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Articles

Promotion Effect of the Protonated Amine Arm of a Ruthenium Complex on Hydrido Migration to CO_2: A Density Functional Study

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The hydrido migration to the carbon of CO_2 on the experimentally synthesized novel N−H···H−Ru H-bonded complex (η^5-$C_5H_4(CH_2)_3NMe_2H^+$)RuH(dppm), **2**, was examined by means of the hybrid density functional method (B3LYP), assuming the following two generally considered reaction paths: (a) the abstraction of the hydrido ligand by an incoming CO_2 without direct coordination of CO_2 to the Ru atom, and (b) the insertion of CO_2 to the Ru−H bond with the η^2-CO precoordination of CO_2 to the Ru atom. Without the contribution of the protonated amine arm of the Ru complex, the reaction is uphill in path a, while 8.1 kcal/mol exothermic in path b, requiring the energy barrier of 6.8 kcal/mol. However, when the proton bonded to N of the amine arm has a H-bonding with an oxygen of CO_2, the energetics in path a completely changes, and the potential energy surface becomes quite smooth, where only the small energy barrier of 2.6 kcal/mol is needed. On the other hand, in path b although the potential energy surface of the reaction is stabilized by about 20−21 kcal/mol, its feature does not change even with the participation of the amine arm with the H-bonding. Consequently, it was found that path a was more facile than path b because the function of the ptotonated amine arm is only effective for path a. This promotion effect of the protonated amine arm in path a originates from the enhancement of the electrophilicity at the carbon of CO_2 by the H-bonding of the proton attached to N of the amine arm with one of the CO_2 oxygens.

Introduction

In the last few years, quite interesting organometallic compounds, which have new types of H-bonding, e.g., where the hydrogen atom instead of the usual nitrogen or oxygen atom is a proton acceptor, have been experimentally found.[1−5] The characteristics of such a new type of H-bonding have been examined in detail by some spectroscopic techniques, and these H-bondings are expected to play an essential role in the control of industrially important organic syntheses and catalytic reactions or of biological reaction processes.

Very recently, Chu et al. synthesized and characterized the novel intramolecular N−H···H−Ru H-bonded complex (η^5-$C_5H_4(CH_2)_nNMe_2H^+$)RuH(dppm) ($n = 2, 3$) **2**.[5] They found that this complex catalyzes the hydrogenation of CO_2, which has intrigued many chemists in recent years from an industrial point of view.[6] The proposed cycle of the catalytic reaction by **2** consisting of some elementary steps, as depicted in Figure 1, has been experimentally well reproduced by the independent stoichiometric reactions of these elementary steps.

The precursor complex, (η^5:η^1-$C_5H_4(CH_2)_nNMe_2$)Ru(dppm), **1**, first rapidly reacts with an H_2 molecule to form **2** at a relatively low temperature (step 1), suggesting that this step readily proceeds. Here, the heterolytic cleavage of the H_2 molecule and the deprotonation by the pendant amino group (amine arm) connected to the cyclopentadienyl (Cp) ring take place. The complex **2** next reacts with CO_2 to form the

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[1] (a) Lough, A. J.; Park, S.; Ramashandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356. (b) Park, S.; Ramashandran, R.; Lough, A. J.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2201.

[2] (a) Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Vorontsov, E. V.; Epstein, L. M.; Gusev, D. G.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105. (b) Belkova, N. V.; Shubina, E. S.; Ionidis, A. V.; Epstein, L. M.; Jacobson, H.; Niedermann, M.; Berke, H. *Inorg. Chem.* **1997**, *36*, 1522.

[3] (a) Lee, J. C.; Peris, E.; Rheingold, A.; Mullar, B.; Pregosin, P. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1021. (b) Lee, J. C.; Peris, E.; Rheingold, A.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014. (c) Peris, E.; Lee, J. C.; Rambo, J. R.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3485. (d) Peris, E.; Wessel, J.; Lee, J. C.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem.* **1995**, *107*, 2711; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2507. (e) Crabtree, R. H.; Eisenstein, O.; Sini, G.; Peris, E. *J. Organomet. Chem.* **1998**, *567*, 7. (f) Lee, D.-H.; Kwon, H. J.; Patel, B. P.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H. *Organometallics* **1999**, *18*, 1615.

