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Density Functional Study of the [2+2+2] Cyclotrimerization of Acetylene Catalyzed by Wilkinson's Catalyst, $RhCl(PPh_3)_3$

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In this work we report density functional calculations at the B3LYP level of the [2+2+2] intermolecular cyclotrimerization of three acetylene molecules catalyzed by Wilkinson's catalyst. This process corresponds to the simplest [2+2+2] cyclotrimerization reaction. The results obtained show that this reaction is thermodynamically very favorable and that the rate-determining step is the initial oxidative coupling between two acetylene molecules with a relatively low Gibbs free energy barrier of 19.8 kcal·mol^{-1}. The energy profile derived from the real $[RhCl(PPh_3)_3]$ Wilkinson's catalyst is compared with that obtained with a model of the catalyst in which the PPh_3 ligands have been substituted by the smaller and computationally less expensive PH_3 molecules. Our results show that, at least for this reaction, this substitution has little influence on the thermodynamics obtained, while the barrier of the rate-determining step is somewhat increased (about 5 kcal·mol^{-1}) in the model system. These results justify the use of this simplified model of the catalyst in theoretical studies of more complex cyclotrimerizations. Finally, we compare the results of the [2+2+2] intermolecular cyclotrimerization of three acetylene molecules catalyzed by $[RhCl(PH_3)_3]$ with those of the [2+2+2] intramolecular cyclotrimerization in a 15-membered azamacrocyclic triyne recently reported (*Chem.*—*Eur. J.* **2009**, *15*, 5289). This comparison shows that the entropic term changes the preference for the intermolecular cyclotrimerization at low temperatures to the intramolecular one at high temperatures.

1. Introduction

The transition-metal-catalyzed [2+2+2] cyclotrimerization of alkynes is an attractive and elegant synthetic method to produce polysubstituted benzene derivatives with important academic and industrial uses.[1] These cycloaddition reactions have been studied extensively by both experimental[1] and theoretical methods.[2−13] In recent years our group has also contributed to the study of these reactions in macrocyclic systems to afford fused tetracycles with benzene and cyclohexadiene cores.[12,14,15] The previously cited theoretical studies have found that the reaction mechanism follows the steps shown in Scheme 1. Initially, a couple of ligand−alkyne substitutions occur. Subsequently, the two alkyne ligands generate metallacyclopentadiene **IIIa** or metallacyclopentatriene **IIIb** complexes through oxidative coupling. This step typically presents a barrier of 10 to 15 kcal·mol^{-1} and,

