CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: A Computational Study of the Intermolecular [2+2+2] Cycloaddition of Acetylene and C60 Catalyzed by Wilkinson's Catalyst

Authors: Albert Artigas, Agustí Lledó, Anna Pla-Quintana, Anna Roglans, and Miquel Solà

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Chem. Eur. J.* 10.1002/chem.201702494

Link to VoR: http://dx.doi.org/10.1002/chem.201702494

Supported by
ACES

WILEY-VCH

10.1002/chem.201702494

WILEY-VCH

FULL PAPER

A Computational Study of the Intermolecular [2+2+2] Cycloaddition of Acetylene and C_{60} Catalyzed by Wilkinson's Catalyst

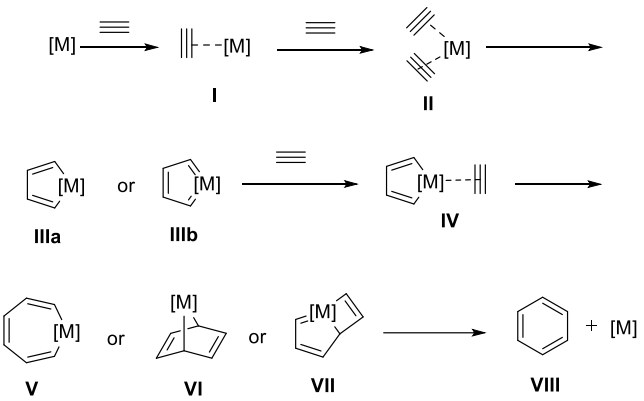
Albert Artigas,[a] Agustí Lledó,[a] Anna Pla-Quintana,[a] Anna Roglans[a] and Miquel Solà*[a]

Abstract: The functionalization of fullerenes helps modulating their electronic and physicochemical properties, generating fullerene derivatives with promising features for practical applications. In this work, we use the density functional theory to explore the attachment of a cyclohexadiene ring to C_{60} via a Rh-catalyzed intermolecular [2+2+2] cycloaddition of C_{60} and acetylene. We analyze all potential reaction paths to conclude that the [2+2+2] cycloaddition of C_{60} and two acetylene molecules catalyzed by $RhCl(PPh_3)_3$ yielding a cyclohexadiene ring fused to a [6,6] bond of C_{60} is energetically feasible.

Introduction

Organic materials are appealing for photovoltaic devices due to the advantages these materials have in comparison with the most commonly used silicon-based systems, such as the low-cost synthesis, easy manufacture, and the possibility to generate flexible, light, and cheap devices.[1] In this regard, fullerenes are attractive organic materials that can efficiently harvest sunlight and transform it into other useful forms of energy. In fact, the production of dye-sensitized solar cells (DSSCs) is currently among the most realistic applications of fullerene derivatives.[2] In the design of DSSCs manufactured using the molecular heterojunction (mHJ) technique,[3] a fullerene, commonly [60]fullerene (C_{60}), is covalently linked to an electron donating group. The use of mHJs allows a better control of the structure of donor and acceptor units and the charge mobility between them.[4] The charge transfer (charge separation and recombination) properties of the donor-C_{60} dyad critically depends on the connection between donor and acceptor.[5] Most of the usual chemical reactions of fullerenes (Diels-Alder, 1,3-dipolar, and Bingel-Hirsch cycloadditions)[6] attach an electron donating group to the fullerenic cages through two C_{sp3}–C_{sp3} bonds. We hypothesize that the communication between donor and acceptor groups could be improved connecting donor and acceptor units through C_{sp3}–C_{sp2} bonds. In this way, the π-system of the cage and electron donor group could interact more effectively by the so-called periconjugation[7] and facilitate charge transfer separation. The transition-metal catalyzed [2+2+2] cycloaddition of C_{60} and two alkynes or a diyne represents a potential way to generate this kind of link between the fullerenic cage and the donor. So far, from a practical point of view, cyclohexadiene-fused fullerene derivatives have been used as synthetic intermediates of the so-called open-cage fullerenes.[8]

The [2+2+2] cycloaddition of three alkynes is an elegant preparative route to polysubstituted benzenes.[9] Scheme 1 shows the widely accepted reaction mechanism for the [2+2+2] cycloaddition of three acetylenes. The reaction begins via a pair of ligand-alkyne substitution reactions. The oxidative addition of the two alkyne ligands in **II** generates a metallacyclopentadiene **IIIa** or a metallacyclopentatriene **IIIb** intermediate. This is commonly the rate-determining step. Subsequent coordination of a third alkyne ligand to **IIIa** or **IIIb** intermediates is followed by either alkyne insertion to form a metallacycloheptatriene **V** (the so-called Schore's mechanism)[10] or metal-mediated [4+2] cycloaddition to yield the metallanorbornadiene **VI** or [2+2] cycloaddition to give a metallabicyclo[3.2.0]heptatriene **VII**. Finally, a reductive elimination of the metal leads to arene **VIII** and recovery of the catalyst. Such [2+2+2] cycloaddition has been also reported between an ene group (or an allene group[11]) and two alkynes or a diyne to yield cyclohexadiene species.[12] Therefore, one can expect that two acetylene molecules could react with C_{60} to generate a six-membered ring attached to C_{60} through two C_{sp3}–C_{sp2} bonds.



