

PAPER

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rsc.li/catalysisComputational studies on the Rh-catalyzed carboxylation of a C(sp²)-H bond using CO₂†Xiangying Lv,^a Linhui Zhang,^a Beibei Sun,^a Zhi Li,^a
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The mechanism and effects of ligands and reagents in Rh-catalyzed C(sp²)-H bond carboxylation with CO₂ were investigated using density functional theory (DFT) calculations. The catalytic cycle involves sequential C-H oxidative addition, CO₂ insertion into the Rh-C(aryl) bond and transmetalation. Among these steps, CO₂ insertion is the rate-determining step. In addition to its role as a methylation reagent, AlMe₂(OMe) can also serve as a Lewis acid to promote the CO₂ insertion step. The greater reactivity of the catalyst with the bulkier P(Mes)₃ ligand than that with PPh₃ benefits from the favorable agostic interaction between the Rh center and the *ortho*-methyl group in the P(Mes)₃ ligand, which can stabilize the transition state of CO₂ insertion.

1. Introduction

The transformation of CO₂ into useful organic chemicals has gained increasing momentum with promise to create new paradigms in synthetic approaches.^{1–21} In this regard, various efforts have been made for CO₂ transformation based on transition metal catalysis.^{22–48} Among these, the direct carboxylation of the C-H bond with CO₂^{49–59} is particularly appealing because of the highly desirable simultaneous functionalization of the C-H bond^{60–85} and CO₂. Recently, the Iwasawa group reported the Rh-catalyzed carboxylation of the C(sp²)-H bond using CO₂.^{86–88} As shown in Scheme 1, CO₂ can insert into the *ortho*-C-H bond of 2-phenylpyridine (**1**) under the experimental conditions, delivering the desired *o*-carboxylated product **2** and byproduct **3**. Compared to the PPh₃ ligand, a bulkier phosphine ligand, P(Mes)₃, can significantly promote the reaction (entry 1 vs. entry 2). In addition, methylmetallic reagents are non-innocent in this reaction; compared to ZnMe₂, AlMe₂(OMe) can dramatically facilitate

the carboxylation process when employing P(Mes)₃ as a ligand (entry 2 vs. entry 3). The effects of these ligands and reagents on the reactivity are still unexplored with computational studies.

Although the reaction can be anticipated to occur through C-H bond metalation, CO₂ insertion into the Rh-C bond and the transmetalation and methylation steps (Scheme 2),⁸⁶ there are still many mechanistic possibilities. For instance, both Rh(I)-Cl and Rh(I)-Me could be the active catalytic species; C-H activation may occur *via* oxidative addition or σ -bond metathesis. After the formation of rhodacycle **A**, CO₂ could directly insert into the Rh-C bond (**B**).⁸⁹ In addition, AlMe₂(OMe) could act as a Lewis acid to promote CO₂ insertion (**C**).⁹⁰ Herein, we performed DFT calculations to study this carboxylation reaction. The computations revealed that AlMe₂(OMe) can act as a Lewis acid to facilitate the CO₂ insertion step. The promoting effect of the P(Mes)₃ ligand is due to the effect of stabilizing the transition state of CO₂ insertion.

