PAPER

NJC
www.rsc.org/njc

Mechanism of the ruthenium-catalyzed formation of pyrane-2-one and their sulfur and selen analogs from acetylene and CX_2 (X = O, S, Se): a theoretical study†

Georg Dazinger, Roland Schmid and Karl Kirchner*

Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060, Vienna, Austria. E-mail: E-mail: kkirch@mail.zserv.tuwien.ac.at

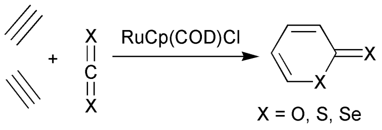
***Received** (in Montpellier, France) 9th July 2003, Accepted 19th September 2003*
First published as an Advance Article on the web 28th November 2003

Complete catalytic cycles for the (actual or potential) cycloaddition of acetylene with CX_2 (X = O, S, Se), mediated by CpRu(COD)Cl as the precatalyst, are proposed on the basis of DFT/B3LYP calculations. The common initial step is the replacement of labile COD by two molecules of acetylene to afford a bisacetylene complex. Oxidative coupling of the acetylene ligands results in the formation a coordinatively saturated metallacyclopentatriene complex. This metallacycle adds the C=X bond of CX_2 directly to the Ru=C bond in a concerted fashion, forming an unusual bicyclic carbene intermediate. The activation energies for this addition are 14.2, 15.3 and 30.0 kcal mol^{-1} for X = O, S and Se, respectively, thus rendering the CSe_2 addition the most difficult. In a subsequent reductive elimination a coordinatively unsaturated metallaheteronorbornene intermediate is formed, which eventually rearranges into RuCpCl complexes bearing pyrane-2-one, thiopyrane-2-thione and selenopyrane-2-selenone ligands coordinated in an η^4 fashion. The energy barrier for the reductive elimination step decreases in the order O > S > Se, being 28.1, 17.7 and 14.6 kcal mol^{-1}, respectively. Overall, the reaction with CS_2 is thus the most favorable. Completion of the cycles is achieved by an exothermic displacement of the respective heterocyclic product by two acetylene molecules, regenerating the bisacetylene complex.

Introduction

The seminal tool that the chemist uses to systematize elemental relationships is the periodic table. Its function is to serve as a framework, as an organizational outline , for the vast and widely diversified information of chemistry. By analyzing the changes in reactivity down a group the behavior of the individual elements is more fully appreciated. This is all the more relevant since it is commonly a combination of factors that are responsible for a particular outcome, for instance, why HF is a much weaker acid than HCl,[1] or why BF_3 is a weaker Lewis acid than BCl_3 .[2]

In the present contribution we focus on the cyclotrimerization of two alkynes with an unsaturated compound, catalyzed by RuCpCl, according to Scheme 1.



Scheme 1

Of these transformations, the reaction with CS_2 has been realized, in fact, recently by Itoh and coworkers, resulting in thiopyrane-2-thiones.[3] Likewise, isocyanates[4] and isothiocyanates[3] have been reacted, giving pyridine-2-ones and thiopyrane-2-imines. Such transition-metal-mediated C–S bond formations would seem highly unusual in view of the strong metal–sulfur bonds prone to deactivate the catalyst. In fact, so far only the ruthenium complexes RuCp(COD)X and RuCp*(COD)X (X = Cl, Br) have proved to be suited for this undertaking.

For the underlying reaction mechanism, Itoh *et al.*[3] invoked a metallacyclopentadiene as a key intermediate. Detailed DFT calculations, however, from our collaboration on similar systems point to the intermediacy of a metallacyclopentatriene complex that is able to easily add a C=S bond of CS_2 in a concerted [2 + 2] fashion directly to the Ru=C double bond.[5,6] Based on this experience we will investigate here, by means of DFT/B3LYP calculations,[7,8] whether the analogous insertions of CO_2 and CSe_2 are conceivable and what atomic properties determine the reactivities. A better understanding of such cyclotrimerizations is desirable since these processes are not only metal-economic but also synthetically useful for obtaining six-membered heterocyclic systems.[9–12] In addition, carbon dioxide is an abundant source of carbon.

