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# 铑(III)催化 *N*-苯氧基乙酰胺与亚甲基氧杂环丁酮氧化还原中性的碳氢活化/环化反应的机理研究

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**摘要** *N*-苯氧基乙酰胺是铑(III)催化无外加氧化剂条件下碳氢活化反应中的一类典型底物. 为了研究这类分子中O-NHAc 部分作为氧化导向基团的起作用方式, 通过密度泛函理论(DFT)计算研究了铑(III)催化 *N*-苯氧基乙酰胺与亚甲基氧杂环丁酮氧化还原中性的碳氢活化/环化反应的机理问题. 结果显示, 在形成铑(III)杂七元环中间体后, 直接的 O—N 键断裂形成铑(V)中间体的过程在能量上是不利的. 相反, 该中间体更容易发生 *β*-氢消除/还原消除, 从而得到铑(I)中间体, 其再通过氢转移/O—N 键断裂可再生活性的铑(III)催化剂. 形成烯基化中间体后, 通过分子内的亲核取代反应即可得到最终产物. 密度泛函理论(DFT)计算揭示的铑(III)/铑(I)/铑(III)催化循环过程为反应结果提供了深入理解.
**关键词** 铑(III)催化; 碳氢活化; 反应机理; 氧化导向基团; 密度泛函理论计算; *N*-苯氧基乙酰胺

# Mechanistic Understanding of Rh(III)-Catalyzed Redox-Neutral C—H Activation/Annulation Reactions of *N*-Phenoxyacetamides and Methyleneoxetanones

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**Abstract** *N*-Phenoxyacetamides represent one category of typical substrates for Rh(III)-catalyzed C—H activation under external oxidant free conditions. To understand how the O-NHAc unit works as the oxidizing directing group, the mechanism for the Rh(III)-catalyzed C—H activation/annulation reactions of *N*-phenoxyacetamides with methyleneoxetanones was studied by density functional theory (DFT) calculations. It was uncovered that after the formation of the 7-membered rhodacycle from irreversible C—H activation and olefin insertion steps, the direct O—N bond cleavage of the internal oxidant unit to form a Rh(V)-nitrenoid species was energetically unfavorable. Instead, this intermediate underwent sequential *β*-H elimination/reductive elimination much more easily and formed a Rh(I) species. Once the hydrogen was transferred to the NAc moiety, the regeneration of Rh(III) occurred easily by O—N bond cleavage. From the olefination intermediate, the final product was formed by an intramolecular nucleophilic substitution reaction, in which the Cp*Rh(III) could be a catalyst. The experimental outcomes are well understood by the density functional theory (DFT)-suggested catalytic cycle of Rh(III)/Rh(I)/Rh(III).
**Keywords** Rh(III) catalysis; C—H activation; reaction mechanism; oxidizing directing group; density functional theory (DFT) calculation; *N*-phenoxyacetamide

## 1 Introduction

The transition metal-catalyzed C—H activations have received much attention in recent decades.[1] Among different types of catalysts, the peculiar catalytic activity of Cp*Rh(III) complexes was widely pursued for C($sp^2$)—H activations.[2] While in most cases the addition of external oxidant was required for C—H activation, notable development was achieved with the introduction of the concept of the oxidizing directing group with Cp*Rh(III) catalysis.[3-4] Thus, the C—H activation reactions with substrates containing N—O,[5] N—N[6] and other polar moieties[7] in the directing groups could be realized under oxidant-free conditions (Scheme 1).[8]

We are interested in mechanistic understanding of the C—H reactions under redox-neutral conditions, and the

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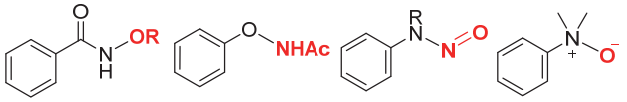


