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## Ab initio Studies on Rh(I)- and Ir(I)-Phenylacetylene Complexes

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The structures and energies for the intramolecular rearrangement in  $d^8\text{-MCl}(\text{PH}_3)_2(\text{HC}\equiv\text{CPh})$ ,  $\text{M}=\text{Rh}$  and  $\text{Ir}$ , complexes were studied by ab initio method at the Hartree-Fock and MP2 levels of theory. Three transition states in two pathways were optimized and characterized by frequency calculations. The activation energies for the process of  $\pi$ -type complex **1** to hydrido-alkynyl **2** have been computed to be relatively low 6.97 and 21.33 kcal/mol at MP2 level for Rh and Ir metals, respectively. However, the activation energies for a 1,2-hydrogen shift via t.s.3 have been computed to be high 50.83 and 60.05 kcal/mol for Rh and Ir metals.

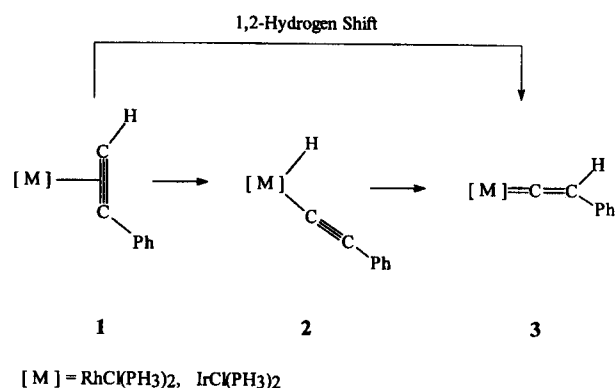
### Introduction

The complexation, rearrangement, and liberation of unsaturated hydrocarbons at a transition metals are the most important reaction sequences in both catalytic and stoichiometric organometallic chemistry. There are numerous reports on the transition metal complexes initiating rearrangement of alkyne derivatives to the corresponding alkynyl and vinylidene complexes.<sup>1</sup> As early as 1985, Silverstre and Hoffmann<sup>2</sup> reported the electronic and geometric features for the process of the rearrangement of transition metal alkynes into vinylidene complexes. The pathway involving hydrido-alkynyl intermediate requires much high activation energy for  $d^6\text{-ML}_5$  fragment at the extended Hückel level. However, they suggested that a direct 1,2-hydrogen shift might be plausible in the metal complex. According to the ab initio calculations by Morokuma and coworkers,<sup>3</sup> the 1,2-hydrogen shift mechanism on  $\text{RuCl}_2(\text{PH}_3)_2(\text{C}_2\text{H}_2)$  system is also supported. Ru metal plays an important role to stabilize the lone pair electrons at the  $\alpha$ -carbon atom in the transition state. Another ab initio calculations by Frenking and coworkers<sup>4</sup> on high oxidation state of Mo and W complexes suggested that the rearrangement of alkyne to vinylidene complexes is thermodynamically unfavorable. Experimentally, there are many evidence for the intermediate alkynyl complexes. It has been reported by Werner and coworkers<sup>5</sup> that Rh- and Ir-alkynyl complexes,  $\text{MCl}(\text{PR}_3)_2(\text{H})(\text{C}\equiv\text{CR}')$  where  $\text{R}'=\text{H}, \text{Ph}, \text{Me}, \text{SiMe}_3$ , rearrange to the vinylidene complexes and three kinds of isomers have been isolated and characterized. It seems to be interesting to investigate the intramolecular pathways of  $\eta^2$ -alkyne to vinylidene complex.

We have recently carried out EHT and ab initio molecular orbital calculations on  $d^8$ -acetylene complexes.<sup>6</sup> We

have focused the electronic and geometric structures of isomers of  $\eta^2\text{-C}_2\text{H}_2$  complex. In this paper we describe the ab initio calculations on the intramolecular pathways (Scheme 1) for  $\text{MCl}(\text{PH}_3)_2(\text{HC}\equiv\text{CPh})$ ,  $\text{M}=\text{Rh}$  and  $\text{Ir}$ , complexes with potential energy surface.

