Carbon Dioxide Reduction by Pincer Rhodium η^2-Dihydrogen Complexes: Hydrogen-Binding Modes and Mechanistic Studies by Density Functional Theory Calculations

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Density functional theory (DFT) calculations using the KMLYP method on a series of pincer PCP−rhodium dihydrogen complexes have been employed to model and examine the proposed mechanisms for the pincer PCP−rhodium complexes mediated hydrogenation of carbon dioxide (CO_2). The relative energies of dihydrogen rotamers and dihydride isomers were evaluated together with T_1 values to determine the molecular structures of these complexes. We have investigated possible pathways for the CO_2 reduction processes involving the formation of rhodium dihydride species. Although the dihydrogen complexes are more stable than the corresponding dihydride isomers, the reduction of CO_2 has to proceed through the dihydride structures.

Introduction

Transition metal-catalyzed homogeneous hydrogenation of carbon dioxide (CO_2) has attracted much interest and continues to receive significant attention because of its relevance in carbon management research and its potential to serve as a source for the C1 feedstock from the abundant gas CO_2.[1−4] A number of effective rhodium and ruthenium complexes have been reported to catalyze the hydrogenation of CO_2 in a variety of solvents.[5−17] Kinetic studies of these systems along with theoretical calculations have greatly improved the mechanistic understanding of the important steps in the catalytic cycles.[18−25] It is well accepted that the first critical step of the reduction is the insertion of a CO_2 molecule into a metal−hydride bond. On the other hand, mechanistic studies on the hydrogenation of carbon dioxide mediated by complexes lacking a metal−hydride bond have not been documented.

In 1988, Kaska and co-workers reported a CO_2 hydrogenation reaction by a pincer rhodium dihydrogen complex that was referred to as "{2,6-bis[(di-*tert*-butylphosphino)methyl]phenyl}-dihydridorhodium(III)" (hereafter denoted as complex **1**).[26] This complex was synthesized by reduction of the {2,6-bis[(di-*tert*-butylphosphino)methyl]phenyl}hydridorhodium chloride precursor[27] with potassium hydride under 1 atm of dihydrogen gas.[28] While these authors did not comment on whether this "dihydrido" complex was a classical or nonclassical dihydrogen complex, they showed that it was capable of reducing CO_2. Interestingly, the first stable intermediate observed was a hydridorhodium hydroxide complex (**3**), presumably through the hydridorhodium formate intermediate **2**. Complex **3** then

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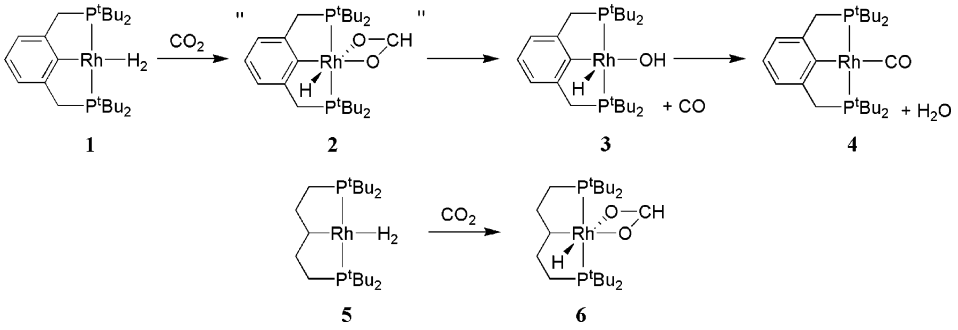
Scheme 1. Reduction of CO_2 by PCP−Rh−H_2 Complexes



further reacted in one week or longer to give a rhodium−carbonyl complex (**4**) and water as final products (Scheme 1). A similar system was studied by Milstein and co-workers in 1996, using a saturated PCP ligand analogue.[29] They demonstrated that complex **5** was a nonclassical dihydrogen complex based on the short T_1 (30−60 ms) observed in ^{1}H NMR. In sharp constrast to Kaska's results, this dihydrogen complex reacted with CO_2 to give a hydridorhodium formate complex (**6**) as the final product without further reactions.