Scheme 1. Most widely accepted reaction mechanism for the transition-metal catalyzed [2+2+2] cycloaddition reaction of three acetylenes ([M] = transition metal catalyst).

[a] A. Artigas, Dr. A. Lledó, Dr. A. Pla-Quintana, Prof. Dr. A. Roglans and Prof. Dr. M. Solà
Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química
Universitat de Girona
C/ Maria Aurèlia Capmany, 69, E-17003, Girona, Catalonia, Spain
E-mail: miquel.sola@udg.edu

Supporting information for this article is given via a link at the end of the document.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

10.1002/chem.201702494

In fact, Murata et al.[13] already formed such a link in a reaction of C_{60} with palladacyclopentadiene complexes that provided cyclohexadiene-type adducts. Moreover, some years ago, Cheng et al.[14] reported a nickel-promoted ene-diyne [2+2+2] cycloaddition reaction on C_{60}. As usual for cycloadditions to C_{60},[15] the addition took place in a [6,6] bond. More than stoichiometric amounts of $NiCl_2(PPh_3)_2$ and excess PPh_3 were needed to get a high yield of cycloadduct. In our group, we have been working for many years on [2+2+2] cycloadditions catalyzed by Rh.[9d, 11a] It is well-known that Rh catalysts are very efficient in [2+2+2] cycloadditions.[9] The main goal of this paper is to explore computationally the rhodium-catalyzed [2+2+2] cycloaddition reaction of two acetylene molecules and C_{60} using Wilkinson's catalyst. All possible routes to cycloaddition products are explored by means of density functional theory (DFT) calculations, to ascertain whether it is possible to reach the cycloadducts of the reaction in catalytic conditions. We also aim to gain insight into the regioselectivity of this [2+2+2] cycloaddition reaction and to have a deeper knowledge of the reaction mechanism, in particular, we pursue to uncover the intermediates present in the process. The results obtained will guide future experimental attempts in our group to carry out the [2+2+2] cycloaddition to C_{60} and higher fullerenes and endohedral metallofullerenes.

Computational Details

Geometries of the reactants, intermediates, transition states (TSs), and products were optimized with the Gaussian 09 program[16] using the DFT B3LYP[17] hybrid exchange-correlation functional. All geometry optimizations were performed without symmetry constraints. The all-electron cc-pVDZ basis set[18] was employed for non-metal atoms and the cc-pVDZ-PP basis set containing an effective core relativistic pseudopotential was used for Rh.[19] The electronic energy was improved by performing single point calculations with the cc-pVTZ (cc-pVTZ-PP for Rh) basis set and the M06L functional. Analytical Hessians were computed to determine the nature of stationary points (one and zero imaginary frequencies for TSs and minima, respectively) and to calculate unscaled zero-point energies (ZPEs) as well as thermal corrections and entropy effects using the standard statistical-mechanics relationships for an ideal gas.[20] These two latter terms were computed at 298.15 K and 1 atm to provide the reported relative Gibbs energies (ΔG). The D3 Grimme energy corrections[21] for dispersion with its original damping function were added in all B3LYP/cc-pVDZ-PP and M06L/cc-pVTZ-PP calculations. Gibbs energies of solvation were not included they were reported to have minor effects in this kind of transformations that are usually carried out in rather nonpolar solvents.[22] However, to assess the importance of solvent effects, we recomputed the reaction profile of the most favorable reaction path in Scheme 3 by adding solvent corrections computed with the SMD continuum solvation model,[23] considering toluene as solvent and using the M06L-D3/cc-pVTZ-PP//B3LYP-D3/cc-pVDZ-PP method. As expected, the results show that changes in Gibbs energy barriers are not larger than 1.5 kcal/mol (see page S40 in the Supporting Information). The most important differences correspond to the dissociation (coordination) of a PPh_3 ligand that are favored (disfavored) by about 5 kcal/mol in solution. These energetic changes, however, do not modify the conclusions reached with the gas-phase profiles. As a summary, the hereafter reported Gibbs energies contain electronic energies calculated at the M06L-D3/cc-pVTZ-PP//B3LYP-D3/cc-pVDZ-PP level together with gas phase thermal corrections and entropic contributions computed at 298.15 K and 1 atm with the B3LYP-D3/cc-pVDZ-PP method.

Abstract in Catalan: *La funcionalització dels ful·lerens permet modular les seves propietats electròniques i fisicoquímiques, generant derivats de ful·lerè amb característiques prometedores per a potencials aplicacions pràctiques. En aquest treball, mitjançant la teoria del funcional de la densitat s'ha explorat la unió d'un anell de ciclohexadiè al C_{60} a través d'una cicloaddició intermolecular [2+2+2] de C_{60} i acetilè catalitzada per rodi. L'anàlisi de tots els possibles camins de reacció ens permet concloure que la cicloaddició [2+2+2] de C_{60} i dues molècules d'acetilè catalitzada per $RhCl(PPh_3)_3$ per generar un anell de ciclohexadiè fusionat a un enllaç [6,6] del C_{60} és un procés energèticament viable.*

