Organometallics **1994,** *13,* 4765−4780

Ab Initio Molecular Orbital Study of Triruthenium Complexes: Geometrical and Electronic Structure of $Ru_3Cp^*_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$, $Ru_3Cp^*_3(\mu\text{-}H)_6^+$, and $Ru_3Cp^*_3(\mu\text{-}H)_3$ and Rearrangement of $Ru_3Cp^*_3(\mu\text{-}H)_3(\mu_3\text{:}\eta^2\text{-}HCCR')$

Jean-Frédéric Riehl,[†] Nobuaki Koga,[†,‡] and Keiji Morokuma*,[†,§]

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan, School of Informatics and Sciences and Graduate School of Human Informatics, Nagoya University, Nagoya 464-01, Japan, and Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received December 7, 1993[®]

A theoretical analysis is presented on the structure and bonding nature of several recently synthesized cyclopentadienyl triruthenium clusters. Using *ab initio* RHF and simulated MP2 geometry optimizations and MP2 energetics, we could calculate structures in good agreement with the experiments for different polyhydrides and alkyne clusters. Using fragment energetics, we also give estimates of the cohesion energy and Ru-H and Ru-Ru binding energies in tri-, penta-, and hexahydrides and of the interaction energy of alkynes with the trihydride $Ru_3Cp_3H_3$. In these trimetallic complexes, the Ru_3 framework is mainly stabilized by three-center two-electron Ru-H-Ru bonds. For the alkyne clusters, the perpendicular conformation has been shown to be more stable than the more common parallel one. Of the perpendicular conformations of the Cp complex, the isomer with the larger substituent "outside" the metallic triangle is more stable than the isomer with the larger substituent "inside". For the Cp* complex, however, an analysis of the steric effects using molecular mechanics shows that the steric effects reverse the trend, making the "inside" isomer more stable, in agreement with the experiment. Finally, the alkyne rearrangement on the top of the metal triangle involving the exchange of the coordinated M-M bond and/or the exchange of the substituents on alkyne has been suggested to occur by the conversion of the stable perpendicular conformation into a parallel conformation intermediate via a shift or rotation of the alkyne and subsequent reversal from the intermediate.

1. Introduction

In the late 80's, Suzuki et al. reported structural properties of various dinuclear polyhydride ruthenium complexes, built from the bimetallic tetrahydride $Ru_2Cp^*_2(\mu\text{-}H)_4$, $Cp^*{=}C_5Me_5$ (**1***; * means the complex has Cp* instead of Cp). This compound reacts with various reagents to cause CH and CP bond activation and to give varieties of bridging ligands.[1,2] More recently, they extended this chemistry to trinuclear compounds. A reaction of the "coordinatively unsaturated" dinuclear species **1*** gives the hexahydride cationic cluster complex $Ru_3Cp^*_3(\mu\text{-}H)_6^+$ (**2***), which decomposes into the neutral pentahydride species $Ru_3Cp^*_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**3***) in basic solution.[3,4] The structures of several di- and trinuclear compounds have been characterized by X-Ray diffraction and NMR experiments.[1−4] Compound **3*** has a high reactivity and reacts with various reagents such as CO, BH_4^-, $CHCl_3$, alkyne, benzene, and Cp with retention of the metallic framework.[4]

Among these reactions, the reactions of **3*** with substituted alkynes RCCR′, (R, R′)=(H, Me, Et, ᵗBu, Ph) give the products written by the general formula of $Ru_3Cp^*_3(\mu\text{-}H)_3(\mu_3\text{:}\eta^2\text{-}RCCR')$ (**4***). These complexes belong to the family of the polymetallic alkyne cluster complexes, which have been the subject of numerous experimental studies in the last decade or two.[5] Such compounds are considered to be important for a better understanding of the carbon-carbon triple bond activation and have been used as models for the chemisorption of small molecules such as ethylene and acetylene on metal surfaces.[6] The alkyne trimetallic clusters are found in two different geometries, differing by the arrangement of the triple bond relative to the metallic framework : a "perpendicular" conformation **5** in which the triple bond lies above the metal-metal bond, perpendicular to it, and a "parallel" conformation **6** in which the triple bond is above and parallel to one of the metal-metal bonds. This latter conformation is experimentally

---

[†] Institute for Molecular Science.

[‡] Nagoya University.

[§] Emory University.

[®] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

(1) (a) Suzuki, H.; Omori, H.; Moro-oka, Y. *Organometallics*, **1988**, 7, 2579. (b) Omori, H.; Suzuki, H.; Take, Y.; Moro-oka, Y. *Organometallics*, **1989**, 8, 2270 (c) Suzuki, H.; Kakigano, T.; Igarashi, M.; Tanaka, M.; Moro-oka, Y. *J. Chem.Soc., Chem.Comm.*, **1991**, 283. (d) Omori, H.; Suzuki, H.; Kakigano, T.; Moro-oka, Y. *Organometallics*, **1992**, 11, 989. (e) Suzuki, H.; Takao, T.; Tanaka, M.; Moro-oka, Y. *J. Chem.Soc., Chem.Comm.*, **1992**, 476.

(2) Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Moro-oka, Y. *Organometallics* **1988**, 7, 2243.

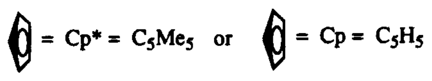
(3) (a) Suzuki, H.; Takaya, Y.; Tanaka, M.; Takemori, T. *40th Symposium of Organometallic Chemistry*, Hokkaido University, **1993**, Japan. (b) Suzuki, H.; Takaya, Y.; Tada, K.; Kakigano, T.; Igarashi, M.; Tanaka, M. *39th Symposium of Organometallic Chemistry*, Waseda University, **1992**, Japan.

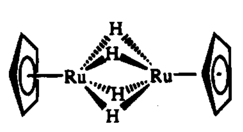
(4) Suzuki, H. *Private communications.*

(5) For a review of alkyne substitued clusters see : (a) Sappa, E.; Tirripicchio, A.; Braunstein, P. *Chem.Rev.* **1983**, 83, 203. (b) Bruce, M. I. *J. Organomet.Chem.* **1983**, 257, 417.

(6) Muetterties, E. L. *Angew. Chem., Int. Ed. Engl.* **1978**, 17, 545.

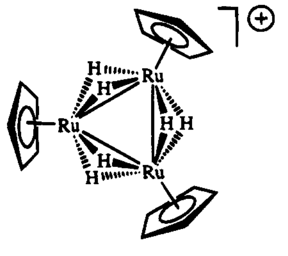
0276-7333/94/2313-4765$04.50/0





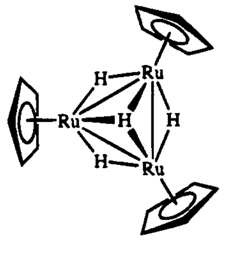
$Ru_2Cp^*_2(\mu\text{-}H)_4$ **1***

$Ru_2Cp_2(\mu\text{-}H)_4$ **1**



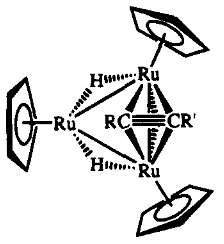
$Ru_3Cp^*_3(\mu\text{-}H)_6^+$ **2***

$Ru_3Cp_3(\mu\text{-}H)_6^+$ **2**

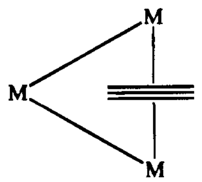


$Ru_3Cp^*_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ **3***

$Ru_3Cp_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ **3**

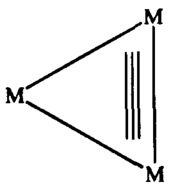


$Ru_3Cp^*_3(\mu\text{-}H)_3(\mu_3{:}\eta^2\text{-}RCCR')$, R > R'



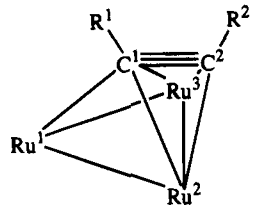
Perpendicular

5



Parallel

6



7

most commonly observed. Using the cluster terminology, **5** can be considered to be in a *closo* arrangement and **6** in a *nido* arrangement.[7] The conformational preference has been rationalized in terms of the number of skeletal electron pairs, as illustrated by Schilling and Hoffmann for $Os_3(CO)_9(C_2H_2)$[8] and Halet et al. for heterometallic M_3C_2 clusters.[9]

Suzuki's alkyne cluster complexes **4*** adopt the unusual perpendicular conformation **5**. These complexes as well as the polyhydrides **2*** and **3*** have Cp* ligands almost "within the metal plane", i.e., the centers X of the C_5 rings are nearly in the Ru_3 plane. X-Ray diffraction experiments have also revealed that in **4*** the alkyne carbon atom having the largest alkyl, or aryl, substituent is unexpectedly located above the center of the Ru_3 triangle.[4] In the following, we will adopt the notation of **7** for the perpendicular conformation **5**. C^1 will refer to the carbon atom of alkyne interacting with the three metal centers or lying above the center of the Ru_3 triangle and C^2 to the other carbon atom interacting only with Ru^2 and Ru^3 and lying outside the Ru_3 triangle. With this notation, the experimentally observed conformation corresponds to R^1 being larger than R^2; the selectivity is complete when the size difference is large, e.g., (R, R′)=(H, Ph) or (Me, Ph), but both isomers are observed in comparable ratio when smaller substituents are used, e.g., (R, R′)=(Me, Et). NMR studies have also shown that at high temperatures, the Cp* ligands become equivalent, suggesting rearrangement process of the triple bond on the top of the Ru_3 framework.[4]

From a theoretical point of view, using *ab initio* molecular orbital (MO) calculations, Koga and Morokuma have recently examined the bonding nature and the H_2 dissociation reaction of the dinuclear species $Ru_2Cp_2(\mu\text{-}H)_4$ (**1**), a model for compound **1***, and established that the four bridging hydrides are almost equivalent.[10] They have also shown that the bonding nature in **1** can be described by four hydride-bridged three-center two-electron bonds (Ru-H-Ru) and that the direct metal-metal interaction using d orbitals is absent, even though the 18-electron rule would rather suggest a metal-metal triple bond. From the study of the H_2 elimination reaction of **1**, calculated to be endothermic by 57 kcal/mol, they estimated a bond energy of 74 kcal/mol for each Ru-H-Ru three-center bond at the MP2 level of calculation; both of which should be taken as upper bounds because they did not consider the basis set superposition error (BSSE). Concerned with trimetallic cluster complexes, we would just mention that we have also recently carried out *ab initio* theoretical studies on the structure and internal rotation of $Os_3(CO)_9(C_6H_6)$[11a] and on the hydrogen exchange reaction in $M_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CH)$, M=Ru, Os.[11b]

In the present paper, we report the results of an *ab initio* MO calculations on the models $Ru_3Cp_3(\mu\text{-}H)_6^+$ (**2**) and $Ru_3Cp_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**3**) of the polyhydrides **2*** and **3***, respectively, on the fragment $Ru_3Cp_3H_3$ (**8**), and on the model alkyne cluster complex $Ru_3Cp_3(\mu\text{-}H)_3(HCCH)$ (**9**) of **4***. The *ab initio* study will be supplemented by molecular mechanics calculations (MM) in order to obtain an estimate of the steric effects, which are expected to be important in **4*** between the alkyl substituents and the Cp* ligands. Our purpose is threefold: (a) to investigate how *ab initio* calculations can reproduce the experimental structures for this kind of large and complicated compounds, (b) to estimate the

---

[7] Albright, T. A; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*, John Wiley & Sons Ed., New York, **1985**.

[8] Schilling, B. E. R.; Hoffmann, R. *J. Am.Chem.Soc.* **1979**, 101, 3456.

[9] Halet, J. F.; Saillard, J.-Y.; Lissillour, R.; McGlinchey, M. J.; Jaouen, G. *Inorg. Chem.* **1985**, 24, 218.

[10] Koga, N.; Morokuma, K. *J. Mol. Str.* **1993**, *12*, 181.

[11] (a) Riehl, J. F.; Koga, N.; Morokuma, K. *Organometallics*, **1993**, *12*, 4788. (b) Riehl, J. F.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 5414.

interaction energy of acetylene with the $Ru_3Cp_3H_3$ fragment as well as the energy difference in **4*** between the perpendicular **5** and the parallel conformation **6**, and (c) to discuss the rearrangement mechanism of the triple bond on top of the metal triangle.

2. Method of Calculations

The geometrical parameters of the metallic cluster complexes have been optimized at the restricted Hartree-Fock (RHF) level of theory with the energy gradient method using the Gaussian-90 and Gaussian-92 packages.[12] Local C_{5v} symmetry has been assumed for the Cp rings in all the calculations; all the C-C bonds, the C-H bonds, and the X-C-H angles, where X is the center of the C_5 ring, in each Cp ring, are assumed to have the same geometrical parameters. Some geometries of acetylene cluster complexes have been optimized with supplementary constraints on the $Ru_3H_3C_2$ unit, such as frozen Ru-Ru distances or frozen Ru_3H_3 unit, as will be described in the corresponding subsections. For the optimization calculations and the potential energy surface scans, the metal centers have been described by the relativistic effective core potential (RECP) of Hay and Wadt including 28 electrons in the core and associated with double-ζ quality valence basis functions.[13] The basis functions used on the spectator Cp ligand is the minimal basis functions STO-3G,[14a] and hydride and alkyne ligands have been described with the split-valence 6-31G basis functions.[14b] This whole basis set will be called BS1. The optimization of the HCCPh clusters has not been possible with BS1 for technical reasons. For this series, we therefore employed a smaller basis set BS2 consisting of the minimal basis functions STO-3G for all the C and H centers and the same basis functions as in BS1 for the metal atoms.