**Scheme 1** Typical oxidizing directing groups for Rh(III)-catalyzed C—H activations

function of the N-OPiv and N-OMe oxidizing directing groups in the Cp*Rh(III)-catalyzed external oxidant-free C—H activations of benzamide derivatives were studied by density functional theory (DFT) calculations.[9] It was found theoretically that the Rh(V)-nitrene intermediates could be involved in the Rh(III)-catalyzed transformations of *N*-acyloxybenzamides via the intramolecular acyloxy migration from N to Rh(III).[10] This was in line with the proposed Rh(V)-nitrene species formed from N—O bond cleavage of the rhodacycle intermediate in DFT studies of the Rh(III)-catalyzed C—H activation reactions of different substrates[11] including *N*-phenoxyacetamides.[12] The involvement of high valent organometallic intermediates was also suggested for external oxidant-free C—H activations with Ru(II),[13] Co(III)[14] and others.[15]

As one example of the recent development of the Rh(III)-catalyzed redox-neutral C—H activations, the efficient synthesis of 2*H*-chromene-3-carboxylic acids **3** by [3+3] cycloaddition between *N*-phenoxyacetamides **1** and methyleneoxetanones **2** was reported by the Yi group (Scheme 2).[16] In this transformation the *α*-methylene-*β*-lactone unit was used as the three carbon synthon through selective alkyl C—O bond cleavage. A Rh(III)-Rh(V)-Rh(III) pathway involving nitrenoid intermediate **C** was proposed based on preliminary mechanistic studies. However, it should be noted that the Rh(V) species are relatively unstable,[17] and its formation by N—O cleavage could be competing with possible reductive eliminations and *β*-eliminations.[18] A full analysis of all possible reaction channels and conformers of key transition states is necessary for reaching a reliable conclusion.

Reported herein is a comprehensive computational mechanistic understanding of the above transformation from *N*-phenoxyacetamide and methyleneoxetanone.[19] It was disclosed that the generation of the Rh(V)-nitrenoid species was much higher in energy than the alternative catalytic cycle of Rh(III)-Rh(I)-Rh(III),[20] from which the experimental outcomes by Yi *et al*. were interpreted in detail.

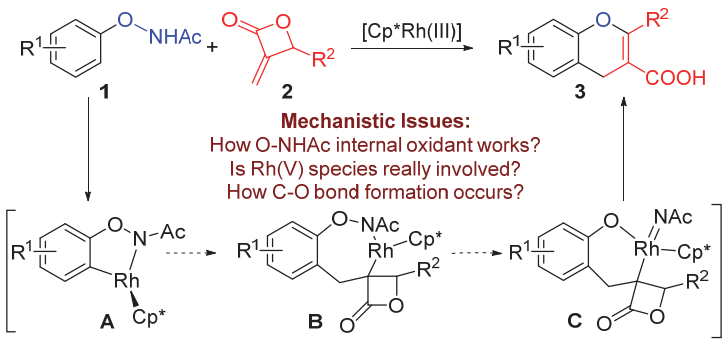
## 2 Results and discussion

### 2.1 Energetic profile for C—H activation/olefin insertion steps

The reaction for generation of **3a** from unsubstituted *N*-phenoxyacetamide (**1a**, $R^1$=H) and *β*-substituted methyleneoxetanone (**2a**, $R^2$=$PhCH_2CH_2$, Scheme 2) was used as the computation model.[21] Cp*Rh$(OAc)_2$ was established as the catalytic active species according to preceding studies.[9] Starting from free **1a** and the Cp*Rh$(OAc)_2$ catalyst, the formation of reactant complex **IN1** is endergonic by 10.5 kcal/mol (Figure 1). The N—H deprotonation occurs facilely via **TS1**, leading to **IN2** and HOAc exergonically. The following C—H activation is a concerted metalation-deprotonation (CMD) process via **TS2** with an activation barrier of 19.3 kcal/mol and the intermediate **IN3** is formed. After releasing HOAc, the five-membered rhodacycle intermediate **IN4** is 6.8 kcal/mol lower in energy than the starting materials. Next, π complex **IN5** could be formed endergonically by coordination of **2a** to the Rh atom. The migratory insertion of the double bond moiety of **2a** into the Rh—$C_{\alpha'}$ bond occurs via **TS3**,[21] with the $C_{\beta'}$—$C_{\alpha'}$ and $C_{\alpha}$—Rh distances being 0.201 and 0.214 nm, respectively (Figure 2). This step requires an activation barrier of 17.5 kcal/mol from **IN4** and generates ring-expanded rhodacycle **IN6** exergonically. Other regio- and stereoisomers of **TS3** are higher in energies.