Although these reactions are not catalytic, the different reactivities of these two ligand systems are intriguing. Mechanistic studies on the CO_2 reduction by such complexes would provide a deeper understanding of these processes and could allow the development of new catalyst models for the reduction of CO_2. In this paper, we report computational studies and experimental evidence to determine the binding modes of these PCP−Rh−H_2 complexes and to address the possible reaction pathway for a bound H_2 molecule to reduce CO_2. By comparing the reaction profiles of the aromatic and saturated PCP−Rh models, a probable key step that may be involved in the formation of complex **4** in the aromatic system is also discussed.

Results and Discussion

Coordination Modes of H_2. The relative energies of rotamers of dihydrogen complexes as well as their dihydride isomers were evaluated by DFT calculations using the KMLYP density functional[30] to determine the most stable coordination modes of complexes **1** and **5**. In addition to the real *tert*-butyl structures, the hypothetical truncated hydrogen models were also studied.

Complex **5** was chosen to be studied first in order to support Milstein's results. Three isomers were located for this saturated PCP model: the η^2-dihydrogen complex **5a**, where the H−H bond is perpendicular to the PCP−Rh plane, the η^2-dihydrogen complex **5b**, where the H−H bond is parallel to the PCP−Rh plane, and the dihydride isomer **5c** (Figure 1). The H(a)−H(b) distances in **5a** and **5b** are 0.830 and 0.821 Å, respectively, and fall into the range of typical H−H bond lengths in nonclassical dihydrogen transition metal complexes.[31−34] The H(a)−Rh and H(b)−Rh bond distances in **5a** and **5b** are ∼0.25 and ∼0.1 Å longer than the H(a)−Rh bond and the H(b)−Rh bond in **5c**, respectively. All the structures of the PCP−Rh framework in these three isomers are similar and comparable to that of the hydridorhodium chloride structure (PCP−Rh(H)-Cl) determined by X-ray crystallography.[35] Frequency calculations were used to verify that calculated structures were indeed minima and to determine zero-point energies and entropic contributions to the free energies. Calculated relative free energies show that **5a** is more stable than **5b** and **5c** by 1.1 and 7.0 kcal/mol at 25 °C (298.15 K), consistent with the experimental observations that complex **5** exists as a η^2-dihydrogen complex.[29]

For the aromatic complex **1**, three isomers were located as well. In general, they show similar structural patterns to their corresponding complex **5** analogues. Noteworthy is that the P1−Rh−P2 planes are distorted from the phenyl rings in these structures to give dihedral angles for P2−Rh−C3−C4 of 12.5°, 12.9°, and 11.1° for **1a**, **1b**, and **1c**, respectively.[28] Moreover, in **1a** the H−H bond is found to be perpendicular to the phenyl plane, and in **1b** the H−H bond is almost parallel to the P1−Rh−P1 plane (Figure 2). In an effort to elucidate the orientation preference of the H−H bond, the molecular orbitals of **1a** and **1b** were analyzed. As shown in Figure 3, both HOMO−7 orbitals in **1a** and **1b** show that the H−H binding angle has no significant effect on the σ interaction of the bonding orbital of H_2 to the Rh center. However, in terms of the dπ back-donation from Rh to the σ^* orbital of H_2, the H−H binding angles can induce different interactions with other ligands. The HOMO−1 of **1a** involves antibonding between the dπ orbital of Rh and the π orbital of the phenyl ring, and the HOMO−4 of **1b** consists of interactions with the Rh−P bonds.[36] These observations suggest that the back-donation from the transition metal−ligand fragment to σ^* of H_2 plays an important role in determining the orientation of the H−H axis.

A similar trend in relative stabilities was observed. The dihydrogen complex **1a** is more stable than complex **1b** and the dihydride complex **1c** by 0.3 and 9.9 kcal/mol, respectively. These results indicate that complex **1** is also a nonclassical dihydrogen complex. To further confirm this assignment, complex **1** was subjected to the T_1 measurement. The synthesis of **1** was carried out by treating the PCP−Rh−(N_2) analogue under 1−2 atm of H_2 to replace the N_2 ligand with H_2.[29] Its ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic properties were identical to those reported in the literature for **1** via a different synthetic route.[28] The T_1 obtained on a Bruker Avance spectrometer (400 MHz) at −45 °C is 26 ± 1 ms,[37] supporting the dihydrogen binding mode.[29] Moreover, the H−H bond distance of **1** was estimated to be 0.874−0.891 Å, in good agreement with the calculation results, by measuring the H−D coupling constant

