

## Mechanism for the Cyclotrimerization of Alkynes and Related Reactions Catalyzed by CpRuCl

Karl Kirchner,<sup>\*,†</sup> Maria José Calhorda,<sup>\*,‡,§</sup> Roland Schmid,<sup>†</sup> and Luís F. Veiros<sup>||</sup>

Contribution from the Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal, ITQB, Av. da República, EAN, Apart. 127, 2781-901 Oeiras, Portugal, and Centro de Química Estrutural, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

Received March 13, 2003; E-mail: mjc@itqb.unl.pt

**Abstract:** A complete catalytic cycle for the cyclotrimerization of acetylene with the CpRuCl fragment has been proposed and discussed based on DFT/B3LYP calculations, which revealed a couple of uncommon intermediates. The first is a metallacyclopentatriene complex RuCp(Cl)(C<sub>4</sub>H<sub>4</sub>) (**B**), generated through oxidative coupling of two alkyne ligands. It adds another alkyne in  $\eta^2$  fashion to give an alkyne complex (**C**). No less than three successive intermediates could be located for the subsequent arene formation. The first, an unusual five- and four-membered bicyclic ring system (**D**), rearranges to a very unsymmetrical metallaheptatetraene complex (**E**), which in turn provides CpRuCl( $\eta^2$ -C<sub>6</sub>H<sub>6</sub>) (**F**) via a reductive elimination step. The asymmetry of **E**, including Cp ring slippage, removes the symmetry-forbidden character from this final step. Completion of the cycle is achieved by an exothermic displacement (21.4 kcal mol<sup>-1</sup>) of the arene by two acetylene molecules regenerating **A**. In addition to acetylene, the reaction of **B** with ethylene and carbon disulfide, the latter taken as a model for a molecule lacking hydrogen atoms, has also been investigated, and several parallels noted. In the case of the coordinated alkene, facile C–C coupling to the  $\alpha$  carbon of the metallacycle is feasible due to an agostic assistance, which tends to counterbalance the reduced degree of unsaturation. Carbon disulfide, on the other hand, does not coordinate to ruthenium, but a C=S bond adds instead directly to the Ru=C bond. The final products of the reactions of **B** with acetylene, ethylene, and carbon disulfide are, respectively, benzene, cyclohexadiene, and thiopyrane-2-thione, the activation energies being lower for acetylene.

### Introduction

Although an exothermic reaction,<sup>1</sup> the cyclotrimerization of acetylene to produce benzene takes place at conditions far from mild, owing to the high activation energy required.<sup>2</sup> A synthetic pathway to produce a great variety of cyclic organic compounds<sup>3</sup> followed the pioneering work of Reppe, who was the first to suggest a metal-catalyzed procedure.<sup>4</sup> It would be logical to expect that the underlying reaction mechanism consists of a [4+2] reaction via the formation of a metallacycle to which the third alkyne molecule is added, rather than a [2+2+2] concerted reaction.<sup>5</sup> Hitherto theoretical attempts at understanding the

intimate conversion mechanism are based on CoCp(L)<sub>2</sub> complexes (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>, L = PR<sub>3</sub>, CO), which from the beginning were found to be active catalysts. While some aspects have been addressed in semiempirical<sup>6</sup> and relatively old ab initio studies,<sup>7</sup> the topic has been more recently treated at density functional theory (DFT) level in the excellent work of Albright and co-workers.<sup>8</sup>

In addition to CpCo-based catalysts also other metal centers, ranging from titanium<sup>9</sup> to palladium,<sup>10</sup> from metal clusters<sup>11</sup> to metal porphyrin derivatives,<sup>12</sup> show relevant catalytic activities.

<sup>†</sup> Institute of Applied Synthetic Chemistry, Vienna University of Technology.

<sup>‡</sup> Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa.

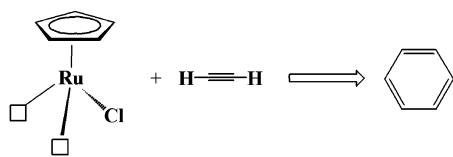
<sup>§</sup> ITQB.

<sup>||</sup> Centro de Química Estrutural, Instituto Superior Técnico.

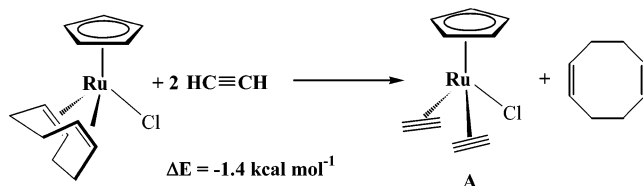
- (1) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968.
- (2) (a) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A.; *J. Am. Chem. Soc.* **1979**, *101*, 6797. (b) Bach, R. D.; Wolber, G. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 2837.
- (3) (a) Vollhardt, K. P. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4996. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.
- (4) (a) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Liebigs Ann. Chem.* **1948**, *560*, 3. (b) Reppe, W.; Schweckendiek, W. *Liebigs Ann. Chem.* **1948**, *560*, 104.
- (5) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081.

- (6) (a) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952. (b) McKinney, R. J.; Thorn, D. L.; Hoffmann, R.; Stockis, A. *J. Am. Chem. Soc.* **1981**, *103*, 2595. (c) Bianchini, C.; Caulton, K. C.; Chardon, C.; Doublet, M.-L.; Eisenstein, O.; Jackson, S.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, *13*, 1910.
- (7) Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuma, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 1907.
- (8) Hardesty, J. H.; Koerner, J. B.; Albright, T. A.; Lee, G.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 6055.
- (9) (a) Suzuki, D.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **2001**, *123*, 7925. (b) Ozerov, O. V.; Ladipo, F. T.; Patrick, B. O. *J. Am. Chem. Soc.* **1999**, *121*, 7941.
- (10) (a) Murakami, M.; Itami, H.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *119*, 7163. (b) Takeda, A.; Ohno, A.; Kadota, I.; Gevorgyan, V.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4547.
- (11) Abbet, S.; Sanchez, A.; Heiz, U.; Schneider, W.-D.; Ferrari, A. M.; Pacchioni, G.; Rösch, N. *J. Am. Chem. Soc.* **2000**, *122*, 3453.
- (12) Fletcher, J. T.; Therien, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 12 393.