### 2.2 Possible reactions from **IN6**

To determine further steps, the activation barriers for possible reaction channels from **IN6** were compared (Scheme 3). The high barrier of 52.7 kcal/mol indicates that the direct reductive elimination for $C_{\alpha}$—N bond formation via **TS4a** is impossible, being consistent with previous finding that the reductive elimination from Rh(III) species is difficult.[9] The originally proposed $O^1$—N bond cleavage via **TS4b** (geometry is given in Figure 2) for generation of **IN7b** was calculated to have an activation barrier of 26.5 kcal/mol. However, this is unfavorable




**Scheme 2** Rh(III)-catalyzed [3+3] cycloaddition between *N*-phenoxyacetamides and methyleneoxetanones and plausible mechanism

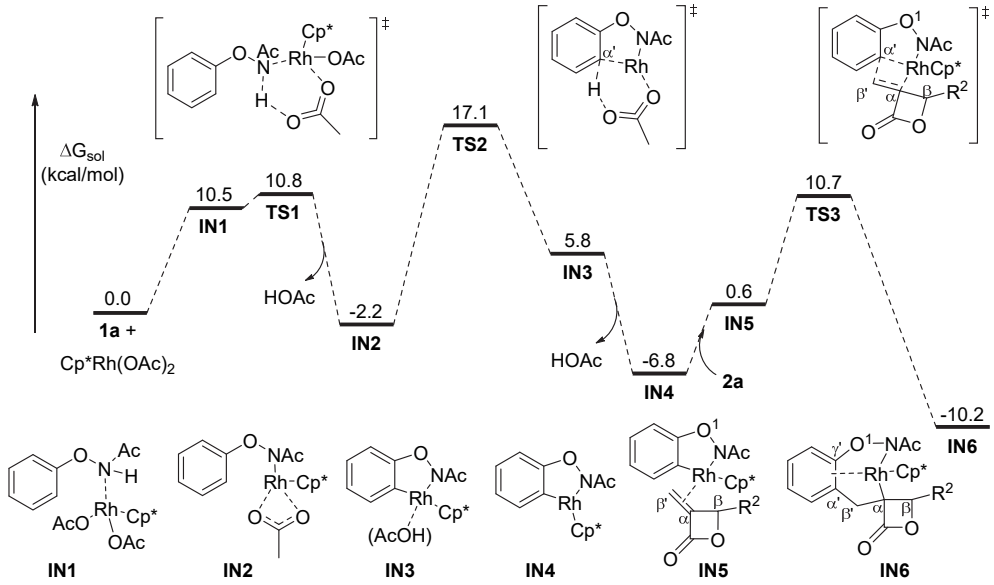



**Figure 1** Potential energy surface for the C—H activation/olefin insertion process ($R^2$=$PhCH_2CH_2$)

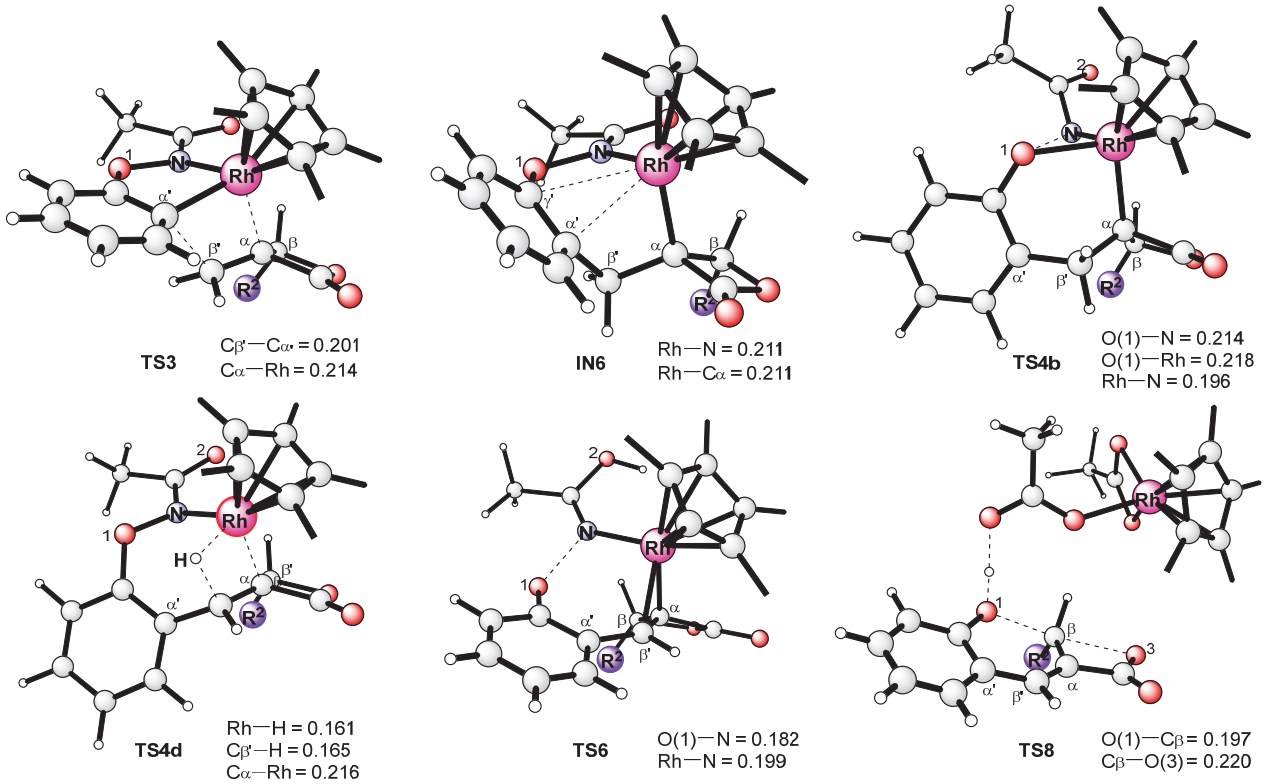


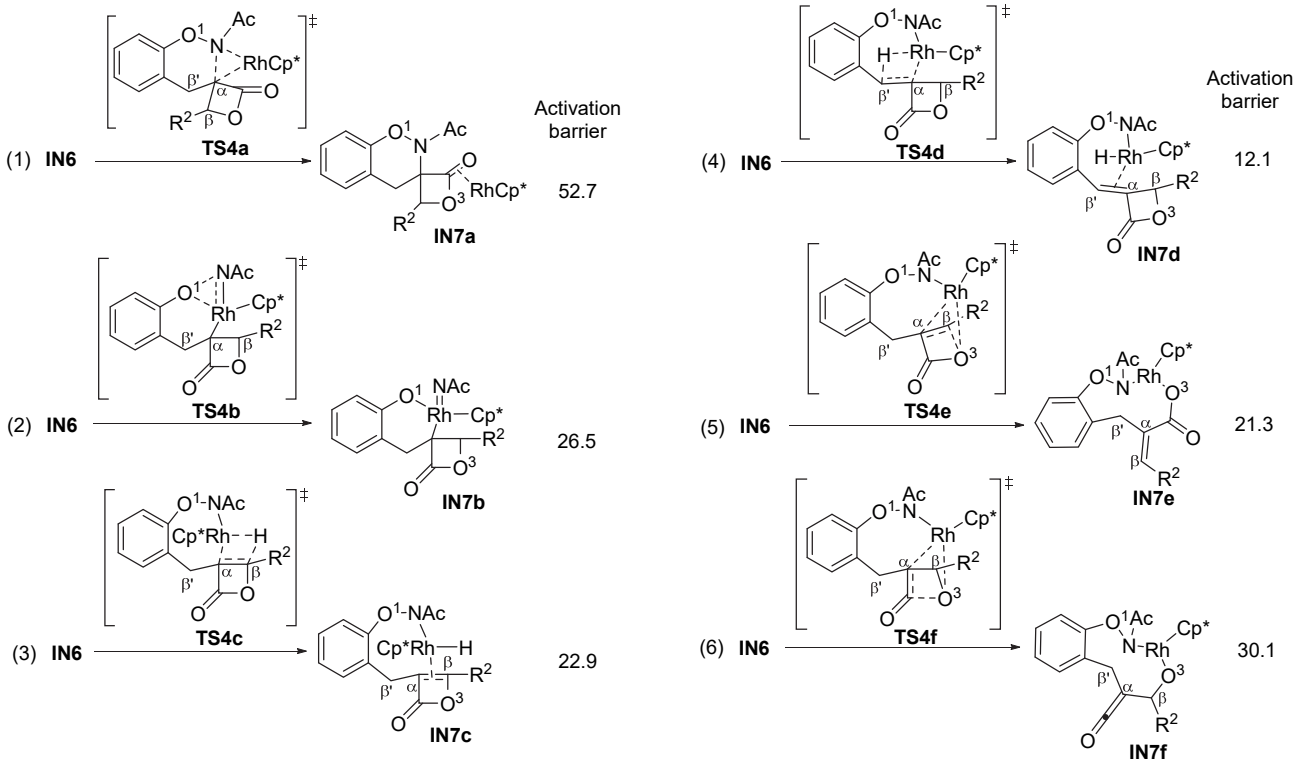

**Figure 2** Geometries for key intermediate and TS (selected distances are in nm; all methyl groups on the Cp* ligand are omitted for clarity; $R^2$=$PhCH_2CH_2$)

compared with the *β*-eliminations.[21] While the *β*-H elimination via **TS4c** ($C_β$—H cleavage) leading to the endocyclic alkene **IN7c** requires a barrier of 22.9 kcal/mol, the barrier for the formation of *exo* alkene **IN7d** via **TS4d** ($C_{β'}$—H cleavage) is only 12.1 kcal/mol, which could be possibly attributed to the more facile cleavage of the benzylic C—H bond in this case. The *β*-O eliminations were calculated, which required barriers of 21.3 and 30.1 kcal/mol for C—O bond cleavage via **TS4e** and **TS4f**, respectively.

## 2.3 Details for generation of the olefination intermediate

The above calculations suggested that the *β*-H elimination via **TS4d** had the lowest energy among possible reactions from **IN6**. Thus, details of this pathway were studied. According to the potential energy surface in Figure 3, prior to **TS4d**, **IN6** would first isomerize to **IN7**, in which the