Results and Discussion

We have analyzed all potential reaction pathways that transform a C_{60} molecule and two acetylenes into the final cyclohexadiene derivative of C_{60}. First, we have considered two possible initial oxidative additions, i.e., path A involving the addition of two acetylenes to yield the rhodacyclopentadiene intermediate **A4** (see Scheme 2) followed by C_{60} insertion or [4+2] cycloaddition and path B in which the oxidative addition takes place between an acetylene and C_{60} to generate intermediate **B4** that subsequently adds a second acetylene molecule. Both in the C_{60} insertion/ [4+2] cycloaddition in path A and in the oxidative addition in path B, we have analyzed the attack to a [6,6] bond and to a [5,6] bond of C_{60}. As usual for C_{60},[15a, c] in all cases, the [6,6] bond has been found to be more reactive than the [5,6] bond. Moreover, all reaction pathways have been studied with three possible active catalysts: $RhCl(PPh_3)_2$, $RhClPPh_3$, and RhCl. This is relevant because, for instance, the preferred oxidative addition between two acetylenes takes place with two phosphines coordinated to Rh, whereas the Rh–C insertion occurs with one coordinated phosphine. It is also worth mentioning that, after oxidative addition, we analyzed the three different possibilities, namely, insertion to form a rhodacycloheptadiene intermediate (analogous to **V** in Scheme 1), Rh-mediated [4+2] cycloaddition to yield a rhodanorbornene complex (**VI** in Scheme 1), and [2+2] cycloaddition to give a rhodabicyclo[3.2.0]heptadiene species (**VII** in Scheme 1). The most favorable reaction paths go through a rhodacycloheptadiene intermediate, but we also found some reaction pathways involving rhodanorbornene and rhodabicyclo[3.2.0]heptadiene intermediates. Finally, for comparison purposes, we also computed the reaction mechanism of the [2+2+2] cycloaddition of three acetylenes catalyzed by Wilkinson's catalyst. This reaction was already studied by some of us some years ago,[24] but here we recompute the Gibbs energy

Accepted Manuscript

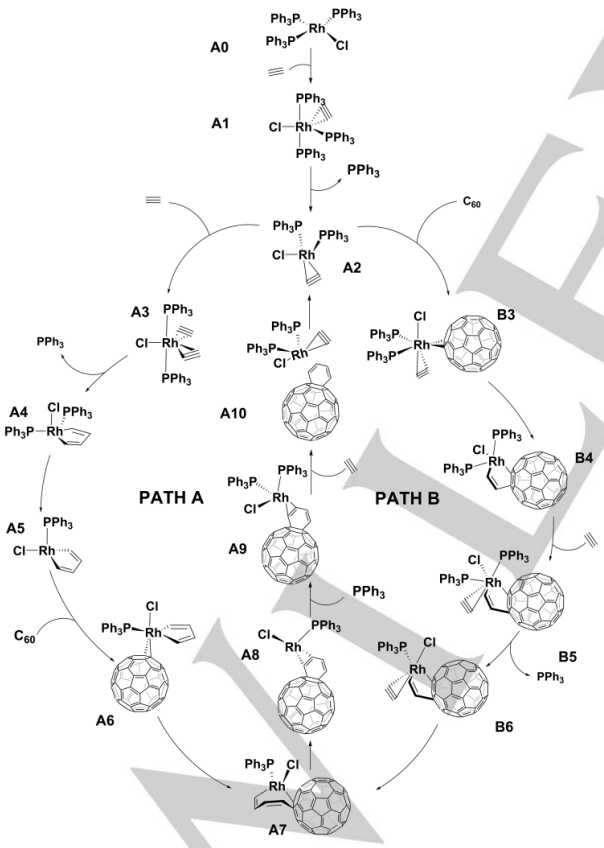
This article is protected by copyright. All rights reserved.

10.1002/chem.201702494

profile to take into consideration dispersion effects in both the geometry and energy of all stationary points. All studied Gibbs reaction profiles are given in the Supporting Information. In the coming paragraphs, we discuss only the two energetically most favorable reaction paths.

As shown in Scheme 2, there is a preactivation of the catalysts before entering the catalytic cycle as the 16-electron species **A2**. To reach **A2**, the initial Wilkinson catalyst coordinates an incoming acetylene molecule and loses a phosphine in a process that is endergonic by 15.0 kcal/mol. The PPh_3 ligand in **A1** that is removed to form **A2** occupies a site *cis* to Cl[25] in the equatorial position of the trigonal bipyramid (tbp).