[4] Alkorta, I.; Rozas, I.; Elguero, J. *Chem. Soc. Rev.* **1998**, *27*, 163, and references therein.

[5] Chu, H. S.; Lau, C. P.; Wong, K. Y. *Organometallics* **1998**, *17*, 2768.

[6] Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259.

10.1021/om0005250 CCC: \$20.00

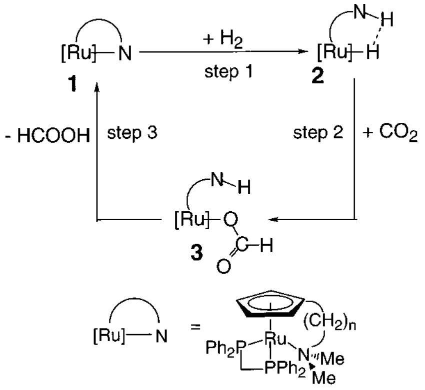
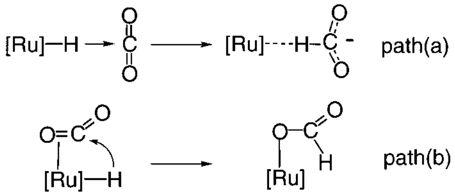


Figure 1. Proposed catalytic cycle of the experimental hydrogenation of CO_2 by (η^5-$C_5H_4(CH_2)_nNMe_2H^+$)RuH(dppm) ($n = 2, 3$), **2**.

transient formate intermediate (η^5-$C_5H_4(CH_2)_nNMe_2H^+$)Ru(HCOO)(dppm), **3** (step 2), which is followed by the immediate liberation of formic acid by the reaction of $HCOO^-$ with the proton attached to the N atom (step 3). Since only **2** is detectable in the solution, step 2 has been thought to be a slow step, although the details of the reaction mechanism have not been clarified. In step 2, one will usually consider the two reaction paths presented below: (a) the abstraction of the hydrido ligand by an incoming CO_2 without direct coordination of CO_2 to the Ru atom, and (b) the insertion of CO_2 to the Ru−H bond with the η^2-CO precoordination of CO_2 to the Ru atom. An insertion reaction similar to path b has already been theoretically reported.[7,8]



In the present study, the hybrid density functional (B3LYP) calculations were performed using a model Ru complex, where the substituents Ph on P and Me on N are replaced by H, for the two reaction paths a and b which can be considered for the important hydrido migration to CO_2. It was found that the unlikely path a is more favorable than path b due to the electronic effect of the protonated amine arm interacting with an oxygen of CO_2, effective only for path a.

Calculation Method

All calculations were performed at the B3LYP level of theory, which consists of a hybrid Becke + Hartree−Fock exchange and Lee−Yang−Parr correlation functional with nonlocal corrections,[9] using the Gaussian 98 program.[10] The basis functions used in the geometry optimizations were the lanl2dz for P, O, N, C, and H atoms, and a valence double-ζ (5s5p4d)/[3s3p2d] for Ru with the relativistic effective core potential (ECP) replacing the core electrons up to 3d determined by Hay and Wadt[11] (basis set I).[12] For the optimized structures, the single-point calculations were performed to obtain the more reliable energies using the higher quality basis set II, namely, a triple-ζ construction (5s5p4d1f)/[3s3p3d1f] augmented by a single set of the f polarization function with the exponent of 1.235[13] for Ru and 6-31G(d,p)[14] for the other atoms.