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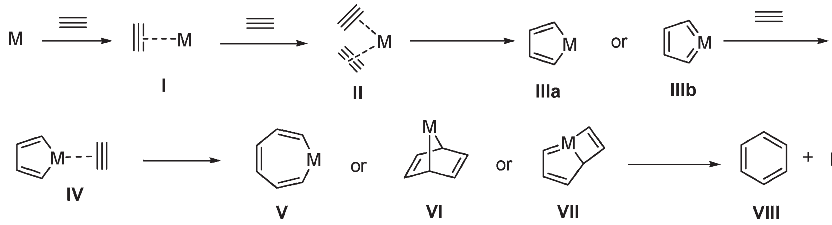
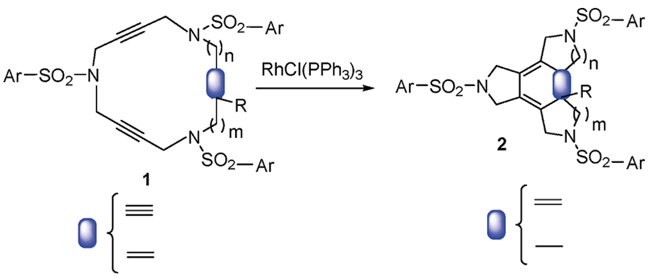
(1) (a) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901–2915. (b) Yamamoto, Y. *Curr. Org. Chem.* **2005**, *9*, 503–519. (c) Kotha, S.; Brahmachary, E.; Lahiri, K. *Eur. J. Org. Chem.* **2005**, 4741–4767. (d) Chopade, P. R.; Louie, J. *Adv. Synth. Catal.* **2006**, *348*, 2307–2327. (e) Gandon, V.; Aubert, C.; Malacria, M. *Chem. Commun.* **2006**, 2209–2217. (f) Tanaka, K. *Synlett* **2007**, 1977−1993. (g) Agenet, N.; Buisine, O.; Slowinski, F.; Gandon, V.; Aubert, C.; Malacria, M. *Org. React.* **2007**, *68*, 1–302. (h) Shibata, T.; Tsuchikama, K. *Org. Biomol. Chem.* **2008**, *6*, 1317–1323. (i) Galan, B. R.; Rovis, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 2830–2834.
(2) (a) Dahy, A. A.; Koga, N. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 781–791. (b) Dahy, A. A.; Suresh, C. H.; Koga, N. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 792–803.
(3) Bianchini, C.; Caulton, K. G.; Chardon, C.; Doublet, M.-L.; Eisenstein, O.; Jackson, S. A.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, *13*, 2010–2023.
(4) Dazinger, G.; Torres-Rodrigues, M.; Kirchner, K.; Calhorda, M. J.; Costa, P. J. *J. Organomet. Chem.* **2006**, *691*, 4434–4445.
(5) Hardesty, J. H.; Koerner, J. B.; Albright, T. A.; Lee, G.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 6055–6067.
(6) (a) Kirchner, K.; Calhorda, M. J.; Schmid, R.; Veiros, L. F. *J. Am. Chem. Soc.* **2003**, *125*, 11721–11729. (b) Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, *125*, 12143–12160.
(7) Orian, L.; van Stralen, J. N. P.; Bickelhaupt, F. M. *Organometallics* **2007**, *26*, 3816–3830.
(8) Agenet, N.; Gandon, V.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2007**, *129*, 8860–8871.
(9) Schmid, R.; Kirchner, K. *Eur. J. Inorg. Chem.* **2004**, 2609–2626.
(10) Varela, J. A.; Saá, C. *J. Organomet. Chem.* **2009**, *694*, 143–149.
(11) Xu, R.; Winget, P.; Clark, T. *Eur. J. Inorg. Chem.* **2008**, 2874–2883.
(12) Dachs, A.; Torrent, A.; Roglans, A.; Parella, T.; Osuna, S.; Solà, M. *Chem.*—*Eur. J.* **2009**, *15*, 5289–5300.
(13) Aubert, C.; Gandon, V.; Geny, A.; Heckrodt, T. J.; Malacria, M.; Paredes, E.; Vollhardt, K. P. C. *Chem.*—*Eur. J.* **2007**, *13*, 7466–7478.
(14) (a) Pla-Quintana, A.; Roglans, A.; Torrent, A.; Moreno-Mañas, M.; Benet-Buchholz, J. *Organometallics* **2004**, *23*, 2762–2767. (b) Torrent, A.; González, I.; Pla-Quintana, A.; Roglans, A.; Moreno-Mañas, M.; Parella, T.; Benet-Buchholz, J. *J. Org. Chem.* **2005**, *70*, 2033–2041.
(15) (a) González, I.; Bouquillon, S.; Roglans, A.; Muzart, J. *Tetrahedron Lett.* **2007**, *48*, 6425–6428. (b) Brun, S.; Garcia, L.; González, I.; Torrent, A.; Dachs, A.; Pla-Quintana, A.; Parella, T.; Roglans, A. *Chem. Commun.* **2008**, 4339–4341.

Scheme 1. Schematic [2+2+2] Reaction Mechanism with M = Transition Metal



Scheme 2. Cycloisomerization Reactions of Macrocyclic Triynes and Enediynes (n, m = 1, 2)



according to all theoretical studies carried out to date, is rate-determining.[2−12] The coordination of a third alkyne then takes place followed by alkyne insertion to yield one of three intermediates: a planar aromatic metallacycloheptatriene **V** (the so-called Schore's mechanism[16]) metal-mediated inter- or intramolecular [4+2] Diels−Alder cycloaddition to form a 7-metallanorbornadiene complex **VI**; or [2+2] cycloaddition to give a metallabicyclo[3.2.0]heptatriene **VII**. At this stage, a reductive elimination is produced generating the arene and recovering the catalyst. The whole process is highly exothermic, the thermodynamic driving force being provided by the new σ-bonds formed and the aromaticity that is gained. Unlike the uncatalyzed [2+2+2] cyclotrimerization of acetylenes, which presents a prohibitive energy barrier,[17] the barriers for the transition-metal-catalyzed [2+2+2] cyclotrimerization are relatively low. This is in agreement with the fact that this reaction experimentally occurs typically under mild conditions.

