Review

CpRuCl- and CpCo-catalyzed or mediated cyclotrimerizations of alkynes and [2+2+2] cycloadditions of alkynes to alkenes: A comparative DFT study

Jesús A. Varela, Carlos Saá *

Departamento de Química Orgánica, Facultad de Química, Universidad de Santiago de Compostela, 15782-Santiago de Compostela, Spain

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ABSTRACT

Computational methods have been used to better understand both the CpRuCl- and CpCo-catalyzed and mediated cyclotrimerization of alkynes and the [2+2+2] cycloaddition of alkynes to alkenes. These studies have allowed more accurate mechanisms to be proposed for each of these transformations and for some previously proposed intermediates to be discarded. The mechanistic rationale of these processes depends on the nature of the metal, ligands and substrate partners.

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Contents

1. Introduction

Stoichiometric and catalytic transition-metal reactions have attracted great interest for their numerous applications in industrial and synthetic processes [1]. Transition-metal-catalyzed reactions are critical in many thermodynamically feasible processes because they accelerate the reaction by opening a lower activation energy pathway, often one that was symmetry forbidden. These metal-centered reactions cover one or more elementary reactions such as substitution, oxidative addition, reductive elimination, migratory insertion, hydrogen exchange, β-hydrogen transfer, σ-bond metathesis, and nucleophilic addition. Numerous experimental and theoretical studies have been undertaken in an effort to under-

stand these fundamental transformations and to elucidate the mechanistic aspects of homogeneous organometallic catalysis. Recent progress in computational chemistry has shown that many important chemical and physical properties of the species involved in these reactions can be predicted from first principles by various computational techniques [2]. This ability is especially important in those cases where experimental results are difficult to obtain, such as the mechanism of the transition-metal-catalyzed or mediated cyclotrimerization of alkynes [3,4] and [2+2+2] cycloaddition of alkynes to alkenes [5].

Many transition-metal complexes catalyze or mediate these transformations and the general mechanism proposed is represented in Scheme 1. Initially, two alkyne partners coordinate to the metal to afford complex II. Subsequent oxidative coupling to metallacyclopentadiene III is followed by coordination of the third unsaturated partner to give complex IV. From IV, two paths can

* Corresponding author. Tel.: +34 98 1563100; fax: +34 981 595012.
E-mail address: carlos.saa@usc.es (C. Saá).
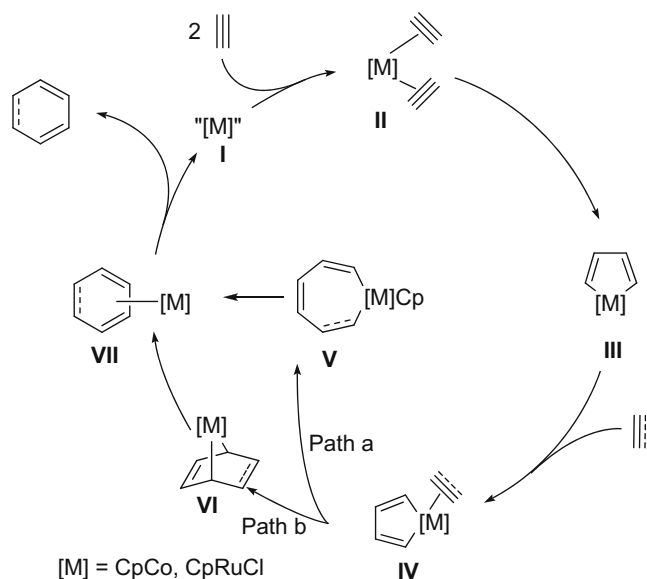
**Scheme 1.** General mechanism proposed for the CpRuCl- and CpCo-catalyzed [2+2+2] cycloaddition reaction.

be envisioned: (a) insertion into the M–C bond gives metallacycle **V**, which after reductive elimination gives complex **VII**; (b) intramolecular [4+2] cycloaddition gives bicyclic complex **VI**, which after isomerization affords complex **VII**. Finally, decoordination of the metal would afford the cycloadduct with recovery of the catalytic species **I**.