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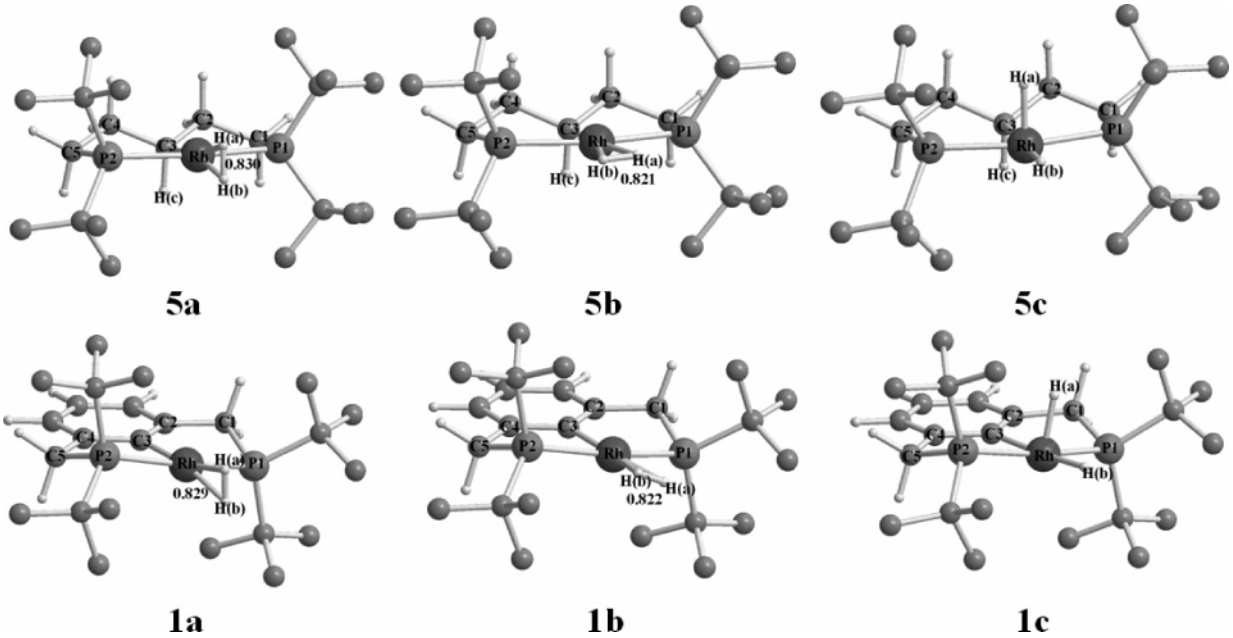

Figure 1. Optimized structures of PCP−Rh−H_2 isomers with hydrogen atoms of the *tert*-butyl groups omitted.

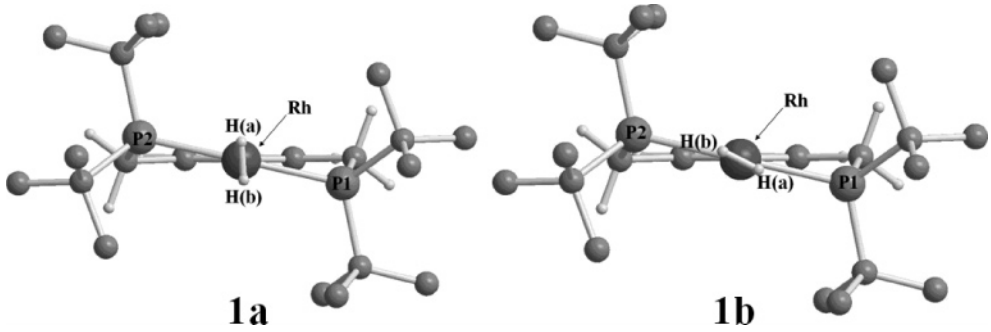

Figure 2. Front views of dihydrogen complexes **1a** and **1b**.