**Computational Methods.** All calculations were carried out using the GAUSSIAN 94 packages<sup>7</sup> on a Cray Y-MP and Indigo 2 workstation. A relativistic effective core potential was used for the core electrons in Rh (up to 4p), Ir<sup>8</sup> (up to 5p), P and Cl<sup>9</sup> (up to 2p). The basis sets used were double- $\zeta$  for valence region with the contraction scheme (21/21/31) for Rh, (21/21/21) for Ir, and (21/21) for P and Cl. The 3-21G basis<sup>10</sup> was used for the alkyne C and H atoms. And STO-3G<sup>11</sup> was used for atoms in phenyl group and the hydrogens in the  $\text{PH}_3$  groups. This combination of basis sets is referred to ECP1. A full geometry optimization at the Hartree-Fock (HF) level was carried out and followed single point calculation at 2nd order Moller-



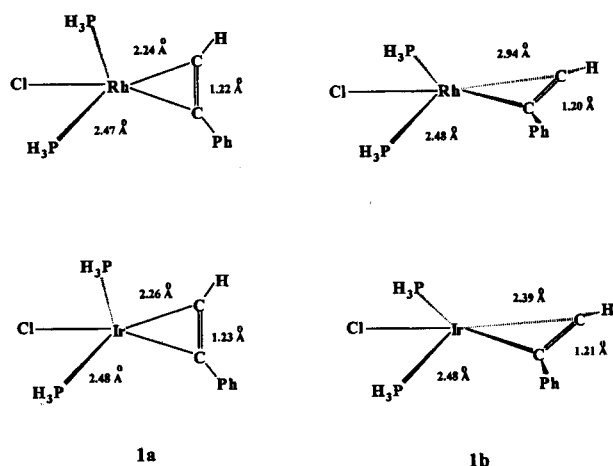
Scheme 1.

Plesset (MP2) perturbation theory on the optimized geometries under  $C_s$  or  $C_{2v}$  symmetry constraint except the local symmetry of  $\text{PH}_3$  groups, kept to  $C_{3v}$ .

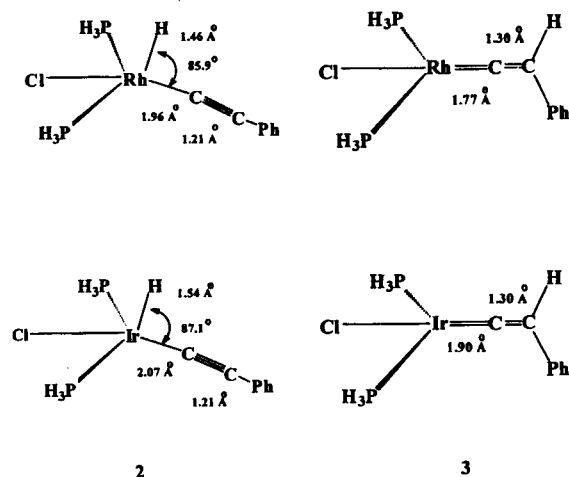
## Results and Discussion

The geometries and energies for the isomerization of phenylacetylene to the corresponding vinylidene complexes with  $d^8$ -transition metal fragment have been studied by *ab initio* calculations.  $\text{MCl}(\text{PH}_3)_2$ ,  $\text{M}=\text{Rh}$  and  $\text{Ir}$ , were chosen for  $d^8$ -metal fragment system. Three stationary points and related transition states have been optimized at HF level followed by MP2 single point calculations for the refinement of energies, that is,  $\pi$ -alkyne (**1**), Hydrido-alkynyl (**2**), and vinylidene (**3**) complexes. The optimized parameters for  $\pi$ -alkyne complexes of  $\text{MCl}(\text{PH}_3)_2(\eta^2\text{-C}_2\text{HPh})$ ,  $\text{M}=\text{Rh}$  and  $\text{Ir}$ , are given in Figure 1.

The difference between **1a** and **1b** conformers in the figure is the orientation of the coordinated phenylacetylene ligand. Alkyne in **1a** conformer is perpendicular to the plane of  $C_{2v}$   $\text{MCl}(\text{PH}_3)_2$  metal fragment. When alkyne ligand is rotated by  $90.0^\circ$  around the extension of M-Cl axis, metal fragment and alkyne are on the same plane to form **1b** conformer. The optimized Rh-C (2.24 Å) and Ir-C (2.26 Å) bond distances in **1a** conformer are much shorter than those (2.94 and 2.39 Å for Rh and Ir complexes, respectively) of **1b**. The C-C bond distances of 1.22 and 1.23 Å in **1a** are longer than those of 1.20 and 1.21 Å in **1b**. These represent that the  $\pi$  back-donation from metal to alkyne in **1a** conformer is much stronger than that in **1b** conformer. While the bond strength between metal and alkyne in **1a** becomes stronger, the C-C bond is weakened to give the elongated bond distance compared with C-C distance in free acetylene ( $\sim 1.20$  Å). In **1b** conformer,  $\pi$  back-donation interaction can not be observed in terms of the optimized bond distances. The rotational energy barriers have been computed to be 40.2 kcal/mol and 35.1 kcal/mol at MP2 level for Rh and Ir metal complexes, respectively. These rotational barriers are much higher than those of unsubstituted alkyne, acetylene complexes, 26.0 and 20.7 kcal/mol for Rh and Ir metal at MP2/ECP1 level, respectively.<sup>6b</sup>



