

- Mater.* 1996, 8, 9.
- Park, J. T.; Kim, Y.; Kim, J.; Kim, K.; Kim, Y. *Organometallics* 1992, 11, 3320.
 - Al-Wassil, A.-A. I.; Hitchcock, P. B.; Sarisaban, S.; Smith, J. D.; Wilson, C. L. *J. Chem. Soc., Dalton Trans.* 1985, 1929.
 - Gosking, K.; Smith, J. D.; Wharmby, D. H. W. *J. Chem. Soc. (A)* 1969, 1738.
 - Wakatsuki, K.; Tanaka, T. *Bull. Chem. Soc. Jpn.* 1975, 48, 1475.
 - (a) Stevens, L. G.; Park, B.; Oliver, J. P. *J. Inorg. Nucl. Chem.* 1964, 26, 97. (b) Elschenbroich, C.; Salzer, A. *Organometallics*; VCH: Weinheim, 1989; pp 86-89.
 - Kawano, Y.; Tobita, H.; Ogino, H. *Organometallics* 1992, 11, 499.
 - Altbach, M. I.; Muedas, C. A.; Korswagen, R. P.; Ziegler, M. L. *J. Organomet. Chem.* 1986, 306, 375. Cowley, A. H.; Jones, R. A.; Ekerdt, J. G. *Chem. Mater.* 1995, 7, 546. (d) Neumayer, D. A.; Ekerdt, J. G. *Chem.*

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

Sung Kwon Kang*, Jin Soo Song, Jung Hyun Moon, and Sock Sung Yun

Department of Chemistry, Chungnam National University, Taejeon 305-764, Korea

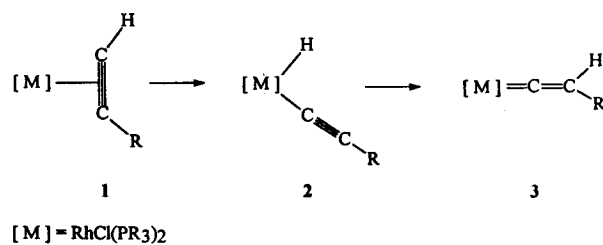
Received September 7, 1996

Ab initio and extended Hückel calculations were carried out on the isomers of *trans*-RhCl(η^2 -C₂H₂)(PH₃)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. Hoffmann³ examined the electronic and structural features of the isomerization of various metal alkynes into vinylidene complexes *via* a 1,2-hydrogen shift. For the d⁶-ML₅ 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(PR₃)₂ moiety produce *trans*-RhCl(η^2 -HCCR)(PR₃)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



Scheme 1.

reaction.

Computational Methods

Calculations were carried out at two levels. For qualitative analysis, the extended Hückel method with the modified Wolfsberg-Helmholz formula⁶ 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 programs⁸ 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 basis¹¹ was used for the alkyne ligand and STO-3G¹² for the hydrogens on the PH₃ groups. A full

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 $\text{trans-RhCl}(\eta^2\text{-C}_2\text{H}_2)(\text{PH}_3)_2$. The geometry around Rh atom in $\text{trans-RhCl}(\eta^2\text{-HCCR})(\text{PR}_3)_2$ 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 $\text{trans-RhCl}(\eta^2\text{-HCCH})(\text{PH}_3)_2$ (1).

The important valence orbitals of C_{2v} $\text{RhCl}(\text{PH}_3)_2$ 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} $\text{RhCl}(\text{PH}_3)_2$ 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 ene-

rgy 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.