**Scheme 3** Activation barriers (in kcal/mol) for possible reactions from **IN6**

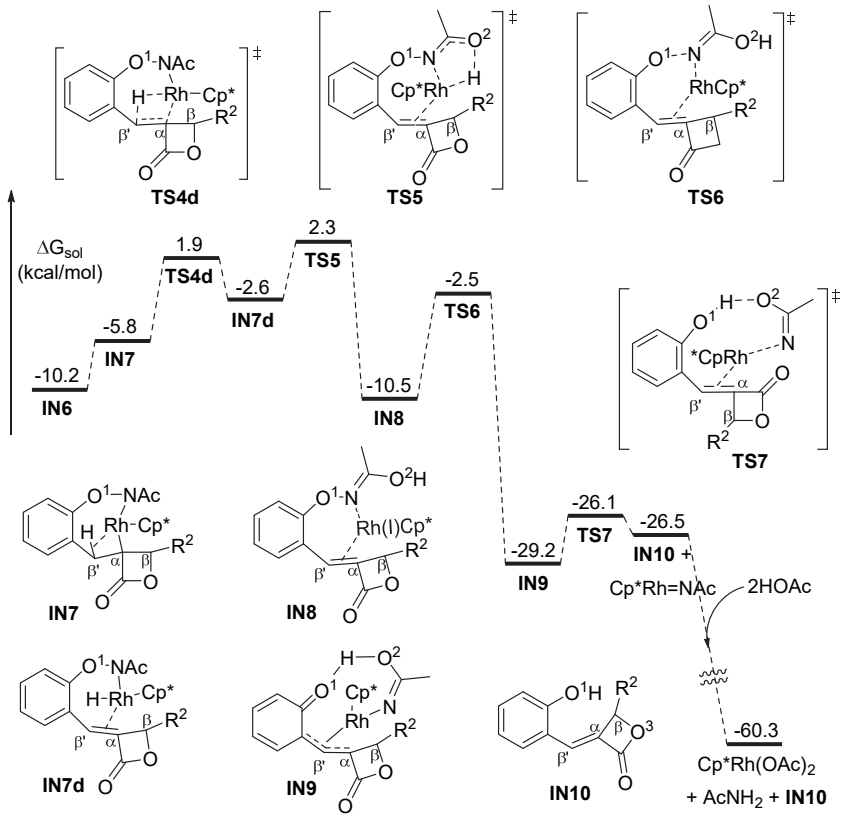



**Figure 3** Energetic profile for generation of the olefination intermediate ($R^2$=$PhCH_2CH_2$)

Rh atom was complexed with the $C_{\beta'}$—H bond. The **TS4d** leads to Rh-hydride **IN7d** endergonically, in which the newly formed double bond adopts the *E*-configuration. This π-complex is unstable and undergoes reductive elimination facilely by hydrogen transfer from Rh to $O^2$ via **TS5**. The relative free energy for **TS5** (2.3 kcal/mol) is

comparable to that of **TS4d** (1.9 kcal/mol), and the formed Rh(I) species **IN8** is slightly more stable than **IN6**. Other intramolecular hydrogen transfers from **IN7** and **IN7d** are much higher in energies than **TS4d** and **TS5**. From **IN8**, the $O^1$—N bond cleavage via **TS6** ($O^1$—N 0.182 nm and Rh—N 0.199 nm, Figure 2) requires a small barrier of 8.0 kcal/mol, leading exergonically to **IN9**. In the next step, oxidation of Rh(I) occurs by an intramolecular hydrogen transfer from $O^2$ to $O^1$ via **TS7**, which affords the Rh(III)-nitrenoid Cp*Rh=NAc and olefination intermediate **IN10**. The regeneration of the Cp*Rh(OAc)$_2$ catalyst is highly energetically favorable by reaction of Cp*Rh=NAc with HOAc.