Results and discussion

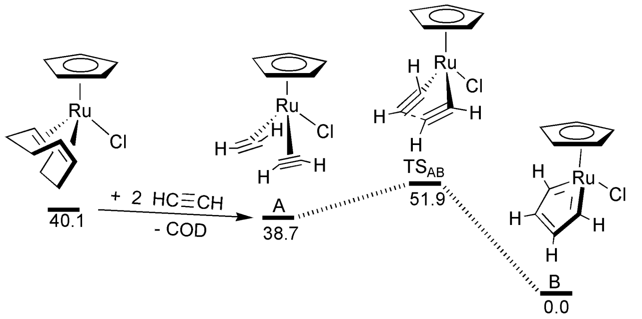
The cyclotrimerization of two molecules of acetylene and CS_2 at RuCp(COD)Cl has been analyzed in detail previously.[6] The initial step is the replacement of labile COD in the Ru complex by two molecules of acetylene to afford, *via* the bisacetylene complex **A**, the metallacyclopentatriene **B** as a result of facile oxidative coupling (Scheme 2, energies in kcal mol^{-1}).

In analogy to CS_2 , **B** also easily adds one C=O bond of the incoming CO_2 molecule in an almost concerted [2 + 2] fashion directly to the Ru=C bond to afford the bicyclic intermediate **C**. This is slightly endothermic, requiring an activation energy of 14.2. kcal mol^{-1} (*cf.* slightly exothermic with an activation energy of 15.3 kcal for CS_2). The energetic profile and the

---

† Electronic supplementary information (ESI) available: coordinates and total energy of the complexes **C**, **D**, **E** and transition states $\mathbf{TS_{BC}}$, $\mathbf{TS_{CD}}$, $\mathbf{TS_{DE}}$. See http://www.rsc.org/suppdata/nj/b3/b307843d/

DOI: 10.1039/b307843d



Scheme 2

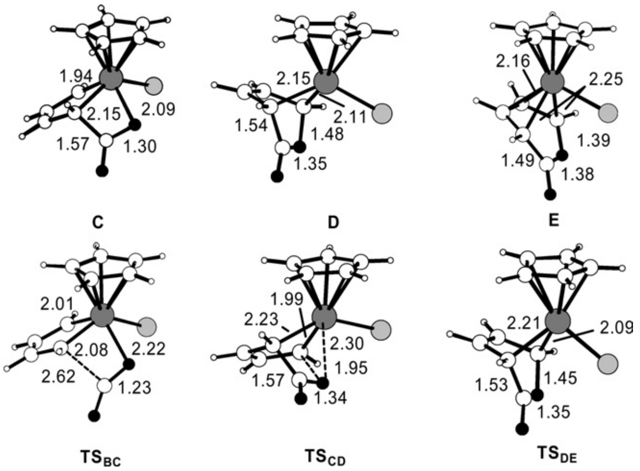


Fig. 1 Optimized B3LYP geometries of the equilibrium structures **C**, **D**, **E** and the transition states $\mathbf{TS_{BC}}$, $\mathbf{TS_{CD}}$, $\mathbf{TS_{DE}}$ (distances in Å) for the reaction of **B** with CO_2.

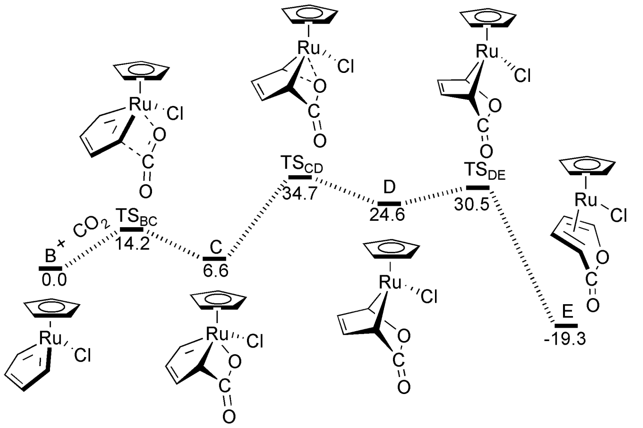
geometries involved are shown in Scheme 3 and Fig. 1. In **C**, two new bonds, Ru–O (2.09 Å) and C–C (1.57 Å), are formed. This is noteworthy since in the transition state $\mathbf{TS_{BC}}$ the carbon dioxide is close to η^1-coordinated with the C···C distance still being very long (2.10 Å), indicating an, at best, weak interaction. The two C=O distances are different because the binding of O to Ru weakens the adjacent C=O bond. In going to **C**, the latter becomes a C–O single bond, while the terminal C–O bond is also weakened since the carbon atom is involved in an additional bond. Both C–O distances remain largely unchanged in the subsequent reactions.

