.6 kcal/mol) for **TS[2-4]**, leading to **5** (see Figure 2a for the computed structures). Therefore, the reaction of **IIIb** with styrene favorably produces **3** (phenylcyclopropane and MTO) via intermediate **2** rather than generates **5** (allylbenzene and MTO) through **TS[2-4]**, showing a hydrogen transfer event.

Considering that **IIIa** features a conventional carbenoid structure and is more stable than **IIIb** (Scheme 2), the conversion of **IIIb** to **IIIa** and the reaction of **IIIa** with styrene have been also investigated for a comparison. As shown in the left part of Figure 1, the transformation of **1** (**IIIb** + styrene) to **6** (**IIIa** + styrene), which is actually the conversion of **IIIb** to **IIIa**,[32] occurs via **TS[IIIb-a]** with an enthalpy barrier of 14.5 kcal/mol (see Figure 2b for computed structures). The reaction of **6** goes through a transition state, **TS[6-3]**, to produce **3**, which could be also derived from **IIIb** (vide supra). This concerted process has an enthalpy barrier of 48.2 kcal/mol. The stepwise pathway is also computed for this reaction. The reaction of **6** overcomes **TS[6-7]**[33] with an enthalpy barrier of

46.3 kcal/mol relative to **6** to give intermediate **7** (left side of Figure 1). Complex **7**, with a five-membered ring motif, could further convert to the more stable complex **8**, during which the metallacycle was retained. This conversion is achieved via the vibration of the methyl group, which made the Me−Re−OCH$_2$ angle smaller in **8** (126.9° in **7** and 74.6° in **8**). The complex **8** further undergoes a hydrogen transfer transition state, **TS[8-5]** (with an enthalpy barrier of 56.7 kcal/mol), leading to **5**. One may note that the reverse conversion, from **6** to **1** (viz., from **IIIa** to **IIIb**), has an enthalpy barrier of 35.0 kcal/mol. This barrier is significantly lower than that for the transformation of **6** to **3** via **TS[6-3]** (48.2 kcal/mol) or to **5** via intermediate **8** (>46 kcal/mol). It is noteworthy that **3** is thermodynamically more stable than **6** by 8.7 kcal/mol. Kinetically, the formation of the former is also more favorable by 2.9 kcal/mol (**TS[2-3]** vs **TS[IIIb-a]**). That is, even if the carbenoid species **IIIa** appears in the reaction system, it could preferably isomerize to **IIIb** and then undergo further reactions. These results also indicate that **IIIb** has a higher reactivity toward styrene, although it is less stable in comparison with **IIIa**.

To assess the possibility for MTO-catalyzed epoxidation in the current system, the oxygen transfer event in the reaction of styrene with **IIIa** has been also investigated. As shown in Figure 3, both the concerted and stepwise pathways have enthalpy barriers of higher than 50 kcal/mol, suggesting that such an oxygen transfer to generate Re carbene speceis[34] seems unlikely. Therefore, methylene transfer rather than oxygen transfer occurs to give the cyclopropanation product in the current system, which is consistent with the experimental result showing the product of phenylcyclopropane derivatives when using $CH(COOEt)N_2$ as a diazo reagent.[14]

As discussed above, the reaction of $MeReO_3(CH_2)$ with styrene preferably produces phenylcyclopropane via a stepwise process showing a transfer of methylene as a terminal form in **IIIb** rather than as a conventional carbenoid fashion in **IIIa**.

Such a stepwise process features a pseudo-metallacyclic intermediate (**2**; Figure 1). More interestingly, the reaction mechanism proposed here stands in sharp contrast to the concerted mechanism of olefin epoxidation with [MeRe-(O)$_2$(η^2-O−O)] (**III$_O$**; Scheme 3a),[16] which is isoelectronic

Scheme 3. MTO-Catalyzed Atom (Group) Transfer Mechanism[16,35]
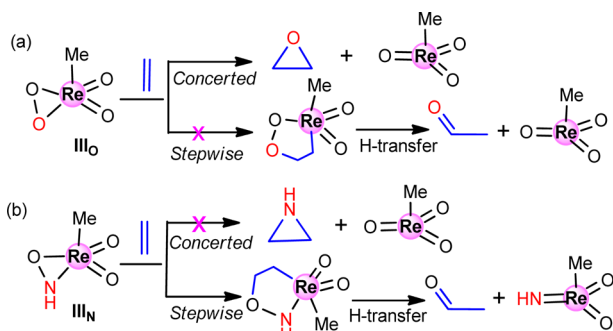
with **IIIa,b**. The result is also obviously different from the stepwise mechanism operating for the reaction of ethylene with another isoelectronic species [MeRe(O)$_2$(η^2-O−NH)] (**III$_N$**; Scheme 3b), giving aldehyde via formation of a metallacyclic intermediate and subsequent hydrogen transfer.[35] The reaction studied here goes through a pseudo-metallacyclic intermediate (**2**) and then encounters a direct ring closure to give the cyclic product rather than cycloaddition and subsequent hydrogen transfer. Such a new stepwise mechanism for cyclopropanation is distinctly different from that previously proposed for either catalytic methylene transfer via metal carbene[1a,c] (or carbene radical[8]) species or the carbenoid-promoted cyclopropanation using a Simmons−Smith-type reagent (RMCH$_2$X).[3−6] This work, for the first time, also demonstrates a d^0 transition metal mediated transfer of the CH$_2$ group as a terminal form rather than a carbenoid or metal carbene fashion,[36] accompanied by cleavage of the H$_2$C═O double bond,[37] which may also provide some new implications for the reaction chemistry of formaldehyde. It is noteworthy that the formation of **2**, which is stabilized by the Re···H−CHCHPh interaction and the phenyl-involved conjugated system (see Figure 2a for the structural parameters of **2**), activates the H$_2$C═O bond. In **2**, the CH$_2$ group of the CH$_2$O moiety attacks the electrophilic benzylidene carbon atom to eventually result in cleavage of the H$_2$C═O double bond. In this sense, both the formation and stability of **2** play an important role in the cleavage of the H$_2$C═O double bond.

