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Theoretical Investigation on the Nature of Intramolecular Interactions in Aminocyclopentadienyl Ruthenium Hydride Complexes

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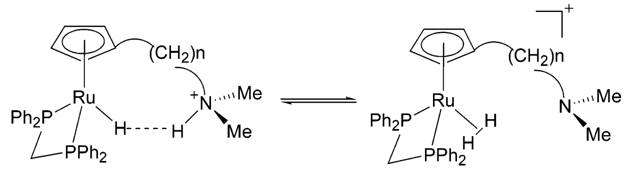
Summary: Aminocyclopentadienyl ruthenium hydride complexes were optimized at the second-order Møller−Plesset (MP2) level of theory with 6-31G(d) and 6-311++G(d,p) basis sets to investigate the nature of intramolecular interactions. The computations show that both Ru−H···H−N dihydrogen bond interactions and Ru···H−N interactions are responsible for the stability of these complexes. The BSSE-corrected interaction energies, computed at the B3LYP and MP2 levels of theory with 6-31G(d), 6-311++G(d,p), and 6-311++G(2d,2p) basis sets, indicate that the dihydrogen bond interaction energy accounts for only 20% of the total interaction energy. Therefore, the Ru···H−N interactions play a key role in stabilizing the aminocyclopentadienyl ruthenium hydride complexes. Topological analysis of electron density at bond critical points confirms the formation of the dihydrogen bonds between oppositely charged hydrogen atoms. Analysis of charge distributions (Mulliken charges) shows there is a strong electronic attraction between Ru and the hydrogen atom.

1. Introduction

The intramolecular and intermolecular E−H···H−X (where E is a transition/alkali metal or boron and X is an electronegative atom/group) bonds, termed dihydrogen bonds, have recently attracted much attention.[1−11] The first unequivocal evidence of a dihydrogen bond involving a transition metal hydride came independently from the groups of Crabtree and Morris in 1994.[2,3] The H···H contact distances and interaction energies for the systems with dihydrogen bonds lie within the range of conventional H-bonds, viz., 1.6−2.2 Å and 3−8 kcal/mol, respectively.[12] It has been observed that dihydrogen-bonded complexes could activate the H_2 ligand and M−H bond, leading to the occurrence of many reactions, such as H/D exchange, proton transfer, and substitution.[13,14] The dihydrogen bonding could also be used in selectively stabilizing transition states and, thereby, plays an important role in controlling the reactivity and stereochemistry of organometallic hydride complexes.[15] Recently, the dppm hydride complex (η^5-$C_5H_4(CH_2)_nNMe_2H^+$)-Ru(dppm)H (n = 2 or 3) (**1**), in which there is a rapid and reversible hydride/proton exchange via the (η^5-$C_5H_4(CH_2)_n$-NMe_2)Ru(dppm)$(H_2)^+$ intermediate (**2**) (Scheme 1), has been synthesized and characterized.[16]

Scheme 1



1 **2**

The intramolecular hydrogen-bonded complex **1** was also characterized by relaxation time T_1 measurements and spin saturation transfer study.[16] Theoretical study shows the protonated amine arm in η^5-$C_5H_4(CH_2)_3NMe_2H^+$)Ru(dppm)H could promote the catalytic hydrogenation of CO_2 to formic acid.[17] However, Sabo-Etienne, Chaudret, and co-workers reported that in the triphenylphosphine analogue of **1** an exchange process between the hydride and the ammonium proton does not involve proton transfer within the dihydrogen bond.[18] The hydride signals of the complexes with dihydrogen bonds usually broaden as the temperature decreases due to strengthening of the M−H···H−X interaction, and sharpen as the temperature increases because of weakening of the dihydrogen bonding.[19] Broadening of the hydride signal of $WH(CO)_2(NO)-(PMe_3)_2$ was observed in the presence of acidic alcohol, due to the formation of an intermolecular M−H···HOR dihydrogen bond.[20]

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Significant broadening of the hydride signals of both cis and trans isomers of $RuH_2(dppm)_2$ was also observed upon addition of excess phenol.[9] However, spectrum changes of the hydride signal in the variable-temperature (VT) ^1H NMR study of the acidification of $[tpmRu(PPh_3)_2H]BF_4$ with aqueous acid are contrary to the behaviors of the hydride signals of complexes containing dihydrogen bonds.[19] Therefore, the interactions stabilizing the intermediate might include other interactions as well as the dihydrogen bonding.