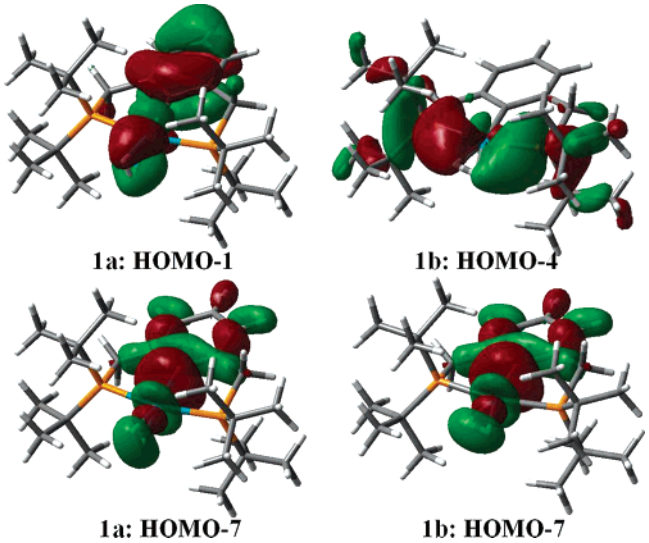

Figure 3. Selected molecular orbitals of dihydrogen complexes **1a** and **1b**.

of the PCP−Rh−(HD) analogue (J_{HD} = 32.7 Hz, at 25 and −45 °C)[37] and using the empirical formulas developed by both Morris[38] and Heinekey.[39]

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Replacement of the *tert*-butyl groups with hydrogen atoms in the truncated models, **7** (H model of **1**) and **8** (H model of **5**), resulted in the complete destabilization of the type **b** dihydrogen rotamers and the type **c** dihydride isomers. All attempts at optimizing these structures led to the type **a** dihydrogen complexes. This could be rationalized by both electronic and steric effects that the *tert*-butyl groups help stabilize the type **b** dihydrogen complexes by increasing the barriers of the Rh−(H_2) bond rotation, and the dihydride complexes by introducing more electron density to the metal center. Nevertheless, the truncated hydrogen models successfully predicted the most stable structures.

Mechanism of CO_2 Reduction. Several important theoretical studies on the Rh-catalyzed hydrogenation of CO_2 to formic acid (HCOOH) have been reported.[19,21,23] The proposed mechanism involves hydride transfer from a Rh−H bond to a η^1-O-coordinated CO_2 to form a Rh−formate intermediate, which can then either undergo oxidative addition of an H_2 molecule to the metal center to form a dihydride intermediate followed by the reductive elimination of HCOOH or undergo σ-bond metathesis with H_2 to release HCOOH and regenerate the catalytically active Rh−H complex. As discussed above, even though complexes **1** and **5** are nonclassical dihydrogen complexes, experimental results have established that they can both reduce CO_2 to afford reduction products. Because the dihydrogen complexes were identified as the most stable species, the way the bound H_2 reduces CO_2 is intriguing. To investigate this question, only complexes **7** and **8**, the truncated hydrogen