The Gibbs energy profile of the transformation from **A2** to **A11** through paths A and B is given in Scheme 3. **A2** adds an acetylene molecule to generate the 18-electron species **A3** in which the two PPh_3 ligands occupy axial positions of the tbp. We have checked that this is the most stable disposition of the ligands. The conversion from **A2** to **A3** is exergonic by merely 2.2 kcal/mol. Oxidative addition from **A3** with two equatorial acetylene ligands has a large Gibbs energy barrier of 37.5 kcal/mol. Thus, this oxidative addition takes place through its less stable isomer **A3**' (Supporting information, S3), in which the acetylene ligands occupy axial and equatorial positions. **A3** and **A3'** are in equilibrium and easily interconvert through a Berry pseudorotation of the tbp.[26] The approach of the two acetylene ligands during oxidative addition is easier when they occupy axial and equatorial coordination sites.[24, 27] The energetic span[28] between the TOF determining intermediate (TDI, **A3**) and TOF determining transition state (TDTS, **TS A3'A4**) is 22.4 kcal/mol. The molecular structure of **TS A3'A4** is depicted in Figure 1a. As it can be seen, the C–C bond to be formed in this step has a bond length of 2.008 Å. This is the highest energy barrier throughout the catalytic cycle through path A and, therefore, oxidative addition is the rate determining step (rds) for this path as found in some other [2+2+2] cycloadditions.[12b, 22c, 27a, 29] Oxidative addition affords the rhodacyclopentadiene species **A4** by releasing 11.0 kcal/mol. In a subsequent step, this intermediate loses a PPh_3 ligand to form **A5** with a cost of 14.6 kcal/mol. Coordination of **A5** to C_{60} to yield **A6** is an exergonic process by 21.6 kcal/mol. Alternatively, **A4** coordinates to a third acetylene molecule (Supporting information, S3) to progress through benzene formation pathway (*vide infra*). π-localization[29b, 30] in **A4** and **A5** as denoted by the large difference between double C=C (1.35 Å) and single C–C (1.47 Å) bond lengths shows that these intermediates are not stabilized by aromaticity of the rhodacyclopentadiene ring. In **A6**, C_{60} is η^2-coordinated to Rh occupying an axial position of a distorted tbp *trans* to Cl. The structure of **A6** resembles that of the first X-ray crystal structure of cobaltacyclopentadiene(alkyne) complex reported.[31] Schore's mechanism[10] is operative in the insertion of the [6,6] bond of C_{60} to the Rh–C bond through **TS A6A7** to yield rhodacycloheptadiene intermediate **A7**. Transformation of **A6** to **A7** is exergonic by 12.4 kcal/mol and takes place through a Gibbs energy barrier of only 6.7 kcal/mol. [4+2] cycloaddition in **A6** leading to intermediate **C7** has also been considered, but this alternative pathway has a much larger barrier of 24.7 kcal/mol.



Scheme 2. The two energetically most favorable catalytic cycles for the [2+2+2] cycloaddition reaction of C_{60} and two acetylenes catalyzed by $RhCl(PPh_3)_3$: 1) path A corresponds to the initial oxidative addition between two acetylenes and 2) path B considers the initial oxidative addition between C_{60} and an acetylene molecule.

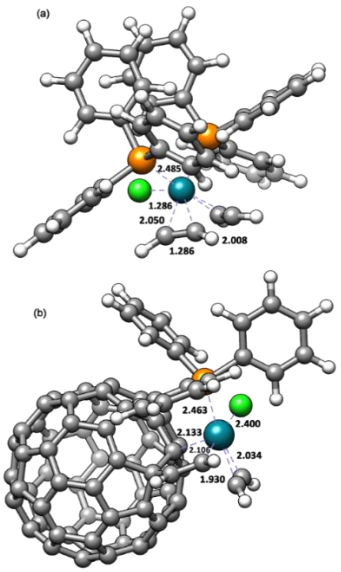
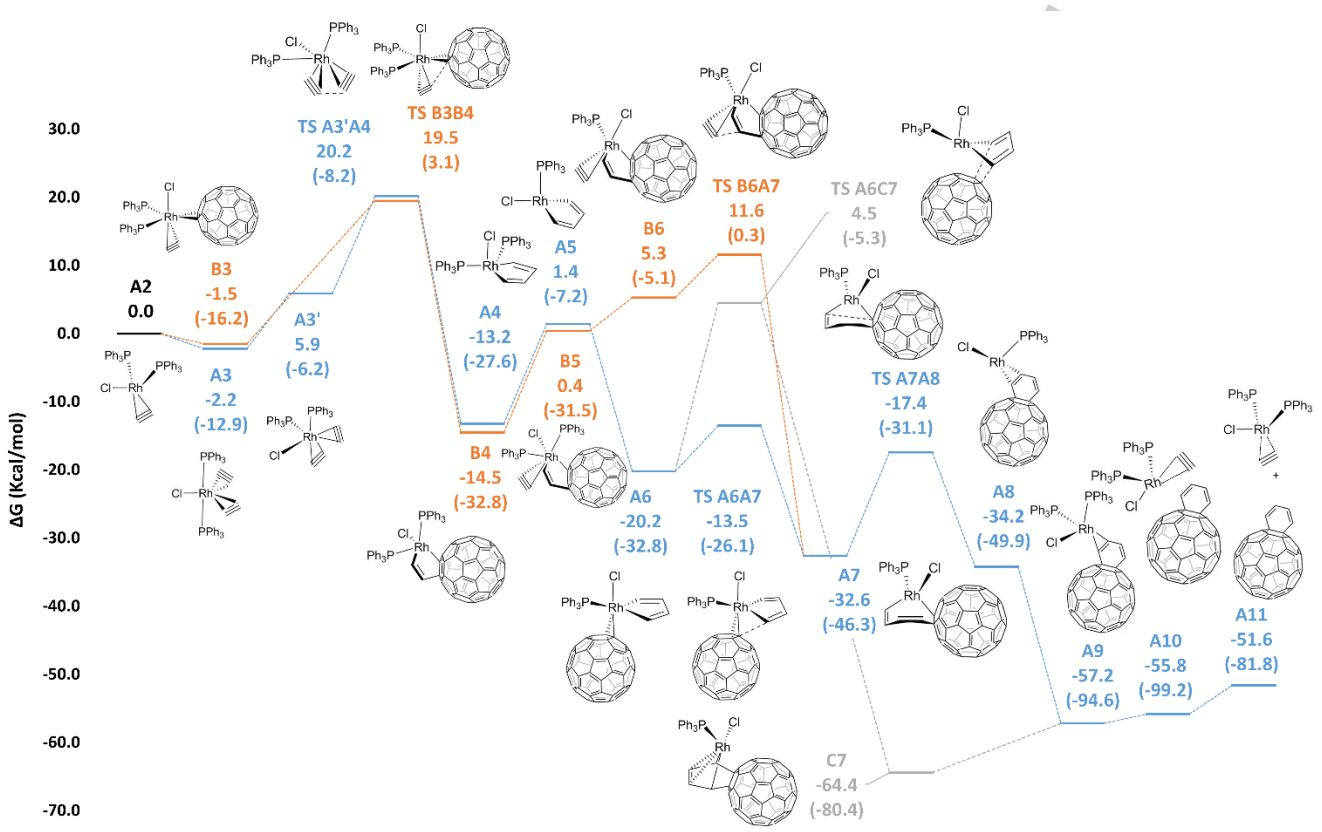