In the onward reaction of **C** the Ru–O bond is eventually broken and concomitantly a C–O bond to the other α carbon of the metallacycle is formed. The transformation of **C** to **D** is essentially a reductive elimination in which a vacant coordination site is created and **D** may be considered as an unsaturated metallaheteronorbornene complex. If the incoming ligand is an alkene[6] this vacant site becomes involved in an agostic interaction. In the present case of CO_2 attack, of course, no such possibility is available apart from a weak Ru–O interaction with the unfavorably positioned oxygen electron lone pair. Therefore, the reaction of **C** to **D** is appreciably endothermic (18.0 kcal mol^{-1}) with a relatively high activation energy (28.1 kcal mol^{-1}). In the case of CS_2 a much smaller activation energy of 17.7 kcal mol^{-1} is needed for the reductive elimination. This difference may be traced to the different atomic radii of O and S (0.66 *vs.* 1.07 Å[13]) controlling the interatomic interactions. The transition state $\mathbf{TS_{CD}}$ largely resembles **D**, having an oxygen atom in a pyramidal environment with the C–O bond partly formed and the Ru–O bond already weakened (0.21 Å longer than in **C**). The C–O bond in **D** is already a normal bond, although on the long side (1.48 Å). It becomes a typical C–O bond (1.39 Å) in the final species **E**, when the Ru–O bond has completely broken and ruthenium binds an η^4-pyrane-2-one. The transformation of **D** into **E** starts with pivoting of the butadiene moiety, moving it from di-σ- to η^4-coordinated as in the CS_2 system. Completion of the cycle is achieved *via* the reaction **E** + 2 HC≡CH → pyrane-2-one + **A**, , which is exothermic by 14.7 kcal mol^{-1} (*cf.* 17.9 kcal mol^{-1} for the CS_2 system).

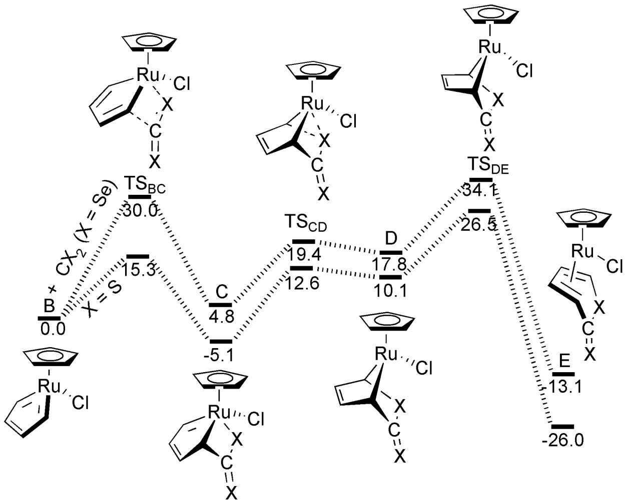
Let us now turn to the reaction of **B** with CSe_2. The energetic profile and the geometries of the species involved are displayed in Scheme 4 and Fig. 2, respectively. While the intermediates **C**, **D** and **E** and the transition states connecting them are very similar to the CO_2 and CS_2 analogs, the energies involved are not. Note that the activation energy required for inserting the C=Se bond into the Ru=C bond of **B** is twice as high (30.0 kcal mol^{-1} *vs.* 14.2 for CO_2 and 15.3 for CS_2). This implies that CSe_2 is a much weaker nucleophile towards ruthenium. The catalytic cycle is completed *via* the reaction **E** + 2 HC≡CH → selenopyrane-2-selenone + **A**, which is exothermic by 17.1 kcal mol^{-1}. The catalytic cycle for the addition of CX_2 (X = O, S, Se) to **B** is shown in Scheme 5.