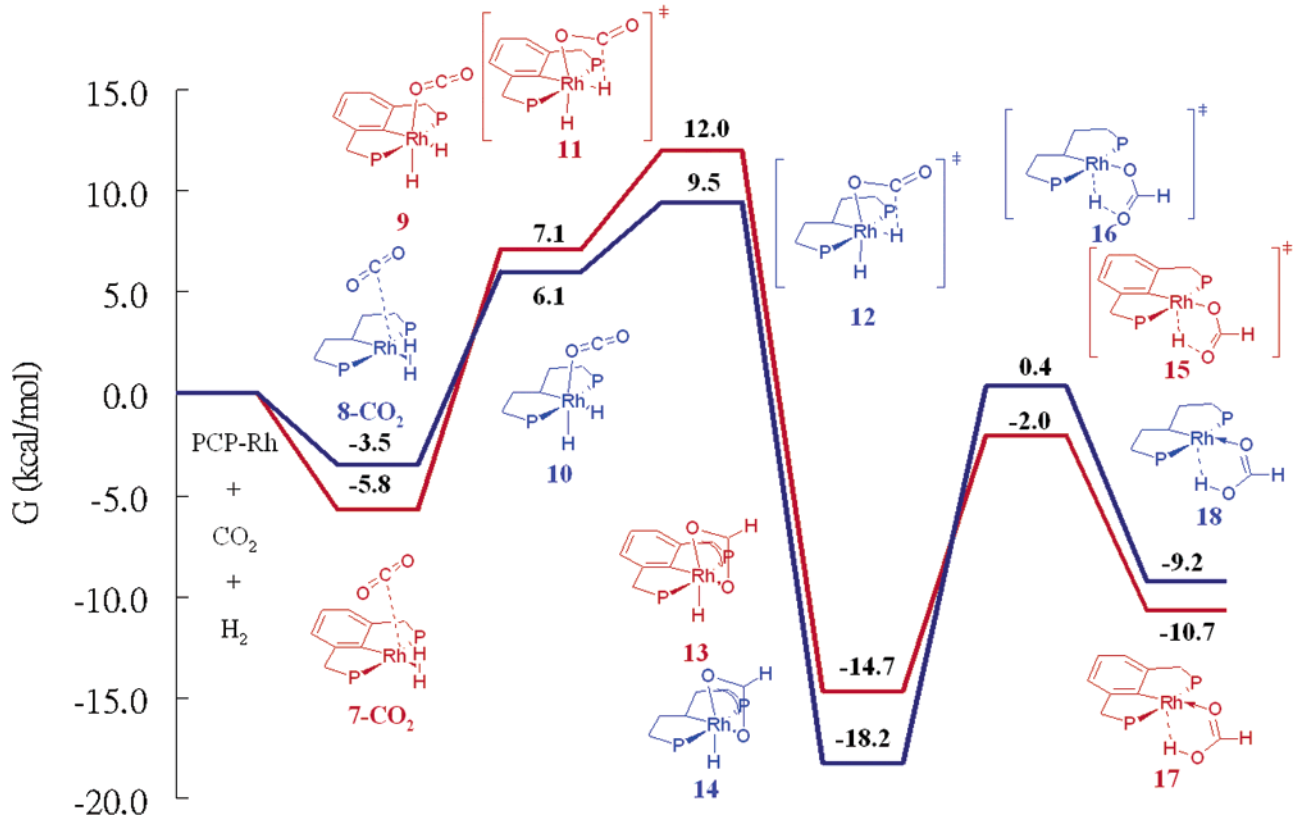

Figure 4. Free-energy changes for the CO_2 reduction processes at 298.15 K. For clarity, the H atoms on the phosphorus atoms have been omitted.

models of **1** and **5**, were employed in the mechanistic study to examine the possible pathways in the interest of computational efficiency. Truncated hydrogen models have been previously applied successfully in other similar pincer systems.[40−43]

We found that η^2-H_2 binding followed by CO_2 coordination to a naked PCP−Rh center to give the dihydrogen complex with a weakly bound η^1-*C*O_2 complex (Figure 4) is thermodynamically favored. This type of η^1 interaction can be viewed as the donation of the HOMO of the Rh−H_2 complex, a d_{z^2} orbital, to the π^* orbital of the CO_2 molecule. However, the CO_2 coordination is expected to be weak because the Rh−*C*O_2 distances are 3.411 and 3.274 Å for **7**-CO_2 and **8**-CO_2, respectively. No intermediates or transition states could be derived to connect these two dihydrogen−Rh-η^1-*C*O_2 complexes to the CO_2 reduction processes.

We then examined the possible routes for the reduction to proceed through the dihydride structures. Similar to the observed relative energies of the dihydrogen and the dihydride isomers of complexes **1** and **5**, the dihydrido−Rh−CO_2 complexes **9** and **10** are 12.9 and 9.6 kcal/mol, respectively, higher in energy than **7**-CO_2 and **8**-CO_2. We predict that CO_2 binds to Rh in an η^1-*O*CO "end-on" fashion in both complexes. Selected bonding parameters and the corresponding atom numberings are summarized in Table 1. Species **9** and **10** both have long Rh−O1 and C2−H(b) distances, but we note that the C2−H(b) distances are 0.3−0.7 Å shorter than those reported in other DFT studies for cationic Rh species.[21,23] These geometrical features might suggest that the hydrido−CO_2 interaction is stronger for the neutral PCP−Rh complex bearing a hydride *trans* to the C ligand (phenyl or alkyl).