In this paper, we investigate the nature of the intramolecular interactions stabilizing the hydride complex (η^5-$C_5H_4(CH_2)_n$-NMe_2H^+)Ru(dppm)H. Five model systems, η^5-$C_5H_4(CH_2)_1$-$(PH_3)_2RuHNH_3^+$ (**A**), η^5-$C_5H_4(CH_2)_2(PH_3)_2RuHNH_3^+$ (**B**), η^5-$C_5H_4(CH_2)_3(PH_3)_2RuHNH_3^+$ (**C**), η^5-$C_5H_5(PH_3)_2RuH\cdots HNH_3^+$ (**D**), and η^5-$C_5H_5(PH_3)_2RuCH_3\cdots HNH_3^+$ (**E**), were chosen to confirm the existence of an intramolecular dihydrogen bond, investigate the effect of the methylene bridge, and study how the dihydrogen bond interactions affect the stability of the systems studied here, respectively. High-level ab initio calculations have been performed on dihydrogen-bonded complexes with hydrogen fluoride (HF) as a proton-donating molecule and simple molecules as proton acceptors (CH_4, SiH_4, BeH_2, MgH_2, LiH, and NaH).[21] A comparison of the calculation results shows that the MP2/6-311++G(d,p) level of theory is sufficient for the description of dihydrogen-bonded complexes.

2. Computational Details

All calculations were carried out with the Gaussian 03[22] package. Geometry optimizations were first performed at the MP2 level with the 6-31G(d) basis set (the relativistic effective core potential with the LANL2DZ basis set was used for the metal Ru), and the nature of the stationary point was confirmed at the same level of theory.[23] Then the equilibrium structures were further optimized at the MP2 level with the 6-311++G(d,p) basis set.[24] The single-point energies were computed at the B3LYP and MP2 levels with 6-31G(d), 6-311++G(d,p), and 6-311++G(2d,2p) basis sets, respectively. The counterpoise (CP) method was used to correct basis set superposition error (BSSE) in the calculation of the binding energy.[25] The intramolecular interactions in A, B, and C were investigated with the conformational analysis method.[26−36] Topological analysis of the electron densities at bond critical points was performed with the AIM2000 program.[37]

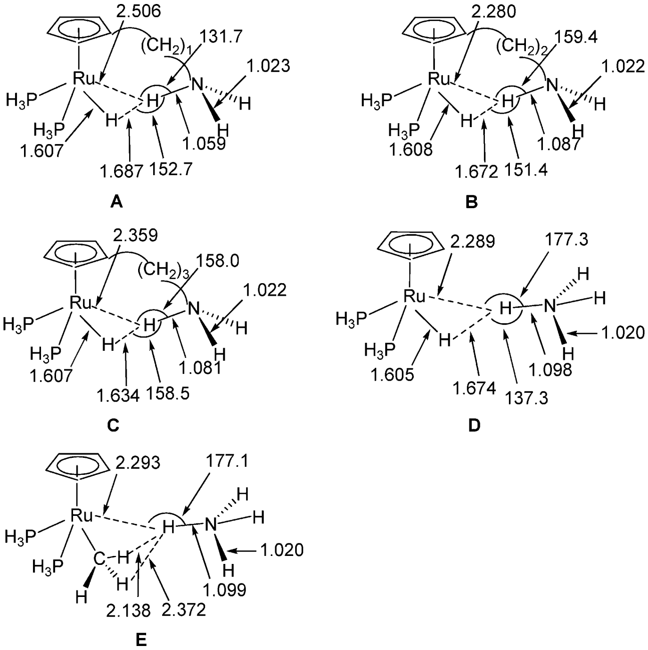

Figure 1. MP2/6-311++G(d,p)-optimized geometries of **A**−**E**. Bond lengths are in Å and angles are in deg.

