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Trans Influence of Boryl Ligands in CO₂ Hydrogenation on Ruthenium Complexes: Theoretical Prediction of Highly Active Catalysts for CO₂ Reduction

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Abstract: In this work, we study the trans influence of boryl ligands and other commonly used non-boryl ligands in order to search for a more active catalyst than the ruthenium dihydride complex Ru(PNP)(CO)H₂ for the hydrogenation of CO₂. The theoretical calculation results show that only the B ligands exhibit a stronger trans influence than the hydride ligand and are along increasing order of trans influence as follows: $-H < -BBr_2 < -BCl_2 \approx -B(OCH)_2 < -Bcat < -B(OCH_2)_2 \approx -B(OH)_2 < -Bpin < -B(NHCH_2)_2 < -B(OCH_3)_2 < -B(CH_3)_2 < -BH_2$. The computed activation free energy for the direct hydride addition to CO₂ and the NBO analysis of the property of the Ru–H bond indicate that the activity of the hydride can be enhanced by the strong trans influence of the B ligands through the change in the Ru–H bond property. The function of the strong trans influence of B ligands is to decrease the d orbital component of Ru in the Ru–H bond. The design of a more active catalyst than the Ru(PNP)(CO)H₂ complex is possible.

Keywords: CO₂ hydrogenation; trans influence; boryl ligand; theoretical calculation



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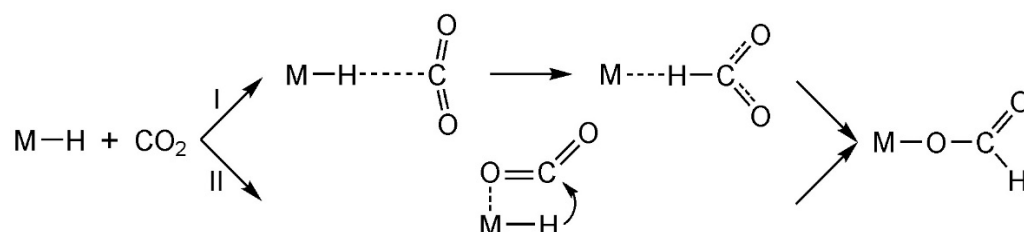
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1. Introduction

The development of high-efficiency catalysts for CO₂ hydrogenation to formic acid or other carbohydrates is still attracting significant attention, as it can address the increasingly severe environmental problems and energy crisis [1–7]. One of the feasible methods is the homogeneous hydrogenation of CO₂ using noble metal catalysts based on Ir, Ru, and Rh [8–14]. In 2009, Nozaki and co-workers reported an impressive iridium catalyst (Ir(PNP)H₃, PNP = 2,6-(diisopropylphosphinomethyl)-pyridine) for CO₂ hydrogenation to formate [8]. The turnover frequency (TOF) and turnover number (TON) reached $1.5 \times 10^5 \text{ h}^{-1}$ and 3.5×10^6 , respectively, at 200 °C and 5.0 MPa. In 2014, Pidko and co-workers achieved this reaction with a Ru(PNP)(CO)H₂ catalyst and greatly increased the TOF to $1.89 \times 10^6 \text{ h}^{-1}$ at a lower temperature and pressure (132 °C and 4.0 MPa) [13]. The catalytic mechanisms for the CO₂ hydrogenation on these catalysts have been intensively studied [15–20]. It is believed that these catalysts are so active and stable because the hydride on these catalysts can be directly added to CO₂, leading to CO₂ reduction, shown as route I in Scheme 1. Another route for CO₂ hydrogenation is via the precoordination of CO₂ to the metal center followed by hydride transfer to CO₂ (route II). In this route, CO₂ should be precoordinated to the metal center before its reaction with the hydride, but CO₂ cannot compete with other molecules in the system to occupy the active site, owing to the weak coordination ability of CO₂. In a word, a highly active hydride is the key to the design of high-efficiency catalysts for the hydrogenation of CO₂.