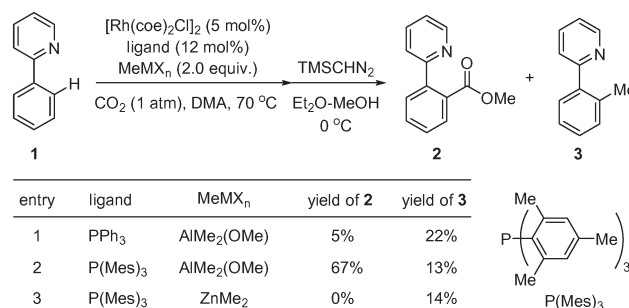
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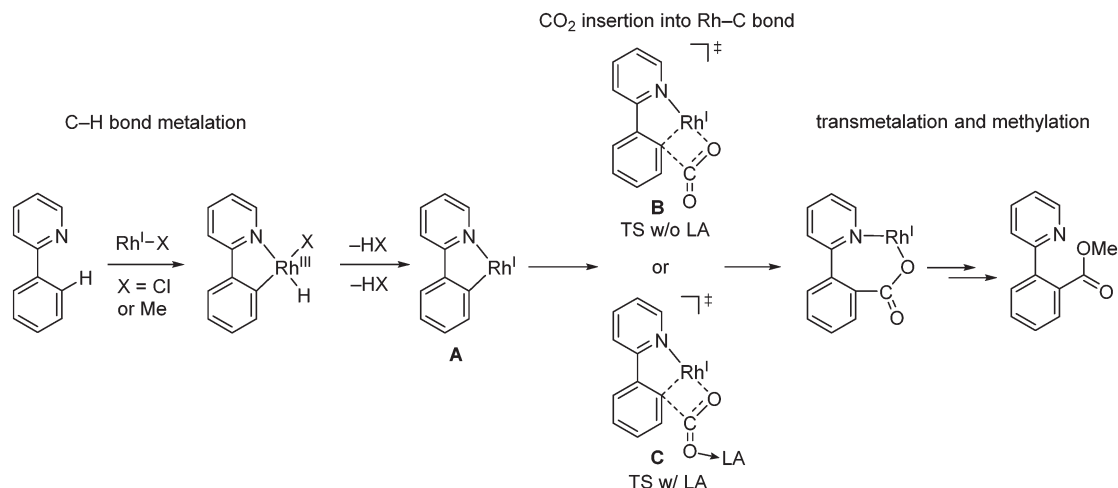
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Scheme 1 Rh-catalyzed carboxylation of the C(sp²)-H bond with CO₂.



Scheme 2 Proposed mechanism of the Rh-catalyzed C-H bond carboxylation.

2. Computational methods

The B3LYP density functional and a mixed basis set of LANL2DZ for Rh and 6-31G(d) for other atoms were used in geometry optimizations. All minima have zero imaginary frequencies and all transition states have only one imaginary frequency. Single-point energies were calculated with M06^{91,92} and a mixed basis set of SDD for Rh, and 6-311+G(d,p) for other atoms. Solvation energy corrections were calculated using the SMD model.⁹³ *N,N*-Dimethylacetamide (DMA) was used as the solvent in the calculations. The same level of theory was used in our recent computational study on Rh-catalyzed reactions.⁹⁴ The natural bond orbital (NBO) charge was calculated at the M06/SDD-6-311+G(d,p) level in DMA solvent using the geometry optimized at the B3LYP/LANL2DZ-6-31G(d) level. All calculations were performed with Gaussian 09.⁹⁵ The 3D structures of the molecules were generated using CYLview.⁹⁶

3. Results and discussion

We first considered several possible active monomeric species of the Rh catalyst and the reactant complex under the experimental conditions (see Fig. S1 in the ESI† for discussion on the chloro-bridged dimeric Rh complex). It is a feasible process for the formation of methylrhodium (Rh(I)-Me) from the catalyst precursor Rh(I)-Cl (Fig. S2†). These Rh(I)-Cl (4

and 6) and Rh(I)-Me (5 and 7) species shown in Fig. 1 have comparable energies, indicating their existence under the reaction conditions. Thus, both 6 and 7 were chosen as starting reactant complexes to study the pathways that lead to the formation of rhodacycle intermediates.

The computed reaction energy profiles for the C-H metalation and reductive elimination steps are shown in Fig. 2. Oxidative addition of C-H bond at Rh(I) requires low barriers, 9.6 (8-TS) and 10.6 (9-TS) kcal mol⁻¹ with respect to 6 and 7, respectively. This is in accordance with other computational studies on the C-H oxidative addition at Rh(I).⁹⁷⁻¹⁰¹ The transition state of the C-H cleavage *via* a σ -bond metathesis mechanism cannot be computationally located. The formed Rh(III) intermediates 10 and 11 are uphill in energy, 4.6 and 5.3 kcal mol⁻¹ higher than the energies of 6 and 7, respectively. The C-H metalation (8-TS, $\Delta G^\ddagger = 7.7$ kcal mol⁻¹) of 6 is reversible due to the higher barrier for the ensuing reductive elimination of HCl from 10 (12-TS, $\Delta G^\ddagger = 23.9$ kcal mol⁻¹). In contrast, the C-H metalation (9-TS, $\Delta G^\ddagger = 10.7$ kcal mol⁻¹) of 7 is irreversible because of the lower barrier for the subsequent reductive elimination of CH₄ (13-TS, $\Delta G^\ddagger = 8.5$ kcal mol⁻¹). This indicates that although 6 has a higher stability and a lower barrier for C-H metalation than 7, the reaction proceeds *via* the reaction pathway derived from the Rh(I)-Me species, shown in black in Fig. 2.