3. Results and Discussion

Geometries and Energies. There are different ways to detect hydrogen bonding. One of the most often used is the application of the geometrical criteria. The (N)H···H(B) contact distances are usually within the range 1.7−2.2 Å, which were found in the analysis of 18 X-ray crystal structures in the Cambridge Structural Database (CSD).[38] From **A** to **D**, the H···H distances are all within the range 1.63−1.69 Å (Figure 1). Therefore, from the geometrical point of view, these systems should form strong intramolecular or intermolecular dihydrogen bonds. The dihydrogen bonds in **A**−**D** should have ionic character because of the existence of the ammonium cation. From **A** to **C**, the H···H contact distances decrease; however, the H−N bond lengths first increase and then decrease. The H−N bond in **B** (1.087 Å) is longer than that in **A** (1.059 Å) or **C** (1.081 Å), and the Ru···H distance in **B** (2.280 Å) is shorter than that in **A** (2.506 Å) or **C** (2.309 Å). As is well known, the shorter the H-bond distance, the larger the H-bond interaction energy and vice versa. Therefore, if we suppose there were only dihydrogen bond interactions in **A**, **B**, and **C**, the shortest H···H distance must correspond to the strongest dihydrogen bond interaction, which results in the longest H−N bond. However, the computational

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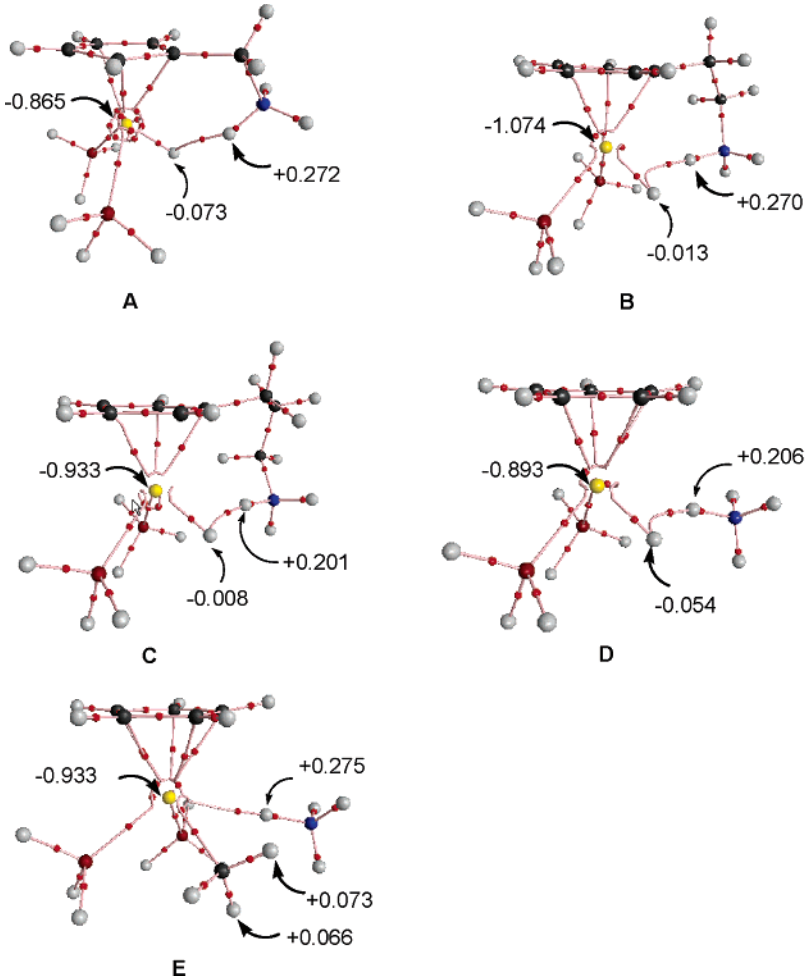

Figure 2. Molecular graphs and Mulliken charges of **A**−**E**. Attractors attributed to the position of the atom and bond critical point (small circles) are shown.

Table 1. BSSE and BSSE-Corrected Interaction Energies, E_{CP} (in kcal/mol), calculated at the B3LYP and MP2 Levels with Different Basis Sets

	BSSE	E^{D}_{CP}	BSSE	E^{E}_{CP}	$E^{D}_{CP} - E^{E}_{CP}$	$E^{D}_{CP} - E^{E}_{CP}/E^{D}_{CP}$
B3LYP						
6-31G(d)	1.15	−29.2	1.28	−24.2	−5.00	0.17
6-311++G(d,p)	0.65	−29.6	0.79	−24.3	−5.37	0.18
6-311++G(2d,2p)	0.44	−29.6	0.53	−24.0	−5.55	0.19
MP2						
6-31G(d)	5.02	−26.5	6.46	−21.6	−4.85	0.18
6-311++G(d,p)	4.97	−28.6	6.19	−23.1	−5.49	0.19
6-311++G(2d,2p)	5.06	−28.1	5.69	−22.0	−6.12	0.21

