citation spectra. An orbital population analysis yields a configuration of $(xy)^{0.95}(xz)^{1.01}(yz)^{0.99}(x^2\text{-}y^2)^{0.02}(z^2)^{0.02}$ for the lowest component of ^2E_g state. The relative *d*-orbital ordering from the calculations is $E(xy, xz)=0$ cm^{-1} < $E(yz)=856$ cm^{-1} < $E(x^2\text{-}y^2)=22882$ cm^{-1} < $E(z^2)=25646$ cm^{-1}. These factors can be used for predicting the photochemical reactivity of mixed-ligand chromium(III) complexes.[21] The following values were finally obtained for the ligand field parameters; $e_\sigma(\mathrm{N_{prim}})=7542\pm85$, $e_\sigma(\mathrm{N_{sec}})=8575\pm68$, $B=613\pm15$, $C=3161\pm30$, $T=121\pm6$, and $\zeta=270\pm20$ cm^{-1}. The parameter values reported here appear to be rather significant, as deduced on the basis of a manifold of sharp-line transitions which were obtained from highly resolved excitation spectrum. The AOM parameters for *trans*-diammac indicate that the primary and secondary nitrogen atoms have very strong σ-donor properties toward chromium(III). The value of 7542 cm^{-1} for the $e_s(\mathrm{N_{prim}})$ is comparable to 7505 cm^{-1} reported for $[\mathrm{Cr(en)_3}]\mathrm{Cl_3}$.[6] However, the value of 8575 cm^{-1} for the $e_s(\mathrm{N_{sec}})$ parameter obtained from the complete ligand field analysis is the largest one among the values reported for nitrogen coordinated chromium(III) complexes. The result is in agreement with the shortest Cr-N bond length of 2.031 Å from X-ray crystal structure analysis.[17] The value of Racah parameter, B is only 66.8% of the value for a free chromium(III) ion in the gas phase. The ligand field parameters given here may be transferable to this type of other complexes as a basis for schematic analysis.

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Ab initio Studies on d^8-$\mathrm{MCl(PH_3)_2(C_2H_2)}$, M=Rh and Ir, Complexes

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The geometries and energies of the isomers in alkyne complexes $\mathrm{MCl(PH_3)_2(\eta^2\text{-}C_2H_2)}$, M=Rh and Ir, are theoretically investigated using *ab initio* methods at the Hartree-Fock and up to MP4 level of theory and relativistic effective core potentials for Rh and Ir metals. The optimized structures of Rh complexes, **1-3** at MP2/ECP1 level are in good agreement with the related experimental data. The binding energies of $\mathrm{C_2H_2}$ to d^8-metal fragments are computed to be ~55 kcal/mol. The vinylidene complexes for Rh and Ir metals are calculated to be much lower in energy than the alkyne complexes. The alkyne-vinylidene rearrangement is possible to proceed exothermically through the intermediate hydrido-alkynyl complexes, **2** or **9**. Detailed comparison is given about the geometries and relative energies on Rh and Ir isomers at the various level *ab initio* calculations with orbital analysis.