Although this mechanism has been the subject of multiple experimental studies, its total elucidation has remained elusive due to the difficulty in isolating some of the proposed intermediates. Nevertheless, to gain further insights into the natures of the species involved in this mechanism, several computational studies have been performed on the metal-catalyzed or mediated cyclotrimerization of alkynes and [2+2+2] cycloaddition of two alkynes to one alkene for the CpRuCl and CpCo fragments. These studies allowed some of the initially proposed pathways to be ruled out and enabled the intermediate steps for these transformations to be defined more accurately.

In this report we would like to describe how a combination of computational techniques and experimental studies is probably the best way to elucidate the mechanism of transition-metal-mediated transformations. As an example, the elucidation of the mechanisms of the CpRuCl- and CpCo-catalyzed trimerization of alkynes and CpRuCl-catalyzed and CpCo-mediated [2+2+2] cycloaddition of alkynes to alkenes is described.

2. CpRuCl-catalyzed [2+2+2] cyclotrimerization of alkynes

Recently, two DFT studies on the Ru(II)-catalyzed [2+2+2] cyclotrimerization of three acetylenes have been published (Scheme 2) [6]. According to these studies, the first step involves the generation of the bisacetylene complex **VIII** by replacement of two of the labile ligands of the initial Ru-complex by two acetylenes. Oxidative coupling to ruthenacyclebiscarbene **IX** subsequently occurs and this can be regarded as a 5-membered aromatic compound rather than a metallacyclopentatriene, making this complex a coordinatively saturated 18 e$^-$ species, according to the X-ray data of the analogous RuCpBr(C$_4$Ph$_2$H$_2$) [7]. Coordination of a third acetylene converts the aromatic ruthenacycle **IX** into a ruthenacyclopentadiene (alkyne) complex **X**. Isomerization of **X** to ruthenabicyclo[3.2.0]heptatriene **XI** then occurs and this can be described as a metal-assisted electrocyclization of the ruthenacy-
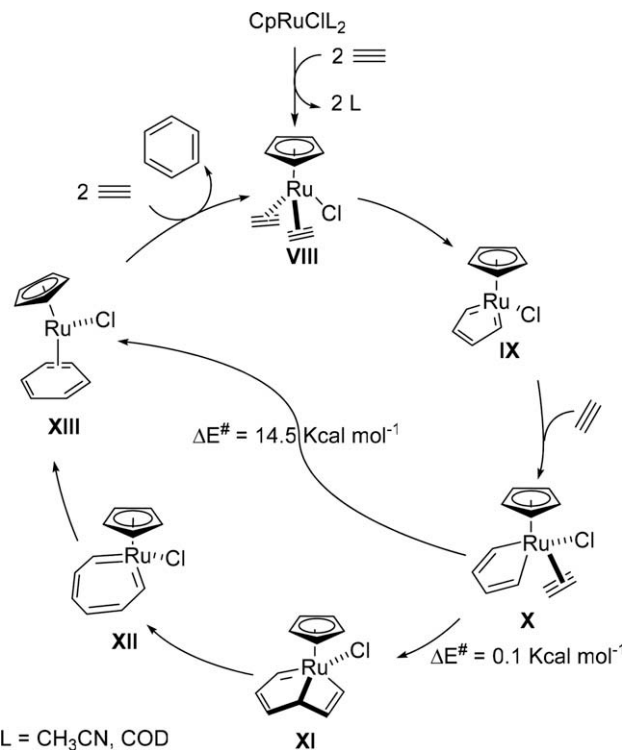

Scheme 2. Catalytic cycle for the CpRuCl-catalyzed cyclotrimerization of alkynes.

