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Molecular Orbital Study of Bonding and Stability on Rh(I)-Alkyne Isomers

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Ab initio and extended Hückel calculations were carried out on the isomers of *trans*-RhCl(η^2-C_2H_2)(PH$_3$)$_2$ (**1**). Due to π-back donation in **1** complex, the rotational energy barrier of alkyne ligand is computed to be in the range of 18.6-25.2 kcal/mol at MP4 levels. The optimized hydrido-alkynyl complex (**2**) at *ab initio* level has the distorted trigonal bipyramidal structure. Vinylidene complex (**3**) is computed to be more stable than **1** complex by 17.1 kcal/mol at MP4//MP2 level. The stabilities of isomers show similar trend at the various level calculations, that is, EHT, MP4//HF, and MP4//MP2 levels. The optimized geometries at *ab initio* level are in reasonable agreement with experimental data. A detailed account of the bonding in each isomers (**1-3**) have been carried out in terms of orbital analyses.

Introduction

The chemistry of alkynes with transition metals has attracted much attention in recent years,[1] due to the usefulness for the reactions of polymerization, cyclization, hydrogenation, and oxidative addition. With various experimental and theoretical approaches, many studies have been carried out to investigate the basic principles of the transformation of alkyne complexes to vinylidene complexes.[2] R. Hoffmann[3] examined the electronic and structural features of the isomerization of various metal alkynes into vinylidene complexes *via* a 1,2-hydrogen shift. For the d^6-ML$_5$ fragment, the alternative pathway for the isomerization involving hydrido-alkynyl complex requires much higher energy. However, recent experimental works[2b,c] support that the rearrangement of alkyne to vinylidene occurs stepwise through the C-H activated intermediates (Scheme 1).

Reactions of alkynes with RhCl(PR$_3$)$_2$ moiety produce *trans*-RhCl(η^2-HCCR) (PR$_3$)$_2$ (**1**), then slowly equilibrate with intermediates (**2**) in benzene or THF at room temperature. The η^2-alkyne complexes can be quantitatively transformed to vinylidene complexes (**3**) on heating in hexane solvent.[4] Recently, the formation of the intermediate hydrido-alkynyl complexes (**2**) has been observed in various systems.[5] In the present paper, we will report the computational results of *ab initio* and extended Hückel molecular orbital methods on Rh(I)-alkyne isomers related to the hydrogen migration

[M] = RhCl(PR3)2
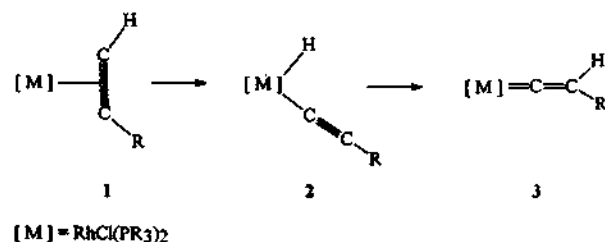
Scheme 1.

reaction.

Computational Methods

Calculations were carried out at two levels. For qualitative analysis, the extended Hückel method with the modified Wolfsberg-Helmholz formula[6] were performed. The atomic parameters for H, C, P, Cl, and Rh were taken from previous work.[7] The *ab initio* calculations used the GAUSSIAN 92 and 94 programs[8] on a Cray Y-MP C916 and Indigo 2 workstation. A relativistic effective core potential was used for the core electrons in Rh (up to 4p),[9] P and Cl (up to 2p).[10] The basis sets used were double-ζ for the valence region with the contraction scheme (21/21/31) for Rh and (21/21) for P and Cl. The 3-21G basis[11] was used for the alkyne ligand and STO-3G[12] for the hydrogens on the PH$_3$ groups. A full

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geometry optimization at the Hartree-Fock (HF) and 2nd order Moller-Plesset (MP2) perturbation theory was carried out on the calculated molecules under C_s or C_{2v} symmetry constraint except that the local symmetry of PH$_3$ groups was kept to C_{3v}. Single point calculations were carried out by using MP4 perturbation theory at the HF and MP2 optimum geometries to obtain the improved relative energies.

Results and Discussion

Extended Hückel Calculations on the isomers of *trans*-RhCl(η^2-C$_2$H$_2$) (PH$_3$)$_2$. The geometry around Rh atom in *trans*-RhCl(η^2-HCCR)(PR$_3$)$_2$ is square planar. In ground state, alkyne ligand is positioned to be perpendicular to the plane of metal fragment. Figure 1 constructs an orbital interaction diagram for *trans*-RhCl(η^2-HCCH)(PH$_3$)$_2$ (1).