Figure 1. Molecular structure of the rate determining transition states of (a) the oxidative addition step in path A (**TS A3'A4**) and (b) the Rh-C insertion step in path B (**TS B6A7**).

Accepted Manuscript

This article is protected by copyright. All rights reserved.

10.1002/chem.201702494



Scheme 3. M06L-D3/cc-pVTZ-PP//B3LYP-D3/cc-pVDZ-PP Gibbs energy profile for paths A (blue) and B (orange) of the [2+2+2] cycloaddition reaction of C_{60} and two acetylenes catalyzed by $RhCl(PPh_3)_3$. Energies given in parenthesis are electronic energies. All energies are relative energies referred to **A2** and are given in kcal/mol.

Paths A and B merge in **A7** and from these intermediate they share the same reaction path until **A11**, the final cyclohexadiene derivative of C_{60}. All attempts to locate the rhodanorbornene and rhodabicyclo[3.2.0]heptadiene intermediates failed and lead to the **A7** complex. A reductive elimination occurs in **A7** to generate intermediate **A8** in which the $Rh^{I}ClPPh_3$ complex is η^2-coordinated to the cyclohexadiene ring attached to C_{60}. The conversion of **A7** into **A8** is exergonic by just 1.6 kcal/mol and takes place through a Gibbs energy barrier of 15.2 kcal/mol. **A8** is a 14-electron species that can accept an incoming PPh_3 ligand to generate the 16-electron **A9** species in an exergonic process by 23.0 kcal/mol. Finally release of the product and recovering of the **A2** species is endergonic by 5.6 kcal/mol. As a whole, the transformation from reactants to products via path A occurs with a Gibbs energy barrier of 22.4 kcal/mol and a Gibbs reaction energy of -51.6 kcal/mol. The fact that **A5** can add C_{60} to give cyclohexadiene-type adducts is in line with the experimental reaction reported by Murata et al.[13] of C_{60} with palladacyclopentadiene complexes to generate an adduct with the cyclohexadiene ring attached to C_{60}.

On the other hand, path B starts with the formation of 18-electron complex **B3** by coordination of C_{60} to $RhCl(PPh_3)_2(C_2H_2)$. The Gibbs reaction energy of this process is -1.5 kcal/mol. The axial coordination sites of the tbp in complex **B3** are occupied by Cl and acetylene. This is the most stable disposition of the ligands We have also analyzed the possibility to generate **B2** (Supporting Information, S2) from **A0** by loss of a PPh_3 ligand and then coordination of C_{60}. Subsequent coordination of acetylene to **B2** forms **B3**. Dissociation of PPh_3 from **A0** and coordination to C_{60} to yield **B2** has a cost of 19.8 kcal/mol. This energetic cost is higher by 4.8 kcal/mol than the cost to generate **A2** from **A0**, and, therefore, **B2** is not expected to play a major role in the reaction mechanism. Oxidative addition in **B3** takes places through **TS B3B4** to yield **B4** with a Gibbs energy barrier of 21.0 kcal/mol and releasing 13.0 kcal/mol. Interestingly, the oxidative addition of an acetylene and C_{60} has almost the same barrier as that between two acetylenes. Similarly, it was found that the oxidative addition of a nitrile and an acetylene molecules catalyzed by RhCp has a similar barrier to that of two acetylenes.[32] In 16-electron intermediate **B4**, C_{60} is fused to a rhodacyclopentene species. This intermediate is moderately stable and we postulate that it could be isolated working at relatively low temperatures. Subsequent coordination of acetylene to **B4** gives the 18-electron **B5** intermediate that is destabilized by 15.9 kcal/mol as compared

Accepted Manuscript

This article is protected by copyright. All rights reserved.

to **B4**. All attempts to locate the transition state of the Rh–C insertion in **B5** failed. On the other hand, if **B5** loses a PPh_3 to give **B6**, the insertion goes through **TS B6A7** with a Gibbs energy barrier of only 6.3 kcal/mol. The energetic span from the TDI **B4** to the TDTS **TS B6A7** is 26.1 kcal/mol. Interestingly, the rds in path B is the insertion of the second acetylene molecule. Despite oxidative addition is generally the rds, there are also some examples in which oxidative addition is not rate determining.[32-33] The energetic span of path B (26.1 kcal/mol) is somewhat higher than that found for path A (22.4 kcal/mol). Therefore, although path A is clearly the most favorable, path B cannot be totally ruled out and both paths could be operative to provide the cyclohexadiene ring attached to C_{60} product. Finally, the reaction pathway from **A7** to **A11** is shared by reaction paths A and B and has been commented in previous paragraphs (*vide supra*).