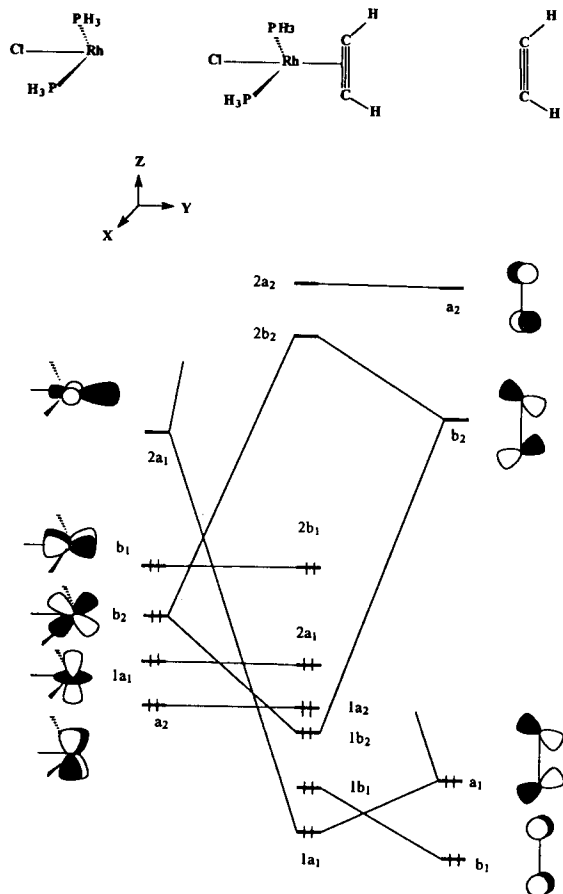
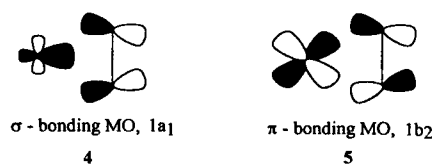


Figure 1. An orbital interaction diagram for the $\text{trans-RhCl}(\eta^2\text{-C}_2\text{H}_2)(\text{PH}_3)_2$ (1).



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 barrier¹⁴ in various olefin complexes.

The molecular orbitals for an hydrido-alkynyl complex, $\text{RhCl}(\text{H})(\text{C}_2\text{H})(\text{PH}_3)_2$ (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 ML_3 strongly interacts with the $2a'$ to form bonding MO $1a'$ (6) and antibonding LUMO $4a'$ (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.

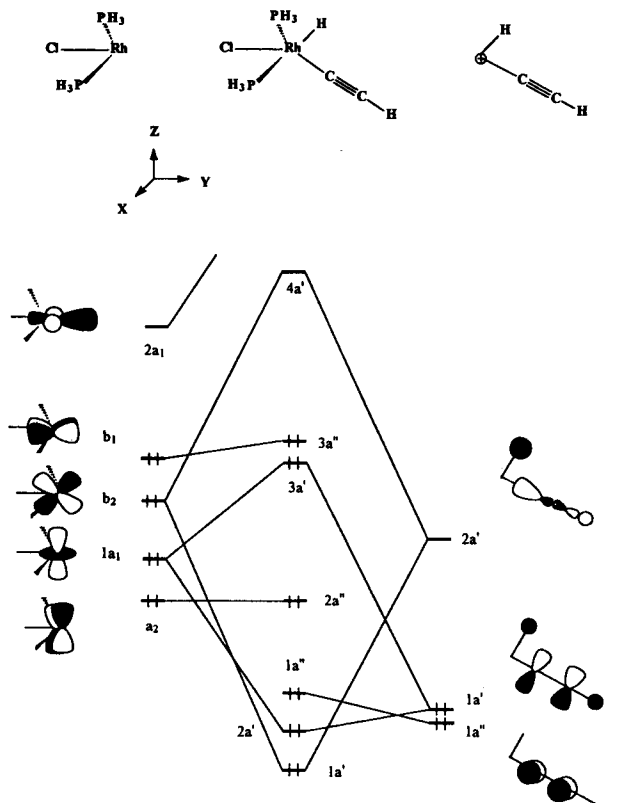


Figure 2. An orbital interaction diagram for the hydrido-alkynyl complex, $\text{RhCl}(\text{H})(\text{C}_2\text{H})(\text{PH}_3)_2$ (**2**).

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

Vinylidene ($:\text{C}=\text{CH}_2$) 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 examples¹⁶ 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 a_1 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 $2a_1$ hybridized orbital on ML_3 and form $1a_1$ σ -bonding molecular orbital (**8**). This interaction is the usual forward donation of ligand. The other important interaction is π -back bonding between b_2 symmetric orbitals. At higher energy the b_2 of vinylidene is mainly p orbital on one C atom. It interacts with an filled b_2 metal fragment orbital to form $1b_2$ and $2b_2$ MO's (**9**). The $2b_2$ is LUMO in $\text{RhCl}(\text{C}=\text{CH}_2)(\text{PH}_3)_2$ (**3**) complex.