All equilibrium structures and transitions states were optimized without any symmetry restrictions and identified by the number of imaginary frequencies calculated from the analytical Hessian matrix. The reaction coordinates were followed from the transition state to the reactant and the product using the intrinsic reaction coordinate (IRC) technique.[15]

Results and Discussion

Structures. The optimized equilibrium structures and the transition states (TSs) involved in paths a and b are presented in Figure 2. Two pathways, (I) one without the contribution of the protonated amine arm, and (II) another with the contribution of the protonated amine arm, were examined to clarify the function of the protonated amine arm in both paths a and b. In path I, the protonated amine arm is completely turned up, avoiding any interaction with CO_2 throughout, while in path II, the N-bound proton has a H-bonding with an oxygen of CO_2, which is retained during the reaction. The analogous structural features with the amine arm rotated up have been experimentally isolated.[16] In path a-I, the stationary point was located only at the reactant, which suggests that this reaction is uphill. Therefore, the structures of the reactant, TS, and the product, **4-I**, **TS1-I**, and **5-I**, displayed in Figure 2, were used for the calculation of the potential energy surface presented below. These structures were artificially obtained from the corresponding optimized reactant, TS, and product, **4-II**, **TS1-II**, and **5-II**, of path a-II, respectively, where only the dihedral angle ∠C−C−C−C(Cp) of the protonated amine arm is changed to 72.8°[17] in **4-II**, **TS1-II**, and **5-II**. However, the selected important optimized parameters of the reactant are shown in parentheses for **4-I** since its geometric features are quite similar to **4-I**. In the reactant, the incoming CO_2 is weakly bound to the hydirdo H^1 with the C^1−H^1 distance of 2.632 Å,

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(7) Torrent, M.; Solà, M.; Frenking, G. *Chem. Rev.* **2000**, *100*, 439, and references therein.

(8) Hutschka, F.; Dedieu, A.; Eichberger, M.; Fornika, R.; Leitner, W. *J. Am. Chem. Soc.* **1997**, *119*, 4432.

(9) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(11) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(12) It was confirmed that the experimentally observed Ru−H- - -H−N H-bond distance of 1.52 Å in **2**[16] was excellently reproduced to be 1.561 Å by the optimization of its model complex at the B3LYP/I level.

(13) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking G. *Chem. Phys. Lett.* **1993**, *208*, 111.

(14) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(15) Fukui, K.; Kato S.; Fujimoto, H. *J. Am. Chem. Soc.* **1975**, *97*, 1.

(16) Ayllon, J. A.; Sayers, S. F.; Sabo-Etienne, S.; Donnadieu, B.; Chaudret, B.; Clot, E. *Organometallics* **1999**, *18*, 3981.

(17) This value was extracted from the optimized parameters of the reactant of path a-I.