In order to include the correlation effects for more reliable energetics, we carried out the single point frozen core Møller-Plesset second order perturbation (MP2) calculation using BS1 for all the structures. The energies of the pentahydride $Ru_3Cp_3H_5$ (**3**), of the trihydride $Ru_3Cp_3H_3$ (**8**), and of $Ru_3Cp_3H_3(HCCH)$ (**9**) have been recalculated using a larger basis set BS3, in order to investigate the basis set effect. For the metal centers, BS3 adopts a triple-ζ d shell, adding an external d primitive (ζ=0.050) to the double-ζ basis functions above.[15] BS3 also uses the split-valence 3-21G basis set[16] for Cp ligands and the 6-31G* basis set for hydride and alkyne ligands.

For molecular mechanics calculations (MM), we used the MM2 program.[17] Since the steric effects are expected to mainly result from the interaction between the alkyl (or aryl) substituents and the Cp (or Cp*) ligands, we have treated the $Ru_3(\mu\text{-}H)_3$ unit as a set of dummy atoms. The electronic factors have been taken into account by redefining new parameters for the triple bond carbon centers, using the calculated C-R distances and C-C-R angles for R=H, Me. For the potential strengths, we used the parameters given for an sp^2 carbon, C-C-R angles being in the range 120°−135°. For Cp, Cp*, and alkyl substituents, we used the standard values for H and sp^2 and sp^3 carbon atoms. Using these definitions, we optimized only the geometrical parameters of the alkyl substituents (R, R′=H, Me, *t*-Bu, Ph) on the two carbon centers of the triple bond and the Cp or Cp* ligands were frozen in a modified geometry of the model complex $Ru_3Cp_3H_3(HCCH)$ (**9**), as precised in the corresponding section.

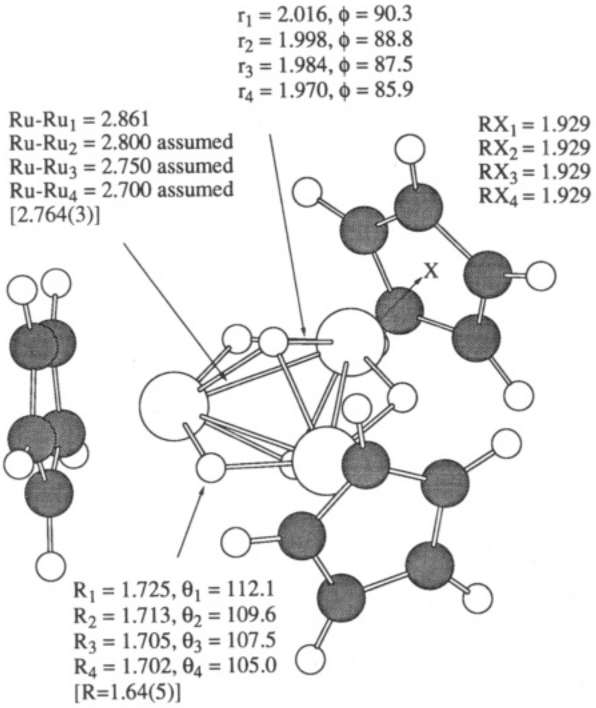


Figure 1. C_{3v}-assumed RHF/BS1 optimized geometries (in Å and deg) of $Ru_3Cp_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**3**) for different Ru-Ru distances. $Ru\text{-}Ru_1$=2.861Å is the optimized distance at the RHF level. R is the Ru-H distance, θ is the Ru-H-Ru angle, r is the Ru-H^c distance, ϕ is the Ru-H^c-Ru angle, and RX is the Ru-X distance. Experimental values for **3*** are shown in brackets. The total energies at Ru-Ru=2.861Å are −851.99872 (RHF/BS1), −853.64621 (MP2/BS1), and −857.71570 (MP2/BS3) hartree.

3. $Ru_3Cp_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$, $Ru_3Cp_3H_6^+$, and $Ru_3Cp_3H_3$ Polyhydride Complexes

A. $Ru_3Cp_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ Complex (3). The first step in our study is the geometry optimization of the pentahydride $Ru_3Cp_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**3**), a model for the experimental starting material **3***. Since the X-ray experiment has shown that the most stable structure is nearly in the C_{3v} symmetry,[4] we assumed this constraint in our calculation. The RHF/BS1 optimized structure is shown in Figure **1**. The RHF calculated Ru-Ru distance is 2.861Å, about 0.1Å longer than the experimental value of 2.764(3)Å. This calculation follows the trend previously observed for other trimetallic clusters. RHF optimizations of Os and Ru trimetallic clusters such as $Os_3(CO)_{12}$, $Os_3(CO)_{10}(\mu\text{-}H)_2$, $Os_3(CO)_9(C_6H_6)$, and $M_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CH)$ (M=Ru, Os) usually reproduced the metal-metal distances within an accuracy of 0.02Å−0.08Å.[11] Though the bonds connecting Ru atoms are represented in Figure 1 for an easier understanding of the structure, the Ru-Ru bonds are

---

[12] (a) Gaussian92, Revision A, Frish, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian, Inc.*, Pittsburgh PA, **1992**. (b) Gaussian90, Frish, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian, Inc.*, Pittsburgh PA, **1990**.

[13] Hay, P. J.; Wadt, W. R. *J. Chem.Phys.* **1985**, 82, 299.

[14] (a) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem.Phys.* **1969**, 51, 2657. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem.Phys.* **1972**, 56, 2257.

[15] This value represents the most external exponent of the original d shell given by Hay and Wadt, divided by 3. Since primitives are usually a geometric progression with a ratio close to 3, this is expected to give a well balance triple-ζ d shell.

[16] Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am.Chem.Soc.* **1980**, 102, 939.

[17] (a) Allinger, N. L.; Yuh, Y. *Quantum Chemistry Program Exchange,* Indiana University, Bloomington, IN, **1980**, 12, 395. (b) Burket, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washigton, DC, **1982**.

however formally broken. As has been discussed in detail by Koga and Morokuma for the dinuclear species **1**,[10] the metal cluster is held together by the three-center two-electron Ru-H-Ru bonds and the four-center Ru-H^c bonds, where H^c are the capping μ_3-H centers.

In agreement with the experimental results, the Cp ligands are nearly planar and almost "within the metal plane"; the Cp centers, Xs, lie only 0.015Å away from the metal plane, leading to an X-Ru-M angle of 179.5°, where M is the center of the Ru_3 triangle. The $Ru_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2X_3$ framework is thus nearly of the D_{3h} symmetry. The μ-H atoms are almost in the metal plane, with an out-of-plane deviation of 0.031Å. These H atoms are slightly in one side of the metal plane, the side not containing the Cp centers Xs. The Ru-H distance and the Ru-H-Ru angle are 1.725Å and 112.1°, respectively. This Ru-H distance is longer than the experimentally proposed average one, 1.64(5)Å. This experimental number may however not be reliable; the location of H atoms by X-Ray diffraction is of poor accuracy, even at low temperature, and often gives too short distances. The calculated value is very close to 1.728Å, given as an average of 22 observations of Ru-(μ-H) distance in cluster complexes by Orpen et al.[18] The capping H^c are located on average 1.157Å above and below the Ru_3 plane, which represents a Ru-H^c distance of 2.016Å and a Ru-H-Ru angle of 90.3°, as shown in Figure **1**.

Because of the substantial error on the Ru-Ru distance at the RHF level, it is essential to estimate the effect of the electron correlation on the geometry. Due to the size of the system, we could not carry out a full optimization with electron correlation taken into account and had to find a more practical way to reduce the error. Assuming that the poor description of the Ru-Ru bond in the RHF calculation is the main cause of the error, we simulated an MP2 geometry optimization by fixing the Ru-Ru distance at different values, optimizing all the other geometrical parameters at the RHF/BS1 level, and recomputing the MP2/BS1 energy at each optimized geometry. We applied this "poor man's optimization" to three Ru-Ru frozen distances, namely 2.800Å, 2.750Å, and 2.700Å. Selected optimized geometrical parameters for these different Ru-Ru distances are shown in Figure **1** and energies in Figure **2**. A third order polynomial fit led to an MP2 estimated distance of 2.748Å, which is in good agreement with the experimental distance of 2.764Å. This shortening increases the MP2 stabilization energy by 4.8 kcal/mol, a very small value considering the number of electrons involved. As shown in Figure **1**, the other parameters are not substantially changed. The $Ru_3H_5X_3$ framework is still roughly in a pseudo-D_{3h} symmetry with the Xs almost in the metal plane. The Ru-Cp distance, shown as RX_i in Figure **1**, is unchanged, but the Ru-H distances are shortened by 0.020Å for Ru-(μ-H) and 0.032Å for Ru-H^c. One should also notice that the distortion of the Ru_3H_5 framework from D_{3h} is enhanced by this shortening of the Ru-Ru distance. For Ru-Ru=2.750Å, the μ-H centers lies around 0.1Å from the metal plane. The Ru-H^c distance is longer for the H^c center lying on the same side of the Ru_3 plane as the Cp ligands than that on the other side, i.e., 1.989Å vs. 1.979Å.

Now we would like to examine the effect of basis sets on the geometry. To clarify this specific point, we recomputed the energies of the four structures discussed above with the larger basis set BS3. A good agreement of the RHF/BS1 geometrical parameters with experiments just discussed above justifies this approximation. The results also shown in Figure **2** shorten the Ru-Ru distance by 0.025Å to 2.723Å. One should notice that the energy stabilization at the MP2 level is slightly larger with BS3 than with BS1, i.e., 8.5kcal/mol vs. 4.8kcal/mol.

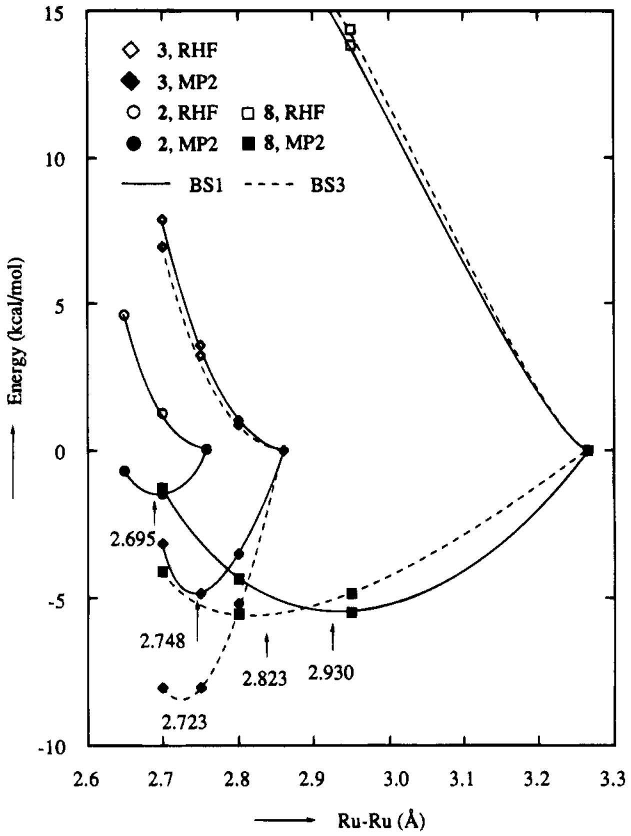


Figure 2. RHF and MP2 energies as functions of Ru-Ru distances for RHF optimized geometries at fixed values of Ru-Ru for $Ru_3Cp_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**3**), $Ru_3Cp_3H_6^+$ (**2**), and $Ru_3Cp_3H_3$ (**8**). Energies are in kcal/mol, relative to the energy of the structure with the Ru-Ru distance obtained by full RHF optimization, 2.861Å for **3**, 2.758Å for **2**, and 3.267Å for **8**.