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

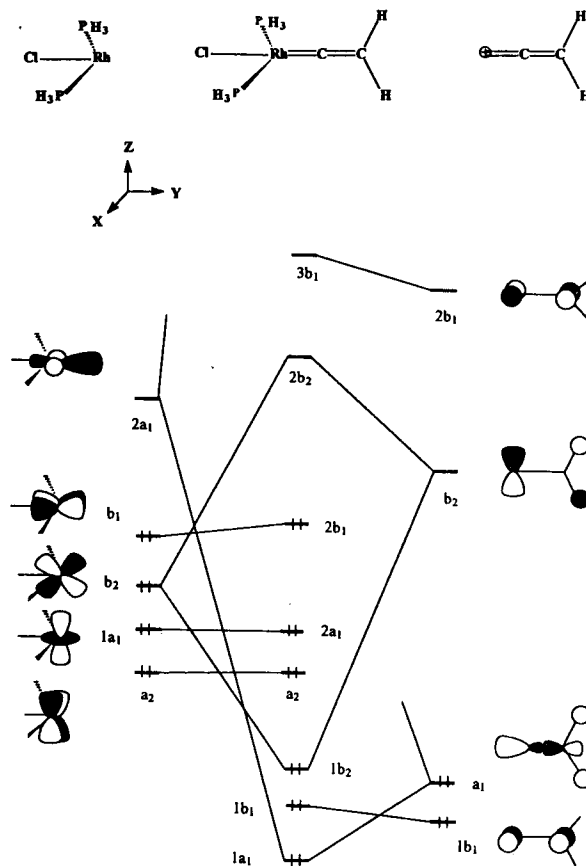
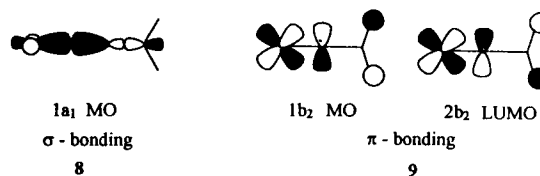


Figure 3. An orbital interaction diagram for the vinylidene complex, $\text{RhCl}(\text{C}=\text{CH}_2)(\text{PH}_3)_2$ (**3**).



back donation does not affect the C-C bond strength because of the non-bonding character in b_2 vinylidene orbital. Interestingly, the overall interaction diagram of **3** is similar with that of the η^2 -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, Vahrenkamp¹⁷ 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*- $\text{RhCl}(\eta^2\text{-HCCH})(\text{PH}_3)_2$ 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

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 η²-alkyne complex are in good agreement with the experimental results¹⁸ 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 d⁸ 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)(PPr₃)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, η²-alkyne complex is able to isomerize to vinylidene complex with d⁸-ML₃ metal fragment. The energies of hydrido-alkynyl complex, **2** are computed to be similar with those of **1a** complex.

Acknowledgment. This research was supported by the Korean Science and Engineering Foundation and by the Korea Research Foundation (BSRI 96-3410).

References

- (a) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (b) Christ, C.S. Jr.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 596. (c) Horton, A. D.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 876. (d) Forsyth, C. M.; Nolan, S. P.; Stern, C. L.; Marks, T. J.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3618. (e) Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1993**, *12*, 1623. (f) Hyla-Kryspin, I.; Niu, S.; Gleiter, R. *Organometallics* **1995**, *14*, 964. (g) Bennett, M. A.; Hockless, D. C. R.; Wenger, E.

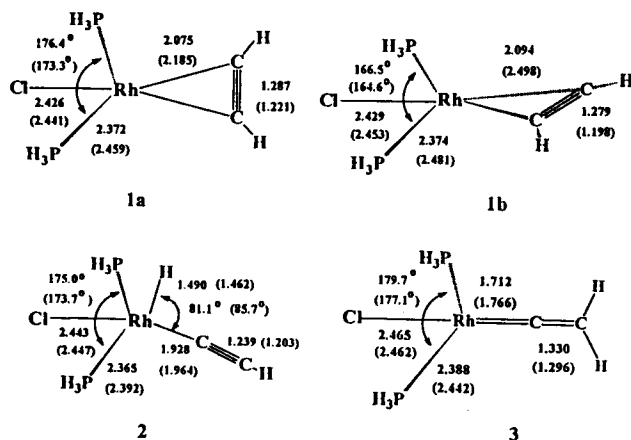


Figure 4. Optimized geometries of **1a-3** complexes calculated at the MP2 level. Geometrical parameters are given in angstroms and degrees. The values in parentheses are at the HF level.

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

Complexes	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

^aMP2 single point calculations at the HF optimized geometries. ^bMP2 optimization calculations. ^cRelative energies at extended Hückel method.