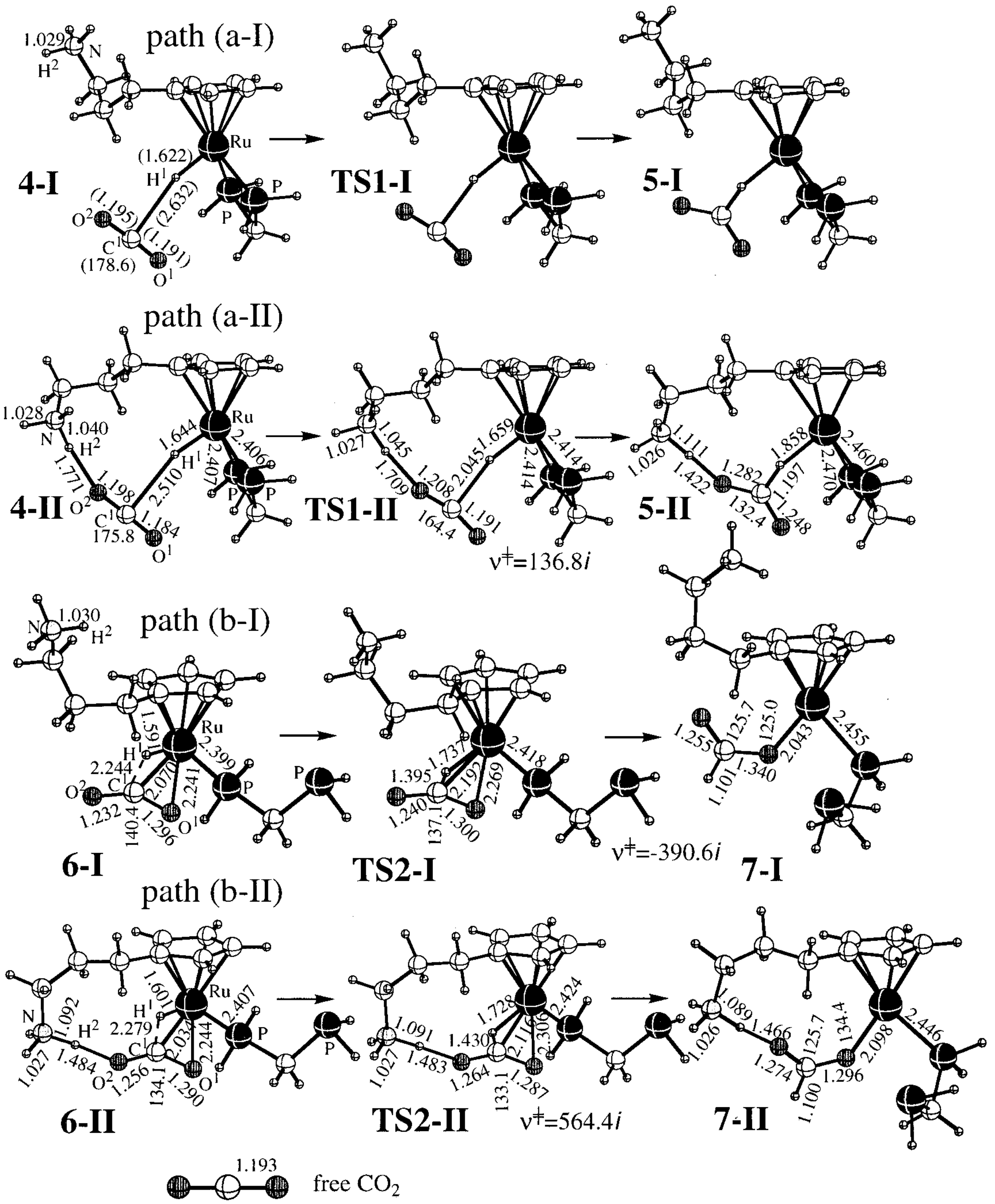


Figure 2. B3LYP/I-optimized structures (in Å and deg) of the reactant, TS, and the product with selected important parameters of paths a and b. The structures **4-I**, **TS1-I**, and **5-I** of path a-I were artificially obtained from the optimized structures **4-II**, **TS1-II**, and **5-II** of path a-II, respectively. See text for details.

because the carbon of CO_2, which has a positive charge, makes an electrostatic interaction with the anionic hydrido ligand. Therefore, the CO_2-axis is also bent by only 1.4°.

On the other hand, in the reactant **4-II** of path a-II, the protonated amine arm somewhat turns up to catch the approaching CO_2 by the N-bound proton. Therefore, the negatively charged O^2 of CO_2 is also weakly bonded to the proton H^2 attached to N of the amine arm by an electrostatic interaction in addition to the positively charged C^1 bonded to the anionic hydrido H^1, which is reflected in the O^2-H^2 distance of 1.771 Å. By this $N-H^2$- - -O^2 H-bonding, both $N-H^2$ and C^1-O^2 distances are slightly stretched compared with those in **4-I**. The C^1-H^1 distance is shorter while the $Ru-H^1$ distance is longer than those in **4-I**, which indicates that the hydrido ligand abstraction by CO_2 is incipiently induced by the incorporation of the protonated amine arm. The angle $\angle O^1-C^1-O^2$ is also reduced to 175.8°. The reaction passes through the TS, **TS1-II**, which is obviously reactant-like, as reflected in the $Ru-H^1$ and C^1-O^2 bond distances stretched only by 0.015 and 0.010 Å, respectively, compared with those in the reactant **4-II**. The C^1-H^1 distance of 2.045 Å is still much longer than that of 1.197 Å in the product, **5-II**. The CO_2-axis is also bent only by 11.4°, and the other parameters are nearly the same as those in **4-II**. The O^2-H^2 distance is remarkably shortened to 1.422 Å in the product, **5-II**, because the negative charge at O^2 increases as a result of the formation of $HCOO^-$, which makes the electro-