Scheme 1



Scheme 2



Other unsaturated molecules can be added at the putative metallacycle intermediate to afford a new source of diversified cyclic species. In recent years, thus, the ruthenium derivatives  $\text{RuCp}(\text{COD})\text{X}$ ,  $\text{RuCp}^*(\text{COD})\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) and  $\text{Ru}(\eta^5\text{-C}_9\text{H}_7)(\text{COD})\text{Cl}$  have been used as efficient pre-catalysts promoting the cyclization of diynes with terminal alkynes,<sup>13</sup> olefins,<sup>14</sup> allylic ethers,<sup>15</sup> dicyanides,<sup>16</sup> tricarbonyl compounds,<sup>17</sup> isothiocyanates, and  $\text{CS}_2$ .<sup>18</sup> At this point the crucial role of the co-ligands to the reaction's outcome should be emphasized. In fact, the use of the 14-electron phosphine derivative  $[\text{RuCp}(\text{PR}_3)]^+$  was found to lead to quite different products, viz. allyl carbenes via phosphine migration.<sup>19</sup> Thus, it is deemed worthwhile to undertake further theoretical studies on the topic. Here, we shall analyze the mechanism of the cyclotrimerization of acetylene to produce benzene in the presence of the 14e fragment  $\text{RuCpCl}$ , based on DFT/B3LYP calculations (Scheme 1).<sup>20,21</sup>

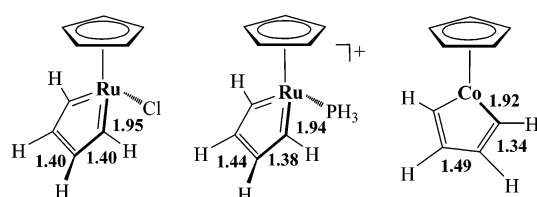
Likewise, the cycloaddition of the unsaturated molecules ethylene and  $\text{CS}_2$  will be analyzed, exposing differences and similarities between the three situations.

## Results and Discussion

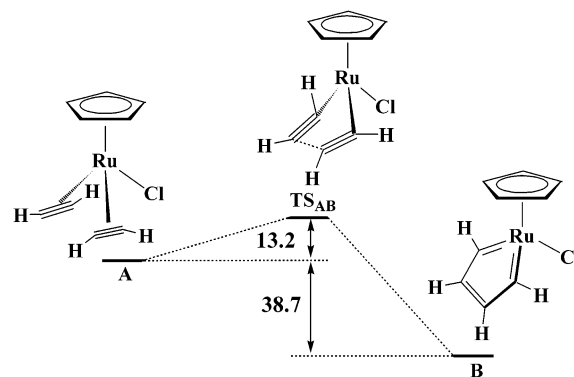
**First Step—Formation of a Metallacyclopentatriene.** The initial step of the reactions is the replacement of labile COD in  $\text{RuCp}(\text{COD})\text{Cl}$  by two molecules of acetylene. The resulting complex **A** in Scheme 2 has a slightly lower energy than the starting materials.

The nevertheless relatively high energy of complex **A** is consistent with the well-known fact that the bisacetylene ruthenium derivatives are rather reactive species. No examples are reported in the CSD.<sup>22</sup> Indeed, the metallacycle derivative **B** forms easily, as can be studied in situ by NMR spectroscopy.

Scheme 3



Scheme 4



In a  $\text{Ru}(\text{II})$ <sup>23</sup> and a  $\text{Co}(\text{I})$  system, **B** could be characterized structurally. According to X-ray data of  $\text{RuCpBr}(\text{C}_4\text{Ph}_2\text{H}_2)$ <sup>23</sup> and the DFT-calculated structure of  $\text{RuCpCl}(\text{C}_4\text{H}_4)$ ,<sup>24</sup> the cycle has been shown to be closer to a metallacyclopentatriene, whereas the corresponding complex in the  $\text{CoCp}$  system is featured by a metallacyclopentadiene.<sup>6c,15–18</sup> The respective distances are displayed, from left to right in Scheme 3, for  $\text{RuCpCl}(\text{C}_4\text{H}_4)$ ,<sup>24</sup>  $[\text{RuCp}(\text{PH}_3)(\text{C}_4\text{H}_4)]^+$ ,<sup>19</sup> and  $\text{CoCp}(\text{C}_4\text{H}_4)$ .<sup>8</sup>

The energetic profile (relative energies in  $\text{kcal mol}^{-1}$ ) and structural details for the conversion of **A** into **B** shown in Scheme 4 has been analyzed in detail previously.<sup>24</sup> Related calculations by other authors on the  $\text{CpCo}$  system are also available.<sup>6,7,8</sup> In  $\text{RuCp}(\text{HC}\equiv\text{CH})_2\text{Cl}$ , the new C–C bond has already started to appear at the transition state ( $\text{TS}_{\text{AB}}$ ) with concomitant strengthening of the initially weak Ru–C bonds as **B** forms, a formulation in line with other recent experimental and theoretical reports.<sup>19,23,24</sup>

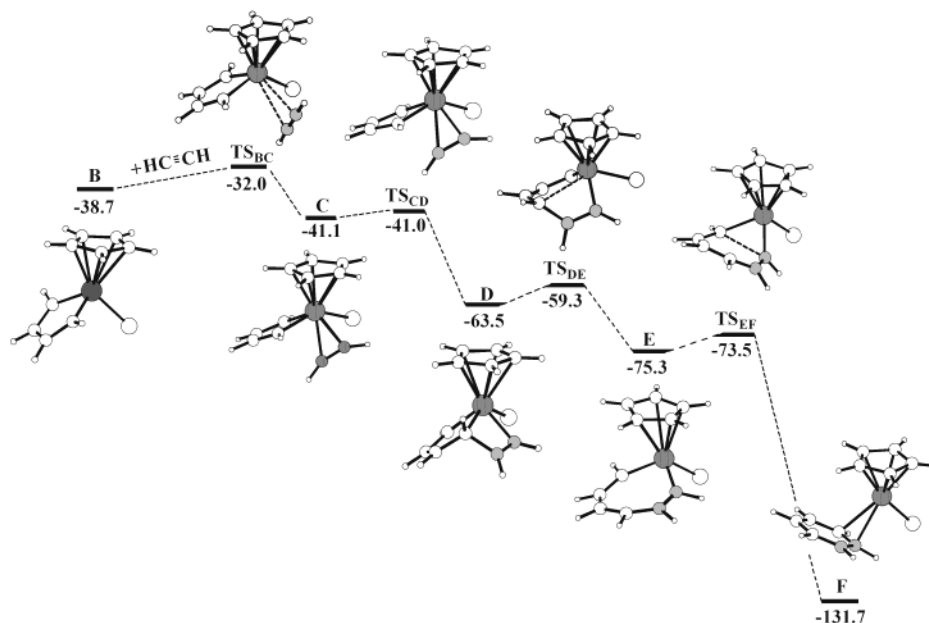
The reactivity of the complex **B** toward unsaturated small molecules will be discussed in the next sections.

**Cyclotrimerization of Acetylene—A [4+2] Reaction.** The reaction of **B** with another alkyne molecule was studied in order to elucidate likely reaction intermediates and transition states. The results are shown in Figure 1. There is a gradual decrease in energy in going from the metallacycle acetylene complex **C**, through intermediate **D**, and the seven-membered metallacycle **E**, to the benzene complex **F**. Selected bond distances for the conversion of **B** into **C** are given in Figure 2.