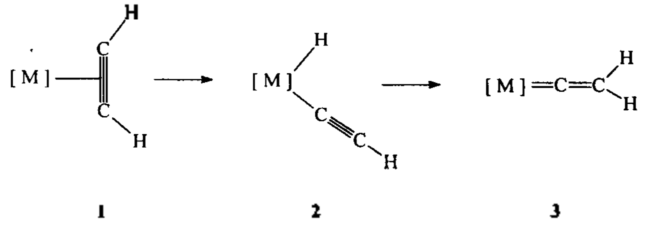
Introduction

The chemistry of unsaturated carbenes, such as vinylidene, allenylidene, and their derivatives which are coordinated to one or more transition metal fragments, has recently drawn substantial attention. Numerous examples of the transition metals initiating rearrangement of alkynes to the corresponding vinylidenes have been reported.[1] Frenking and coworkers[2] have reported the geometric parameters and stabilities of the alkyne and vinylidene complexes of molybdenum and tungsten in high oxidation states. According to the ab initio calculations, the vinylidene complexes are computed to be slightly higher in energy than the alkyne complexes. It suggests that the rearrangement of alkyne to vinylidene complex in Mo and W systems is thermodynamically unfavorable. Another theoretical studies on the rearrangement are given by R. Hoffmann and J. Silverstre[3] with the extended Hückel method. They examined the electronic and structural features of the isomerization of various alkyne into vinylidene complexes *via* 1,2-hydrogen shift process. In these studies, the alternative pathway through a hydrido-alkynyl species needs much activation energy for d^6-ML_5 fragment. However, if ML_n is rhodium or iridium fragments, the alkyne complex (**1**) and the hydrido-alkynyl complex (**2**) exists in equilibrium.[4] And it is experimentally known that on addition of basic substance such as pyridine this equilibrium is completely shifted to the hydrido-alkynyl complex. Recently, the intermediate hydrido-alkynyl complexes have been known in various Rh and Ir systems.[5-7] The existence of the intermediate supports that the rearrangement of alkyne to vinylidene complex (**3**) occurs stepwise as shown on Scheme 1.

In previous studies,[8] we have investigated the electronic structures, molecular geometries, and energies of the isomers of $RhCl(PH_3)_2(C_2H_2)$ complex with the extended Hückel and preliminary *ab initio* calculations. We have focused on the chemical bonding of isomers. We have found that σ-bond interaction in **2** and **3** complexes is much stronger than that in **1**. As a result, the alkyne complex is computed to be less stable by 32.3 kcal/mol at EHT and 17.1 kcal/mol at *ab initio* level relative to the vinylidene complex. In the present paper, molecular structures and energies of the isomers of Rh(I) and Ir(I) systems shown on Scheme 1 shall be examined using *ab initio* methods with the various levels of calculations.

Computational Methods

All calculations were carried out using the GAUSSIAN 92 and 94 packages[9] on a Cray Y-MP and Indigo 2 workstation. Two kinds of basis sets were used for the rhodium and iridium complexes. A relativistic effective core potential was used for the core electrons in Rh[10] (up to 4p), Ir[10] (up to 5p), P and Cl[11] (up to 2p). The basis sets used were double-ζ 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[12] was used for the alkyne C and H atoms and STO-3G[13] for the hydrogens on the PH_3 groups. This combination of basis sets is referred to as ECP1. In the second basis set, referred to as ECP2, better effective core potentials are used for Rh and Ir, treating explicitly the outermost core electrons (3s3p for Rh and 4s4p for Ir).[14] Metal basis sets were contracted to (341/321/31) and (341/321/21) for Rh and Ir, respectively. The 6-31G* basis[15] was used for C and H in alkyne. A full geometry optimization at the Hartree-Fock (HF) and 2nd order Moller-Plesset (MP 2) perturbation theory was carried out on the calculated



[M] = $RhCl(PH_3)_2$, $IrCl(PH_3)_2$

Scheme 1.

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

The coordinatively unsaturated 14-electron compounds $MCl(PR_3)_2$, M=Rh or Ir,[16] are useful species to investigate the reaction with alkynes. They easily produce the various square planar alkyne complexes and smoothly rearrange to the vinylidene complexes.[4,6] The valence orbitals of C_{2v} $RhCl(PH_3)_2$ were analyzed in detail.[17] At higher energy the vacant $2a_1$ valence orbital is the hybridized d orbital by metal s and p towards the entering ligand. This orbital is able to accept electrons from ligand and make a strong σ-interaction. At low energy are the four filled orbitals associated with a square planar splitting pattern. One of them, b_2 metal d orbital is associated with the back-donation to the ligand empty orbital. We will describe these interactions in the discussion of the optimized geometries later.

The optimized molecular structures of Rh complexes (**1-3**) at the HF/ECP1 level are illustrated in Figure 1. And the important optimized bond distances and angles are reported in Table 1.