clopentadiene to acetylene, a process that has an activation energy of only 0.1 kcal mol^{-1} [8]. Subsequent scission of the central Ru–C single bond in **XI** leads to the 7-membered ruthenacycle **XII** [9] and this is followed by reductive elimination to give the η^2-benzene complex **XIII**. Finally, coordination of the ruthenium to two new acetylenes liberates the benzene product and regenerates the catalytic species **VIII**. This study shows that Ru-catalyzed cyclotrimerization of acetylenes to benzenes does not proceed either through an acetylene insertion or a Diels–Alder type route from ruthenacyclopentadienes **X**. The Diels–Alder route can be discarded on the basis of the higher activation energy for the direct transformation of **X** to **XIII** (14.5 kcal mol^{-1}) compared to 0.1 kcal mol^{-1} for the transformation of **X** to **XI**.
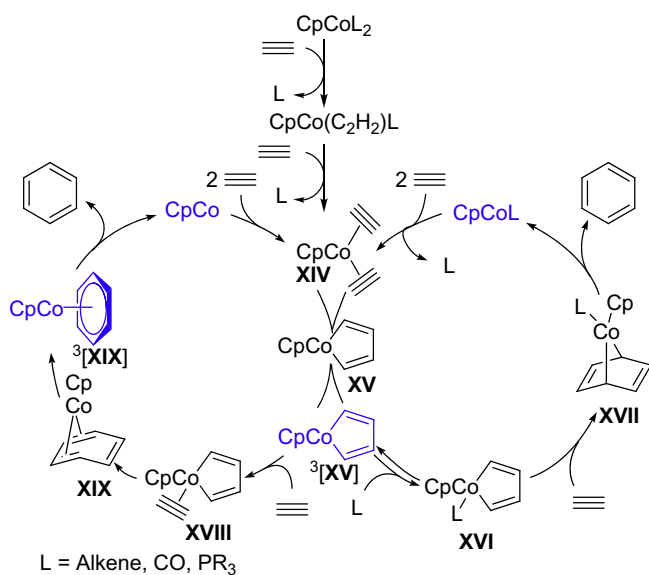
3. CpCo-catalyzed [2+2+2] cyclotrimerization of alkynes

Cobalt complexes of the type CpCoL$_2$ (L = CO, PR$_3$, alkenes) have been used extensively for the cyclotrimerization of alkynes and they are probably the most studied catalysts for the [2+2+2] cyclotrimerization of alkynes [10]. In these experimental studies some intermediates have been isolated and characterized. When 2-butyne was treated with CpCo(PPh$_3$)$_2$ at room temperature, the monoalkyne complex **1** was detected in the mixture and the cobaltacyclopentadiene **2** was isolated (Eq. (1), Scheme 3) [11]. The reaction of 2-butyne with CpCo(C$_2$H$_4$)$_2$ gave the paramagnetic 20-electron sandwich complex **3** at −10 °C (Eq. (2), Scheme 3) [12]. η^4-Arene complexes of type **4** were isolated from the reaction of DMAD with Cp*Co(C$_2$H$_4$)$_2$ (Eq. (3), Scheme 3) [13]. The alkyne-cobaltacyclopentadiene **6** has also been isolated in the reaction of triyne **5** with various CpCo species (Eq. (4), Scheme 3). Heating of complex **6** afforded the Cp*Co(η^4-arene) **8**, which after further heating afforded the free arene **9** [14].