As aforementioned, we have studied the oxidative addition of three acetylene molecules catalyzed by $RhCl(PPh_3)_3$ to generate benzene (see Supporting Information). The reaction mechanism from **A0** to **A4** is the same as path A discussed in previous paragraphs. In both reaction pathways the oxidative addition is the rds. The two main differences are: 1) path A of Scheme 3 involves loss of a PPh_3 ligand in **A4** to form **A5** before insertion and this dissociation costs 14.6 kcal/mol, whereas PPh_3 in **A4** is not released in the cycloaddition of three acetylene molecules, and 2) the Rh–C insertion has an energy barrier of 13.0 kcal/mol when acetylene is inserted and of only 6.7 kcal/mol when C_{60} is inserted in **A6**. Subsequent steps are almost barrierless in the [2+2+2] cycloaddition of three acetylenes, whereas a barrier of 15.2 kcal/mol is found in the transformation of **A7** to **A8** (Scheme 3). We conclude that insertion of C_{60} and acetylene can compete and, therefore, to avoid benzene formation which is somewhat easier, it would be advisable to work with an excess of C_{60}.

Finally, we have analyzed the possible attack to the [5,6] bond of C_{60} (see Supporting Information). Again, both paths A and B have been considered. The lowest in energy reaction pathway for the attack to a [5,6] is kinetically and thermodynamically less favored than the addition to a [6,6] bond. The product of the [5,6] addition is 15.3 kcal/mol less stable in Gibbs energy than that of the [6,6] attack. From a kinetic point of view, for path A, the main difference corresponds to the insertion of C_{60} to Rh–C bond. In the [5,6] addition, the Gibbs energy barrier is 21.9 kcal/mol, whereas for the [6,6] attack is 15.2 kcal/mol. For path B, the energetic span in the [5,6] attack is 29.7 kcal/mol and that of the [6,6] attack is 26.1 kcal/mol. Our conclusion is that the major (or the only) product of the [2+2+2] cycloaddition will be the one generated in the [6,6] attack, although the presence of traces of the [5,6] addition cannot be totally ruled out.

Conclusions

We have shown here that Wilkinson's complex catalyzed [2+2+2] cycloaddition of C_{60} and two acetylene molecules to form a cyclohexadiene ring fused to a [6,6] bond of C_{60} is possible. The most likely reaction pathway involves an oxidative addition of the two acetylene molecules followed by insertion of C_{60} into a Rh–C bond of the rhodacyclopentadiene intermediate formed. The reaction yield can be improved by using an excess of C_{60} to avoid side reactions such as the formation of benzene. Moreover, the energy barriers could be entropically reduced by using diynes instead of acetylene molecules.[34] Capitalizing on all this information, work is underway in our laboratories to develop a Rh-catalyzed [2+2+2] cycloaddition involving fullerene. Results will be reported in due course.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgements

Financial support from the Spanish Ministry of Economy and Competitivity (MINECO) and European Social Fund (ESF) (Project No. CTQ2014-54306-P, FPI fellowship to A.A., and RyC contract RYC2012-11112 to A.L.) and the DIUE of the Generalitat de Catalunya (Project No. 2014SGR931 and ICREA Academia 2014 to M.S.) are acknowledged. The EU under the FEDER grant UNGI10-4E-801 has also funded this research.

Keywords: [2+2+2] cycloaddition • transition metal catalysis • fullerenes • oxidative addition • Rh–C insertion

[1] a) A. J. Heeger, *Adv. Mater.* **2014**, *26*, 10-28; b) D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks and M. C. Hersam, *Chem. Soc. Rev* **2013**, *42*, 2824-2860; c) S. Günes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.* **2007**, *107*, 1324-1338.

[2] a) D. M. Guldi, B. M. Illescas, C. M. Atienza, M. Wielopolski and N. Martín, *Chem. Soc. Rev* **2009**, *38*, 1587-1597; b) N. Martín, *Adv. Energy Mater.* **2017**, *2*, 1601102; c) K. Wojciechowski, T. Leijtens, S. Siprova, C. Schlueter, M. T. Hörantner, J. T.-W. Wang, C.-Z. Li, A. K. Y. Jen, T.-L. Lee and H. J. Snaith, *J. Phys. Chem. Lett.* **2015**, *6*, 2399-2405.

[3] J. L. Segura, N. Martin and D. M. Guldi, *Chem. Soc. Rev* **2005**, *34*, 31-47.

[4] a) J. P. Martínez, M. Solà and A. A. Voityuk, *J. Comput. Chem.* **2016**, *37*, 1396-1405; b) J. P. Martínez, M. Solà and A. A. Voityuk, *Chem. Eur. J.* **2016**, *22*, 17305-17310.