Conclusions

According to the present DFT/B3LYP calculations the mechanisms of the hypothesized cyclotrimerization of alkynes with CO_2, CS_2 and CSe_2 catalyzed by the CpRuCl fragment should be very similar. The metallacyclopentatriene **B**, appearing as a common key intermediate from oxidative coupling of



Scheme 3



Scheme 4

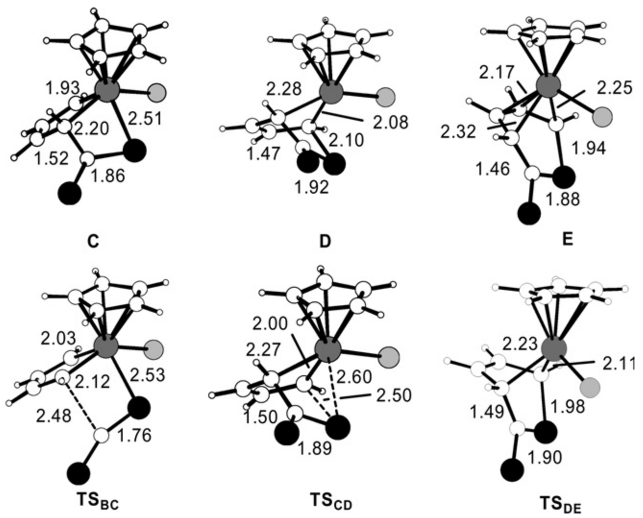
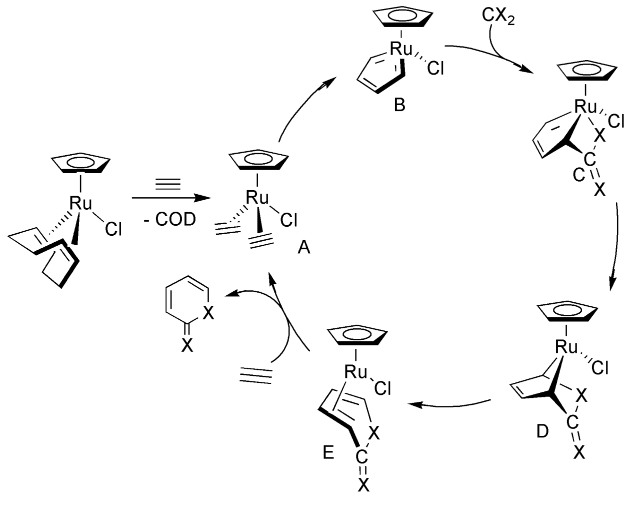


Fig. 2 Optimized B3LYP geometries of the equilibrium structures **C**, **D**, **E** and transition states $\mathbf{TS_{BC}}$, $\mathbf{TS_{CD}}$, $\mathbf{TS_{DE}}$ (distances in Å) for the reaction of **B** with CSe_2.

two alkyne ligands, is capable of adding CX_2 in a concerted fashion to the Ru=C bond to give a new bicyclic carbene intermediate **C**. However, there are notable energetic differences. Whereas the barrier for the [2 + 2] addition of a C=X bond to the Ru=C bond of **B** is low in the case of X = O and S, for X = Se the addition is the rate-limiting step. Conversely, the subsequent reductive elimination (**C** → **D**) is facile for X = S and Se but difficult for X = O, in which case the transformation of a Ru–O into a C–O bond is unfavorable and constitutes the rate-determining step. Therefore, the overall reaction with CS_2 is the most favorable.