- Organometallics* **1995**, *14*, 2091. (h) Abdelrehim, I. M.; Thornburg, N. A.; Sloan, J. T.; Caldwell, T. E.; Land, D. P. *J. Am. Chem. Soc.* **1995**, *117*, 9509. (i) Hodge, A. J.; Ingham, S. L.; Kakkar, A. K.; Kan, M. S.; Lewis, J.; Long, N. J.; Parker, D. G.; Raithby, P. R. *J. Organomet. Chem.* **1995**, *448*, 205.
2. (a) Bruce, M. I.; Swingler, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077. (c) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (d) Delbecq, F. *J. Organomet. Chem.* **1991**, *406*, 171. (e) Rappert, T.; Nurnberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992**, *11*, 4156. (f) Braun, T.; Steinert, P.; Werner, H. *J. Organomet. Chem.* **1995**, *448*, 169.
3. Silverstre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.
4. (a) Werner, H.; Wolf, J.; Hohn, A. *J. Organomet. Chem.* **1985**, *287*, 395. (b) Werner, H.; Alonso, F. J. G.; Otto, H.; Wolf, J. *Z. Naturforsch. B* **1988**, *43*, 722.
5. (a) Hohn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852. (b) Chin, C. S.; Yoon, J.; Song, J. *Inorg. Chem.* **1993**, *32*, 5901. (c) Bianchini, C.; Barbaro, P.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1993**, *12*, 2505. (d) Rahim, M.; Bushweller, C. H.; Ahmed, K. J. *Organometallics* **1994**, *13*, 4952.
6. Ammeter, J. H.; Bürgi, H. B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.
7. (a) Lauher, J. W.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (b) Yun, S. S.; Kang, S. K.; Suh, I. H.; Choi, Y. D.; Chang, I. S. *Organometallics* **1991**, *10*, 2509. (c) Kang, S. K.; Ahn, B. G. *Bull. Korean Chem. Soc.* **1994**, *15*, 658.
8. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. B.; Foresman, J.; Cioslowski, B.; Stefanov, B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, W.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1995.
9. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.
10. Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.
11. Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.
12. Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.
13. (a) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952. (b) Kang, S. K.; Albright, T. A.; Silvestre, J. *Croat. Chim. Acta*, **1984**, 1355. (c) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*, Wiley; New York, 1985.
14. (a) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801. (b) Demuynck, J.; Strich, A.; Veillard, A. *Nouv. J. Chim.* **1977**, *1*, 217.
15. (a) Reisen, C.; Lussier, F. M.; Jensen, C. C.; Steinfeld, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 350. (b) Duran, R. P.; Amorebieta, V. T.; Colussi, A. *J. Am. Chem. Soc.* **1987**, *109*, 3154. (c) Stang, P. L. *Chem. Rev.* **1978**, *78*, 383; *Acc. Chem. Res.* **1982**, *15*, 348.
16. (a) Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, *13*, 1089. (b) Gamasa, M. P.; Gimeno, J.; Martin-Vaca, B. M.; Borge, J.; Garcia-Granda, S.; Perez-Carreño, E. *Organometallics* **1994**, *13*, 4045. (c) Schubert, U.; Gronen, J. *J. Chem. Ber.* **1989**, *122*, 1237. (d) Brower, D. C.; Stoll, M.; Templeton, J. L. *Organometallics* **1989**, *8*, 2786. (e) Bruce, M. I.; Humphrey, M. G.; Liddell, M. J. *J. Organomet. Chem.* **1987**, *321*, 91.
17. (a) Bernhardt, W.; Vahrenkamp, H. *Angew. Chem. Int. Ed.* **1984**, *23*, 141. (b) Roland, E.; Bernhardt, W.; Vahrenkamp, H. *Chem. Ber.* **1985**, *118*, 2858.
18. Werner, H.; Gevert, O.; Steinert, P.; Wolf, J. *Organometallics* **1995**, *14*, 1786.
19. The optimized C-C bond distance in free acetylene is 1.19 Å at 3-21G basis set.
20. Baum, M.; Mahr, N.; Werner, H. *Chem. Ber.* **1994**, *127*, 1877.
21. Alonso, F. J. G.; Höhn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 406.
22. (a) Stegmann, R.; Neuhaus, A.; Frenking, G. *J. Am. Chem. Soc.* **1993**, *115*, 11930. (b) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105.