It is well known that the calculation of the absolute value of a binding energy is not an easy task, requiring a large basis set with higher polarization functions and the consideration of BSSE. Here at the present relatively low level of calculation, we would like to make a qualitative estimate of the total cohesion energy of this complex. The total cohesion energy ΔE of the cluster complex can be defined, using the energies of the complex and the fragments, as

$$\begin{aligned}-\Delta E(\mathbf{3}) &= E(\mathbf{3}) - 5\,E(H) - 3\,E(RuCp)\\ &= 6\,D(Ru\text{-}H, \mathbf{3}) + 6\,D(Ru\text{-}H^c, \mathbf{3}) + \\ &\qquad 3\,D(Ru\text{-}Ru, \mathbf{3}) \quad (1)\end{aligned}$$

The second equal sign, which will be discussed in a succeeding subsection, represents the total cohesion energy in terms of Ru-H, Ru-H^c, and Ru-Ru bond energies. Using the appropriate UHF or UMP2 energies of RuCp calculated at the RHF optimized geometry of the closed-shell $RuCp^+$ fragment, we obtained the

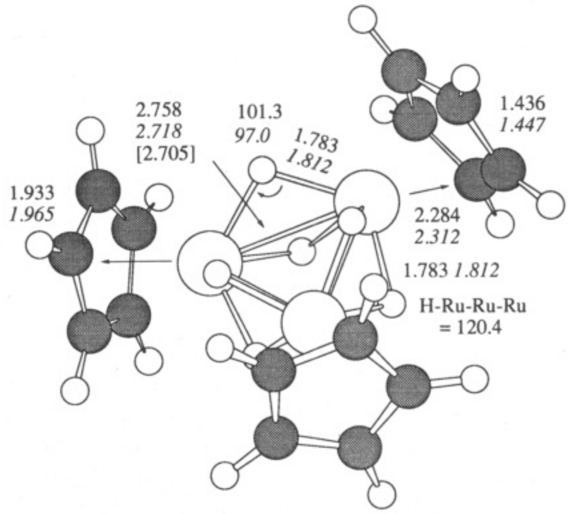


Figure 3. C_{3v}-assumed RHF/BS1 optimized geometries (in Å and deg) of $RuCp_3(\mu\text{-}H)_6^+$ (**2**) and $Ru_3Cp_3(\mu\text{-}H)_6^{3+}$ (**2′**). Values for **2′** are in *italic*. Experimental values for **2*** are given in brackets. The total energies for **2** are −852.40325 (RHF/BS1) and −854.144374 (MP2/BS1) hartree.

following values for ΔE(**3**) : 366.4kcal/mol at RHF/BS1 level, 365.9kcal/mol at RHF/BS3 level, 548.6kcal/mol at MP2/BS1 level, and 588.4kcal/mol at MP2/BS3 level. These results show that the correlation energy is essential for any qualitative estimation of this energy. Though these values are useful in comparing bond strengths among different systems, as we warned at the beginning of the paragraph, the absolute numbers of these cohesion energies should not be taken too seriously. First reason is that we have used the RHF geometry of the assumed fragment, which may have little relationship with the "experimental" fragments for which binding energies could be measured. Secondly, the BSSE could be substantial. A conventional method of the counterpoise correction (CPC) using the ghost orbitals can reduce these values as much as a factor of two,[11] but the CPC itself is considered to be a vast overestimation of the true BSSE.

B. $Ru_3Cp_3(\mu\text{-}H)_6^+$ Complex (2). Figure **3** shows the RHF/BS1 optimized structure of $Ru_3Cp_3(\mu\text{-}H)_6^+$ (**2**), a model of the experimental hexahydride cationic complex **2***. Since the experimental structure of **2*** is nearly in the C_{3v} symmetry, we assumed this constraint in our calculation. Geometry optimization brought the center X of the Cp ligand within 1° of the Ru_3 plane, the six bridging H's being nearly equivalent. The calculated Ru-Ru distance is 2.758Å, in good agreement with the experimental value of 2.705(1)Å. Thus, the desirable trend observed in most of our previous optimizations of cluster complexes is followed also for this complex; tFigure **1** and Figure **2** here is an error of only 0.05Å in the Ru-Ru distance. The bridging H is at the distance of 0.973Å from the metallic plane, giving the distance of 1.986Å between the H atoms bridging the same Ru-Ru bond. This large distance, which is consistent with the expected hydridic character of the hydrogen atoms, implies that the geometry of Ru_2H_2 group is subject to a cyclic constraint; short Ru-H distances with a large H---H separation requires a short Ru-Ru distance. This is consistent with the shortening of the Ru-Ru bonds when going from **3** to **2** (or experimentally from **3*** to **2***), despite the expectation that the direct metal-metal interaction should be weaker for a doubly-bridged bond than for a singly-bridged bond with capping ligands. The even shorter Ru-Ru distance of 2.47Å has been observed in the dinuclear species **1***. In **1** Koga and Morokuma have shown that no direct interaction exists between the two metal atoms; the three-center two-electron Ru-H-Ru bonds cause this shortening.[10]

In order to illustrate the correlation effect on the metal-metal bond distances, as we did for **3**, we carried out the "poor man's optimization" for this compound. We reoptimized the structure of this complex for two supplementary fixed Ru-Ru distances (2.70Å and 2.65Å) at the RHF/BS1 level, recomputing the energy at the MP2/BS1 level. Energies are shown in Figure **2**. Such a simulated optimization leads to an MP2 estimated Ru-Ru bond distance of 2.695Å, quite close to the experimental value of 2.705Å. The other parameters remain to be very similar to the previous ones. The extra stabilization due to this small reoptimization is only 1.5kcal/mol. For this compound, we did not perform the calculation with BS3, but results for **3** will suggest a further shortening of the Ru-Ru bond if BS3 were employed.

In this paragraph, we make a brief detour to the tricationic complex $Ru_3Cp^*_3(\mu\text{-}H)_6^{3+}$, **2*′**. When **2*** was synthesized, its charge could not be readily assigned, and it was first written as $Ru_3Cp^*_3(\mu\text{-}H)_6^{3+}$.[4] Even though the problem is now solved, it is interesting to see how theoretical calculations could answer the question and what kind of geometrical changes are expected when two electrons are removed. In the *ab initio* calculation of model complex **2**, the highest occupied orbitals are $(e)^4(a_2)^2$. This suggests two possible states for the $Ru_3Cp_3(\mu\text{-}H)_6^{3+}$ (**2′**) ground state: a singlet state consisting mainly of the $(e)^4$ configuration or a triplet state with the configuration $(e)^2(a_2)^2$. Since the HF calculation using the geometry of **2** showed that the UHF triplet state is less stable by 52.8 kcal/mol than the closed-shell RHF singlet state, we optimized the geometry of the singlet, shown also in Figure **3**. Compared to **2**, Ru-Ru bonds are 0.04Å shorter and Ru-H bonds are 0.03Å longer, as are the Ru-Cp distances (+0.03Å). These small changes are consistent with the mainly lone pair nature we expect for the highest occupied d orbitals on the metals. If we assume that for this kind of complex RHF optimization overestimates the M-M bond distances by at least 0.03Å−0.05Å as seen for **2** above, the calculated Ru-Ru distance in **2′** is less compatible, i.e. too short, with the experimental data than the value calculated for **2**. Finally, **2′** presents a small HOMO-LUMO gap, not consistent with the observed good stability of **2***. Based on these two points, we could say that **2*** is preferred to **2*′**, as representing the electronic structure of the compound.

This geometrical argument is supported by an analysis of the energetics. As in **3**, we have estimated the total cohesion energy ΔE for **2** and **2′**, using the energies of RuCp and $RuCp^+$ at the geometry of $RuCp^+$.

$$
\begin{aligned}
-\Delta E(\mathbf{2}) &= E(\mathbf{2}) - 6\,E(H) - E(RuCp^+) - 2\,E(RuCp) \\
&= 12\,D(\text{Ru-H}, \mathbf{2}) + 3\,D(\text{Ru-Ru}, \mathbf{2}) \qquad (2)
\end{aligned}
$$

For **2**, we obtain an energy of 397.9 kcal/mol and 632.4 kcal/mol at the RHF/BS1 and MP2/BS1 level, respectively, without compensating the BSSE. Discarding the RHF values and dividing MP2 values by 3, this cor-

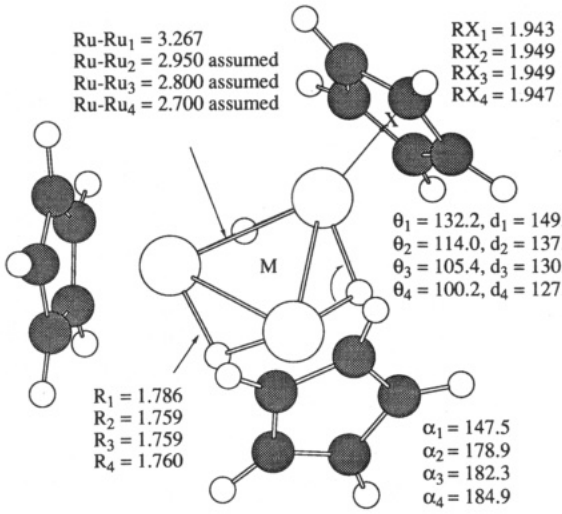


Figure 4. C_{3v}-assumed RHF/BS1 optimized geometries (in Å and deg) of $Ru_3Cp_3(\mu\text{-}H)_3$ (**8**) for different Ru-Ru distances. $Ru\text{-}Ru_1$=3.267Å is the optimized distance at the RHF level. R is the Ru-H distance, θ is the Ru-H-Ru angle, d is the angle between the RuHRu and the Ru_3 planes, RX is the Ru-X distance and α is the angle M-Ru-X, the angle of Cp center X with respect to the metal plane. The total energies at Ru-Ru=3.267Å are −850.87503 (RHF/BS1), −852.33986 (MP2/BS1), and −856.39820 (MP2/BS3) hartree.

responds to an energy of 210.8 kcal/mol per RuH_2Ru subunit at the MP2/BS1 level. In **2′**, using the equation $-\Delta E(\mathbf{2'}) = E(\mathbf{2'}) - 6\ E(H) - 3\ E(RuCp^+)$, we obtain a cohesion energy of 39.6 kcal/mol at the RHF/BS1 level and 9.4kcal/mol at the MP2/BS1 level, suggesting a poor intrinsic stability of **2′**, compared to **2**. This instability of **2′** can be explained by the large ionization potential, 7.4 eV or 172 kcal/mol with the Koopmans approximation, of **2** (or **2***), compared to the ionization potential of RuCp, 4.5eV or 103 kcal/mol, which has an electron in a d orbital high in energy. From an energetic point of view, **2*** must therefore also be preferred to **2*′**.

C. $Ru_3Cp_3(\mu\text{-}H)_3$ Complex (8). In the early stage of experimental analysis, the product of decomposition of the hexahydride cationic cluster complex **2*** was considered to be the $Ru_3Cp^*{}_3(\mu\text{-}H)_3$ complex. We would like to compare the skeletal geometrical parameters, in particular, the Ru-Ru distance, between the experiment for the product and the calculated for $Ru_3Cp_3(\mu\text{-}H)_3$ (**8**). The optimized structure of **8** is also needed to calculate its interaction energy with acetylene in the $Ru_3Cp_3(\mu\text{-}H)_3(HCCH)$ complex (**9**), a model for **4***. The RHF/BS1 optimization led to a structure shown in Figure **4**, with a long Ru-Ru distance of 3.267Å and with the centers X of the Cp rings lying 1.043Å out of the Ru_3 plane (above the Ru_3 plane if the H's are under it). This represents an X-Ru-M angle of 147.5°, where M is the center of the Ru_3 plane. Ru-H distances and Ru-H-Ru angle are 1.786Å and 132.2°, respectively.

Though one cannot compare directly our calculated structure of the Cp complex with the experiment for a Cp* complex, it is obvious that the calculated Ru-Ru is too long. Single bridge bonds are usually intrinsically longer than non-bridged or doubly-bridged,[18] but 3.25Å seems to be a large overestimate, suggesting a failure of the RHF level calculation for this compound. Compared with the two previous cases, **8** presents two dissadvantages: no strong direct interaction to maintain a short Ru-Ru bond and no constraint requiring a cyclic structure as in systems having doubly-bridged metal-metal bonds. As was done for **3** and **2**, we thus also performed the "poor man's optimization" at the MP2 level, as shown in Figure **4** and energies in Figure **2**.

As shown in Figure **2**, the MP2/BS1 estimate of the Ru-Ru distance is around 2.930Å, which represents a substantial shortening by 0.34Å. One should notice that the Ru-H distance is not very sensitive to the metal-metal separation; in particular for Ru-Ru distance shorter than 3.0Å, the Ru-H distance stays unchanged at 1.76Å, close to the 1.782Å average value given by Orpen et al.[19] As the Ru-Ru distance is changed, the complex rather adjusts its geometry through the Ru-H-Ru angle and H-Ru-Ru-Ru dihedral angle; H is out of the Ru_3 plane by 0.650Å and 0.890Å for Ru-Ru=2.95Å and 2.70Å, respectively. The centers of the Cp ligands are located nearly in the metallic plane when the Ru-Ru distance is shortened; when Ru-Ru is shorter than 3.0Å, the deviation never exceeds 2°.

The basis set effect was also examined by MP2/BS3 calculations at four RHF/BS1 geometries. As shown in Figure **2**, the Ru-Ru distance is now estimated to be 2.823Å. Compared with the experimental Ru-Ru distance of 2.764Å of the product of the decomposition of the hexahydride complex **2***, this is still very long. Thus, during the course of our study, we have not endorsed an early proposed assignment of the product to the trihydride $Ru_3Cp^*{}_3(\mu\text{-}H)_3$ complex. As discussed in a preceding subsection, it is now reassigned to **3***, and our calculation supports this assignment. The change in stabilization energy upon the shortening of the Ru-Ru distance is small, indicating that the potential energy curve with respect to the Ru-Ru distance variation is relatively flat, as is clearly seen in Figure **2**, and that the $Ru_3Cp^*{}_3(\mu\text{-}H)_3$ fragment has a good flexibility to adapt to geometry changes when it interacts with other ligands.