The important valence orbitals of C_{2v} RhCl(PH$_3$)$_2$ metal fragment are displayed on the left side of the figure. The valence orbitals of C_{2v} ML$_3$ fragment are extensively studied by many groups.[13] During the rearrangement of hydrogen in alkyne complex, C_{2v} RhCl(PH$_3$)$_2$ fragment was almost kept constantly. Therefore, we will briefly describe the important features of the fragment orbital analysis. At low energy level there are four filled orbitals (a$_2$, 1a$_1$, b$_2$, and b$_1$) associated with a square planar splitting pattern. The b$_2$ and b$_1$ orbitals in metal fragment are pushed up somewhat in energy from a$_2$ because of antibonding from the Cl ligand. At higher energy the 2a$_1$ fragment orbital is primarily the metal-ligand antibonding x^2-y^2 orbital with cartesian coordinate given on figure. However, it is also hybridized by metal s and p character towards the entering ligand in complex. On the right side of figure 1, there are the typical π-type orbitals of alkyne, two bonding and two antibonding orbitals. Two filled orbitals are not degenerate because of the bent-back of hydrogen atoms in alkyne. There are two strong interactions between fragments. The 2a$_1$ hybrid on ML$_3$ interacts strongly with the a$_1$ π-orbital of alkyne to produce the stabilized 1a$_1$ molecular orbital. We also find that there is some back donation of electron density from the filled b$_2$ fragment orbital of ML$_3$ into the empty π^* orbital, b$_2$, of alkyne. It was computed that 0.42 electrons are transferred from b$_2$ on ML$_3$ to b$_2$ of alkyne ligand. This means that the Rh-C distance should be shorter than normal one. Furthermore, since the b$_2$ of alkyne is antibonding between two C atoms, C-C distance should be increased. We shall show this distortions later in *ab initio* calculations. The 1a$_1$ and 1b$_2$ molecular orbitals at the center of figure 1 are represented by 4 and 5, respectively.
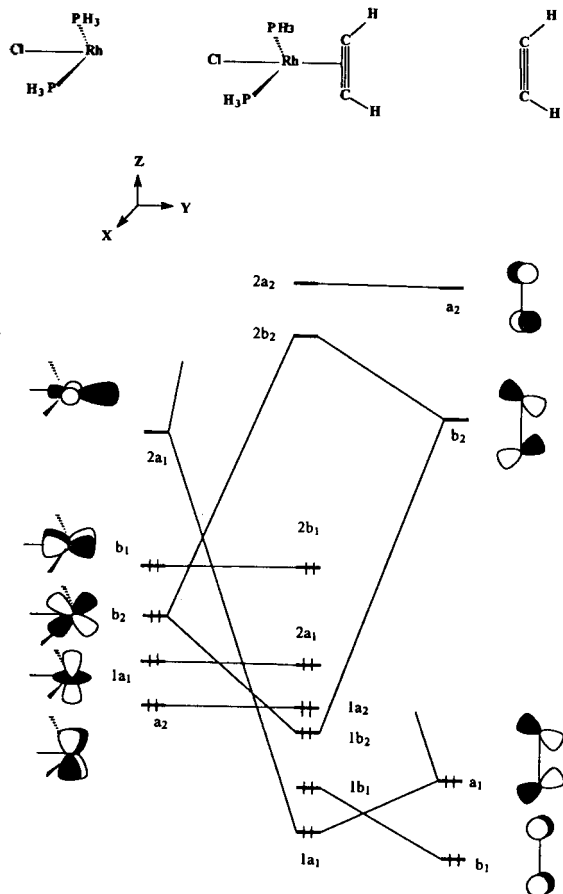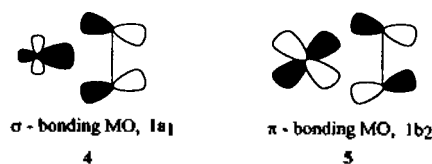

σ - bonding MO, 1a$_1$ π - bonding MO, 1b$_2$

4   5

As shown in **4**, the 1a$_1$ MO is cylindrically symmetrical with respect to the Rh-alkyne axis. Therefore, energy of this MO must be constant as a function of rotation. When the alkyne ligand is rotated by 90.0°, the interaction producing 1b$_2$ MO (5) will disappear. The rotational energy barrier of alkyne ligand is computed to be 13.8 kcal/mol at the extended Hückel level. This barrier is almost half of the computational barrier[14] in various olefin complexes.