However, not all hydrides on transition metal complexes are active enough for the direct addition to CO₂. When we studied Nozaki's Ir(PNP)H₃ catalyst, we found that there exist two types of Ir–H bond, and only the hydride on the Ir–H bond formed from

the mixing of the sd^2 orbital of Ir with the $1s$ orbital of H is active enough [17]. Then, we checked several Ru complexes and concluded that, if the Ru–H bond is formed from the mixing of the sd^3 orbital of Ru with the $1s$ orbital of H, the hydride is not active for the direct addition to CO_2 [21]. It only can take place for the hydride contained by a Ru–H bond formed from the mixing of the sd^2 orbital of Ru with the $1s$ orbital of H, the same as the situation on the Ir complex. Moreover, we noticed that, if less d orbital component is involved in the formation of Ru–H bond, the hydride will be more active. Inspired by these findings, we thought the property of the Ru–H bond could be influenced by its trans ligand because this ligand shares the same orbital of Ru combined with the hydride. We tested two boryl ligands (Bcat and Bpin, cat = catecholate, pin = pinacolate) as the trans ligand to the hydride, and found that the activation barriers for the direct hydride addition to CO_2 on the $Ru(PNP)(CO)HBcat$ and $Ru(PNP)(CO)HBpin$ complexes are both lower than that on the $Ru(PNP)(CO)H_2$ complex [22]. Further, we explored the whole pathway for the hydrogenation of CO_2 to formate. The advantage of the $Ru(PNP)(CO)HBcat$ or $Ru(PNP)(CO)HBpin$ complex is more remarkable; the overall activation free energy for CO_2 hydrogenation to formate on the complexes $Ru(PNP)(CO)H_2$, $Ru(PNP)(CO)HBcat$, and $Ru(PNP)(CO)HBpin$ were calculated to be 18.2, 16.4, and 13.0 kcal·mol^{−1}, respectively.



Scheme 1. Two routes for CO_2 insertion into the M–H bond.

In this paper, we would like to examine the trans influence of more boryl ligands, together with that of various commonly used non-boryl ligands, in the direct addition of hydride to CO_2 . It is shown only the B ligands exhibit a stronger trans influence than the hydride. We then calculated the activation free energy for the addition of hydride to CO_2 on the Ru complexes with several selected trans B ligands, in comparison with that on the $Ru(PNP)(CO)H_2$ complex. The properties of Ru–H bonds on these complexes were studied with natural bond orbital (NBO) analysis. It is indicated that the activity of the hydride can be systematically enhanced by the strong trans influence of the B ligands through the modification of the Ru–H bond property. In addition, we studied the case on another Ru dihydride complex $trans-[Ru(dmpe)_2H_2]$ ($dmpe = Me_2PCH_2CH_2PMe_2$) [23]. The trans influence of B ligands on this complex is not as significant as that on the $Ru(PNP)(CO)H_2$ complex. We will discuss this in the main text.

2. Results and Discussion

2.1. Trans Influence of Non-Boryl and Boryl Ligands

The bond distance of the Ru–H bond is an index for the trans influence of the trans ligand, as well as an index for the activity of the hydride on the Ru–H bond. In general, the longer the distance of the Ru–H bond, the stronger the trans influence of the ligand trans to this Ru–H bond, the weaker the Ru–H bond, and the more active the hydride on it [24]. We first examined various commonly used non-boryl ligands, and compared the computed distance of the Ru–H bond on each complex with that on the $Ru(PNP)(CO)H_2$ complex, in which two hydrides are trans to each other. The results are collected in Table 1. The optimized geometries of all the species are given in the Supplementary Materials. It is shown that the order of increasing trans influence of non-boryl ligands is as follows: $-NO_3 \approx -Br < -Cl < -SCN < -ONO \approx -F < -OMe < -OH \approx -NO_2 < -NH_2 < -CN < -SiH_3 < -Ph < -Me < -Et < -H$. Greif et al. studied the trans influence of several ligands on a square-planar Pt complex and provided a sequence of increasing trans influence as follows:

$-\text{NO}_3 < -\text{ONO} < -\text{Cl} < -\text{Br} < -\text{SCN} < -\text{NO}_2 < -\text{CN} < -\text{Ph} < -\text{Me}$ [25]. Sajith and Suresh quantified the trans influence of various ligands on a hypervalent iodine complex and found a sequence of increasing trans influence as follows: $-\text{NO}_3 < -\text{F} < -\text{Cl} < -\text{OH} < -\text{Br} < -\text{OMe} < -\text{NO}_2 < -\text{NH}_2 < -\text{Me} < -\text{Ph} < -\text{Et}$ [26]. Our result is in reasonable agreement with the above two results. However, there is an inverse trans influence of $-\text{Br} < -\text{Cl} < -\text{F}$ in this case. The inverse trans influence of the $-\text{Br}$, $-\text{Cl}$, and $-\text{F}$ ligand was observed by the experimental and theoretical studies [27,28]. All the Ru–H bonds on the complexes with these trans non-boryl ligands are shorter than that on the $\text{Ru}(\text{PNP})(\text{CO})\text{H}_2$ complex, thus we deduce that the hydride on these complexes will be less active for CO_2 hydrogenation than that on the $\text{Ru}(\text{PNP})(\text{CO})\text{H}_2$ complex.

Table 1. Bond distance of the Ru–H bond on the Ru PNP-type complex with different trans ligands.

Trans Ligand	Distance of Ru–H Bond (Å)	Trans Ligand	Distance of Ru–H Bond (Å)
–H	1.697	–H	1.697
–Et	1.683	–BBr ₂	1.711
–Me	1.682	–BCl ₂	1.713
–Ph	1.678	–B(OCH) ₂	1.713
–SiH ₃	1.676	–Bcat	1.714
–CN	1.662	–B(OCH ₂) ₂	1.715
–NH ₂	1.656	–B(OH) ₂	1.715
–NO ₂	1.637	–Bpin	1.716
–OH	1.637	–B(NHCH ₂) ₂	1.717
–OMe	1.636	–B(OCH ₃) ₂	1.720
–F	1.621	–B(CH ₃) ₂	1.726
–ONO	1.621	–BH ₂	1.739
–SCN	1.616		
–Cl	1.611		
–Br	1.609		
–NO ₃	1.609		

Some studies in the literature have reported that the boryl ligands have a very strong trans influence [29–33]. Thus, we examined the trans influence of some usual boryl ligands. The computed distances of Ru–H bonds on these complexes with trans B ligands are collected in Table 1. The diagrams of some boryl ligands are given in Chart 1. Their optimized geometries are presented in the Supporting Information. It can be seen that the B ligands actually have a stronger trans influence than the hydride, judged by the longer distance of the Ru–H bond. Bcat and Bpin ligand are among the most popular B ligands found in transition metal complexes, thus we tested them in our previous work [22]. However, the trans influences of Bcat and Bpin ligands are not the strongest; the BH₂, B(CH₃)₂, and B(OCH₃)₂ ligands show a stronger trans influence than the Bcat and Bpin ligands. The total order of increasing trans influence of boryl ligands considered here is as follows: $-\text{H} < -\text{BBr}_2 < -\text{BCl}_2 \approx -\text{B(OCH)}_2 < -\text{Bcat} < -\text{B(OCH}_2)_2 \approx -\text{B(OH)}_2 < -\text{Bpin} < -\text{B(NHCH}_2)_2 < -\text{B(OCH}_3)_2 < -\text{B(CH}_3)_2 < -\text{BH}_2$. Zhu and Lin investigated the trans influence of boryl ligands on a square-planar Pt complex and reported a sequence of increasing trans influence as follows: $-\text{H} < -\text{BBr}_2 \approx -\text{BCl}_2 \approx -\text{Bcat} \approx -\text{B(OCH)}_2 < -\text{B(OCH}_2)_2 < -\text{Bpin} < -\text{B(NHCH}_2)_2 < -\text{BH}_2 < -\text{B(CH}_3)_2$ [29]. In that case, B(CH₃)₂ shows the strongest trans influence.