Recently, a detailed DFT study into the CpCoL$_2$-catalyzed cyclotrimerization of ethyne has been published that fully explains all of the experimental findings [15]. In this study two parallel mechanisms for the Co-catalyzed [2+2+2] cyclotrimerization of
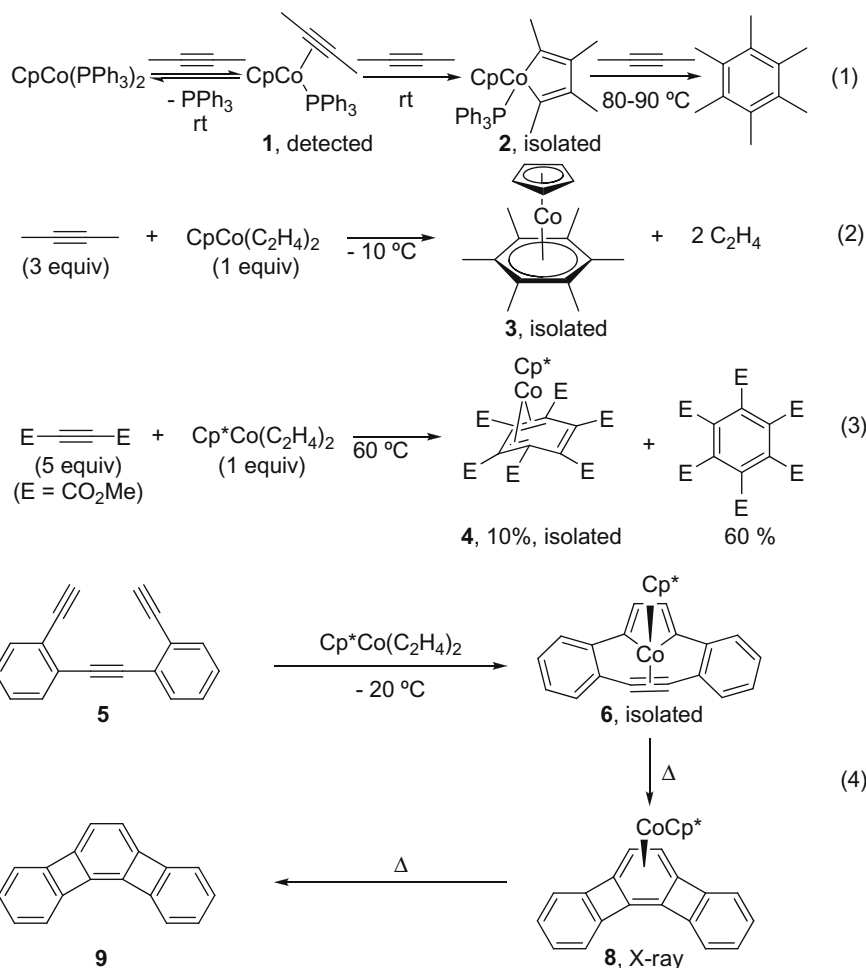
Scheme 3. Experimental results of the cyclotrimerization of 2-butyne, dimethyl acetylenedicarboxylate (DMAD) and triyne **5** with CpCo catalysts.

Scheme 4. Two parallel mechanisms for the CpCo-catalyzed [2+2+2] cyclotrimerization of alkynes.

acetylene were investigated (Scheme 4). In both paths the initially formed bisalkyne-complex **XIV** undergoes oxidative coupling to the cobaltacyclopentadiene **XV**, which spontaneously relaxes to the triplet ground state ³[**XV**]. From this point two alternatives are possible depending on the nature of the ligands [16]: (a) with strong σ-donor solvents or ligands such as PR₃ or CO, complex ³[**XV**] is trapped to give the 18 e⁻ complex **XVI** [17], which affords the cobaltanorbornadiene **XVII** by intermolecular [4+2] cycloaddition with an electron-poor alkyne; (b) in the absence of strong σ-donors and electron-poor alkynes, ³[**XV**] reacts with the alkyne to give **XVIII**, which subsequently evolves to the CpCo(η⁴-arene) complex **XIX** through an intramolecular metal-assisted [4+2] cycloaddition [18]. A spin change affords the 20-electron sandwich complex ³[**XIX**] and dissociation of this species provides the free arene and CpCo **XIV**, which reinitiates the catalytic cycle after coordination with new alkynes [19].