As in **3** and **2**, one can also give an estimate for the cohesion energy using the formula

$$\begin{aligned}-\Delta E(\mathbf{8}) &= E(\mathbf{8}) - 3\ E(H) - 3\ E(RuCp)\\ &= 6\ D(Ru\text{-}H, \mathbf{8}) + 3\ D(Ru\text{-}Ru, \mathbf{8}) \quad (3)\end{aligned}$$

Using the appropriate UHF or UMP2 energies of RuCp, we obtained the following values for $\Delta E(\mathbf{8})$: 288.9kcal/mol at RHF/BS1 level, 285.1kcal/mol at RHF/BS3 level, 357.3kcal/mol at MP2/BS1 level, and 383.2kcal/mol at MP2/BS3 level. Discarding the RHF values and dividing by three, one obtains 119.1kcal/mol at MP2/BS1 level and 127.7 kcal/mol at MP2/BS3 level as an estimate of the cohesive energy per RuHRu unit.

D. Ru−H and Ru−Ru Bond Energies. Having calculated energetic parameters for compounds **3**, **2**, and **8**, we can try to analyze them further. The correlation energy is obviously essential for any qualitative estimation of this energy. We do not have the MP2/BS3 energies for **2** and therefore will use the MP2/BS1 ones.

We first focus **2** and **8**, both containing only μ-H type H centers. First (assumption 1), we assume that the

---

[18] (a) Schultz, A. J.; Williams, J. M.; Calvert, R. B.; Shapley, J. R.; Stucky, G. D. *Inorg.Chem.* **1979**, 18, 319. (b) Broach, R. W.; Williams, J. M. *Inorg.Chem.* **1979**, 18, 314. (c) Churchill, M. R.; DeBoer, B. G. *Inorg.Chem.* **1977**, 16, 878.

[19] Orpen, A. G.; Brummer, L.; Allen, F. A.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem.Soc., Dalton Trans.* **1989**, Supplement, S1.

Ru-H bond energies D(Ru-H) are the same in both compounds and so are the Ru-Ru bond energies D(Ru-Ru). Then, from eqs(2) and (3) one can obtain D(Ru-H) = 45.8 kcal/mol and D(Ru-Ru) = 27.4 kcal/mol. Alternatively (assumption 2), we also can make the hypothesis that the Ru-Ru bond in **8** is stronger than in **2** because of the presence of only one bridging H, and assume that it is, say, twice as strong. This leads to: D(Ru-H) = 50.4 kcal/mol, D(Ru-Ru, **8**) = 18.3 kcal/mol and D(Ru-Ru, **2**) = 9.2 kcal/mol. Though the metal-metal bond is formally broken,[10] both estimations suggest that the metal-metal interaction is attractive, with a non-negligible bond energy of 10−20 kcal/mol and that the Ru-H bond energy is around 50 kcal/mol. On the other hand, since the metal-metal bonds are formally broken, one may also assume (assumption 3) that there is no direct Ru-Ru bond, i.e., D(Ru-Ru) = 0. In this case one is led to D(Ru-H, **8**) = 59.6 kcal/mol and D(Ru-H,**2**) = 52.7 kcal/mol, suggesting that the Ru-H bonds are stronger in the trihydride than in the hexahydride. For the evaluation of the absolute values of the bond energies, of course one has to take the correction for the BSSE into account.[11]

One can compare these results with the corresponding dinuclear complex $Ru_2Cp_2H_4$, **1**, a model for **1***, studied by Koga and Morokuma.[10] Based on the H_2 elimination reaction, they estimated a bonding energy of 74 kcal/mol for each Ru-H-Ru subunit, H being a leaving hydrogen. This energy cannot be directly compared to our estimates, since Koga and Morokuma calculation takes into account the relaxation energy of the $Ru_2Cp_2H_2$ remaining fragment. The data reported by these authors being not sufficient to estimate the cohesion energy ΔE(**1**) defined, as for the previous compounds, by

$$\begin{aligned} -\Delta E(\mathbf{1}) &= E(\mathbf{1}) - 4\,E(H) - 2\,E(RuCp) \\ &= 8\,D(Ru\text{-}H, \mathbf{1}) + D(Ru\text{-}Ru, \mathbf{1}) \qquad (4) \end{aligned}$$

we reoptimized **1** with the basis set BS1. Using the energies of RuCp at the geometry of $RuCp^+$, the MP2/BS1 cohesion energy ΔE(**1**) is 374.4 kcal/mol. If we assume D(Ru-Ru,**1**)=0 for this Ru-Ru bond bridged by four hydrogen atoms, one obtains D(Ru-H,**1**)=46.8 kcal/mol. This binding energy is 6 kcal/mol weaker than that calculated above for the trinuclear species **2** under the assumption D(Ru-Ru, **2**)=0. This trend can not be explained by considering just the ratios of the number of hydrides to the number of metal centers; they are equal in **1** (4 H / 2 Ru = 2) and in **2** (6 H / 3 Ru = 2). However, structure **2** is less compact than the dinuclear species **1**. In our optimized structures, the H-Ru-H angle is around 60° in **1** and 85° in **2**, suggesting that the arrangement in **2** is more suitable for a better use of the metal orbitals.

Having an estimate of the Ru-H bond strength in **8**, one can now give an estimate of the Ru-H^c bond strength in **3**. Assuming that D(Ru-H,**8**)=D(Ru-H,**3**) and D(Ru-Ru,**3**)=0, one obtains an energy of 191.0kcal/mol for the six Ru-H^c bonds, i.e., 31.8kcal/mol per Ru-H^c bond. This shows that the Ru-H^c bonds are much weaker than the Ru-H bonds, which is consistent with the four-center two-electron bond nature of the Ru-H^c bonds. From the fragment energies, one can also estimate the reaction energy of the decomposition reaction

$$Ru_3Cp_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2\ (\mathbf{3}) \rightarrow Ru_3Cp_3(\mu\text{-}H)_3\ (\mathbf{8}) + H_2$$

Using the MP2 energy of H_2 calculated with the RHF geometry, one obtains that this decomposition reaction is endothermic by 96.1kcal/mol. Again for a more accurate absolute value, one has to take the BSSE into account.

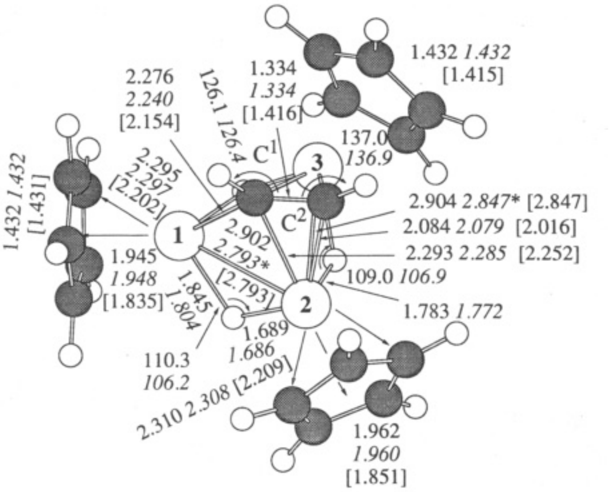


Figure 5. C_s-assumed RHF/BS1 optimized geometries (in Å and deg) of the structures **9**⊥ and **9**⊥′ of $Ru_3Cp_3(\mu\text{-}H)_3$-(HCCH) in the experimentally observed perpendicular conformation **5**. Values for **9**⊥′ are in *italic*, where assumed values are followed by *, and average experimental values for $Ru_3Cp^*_3(\mu\text{-}H)_3$(MeCCPh) are in brackets. H-Ru^1-Ru^2-Ru^3 and H-Ru^2-Ru^3-Ru^1 dihedral angles are 130.7° and 105.9° in **9**⊥, and 129.0° and 108.6° in **9**⊥′. The total energies for **9**⊥ are −927.71337 (RHF/BS1), 929.54841 (MP2/BS1) hartree.

4. $Ru_3Cp_3(\mu\text{-}H)_3$(alkyne) Clusters

A. $Ru_3Cp_3(\mu\text{-}H)_3$(HCCH) complex (9). As mentioned in the Introduction, alkyne trimetallic clusters can exist in two conformations **5** and **6**, differing in the orientation of the triple bond relative to the metal triangle. Suzuki's complexes adopt the perpendicular or *closo* conformation **5**. We have optimized at the RHF/BS1 level the two conformations of $Ru_3Cp_3(\mu\text{-}H)_3$-(HCCH) (**9**), a model for the experimental complexes **4***. Labels **9**⊥ and **9**// will respectively refer to the perpendicular and parallel conformations of this model compound. Structures, optimized under C_s constraint, are shown in Figures **5** and **6**, respectively. For these complexes, we adopted the Cp orientation proposed for the Cp* ligands in the experimental complexes and shown in **4***.

We focus our attention first on the perpendicular conformation **9**⊥ in Figure **5**. Though we do not find a large discrepancy from the experiment, the metal-metal distances are too long by 0.109Å for Ru^1-Ru^2=Ru^1-Ru^3 and by 0.057Å for Ru^2-Ru^3. The average values of the metal-Cp distances are also too long by 0.10Å, compared to the experiment for $Ru_3Cp^*_3H_3$(PhCCMe). The center X^1 of the Cp connected to Ru^1 (Cp^1) is nearly within the metal plane, the X^1-Ru^1 axis deviating only by 1° from the metallic plane. For Cp^2 and Cp^3, respectively attached to Ru^2 and Ru^3, this deviation is 7°. From here, a positive value will represent a Cp motion to the side of the Ru_3 plane not containing the alkyne ligand. These deviations are smaller than in the experimental

Table 1. RHF/BS1 Selected Optimized Geometrical Parameters for Structures 9⊥, 10⊥, 11⊥, and 12⊥ and Relative Energies for Each Series of Compounds[a]

	calculated structures													
	H, H		Me, H		H, Me		^{t}Bu, H		H, ^{t}Bu		Ph, H		H, Ph	exptl
R^1, R^2 Label	**9⊥**	**9⊥′**	**10⊥i**	**10⊥i′**	**10⊥o**	**10⊥o′**	**11⊥iA**	**11⊥iA′**	**11⊥oB**	**11⊥oB′**	**12⊥ih**	**12⊥iv**	**12⊥ov**	Ph, Me
Ru^1-Ru^2=Ru^1-Ru^3	2.902	*2.793*	2.886	*2.793*	2.898	*2.793*	*2.793*	*2.793*	*2.793*	*2.793*	*2.793*	*2.793*	*2.793*	2.7932(8)
Ru^2-Ru^3	2.904	*2.846*	2.909	*2.846*	2.899	*2.846*	*2.846*	*2.846*	*2.846*	*2.846*	*2.846*	*2.846*	*2.846*	2.8467(8)
Ru^1-C^1	2.276	2.240	2.302	2.266	2.278	2.242	2.350	*2.240*	2.215	*2.240*	*2.240*	*2.240*	*2.240*	2.132(5)
Ru^2-C^1=Ru^3-C^1	2.293	2.285	2.332	2.318	2.279	2.271	2.344	*2.285*	2.281	*2.285*	*2.285*	*2.285*	*2.285*	2.254(5)
Ru^2-C^2=Ru^3-C^2	2.084	2.079	2.074	2.066	2.100	2.089	2.053	*2.079*	2.134	*2.079*	*2.079*	*2.079*	*2.079*	2.034(5)
C^1-C^2	1.334	1.334	1.337	1.338	1.333	1.336	1.343	*1.334*	1.341	*1.334*	*1.334*	*1.334*	*1.334*	1.418(8)
C^1-R^1	1.073	1.072	1.515	1.514	1.074	1.074	1.549	1.573	1.075	1.073	1.510	1.549	1.085	1.497
C^2-R^2	1.066	1.066	1.068	1.068	1.492	1.491	1.065	1.062	1.529	1.538	1.082	1.075	1.498	1.493
C^1-C^2-R^2	137.0	136.1	134.5	134.5	136.7	136.1	134.9	137.7	130.1	125.4	135.1	137.6	134.9	116.2
C^2-C^1-R^1	126.1	126.4	124.6	124.8	125.8	125.9	121.5	116.4	124.4	127.4	125.2	114.8	124.9	126.6
Ru^1-Cp	1.945	1.948	1.951	1.953	1.946	1.948	1.974	*1.948*	1.949	*1.948*	*1.948*	*1.948*	*1.948*	1.835
Ru^2-Cp=Ru^2-Cp	1.962	1.960	1.962	1.961	1.965	1.963	1.962	*1.960*	1.979	*1.960*	*1.960*	*1.960*	*1.960*	1.851
X^1-Ru_3[b]	−1.2	−1.3	0.7	0.7	−1.4	−1.4	7.9	9.6	0.8	−0.5	1.3	9.2	−1.9	7.1
X^2-Ru_3=X^3-Ru_3[b]	6.2	6.8	7.2	7.4	6.7	7.3	8.3	7.6	13.4	14.0	6.5	6.8	7.1	13.3
RHF/BS1 Energy[c]	0.0	2.1	0.0	1.8	−3.8	−1.7	0.0	3.6	0.3	1.9	0.0	12.9	−1.7	–
MP2/BS1 Energy[c]	0.0	−7.3	0.0	−4.6	−1.7	−6.9	0.0	−1.8	−6.5	−6.3	0.0	11.5	1.0	–

[a] Frozen parameters are given in italics. Distances are given in Å, angles in degrees and energies in kcal/mol. [b] X^i-Ru_3 is the angle of deviation of the X^i-Ru^i axis from the plane of Ru_3, where X^i is the center of the Cp ring attached to Ru^i. [c] Energies in kcal/mol relative to the left most isomer of each complex.