To rationalize the proposed mechanism in this study, we further calculated the CHR-transfer process by using CH-(COOEt)N$_2$ as the dizao reagent to react with MTO. As expected, the stepwise pathway leading to **IIIb′** (analogous to **IIIb**, see Chart 1 and Scheme 2) is more kinetically favorable than the concerted pathway giving **IIIa′** (analogues to **IIIa**) by 6.2 kcal/mol (see Scheme S1 in the Supporting Information). **IIIb′** is less stable than **IIIa′** only by 8.0 kcal/mol (20.5 kcal/mol for the case of **IIIa,b**; Scheme 2) because of the coordination of the O atom of carbonyl to the metal in **IIIb′** (Chart 1). The calculation results also indicate that **IIIb′** is more reactive than **IIIa′** toward styrene, and the stepwise mechanism demonstrated here works for the reaction of **IIIb′** with styrene to yield the cyclopropanation product (see Figures S1 and S2 in the Supporting Information), which is in line with

Chart 1. Structures^a of IIIa′,b′
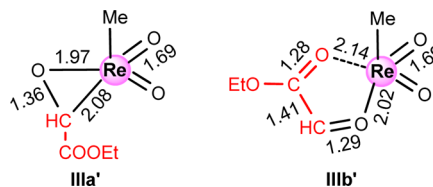
^{a}Distances are given in Å.

the experimental results showing the product of phenyl-cyclopropane derivatives.[14]

■ CONCLUSION

In summary, the MTO-catalyzed styrene cyclopropanation has been computationally found to proceed via formation of the MeRe(O)$_2$(η^1-O═CH$_2$) species and the subsequent transfer of the terminal methylene group through cleavage of the H$_2$C═O double bond. The catalytic transfer of terminal methylene to styrene follows a stepwise mechanism characterized by a pseudo-metallacycle and alkylative cyclization leading to phenylcyclopropane, which is distinctly different from the carbenoid or metal carbene promoted methylene transfer and is also in contrast to the MTO-catalyzed transfer of the isoelectronic atom (group) in MeRe(O)$_2$(η^2-O−O) or MeRe-(O)$_2$(η^2-O−NH) reported previously. The present result serves as the first theoretical evidence for d^0 transition metal mediated methylene transfer via a terminal form rather than a metal carbene or carbenoid fashion. This study not only enriches the chemistry of olefin cyclopropanation and the MTO-catalyzed group (atom) transfer event but also sheds new light on the reaction chemistry of formaldehyde. The mechanism demonstrated here is being tested for analogous systems, in which the more C-based transferring groups and various substrates containing the C═X (X = C, N, O) unsaturated bond would be considered.

■ ASSOCIATED CONTENT

⬡ Supporting Information
Figures, tables, and an xyz file giving a scheme for the formation of **IIIa′** and **IIIb′**, PES for the reaction of styrene with **IIIa′** and **IIIb′**, profiles of energy in solution, relative free energies, 3D structures and parameters, and all computed molecule Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(33) The process for 1,2-insertion of styrene into the Re–C bond of **IIIa** was also calculated, and the result indicates that the enthalpy barrier is similar to that for **TS[6-7]** (more than 45 kcal/mol; see Figure S3 in the Supporting Information).

(34) It is noted that the formations of Re carbene species $MeRe(=CH_2)O_2$ via oxygen transfer (Figure 3) and $MeRe(=CH_2)O_3$ via the reaction of MTO with CH_2N_2 (Scheme 2) are inaccessible, and further reactivities of these species were not calculated in this study. For references on the reaction of $MeRe(=CH_2)O_2$ with olefin, see: (a) Haunschild, R.; Loschen, C.; Tüllmann, S.; Cappel, D.; Hölscher, M.; Holthausen, M. C.; Frenking, G. *J. Phys. Org. Chem.* **2007**, *20*, 11. (b) Haunschild, R.; Frenking, G. *J. Organomet. Chem.* **2008**, *693*, 3627.

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