These dihydride structures can then undergo the hydride transfer from the Rh center to the C center of CO_2 with low-energy barriers. Most of the structural variables of the transition states **11** and **12** do not vary significantly from those of the starting intermediates, except that the C2−H(b) distances become 0.8−0.9 Å shorter and the O1−C2−O2 angles change from linear to ∼155°. The overall energy barriers for the reduction of CO_2 by the PCP−Rh η^1-H_2 complexes are calculated to be 17.8 kcal/mol for **7** and 13.0 kcal/mol for **8**, consistent with the fact that the reactions of CO_2 with **1** and **5** occur instantly at room temperature.[26,29] After the hydride insertion event, the kinetic products formed are hydridorhodium η^1-formate complexes, which should transform into the most stable η^2-formate coordination compounds, as the d^6 rhodium center prefers the d^2sp^3 octahedral structure. The transition state energy of such transformations has been previously estimated to be 2−5 kcal/mol above the η^1-formate complex by Musashi and Sakaki.[21] Thus, these calculations were not performed in this study. However, as expected, complexes **13** and **14** were predicted to be the most thermodynamically stable products for the CO_2 reduction reactions. They both have similar C2−O1 and C2−O2 bond lengths and the C2 centers are now sp^2 hybridized.

Complex **6** has been shown as the final product of the reaction of complex **5** and CO_2.[29] In order to verify that the rhodium formate complex **2** was an intermediate formed in the reaction of complex **1** and CO_2, this reaction was monitored by NMR. It was found that complex **2** was formed immediately together with a small amount of an intermediate and the PCP−Rh−CO complex **4**. The lifetime of **2** was long enough under such

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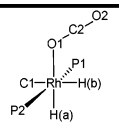
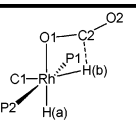
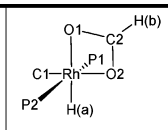
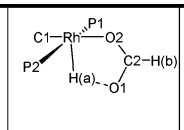
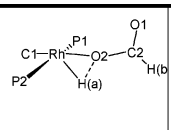
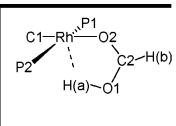
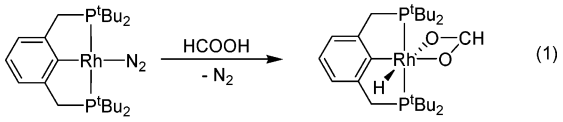
Table 1. Selected Geometrical Parameters for Complexes 9−18[a]

												
	9	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**15'**	**16'**	**17**	**18**
Rh-C1	2.059	2.148	2.063	2.117	2.006	2.061	2.025	2.076	2.018	2.054	2.017	2.067
Rh-P1	2.268	2.261	2.275	2.269	2.281	2.281	2.282	2.287	2.281	2.287	2.273	2.273
Rh-O1	2.424	2.399	2.315	2.308	2.257	2.232	-	-	-	-	-	-
Rh-O2	-	-	-	-	2.215	2.272	2.146	2.184	2.168	2.208	2.220	2.249
Rh-H(a)	1.510	1.514	1.520	1.523	1.537	1.543	1.575	1.605	1.569	1.569	2.181	2.147
Rh-H(b)	1.641	1.654	1.692	1.698	-	-	-	-	-	-	-	-
C2-H(b)	2.672	2.611	1.743	1.811	1.093	1.094	1.092	1.092	1.100	1.103	1.085	1.086
C2-O1	1.157	1.159	1.189	1.186	1.243	1.247	1.240	1.246	1.193	1.194	1.292	1.292
C2-O2	1.143	1.143	1.161	1.159	1.243	1.239	1.243	1.238	1.295	1.292	1.204	1.204
O1-H(a)	-	-	-	-	-	-	1.535	1.457	-	-	0.998	1.004
O2-H(a)	-	-	-	-	-	-	-	-	1.435	1.424	-	-
O1-C1-O2	175.9	174.8	153.4	155.1	122.2	122.6	125.4	125.1	125.1	125.6	124.1	124.0
P1-Rh-P2	159.8	161.8	161.0	162.8	163.2	167.5	161.1	156.2	162.2	162.7	161.5	162.5

[a] Reported in deg and Å.