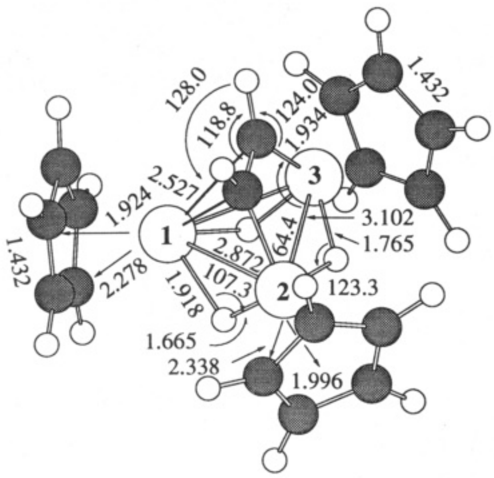


Figure 6. C_s-assumed RHF/BS1 optimized geometry (in Å and deg) of the parallel conformation **9//** of $Ru_3Cp_3(\mu$-$H)_3(HCCH)$. The acetylene C-C distance is 1.435Å and the H-$Ru^1Ru^2Ru^3$ and H-$Ru^2Ru^3Ru^1$ dihedral angles of 114.7° and 123.3°, respectively.

complexes, probably because of the absence of the steric effects due to Cp*. In $Ru_3Cp^*{}_3H_3(PhCCMe)$, the X^1-Ru^1 and X^2-Ru^2=X^3-Ru^3 deviations are of 7.1° and 13.3°, respectively, as given as the X^1-Ru_3 and X^2-Ru_3 entries in Table 1. The C^1-C^2 bond is not parallel to the Ru_3 plane, C^1 lying 0.138Å higher than C^2. The C^1-C^2 bond distance of 1.334Å is shorter than the experimental 1.416Å in $Ru_3Cp^*{}_3H_3(PhCCH)$ and 1.418Å in $Ru_3Cp^*{}_3H_3(PhCCMe)$, but is much longer than the C-C distance 1.194Å in acetylene and even longer than 1.315Å in ethylene calculated with the same basis set. The C-C-H angles are larger than the C-C-C angles in the experimental complexes; in **9⊥**, C^1-C^2-H and C^2-C^1-H are respectively 137.0° and 126.1° to be compared with the C^1-C^2-C and C^2-C^1-C angles of 126.6° and 116.2° in $Ru_3Cp^*{}_3H_3(PhCCMe)$ and $Ru_3Cp^*{}_3H_3(PhCCH)$, respectively and with the C^2-C^1-C angle of 118.2° in $Ru_3Cp^*{}_3H_3(PhCCH)$. These trends suggest the existence of substantial steric repulsion between the Cp* ligands and alkyl (or aryl) substituents, which we are unable to reproduce with this Cp model. Calculations on other model complexes, to be described in the following subsections, will show that this discrepancy between calculated and experimental values is not caused by the failure of the RHF method. The bridging H atoms are under the metallic plane. The effect of the C atoms bridging a Ru-Ru bond is to narrow the dihedral H-Ru-Ru-Ru angle associated with this bond, confirming the trend found by X-Ray experiments for **4***;[4] the H atom bridging Ru^2-Ru^3 lies almost under the metal-metal bond, the dihedral angle H-Ru^2-Ru^3-Ru^1 being 105.9° vs. 130.7° for the dihedral angle H-Ru^1-Ru^2-Ru^3.

In order to assess the electron correlation effects on the geometry, we carried out two constrained optimizations. In the first calculation, we froze the Ru-Ru distances to their experimental value in $Ru_3Cp^*{}_3H_3(MeCCPh)$, i.e., Ru^1-Ru^2=Ru^1-Ru^3=2.793Å and Ru^2-Ru^3=2.847Å, optimized at the RHF/BS1 level all the other parameters, and obtained the structure **9⊥′**. Selected parameters are given in Figure **5** and Table 1. In this model optimization, Cp parameters are nearly unchanged, with variations smaller than 0.002Å. The C^1-C^2 bond length is also unchanged and still shorter than the experimental one, suggesting that the interaction is not strengthened by an artificial Ru-Ru bond shortening. One can however notice that the Ru^1-C^1 distance is shortened to 2.240Å from 2.276Å in **9⊥′**, suggesting that a part of the error on these parameters is the consequence of the error in the Ru-Ru distances. This model optimization stabilizes the system by 7.3 kcal/mol at the correlated MP2/BS1 level. Since the shape of the PES with respect to Ru-Ru distances is relatively flat as seen in Figure **2**, one can attribute this energy gain to a strengthening of the interaction between the alkyne and the metallic frame at the correlated MP2 level. In the second model **9⊥″**, we keep the experimental Ru-Ru distances used in **9⊥′** and also freeze the C^1-C^2 bond length to the experimental value of 1.418Å in $Ru_3Cp^*{}_3H_3(MeCCPh)$. Such an optimization further shortens the Ru-C distances: Ru^1-C^1=2.185Å, Ru^2-C^1=Ru^3-C^1=2.290Å ; Ru^2-C^2=Ru^3-C^2=2.053Å and stabilizes the MP2 energy by 3.3 kcal/mol. However, this model is not satisfactory with respect of the positioning of the C^1-C^2 bond; C^2 is right above the Ru^2-Ru^3 bond, slightly inside the Ru_3 triangle, the angle between Ru^1-C^1 and the metal plane being too large, while in **9⊥** and **9⊥′** as well as in the experimental structures, a third of C^1-C^2 bond is outside the metal triangle, C^1-C^2 and Ru^2-Ru^3 bonds crossing each other.

In the parallel conformation **9//**, in which the two C centers of the triple bond are equivalent, the Ru^2-Ru^3 bond is stretched to 3.102Å vs. 2.904Å in **9⊥**. Likewise, the C-C bond becomes longer, of which the distance is 1.435Å vs 1.334Å in **9⊥**. Ru^1-Ru^2 = Ru^1-Ru^3 distances are 2.872Å, not far from 2.902Å for **9⊥**, and Ru^1-C^1 = Ru^1-C^2 distances are 2.527Å, which is compatible with the existence of Ru-C bonds. The alkyne C-H bonds are bent with a bending angle of 61° which is larger than in the perpendicular conformation. The H-C-Ru angles being of 124.0°, the C centers have the characteristics of sp^2 carbon atoms. The Cp^1 center X^1 is still close to the metal plane, while the out-of-plane deviation associated to Cp^2 and Cp^3 is around 10°. One should notice that in this structure, Ru^2-Cp^2 = Ru^3-Cp^3 distances are longer than the Ru^1-Cp^1 distance by 0.07Å, suggesting an important *trans* influence of the carbon atoms in this conformation. In this structure, the arrangement of the bridging H is slightly more outside the Ru$_3$ triangle than in **9⊥**; the H-Ru^1-Ru^2-Ru^3 dihedral angle is 114.7° in **9//** vs. 130.7° in **9⊥**, and the H-Ru^2-Ru^3-Ru^1 dihedral angle is 123.3° in **9//** vs. 105.9° in **9⊥**.

Structure **9//** can be compared to experimentally available parallel structures. For instance, in Os$_3$(CO)$_9$-(μ-H)(HCCPMe$_2$Ph),[20] the distance of the Os-Os bond bridged by the triple bond is 2.980(1)Å, while the distances of the others are 2.781(1)Å on average. Thus, the magnitude of the bond length difference observed in this compound (0.199Å) is in good agreement with that found in our calculations, 0.198Å in **9//**, even though the calculated bond distances are generally overestimated. The experimental Os^2-C and Os^3-C distance of 2.090(17)Å is longer than the calculated one (1.934Å), but the C-C distances show good agreement, namely 1.411(23) experimental vs. 1.435Å in **9//**.

Energetically, using the full optimized structures **9⊥** and **9//**, the perpendicular conformation is more stable by 32.2 kcal/mol at the RHF/BS1 level and 4.6 kcal/mol at the MP2/BS1 level than the parallel one. For the perpendicular conformation, one can also estimate the interaction energy of acetylene with Ru$_3$Cp$_3$H$_3$ using the energies of the optimized fragments. To calculate the RHF energy, we used the fully optimized structure and for the MP2 energy, the model structures, **9⊥′** for Ru$_3$-Cp$_3$H$_3$(HCCH) and the fitted energy for Ru$_3$Cp$_3$H$_3$. The interaction energy is 29.2 kcal/mol at the RHF/BS1 level and 153.2 kcal/mol at the MP2/BS1 level. Recomputed with BS3, the MP2 interaction energy is 168.6 kcal/mol. The very large difference in the binding energy between the RHF and MP2 levels clearly indicates the importance of the correlation energy. For the strong interaction such as this where new M-C bonds are formed, the electron correlation is essential.

As discussed before, the accurate estimation of the absolute value of the binding energy is rather difficult; a very large basis set including higher order polarization functions is needed to recover the correlation energy contribution, and the BSSE has to be taken into account. However, the order of magnitude is qualitatively understandable. Acetylene is interacting with three metal centers and has two π systems which can interact with the metallic frame: one perpendicular to the metal plane and one parallel to it. Therefore, one expects an interaction stronger than the interaction of an ethylene molecule, which is able to have an interaction energy up to 50 kcal/mol when interacting with a monometallic fragment.[21] The interaction between Ru^1 and C^1 is strong, and the structure suggests that there should exist a σ bond between these two atoms. The interaction of C^2 with the metallic frame is of the same order as the interaction of C^1 because of the presence of two π systems interacting with two metals. The total interaction energy should therefore be comparable to the energy of two M-C σ bonds. The second model optimization (**9⊥″**) suggests that the system would be further stabilized by an optimization at a correlated level by 5−10kcal/mol, and a larger basis set may increase this further. On the other hand, one also expects a substantial BSSE effect at the MP2 level; in the calculation of the interaction energy between benzene and the Os$_3$-(CO)$_9$ fragment,[11a] we estimated by a counterpoise correction (CPC) a BSSE of 80 kcal/mol at the MP2 level. For acetylene with four π electrons, two over three times smaller than benzene, one thus expects a BSSE of 50−70kcal/mol at the MP2 level, which will substantially reduce the true interaction energy. The cancellation of these two errors make us think that the calculated interaction energy is probably an upper limit, but represents a reasonable qualitative estimate.

This conformational preference is consistent with the Extended Hückel (EH) analysis proposed by others.[8,9] According to these studies, the perpendicular conformation, or *closo* structure, should be preferred in a complex with 6 skeletal electron pairs (SEPs), while the parallel conformation, or *nido* structure, is observed for 7 SEPs. The Ru$_3$Cp$_3$H$_3$(HCCH) complex has 6 SEPs : the three Ru$_3$Cp$_3$H$_3$ orbitals responsible for the Ru-H bonds, the acetylene $\sigma_{c\text{-}c}$ orbital and the two acetylene $\pi_{c\text{-}c}$ orbitals, and should thus adopt the perpendicular structure. We performed some EH calculations on the two conformations. Even though EH energetics are usually not very meaningful, the perpendicular conformation is found to be 21 kcal/mol more stable. If we add two supplementary electrons, the parallel conformation becomes more stable by 16kcal/mol, because of a large lowering of the LUMO energy. Our EH calculations also revealed that the sums of the three Ru-C overlap populations are similar for both C centers, suggesting that the interaction between HCCH and the metallic fragment is well balanced between the two C atoms.

B. Ru$_3$Cp$_3$(μ-H)$_3$(HCCMe) Model Complex (10). In this subsection, we present the optimized structures of Ru$_3$Cp$_3$(μ-H)$_3$(HCCMe) (**10**) at the RHF/BS1 level. Since the methyl substituent is still too small to let large steric effects to take place, we will be able to measure the electronic effect of a substituted triple bond, and obtain C-C-C equilibrium structures to be used in the MM calculations. As mentioned in the Introduction, the perpendicular conformation presents two isomers when the triple bond substituents are different. The one experimentally observed is the isomer with the largest alkyl (or aryl) substituent connected to the carbon lying

---

(20) Henrick, K.; McPartlin, M.; Deeming, A. J.; Hasso. S.; Manning, P. *J. Chem.Soc., Dalton Trans.* **1982**, 899. See also references therein.

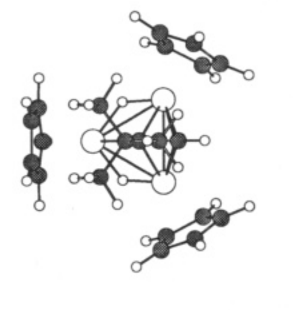
(21) Koga, N.; Morokuma, K. *Chem.Rev.* **1991**, 91, 823.

above the metal triangle (C^1). We have determined both isomers, i.e., R^1=Me, R^2=H (**10⊥i**; **i** means that the methyl group is on the inside carbon, C^1) and R^1=H, R^2=Me (**10⊥o**; **o** designates that the methyl group is on the outside carbon, C^2). The experimental conformation of the Cp* clusters **4*** should be better represented by **10⊥i**.