The values at ECP2 basis sets are given in parentheses. There are two conformers for **1** and **3** depending on the orientations of alkyne or vinylidene ligands. In **1a** or **3a**, unsaturated hydrocarbon ligand, alkyne or vinylidene, is perpendicular to the plane of $RhCl(PH_3)_2$ fragment. According to the ligand rotation by 90°, it can be formed **1b** or **3b** (not shown on Figure 1) conformers.

It is known that **1** complex is produced by the reaction of C_2H_2 with a coordinatively unsaturated $RhCl(PH_3)_2$ (eqs. 1).

$$C_2H_2 + RhCl(PH_3)_2 \rightarrow RhCl(PH_3)_2(\eta^2\text{-}C_2H_2) \qquad (1)$$

At ECP1 basis, the optimized bond distances of Rh-C and C-C in **1a** are 2.185 Å and 1.221 Å, respectively. These values for 2-alkyne complex are reasonable distances compared with the X-ray structure[7] of $[Rh(CO)(PPr^i_3)_2(\eta^1,\eta^2\text{-}C\equiv C\text{-}C\equiv CPh)RhCl(PPr^i_3)_2]$ (Rh-C; 2.098 Å, C-C; 1.271 Å). The C-C distance of 1.221 Å in **1a** is elongated by 0.033 Å than the optimized free acetylene[18] because of π-back donation (**4**) from the filled metal d orbital to the empty π*-orbital of C_2H_2.

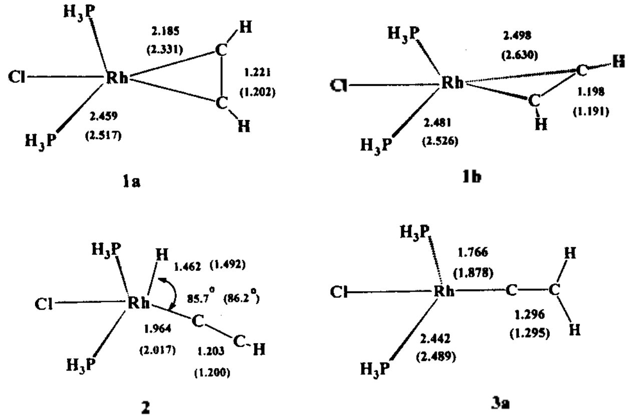
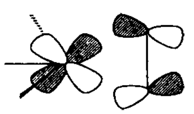


Figure 1. Optimized geometries of **1-3** at the HF/ECP1 level. Geometrical parameters are given in angstroms and degrees. Numbers in parentheses are at the HF/ECP2 level.

Table 1. The optimized parameters for Rhodium complexes (**1-3**) at HF/ECP1 and HF/ECP2 levels. The bond distances are in angstroms and angles in degrees. Numbers in parentheses are at the HF/ECP2 level

	1a	**1b**	**2**	**3a**	**3b**
Rh-Cl	2.449 (2.484)	2.453 (2.493)	2.447 (2.460)	2.462 (2.478)	2.494 (2.507)
Rh-P	2.459 (2.517)	2.481 (2.526)	2.392 (2.443)	2.442 (2.489)	2.450 (2.486)
Rh-C	2.185 (2.331)	2.498 (2.630)	1.964 (2.017)	1.766 (1.878)	1.777 (1.904)
C-C	1.221 (1.202)	1.198 (1.191)	1.203 (1.200)	1.296 (1.295)	1.294 (1.292)
Rh-H			1.462 (1.492)		
∠P-Rh-P	173.3 (172.2)	164.6 (165.8)	173.7 (179.2)	177.1 (174.5)	170.4 (169.4)
H-Rh-C			85.7 (86.2)		



4

π - back bonding

When the optimized **1b** structure is compared with **1a**, Rh-C distance of 2.498 Å is much increased by 0.313 Å and C-C distance of 1.198 Å is shortened. As a result, the alkyne ligand in **1b** is weakly coordinated to the metal fragment. It is caused by the weakening of π-back donation in **1b** by the rotation of alkyne ligand. As given in parentheses at Table 1, the optimized parameters for **1a** and **1b** at ECP2 level are analyzed to have similar phenomena with ECP1 level for Rh-C and C-C distances.[18] The calculated energies at the various level theory are summarized in Table 2.