### 2.4 Intramolecular nucleophilic substitution

Transformation of intermediate **IN10** to the final product **3a** was investigated. As the double bond ($C_\alpha$=$C_{\beta'}$) in **IN10** has an *E*-configuration, first transferring of the phenolic proton to the lactone moiety to form a phenoxide ion is not possible. Attempts to locate **TS** for direct nucleophilic attack of the phenolic hydroxyl group to the alkyl carbon ($C_\beta$) of the lactone was failed. If the Cp*Rh(OAc)$_2$ catalyst was involved, hydrogen-bonding complex **IN11** could be formed (Figure 4). Then, a concerted $C_\beta$—$O^1$ bond formation/ring-opening process via **TS8** ($O^1$—$C_\beta$ 0.197 nm and $C_\beta$—$O^3$ 0.220 nm, Figure 2) could be possible, requiring an activation barrier of 24.8 kcal/mol from **IN10**. Other pathways for $C_\beta$—$O^1$ formation and $C_\beta$—$O^3$ cleavage are higher in energies.

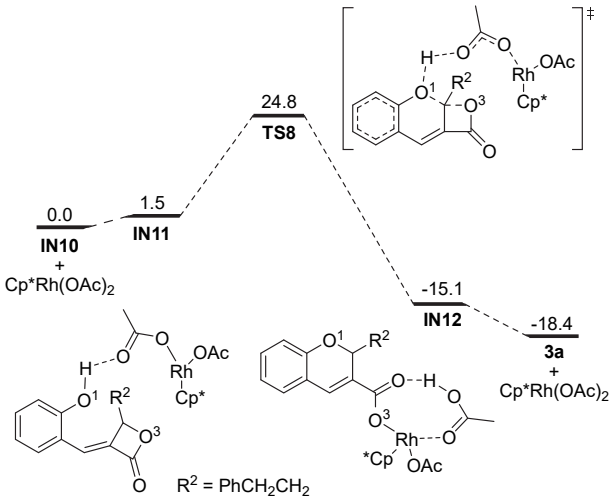
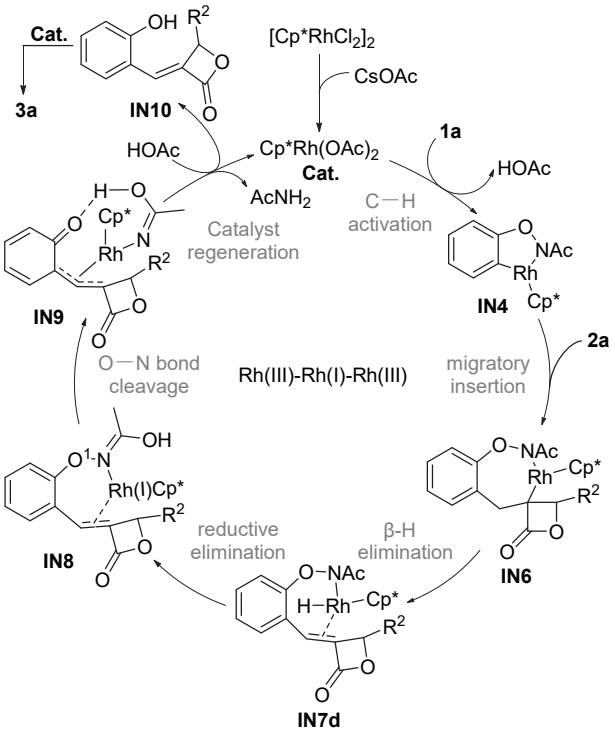