In addition to the reductive elimination of CH₄ (13-TS) from the Rh(III) intermediate 11, we also studied the reductive elimination pathway for generating the byproduct 3 (the red pathway in Fig. 2). The computed barrier (16-TS, $\Delta G^\ddagger = 16.8$ kcal mol⁻¹) is higher than that of 13-TS ($\Delta G^\ddagger = 8.5$ kcal mol⁻¹). This is in line with the experimentally observed lower yield of 3 (entry 2 in Scheme 1). Furthermore, the reductive elimination of CH₄ is highly exothermic ($\Delta G = -24.4$ kcal mol⁻¹). This suggests that the reverse process of 14 + CH₄ → 13-TS → 11, which has a barrier of 32.9 kcal mol⁻¹, is impossible.

After the formation of rhodacycle 14, we first considered the mechanism of direct CO₂ insertion into the Rh(I)-C(sp²)

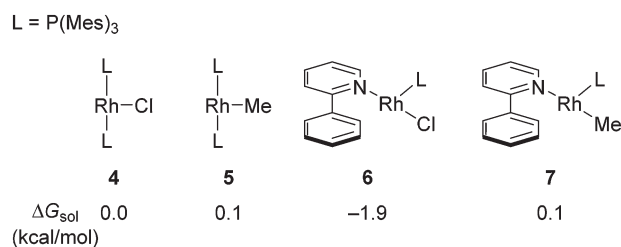


Fig. 1 Possible Rh(I) species involved in the reaction.

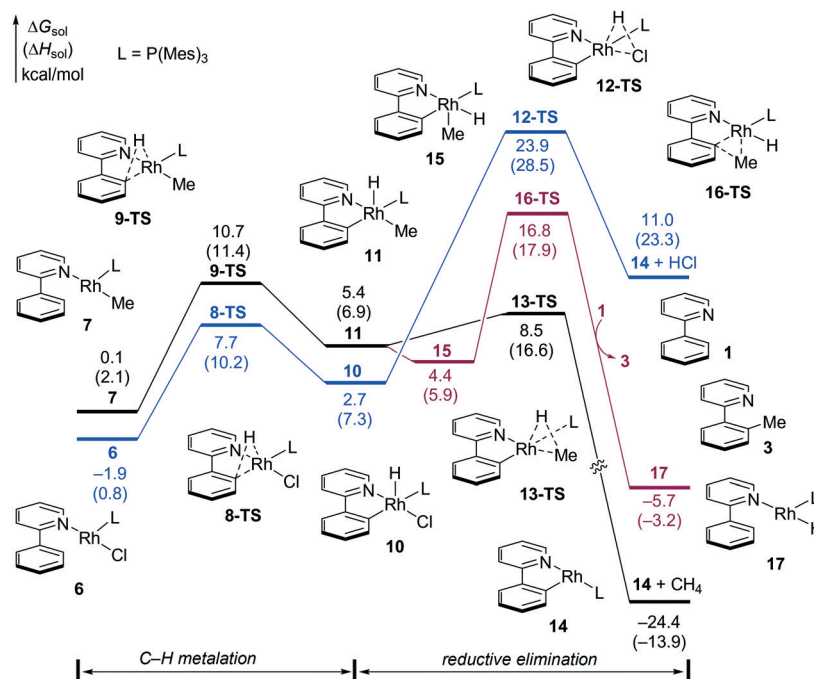


Fig. 2 Energy profiles for C-H metalation and reductive elimination. Energies are shown with respect to the separated substrate 1 and catalyst precursor 4.