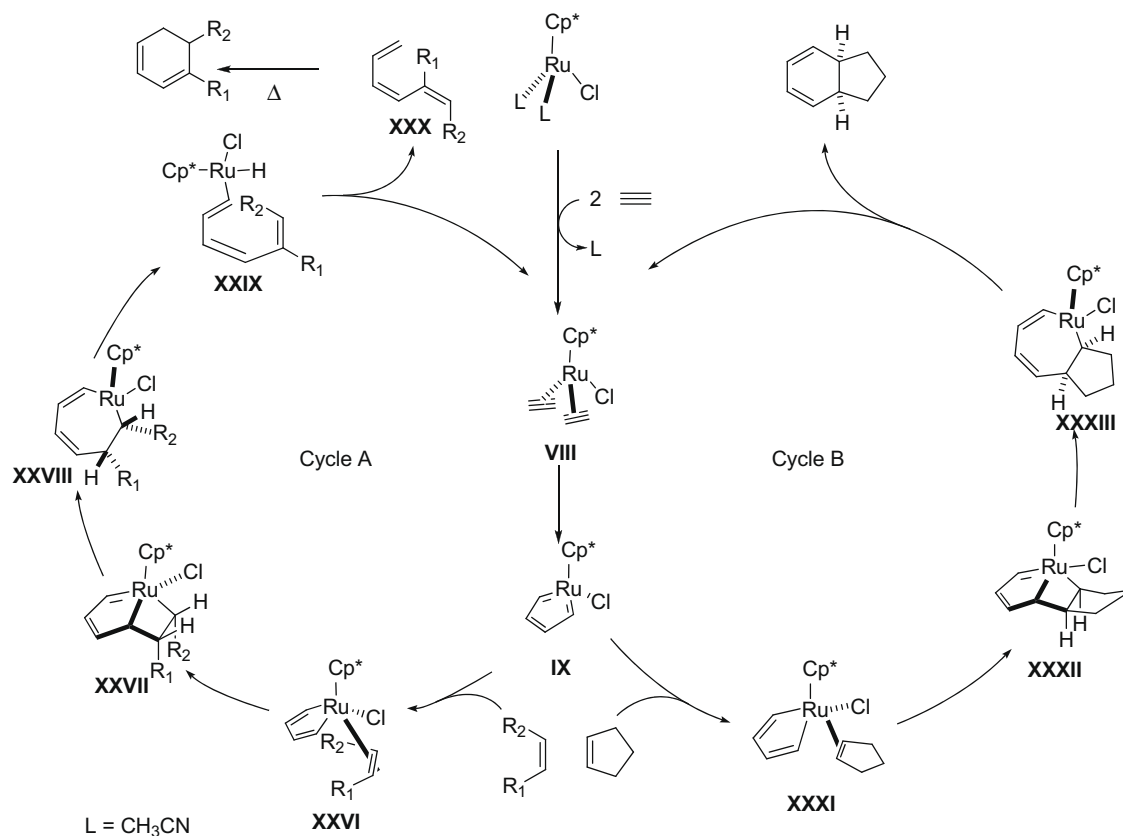## 4. CpRuCl-catalyzed [2+2+2] cycloaddition of alkynes to alkenes

The mechanism of the metal-catalyzed [2+2+2] cycloaddition of alkynes to alkenes to afford 1,3-cyclohexadienes has been less widely studied than the previous cyclotrimerization of three al-kynes to benzenes. Two DFT studies on the Ru(II)-catalyzed [2+2+2] cycloaddition of two acetylenes and norbornene [6b] and ethylene [6a] have recently appeared in the literature. In both studies the behaviour of the alkene in the initial stages is seen to parallel closely that of acetylene, as shown in Scheme 2: i.e. replacement of labile cod in CpRu(cod)Cl by two molecules of acet-ylene affords complex **VIII**, which undergoes oxidative addition to form biscarbene **IX**, followed by coordination to the double bond of ethylene or norbornene to give the ruthenacyclopentadienes **XX** and **XX′**, respectively. A Ru-assisted electrocyclization of **XX** and