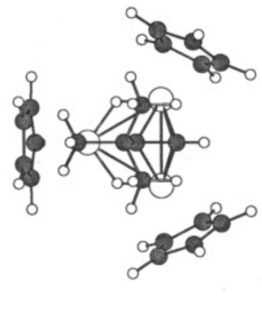
At first, the structures of **10⊥i** and **10⊥o** have been fully optimized with the methyl group eclipsed with the C^1-C^2 bond in **10⊥i** and staggered in **10⊥o**. The methyl group in these structures are nearly freely rotating, and the choice here is to correspond with what is used later for ^{t}Bu. As shown in Table 1, both compounds give geometrical characteristics very similar to the acetylene complex **9⊥**. These calculations show that from the electronic point of view, C-C-R angles are not sensitive to the nature of R : C^1-C^2-R^2 is in the range 134°−137° and C^2-C^1-R^1 in the range 124°−127° for **9⊥**, **10⊥i**, and **10⊥o**. We also performed a constrained optimization, denoted by **10⊥i′** and **10⊥o′**, using the experimental Ru-Ru distances in Ru$_3$Cp*$_3$H$_3$(MeCCPh) and the positions of the bridging H's calculated for **9⊥′**. These bridging H's are associated to soft vibration modes, slowing down the optimization process. In order to save CPU time for this and subsequent model complexes, we decided to freeze their motion. This model is reasonable, since the gradient associated to these bridging H's is still small after optimization of the rest of the molecule. As shown in Table 1, these model optimizations show the same trend as that found for **9⊥** and **9⊥′**, namely a shortening of the Ru-C distances, with a similar C^1-C^2 separation. The C-C-H and C-C-C angles are also nearly unchanged.

From an energetic point of view, **10⊥o** is more stable than **10⊥i** by 2 kcal/mol; electronically the structure with the methyl substituent outside the Ru$_3$ triangle is slightly more favored. This trend is similar for the model **10⊥i′** and **10⊥o′**, both more stable than **10⊥i** and **10⊥o** to the similar extent, 5 kcal/mol. Using the most stable structure, we obtain a BSSE uncorrected interaction energy between HCCMe and Ru$_3$Cp$_3$H$_3$ of 155.1 kcal/mol at the MP2/BS1 level, slightly larger than 153.2kcal/mol for unsubstituted acetylene.

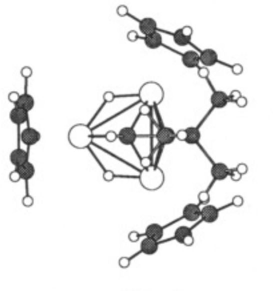
C. Ru$_3$Cp$_3$(μ-H)$_3$(HCC^{t}Bu) Model Complex (11). The third compound treated by *ab initio* optimization is the *tert*-butyl substituted alkyne cluster Ru$_3$Cp$_3$(μ-H)$_3$(HCC^{t}Bu) (**11**) with a perpendicular conformation. As for the propyne case, one can build two isomers, one with ^{t}Bu attached to C^1 and one with ^{t}Bu attached to C^2. Moreover, each isomer can exist in two conformations. Structures **11⊥iA** and **11⊥iB** correspond to the isomer R^1=^{t}Bu, R^2=H; the ^{t}Bu substituent is eclipsed with the C^1-C^2 bond in **11⊥iA** and staggered in **11⊥iB**. Structures **11⊥oA** and **11⊥oB** correspond to the isomer R^1=H, R^2=^{t}Bu, with the ^{t}Bu substituent eclipsed in **11⊥oA** and staggered in **11⊥oB**. Since preliminary MM calculations have shown that **11⊥oB** should be more stable than **11⊥oA**, we optimized only **11⊥oB** and **11⊥iA**, the structure experimentally observed.[4] For these compounds, we adopted the constrained model with the frozen Ru$_3$H$_3$ unit. One can see in Table 1 some steric effects in **11⊥iA**, the C^2-C^1-C angle being reduced to 121.5° from 126.4° in **9⊥′**. The same trend is found in **11⊥oB** in which the C^1-C^2-C angle is reduced by 6° to 130.1° from 136.1° in **9⊥′**. One can see in Table 1, however, the Ru-C and Ru-Cp bonds are stretched in **11⊥iA**, compared to in **9⊥′**. One may suspect that the steric strain is in part relieved by these stretches, which are easier at the RHF level than they really are.



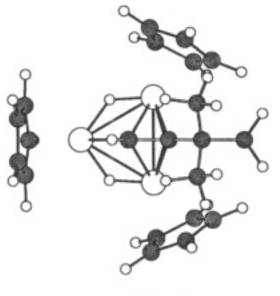
11⊥iA



11⊥iB



11⊥oA



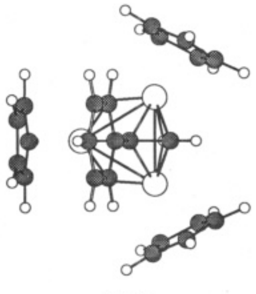
11⊥oB

We thus carried out a supplementary optimization with additional constraints that the Ru-C and the Ru-X distances as well as the C^1-C^2 distance are frozen at the optimized values in **9⊥′**. The resultant structures **11⊥iA′** and **11⊥oB′** with these constraints on the distances in Table 1 show much more pronounced changes in bond angles than in **11⊥iA** and **11⊥oB**. Their C-C-^{t}Bu angles are about 10° smaller than the C-C-H angle in **9⊥′**. The constraints on the distances are also compensated by a larger out-of-plane deviation of the Cp center X, as seen in the X^i-Ru$_3$ angles in Table 1.

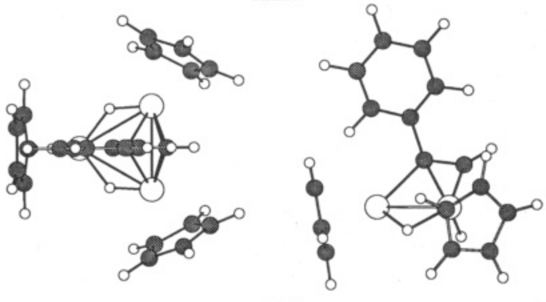
From the energetical point of view, **11⊥oB** is more stable than **11⊥iA** about 7 kcal/mol at the MP2/BS1 level. The same order is found for **11⊥iA′** and **11⊥oB′**, 5 kcal/mol. The present result is compatible with experimental preference for similar clusters with ligands not so bulky as Cp*.[5] For instance, in NiFe$_2$Cp(CO)$_6$-(HCC^{t}Bu), Ru$_3$H(CO)$_9$(HCC^{t}Bu), and Ru$_3$(CO)$_9$(PPh$_2$)-(HCCPr^i), the butyl or propyl ligand is experimentally found on the outside carbon C^2. This energy difference of 7 kcal/mol is larger than what we found for the HCCMe clusters, 2 kcal/mol. One should also notice that the MP2 energies of **11⊥iA** and **11⊥oB** are similar to those of **11⊥iA′** and **11⊥oB′**, respectively, suggesting that a coupling between the M-C stretches and the C-C-R bend makes the motion of the triple bond on the top of the triangle an easy motion.

The existence of steric strain also modifies the interaction energy. Using the most stable structure **11⊥oB** and the fitted MP2 value for the metallic fragment Ru$_3$Cp$_3$H$_3$, the interaction energy is calculated to be 142.2 kcal/mol, about 11kcal/mol smaller than that for the acetylene complex.

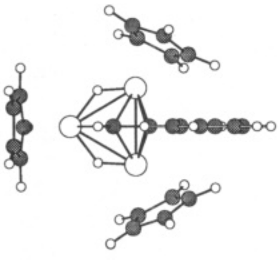
D. Ru$_3$Cp$_3$(μ-H)$_3$(HCCPh) Model Complex (12). The last of the model compounds is the phenyl substituted alkyne cluster. For this species, one can consider for each isomer two conformations of the phenyl group: a "horizontal" conformation, in which the C$_6$ plane is perpendicular to the mirror plane of the cluster and a "vertical" conformation, in which the C$_6$ plane is within the mirror plane of the cluster. Several compounds adopting the vertical conformations have been observed experimentally.[5] For the isomer R^1=Ph, R^2=H, the horizontal and vertical conformations will be respectively denoted by **12⊥ih** and **12⊥iv**. The vertical conformation of the isomer R^1=H, R^2=Ph will be labeled **12⊥ov**. The horizontal conformation of this isomer is not possible, because of very short distances between H of Cp and H of Ph. Structures of **12**s have been optimized using the model adopted for **11⊥iA′** and **11⊥oB′**, namely with frozen Ru$_3$H$_3$C$_2$ unit and frozen Ru-X, Ru-C and C^1-C^2 distances. We used a smaller basis set BS2, as mentioned in the Method section; this could be justified as we froze most of the geometrical parameters of the metal cluster-acetylene part of the complex. Structures and energies thus obtained are summarized in Table 1. Energies have been recomputed with the basis set BS1, using the RHF/BS2 structures.



12⊥ih



12⊥iv



12⊥ov

In **12⊥ih**, the C^2-C^1-C angle of 125.2° suggests that, in spite of the large size of the phenyl ligand, this conformation does not suffer from a large steric energy. This is related to the 2-dimensional nature of phenyl and Cp ligands which can ignore each other, if they are nearly in parallel planes with a reasonable separation. Even though the C^1 center is not far from Cp^1, the system would still be able to minimize the steric repulsion by a simultaneous change in the C^2-C^1-C angle and the Cp bending angle. The steric repulsion is clearly larger in **12⊥iv** where Ph is in a vertical position; the C^2-C^1-C angle is bent strongly to 114.8° and Cp^1 is out of the Ru$_3$ plane by 9°. The structure **12⊥iv** is about 12 kcal/mol less stable than **12⊥ih** at the MP2/BS1 level. The structure **12⊥ov** with the C^1-C^2-C angle of 134.9° suggests the absence of steric repulsion between Ph and the Cp ligands attached to Ru^2 and Ru^3, which once again can be attributed to the planar nature of Ph and Cp. Energetically, structures **12⊥ih** and **12⊥ov** are almost degenerate, suggesting that both of them could exist in solution. These findings suggest a weak electronic influence of the phenyl substituent and a weak coupling between the π systems of the C-C triple bond and of the aryl ring; the aryl π orbitals can mix with different π orbitals of the C-C triple bond, depending on Ph orientation. Calculated from the total energy of **12⊥ih** and the energy of a free HCCPh molecule optimized at the RHF level, the interaction energy of HCCPh with the metallic fragment is 162.0 kcal/mol at the MP2/BS1 level. This value is about 9 kcal/mol larger than calculated for the acetylene compound, but has probably to be attributed in part to an increase in the BSSE because of the larger size of HCCPh compared to acetylene.

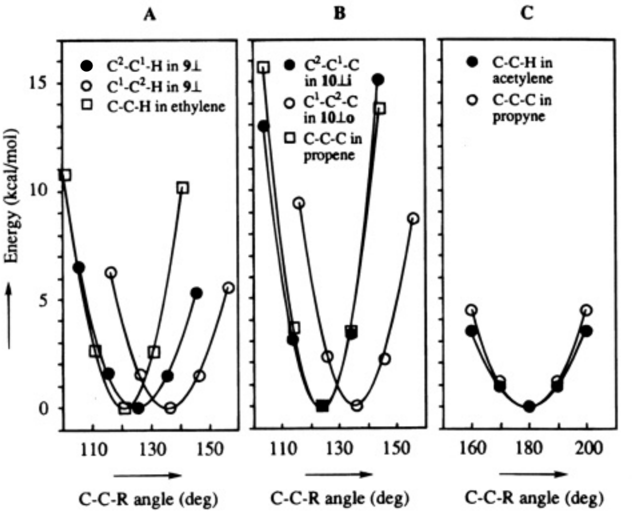
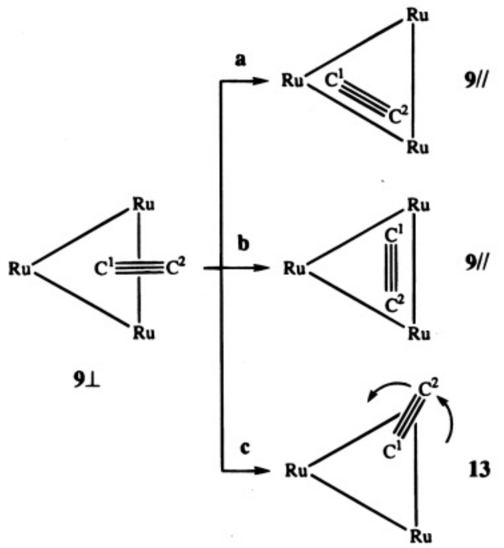


Figure 7. Energy variation (in kcal/mol) as a function of the C-C-R angle for various systems. Every curve covers a range of ±20° around the minimum.