bond. The calculated energy profiles are shown in Fig. 3. The coordination of CO_2 to Rh is endothermic by 9.6 kcal mol⁻¹ (18), and the subsequent insertion transition state has a high barrier (20-TS, $\Delta G^\ddagger = 28.9$ kcal mol⁻¹ with respect to 14). In

this transition state, the phosphine ligand is *trans* to the aryl group (Fig. 4). The conformer with the phosphine ligand *cis* to the aryl group is much less favorable (21-TS, $\Delta G^\ddagger = 34.3$ kcal mol⁻¹ with respect to 14). This is due to steric repulsion

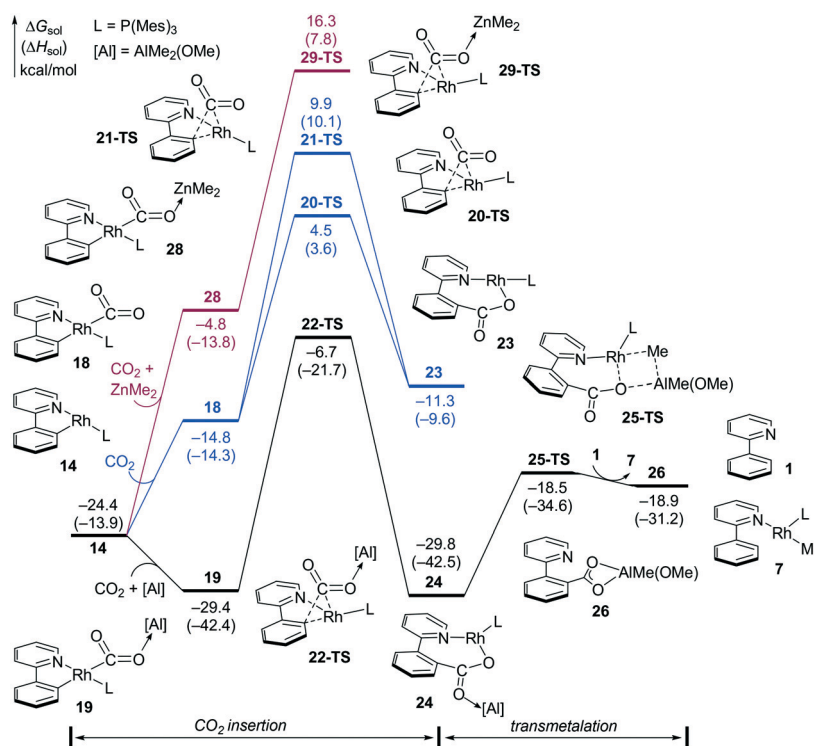


Fig. 3 Energy profiles for CO_2 insertion into the Rh-C bond, with and without $\text{AlMe}_2(\text{OMe})$ and ZnMe_2 . Energies are shown with respect to the separated substrate 1 and catalyst precursor 4.

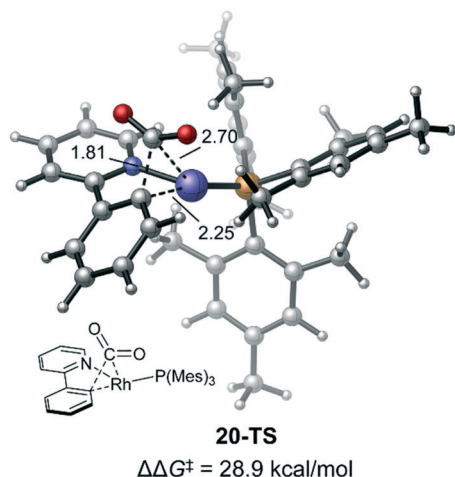


Fig. 4 Optimized geometry of transition state 20-TS.

caused by the closer proximity of the bulky $\text{P}(\text{Mes})_3$ ligand to the aryl group and CO_2 (Fig. S3†). Compared to the CO_2 insertion into the $\text{Rh}(\text{I})-\text{C}(\text{sp}^2)$ bond, the insertions into the $\text{Rh}(\text{III})-\text{C}(\text{sp}^2)$ bond in **10** and **11** are more disfavored due to the steric congestion around six-coordinated $\text{Rh}(\text{III})$ in the transition states (Fig. S4†).