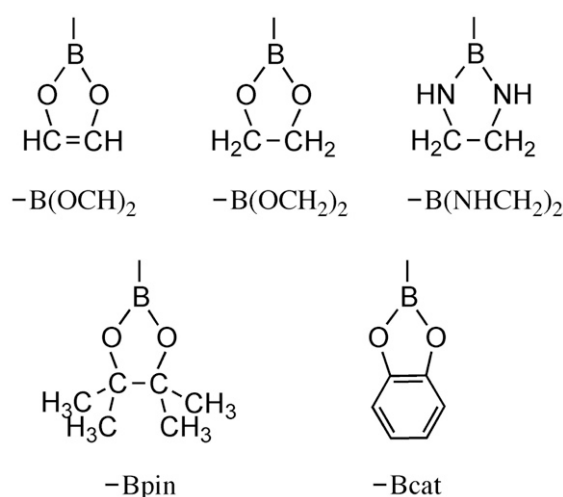


Chart 1. Diagram of some boryl ligands.

2.2. Activity of the Hydride under Trans Influence

As the B ligands exhibit a stronger trans influence than the hydride, we expected to confirm the activity of the hydride under the trans influence of B ligands. For this purpose, we calculated the activation free energy for the addition of hydride to CO₂ on the Ru PNP-type complexes with four selected trans B ligands. The activation barrier for the direct hydride addition to CO₂ on the Ru(PNP)(CO)H₂ complex was also computed for comparison. The results are collected in Table 2. To show this information more clearly, we drew a picture of the free energy profile for the direct hydride addition to CO₂ on the Ru(PNP)(CO)H₂ complex and four Ru complexes with trans B ligands, presented as Figure 1. The optimized geometries of all the species involved in Figure 1 are provided in Figure 2 and in the Supporting Information. When CO₂ approaches the hydride on the Ru(PNP)(CO)H₂ complex, an association complex (IS) will be formed, in which CO₂ is fixed by the interaction between CO₂ with the hydride and the hydrogen bonding of CO₂ with the methyl group H atoms on P atoms. The angle of CO₂ is 176.5°, indicating that CO₂ is just weakly activated. After the addition of hydride to CO₂, an H-bound formate complex (FS) is formed. In this state, the angle of OCO is decreased to 138.0°, indicating that CO₂ is already reduced. This step is endergonic by 6.7 kcal mol^{−1} and is involved with an activation free energy of 7.0 kcal mol^{−1}. It should be mentioned that the whole process of CO₂ insertion into the Ru–H bond to form a formate complex (Scheme 1) is exergonic, but the step of hydride addition to CO₂ is always an endergonic step; the less endergonic the step of hydride addition to CO₂, the more favorable the formation of the formate complex, by lowering the energetics of the whole catalytic cycle [15–19,34]. When CO₂ approaches the hydride on the Ru complex with Bcat, Bpin, B(NHCH₂)₂, or B(OCH₃)₂ as trans ligand, a similar mechanism will occur. The angle of CO₂ in the association complexes with these trans B ligands is 176.8°, 176.6°, 176.3°, and 176.4°, respectively, very close to that on the Ru(PNP)(CO)H₂ complex, but the angle of OCO in the final state is 137.3°, 136.3°, 136.1°, and 135.9°, respectively, less than that on the Ru(PNP)(CO)H₂ complex. The activation barrier for the hydride addition to CO₂ is 5.9, 5.6, 5.2, and 4.9 kcal·mol^{−1}, respectively. These values are lower than that on the Ru(PNP)(CO)H₂ complex and along a decreasing order in accordance with the increasing order of trans influence of these B ligands. Moreover, these steps are endergonic by 5.3, 4.5, 3.6, and 3.1 kcal mol^{−1}, respectively, indicating that the formed formate complexes are more thermodynamically stable. The addition of hydride to CO₂ is the first and the key step for the hydrogenation of CO₂. If the whole pathway for the CO₂ hydrogenation to formate is explored, the advantage will be more remarkable, as we reported on the Ru(PNP)(CO)HBcat and Ru(PNP)(CO)HBpin complexes [22].