XX′ then gives rise to ruthenabicyclo[3.2.0]heptadienes **XXI** and **XXI′**, respectively (Scheme 5) [20]. From this point there are two different paths depending on the alkene used in the cyclization reaction: path A for ethylene and path B for norbornene. In path
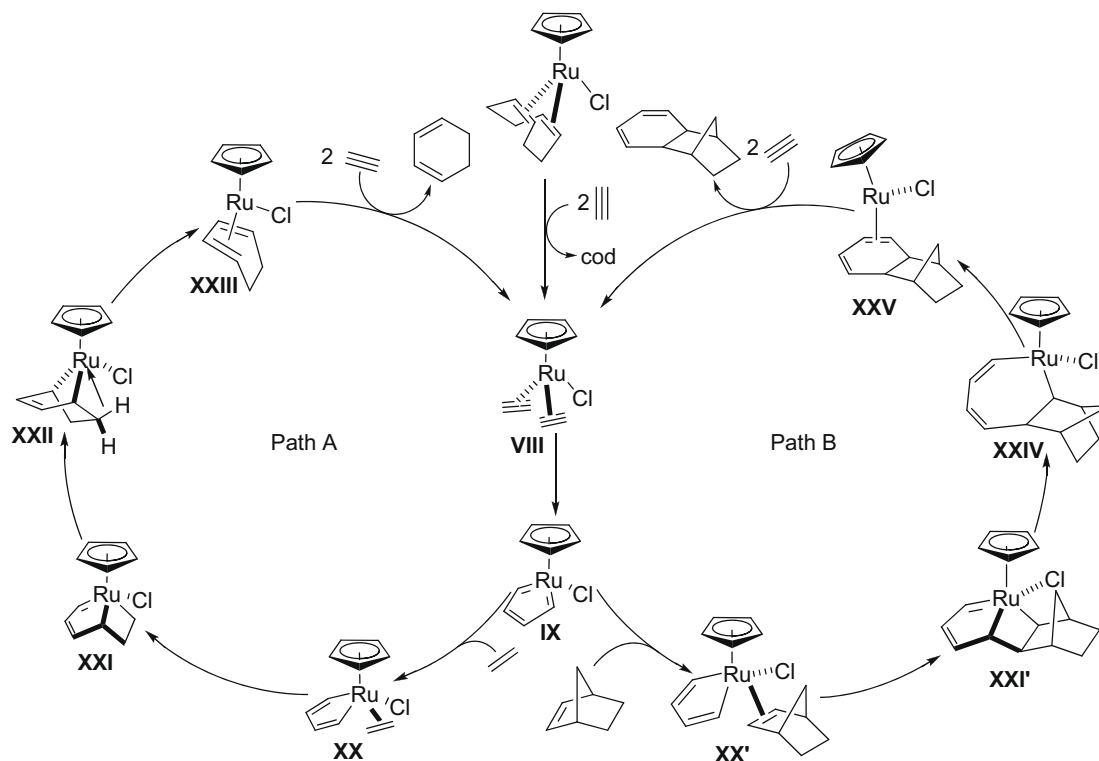
Scheme 5. Proposed mechanism for the CpRuCl-catalyzed [2+2+2] cycloadditions of two acetylenes to ethylene and norbornene.

Scheme 6. Proposed mechanisms for the "formal" and standard Ru-catalyzed [2+2+2] cycloadditions of alkynes to acyclic and cyclic alkenes.

A, the most favorable step seems to be the reductive elimination from **XXI** to give the Ru species **XXII**, which is stabilized by an agostic interaction between a hydrogen and the ruthenium. A change in hapticity from η^2 to η^4 followed by decomplexation of the ruthenium affords the final cyclohexadiene. On the other hand, in the case of norbornene (path B), the most favorable step involves ring expansion of the ruthenabicycle **XXI**′ (by cleavage of the central Ru–C bond) to the ruthenacycloheptadiene **XXIV**, which is the key intermediate in the cocyclotrimerization of acetylene with norbornene. Reductive elimination and decomplexation affords the final cyclohexadiene (Scheme 5).

More recently, we have published a DFT study on the CpRuCl-catalyzed [2+2+2] cycloaddition reaction of alkynes to alkenes, which involves two possible pathways depending on the alkene used (Scheme 6) [21]. Coordination of the Ru catalyst to alkynes followed by oxidative coupling gives the biscarbene species **IX**. Two pathways can be envisioned depending on the nature of the alkene: (a) coordination of **IX** to an acyclic alkene to give ruthenacyclic species **XXVI** (*endo* approach); (b) coordination of **IX** to cyclic alkenes to give ruthenacyclic species **XXXI** (*exo* approach). Subsequent formation of Ru-bicyclic complexes **XXVII** [22] and **XXXII** followed by electrocyclic opening would afford ruthenacy-

cloheptadienes **XXVIII** and **XXXIII**, respectively. The final steps of the catalytic cycle are: (a) the well-established reductive elimination from **XXXIII** to cyclohexadienes in the case of cyclic alkenes (standard cycloaddition) [23]; (b) a new β-elimination from **XXVIII** to give the ruthenium hydride **XXIX**, followed by reductive elimination to the open hexatriene **XXX** in the case of acyclic alkenes. The hexatriene **XXX** undergoes a pure thermal disrotatory $6e^-\pi$-electrocyclization to give the observed cyclohexadiene. The whole cascade process could be considered as a "formal" [2+2+2] cycloaddition of alkynes to alkenes [24].