The molecular orbitals for an hydrido-alkynyl complex, RhCl(H)(C$_2$H)(PH$_3$)$_2$ (2), are constructed in Figure 2.

As shown in Scheme 1, hydrido-alkynyl complex is an important intermediate for the rearrangement of alkyne to vinylidene complex. It is formed by an oxidative addition to metal fragment across the C-H bond in alkyne ligand. At lower energy in Figure 2, there are two filled orbitals (1a″ and 1a′) which are mainly π-bonding of alkynyl ligand. These are weakly interacting with the filled metal fragment orbitals and a little destabilized. The b$_2$ (yz orbital) on ML3 strongly interacts with the 2a′ to form bonding MO 1a′ (6) and antibonding LUMO 4a′ (7).

1a′ MO   4a′ MO

6   7

This interaction is a main driving force for the stabilization of hydrido-alkynyl complex. The stabilization energy produced by this interaction is computed to be 108.0 kcal/mol.
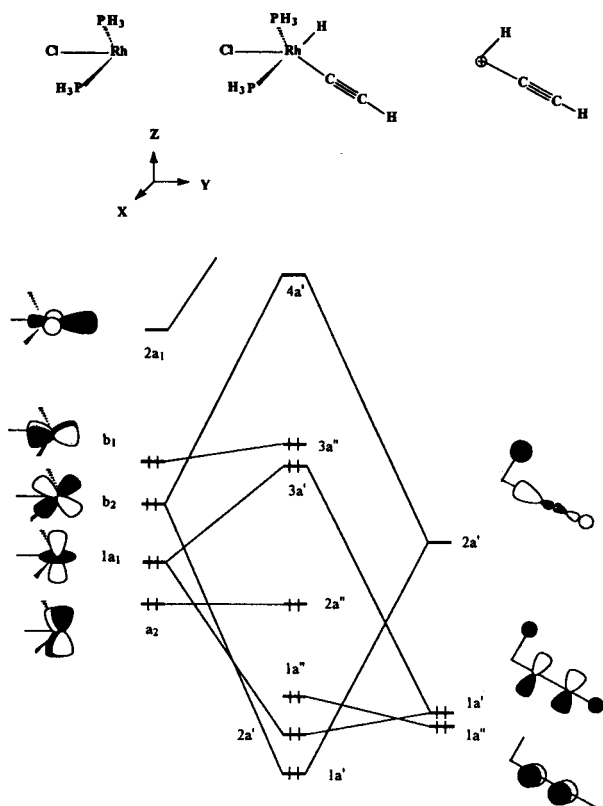

Figure 1. An orbital interaction diagram for the *trans*-RhCl-(η^2-C$_2$H$_2$)(PH$_3$)$_2$ (1).

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Figure 2. An orbital interaction diagram for the hydrido-alkynyl complex, RhCl(H)(C₂H)(PH₃)₂ (2).

In terms of total energy at EHT level, hydrido-alkynyl complex (2) is more stable than η²-alkyne complex (1) by 26.5 kcal/mol.

Vinylidene (:C=CH₂) is tautomeric with ethyne and the simplest unsaturated carbene. Ethyne-vinylidene rearrangement systems have been studied by many groups.[15] There are some evidence supporting the existence of a vinylidene species. Specially, numerous examples[16] with various transition metal fragments have been reported. Vinylidene itself is very unstable species. However, the transition metals stabilize the vinylidene species by forming stable metal complexes. In order to investigate the influence of a transition metal fragments, we need to understand the electronic structures from an orbital point of view. The important valence orbitals of vinylidene ligand are displayed on the right side of Figure 3.

The a₁ on the right side of figure 3 is corresponding to the lone pair electrons on C atom which is hybridized toward the empty space. This orbital strongly interacts with the 2a₁ hybridized orbital on ML₃ and form 1a₁ σ-bonding molecular orbital (8). This interaction is the usual forward donation of ligand. The other important interaction is π-back bonding between b₂ symmetric orbitals. At higher energy the b₂ of vinylidene is mainly p orbital on one C atom. It interacts with an filled b₂ metal fragment orbital to form 1b₂ and 2b₂ MO's (9). The 2b₂ is LUMO in RhCl(C=CH₂)(PH₃)₂ (3) complex.