We further studied whether the interaction of $\text{AlMe}_2(\text{OMe})$ with CO_2 could facilitate CO_2 insertion. The interaction of Rh in **18** with CO_2 is disfavored, although the computed NBO charge on Rh in **14** is negative ($-0.281e$). However, in the presence of $\text{AlMe}_2(\text{OMe})$, the coordination of aluminum to one of the oxygen atoms in CO_2 can further polarize CO_2 and thus increase the electrophilicity of the carbon atom in CO_2 . The synergetic effects of rhodium and aluminum on CO_2 result in a favorable interaction in **19**, $5.0 \text{ kcal mol}^{-1}$ lower than **14**. The subsequent CO_2 insertion with $\text{AlMe}_2(\text{OMe})$ coordination has a barrier of $22.7 \text{ kcal mol}^{-1}$ (22-TS, Fig. 5) with respect to **19**, which is $6.2 \text{ kcal mol}^{-1}$ lower than that of 20-TS without $\text{AlMe}_2(\text{OMe})$. This result indicates that $\text{AlMe}_2(\text{OMe})$ not only acts as a methylmetallic reagent to generate methylrhodium(i), but also dramatically promotes CO_2 insertion *via* the Lewis acid effect.

The transmetalation of **24** with $\text{AlMe}_2(\text{OMe})$ has a low barrier (25-TS, $\Delta G^\ddagger = 11.3 \text{ kcal mol}^{-1}$ with respect to **24**). This is in agreement with the experimental observation that the transmetalation of rhodium carboxylate with $\text{AlMe}_2(\text{OMe})$ is a fast process and can happen even at room temperature.⁸⁶ The formed aluminum carboxylate **26** can be methylated using TMSCHN_2 to give the desired product. In addition, the carboxylate-assisted C–H activation of **1** by **24** cannot be computationally located, although rhodium carboxylates are usually employed for C–H activation *via* the concerted metalation deprotonation mechanism.⁸⁵

The energy profiles shown in Fig. 2 and 3 indicate that CO_2 insertion is the rate-determining step in the overall catalytic cycle. Thus, we further investigated the effects of different ligands and reagents based on this step. Fig. 5 shows the optimized transition state geometries (22-TS and 27-TS) of

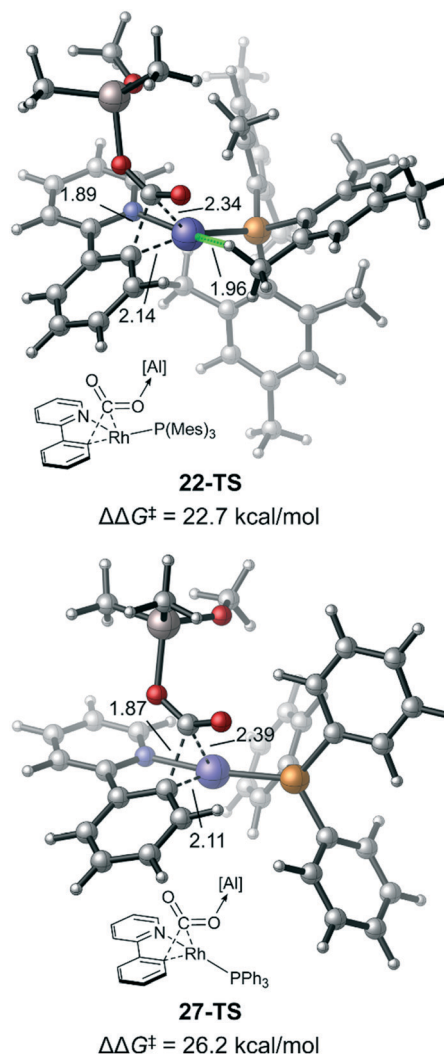


Fig. 5 Optimized geometries of transition states 22-TS and 27-TS.