5. CpCo-mediated [2+2+2] cycloaddition of alkynes to alkenes

A DFT study of the cobalt-mediated cocyclization of two acetylenes and ethylene to 1,3-cyclohexadiene and 1,3,5-hexatriene has recently been published [25]. According to this study, the mechanism of the cobalt-mediated [2+2+2] cycloaddition of two acetylenes to ethylene to give CpCo-complexed 1,3-cyclohexadiene proceeds through coordination of the alkene to **XV** followed by insertion into a σ Co–C-bond of the resulting cobaltacyclopentadiene **XXXIV** rather than inter- or intramolecular [4+2] cycloaddition between **XV** and the alkene (path B versus path A, cycle A, Scheme
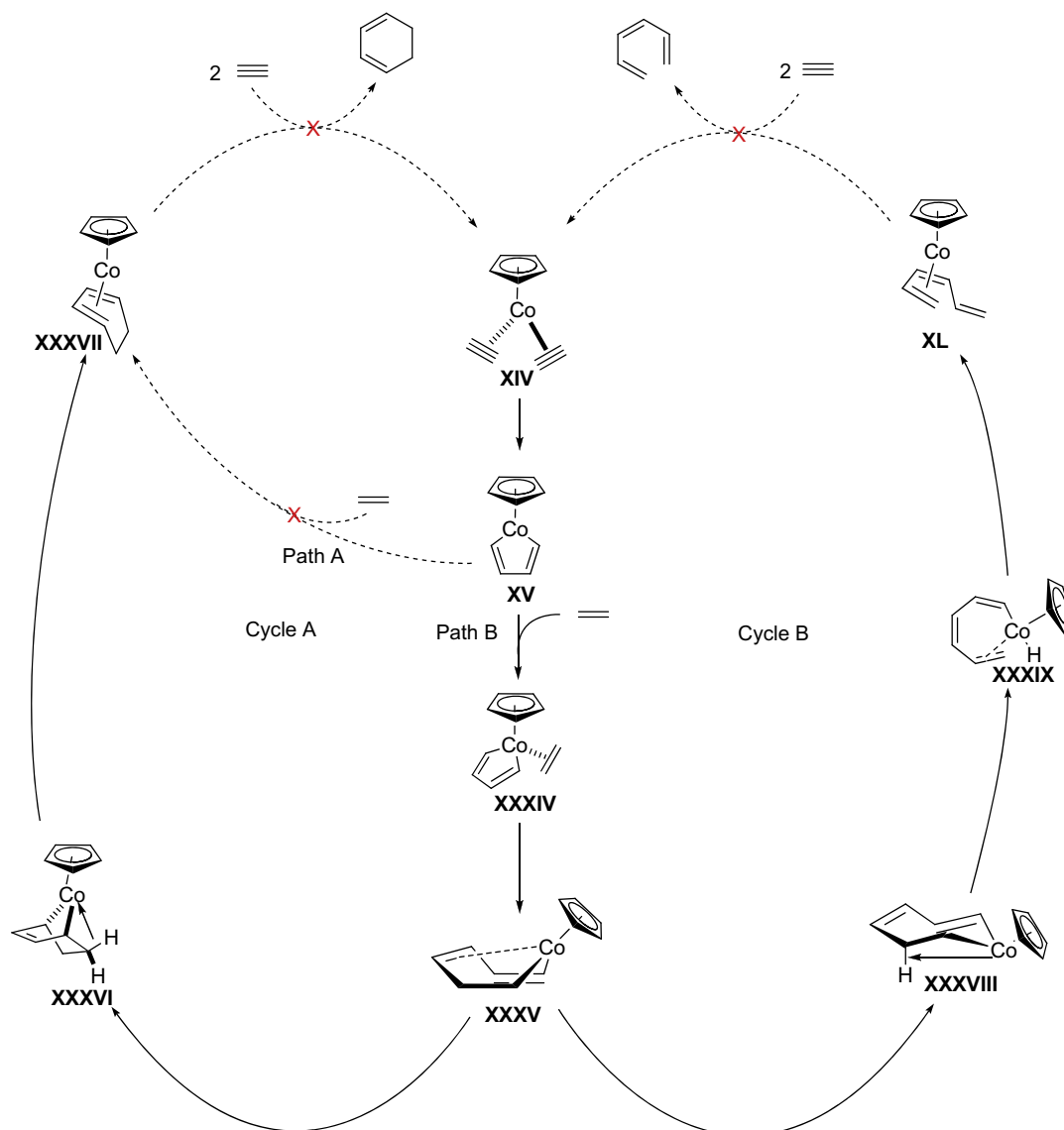
Scheme 7. Proposed mechanism for the CpCo-mediated cocyclization of two acetylenes and ethylene.