Our calculation shows that 0.68 electrons are transferred from metal to vinylidene ligand in this interaction. The π-

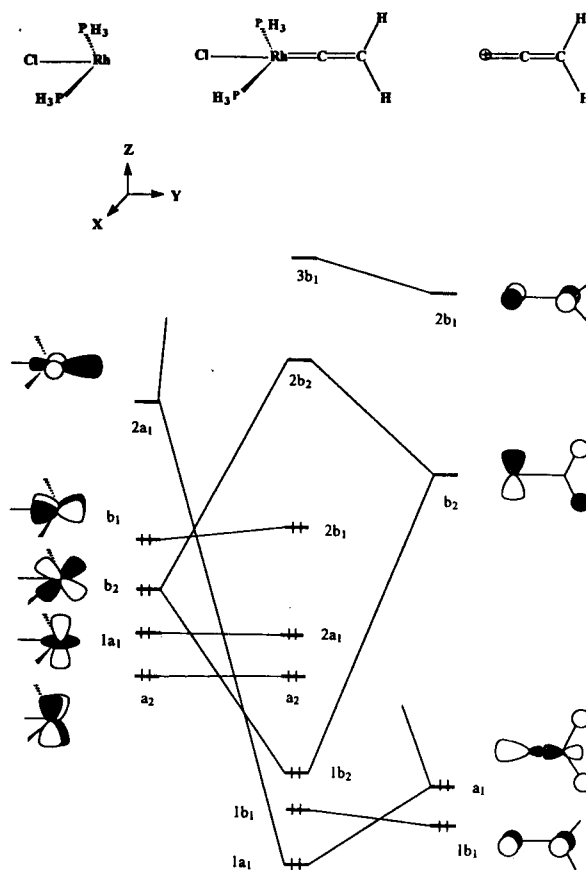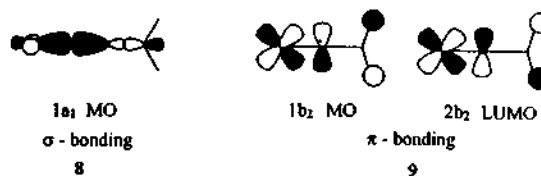**Figure 3.** An orbital interaction diagram for the vinylidene complex, RhCl(C=CH₂)(PH₃)₂ (3).

1a₁ MO   1b₁ MO   2b₂ LUMO
σ - bonding   π - bonding
8   9

back donation does not affect the C-C bond strength because of the non-bonding character in b₂ vinylidene orbital. Interestingly, the overall interaction diagram of 3 is similar with that of the η²-alkyne complex given in Figure 1. However, the strength of interaction between fragmental orbitals are quite different. The vinylidene complex is computed to be more stable than 1 and 2 complexes by 32 kcal/mol and 6 kcal/mol, respectively. This means that the vinylidene is much more stabilized than the alkyne by a transition metal fragment. Experimentally, Vahrenkamp[17] observed the interconversion of alkyne-vinylidene complex on a trinuclear clusters. So far, we have analyzed the results of qualitative calculations. We will shift to *ab initio* studies.

Ab initio calculations. On the basis of orbital analysis, *ab initio* calculations on the isomers of *trans*-RhCl(η²-HCCH)(PH₃)₂ have been carried out to investigate molecular geometries and quantitative energies. The important optimized bond distances and angles of the isomers (**1a**, **1b**, **2**, and **3**) at the HF and MP2 levels are given in Figure 4.

The difference between **1a** and **1b** is the orientation of the coordinated alkyne ligand. Alkyne in **1a** is perpendicular