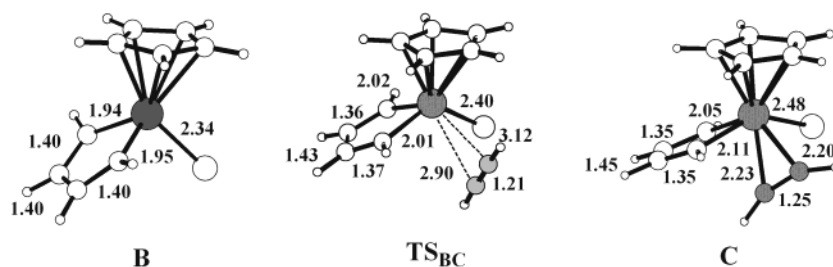
The acetylene molecule approaches **B** in an unsymmetrical mode since in the transition state one Ru–C bond is considerably longer than the other (3.12 vs 2.90 Å). At the same time the  $\text{Ru}=\text{C}$  bonds become weaker, the cycle becoming a metallacyclopentadiene. Interestingly, the Ru–C bond length between the metal center and the third acetylene molecule in **C**

- (13) Yamamoto, Y.; Ogawa, R.; Itoh, K. *Chem. Commun.* **2000**, 549.  
 (14) (a) Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Kawaguchi, H.; Tatsumi, K.; Itoh, K. *J. Am. Chem. Soc.* **2000**, *122*, 4310. (b) Yamamoto, Y.; Kitahara, H.; Hattori, R.; Itoh, K. *Organometallics* **1998**, *17*, 1910.  
 (15) Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Itoh, K. *J. Org. Chem.* **1998**, *63*, 9610.  
 (16) Yamamoto, Y.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2001**, *123*, 6189.  
 (17) Yamamoto, Y.; Takagishi, H.; Itoh, K. *J. Am. Chem. Soc.* **2002**, *124*, 6844.  
 (18) Yamamoto, Y.; Takagishi, H.; Itoh, K. *J. Am. Chem. Soc.* **2002**, *124*, 28.  
 (19) (a) Rüba, E.; Mereiter, K.; Schmid, R.; Sapunov, V. N.; Kirchner, K.; Schottenberger, H.; Calhorda, M. J.; Veiros, L. F. *Chem. Eur. J.* **2002**, *8*, 3948. (b) Rüba, E.; Mereiter, K.; Schmid, R.; Kirchner, K. *Chem. Commun.* **2001**, 1996.  
 (20) Parr, R. G.; Wang, Y. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.  
 (21) (a) Becke, A. D.; *J. Chem. Phys.* **1993**, *98*, 5648. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (c) Lee, C.; Yang, W.; Parr, G. *Phys. Rev. B* **1988**, *37*, 785.  
 (22) Allen, F. H.; Kennard, O. *Chem. Design Autom. News*, **1993**, *8*, 31.

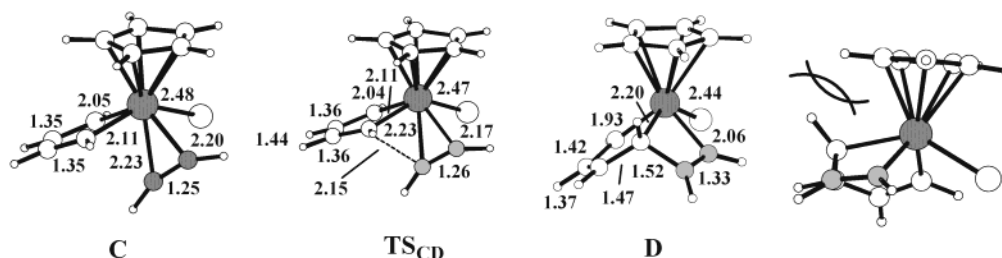
- (23) Albers, M. O.; de Waal, D. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680.  
 (24) Calhorda, M. J.; Kirchner, K.; Veiros, L. F. In *Perspectives in Organometallic Chemistry*; Scretta, C. G., Steele, B. R., Eds.; The Royal Society of Chemistry, Cambridge, **2003**, p 111–119.



**Figure 1.** Energy profile for the cyclotrimerization of acetylene in the metallacycle **B** (energies in kcal mol<sup>-1</sup>, relative to the bisacetylene complex, **A**).



**Figure 2.** Relevant distances (Å) in the optimized geometries for going from **B** to **C**.

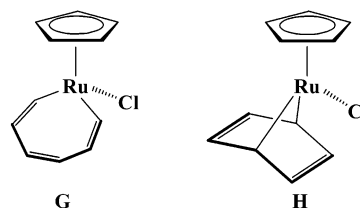


**Figure 3.** Relevant distances (Å) in the optimized geometries for going from **C** to **D**.

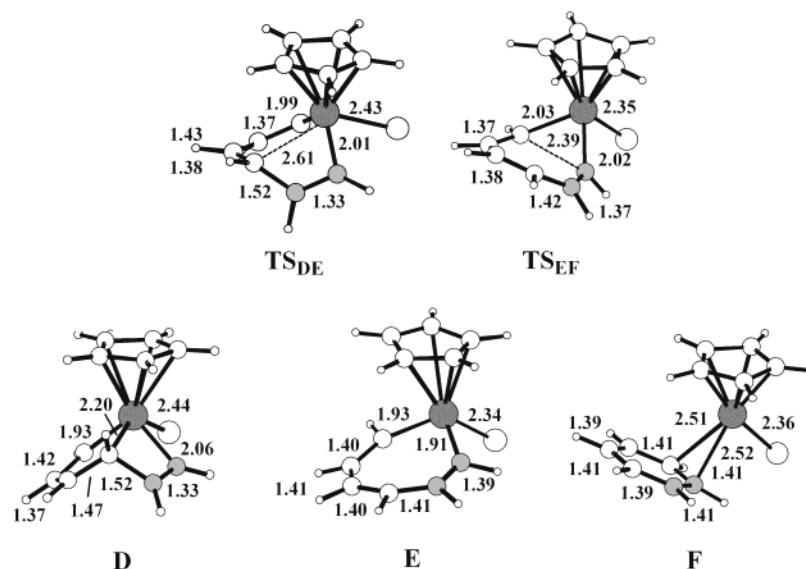
is just as long as in **A** (2.20 Å).<sup>24</sup> Furthermore, the Ru–Cl bond becomes weaker, while the Ru bonds to the ring remain essentially unchanged. It may be noted that **C** is 2.4 kcal mol<sup>-1</sup> more stable than the metallacyclopentatriene plus free acetylene.

The next step is a facile C–C coupling between the coordinated acetylene and the metallacyclopentadiene to afford **D** featuring an unusual five and four-membered bicyclic ring system (Figure 3). Energetically, the transition state for this reaction is merely 0.1 kcal/mol higher in energy than **C**. Although no bonds are formally broken (it is essentially a rotation of the acetylene by about 5°), the acetylene C≡C bond becomes weaker, tending toward a double bond and the bonding pattern is inverted relative to the former metallacycle: one Ru–C bond is carbenic (1.93 Å) and is adjacent to a weak C–C bond. In the transition state, these features are not yet observed, with TSCD being closer to **C** than to **D**. The second Ru–C bond of the former metallacycle involving the coupling carbon atom

#### Chart 1



becomes longer (2.11, 2.11, and 2.20 Å, in **C**, TSCD, and **D**, respectively) and will be broken in the following step. The crucial intermediate **D** is shown in a different perspective at the right-hand side of Figure 3, to emphasize the steric constraints between the hydrogen of the metallacycle (i.e., from the first acetylene molecule) and that of the Cp ring. It is easy to see that this intermediate controls the selectivity of the overall cyclotrimerization process. Acetylene molecules carrying two