Theoretical

All calculations were performed using the Gaussian 98 software package[14] on a Silicon Graphics Cray Origin 2000 at the Vienna University of Technology. The geometry and energy of the model complexes and the transition states were optimized at the B3LYP level with the Stuttgart/Dresden ECP (sdd) basis set[15] to describe the electrons of the ruthenium atom. For all other atoms the 6-31G** basis set was employed.[16] 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 reaction energy profiles. All geometries were optimized without constraints (C_1 symmetry) and the energies were zero-point corrected. Relative energies were compared taking into account the total number of molecules present.



Scheme 5

Acknowledgement

Financial support by the "Fonds zur Förderung der wissenschaftlichen Forschung" is gratefully acknowledged (Project No. P14681-CHE).

References

1 R. Schmid and A. M. Miah, *J. Chem. Educ.*, 2001, **78**, 116.
2 H. Hirao, K. Omoto and H. Fujimoto, *J. Phys. Chem. A*, 1999, **103**, 5807.
3 Y. Yamamoto, H. Takagishi and K. Itoh, *J. Am. Chem. Soc.*, 2002, **124**, 28.
4 Y. Yamamoto, H. Takagishi and K. Itoh, *Org Lett.*, 2002, **13**, 2117.
5 M. J. Calhorda, K. Kirchner and L. F. Veiros, in *Perspectives in Organometallic Chemistry*, eds. C. G. Screttas and B. R. Steele, The Royal Society of Chemistry, Cambridge, 2003, p. 111–119.
6 K. Kirchner, M. J. Calhorda, R. Schmid and L. F. Veiros, *J. Am. Chem. Soc.*, 2003, **125**, 11 721.
7 R. G. Parr and Y. Wang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.
8 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett*, 1989, **157**, 200; (*b*) C. Lee, W. Yang and G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
9 (*a*) P. Hong and H. Yamazaki, *Tetrahedron Lett.*, 1977, **18**, 1333; (*b*) P. Hong and H. Yamazaki, *Synthesis*, 1977, 50; (*c*) R. A. Earl and K. P. C. Vollhardt, *J. Org. Chem.*, 1984, **49**, 4786; (*d*) P. Diversi, G. Ingrosso, A. Lucherini and S. Malquori, *J. Mol. Catal.*, 1987, **40**, 267.
10 (*a*) H. Hoberg and B. W. Oster, *Synthesis*, 1982, 324; (*b*) H. Hoberg and B. W. Oster, *J. Organomet. Chem.*, 1982, **234**, C35; (*c*) H. Hoberg and B. W. Oster, *J. Organomet. Chem.*, 1983, **235**, 359.
11 S. T. Flynn, S. E. Hasso-Henerson and A. W. Parkins, *J. Mol. Catal.*, 1985, **32**, 101.
12 (*a*) Y. Wakatsuki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 1973, 280; (*b*) H. Yamazaki, *J. Synth. Org. Chem. Jpn.*, 1987, **45**, 244.
13 C. H. Suresh and N. Koga, *J. Phys. Chem. A*, 2001, **105**, 5940.
14 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, *GAUSSIAN 98 (Revision A.7)*, Gaussian, Inc., Pittsburgh, PA, 1998.
15 (*a*) U. Haeusermann, M. Dolg, H. Stoll, H. Preuss, P. Schwerdtfeger and R. M. Pitzer, *Mol. Phys.*, 1993, **78**, 1211; (*b*) W. Kuechle, M. Dolg, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1994, **100**, 7535; (*c*) T. Leininger, A. Nicklass, H. Stoll, M. Dolg and P. Schwerdtfeger, *J. Chem. Phys.*, 1996, **105**, 1052.
16 (*a*) A. D. McClean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639; (*b*) R. Krishnan, J. S. Binkley, R. Seeger and J. Pople, *J. Chem. Phys.*, 1980, **72**, 650; (*c*) A. J. H. Wachters, *J. Chem. Phys.*, 1970, **52**, 1033; (*d*) P. J. Hay, *J. Chem. Phys.*, 1977, **66**, 4377; (*e*) K. Raghavachari and G. W. Trucks, *J. Chem. Phys.*, 1989, **91**, 2457; (*f*) M. P. McGrath and L. Radom, *J. Chem. Phys.*, 1991, **94**, 511.