**Figure 1.** Optimized structures of  $\text{MCl}(\text{PH}_3)_2(\eta^2\text{-C}_2\text{HPh})$ ,  $\text{M}=\text{Rh}$  and  $\text{Ir}$ , at HF/ECP1 level.



**Figure 2.** Optimized structures of Hydrido-alkynyl (**2**) and Vinylidene (**3**) for Rh and Ir metal complexes at HF/ECP1 level.

One pathway for the alkyne-vinylidene rearrangement is through the oxidative addition reaction across the C-H bond, forming hydrido-alkynyl intermediate (**2**), and subsequent migration to produce vinylidene complex. The optimized structures of hydrido-alkynyl (**2**) and vinylidene (**3**) complexes are displayed in Figure 2.

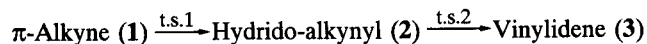
The optimized geometry of **2** for Rh and Ir metals forms a distorted trigonal bipyramidal. The M-H bond distances (Rh; 1.46 Å and Ir; 1.54 Å) are within the range of typical bond distances of specific metal and hydrogen atom. The five coordinated hydrido-alkynyl Rh and Ir complex corresponding to **2** has not been known experimentally. For comparison, the Rh-H distances observed in binuclear complex  $\text{Rh}_2\text{H}_2(\text{O}_2\text{CO})(\text{PhC}\equiv\text{CPh})(\text{P}(i\text{-Pr})_3)_3$  are 1.42 and 1.48 Å.<sup>12</sup> The Rh-H distance of 1.46 Å that we calculated in agreement with the observed value. The optimized Rh-C distance of 1.96 Å and C≡C distance of 1.21 Å are also in good agreement with the experimental values of 1.958 and 1.206 Å in  $\text{RhCl}(\text{Py})(\text{P}(i\text{-Pr})_3)_2(\text{C}\equiv\text{C}-\text{CMe}=\text{CH}_2)_2$  complex.<sup>13</sup> Distances between C and H atoms which are both coordinated to Rh or Ir metals have been optimized to be very long. Obviously, there is no interaction between two atoms. The C-C distance of 1.21 Å in Rh and Ir complex is not affected by metal fragment. There is no  $\pi$  back-donation interaction in hydrido-alkynyl complex.

The optimized vinylidene complex **3** shows double bonding character in M-C. The M-C bond distance in **3** (1.77 Å and 1.90 Å for Rh and Ir, respectively) is significantly shortened than those in the corresponding complex **2**. The optimized C-C bond is elongated to be 1.30 Å to represent double bond character shown in Figure 2. The optimized values are very close to the experimentally determined distances of 1.775 and 1.32 Å for Rh-C and C=C distances in  $\text{RhCl}(\text{P}(i\text{-Pr})_3)_2(\text{C}=\text{CHMe})$  complex.<sup>5d</sup>

Two types of transition states (t.s.1 and t.s.2) have been optimized and characterized with frequency calculational analysis to investigate the potential energy surface for the intramolecular process. t.s.1 appears in the process of transformation of  $\pi$ -alkyne (**1**) to hydrido-alkynyl (**2**) complexes and t.s.2 is in the middle of hydrido-alkynyl and vinylidene complexes.