**Figure 4.** Relevant distances (Å) in the optimized geometries in going from **D** to **F**.

bulky substituents will therefore experience considerable repulsions at this stage. In fact, cyclotrimerization is found to work well only when parent 1,6-diynes or unsymmetrical 1,6-diynes react with terminal alkynes.<sup>12</sup>

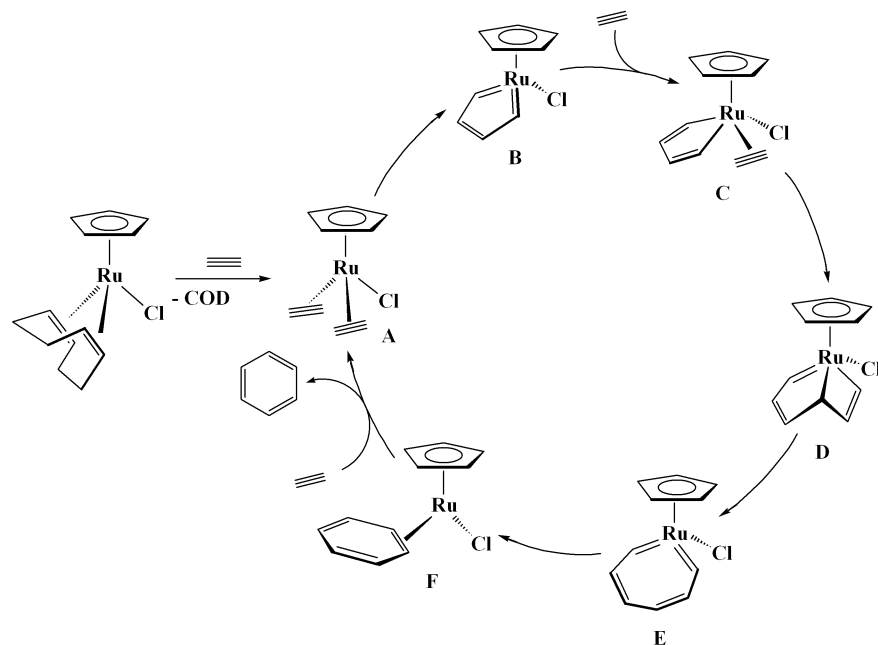
For the structure of **D** we also considered the two alternative possibilities shown in Chart 1. The first would follow a classical insertion of an alkyne into the Ru–C $_{\alpha}$  single bond of **C** to give the coordinatively unsaturated metallacycloheptatriene **G**. Such species have indeed been frequently proposed as intermediates in cyclotrimerization reactions of alkynes referred to as Schore's mechanism.<sup>5</sup> Notice that **G** differs from the coordinatively saturated biscarbenic intermediate **E** (see Scheme 5 below).

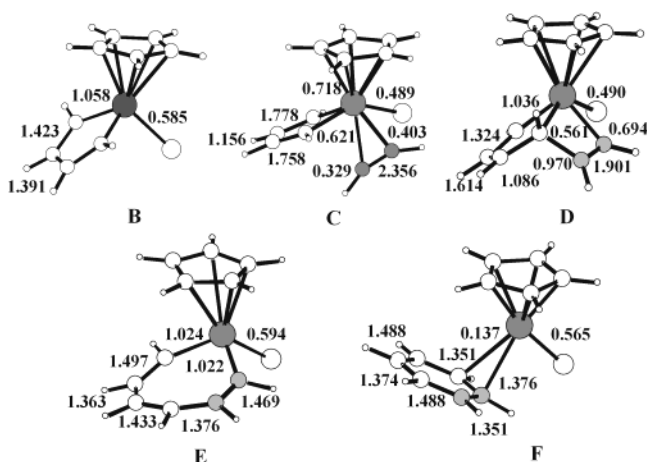
The other one is the metallanorbadiene **H**. For the present system, however, we were unable to locate stationary points for any of them at the DFT/B3LYP level. It should be mentioned in this context that arene formation via a reductive elimination

from **G** as well as from **H** is symmetry-forbidden (if  $C_3$  symmetry is maintained) and thus energetically prohibitive. This has also been noted for the related CoCp system.<sup>8</sup> By the same token, the intermediacy of a cyclobutadiene complex<sup>8,25,26</sup> can be ruled out. The activation energy ( $>50$  kcal mol<sup>-1</sup>) involved in its formation (or destruction if the reaction is to proceed) is much higher than the energies calculated across the path of Figure 1. A detailed discussion will be given elsewhere.<sup>26</sup> In the present case, the energetically favorable formation of benzene takes place in two successive steps as shown in Figure 4.

First, the central Ru–C bond is cleaved, yielding the metallacycle **E**, which undergoes facile reductive elimination to give **F** containing an  $\eta^2$ -coordinated benzene ligand. Complex **E** features an unusual nonplanar asymmetric seven-membered metallacyclic moiety with two short Ru=C bonds (1.93 and 1.91 Å). The strengthening of these bonds compensates for the

**Scheme 5.** Catalytic Cycle for the Cyclotrimerization of Acetylene Mediated by [RuCpCl(HC≡CH)<sub>2</sub>]<sup>+</sup> (**A**).





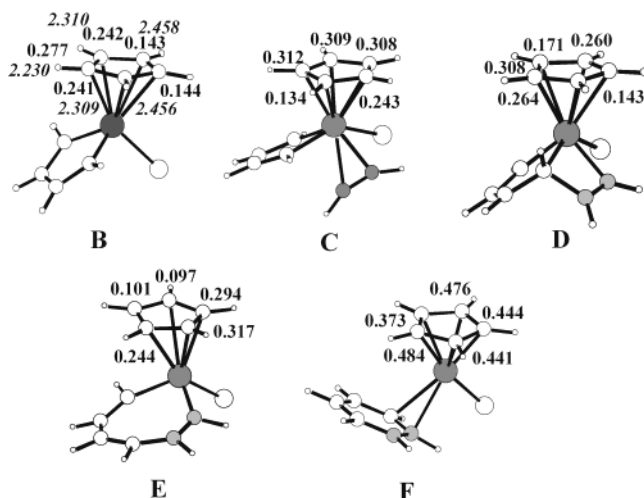
**Figure 5.** Wiberg indices (WIs) for the bonds involving the metallacycle in the intermediates **B** to **F** for the cyclotrimerization of acetylene.

loss of the other Ru–C bond. The C–C bond distances within the metallacycle are very similar, ranging from 1.39 to 1.41 Å. The Ru–Cl distance is essentially the same as the one in **B** (2.34 Å), while it is longer (ca. 0.1 Å) in the other species **C** and **D**, in which Ru is engaged in more bonds.

In the following, we shall characterize the progress of reaction by NPA (natural population analysis<sup>27</sup>) using Wiberg indices (WI).<sup>28</sup> Instead of distances, the WIs measure the bond strengths allowing easy comparisons of equivalent bonds within the reacting molecules. They are also more sensitive to a change in bond order than are distances. The respective values for the complexes **B** to **F** are shown in Figure 5.