conditions to allow a ^{1}H, ^{13}C, and ^{31}P NMR analysis. The ^{13}C-{^{1}H} NMR chemical shift of the formate carbon atom is δ 172.4 ppm, consistent with Kaska's observation when using $^{13}CO_2$.[26] The ^{31}P{^{1}H} NMR chemical shift at δ 78.0 ppm, with a J_{RhP} coupling constant of 118.4 Hz, indicates a Rh(III) formal oxidation state. Unfortunately, due to its instability, complex **2** could not be isolated and purified. Thus, to further confirm that the intermediate we observed was indeed the rhodium formate complex, complex **2** was also prepared by treating PCP−Rh−(N_2) with an excess amount of HCOOH (eq 1). The resulting ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic properties were identical to those observed from the reaction of complex **1** and CO_2. Furthermore, when HCOOD was used, the proton NMR signal for Rh−*H* at δ −22.51 ppm was not detected, and when DCOOH was used, the signal of the formyl hydrogen (Rh−O_2C*H*) at δ 8.64 ppm was not observed. Using H^{13}COOH led to a doublet signal for Rh−O_2C*H* at δ 8.64 ppm with a J_{CH} coupling constant of 194 Hz, consistent with the literature value measured by ^{13}C NMR.[26]



(1)

2

Reductive Elimination of Formic Acid. Kaska and coworkers have demonstrated that the short-lived complex **2** further decomposed to give the Rh−CO complex **4** and water as the final products under CO_2.[26] The two major reactions of hydrido transition metal formate complexes reported in the literature are decarboxylation via β-hydride elimination to lose CO_2,[44] a reverse reaction of the hydride transfer to CO_2, and the reductive elimination of formic acid.[2,6] Since the decarboxylation reaction will result in the regeneration of complex **1** and CO_2, it is inferred that the formation of complex **4** can only occur after the reductive elimination of a formic acid molecule from **2** followed by the decarbonylation of the formyl functional group of the formic acid by the reduced Rh(I) center, given the fact that Rh(I) compounds are excellent decarbonylation reagents for aldehydes and formate esters.[45−49]

The reductive elimination reactions were examined by DFT for the hydrogen analogues **13** and **14** (Table 1 and Figure 4). Only the five-centered transition states, **15** and **16**, and the three-centered ones, **15′** and **16′**, were studied because the dihydrogen-induced σ-bond metathesis for the elimination of a formic acid molecule was not possible in these reaction conditions.[26,29] Consistent with Musashi and Sakaki's observations,[23] transition states **15′** and **16′** are of much higher energies than **15** and **16** by 24.3 and 19.9 kcal/mol, respectively, thus indicating that the five-centered transition states are also more favored for these pincer complexes. The reductive elimination reactions through the five-centered transition states led to the most stable Rh(I)−κ^2-formic acid adducts, **17** and **18**. Despite the fact that the reaction patterns of the aromatic and saturated PCP complexes are similar, it should be noted that the transition state barrier for reductive elimination of **14** is 5.9 kcal/mol higher than that of **13**, and the energy difference between the hydridorhodium η^2-formate complex and the Rh(I)−κ^2-formic acid product for **14** and **18** is also 5.0 kcal/mol larger than those for **13** and **17**. We rationalize this by noting that the saturated PCP ligand makes the rhodium center more electron rich and, thus, disfavors the reductive elimination reaction.[50] These results suggest that if the elimination reaction of formic acid is an essential step for a subsequent decarbonylation reaction to occur, complex **2** will be much more reactive than complex **6**.

Conclusion

In summary, we have employed the KMLYP DFT functional to perform a mechanistic study of CO_2 reduction reactions

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mediated by pincer PCP−Rh dihydrogen complexes. Consistent with the experimental observations, complexes **1** and **5** were both identified as *nonclassical dihydrogen complexes*. Although the η^2-dihydrogen structures are thermodynamically favored over dihydride isomers, in order to reduce the bound CO_2 molecule, *hydride transfer from the Rh center to carbon must proceed through the dihydride intermediate*. These results further suggest that CO_2 reduction by hydrogen does not necessarily require a metal hydride precursor as long as a hydride intermediate is thermodynamically accessible. The formation of hydridorhodium formate **2** was confirmed experimentally by NMR in the reaction of the η^2-dihydrogen complex **1** with CO_2. Complex **2** was also prepared independently and characterized by NMR techniques. Investigations on the probable HCOOH reductive elimination reactions from the truncated hydridorhodium formate models **13** and **14** revealed that the energy barrier and the corresponding free energy of reaction for the saturated PCP model **14** are 5.9 and 5.0 kcal/mol higher, respectively, than those of the aromatic analogue **13**. This observation suggests that the more electron-donating saturated PCP complex disfavors the reductive elimination. Computational and experimental investigations of the mechanism of the subsequent decarbonylation from complex **2** are currently ongoing in our laboratories.