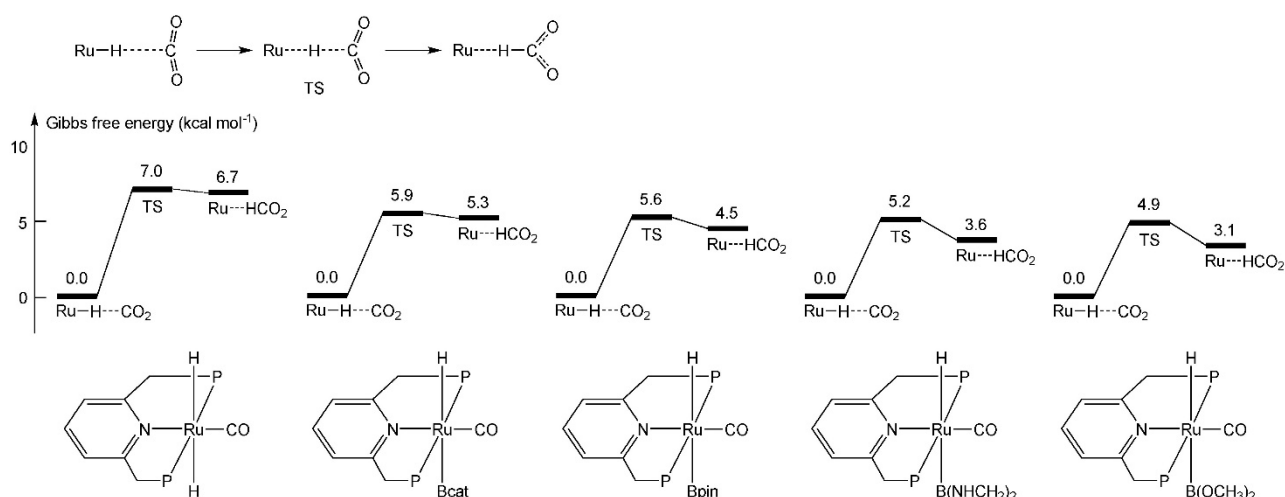


Figure 1. Free energy profile for the addition of hydride to CO_2 on the Ru PNP-type complex with different trans ligands. The substituent on phosphorus is omitted for clarity.

Table 2. Bond distance of the Ru–H bond, bonding parameter of the Ru–H bond, and activation free energy for hydride addition to CO_2 on the Ru PNP-type complex with different trans ligands.

Trans Ligand	Distance of Ru–H Bond (Å)	Coefficients/Hybrids of Ru–H Bond Orbital	Activation Free Energy for Hydride Addition to CO_2 (kcal mol ^{−1})
–H	1.697	0.706 Ru($\text{sd}^{2.11}$) + 0.709 H(s)	7.0
–Bcat	1.714	0.702 Ru($\text{sd}^{1.83}$) + 0.712 H(s)	5.9
–Bpin	1.716	0.699 Ru($\text{sd}^{1.80}$) + 0.715 H(s)	5.6
–B(NHCH ₂) ₂	1.717	0.699 Ru($\text{sd}^{1.76}$) + 0.715 H(s)	5.2
–B(OCH ₃) ₂	1.720	0.686 Ru($\text{sd}^{1.63}$) + 0.728 H(s)	4.9

To confirm the origin of the trans influence of B ligand, we investigated the properties of the Ru–H bonds in the above complexes with NBO analysis. The bonding parameters are collected in Table 2. As reported in our previous work [21], if less d orbital component of Ru is involved in the formation of the Ru–H bond, the hydride will be more active for direct addition to CO_2 . The ligand trans to the hydride is an important factor influencing the Ru–H bond property, because this ligand shares the same orbital of Ru with the hydride. The Ru–H bond in the $\text{Ru}(\text{PNP})(\text{CO})\text{H}_2$ complex is a σ bond formed via the mixing of the $\text{sd}^{2.11}$ hybrid orbital of Ru with the 1 s orbital of H. The Ru–H bond in the complex with Bcat, Bpin, $\text{B}(\text{NHCH}_2)_2$, or $\text{B}(\text{OCH}_3)_2$ trans ligand is also a σ bond, but the d orbital component of Ru–H bond in these complexes is 1.83, 1.80, 1.76, and 1.63, respectively, in a decreasing order that is also in accordance with the increasing order of trans influence of these B ligands. Consequently, the B ligands can modify the property of the Ru–H bond to improve the activity of the hydride. The essence of the strong trans influence of B ligands is to decrease the d orbital component of Ru in the Ru–H bond.