the $\text{AlMe}_2(\text{OMe})$ -assisted CO_2 insertion with $\text{P}(\text{Mes})_3$ and PPh_3 ligands. The barrier of 27-TS with the PPh_3 ligand is $3.5 \text{ kcal mol}^{-1}$ higher than that of 22-TS with the $\text{P}(\text{Mes})_3$ ligand, which agrees with the experimentally observed reactivity (entry 1 *vs.* entry 2 in Scheme 1). Due to the larger size of $\text{P}(\text{Mes})_3$ compared to PPh_3 , in 22-TS, the phosphine ligand is *trans* to the aryl group to relieve the steric congestion. In contrast, the smaller PPh_3 ligand favors the *cis* position of the aryl group in 27-TS. The disfavored conformers of 22-TS and 27-TS are given in Fig. S5†. Because CO_2 attacks the $\text{Rh}-\text{C}(\text{aryl})$ bond above the plane consisting of Rh , P , N and C atoms, there is an empty site on Rh , which is *cis* to the phosphine ligand. This site is precisely occupied by the *ortho*-methyl group of $\text{P}(\text{Mes})_3$, as evidenced by the short $\text{Rh}\cdots\text{H}$ distance in 22-TS ($1.96 \text{ \AA}$, shown in green, Fig. 5). We performed a topological analysis of this $\text{Rh}\cdots\text{H}$ interaction using the Multiwfn program.¹⁰² The electron density (0.044 a.u.) and Laplacian (0.16 a.u.) values at the bond critical point between the Rh and H atoms indicate that the $\text{Rh}\cdots\text{H}$ interaction is a typical agostic interaction (Fig. S6†).^{103–105} We

further simply replaced the *ortho*-methyl substituent in 22-TS with a H atom to generate 22-TSb without the agostic interaction (Fig. S7†). A higher barrier was obtained for 22-TSb. This result indicates that the agostic interaction of C–H⋯Rh can stabilize 22-TS, thus enhancing the reactivity. In contrast, this type of stabilization derived from the agostic interaction is not observed in the transition state with the PPh₃ ligand (27-TS). Therefore, the *ortho*-methyl group in the P(Mes)₃ ligand is critical for the promoting effect of the ligand.

Next, we compared the energetics of CO₂ insertion using ZnMe₂ and AlMe₂(OMe) (Fig. 3). Both the CO₂ coordination (28, $\Delta G = 19.6 \text{ kcal mol}^{-1}$ with respect to 14) and insertion (29-TS, $\Delta G^\ddagger = 40.7 \text{ kcal mol}^{-1}$ with respect to 14) steps are highly disfavored for ZnMe₂. Since the enthalpy energies are comparable with those of direct CO₂ coordination (18) and insertion (20-TS), the significant increase in the activation free energies is mainly caused by the entropic penalty due to the reaction involving three molecules, 14, CO₂ and ZnMe₂. In contrast, the reaction with AlMe₂(OMe) is favored due to the significantly strong interactions of AlMe₂(OMe) with CO₂ in the CO₂ coordination (19) and insertion (22-TS) steps, which are 24.6 and 23.0 kcal mol^{−1} more stable than 28 and 29-TS, respectively.

4. Conclusions

In summary, DFT calculations were performed to study the mechanism and the effect of the ligands and reagents in Rh-catalyzed C–H bond carboxylation using CO₂. The reaction proceeds *via* C–H oxidative addition on the active Rh(I)–Me catalyst, AlMe₂(OMe)-promoted CO₂ insertion into the Rh–C(aryl) bond and transmetalation with AlMe₂(OMe) to give aluminum carboxylate and regenerate Rh(I)–Me. CO₂ insertion is the rate-determining step in the overall catalytic cycle. The Lewis acid effect of AlMe₂(OMe) facilitates the CO₂ insertion step. The origin of the promoting effect of P(Mes)₃ on the reactivity is derived from the stabilizing effect due to the favorable agostic interaction of Rh with the *ortho*-methyl group of P(Mes)₃. These theoretical insights may have useful implications for the development of transition metal catalyzed CO₂ transformations.

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