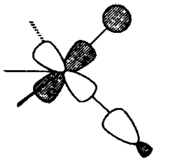
Table 2. Energies (in kcal/mol) for the isomerization of $RhCl(PH_2)_2(C_2H_2)$ (**1a**) Relative to the reactants ($RhCl(PH_3)_2+HC\equiv CH$) at HF optimum geometries

		Reactants[a]	**1a**	**1b**	**2**	**3a**	**3b**
ECP1	HF	−129.29151	−27.9	−16.6	−22.5	−30.9	−22.4
	MP2	−129.72139	−56.0	−30.0	−63.3	−74.4	−59.1
	MP4	−129.80337	−55.1	−29.8	−58.7	−79.0	−68.2
ECP2	HF	−216.27290	−11.6	−4.2	+7.3	−9.6	−3.6
	MP2	−216.78951	−37.7	−18.1	−45.7	−58.0	−41.7
	MP4	−216.87663	−39.9	−19.3	−43.0	−72.7	−57.7

[a] In hartrees

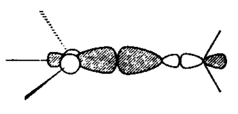
The total energies of reactants in Hartree unit is the sum of energy for $HC\equiv CH$ and $RhCl(PH_3)_2$. The other energies given in kcal/mol for **1a-3b** are the relative values to the reactants. As mentioned in calculational methods, MP2 or MP4 energies are obtained through the single point calculations at the HF optimum geometries. In general, HF energy is underestimated and is no good choice to analyze potential energy surfaces in a series of transition metal complex reactions. MP2 or MP4 energies usually give resonable values for transition metal complexes.[19] The binding energy of C_2H_2 in **1a** is computed to be 56.0 and 55.1 kcal/mol at MP2/ECP1 and MP4/ECP1 levels, respectively. Previously, we have analyzed the origin of this binding energy with an orbital interaction diagram at EHT calculations.[8] Two important interactions, σ- and π-bonding exist between alkyne ligand and $RhCl(PH_3)_2$ fragment. The vacant hybridized d orbital of metal fragment strongly interacts with the filled alkyne π orbital to form σ-bonding molecular orbital. The other contribution originates from the π-back donation shown in **4**. The computed rotational barriers, the energy difference between **1a** and **1b**, are 25.3 and 20.6 kcal/mol at the MP4/ECP1 and MP4/ECP2 levels, respectively.

The C-H bond activation, oxidative addition of C_2H_2, by $RhCl(PH_3)_2$ fragment produce a hydrido-alkynyl complex, **2**. The geometry around Rh atom is a distorted trigonal bipyramidal (Figure 1). The optimized Rh-C distance of 2.017 Å at ECP2 (1.964 Å at ECP1) is within the range of experimentally determined values 1.99-2.03 Å.[6,20] And the Rh-H distance of 1.492 Å at ECP2 (1.462 Å at ECP1) is slightly shorter than that, 1.542 Å, of the X-ray crystal structure[6] of $Rh(PPr^i_3)_2(py)H(C\equiv CSiMe_3)_2$. The experimental data is an estimated value in six-coordinated octahedral Rh complex. The optimized C-C bond distance indicates a typical triple bond. The energy of hydrido-alkynyl complex is calculated to be *ca.* 4 kcal/mol more stable than η^2-alkyne complex **1a** at MP4 levels. According to the orbital analysis, the main reason for the stabilization in **2** complex is to form a strong σ-bonding molecular orbital, **5**.



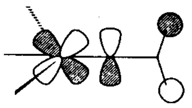
5

One of the metal d orbitals strongly interacts with both s orbital of H atom and the hybridized p orbital on C atom in alkynyl ligand. In terms of thermodynamic point, alkyne complex **1a** can exist in equilibrium with or rearrange to hydrido-alkynyl complex **2**. Werner[21] also observed the similar reactions in the alkyne complexes in solution. And on addition of pyridine they obtained the octahedral hydrido-alkynyl complexes.