The Ru–C carbenic bonds in the intermediates **B**, **D**, and **E** exhibit WIs greater than unity, whereas the Ru–C(metallacycle) single bonds in **C** and **D** are characterized by numbers between 0.5 and 0.7. Interestingly, the Ru–C(alkyne) bonds, with WIs of 0.329 and 0.403, are weaker. Even weaker are the two symmetrical Ru bonds to the  $\eta^2$ -coordinated benzene ring in the final species **F**. The C–C bonds are changing in a related way. A WI of 2.250 is found for the alkyne C≡C bond in the transition state **TS<sub>CD</sub>**, indicating a barely activated triple bond (WI of free acetylene is 2.993). It has not weakened significantly from **C** (2.36), although it becomes closer to a double bond in **D** (1.90). For comparison, the WI of free ethylene is 2.039. Notice that the C–C bonds in the metallacycle are weaker as expected, featuring an alternation of single and double bonds in **C**, but otherwise exhibiting a stronger delocalization, especially in **E**. The incipient C···C bond formed in **TS<sub>EF</sub>** is characterized by a very low WI of 0.297, in agreement with the long distance calculated, similarly to the Ru···C bond breaking in **TS<sub>DE</sub>** (WI = 0.192).

The role of the cyclopentadienyl ring should also be appreciated. A closer look at the Ru–C(Cp) distances and the respective



**Figure 6.** WIs for the Ru–C(Cp) bonds in the intermediates **B** to **F** in the cyclotrimerization of acetylene, and Ru–C(Cp) distances (italics) in **B**.

WIs (Figure 6) reveals that these vary significantly while the reaction proceeds.

The five Ru–C bonds in **B** range between 2.23 and 2.46 Å, with the respective WIs varying from 0.277 for the shorter and stronger bond to 0.143 for the longer and weaker bond. This coordination mode can be considered typical of  $\eta^5$  Cp in a distorted environment. The addition of acetylene introduces an even larger asymmetry in **C**, but the ring becomes more strongly bound to the metal. When **D** is formed, there are small changes of the Ru–C bond lengths, those to the Cp becoming slightly weaker on average. The relatively short contact between the hydrogen from the metallacycle (see Figure 3, right) and the Cp ring does not affect these bonds. Most interesting is intermediate **E** insofar as it reveals a notable asymmetry of the Cp bonding, or, in other words, ring slippage. The coordination of the ring is no longer  $\eta^5$ , because there are two very weak Ru–C(Cp) bonds (WI 0.097 and 0.101; distances 2.721, 2.670 Å) and only three normal ones (WI 0.244, 0.294, 0.317; distances 2.196, 2.311, 2.391 Å), but it is still far from a typical  $\eta^3$  coordination, where two Ru–C distances should be close to 3 Å. This ring can be considered as having a hapticity between  $\eta^3$  and  $\eta^5$ , as has been described in other systems.<sup>29</sup>

Judging from the Ru=C and Ru–Cl bond distances one would expect **E** to be reluctant to a reductive elimination, as is **B**. But the loss of symmetry, reflected in the asymmetric bonds of Ru to the carbon atoms in Cp ring, facilitates subsequent C–C coupling in sharp contrast to **B**. On the other hand, the WI sums are comparable in **B** (1.047) and **E** (1.053) a finding which might erroneously point to an overall similar Ru–Cp binding in the two metallacycles. The larger bite angle of the metallacycle in **E** prevents the Ru–C interactions to be the same as in **B**.

The final complex **F** looks surprising, in what concerns the 18e rule, because the benzene is  $\eta^2$ -bonded rather than  $\eta^4$ . The two Ru–C bonds are long (2.52 Å), with a WI of 0.137, which is less than the incipient bonds in **TS<sub>DE</sub>** and **TS<sub>EF</sub>**. Notice, however, that all of the five Ru–C(Cp) bonds in **F** have significantly contracted as reflected by the WIs given in Figure

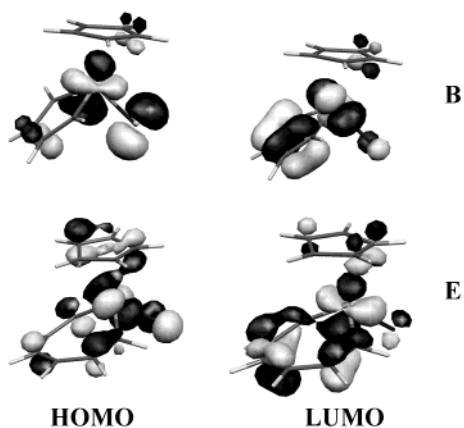
(25) Lippmann, E.; Kerscher, T.; Aechter, B.; Robl, C.; Beck, W.; Price, D. W.; Metz, M.; Hofmann, P. *J. Organomet. Chem.* **1998**, 556, 207.

(26) Veiros, L. F.; Calhorda, M. J.; Kirchner, K., manuscript in preparation.

(27) (a) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1988**, 169, 41. (b) Carpenter, J. E. *Ph.D. Thesis*, University of Wisconsin (Madison WI), **1987**. (c) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, 102, 7211. (d) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, 78, 4066. (e) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, 78, 1736. (f) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, 83, 735. (g) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899. (h) Weinhold, F.; Carpenter, J. E. *The Structure of Small Molecules and Ions*; Plenum: New York, 1988, 227.

(28) Wiberg, K. B. *Tetrahedron* **1968**, 24, 1083.

(29) Stoll, M. E.; Belanzoni, P.; Calhorda, M. J.; Drew, M. G. B.; Félix, V.; Geiger, W. E.; Gamelas, C. A.; Gonçalves, I. S.; Romão, C. C.; Veiros, L. F. *J. Am. Chem. Soc.* **2001**, 123, 10 595.



**Figure 7.** HOMO and LUMO of the intermediates **B** and **E** in the cyclotrimerization of acetylene.

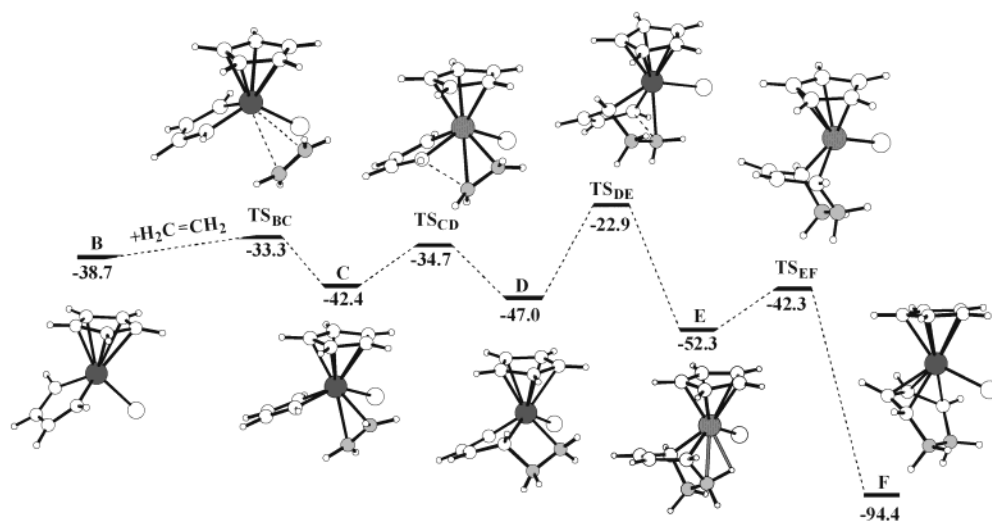
6 and by the distances (ca. 2.14 Å). As an important consequence, the two Ru–C arene bonds are easily replaced, even by an alkyne molecule, with regeneration of the catalyst. The reactivity of  $\eta^2$ -benzene has been discussed in other systems as

well.<sup>6c</sup> In the transition states, the Ru–C(Cp) rings are stronger than in the intermediates, making up for the loss of other bonds to ruthenium. It is noteworthy that in the isoelectronic CoCp system an 18e  $\eta^4$ -benzene complex has been calculated to be the final species in the catalytic cycle.<sup>8</sup>