**Table 1.** The Optimized parameters for  $MCl(PH_3)_2(C_2HPh)$  ( $M=Rh, Ir$ ) complexes at HF/ECP1 level. The bond distances are in angstroms and angles in degrees. Numbers on top and bottom are for Rh and Ir complexes, respectively

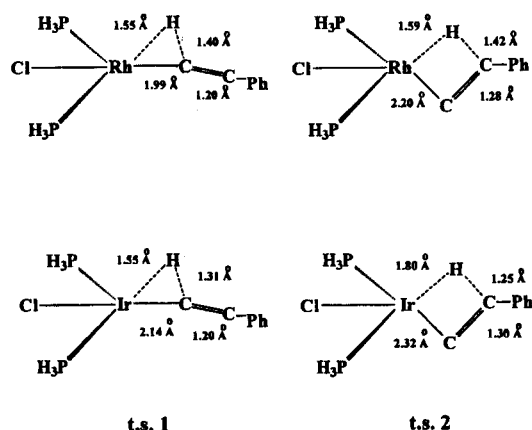
	1a	1b	t.s.1	2	t.s.2	3	t.s.3
M-C	2.24	2.94	1.99	1.96	2.20	1.77	2.00
	2.26	2.39	2.14	2.07	2.32	1.90	2.10
C-C	1.22	1.20	1.20	1.21	1.28	1.30	1.24
	1.23	1.21	1.20	1.21	1.30	1.30	1.24
C-H	1.05	1.05	1.40	2.54	-	-	1.20
	1.06	1.05	1.31	2.52	-	-	1.20
C-C <sub>Ph</sub>	1.44	1.43	1.43	1.46	1.47	1.49	1.44
	1.45	1.45	1.43	1.44	1.49	1.50	1.44
M-H	-	-	1.55	1.46	1.59	-	-
	-	-	1.70	1.54	1.80	-	-
C-H	-	-	-	-	1.42	1.08	1.51
	-	-	-	-	1.25	1.08	1.52
$\angle P-M-P$	170.7	165.5	176.1	173.5	174.9	175.1	169.4
	173.0	154.3	175.6	173.9	175.1	175.5	169.0
$\angle Cl-M-C$	166.5	172.7	166.5	172.8	154.9	178.5	178.8
	166.0	159.4	168.0	172.8	135.5	178.7	179.2
$\angle M-C-C$	-	-	169.6	178.2	82.0	180.0	170.6
	-	-	165.3	179.3	79.0	180.0	172.7
$\angle H-M-C$	-	-	48.5	85.9	67.1	-	-
	-	-	37.5	87.1	61.6	-	-
$\angle H-C-C$	166.7	175.1	-	-	-	-	76.4
	161.3	163.1	-	-	-	-	76.9
$\angle C-C-C_{Ph}$	165.1	177.0	180.0	180.0	150.1	128.1	179.1
	160.4	156.0	180.0	180.0	139.9	128.1	179.7



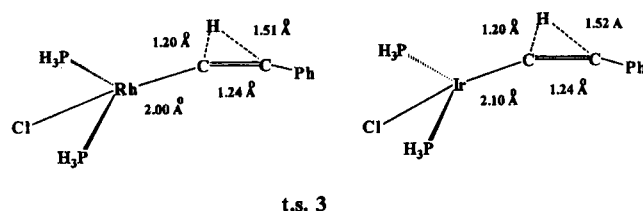
The optimized parameters of 1-3 and three transition states for  $MCl(PH_3)_2(C_2HPh)$  ( $M=Rh, Ir$ ) complexes at HF/ECP1 level are summarized in Table 1.

The optimized geometries of t.s.1 and t.s.2 for  $MCl(PH_3)_2(C_2HPh)$ ,  $M=Rh$  and  $Ir$ , are displayed on Figure 3 at HF/ECP1 calculations.

Transferring H atom in t.s.1 is positioned between Rh and C atoms. While the C-H bonding with the optimized



**Figure 3.** Optimized structures of t.s.1 and t.s.2 for Rh and Ir metal complexes at HF/ECP1 level.



**Figure 4.** Optimized structures of t.s.3 for Rh and Ir metal complexes at HF/ECP1 level.

distance of 1.40 and 1.31 Å for Rh and Ir complex are much weakened, the interaction between metal and H atoms becomes stronger. The optimized M-H distances are 1.55 Å for both metal systems. We can easily observe that H atom is moving from C to metal atom in the optimized t.s.1 structure. It has been characterized that t.s.1 is the transition state for the process of  $\pi$ -Alkyne (1)  $\rightarrow$  Hydrido-alkynyl (2) by the analysis of frequency calculations. t.s.2 structure formed four-membered ring complex shows that one H atom is transferring from metal to the uncoordinated C atom. The bond distances of M-H are computed to be 1.59 Å and 1.80 Å for Rh and Ir metal, respectively. And the optimized C-H distance is 1.42 and 1.25 Å for Rh and Ir systems.