σ - bonding

6



π - bonding

7

According to the EHT analysis for **3a** complex, there are two strong interaction, **6** and **7**, between vinylidene ligand and $RhCl(PH_3)_2$ fragment.

6 molecular orbital is a very strong σ-interaction between two hybrid orbitals. And in **7** MO, one d orbital interacts with the non-bonding p orbital in vinylidene as π-type. Consequently, it is easily expected to form strong Rh-C bond. We also observed strong Rh-C bond in the optimum geometries at the *ab initio* calculations. The Rh-C bond distance in **3a** is optimized to 1.766 Å at ECP1 which is in good agreement with the X-ray crystal analysis[4a)] (1.775 Å) for trans-[RhCl(=C=CHMe)(PPr^i_3)$_2$]. This much shorter distance than **1** or **2** indicates forming a strong Rh=C bonding. The C-C distance of 1.296 Å is obviously a double bond character. It is a reasonable distance compared with the experimental value[4c)] (1.32 Å) and the theoretical data[2] (1.29-1.33 Å) for Mo and W vinylidene complexes. The optimized parameters for **3b** formed by the rotation of vinylidene ligand are very close to those of **3a** given in Table 1. However, the rotational barrier of vinylidene ligand in **3** complex is computed to be 11-15 kcal/mol at MP4 levels. The energy barrier comes from the weakening of π-interaction. Among three Rh isomers in Scheme 1, **3a** is most stable one. It is computed at MP4/ECP1 levels that **3a** is 23.9 and 20.3 kcal/mol more stable than **1a** and **2**, respectively. As experimentally observed, our calculations also indicates that η^2-alkyne Rh complex(**1**) can be isomerized to vinylidene complex(**3**) through the intermediate hydrido-alkynyl complex(**2**) in terms of thermodynamic point.

Ir metal has been chosen to investigate the effects of metal itself in d^8-metal fragments. The optimized structures of Ir complexes (**8-10**) at the applied basis sets are given in Figure 2. And the detailed parameters are summarized in Table 3.

The back-donation ability of Ir complex is larger than that of Rh because of metal softness. We also observed this property in the optimum structure of **8a**. The C-C bond distance in **8a** is optimized to 1.235 Å at HF/ECP1. This value is 0.014 Å longer than the C-C distance in Rh complex, **1a**. The elongation of C-C length indicates that the bond is weakened because of larger π-back donation to the empty C-C π*-bonding orbital. In general, the optimized Ir-C bond distances at HF/ECP1 level is longer than those at HF/ECP2 level. It is the exactly opposite result to Rh complexes. The only explanation we think might be basis sets effect. The computed binding energy of C_2H_2 in Ir complex **8a** is 55.0 kcal/mol at MP4/ECP1 level (Table 4). It is almost same with that of Rh complex, **1a**.

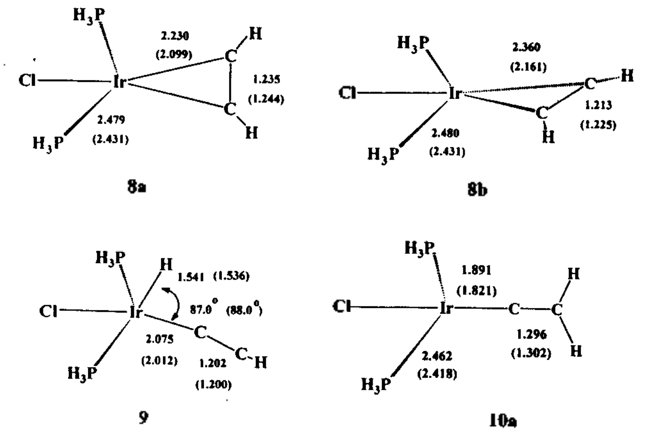


Figure 2. Optimized geometries of 8-10 at the HF/ECP1 level. Geometrical parameters are given in angstroms and degrees. Numbers in parentheses are at the HF/ECP2 level.