E. Potential Curve for the C−C−R Angle. In this section, we would like to report an analysis of the PES around the equilibrium structure for the C-C-R angles. Since the presence of larger substituents or the use of Cp* would increase the steric effects and decrease the C-C-R angles, the strength of this motion and a comparison between the centers C^1 and C^2 are of interest. We also can make the comparison with free acetylene and ethylene. For this purpose, using the optimized geometries, we scanned the C-C-R angles, the other parameters of the system being frozen. Figure **7** shows the energy curves obtained for complexes **9⊥** (R^1=H, R^2=H), **10⊥i** (R^1=Me, R^2=H) and **10⊥o** (R^1=H, R^2=Me). The shape of the potential curves associated with the C^1-C^2-H and C^2-C^1-H angles in **9⊥** are similar to each other and lie between those of an sp^2 (ethylene) and an sp (acetylene) carbon; a deformation of C^1-C^2-H or C^2-C^1-H of 20° costs about 7kcal/mol, more than a similar deformation in acetylene (3 kcal/mol) but less than in

Scheme 1



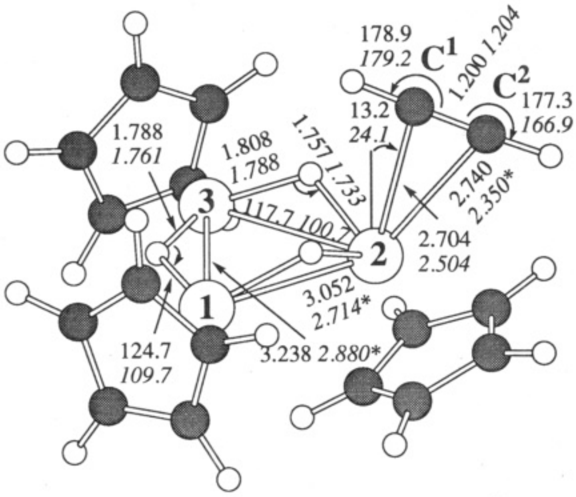


Figure 8. RHF/BS1 optimized structures (in Å and deg) of the transition states **13** and **13′**. Values for the partly optimized structure **13′** are given in *italic*, where assumed values are followed by *. The H-Ru^1-Ru^3-Ru^2 and H-Ru^2-Ru^3-Ru^1 dihedral angles are 175.5° and 124.9°, respectively, for the full optimized structure **13**, and 139.4° and 123.4° for **13′**.

ethylene (10 kcal/mol). For C-C-C angles, the C^2-C^1-C potential curve is slightly steeper than the C^1-C^2-C curve and fits quite well with that in propene $H_2C{=}CH{-}CH_3$; a deformation of 20° costs around 10−15 kcal/mol, substantially more than that, 5kcal/mol, in propyne.

C-C-R deformations are energetically more expensive for the ^{t}Bu clusters. A distortion of 10° in **11⊥iA** (R^1=^{t}Bu, R^2=H) costs around 20 kcal/mol; an opening of the C^2-C^1-C angle gives rise to a rapid increase of the steric repulsion and a closing of the angle leads to a steep increase in the energy since the equilibrium structure is far away from the electronic energy minimum. The structure **11⊥oB** (R^1=H, R^2=^{t}Bu) behaves like its HCCMe analogous **10⊥o**. Calculations have not been performed for the Ph compounds, but the absence of steric repulsion in **12⊥ih** and **12⊥ov** suggests that this species will behave like the propyne cluster around the equilibrium position.

F. Alkyne Rearrangement. As mentioned in the Introduction, experimentally the Cp* ligands become equivalent at high temperatures, suggesting a motion of the triple bond "jumping" from a metal-metal bond to another. In spite of the large number of degrees of freedom, one can easily consider two simple intramolecular mechanisms of the rearrangement of coordinated alkyne. The first mechanism involves the parallel conformation as a transition state or an intermediate. The interconversion between the perpendicular and parallel conformation can take place through a shift, as shown as **a** in Scheme 1, or a rotation (**b**) of the alkyne. Diagonalization of a partial Hessian matrix indicates that the parallel conformation **9//** should be a local minimum on the PES. We did not determine the possible C_1 transition states converting the two conformations by shift or by rotation. However, since the chemical nature of the compound is not modified during the transformation, i.e. Ru^1-C^1 and Ru^2-C^2 bonds remain intact, and since the energy difference between the perpendicular and parallel conformations is relatively small (4.6 kcal/mol at the MP2 level), one may expect that these transition states will also be low in energy. The rearrangement can take place in two consecutive shift or rotation steps via the parallel intermediate. Any two consecutive rotations exchange the inside and the outside substituents on alkyne on the same M-M bond; any two consecutive shifts lead to a simultaneous exchange of the substituents and of the coordinated M-M bond, and a shift followed by rotation or vice versa give the M-M coordinated bond exchange and a mixture of exchanged and unexchanged substituents. For the model Cp compounds where the two isomers of the perpendicular conformation are nearly equal in energy, one may expect that the shift and the rotation pathways would have similar barriers and be competitive, and all the rearrangement mechanisms discussed above may take place. For the more bulky Cp* compounds, one isomer is much more favored in energy than the other by the steric effects, and the rearrangement has to follow an "asymmetric" mechanism consisting of one shift and one rotation, resulting in the exchange of only the coordinated M-M bond but not of the substituents.

Another mechanism can take place through a $\mu_1{:}\eta^2$ coordination mode of the triple bond, obtained by the rotation of the triple bond in a horizontal plane roughly around the C^1 center, as shown as **c** in Scheme 1. This mechanism exchanges only the coordinated M-M bond but not the substituents on alkyne. The geometry of this structure **13** for our model compound has been optimized under the C_s constraint, as shown in Figure **8**. In this structure, the triple bond being not in direct interaction with the metal triangle, the Ru-Ru distances fall in the range of what we found for the trihydride **8**, over 3.2Å. Moreover, the interaction between acetylene and the metallic fragment is weak, leading to two very long Ru^2-C distances, over 2.7Å, and a C-C distance of 1.204Å close to the distance in a free acetylene, 1.194Å. Acetylene is also nearly linear. To provide the metal center bonded to acetylene (Ru^2) with a proper ligand field, the Cp^2 bending of 63.1° is very large and the hydrogen atoms bridging Ru^1-Ru^2 and Ru^2-Ru^3 are on the same side of the metal plane with acetylene. In this peculiar arrangement, the ligand field on Ru^2 should be close to an octahedral. The H center bridging Ru^1-Ru^3 is nearly coplanar with the metal atoms and the Cp ligands attached to Ru^1 and Ru^3 are out of plane by −2.9°.

Table 2. Equilibrium Parameters, in Å and Degrees, Used for the MM2 Calculations

parameter	perpendicular	parallel
C^1-C^2	1.334(fixed)	1.434(fixed)
C^1-H=C^2-H	1.072	1.072
C^1-C=C^2-C	1.514	1.514
C^2-C^1-H	126.4	118.7
C^1-C^2-H	136.1	118.7
C^2-C^1-C	125.9	118.7
C^1-C^2-C	134.5	118.7

In order to precise the nature of this conformation **13**, which is a minimum under the C_s constraint, we have diagonalized an approximate Hessian matrix consisting of values obtained by numerically differentiating the gradient for the acetylene ligand internal coordinates and of estimated values obtained with the optimization for the other degrees of freedom. This diagonalization has led to a negative eigenvalue associated to an a″ eigenvector, suggesting that **13** is a transition state associated with an out-of-plane motion of the triple bond, which is the reaction coordinate of the rotational motion. The energy of this structure relative to **9⊥** is quite low at the RHF level, 20.9 kcal/mol, which is lower than the energy of the parallel conformation **9//**, but is very high, 120.8 kcal/mol, at the MP2 level. Compared to the metallic fragment and acetylene, this corresponds to the binding energy of 32.4 kcal/mol.

The RHF optimized distance between Ru^2 and acetylene for **13** being abnormally long, we performed a model restricted optimization of structure **13′**. We first reduce the Ru^1-Ru^3 distance to 2.88Å, a value close to what is deduced for **8**, shrink the Ru^1-Ru^2 and Ru^2-Ru^3 distance in proportion to 2.714Å, and further assume arbitrarily the Ru^2-C^2 distance at 2.350Å. Other geometrical parameters are optimized at the RHF level as shown in Figure **8**. Relative to **13**, **13′** is stabilized by 14.3 kcal/mol at the MP2 level, but the barrier height remains very high, making such a pathway quite unlikely. The mechanism involving the parallel conformation **9//** seems to be preferred.

5. Molecular Mechanics Calculations. Results and Discussion

In this section, we use the molecular mechanics with the MM2 force field to investigate the steric effects in the alkyne clusters. We optimized the position of the alkyl or aryl substituents in the two series $Ru_3(\mu\text{-}H)_3(Cp_3)(RCCR')$ and $Ru_3(\mu\text{-}H)_3(Cp^*{}_3)(RCCR')$ for varieties of (R, R′) couples. As described in the Method section, metal atoms and bridging H are treated as dummy atoms, because the steric effects are expected mainly between the Cp or Cp* ligands and the alkyl or aryl substituents. In order to take into account the electronic effects of the metallic fragment interaction on the structure of the alkyne, we used the averages of the RHF optimized parameters, shown in Table 2, as the equilibrium geometries involving the C^1 and C^2 atoms. For the compounds involving Ph, we redefined the potential energy for the C^1-C^2-C-C and C^2-C^1-C-C dihedral angles using a small arbitrary value for V_4=0.5kcal/mol with V_1=V_2=V_3=0. Such a definition corresponds to a periodicity of 90° for the rotation of the phenyl around the C^1-C or C^2-C axis and conveniently allows to describe both vertical and horizontal conformations. For all the calculations, we fixed the geometry of the $Cp_3C^1C^2$ and $Cp^*{}_3C^1C^2$ unit at the *ab initio* calculated geometry of $Ru_3(Cp)_3(HCCH)$, **9⊥′** for the perpendicular and **9//** for the parallel conformation. The only exceptions are that the out-of-plane angles of the centers X of Cp and Cp* rings for the perpendicular conformations are fixed at the *ab initio* calculated values for the ^{t}Bu compounds, 9.4° for Cp^1 and 14.0° for Cp^2 and Cp^3, and that for the Cp* complexes the Me groups of Cp* are fixed at the *ab initio* geometries in a free Cp* and the C-C(Me) bonds are bent like the C-H bonds in the *ab initio* optimized $Ru_3(Cp)_3(HCCH)$ with a local C_{5v} symmetry constraint for Cp.

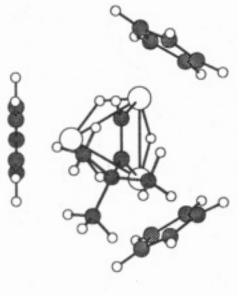
A. Cp Complexes. As shown in Table 3, because of the nearly negligible steric interaction between the Cp ligands and the hydrogen atom or the methyl substituent on the acetylene carbons, MM calculations for acetylene complex **9⊥** and propyne complexes, **10⊥i** and **10⊥o**, give back only very small changes over the input C-C-H and C-C-C bending angles given in Table 2. The two isomers of the propyne complex, **10⊥i** and **10⊥o**, have nearly the same total steric energy, suggesting that the conformational preferences in such a compound is determined by the electronic energies not included in Table 3; the *ab initio* energy that includes both electronic and steric energies favored **10⊥o** over **10⊥i** by about 2kcal/mol, as discussed in Table 1.

For the ^{t}Bu series (**11**), one can find some changes in the angular parameters. For the isomer R^1=^{t}Bu, R^2=H, Table 3 indicates that the ^{t}Bu conformation we have chosen for the *ab initio* calculation, **11⊥iA**, in which ^{t}Bu is eclipsed with the triple bond, is slightly more favorable than the conformation **11⊥iB** in which the ^{t}Bu substituent is staggered with the triple bond. The C^2-C^1-C angle 111.6° in **11⊥iB** is smaller than 114.8° in **11⊥iA**, consistent with a slightly larger total steric energy: 89.1 kcal/mol in **11⊥iB** vs 88.9 kcal/mol in 11⊥iA. The MM calculated C^2-C^1-C angle of 114.8° in **11⊥iA** is in good agreement with the *ab initio* calculated value of 116.4° in model **11⊥iA′**. In the structure **11⊥iA**, each methyl group on ^{t}Bu points between two Cp rings, giving a pseudo-C_3 axis to the system. One should also notice in Table 3 that the repulsion between the H atom on C^2 and one methyl on ^{t}Bu causes the C^1-C^2-H angle to become larger, 141.5°. Such an effect, though smaller, has already seen in the *ab initio* calculations in Table 1. The steric effect is more clearly seen in the isomers R^1=H, R^2=^{t}Bu, in which ^{t}Bu is on the more crowded C^2. The conformation we treated by *ab initio* calculations, **11⊥oB**, in which the ^{t}Bu substituent is staggered with the triple bond, presents a lower steric energy 90.2 kcal/mol than the conformation **11⊥oA** in which ^{t}Bu is eclipsed, 95.9 kcal/mol. Structure **11⊥oA** is high in energy, two methyl groups on ^{t}Bu being oriented in the direction of the Cp ligands, whereas **11⊥oB** has a lower steric energy, the methyl groups pointing to the direction of the Cp ligands being further away from them than in **11⊥oA**. The steric energy difference between the most stable conformation of the two isomers, **11⊥iA** and **11⊥oB**, is less than 2kcal/mol in favor of **11⊥iA**. Here again, the *ab initio* energy difference that includes both electronic and steric energies is in favor of **11⊥oB** by 7kcal/mol. The role of steric energy is insignificant. In the parallel conformation **11//**, the steric energy is of the same magnitude as in **11⊥iA** and **11⊥iB**, suggesting that the energy difference between the perpendicular

Table 3. Total and Relative Steric Energy, in kcal/mol, and C-C-R Optimized Angles, in Degrees, Calculated by MM2