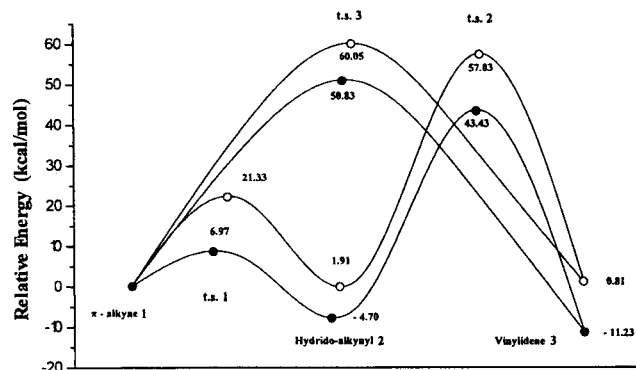
Figure 4 displays the optimized transition state structure (t.s.3) for 1,2-hydrogen shift process between 1 and 3. The bond distances are optimized to be 1.20 and 1.51 Å in the middle of C-C bond for Rh and Ir systems. Structurally, our optimized transition states are very close to Morokuma's optimum values<sup>14</sup> about  $RhCl(PH_3)_2(C_2H_2)$  system.

The computed relative energies at MP2 level are given in Table 2 in the unit of kcal/mol. And potential energy surfaces for  $MCl(PH_3)_2(C_2HPh)$ ,  $M=Rh$  and  $Ir$  complexes at MP2 calculations are displayed in Figure 5.

The computed total energy of hydrido-alkynyl intermediate 2 is close to that of 1a complex for both Rh and Ir systems. The activation energy for the process of 1a to 2

**Table 2.** The relative energies for  $MCl(PH_3)_2(C_2HPh)$ ,  $M=Rh$  and  $Ir$ , at MP2/ECP1 level. The energies are listed in kcal/mol

	1a	1b	t.s.1	2	t.s.2	3	t.s.3
Rh	0.00	40.23	6.97	-4.70	43.43	-11.23	50.83
Ir	0.00	35.13	21.33	1.91	57.03	0.81	60.05



**Figure 5.** Potential energy Surface for  $MCl(PH_3)_2(\pi-C_2HPh) \rightarrow MCl(PH_3)_2(C_2HPh)$ , ( $M=Rh \circ, Ir \circ$ ) at MP2/ECP1 calculation.

via t.s.1 is computed to be relatively low; 6.97 and 21.33 kcal/mol for Rh and Ir metals, respectively. The activation energy of 6.97 kcal/mol for the Rh-phenylacetylene system is much lower than the computed energy of 36.3 kcal/mol for Morokuma's Rh-acetylene system.<sup>14</sup> For the 2 to 3 process through t.s.2, the computed activation energies are 48.13 and 55.12 kcal/mol for Rh and Ir metal complexes, respectively. These high activation energies indicate that the reaction through t.s.2 does not easily process at normal reaction condition. Rh vinylidene complex 3 is most stable one in terms of energy. Numerous Rh vinylidene complexes have been known experimentally. The activation energies for a 1,2-hydrogen shift via t.s.3 have been computed to be also high 50.83 and 60.05 kcal/mol for Rh and Ir complexes, respectively. In general,  $\text{RhCl}(\text{PH}_3)_2(\text{C}_2\text{HPh})$  complex has lower energy pathway compared with the corresponding Ir complex as shown on Figure 5. It has been known that the reaction rate of Rh complexes is usually faster than Ir complexes.

### Conclusions

*Ab initio* calculations have been carried out to study geometries and energies on the intramolecular rearrangement of Rh and Ir-phenylacetylene complexes, 1-3. The optimized stationary points for the Rh complexes ( $\pi$ -Alkyne (1), Hydrido-alkynyl (2), and Vinylidene (3)) are in good agreement with the corresponding experimental and theoretical values. Three transition states (t.s.1, t.s.2, and t.s.3) for two different intramolecular process have been optimized and characterized by frequency calculational analysis. The activation energies for the process of  $\pi$ -type complex 1a to hydrido-alkynyl 2 have been computed to be relatively low 6.97 and 21.33 kcal/mol at MP2 level for Rh and Ir metals, respectively. However, the other pathways have high activation energies for both Rh and Ir metals.

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