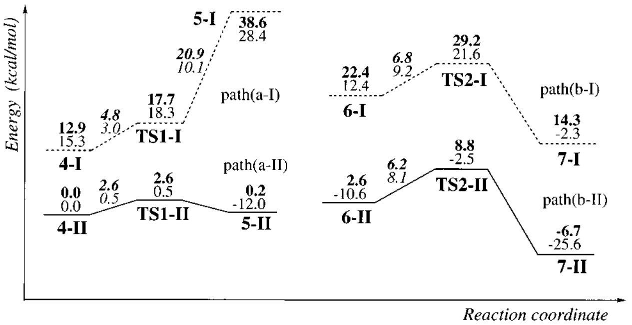


Figure 3. Potential energy surfaces of paths a and b with (solid line) and without (dotted line) the contribution of the protonated amine arm at the B3LYP/I (plain) and B3LYP/II (bold) levels.

static interaction with the proton H^2 stronger. As a result, the N$-H^2$ distance is longer by 0.071 Å than that in **4-II** and the single-bond-like C^1-O^2 is longer by 0.034 Å than the double-bond-like C^1-O^1. The short Ru$-H^1$ distance of 1.858 Å and the long C^1-H^1 distance of 1.197 Å indicate an interaction of the hydrogen of $HCOO^-$ with the Ru atom.

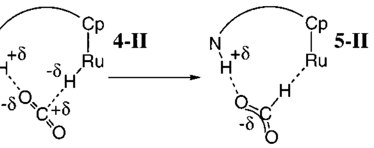
In the other path, b, a phosphine of the bidentate ligand has to dissociate to prepare an empty site for the η^2-CO precoordination of CO_2 to the Ru atom. It is well known that such ligand dissociation very often occurs in the solution reaction of transition metal complexes.[18] In the reactant **6-I** in path b-I without the contribution of the protonated amine arm, the coordinated C^1-O^1 bond is elongated by 0.103 Å compared with that of the free CO_2 due to the well-known interaction by the electron donation from the occupied pπ orbital of the C=O double bond to the unoccupied d orbital of the Ru atom and back-donation from the occupied d orbital of the Ru atom to the pπ* orbital of the C=O double bond. It should be noted here that the C^1-Ru bond is nearly formed, as shown in the short distance of 2.070 Å, which suggests the formation of $RuCOO^-$. Indeed, the CO_2-axis is largely bent so that the $\angle O^1-C^1-O^2$ angle of 140.4° is already small, which is similar to the case of the Rh complex system reported by Dedieu et al.[8] The C^1-O^2 bond is also stretched by 0.039 Å. In the complex **6-I**, the hydrido H migrates to the C^1 atom to form the C^1-H^1 bond and the Ru$-H^1$ and Ru$-C^1$ bonds are broken passing through the TS, **TS2-I**. Although the distance of Ru$-O^1$ as well as those of Ru$-H^1$ and Ru$-C^1$ is stretched only by 3% in **TS2-I**, it becomes shorter in **7-I** with the rotation of the produced $HCOO^-$ to provide a better overlap of the oxygen orbital with the Ru orbital. The C^1-H^1 distance in **TS2-I** is still longer by 0.294 Å compared with that in the product, **7-I**. In contrast with the case of the hydrido ligand abstraction, even in path b-II, where the protonated amine arm participates in the reaction, there is no significant change in the geometric features of the equilibrium structures and the TS, even though the N-bonded proton is strongly bound to the O^2 atom of CO_2 during the reaction with the short distance of 1.47−1.48 Å.