7). The resulting 7-membered cobaltacycle **XXXV** is the key intermediate and this leads either to CpCo-complexed cyclohexadiene (cycle A) or 1,3,5-hexatriene (cycle B). The metallacycle **XXXV** can be connected to the bicyclic intermediate **XXXVI** (with an agostic interaction analogous to intermediate **XXII** for the ruthenium) and this ultimately leads to the CpCo-complexed cyclohexadiene **XXXVII** by breaking the agostic interaction and changing the hapticity of the ligand (Cycle A). On the other hand, the metallacycle **XXXV** can undergo a conformational change to the more stable cobaltacycloheptadiene **XXXVIII**, in which an agostic Co–H_β interaction replaces a double bond coordination. Finally, β-hydride elimination followed by reductive elimination leads to the CpCo-complexed 1,3,5-hexatriene **XL** (cycle B). The completion of both catalytic cycles requires the dissociation of the diene ligands followed by coordination of two acetylenes to regenerate complex **XIV**. These processes have been calculated to be slightly exothermic [25], which could explain why this reaction is catalytic only under specific conditions [26].

6. Conclusion

In summary, DFT computational methods have been used to better understand the CpRuCl- and CpCo-catalyzed or mediated cyclotrimerization of alkynes and [2+2+2] cycloaddition of alkynes to alkenes. These theoretical studies have enabled more detailed catalytic cycles to be proposed and have allowed putative intermediates frequently invoked in the literature as part of those catalytic cycles to be ruled out. These examples show the potential that the computational methods actually have in elucidating cases where experimental results are difficult to obtain.

Acknowledgements

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Carlos Saá, born in Lugo (Spain), studied chemistry at the Universidad de Santiago de Compostela (Spain), where he received his Ph.D. in 1985 under the supervision of Profs. L. Castedo, R. Suau and J.M. Saá for research on synthesis of isoquinoline alkaloids. He spent two-year (1987–1988) as a NATO postdoctoral research associate at the University of California, Berkeley, working with Prof. K.P.C. Vollhardt on Co(I)-catalyzed [2+2+2] cycloaddition of alkynes to nitriles: synthesis of ergot alkaloids. Since 1990, he joined the faculty at the Universidad de Santiago de Compostela (Spain) as Profesor Titular, and since 2004 as full Professor. His research interest centers on the discovery of new reactions using transition-metal catalysts and the organometallic chemistry of unsaturated compounds.

Jesús A. Varela was born in 1971 in Lugo, Spain, and studied chemistry at the Universidad de Santiago de Compostela, Spain. He completed his M.Sc. in 1994 and his Ph.D. thesis in 1999 (excellent award) both under the supervision of Prof. Dr. Carlos Saá for research on synthesis of oligopyridines via cobalt chemistry. He spent a predoctoral research training period in Harvard University under supervision of Prof. Dr. Matthew Shair working on polyol synthesis by C–H insertion of metal-carbenes. From 1999 to 2001, he spent a postdoctoral period as an Alexander Von Humboldt and Marie Curie Fellow with Prof. Dr. Paul Knochel at Ludwig Maximilians Universität in Munich (Germany), working on remote C–H activation via hydroboration. He is currently assistant professor at the Universidad de Santiago de Compostela. His research interests are focused in metal-catalyzed cycloaddition reactions towards medium-sized carbo- and heterocycles.