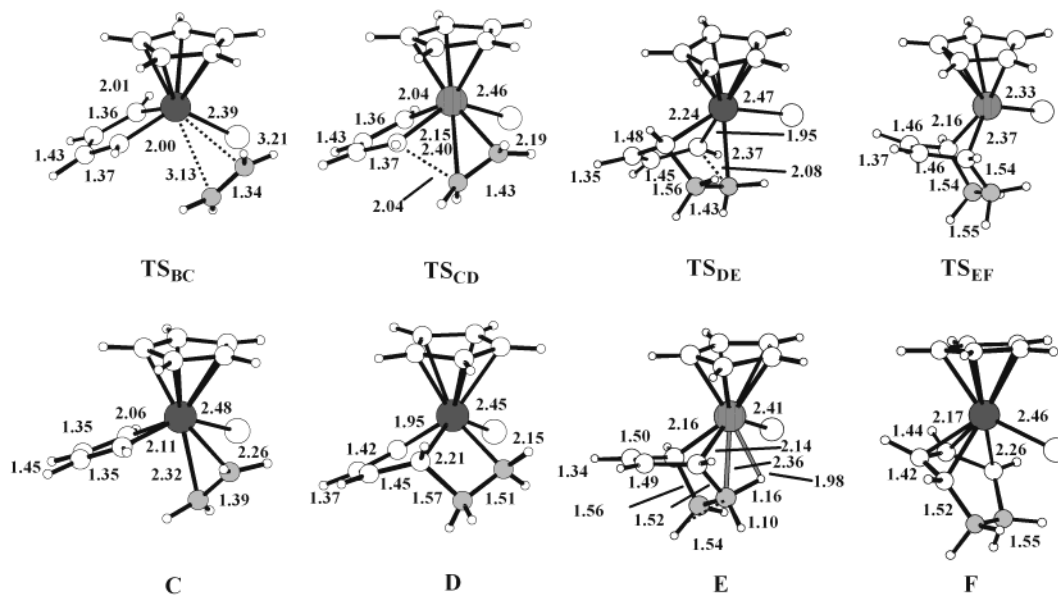
Clearly, the key steps in acetylene cyclotrimerization are the two metallacycles **B** and **E**, whose properties are very divergent, as a consequence of their frontier orbitals (Figure 7).

Indeed, for complex **B**, the HOMO is not localized on the terminal carbon atoms of the metallacycle, while the LUMO is antibonding between them. This explains why there is no tendency to form a cyclobutadiene, whereas the strong localization of these orbitals on ruthenium favors the coordination of acetylene or another molecule. The frontier orbitals of **E** are both bonding between the two terminal carbon atoms of the metallacycle ( $\alpha$  carbon atoms) thus favoring the creation of a new C–C bond between them to give benzene.

Summing up, the catalytic cycle outlined in Scheme 5 is proposed. Completion of the cycle is achieved via the reaction  $\mathbf{F} + 2 \text{HC}\equiv\text{CH} \rightarrow \text{benzene} + \mathbf{A}$ , which is exothermic by

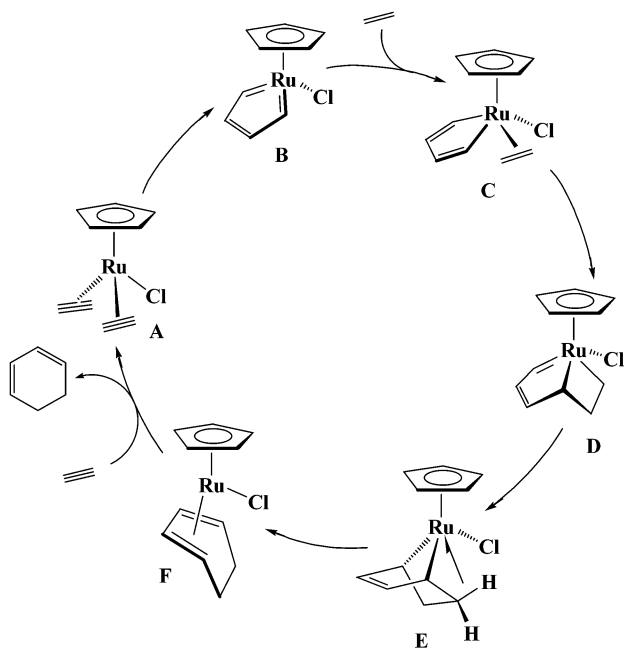


**Figure 8.** Energy profile for the addition of ethylene to the metallacycle **B** (energies in kcal mol<sup>-1</sup>, relative to the bisacetylene complex, **A**).



**Figure 9.** Relevant distances (Å) in intermediate products and transition states for adding ethylene to the metallacycle **B**.

**Scheme 6.** Catalytic Cycle for the [4+2] Addition of Ethylene to the Metallacycle B.



21.4 kcal mol<sup>-1</sup>. Experimentally, the reaction proceeds under mild conditions, namely at, or even below, room temperature.<sup>12</sup>

**Ethylene and the Metallacyclopentatriene—A [4+2] Reaction.** Let us now discuss the differences in behavior when ethylene is added to **B** instead of acetylene. The most relevant structural features of the intermediate products and transition states are presented in Figures 8 and 9.

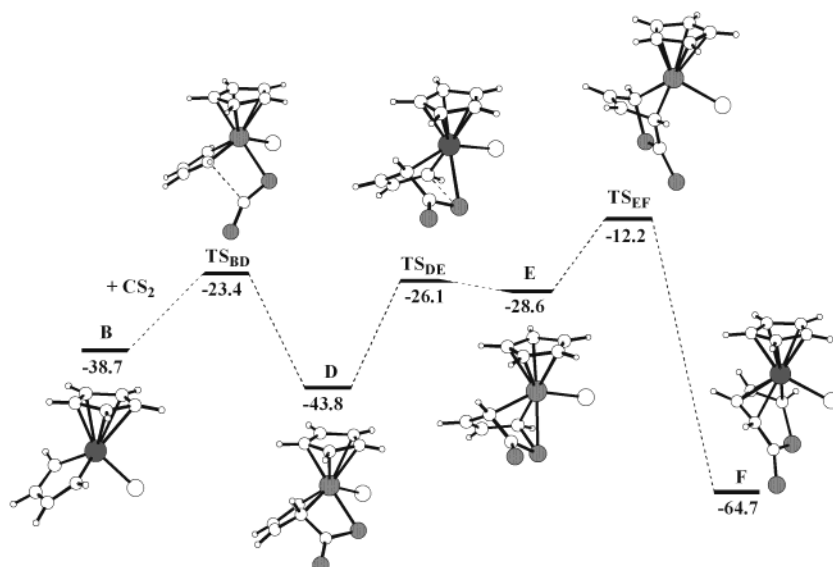
In the initial stages, from **B** to **D**, the behavior of ethylene is seen to parallel closely that of acetylene. Some differences are noted, though: (i) the Ru—C distances of coordinated ethylene are slightly longer (2.32 and 2.26 vs 2.23 and 2.20 Å); (ii) ethylene binding is marginally more exothermic (by 1.3 kcal mol<sup>-1</sup>); (iii) the C···C distance in the transition state **TS<sub>CD</sub>** is smaller for ethylene (2.04 vs 2.15 Å); (iv) the step **C** → **D** is kinetically less facile ( $E_a = 7.7$  vs 0.1 kcal mol<sup>-1</sup>) and less