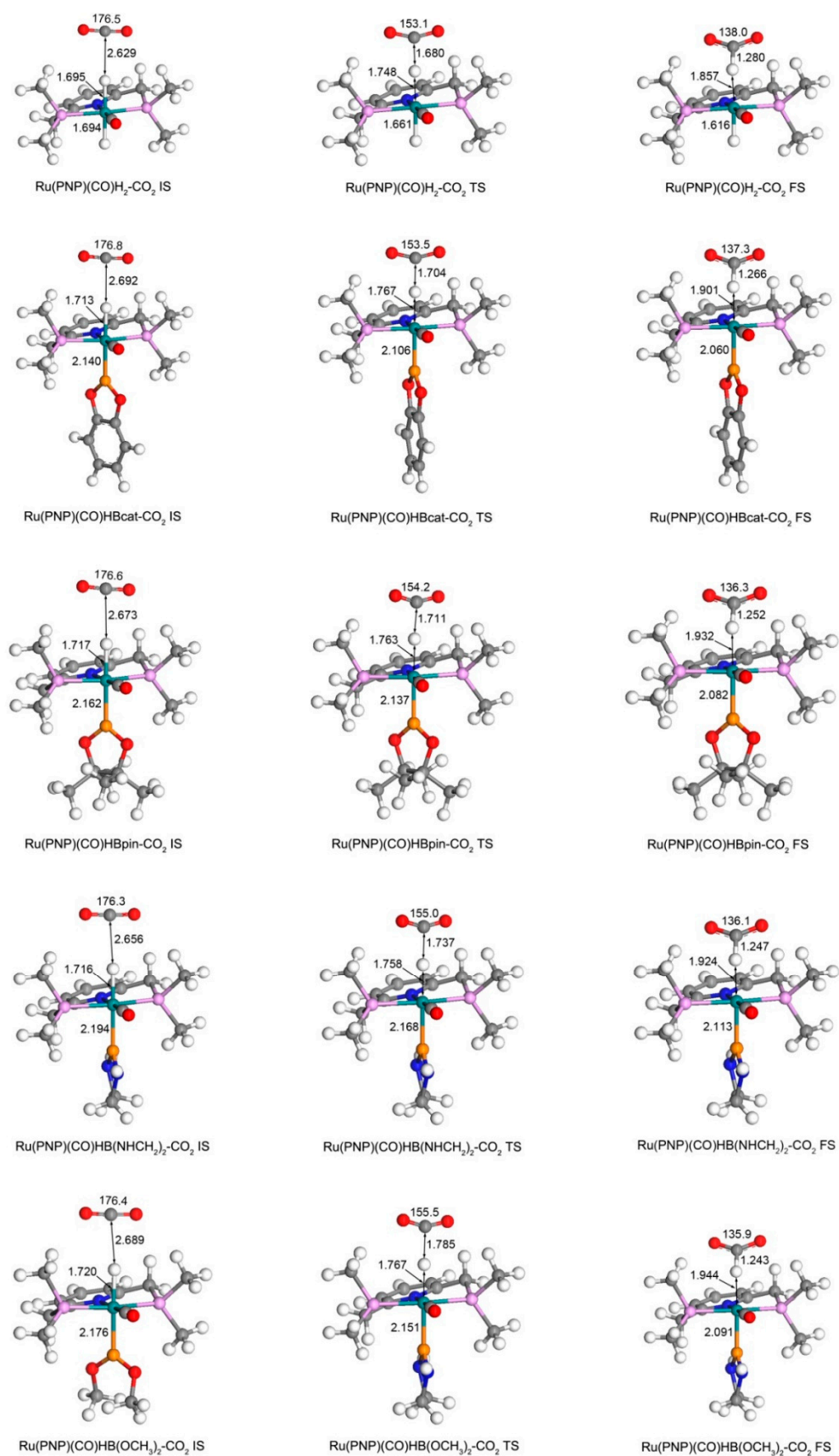


Figure 2. Optimized geometries of the species involved in the addition of hydride to CO₂ on selected Ru PNP-type complexes. Bond distances are given in angstrom (Å) and bond angles are in degree (°) (green balls: Ru; violet: P; red: O; blue: N; grey: C; orange: B; white: H).