results are contrary to the hypothesis. The fact is, the shortest Ru···H distance corresponds to the longest H−N bond. This suggests that the changes of structure might have something to do with the Ru···H−N interactions. In addition, the angle of Ru···H−N in **B** is closer to 180° than that of H···H−N, which also suggests the intramolecular Ru···H−N interactions cannot be ignored. The angles of Ru···H−N and H···H−N could be affected by the methylene bridge; therefore, we investigate the intermolecular interactions in complex **D**. As shown in Figure 1, the angle of Ru···H−N in **D** computed at the MP2/6-311++G(d,p) level is 177.3°, which is more linear than the angle of H···H−N (137.3°), indicating the Ru···H−N interaction might be more prominent than that of the dihydrogen bond interaction in **D**. It is also observed that, compared with the geometrical parameters of **A** and **C**, the geometrical parameters of **B** are closer to those of **D**. This shows the methylene bridge has less effect on **B** than on **A** or **C**. To get more insight into the nature of the interactions of η^5-$C_5H_4(CH_2)_n(PH_3)_2RuHNH_3^+$, we computed the model complex **E**. Although no dihydrogen bond was formed in **E**, the Ru···H distance and Ru···H−N angle are almost the same as those of **D**. This further confirms that the Ru···H−N interaction plays a key role in stabilizing the η^5-$C_5H_4(CH_2)_n(PH_3)_2RuHNH_3^+$ complex. There is little structure difference between complexes **D** and **E**; therefore, the interactions in **D** include both the Ru···H−N interaction, which is approximately equal to that in **E**, and the dihydrogen bond interaction.

The interaction energies of **D** and **E** computed at the B3LYP and MP2 levels with different basis sets are listed in Table 1. As shown in Table 1, the DFT calculations have less BSSE than the MP2 calculations. For the B3LYP calculations, the larger the basis set, the less the BSSE. The differences of the interaction energies calculated at the B3LYP/MP2 level with different basis sets are less than 0.5/2.0 kcal/mol, which indicates the interaction energies are not sensitive to the selection of the methods and basis sets. In all cases, the interaction energy differences between **D** and **E** are approximately 6.0 kcal/mol and account for 20% of the total interaction energy. This implies that the dihydrogen bond interaction in **D** accounts for approximately 20% of the total interaction energy. Therefore, the Ru···H−N interactions play a dominant role in these systems. Similar agostic interactions have also been found in other systems.[39−43] The strength of the dihydrogen bonding in the systems investigated here is close to that in the W−H···HOR system.[20]

Table 2. Selected Topological Properties (in au) of BCPs

	ρ_b	$\nabla^2\rho$	λ_1	λ_2	λ_3	ϵ
A	0.0281	0.0486	−0.0320	−0.0240	0.1046	0.3333
B	0.0343	0.0508	−0.0364	−0.0106	0.0978	2.4340
C	0.0349	0.0488	−0.0423	−0.0275	0.1186	0.5381
D	0.0345	0.0461	−0.0377	−0.0124	0.0962	2.0403

According to the calculations, the total interactions should be more sensitive to the changes of Ru···H distance and Ru···H−N angle than to other geometrical parameters. The H···H contact distance in **B** is shorter than that in **C** and the Ru···H−N angle in **B** is larger than that in **C**, which means that the interaction in **B** should be stronger than that in **C**. The Ru···H distance in **A** is shorter than that in **B** or **C**, and the intramolecular interaction energy in **A** should less than that in **B** or **C**. Analysis of charge distributions (Figure 2) also shows that the electronic attraction in **B** is larger than that in **C**. The intramolecular interaction energies in **A**, **B**, and **C**, computed at the B3LYP/6-311++G(2d,2p) level with the conformational analysis method, are −12.6, −17.4, and −16.8 kcal/mol, respectively, which confirms our hypothesis. The methylene bridge makes the system have angle strain and thereby decreases the total interaction. This effect is more obvious on **A** than on **B** or **C**. This is also consistent with the (VT) ^{1}H NMR experiment results, in which stronger Ru−H···H−N interaction in η^5-$C_5H_4(CH_2)_2NMe_2H^+$)Ru(dppm)H than in η^5-$C_5H_4(CH_2)_3$-NMe_2H^+)Ru(dppm)H is reflected by the smaller T_1 value (in THF-d_8 or chlorobenzene-d_5) of the hydride signal of the former.[16] In **E**, two hydrogen atoms of the methyl ligand are positive and will repel the adjacent H atom of ammonium. This repulsive interaction decreases the contribution of the dihydrogen bond interaction to the total interaction, and thereby the dihydrogen bond interaction in D should accounts for less than 20% of the total interaction energy.