exothermic ( $\Delta E = 4.6$  vs 22.4 kcal mol<sup>-1</sup>) in the ethylene case. This can be rationalized in terms of the carbon atoms having become saturated. Accordingly, the C—C distance in coordinated ethylene points to a single bond (1.51 Å), whereas in acetylene it is a double bond (1.33 Å). Thus, the formation of complex **D** for ethylene is made more difficult by the lack of flexibility introduced by the higher number of hydrogen atoms present, since the steric constraints of the metal environment must be accommodated.

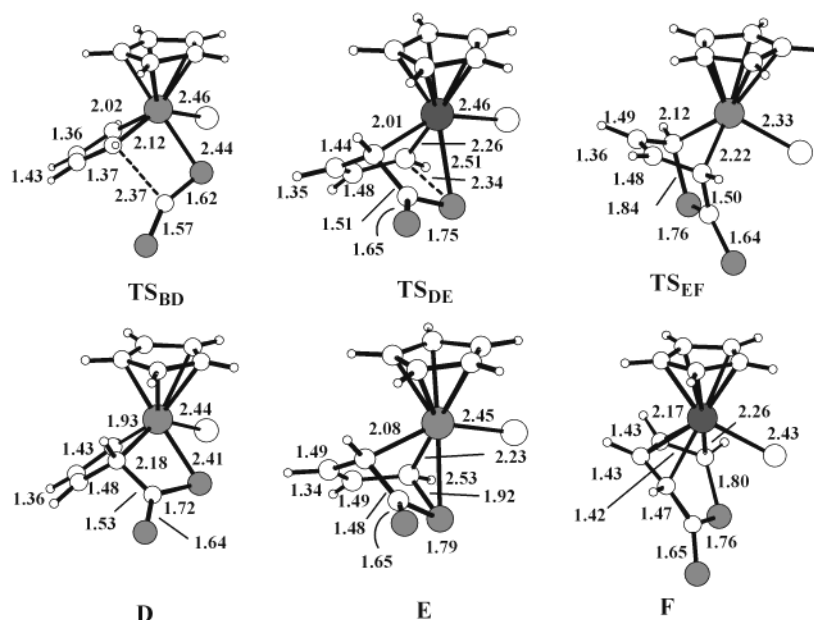
For the onward reaction of **D**, the two systems differ greatly of course, because the carbon atoms stemming from the ethylene molecule are already saturated, making the generation of a metallacycle impossible. Nevertheless, also in the ethylene case there is a C—C bond formed and a Ru—C bond broken, assisted now by the agostic interaction (1.98 Å) which prevents the Ru center from being unsaturated. The Ru···H distance amounts to 2.59 Å already in the transition state **TS<sub>DE</sub>**. The final transformation involves breaking the agostic interaction and converting the di- $\sigma$ -metallacycle into an  $\eta^4$ -cyclohexadiene **F**. At the transition state **TS<sub>EF</sub>**, the Ru—H distance has increased to 2.80 Å. This last step is formally a reductive elimination changing the formal oxidation state from Ru(IV) in **E** to Ru(II) in **F**. The metal NPA charge decreases from 0.444 in **TS<sub>EF</sub>** to 0.304 in complex **F**. The movement from **TS<sub>EF</sub>** to **F** is essentially a slippage of the butadiene from  $\eta^2$ -coordinated (through its terminal carbons) to  $\eta^4$ -butadiene, a species which exhibits a mirror plane (despite the calculations having been performed without any symmetry constraints). Finally it may be remarked that the conversion barriers for the steps **D** → **E** and **E** → **F** are higher by 19.9 and 8.2 kcal mol<sup>-1</sup>, respectively, for the ethylene case than for acetylene.

Likewise, the completion of the catalytic cycle given by **F** + 2 HC≡CH → cyclohexadiene + **A** is less exothermic (4.2 kcal mol<sup>-1</sup>) than the corresponding part in the acetylene system. A proposal for a catalytic cycle of cyclohexadiene formation from two molecules of alkyne and one molecule of alkene is presented in Scheme 6.

**CS<sub>2</sub> and the Metallacyclopentatriene — a [4+2] Reaction.** The last reaction studied is the addition of a C=S bond to **B**. This type of reaction is relevant since the generation of many



**Figure 10.** Energetic profile for the addition of carbon disulfide to the metallacycle **B** (energies in kcal mol<sup>-1</sup>, relative to the bisacetylene complex, **A**).



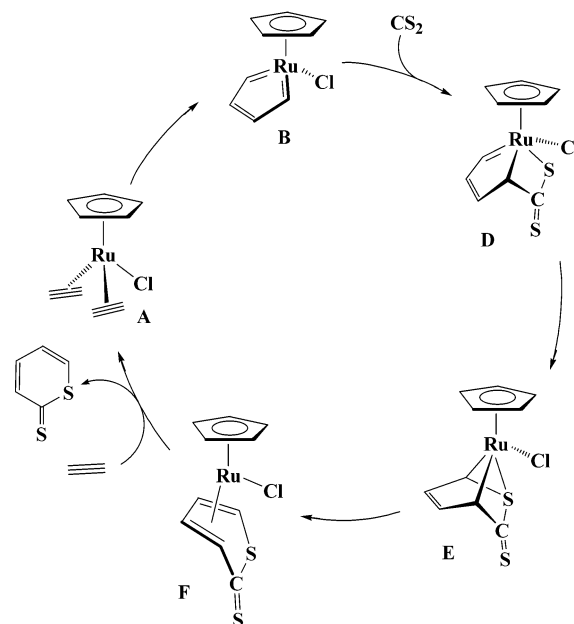
**Figure 11.** Relevant distances (Å) in intermediate products and transition states for adding CS<sub>2</sub> to the metallacycle **B**.

unsaturated organic ring compounds is achieved through the reaction of unsaturated substrates of several kinds (C=S, C≡N, etc) with the appropriate metallacycle.<sup>13,14</sup> The reaction of **B** with CS<sub>2</sub> differs from the two others in that there is no coordination of the molecule to the ruthenium center prior to coupling. Instead, the C=S bond adds in an almost concerted fashion to the Ru=C bond of the metallacycle, to afford in only one step the intermediate controlling the stereochemistry of the addition, which we will still call complex **D** (in this path there is no complex analogous to **C**). The energetic profile and the geometries of the entities involved are shown in the Figures 10 and 11.