Table 3. The optimized parameters for Iridium complexes (8-10) at HF/ECP1 and HF/ECP2 levels. The bond distances are in angstroms and angles in degrees. Numbers in parentheses are at the HF/ECP2 level

	8a	8b	9	10a	10b
Ir-Cl	2.527 (2.480)	2.531 (2.516)	2.533 (2.490)	2.542 (2.500)	2.574 (2.522)
Ir-P	2.479 (2.431)	2.480 (2.431)	2.446 (2.418)	2.462 (2.418)	2.465 (2.420)
Ir-C	2.230 (2.099)	2.360 (2.161)	2.075 (2.012)	1.891 (1.821)	1.902 (1.829)
C-C	1.235 (1.244)	1.213 (1.225)	1.202 (1.200)	1.296 (1.302)	1.293 (1.301)
Ir-H			1.541 (1.536)		
∠P-Ir-P	174.7 (174.8)	162.8 (159.5)	174.8 (176.4)	176.9 (175.6)	168.1 (167.6)
∠H-Ir-C			87.0 (88.0)		

At MP2/ECP1 and MP4/ECP1 calculations, the other relative energies of Ir complexes (**8-10**) are pretty close to those of Rh complexes given in Table 2.

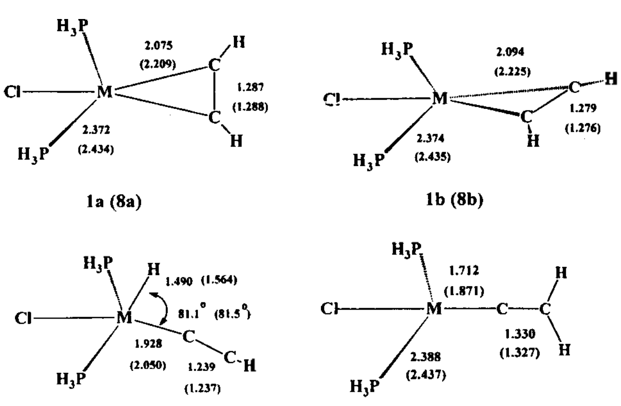
MP2/ECP1 optimizations have been carried out to examine the effects of computational methods on structures and energies. The optimized geometries of Rh and Ir complexes at MP2/ECP1 level are illustrated in Figure 3. The bond distances of Ir complexes (**8-10**) are given in parentheses.

The important features are on the Rh-C and C-C bond distances. For all isomers of Rh and Ir complexes, the optimized Rh-C distances at MP2/ECP1 level are a little shortened than those at HF/ECP1 level. However, the C-C bond distances are much increased at the MP2 optimizations. For examples, the Rh-C distance in **1a** is optimized to be 2.075 and 2.185 Å at MP2/ECP1 and HF/ECP1 levels, respectively. MP2 value of 2.075 Å is in good agreement with the

Table 4. Energies (in kcal/mol) for the isomerization of $IrCl(PH_3)_2(C_2H_2)$ (**8a**) Relative to the reactants ($IrCl(PH_3)_2$+$HC{\equiv}CH$) at HF optimum geometries

		Reactants[a]	**8a**	**8b**	**9**	**10a**	**10b**
ECP1	HF	−127.27881	−35.4	−21.6	−38.8	−36.6	−25.5
	MP2	−127.72431	−57.6	−36.9	−61.5	−66.8	−49.9
	MP4	−127.80626	−55.0	−35.6	−56.9	−68.7	−55.6
ECP2	HF	−211.40010	−35.2	−17.7	−40.9	−50.0	−38.1
	MP2	−211.93642	−75.6	−52.7	−74.1	−96.2	−79.9
	MP4	−212.02260	−72.0	−50.5	−70.1	−99.2	−87.8

[a] In hartrees



1a (8a) 1b (8b)

2 (9) 3a (10a)

Figure 3. Optimized geometries of Rh complexes, **1-3** at the MP2/ECP1 level. The values in parentheses are of Ir complexes, **8-10** at the MP2/ECP1 level.

experimental value of 2.098 Å.[7] And the C-C distance of 1.287 Å at MP2 level is much close to the experimental 1.271 Å compared with the HF value of 1.221 Å. The calculated energies for Rh and Ir complexes (**1-3** and **8-10**) at MP4/ECP1//MP2/ECP1 (abbreviated to MP4//MP2) levels are summarized on Table 5.