2.3. Trans Influence of B Ligands on Trans-[Ru(dmpe)₂HX] Complexes

The trans-[Ru(dmpe)₂H₂] dihydride complex is another highly active complex in that the direct addition of hydride to CO₂ can occur as well, as reported by Baiker and co-workers [23]. Trans-[Ru(dmpe)₂H₂] is one of two isomers of Ru(dmpe)₂H₂, but cis-[Ru(dmpe)₂H₂] is not that active. We wondered about the trans influence of B ligands on this complex. Thus, we selected four B ligands as trans ligands to substitute one hydride of trans-[Ru(dmpe)₂H₂]. We optimized their geometries and calculated the activation free energy for hydride addition to CO₂ on these complexes. The free energy profile for this step on the trans-[Ru(dmpe)₂HX] complexes (X may be hydride or B ligand) is presented in Figure 3. The optimized geometries of all the species involved above are provided in the Supporting Information. On trans-[Ru(dmpe)₂H₂], the addition of hydride to CO₂ is endergonic by 2.5 kcal mol^{−1}, with an activation free energy of 3.6 kcal mol^{−1}. This activation barrier is even lower than that on Ru(PNP)(CO)H₂. This is because the assistance of hydrogen bonding for the fixation and the activation of CO₂ in this system is more significant than that on Ru(PNP)(CO)H₂. On trans-[Ru(dmpe)₂H₂], CO₂ can be fixed and assisted by at least four hydrogen bonds, but on Ru(PNP)(CO)H₂, there are only two hydrogen bonds. However, one may notice that the activation barrier for this step on the complexes with Bcat, Bpin, B(CH₃)₂, or BH₂ as trans ligand is not lower than that on trans-[Ru(dmpe)₂H₂]. The value on trans-[Ru(dmpe)₂HBpin] is even as high as 5.8 kcal mol^{−1}. It is usually believed that the help of hydrogen bonding is positive for the hydrogenation of CO₂ and some big groups on the complexes can provide more hydrogen atoms for the formation of hydrogen bonding. However, the big groups might bring greater steric hindrance on the other hand. Considering that the interaction of CO₂ with the hydride is very weak, the steric hindrance of big groups might offset the assistance of hydrogen bonding. In this sense, the effects of big groups for the hydrogenation of CO₂ are not always positive. Anyway, the formation of the H-bound formate complexes is thermodynamically favorable compared with that on trans-[Ru(dmpe)₂H₂].