Energetics. As demonstrated by the potential energy surface made by connecting the relative energies of the structures **4-I**, **TS1-I**, and **5-I**, the hydrido ligand abstraction without the contribution of the protonated amine arm (path a-I) is obviously uphill (Figure 3). When the protonated amine arm contributes to the reaction (path a-II), the features of the potential energy surface are completely different. The potential energy surface is largely stabilized because the reactant, TS, and product become much more stable by the interaction of the O^2 of CO_2 with the N-bonded proton H^2. It should be noted that the stabilization in energy is the largest between the products **5-I** and **5-II** (38.4 kcal/mol). Accordingly, the potential energy surface is quite smooth, requiring an energy barrier of only 2.6 kcal/mol.

On the other hand, the insertion of CO_2 into the Ru−H bond is 8.1 kcal/mol exothermic and the energy barrier is 6.8 kcal/mol even without the participation of the protonated amine arm (path b-I). The features of the potential energy surface do not change even if the protonated amine arm participates in the N$-H^2$- - -O^2 H-bonding, although the potential energy surface in path b-II shifts down by 20−21 kcal/mol. This indicates that the N-bound proton does not function during the insertion reaction, path b, at all. The calculated energy barrier of 6.2 kcal/mol for path b-II, which is similar to that in the Rh system previously reported,[8] is larger than that of path a-II. Thus, the unlikely hydrido ligand abstraction by CO_2, path a, is more favorable than the insertion of CO_2 into the Ru−H bond, path b, due to the promotion effect of the protonated amine arm effective only for path a.

Origin of the Promotion Effect. To clarify the function of the protonated amine arm, the analysis of the Mulliken atomic charge was performed at the B3LYP/I level. The selected and important atomic charges on the reactants **4** and **6** and the products **5** and **7** of paths a and b are presented in Figure 4.

For the reactant **4-I**, without the N$-H^2$- - -O^2 H-bonding, in the hydrido ligand abstraction, path a, the atomic charges on both the carbon and oxygen atoms of CO_2 are nearly the same as those of free CO_2, the carbon and oxygen atoms having positive and negative charges, respectively. In **4-II**, with N$-H^2$- - -O^2 H-bonding, the negative charge at the O^2 atom rises by 0.05*e* and the positive charge at the C^1 atom rises by 0.03*e* compared with those in **4-I** due to the electronic effect of the proton H^2. Thus, CO_2 is obviously induced by the formation of the H-bond with the proton H^2 to abstract the hydrido H^-, as presented below, since the electrophilicity of the C^1 of CO_2 is enhanced.



The negative charge at the O^2 atom significantly increases in **5-II** after the formation of $HCOO^-$ by the transmission of the negative charge from the hydrido H^1 to the O^2 atom through the $H^1-C^1-O^2$ linkage. The negative charge at the O^1 also increases by 0.18*e* due to the delocalization of the negative charge along the CO_2-axis. The formed $HCOO^-$ in **5-II** is stabilized by the N$-H^2$- - -O^2 H-bonding and the O^2-H^2 distance is shortened to 1.422 Å as mentioned above. The bond population in the O^2-H^2 also consistently increased by 0.08*e*. On the contrary, in **5-I**, the formed $HCOO^-$ cannot be stabilized without such a N$-H^2$- - -O^2 H-bonding.