[5] G. Sauvé and R. Fernando, J. Phys. Chem. Lett. 2015, 6, 3770-3780.

[6] a) A. Hirsch, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1138-1141; b) A. Hirsch, *The Chemistry of Fullerenes*, Thieme, Sttutgart, Germany, **1994**; c) A. Hirsch and M. Brettreich, *Fullerenes: Chemistry and Reactions*, John Wiley & Sons, Weinheim, **2004**; d) N. Martín, *Chem. Commun.* **2006**, 2093-2104; e) S. Osuna, M. Swart and M. Solà, *Phys. Chem. Chem. Phys.* **2011**, *13*, 3585-3603.

[7] T. Ohno, N. Martín, B. Knight, F. Wudl, T. Suzuki and H. Yu, *J. Org. Chem.* **1996**, *61*, 1306-1309.

[8] G. C. Vougioukalakis, M. M. Roubelakis and M. Orfanopoulos, *Chem. Soc. Rev* **2010**, *39*, 817-844.

[9] For selected reviews, see: a) S. Saito and Y. Yamamoto, *Chem. Rev.* **2000**, *100*, 2901-2916; b) Y. Yamamoto, *Curr. Org. Chem.* **2005**, *9*, 503-519; c) B. R. Galan and T. Rovis, *Angew. Chem. Int. Ed.* **2009**, *48*, 2830-2834; d) A. Pla-Quintana and A. Roglans, *Molecules* **2010**, *15*, 9230-9251; e) Y. Shibata and K. Tanaka, *Synthesis* **2012**, *44*, 323-350; f) D. L. J. Broere and E. Ruijter, *Synthesis* **2012**, *44*, 2639-2672; g) G. Dominguez and J. Perez-Castells, *Chem. Soc. Rev* **2011**, *40*, 3430-3444; For a monograph, see: h) K. Tanaka, *Transition-Metal-Mediated Aromatic Ring Construction*, (Ed. K. Tanaka), John Wiley & Sons, Inc., **2013**.

[10] N. E. Schore, *Chem. Rev.* **1988**, *88*, 1081-1119.

[11] For a review, see: a) A. Lledó, A. Pla-Quintana and A. Roglans, *Chem. Soc. Rev* **2016**, *45*, 2010-2023 and references cited therein. For contributions of our group, see: b) E. Haraburda, M. Fernández, A. Gifreu, J. Garcia, T. Parella, A. Pla-Quintana and A. Roglans, *Adv. Synth. Catal.* **2017**, *359*, 506-512; c) E. Haraburda, A. Lledó, A. Roglans and A. Pla-

Accepted Manuscript

This article is protected by copyright. All rights reserved.

Quintana, *Org. Lett.* **2015**, *17*, 2882-2885; d) E. Haraburda, O. Torres, T. Parella, M. Solà and A. Pla-Quintana, *Chem. Eur. J.* **2014**, *20*, 5034-5045.

[12] For a review, see: a) G. Domínguez and J. Pérez-Castells, *Chem. Eur. J.* **2016**, *22*, 6720-6739 and references cited therein. For selected examples, see: b) A. Dachs, A. Pla-Quintana, T. Parella, M. Solà and A. Roglans, *Chem. Eur. J.* **2011**, *17*, 14493-14507; c) A. Torrent, I. González, A. Pla-Quintana, A. Roglans, M. Moreno-Mañas, T. Parella and J. Benet-Buchholz, *J. Org. Chem.* **2005**, *70*, 2033-2041; d) S. Brun, L. Garcia, I. González, A. Torrent, A. Dachs, A. Pla-Quintana, T. Parella and A. Roglans, *Chem. Commun.* **2008**, 4339-4341; e) J. A. Varela, S. G. Rubín, L. Castedo and C. Saá, *J. Org. Chem.* **2008**, *73*, 1320-1332; f) J. A. Varela, S. G. Rubín, C. González-Rodríguez, L. Castedo and C. Saá, *J. Am. Chem. Soc.* **2006**, *128*, 9262-9263; g) T. Shibata, H. Kurokawa and K. Kanda, *J. Org. Chem.* **2007**, *72*, 6521-6525; h) S. García-Rubín, J. A. Varela, L. Castedo and C. Saá, *Chem. Eur. J.* **2008**, *14*, 9772-9778; i) M. Fernández, M. Parera, T. Parella, A. Lledó, J. Le Bras, J. Muzart, A. Pla-Quintana and A. Roglans, *Adv. Synth. Catal.* **2016**, *358*, 1848-1853.

[13] H. Inoue, H. Yamaguchi, T. Suzuki, T. Akasaka and S. Murata, *Synlett* **2000**, *2000*, 1178-1180.

[14] T.-Y. Hsiao, K. C. Santhosh, K.-F. Liou and C.-H. Cheng, *J. Am. Chem. Soc.* **1998**, *120*, 12232-12236.

[15] a) M. Solá, J. Mestres, J. Martí and M. Duran, *Chem. Phys. Lett.* **1994**, *231*, 325-330; b) S. Osuna, J. Morera, M. Cases, K. Morokuma and M. Solà, *J. Phys. Chem. A* **2009**, *113*, 9721-9726; c) I. Fernández, M. Solà and F. M. Bickelhaupt, *Chem. Eur. J.* **2013**, *19*, 7416-7422.