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to the plane of metal fragment, whereas alkyne ligand in **1b** is rotated by 90° to be on the same plane with metal fragment. The optimized Rh-P bond distances at MP2 level in figure 4 are reasonable values compared with the experimental 2.35 Å. The Rh-C and C-C bonds in **1a** have been optimized to be 2.075 Å and 1.287 Å, respectively. These distances for η^2-alkyne complex are in good agreement with the experimental results[18] of *ca.* 2.09 Å and 1.27 Å. The C-C bond is elongated by *ca.* 0.08 Å compared with that in the optimum free acetylene.[19] As mentioned in orbital analyses, this is the result of π back-donation from metal to the empty C-C π^* orbital of alkyne ligand. The back-donation is diminished by the rotation of alkyne ligand. From the optimized geometry of **1b**, we can easily observe the reduction of this back-donation interaction. Specially, at the HF level, Rh-C bond distance of 2.498 Å is significantly longer and C-C bond of 1.198 Å is shorter than those in **1a** complex. The optimum geometry of hydrido-alkynyl complex, **2**, is a distorted trigonal bipyramidal. The Rh-C bond distance of 1.928 Å is slightly shorter than that experimentally observed in the alkynyl complexes (1.99-2.03 Å).[18,20] Rh-C bond in **2** is, however, much stronger than that in **1a**, in which distance is shortened by 0.147 Å at MP2 level. The C-C bond distance

of 1.239 Å (MP2) and 1.203 Å (HF) is not affected by the d^8 metal fragment. There is no π back-donation interaction in hydrido-alkynyl complex. The optimized vinylidene complex (3) shows Rh=C double bonding character. The Rh-C bond distance of 1.712 Å in **3** is shortened by more than 0.2 Å compared with **1a** and **2** complexes. As shown in EHT studies (**8** and **9**), there are strong σ- and π-type interactions between metal and carbon atoms. The C-C bond length of the vinylidene ligand in **3** (1.330 Å at MP2 level) is nearly same as that in the *trans*-[RhCl(C=CHMe)(PPr'$_3$)$_2$] (1.32 Å)[21] and computed data (1.29-1.33 Å)[22] for Mo, W, and Ru vinylidene complexes.

The total energies (in Hartrees) and relative energies (in kcal/mol) at the MP2 and MP4 levels are listed in Table 1. The optimum geometries at HF and MP2 levels have been used to calculate MP4 energies. The rotational energy barriers have been computed to be in the range of 18.6-25.2 kcal/mol at MP4 levels. The barrier at EHT calculations is 13.8 kcal/mol. EHT method has been used for the qualitative comparisons in terms of the orbital analyses. Therefore, the optimization process has not been applied to our systems. Most stable complex in Table 1 is vinylidene complex, **3** at various level calculations. **3** is 17.1 kcal/mol more stable than **1a** at our best calculations of MP4//MP2. Thermodynamically, η^2-alkyne complex is able to isomerize to vinylidene complex with d^8-ML$_3$ metal fragment. The energies of hydrido-alkynyl complex, **2** are computed to be similar with those of **1a** complex.

Figure 4. Optimized geometries of **1a-3** complexes calculated at the MP2 level. Geometrical parameters are given in angstroms and degrees. The values in parentheses are at the HF level.

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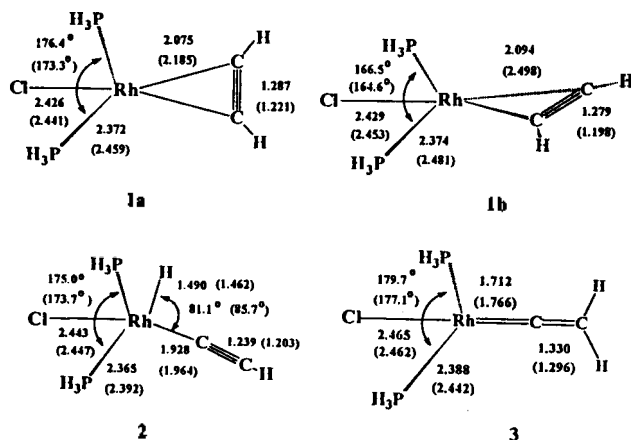
Table 1. Calculated Total Energies (Hartrees) and Relative Energies (kcal/mol) of complexes **1a-3** at the MP2 and MP4 levels

Complexes / Methods	1a	1b	2	3
MP2//HF[a]	−129.81068	−129.76925	−129.82226	−129.84001
	18.4	44.4	11.2	0.0
MP4//HF	−129.89111	−129.85093	−129.89690	−129.92932
	24.0	49.2	20.3	0.0
MP2[b]	−129.82758	−129.79604	−129.82679	−129.84574
	11.4	31.2	11.9	0.0
MP4//MP2	−129.90483	−129.87517	−129.90193	−129.93211
	17.1	35.7	19.0	0.0
EHT[c]	32.3	46.1	5.8	0.0

[a] MP2 single point calculations at the HF optimized geometries. [b] MP2 optimization calculations. [c] Relative energies at extended Hückel method.

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