Computational and Experimental Details

Computational Details. DFT calculations on the PCP−rhodium complexes were performed using the Gaussian 03 program (revision C.02).[51] The KMLYP hybrid DFT method was employed.[30] This method combines the HF and Slater exchange functionals[52] for the exchange energy and the VWN[53] and LYP[54] correlation functionals for the correlation energy. The mixing parameters were obtained in an attempt to reduce self-interaction errors generally present in most DFT methods by reproducing the ground state energy of atomic hydrogen, while simultaneously describing electron−electron interactions by reproducing the electron affinity of atomic oxygen. KMLYP has been shown to correctly determine a wide variety of molecular properties for significantly different systems.[55−58] Geometry optimizations were performed using the default convergence criteria without any geometric constraints. The LANL2DZ ECP basis set[59−61] was used for the rhodium atom, while the all-electron 6-31G+(d) Pople basis set was employed for all other atoms.[62−64] Frequency calculations were used to characterize the stationary points as minima or transition state structures, to determine zero-point energies (ZPEs), and for free-energy calculations. Gibbs free energies were calculated at 25 °C (298.15 K).

General Procedures. All manipulations were carried out under an atmosphere of nitrogen using Schlenk techniques or in a MBraun drybox. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance spectrometer (400 MHz for ^1H, 125 MHz for ^{13}C, and 161.98 MHz for ^{31}P). ^1H NMR chemical shifts were referenced to the residual proton peak of d_6-benzene (C_6D_6) at δ 7.15, ^{13}C NMR chemical shifts were referenced to C_6D_6 at δ 128.0, and ^{31}P NMR chemical shifts were referenced to an external 85% H_3PO_4 sample at δ 0.0. C_6D_6 was distilled from purple sodium/benzophenone solution and stored under N_2 prior to use. Complexes **1** and **5** were synthesized from their dinitrogen analogues upon treatment of dihydrogen atmosphere according to the literature procedures.[29] Research grades of N_2, H_2, and CO_2 were used without further purification. HCOOD (98% D, <5% D_2O), DCOOH (98% D, <5% H_2O), and $H^{13}COOH$ (99% ^{13}C, <5% H_2O) were purchased from Cambridge Isotope Laboratories, Inc. and degassed by three freeze−pump−thaw cycles prior to use.

{2,6-Bis[(di-*tert*-butylphosphino)methyl]phenyl}hydridorhodium Formate, 2. A solution of PCP−Rh−(H_2) complex **1**, synthesized by treating 1.0 mg of {2,6-bis[(di-*tert*-butylphosphino)-methyl]phenyl}rhodium dinitrogen complex in 0.7 mL of d_6-benzene under 1 atm of H_2, was fully degassed and then saturated under 2 atm of CO_2 at room temperature. Complex **2** was formed immediately together with a small amount of an intermediate and PCPRh−CO **4** (less than 5%). ^1H NMR (C_6D_6): δ −22.51 (dt, 1H, J_{RhH} = 31.7 Hz , J_{PH} = 12.2 Hz), 1.21 (t, 18H, J_{PH} = 6.7 Hz), 1.30 (t, 18H, J_{PH} = 6.4 Hz), 2.85 (dt, 2H, J_{RhH} = 17.1 Hz , J_{PH} = 3.6 Hz), 3.13 (dt, 2H, J_{RhH} = 17.1 Hz , J_{PH} = 3.6 Hz), 6.85−7.00 (m, 3H), 8.64 (s, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 29.7 (t, J_{PC} = 2.7 Hz), 30.0 (t, J_{PC} = 3.1 Hz), 33.3 (dt, J_{RhC} = 3.0 Hz , J_{PC} = 10.7 Hz), 35.1 (dt, J_{RhC} = 1.5 Hz , J_{PC} = 8.5 Hz), 36.5 (t, J_{PC} = 6.8 Hz), 122.1 (t, J_{PC} = 8.5 Hz), 122.8 (s), 149.5 (t, J_{PC} = 10.0 Hz), 155.5 (d, J_{RhC} = 42.9 Hz), 172.4 (s). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 78.0 (d, J_{RhP} = 118.4 Hz). Treatment of the PCP−Rh−(N_2) d_6-benzene solution with 25 equiv of formic acid afforded a complex with the NMR properties identical with those of complex **2**.

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Supporting Information Available: Further details of the DFT computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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