In **D**, the two bonds Ru–S (2.41 Å) and C–C (1.53 Å) are formed. This is noteworthy because in the transition state **TS<sub>BD</sub>** the carbon disulfide is close to η<sup>1</sup>-coordinated with the C⋯C distance being still very long (2.37 Å), indicating at most a weak interaction. The two C=S distances are already different, because the binding of S to Ru weakens the adjacent C=S bond. In complex **D**, this has become a C–S single bond, whereas the terminal C–S bond is also weakened since the carbon atom is involved in an additional bond. Both C–S distances remain rather unchanged in the subsequent reactions.

The onward reaction of **D** parallels the behavior of the alkene scheme, in that the Ru–S bond is being broken and concomitantly a C–S bond to the other α carbon of the metallacycle is being formed. The transformation of **D** to **E** is essentially a reductive elimination in which a vacant coordination site is created. In the corresponding reaction of alkenes this vacant coordination site is occupied by an agostic interaction, whereas in the CS<sub>2</sub> system no such possibility is available except a Ru–S interaction which is weak owing to the unfavorable position of the sulfur lone-pair. Although its length of 2.53 Å might point to a genuine bond the low WI of 0.087 tells the contrary (for comparison, the Ru–S bond in **D** is 2.41 Å long and has a WI of 0.597). As a consequence, the reaction of **D** to **E** is appreciably endothermic (15.2 kcal mol<sup>-1</sup>, Figure 10), unlike the corresponding conversion in the olefin system (Figure 8). The transition state **TS<sub>DE</sub>** largely resembles **E** having a sulfur

**Scheme 7.** Catalytic Cycle for the [4+2] Addition of CS<sub>2</sub> to the Common Metallacycle Intermediate **B**.



atom in a pyramidal environment, with the C–S bond partly formed and the Ru–S bond still strong (only 0.1 Å longer than in **D**). The C–S bond in **E** is already a normal bond, although on the long side (1.92 Å). It becomes a typical C–S bond (1.80 Å) in the final species **F**, when the Ru–S bond has vanished and ruthenium binds a η<sup>4</sup>-thiopyrane-2-thione. The transformation of **E** into **F** starts indeed by cleaving the Ru–S bond (already achieved in the transition state **TS<sub>EF</sub>**), followed by a pivoting of the butadiene moiety, moving it from di-σ to η<sup>4</sup>-coordinated.

The overall reaction **F** + 2 HC≡CH → thiopyrane-2-thione + **A** is exothermic by 17.9 kcal mol<sup>-1</sup>, closer to the alkyne than to the alkene reaction. A catalytic cycle for the addition of carbon disulfide to **B** is shown in Scheme 7.



## Conclusions

Upon summarizing the present theoretical study of the acetylene trimerization catalyzed by the CpRuCl fragment, some general conclusions can be drawn and compared with those from the study of Albright and co-workers of the CpCo system.<sup>8</sup> The formulation of the metallacycle **B** appearing as the first key intermediate from oxidative coupling of two alkyne ligands can vary with the metal fragment: with CpRuCl it is a metallacyclopentatriene, but with CpCo it is a metallacyclopentadiene. Both complexes add another alkyne in  $\eta^2$  fashion (giving intermediate **C**), but the mode of subsequent arene formation differs markedly. For the CpCo system, direct rearrangement to CpCo( $\eta^4$ -C<sub>6</sub>H<sub>6</sub>) has been suggested. In the CpRuCl system, in contrast, no less than three further intermediate products could be located. First, a novel bicyclic ring system (**D**) is formed, rearranging next to an unsymmetrical metallaheptatetraene complex (**E**). Owing to its asymmetry, the final reductive elimination to give RuCpCl( $\eta^2$ -C<sub>6</sub>H<sub>6</sub>) (**F**) is no longer symmetry-forbidden.

The differences between the two systems, namely the larger variety of intermediates envisaged for the ruthenium system as compared to cobalt, may be partly related to the atomic radii. The smaller radius of Co (1.25 vs 1.33 Å for Ru)<sup>30</sup> may control interligand interactions (through-space coupling)<sup>31</sup> in a different way. In this respect it might be relevant to undertake investigations on the rhodium analogue CpRh.

Finally, it is interesting to see the many parallels between the reactivity of **B** toward acetylene, ethylene and carbon sulfide, the latter being taken as a model for a molecule lacking hydrogen atoms. Since new bonds to these incoming molecules are formed, the bonds between the metal and the former cycle are weakened. The tuning of the strengths of these Ru–C bonds is a critical factor for the course of the catalytic pathway, and is complemented by the Ru–C bonds to the ring. Also, in the case of the coordinated alkene facile C–C coupling to the  $\alpha$  carbon of the metallacycle becomes feasible owing to an agostic assistance which tends to counterbalance the reduced degree of saturation at the metal. Carbon disulfide, on the other hand, does not coordinate to ruthenium, but instead adds directly to the Ru=C bond. The resulting complexes (**D**) play a determining role in the stereoselectivity control of the reaction. It would

appear that the steric repulsion between hydrogen atoms in the Cp ring and in the metallacycle has a notable influence on the outcome of the coupling of the two initial acetylene molecules. The final steps of the conversion of **D** into the final species are energetically more favorable for acetylene.

## Computational Details

All calculations were performed using the Gaussian 98 software package<sup>32</sup> on the Silicon Graphics Cray Origin 2000 of the Vienna University of Technology, at IST and ITQB. The geometry and energy of the model complexes and the transition states were optimized at the B3LYP level<sup>21</sup> with the Stuttgart/Dresden ECP (sdd) basis set<sup>33</sup> to describe the electrons of the ruthenium atom. For all other atoms the 6-31G\*\* basis set was employed.<sup>34</sup> Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides, and obtaining the minima presented on the reactions energy profile. All geometries were optimized without constraints (C<sub>1</sub> symmetry) and the energies were zero point corrected. Relative energies were compared taking into account the total number of molecules present. A Natural Population Analysis (NPA)<sup>27</sup> and the resulting Wiberg indices<sup>28</sup> were used for a detailed study of the electronic structure and bonding of the optimized species.

**Acknowledgment.** Financial support by the “Fonds zur Förderung der wissenschaftlichen Forschung” is gratefully acknowledged (Project No. P14681-CHE). M.J.C. and K.K. thank Acordo Cultural Luso-Austriaco.

JA035137E

(30) Ping, M.; Xiubin, L.; Yuankai, W. *J. Chem. Educ.* **1990**, *67*, 218.

(31) Sapunov, V. N.; Schmid, R.; Kirchner, K.; Nagashima, H. *Coord. Chem. Rev.* **2003**, in press.

- (32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (33) (a) Haeusermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *78*, 1211. (b) Kuechle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994**, *100*, 7535. (c) Leininger, T.; Nicklass, A.; Stoll, H.; Dolg, M.; Schwerdtfeger, P.; *J. Chem. Phys.* **1996**, *105*, 1052.
- (34) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209. (d) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163. (e) Hariharan, P. C.; Pople, J. A. *Theo. Chim. Acta* **1973**, *28*, 213.