AIM Analysis. Eight atoms-in-molecules (AIM) criteria have been proposed to study and characterize hydrogen bonds.[44] To further understand the nature of intramolecular interactions in the (η^5-$C_5H_4(CH_2)_nNMe_2H^+$)Ru(dppm)H system, we performed the AIM analysis to investigate whether there exist dihydrogen bonds in systems studied here.

Figure 2 clearly demonstrates the existence of a bond critical point (BCP) for every dihydrogen bond in **A**−**D**. For complex **E**, there is a BCP for Ru···H−N but no BCP for the dihydrogen bond. The bond paths between two hydrogen atoms of **B** and **D** obviously bend toward the Ru atoms, which shows that there is obvious interaction between Ru and the $H_{(N)}$ atom, although no (3,−1) critical point could be located between Ru and the $H_{(N)}$ atom.

The electron densities at H···H bonds are listed in Table 2. The corresponding values of the Laplacians are also collected. All values of electron densities at H···H bonds do fall within the proposed range of 0.002−0.035 au.[45] Among **A**, **B**, and **C**, the electron density of H···H critical point in **B** (0.0343 au) is closest to that in **D** (0.0345 au). The Laplacian $\nabla^2\rho$ is simply the sum of the eigenvalues λ. It has been observed that for ionic bonds, hydrogen bonds, and van der Waals interactions $\nabla^2\rho$ is positive. The ellipticity ϵ is defined as $\lambda_1/\lambda_2 - 1$ and measures the extent to which charge is preferentially accumulated. In Table 2, we see that ϵ of **B** or **D** is much larger than that of **A** or **C**, confirming that the former Ru−H···H−N bonds are weaker than those of the latter. Both analyses of electron densities and that of Laplacians show that the effect of the methylene bridge on **B** is less than that on **A** or **C**.

Table 3. Atomic Properties (in au) for Proton Donor Hydrogen Atoms

	$\Delta r_{H(N)}$	$\Delta r_{H(Ru)}$	$q(\Omega)$	$E(\Omega)$	$V(\Omega)^a$	$M(\Omega)$
A	0.383	0.709	0.5686	−0.3555	17.03	0.1399
B	0.439	0.088	0.5667	−0.3454	13.34	0.1281
C	0.478	0.745	0.5472	−0.3426	13.32	0.1282
D	0.450	0.371	0.5877	−0.3247	13.13	0.1242
H_{NH4+}			0.5155	−0.3941	23.44	0.1263

[a] For the 0.001 au contour.

The penetration Δr(**A**) is defined as the nonbonded radius minus the bonded radius. The nonbonded radii of the hydride and ammonium proton are about 2.650 and 1.774 Å, respectively. All the penetrations listed in Table 3 are positive, which is in agreement with previous studies on related systems.[46,47]

Another necessary condition for the formation of an H bond is the loss of charge of the hydrogen atom. The values of the net charge for the hydrogen atom, $q(\Omega)$, in the isolated ammonium cation and in the systems are shown in Table 3. Compared with the ammonium cation, the H atoms in all systems studied here lose some charge and thereby are more positive. Both energetic destabilization of the hydrogen atom, $\Delta E(\Omega)$, and decrease of the hydrogen atom's volume, $\Delta V(\Omega)$, confirm the formation of a dihydrogen bond.

In addition to the preceding integrated properties, the first moment of the hydrogen atom, $M(\Omega)$, must decrease upon formation of an H bond. The value of $M(\Omega)$ for the hydrogen in the isolated ammonium cation is 0.1263 au and decreases to 0.1242 au in **D**. However, it increase in **A**, **B**, or **C** because of the Ru···H−N interactions.

4. Conclusion

Topological analysis shows that there is formation of a dihydrogen H-bond in the η^5-$C_5H_4(CH_2)_n(PH_3)_2RuHNH_3^+$ (n = 1, 2, and 3) system, but structure and energy analyses indicate that the Ru···H−N interaction overwhelms the dihydrogen H-bond interaction. So it is the Ru···H−N interactions that play a key role in stabilizing these structures. The BSSE-corrected interaction energies, computed at the B3LYP and MP2 levels with different basis sets, indicate that the dihydrogen bond interaction energy accounts for only 20% of the total interaction energy.

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

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