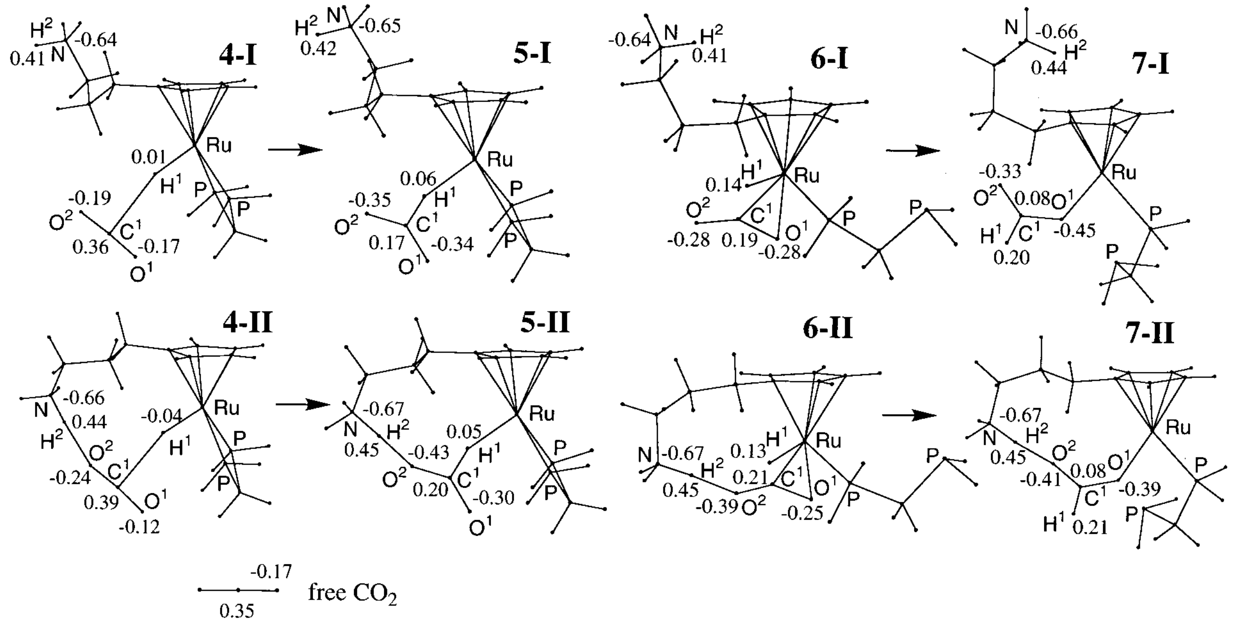


Figure 4. Mulliken atomic charges calculated at the B3LYP/I level in the reactants, **4** and **6**, and the products, **5** and **7**, of paths a and b.

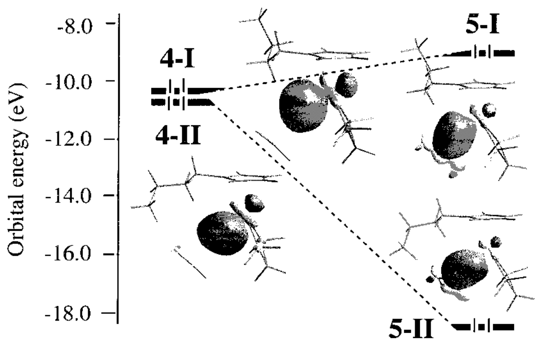


Figure 5. LMOs and their energy levels calculated at the B3LYP/I level for the C^1-H^1-Ru bonding in the reactants, **4**, and the products, **5**, of path a.

The electronic effect of the protonated amine arm also explicitly appears in the C^1-H^1-Ru bonding. The localized molecular orbitals (LMOs) for the C^1-H^1-Ru bonding and their energy levels in the reactants **4** and the products **5** calculated at the B3LYP/I level are presented in Figure 5.