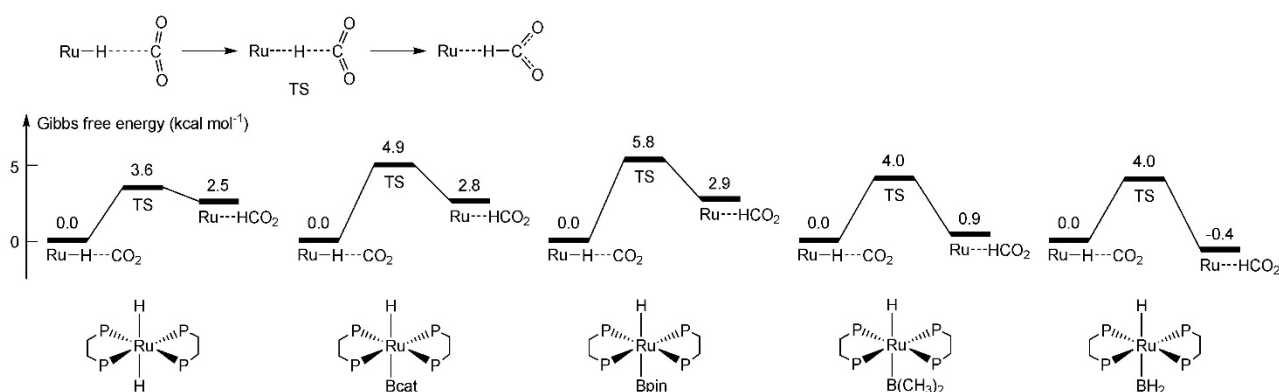


Figure 3. Free energy profile for hydride addition to CO₂ on trans-[Ru(dmpe)₂HX] complexes (X may be hydride or B ligand). The substituent on phosphorus is omitted for clarity.

3. Computational Methods

All calculations were implemented with the Gaussian 09 programs [35]. The B3LYP hybrid functional [36] was used. For Ru, the Stuttgart–Dresden basis set-relativistic effective core potential (RECP) combination [37], supplemented with two sets of *f* functions and a set of *g* functions [38], was applied. For the P, O, N, C, B, or H element, the Dunning cc-pVDZ basis set [39] was applied. Each stationary point was confirmed as a minimum or transition state by calculating the vibrational frequency, and all transition states were verified by intrinsic reaction coordinate (IRC) calculations. The Ru–H bond properties were characterized using NBO analysis with NBO 5.9 version [40]. For the Ru PNP-type complexes, the groups on P atoms are methyl groups. Gibbs free energies of all species were computed at 298.15 K and 1 atm.

4. Conclusions

For the purpose of the design of high-activity catalysts for the hydrogenation of CO₂, we have studied the trans influence of boryl ligands and various commonly used non-boryl ligands. Our calculation results show that, on the Ru PNP-type dihydride complex, the order of increasing trans influence of non-boryl ligands is as follows: $-\text{NO}_3 \approx -\text{Br} < -\text{Cl} < -\text{SCN} < -\text{ONO} \approx -\text{F} < -\text{OMe} < -\text{OH} \approx -\text{NO}_2 < -\text{NH}_2 < -\text{CN} < -\text{SiH}_3 < -\text{Ph} < -\text{Me} < -\text{Et} < -\text{H}$ and the sequence of increasing trans influence of boryl ligands is as follows: $-\text{H} < -\text{BBr}_2 < -\text{BCl}_2 \approx -\text{B}(\text{OCH})_2 < -\text{Bcat} < -\text{B}(\text{OCH}_2)_2 \approx -\text{B}(\text{OH})_2 < -\text{Bpin} < -\text{B}(\text{NHCH}_2)_2 < -\text{B}(\text{OCH}_3)_2 < -\text{B}(\text{CH}_3)_2 < -\text{BH}_2$. Only the B ligands exhibit a stronger trans influence than the hydride ligand. The computed activation free energy for the hydride addition to CO₂ and the NBO analysis of the property of the Ru–H bond indicate that the activity of the hydride can be systematically enhanced by the strong trans influence of the B ligands through the modification of the Ru–H bond property. The purpose of the strong trans influence of B ligands is to decrease the d orbital component of Ru in the Ru–H bond. In addition, we investigated the case on another Ru dihydride complex $\text{trans}[\text{Ru}(\text{dmpe})_2\text{H}_2]$. In this case, B ligands fail to lower the activation barrier for the hydride addition to CO₂. We think it is because the large groups on this kind of complex bring hydrogen bonding that is positive for the activation of CO₂, and at the same time form steric hindrance that is negative for the approaching of CO₂ to the hydride. Nevertheless, the design of a more active catalyst than the dihydride complex is possible.

Our next work is to probe the property of the Ru–B bond and the factors that can influence the Ru–B bond property, and then summarize some rules for the design of boryl-ligand-containing complexes with high activity for the hydrogenation of CO₂.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11111356/s1>, Figure S1: Optimized geometries of the species involved in the addition of hydride to CO₂ on $\text{trans}[\text{Ru}(\text{dmpe})_2\text{HX}]$ complexes; Table S1: Cartesian coordinates for the optimized geometries of all the species.

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