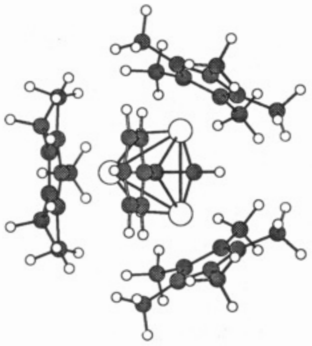
		R^1=R′; R^2=R					R^1=R; R^2=R′				
R, R′	conformation[a]	Label	C^1-C^2-R	C^2-C^1-R′	E	ΔE	Label	C^1-C^2-R′	C^2-C^1-R	E	ΔE
				Cp compounds							
R=H, R′=H		**9⊥**	136.6	126.9	81.2	0.0					
R=H, R′=Me		**10⊥i**	136.6	127.6	79.7	0.0	**10⊥o**	135.4	126.7	79.9	0.2
R=H, R′=^{t}Bu ecl.		**11⊥iA**	141.5	114.8	88.9	0.0	**11⊥oA**	120.4	132.6	95.9	7.0
	sta.	**11⊥iB**	140.4	111.6	89.1	0.2	**11⊥oB**	128.3	127.8	90.2	1.3
		11//	125.0	114.7	88.5	−0.4					
R=H, R′=Ph	hor.	**12⊥ih**	136.5	126.7	74.2	0.0					
	ver.	**12⊥iv**	142.5	114.3	83.5	9.3	**12⊥ov**	132.9	128.4	76.3	2.1
		12//	119.9	115.9	77.4	2.8					
				Cp* compounds							
R=H, R′=H		**9⊥***	136.6	127.1	82.5	0.0					
R=H, R′=Me		**10⊥i***	136.8	123.9	80.0	0.0	**10⊥o***	127.0	127.2	83.8	3.8
R=H, R′=^{t}Bu	ecl.	**11⊥iA***	145.6	109.6	108.3	0.0	**11⊥oA***	102.5	144.9	162.8	54.5
	sta.	**11⊥iB***	142.7	103.3	110.4	2.1	**11⊥oB***	105.8	134.7	126.3	18.0
		11//*	133.1	99.1	113.2	4.9					
R=H, R′=Ph	hor.	**12⊥ih***	136.6	122.7	74.1	0.0					
	ver.	**12⊥iv***	145.3	105.1	96.4	22.3	**12⊥ov***	117.7	134.6	90.8	16.7
		12//*	123.1	108.8	75.8	1.7					
R=Me, R′=Ph	hor.	**15⊥i***	130.9	117.5	105.2	0.0	**15⊥o***	121.2	134.6	98.7	−6.5
R=Me, R′=^{t}Bu	ecl.	**16⊥i***	140.4	112.8	110.9	0.0					
	sta.						**16⊥o***	109.0	137.9	135.1	24.2

[a] ecl. = *ter*-Bu eclipsed with the C-C bond; sta.=*ter*-Bu staggered with the C-C bond; hor.=horizontal phenyl.; ver.=vertical phenyl.



11//

12//



12⊥ih*

and parallel conformations is not much affected by the steric interaction. In our MM optimization, the absence of metal parameters makes in general the rotation of the alkyl group around the triple bond free. The MM optimization of **11//**, however, gives the H-C^2-C^1-C dihedral angle only of 2°, similar to what we found in the *ab initio* optimization; the ^{t}Bu group is trapped between two Cp groups. The C^2-C^1-C bond angle of 114.7° in Table 3 is, however, smaller than in the parallel conformation of the acetylene compound, 118.7°, suggesting a steric effect within this trap.

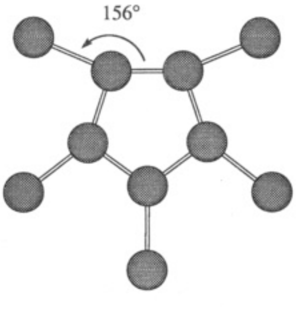
In Ru$_3$Cp$_3$H$_3$(HCCPh) (**12**), since we redefined the dihedral potential associated to the phenyl rotation, we are able to describe the vertical and horizontal phenyl conformations as two local minima on the PES. We do not know whether or not this corresponds to the reality, because we did not determine the true nature of **12⊥iv** optimized under C$_s$ constraint. It is quite likely that **12⊥iv** is a transition state with respect of the phenyl rotation, since it is higher in energy than **12⊥ih**. Such a procedure however allows us to measure the steric energy in both conformations. The total steric energy in **12⊥iv** is 9 kcal/mol higher than in **12⊥ih**, with a smaller C^2-C^1-C angle of 114.3° vs 126.7° in **12⊥ih**. These values are in very good agreement with the *ab initio* results in Table 1, suggesting once more that the conformational preferences are entirely governed by the steric effects and that the electronic influence of the C$_6$ ring orientation is a minor point. Table 3 also shows that **12⊥ih** and **12⊥ov** have very similar total steric energies suggesting that **12⊥ih** and **12⊥ov** may coexist, in agreement with the *ab initio* results in Table 1 that their energies are nearly degenerate. As in the case of the ^{t}Bu complex, the parallel conformation **12//** has an only slightly larger total steric energy, by 2.8 kcal/mol, than **12⊥ih**. This would suggest that, in spite of the large size of the substituents, the energy difference between the perpendicular and parallel conformations is not very sensitive to the nature of the substituents and that it would not be easy to upset the electronic energy difference of about 5 kcal/mol discussed in the previous section by the steric effects. This also implies that the triple bond exchange mechanism will not be very sensitive to the nature of the alkyne, the barrier height being not dependent of the size of the substituent. The similar steric energies for both conformations suggests that a similar effect may be expected for the transitions states of the exchange reaction.

B. Cp* Compounds. One can expect that replacing Cp by Cp* will add a substantial steric energy to the system. As seen in Table 3, the acetylene complex **9⊥*** is apparently not affected by this change. Some steric effect can be seen in propyne complexes. In the isomer **10⊥i*** with R^1=Me, R^2=H, the C^2-C^1-C angle is smaller by 3° than in **10⊥i**; in the isomer **10⊥o*** with R^1=H, R^2=Me, the C^1-C^2-C angle is smaller by 8° than in **10⊥o**. The difference between **10⊥i*** and **10⊥o*** in the total steric energy is still small, about 3 kcal/mol, which is consistent with the fact that both isomers of the MeCCEt cluster have been experimentally observed.[4]

With a ^{t}Bu substituent the trend found in the preceding subsection in the Cp complex is very enhanced in the Cp* complex. In the isomer with R^1=^{t}Bu, R^2=H the eclipsed conformation **11⊥iA*** is more stable than the staggered conformation **11⊥iB***, and the C^2-C^1-C angles in Cp* complexes are genenrally smaller than in the corresponding Cp complexes, e.g., 109.6° in **11⊥iA*** and 103.3° in **11⊥iB*** vs. 114.8° in **11⊥iA** and 111.6° in **11⊥iB**. The isomer with R^2=^{t}Bu in the crowded region has a much higher steric energy. The eclipsed **11⊥oA*** and the staggered conformation **11⊥oB*** of this R^2=^{t}Bu isomer have a steric energy of 54 and 18 kcal/mol, respectively, relative to the most stable conformation of the R^1=^{t}Bu isomer **11⊥iA*** and their changes in the C^1-C^2-C angle are much more pronounced. Such a steric energy is sufficient to upset the electronic effect which, according to the *ab initio* calculation for the Cp complexes, favors the R^2=^{t}Bu isomer by 5 kcal/mol. Thus the conformation **11⊥iA***, most favorable with R^1=^{t}Bu, is estimated to be lower by about 13 kcal/mol than that **11⊥oB*** with R^2=^{t}Bu, suggesting the dominance of the former. The parallel conformation **11//*** also shows a larger steric energy than **11⊥iA*** with a very small C-C-C angle of 99.1°. This result would suggest that, when Cp* ligands are used, the perpendicular conformation is sterically more stable than the parallel one. Calculations on Cp compounds suggested similar steric effects in both conformations.

In the isomer R^1=Ph, R^2=H of the HCCPh complex, the phenyl retains the horizontal conformation **12⊥ih***, with a small change in the C^2-C^1-C angle. The vertical conformation **12⊥iv*** is 22 kcal/mol higher than **12⊥ih***, with a very small C^2-C^1-C angle of 105.1°, consistent with a larger steric energy than in the Cp compound with a C^1-C^2-C angle of 114.3°. The vertical conformation **12⊥ov*** of the isomer R^1=H, R^2=Ph is substantially higher than **12⊥ih***, showing a clear effect of the Cp* ligand size; an energy difference of 17 kcal/mol is sufficient to lead to a total dominance of the R^1-horizontal Ph complex **12⊥ih***. The parallel conformation **12//*** does not suffer from a high steric energy and is almost degenerate with **12⊥ih***.

We would like to comment here on one of the limitations of our model. In our calculations, we assumed a fixed geometry for the Cp* ligands, with a C-CH_3 bend equal to the ab initio calculated C-H bend in the Cp complex and with a local C_{5v} symmetry. According to the X-Ray diffraction on MeCCPh complex,[4] the Cp* group in direct interaction with the phenyl group is distorted. The Cp* rings are nearly coplanar but two C-C-CH_3 angles are open with a value of 156° (**14**), to be compared with the value in a C_{5v} Cp*, 126°. Such a distortion should reduce the steric repulsion between Cp* and the phenyl group. When we allow in our MM calculation the relaxation of the methyl group of the Cp* attached to Ru^1, the total steric energy of **12⊥ih*** is reduced by 3 kcal/mol, but the relaxation mainly occurs through a reduction of the C-CH_3 bend. This is costly in the electronic energy; this bend is essential to a good interaction between the C_5 ring π orbitals and the metal d orbitals. Overall, the reduction in steric energy due to the Cp* relaxation will not be able to compensate the loss in the electronic energy and should not modify the trend obtained with the frozen Cp* geometry.



14

We also optimized structures **15** and **16** of complexes with doubly-substituted alkynes. These calculations show an increased total steric energy and its correlation with the changes in C^1-C^2-C and C^2-C^1-C angles caused by the repulsion between the substituents.

6. Conclusions

The present study has shown that *ab initio* calculations are able to reproduce the geometry and relative stability of complicated and large molecules such as the present trimetallic polyhydride compounds of second row transition metal, at a relatively low level of calculation, such as RHF or simulated MP2 optimization with MP2 single point energy using valence double-ζ type basis functions. For instance, while the optimized Ru-Ru distance of 2.758Å at the RHF level in $Ru_3Cp_3H_6^+$ is not bad, the MP2 estimated value of 2.695Å is in good agreement with the experimental value of 2.705Å for $Ru_3Cp^*_3H_6^+$. The RHF optimized Ru-Ru distance, 2.861Å, for $Ru_3Cp_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ is substantially longer than the experimental value, 2.764Å, for $Ru_3Cp^*_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**3***) but the MP2 estimated distance, 2.748Å, is in good agreement with experiment. The calculated geometry could not support an early proposed assignment of **3*** to $Ru_3Cp^*_3(\mu\text{-}H)_3$.

In all the trimetallic complexes we have studied, the Ru-Ru framework is held together by strong Ru-H-Ru three-center two-electron bonds as in the related bimetallic compound $Ru_2Cp_2H_4$ previously studied. Our calculations suggest that the μ-H-Ru bond energy in the polyhydrides, $Ru_3Cp_3H_3$, $Ru_3Cp_3H_6^+$ and $Ru_3Cp_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$, is of the order of 50 kcal/mol before the correction due to BSSE, which should reduce the absolute value substantially. The μ_3-H-Ru bonds are substantially weaker. The μ-H-Ru bond in the dinuclear complex $Ru_2Cp_2H_4$ is several kcal/mol weaker than that in the present trimetallic complexes. Though the Ru-Ru bonds are formally broken in these compounds, the direct interaction is estimated to be still attractive by 10−20 kcal/mol/bond, before BSSE correction.

We have shown that the perpendicular conformation of the acetylene $Ru_3Cp_3H_3$(HCCH) complex is more stable than the more common parallel conformation by about 5 kcal/mol. The estimated binding energy of the alkyne ligand with the trimetallic fragment $Ru_3Cp_3H_3$, 150kcal/mol, is obviously an overestimation due to the BSSE, but is qualitatively understandable since it should be comparable to twice the energy of an M-C σ bond. Optimizations of complexes of substituted alkynes show that the steric effect is small in the Cp complexes, and that the isomer with the larger substituent "outside" the metallic triangle, i.e., on the C center denoted

C^2, is generally more stable than the isomer with the larger substituent "inside", i.e., connected to C^1. The difference for HCC^{t}Bu cluster is as large as 5 kcal/mol at the MP2 level. An MM analysis has shown however that this trend is reversed in the Cp* compounds and that the sterically more favored structure with the larger alkyl connected to C^1 is what is observed experimentally.

Finally the mechanism of alkyne rearrangement on the top of the metal triangle involving the exchange of coordinated M-M bond and/or the exchange of substituents on alkyne has been discussed. A brief consideration of a structure containing a μ_1:η^2 alkyne shows that such a structure is too high in energy to participate. The rearrangement should rather occur by conversion of the stable perpendicular conformation into a parallel conformation intermediate via a shift or rotation of the alkyne and subsequent reversal from the intermediate to the perpendicular product.

Acknowledgment. We thank Professor H. Suzuki of the Tokyo Institute of Technology for the communication of experimental results before publication and helpful discussions. A part of numerical calculations was carried out at the Computer Center of IMS. R.J.F. acknowledges the Japan Society of Promotion of Science for his postdoctoral fellowship. The present research was in part supported by a Grant-in-Aid for Scientific Research in the Priority Area of "Theory of Chemical Reactions" from the Ministry of Education, Science and Culture of Japan.

OM9308250