[16] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox in *Gaussian 09, Revision D.1*, Gaussian, Inc., Wallingford CT, **2009**.

[17] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652; b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789; c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623-11627.

[18] a) T. H. Dunning Jr., *J. Chem. Phys.* **1989**, *90*, 1007-1023; b) D. E. Woon and T. H. Dunning Jr., *J. Chem. Phys.* **1993**, *98*, 1358-1371.

[19] K. A. Peterson, D. Figgen, M. Dolg and H. Stoll, *J. Chem. Phys.* **2007**, *126*, 124101.

[20] P. Atkins and J. De Paula in *Physical Chemistry*, Oxford University Press, Oxford, **2006**.

[21] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

[22] a) L. Orian, J. N. P. van Stralen and F. M. Bickelhaupt, *Organometallics* **2007**, *26*, 3816-3830; b) L. Orian, L. P. Wolters and F. M. Bickelhaupt, *Chem. Eur. J.* **2013**, *19*, 13337-13347; c) C.-H. Guo, H.-S. Wu, M. Hapke and H. Jiao, *J. Organomet. Chem.* **2013**, *748*, 29-35.

[23] A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

[24] A. Dachs, S. Osuna, A. Roglans and M. Solà, *Organometallics* **2010**, *29*, 562-569.

[25] J. Goodman, V. V. Grushin, R. B. Larichev, S. A. Macgregor, W. J. Marshall and D. C. Roe, *J. Am. Chem. Soc.* **2010**, *132*, 12013-12026.

[26] a) J. M. Brown and A. G. Kent, *J. Chem. Soc., Perkin Trans. 2* **1987**, 1597-1607; b) N. Koga, S. Q. Jin and K. Morokuma, *J. Am. Chem. Soc.* **1988**, *110*, 3417-3425; c) L. A. van der Veen, M. D. K. Boele, F. R. Bregman, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, H. Schenk and C. Bo, *J. Am. Chem. Soc.* **1998**, *120*, 11616-11626.

[27] a) A. Dachs, A. Roglans and M. Solà, *Organometallics* **2011**, *30*, 3151-3159; b) Ò. Torres, A. Roglans, A. Pla-Quintana, J. M. Luis and M. Solà, *J. Organomet. Chem.* **2014**, *768*, 15-22.

[28] a) S. Kozuch and S. Shaik, *J. Phys. Chem. A* **2008**, *112*, 6032-6041; b) S. Kozuch and S. Shaik, *Acc. Chem. Res.* **2010**, *44*, 101-110.

[29] a) K. Kirchner, M. J. Calhorda, R. Schmid and L. F. Veiros, *J. Am. Chem. Soc.* **2003**, *125*, 11721-11729; b) J. H. Hardesty, J. B. Koerner, T. A. Albright and G.-Y. Lee, *J. Am. Chem. Soc.* **1999**, *121*, 6055-6067; c) A. Dachs, A. Torrent, A. Roglans, T. Parella, S. Osuna and M. Solà, *Chem. Eur. J.* **2009**, *25*, 5289-5300.

[30] A. A. Dahy and N. Koga, *Organometallics* **2015**, *34*, 4965-4974.

[31] P. I. Dosa, G. D. Whitener, K. P. C. Vollhardt, A. D. Bond and S. J. Teat, *Org. Lett.* **2002**, *4*, 2075-2078.

[32] G. Dazinger, M. Torres-Rodrigues, K. Kirchner, M. J. Calhorda and P. J. Costa, *J. Organomet. Chem.* **2006**, *691*, 4434-4445.

[33] a) H. Zhou, J. Liu, S. Du, L. Zhang, G. Li, Y. Zhang, B. Z. Tang and H.-J. Gao, *J. Am. Chem. Soc.* **2014**, *136*, 5567-5570; b) A. Dachs, A. Torrent, A. Pla-Quintana, A. Roglans and A. Jutand, *Organometallics* **2009**, *28*, 6036-6043.

[34] Y. Yamamoto, T. Arakawa, R. Ogawa and K. Itoh, *J. Am. Chem. Soc.* **2003**, *125*, 12143-12160.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

10.1002/chem.201702494

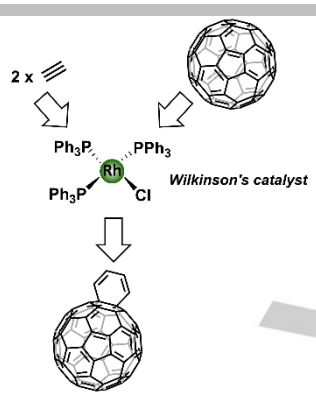
WILEY-VCH

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

The [2+2+2] cycloaddition between two acetylene molecules and C_{60} catalyzed by Wilkinson's catalyst to afford a cyclohexadiene ring attached to the fullerenic cage has been studied computationally. Results show that the reaction is feasible.



*Albert Artigas, Agustí Lledó, Anna Pla-Quintana, Anna Roglans and Miquel Solà**

Page No. – Page No.

A Computational Study of the Intermolecular [2+2+2] Cycloaddition of Acetylene and C_{60} Catalyzed by Wilkinson's Catalyst

WILEY-VCH Accepted Manuscript

This article is protected by copyright. All rights reserved.