The MO for the C^1-H^1-Ru bonding in **4-II** is slightly lower in energy than that in **4-I**, because the increase in the positive charge of the C^1 by the $N-H^2\text{- - -}O^2$ H-bonding makes the interaction of the C^1 with the anionic hydrido H^1 stronger. The corresponding MO is quite stabilized in **5-II** with the contribution of the protonated amine arm, but is somewhat destabilized in **5-I** without the contribution of the protonated amine arm. Also, due to the migration of the hydrido H^1 to the C^1 of CO_2, the bond population of $Ru-H^1$ decreased and that of C^1-H^1 increased in path a-II, while both of them did not change in path a-I. These results indicate that the support of the N-bound proton H^2 is indispensable for the C^1-H^1 bond formation in path a. Thus, it is obvious that the interaction of the N-bound proton with an oxygen of CO_2, which enhances the positive charge at the C^1 atom of CO_2, makes the hydrido H^- abstraction facile.

The experimental reports of the enhancement of the homogeneous hydrogenation of CO_2 with other transition metal complex catalysts by the addition of H_2O or CH_3OH are quite interesting.[19,20] For an understanding of this enhancement, a TS with a H-bonding between the coordinated ROH and oxygen of the approaching CO_2, $\overline{RHO-M(L)_n\text{- - -}H\text{- - -}CO}_2$, has been proposed in the step of the hydrido migration to the carbon of CO_2. In this TS, the electrophilicity of the carbon of CO_2 would increase by the H-bonding in the same manner as mentioned above, which makes the hydrido migration easy. In this context, the coordinated H_2O or CH_3OH plays the same role as that of the amine arm in the present case.

In the case of the insertion reaction, path b, both the O^2 and O^1 atoms of the reactant **6-I** without the $N-H^2\text{- - -}O^2$ H-bonding already have a large negative charge of $-0.28e$ as shown in Figure 4, suggesting the formation of the $RuCOO^-$, which is stabilized by the interaction of the negatively charged O^1 with the Ru atom, which is divalent. The negative charge delocalized along the CO_2-axis is provided by the hydrido H^1 via Ru, so that the hydrido H^1 atom has a large positive charge ($+0.14e$). The protonic hydrido is transferred to the C^1 atom to form the formate complex **7-I**. Even with the $N-H^2\text{- - -}O^2$ H-bonding, there is no significant change in the distribution of the atomic charge in both the reactant **6-II** and product **7-II**, as presented below, although the negative charge is larger at the O^2 atom than at the O^1 atom (see Figure 4). Since CO_2 has already obtained enough negative charge to form a $RuCOO^-$ in the reactant without support of the N-bound proton H^2, the protonated amine arm does not function in the insertion reaction, path b.

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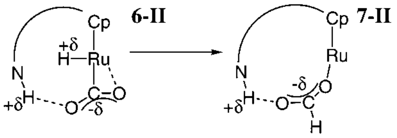
(18) For example, see: Halpern, J.; Wang, C. S. *J. Chem. Soc., Chem. Commun.* **1973**, 629.

(19) Tsai, J.-C.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 5117.

(20) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 344.



Conclusion

The hybrid density functional (B3LYP) calculations were performed for the hydrido migration to the carbon of CO_2 on the experimentally synthesized novel N−H···H−Ru H-bonded complex (η^5-$C_5H_4(CH_2)_3$-NMe_2H^+)RuH(dppm), **2**, assuming the two generally accepted different reaction paths, i.e., (a) the abstraction of the hydrido ligand by an incoming CO_2 without direct coordination of CO_2 to the Ru atom, and (b) the insertion of CO_2 to the Ru−H bond with the η^2-CO precoordination of CO_2 to the Ru atom. Although the unlikely path a was significantly promoted by the contribution of the protonated amine arm of the Ru complex, path b was not. As a result, path a, with only the small energy barrier of 2.6 kcal/mol, was more favorable than path b, with the energy barrier of 6.2 kcal/mol. It was found that the promotion effect of the protonated amine arm in path a originates from the enhancement of the electrophilicity at the carbon of CO_2 by the H-bonding of the proton attached to N of the amine arm with one of the oxygens of CO_2.

Acknowledgment. Part of the calculations were carried out at the Computer Center of the Institute for Molecular Science, Japan.

Supporting Information Available: The Cartesian coordinates of all structures presented in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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