**Figure 4** Energetic profile for the intramolecular nucleophilic substitution from **IN10**

Thus, as outlined in Scheme 4, the full catalytic cycle based on the current DFT calculation is a Rh(III)-Rh(I)-Rh(III) process including key steps of C—H activation, migratory insertion, *β*-H elimination, reductive elimination, O—N bond cleavage and catalyst regeneration. It should be noted that although the catalyzed intramolecular nucleophilic substitution of **IN10** requires the highest activation barrier in the whole transformation (Figure 4), the calculated energies indicate that the transition state for C—H activation (**TS2**) has the highest relative free energy along the potential energy profile (Figure 1), suggesting that the C—H activation is irreversible as the TS for all following steps are lower in energies. These are consistent with results of the deuterium incorporation and kinetic isotope study in original experiments.[21]




**Scheme 4** Full catalytic cycle uncovered by DFT

## 3 Conclusions

In summary, the mechanism for the Cp*Rh(III)-catalyzed redox-neutral C—H activation/annulation reactions of *N*-phenoxyacetamides with methyleneoxetanones was studied by DFT calculations. The reaction initiates with the irreversible steps of C—H activation and olefin insertion to form the 7-membered rhodacycle species as a key intermediate (**IN6**). All possible reaction channels from **IN6** were analyzed in detail, and the direct O—N bond cleavage to generate a Rh(V)-nitrenoid species was found to be relatively difficult. Instead, the most favorable pathway involves sequential *β*-H elimination/reductive elimination to form a Rh(I) intermediate, which could be oxidized easily to Rh(III) by O—N bond cleavage of the internal oxidant moiety. After generation of the olefination intermediate, the intramolecular nucleophilic substitution leading to the final product is a concerted process when catalyzed by Cp*Rh(III). These theoretical findings may have implications for mechanistic studies of related transformations.

## 4 Experimental section

All calculations were carried out by using the Gaussian 09 suite of computational programs.[22] All stationary

points along the reaction coordinate were fully optimized at the DFT level using the B3LYP hybrid functional.[23] The 6-31G(d) basis set[24] was applied for all atoms except Rh, which was described by the Lanl2dz basis set and effective core potential implemented.[25] Frequencies were analytically computed at the same level of theory to get the thermodynamic corrections and to confirm whether the structures are minima (no imaginary frequency) or transition states (only one imaginary frequency). The solvation effect was examined by performing single-point self-consistent reaction field (SCRF) calculations based on the SMD solvation model for gas-phase optimized structures. Acetonitrile was used as the solvent, corresponding to the original experimental conditions. All SCRF calculations were done at the M06 level[26] by using a larger basis set of SDD[27] for Rh and 6-311＋G(d,p)[28] for the rest elements. The relative free energies corrected by solvation effects are used for discussion, and for species that has more than one conformer, only the one having the lowest energy value is given unless stated otherwise.

**Supporting Information** Additional computational results, calculated energies and Cartesian coordinates. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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