The binding energy of C_2H_2 to $RhCl(PH_3)_2$ fragment in 1a is computed to be 59.5 and 56.2 kcal/mol at MP2//MP2 and MP4//MP2 calculations, respectively. These energies are similar with the binding energies given in Table 2 (MP2//HF; 56.0 kcal/mol, MP4//HF; 55.1 kcal/mol). When the relative energies in Table 5 are compared with those in Table 2 and Table 4, we can not find out any significant difference. While the electron correlation (at least MP2 level) needs to obtain the better molecular structures for Rh and Ir complexes, it is good enough to investigate energies using HF optimization followed by MP2 or MP4 single point calculations.

Conclusions

Ab initio calculations have been carried out to investigate geometries and energies on the isomers of Rh and Ir-alkyne complexes, **1-3** and **8-10**. ECP1 and ECP2 basis sets are

Table 5. Energies (in kcal/mol) for the isomerization of $MCl(PH_3)_2(C_2H_2)$, M=Rh and Ir, (**1a** and **8a**) Relative to the reactants ($MCl(PH_3)_2$+$HC{\equiv}CH$) at MP2 optimum geometries

		MP2	MP4
M=Rh	Reactant[a]	−129.73284	−129.81525
	1a	−59.5	−56.2
	1b	−39.7	−37.6
	2	−59.0	−54.4
	3a	−70.8	−73.3
	3b	−58.2	−64.9
M=Rh	Reactant	−127.73169	−127.81331
	8a	−57.8	−55.1
	8b	−39.7	−37.9
	9	−59.4	−55.6
	10a	−64.1	−66.1
	10b	−48.4	−53.9

[a] In hartrees

used with the various level calculations up to MP4 level. The optimized geometries of the Rh complexes, **1-3**, at MP2/ECP1 level are in good agreement with the related experimental data. The binding energies of C_2H_2 to $MCl(PH_3)_2$ fragment, M=Rh and Ir, are computed to be ~55 kcal/mol at both MP2 and MP4 levels. The Rh-vinylidene complex, **3a** is 23.9 kcal/mol more stable than the alkyne complex, **1a** and Ir complex, **10a** is 13.7 kcal/mol more stable at MP4/ECP1 levels. In terms of thermodynamic point, the alkyne-vinylidene rearrangement with $MCl(PH_3)_2$, M=Rh and Ir, is possible through the intermediate hydrido-alkynyl complexes (**2** or **9**). The geometries and energies for Rh and Ir isomers at the various level *ab initio* calculations are compared in detail using orbital analysis.

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Analytical Characteristics and Applications of Laser Ionization Mass Spectrometry

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We have built a laser ionization mass spectrometer (LIMS) for chemical composition analysis of solid samples, which employs an Nd:YAG laser and a time-of-flight mass analyzer. In this spectrometer, the maximum mass we identified clearly is higher than 2000 amu. A mass resolution of 230 has been achieved at m/z 208 (Pb element) in the linear TOFMS and can be even improved up to 1550 by employing a reflectron. The detection limit is determined to be on the order of ppm for Fe and In. The depth resolution is found to be about 20 Å/spectrum with a laser power of 0.5 J/cm^2. We also report a preliminary application of the LIMS to identifying impurities resident in several solid samples.

Introduction

Recently, the development of chemical composition analysis technique for solid samples has rapidly grown. The techniques have adapted sputtering method to take off compositional elements or molecules from the surface of a sample. Among them, laser ionization mass spectroscopy (LIMS)[1] is one of the promising analytical techniques. In this technique, the composition of a solid sample can be identified by measuring the mass of elemental or molecular ions produced by the interaction between a focused high-power laser pulse and a target surface. This technique has

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