We previously reported the [2+2+2] intramolecular cycloisomerization of 15-,[14,15a] 16-,[15b] 17,[15b] 20-,[12] and 25-membered[12] azamacrocyclic triynes and enediynes catalyzed by different transition metals (Scheme 2). In these studies we found that the best experimental results were obtained using Wilkinson's catalyst, [RhCl(PPh$_3$)$_3$]. The metal-catalyzed [2+2+2] cyclotrimerization of three acetylenes has been theoretically studied in the case of the [CoCp(L)$_2$] (L = CO, PR$_3$, THF, and olefin),[2,5,8,10,13] [CpRuCl],[4,6,9,10] and LRh (L = Cp and indene)[4,7] catalysts but, to the best of our knowledge, not for Wilkinson's catalyst. We therefore decided to initiate a density functional theory (DFT) study of the mechanism of the simplest [2+2+2] cyclotrimerization catalyzed by [RhCl(PPh$_3$)$_3$], i.e., a study involving three acetylene molecules to yield benzene. Our main goal is to discuss whether the widely accepted mechanism of Scheme 1 also holds for Wilkinson's catalyst and to analyze similarities and differences between the mechanism found for Wilkinson's catalyst and the mechanisms proposed in previous works using other catalysts.

In many theoretical organometallic chemistry studies involving Wilkinson's catalyst or similar catalysts, the PPh$_3$ ligands are substituted by PH$_3$ molecules.[5,12,18−20] The replacement of PPh$_3$ by PH$_3$ in DFT studies is appealing because it significantly reduces the computational cost. This notwithstanding, the electronic and steric effects produced by the PPh$_3$ ligands are quite different from those created by the PH$_3$ ligands.[21] For instance, it is well-known that PH$_3$ is a poorer σ-donor and a stronger, although still modest, π-acid than PPh$_3$,[21] not to mention the different steric effects. Therefore, one can expect that the PPh$_3$ groups, having larger σ-donation and smaller π-back-donation, might enhance the electron density of the metal when compared to the PH$_3$ ligands.[22] This different electronic and steric behavior may have an important impact on the whole reaction mechanism, so that modeling PPh$_3$ by PH$_3$ could lead to unreliable results. On the other hand, a recent study[18] comparing the geometric parameters of the optimized structure at the B3LYP level for [RhCl(PH$_3$)$_3$] with the experimental X-ray structure of [RhCl(PPh$_3$)$_3$] established by Bennett and Donaldson[23] shows that the two geometries agree well and, therefore, that substitution of PPh$_3$ by PH$_3$ in the theoretical model is acceptable at least from a geometrical point of view. Thus, as a second and additional goal we aim to compare the reaction mechanisms catalyzed by the [RhCl(PPh$_3$)$_3$] and [RhCl(PH$_3$)$_3$] complexes and to discuss whether the substitution of PPh$_3$ by PH$_3$ leads to very different or comparable energy profiles. This is also an important goal for us since we are interested in theoretically studying reactions such as those shown in Scheme 2. Therefore, to study these relatively large macrocycles with a DFT method, it is necessary to substitute PPh$_3$ by PH$_3$ in order to finish the study in a reasonable period of time. Finally, as a third goal, we want to discuss the similarities and differences between the intermolecular [2+2+2] cyclotrimerization of three acetylene molecules

(16) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081–1119.
(17) (a) Ioffe, A.; Shaik, S. *J. Chem. Soc., Perkin Trans. 2* **1992**, 2101–2108. (b) Santos, J. C.; Polo, V.; Andrés, J. *Chem. Phys. Lett.* **2005**, *406*, 393–397.
(18) Yoo, K.; Jun, C.-H.; Choi, C. H.; Sim, E. *Bull. Korean Chem. Soc.* **2008**, *29*, 1920–1926.
(19) Gandon, V.; Agenet, N.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2006**, *128*, 8509–8520.
(20) (a) Veiros, L. F.; Dazinger, G.; Kirchner, K.; Calhorda, M. J.; Schmid, R. *Chem.—Eur. J.* **2004**, *10*, 5860–5870. (b) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1997**, *16*, 1355–1364. (c) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 742–751. (d) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 1383–1392. (e) Zheng, W.; Ariafard, A.; Lin, Z. *Organometallics* **2008**, *27*, 246–253. (f) Abe, Y.; Kuramoto, K.; Ehara, M.; Nakatsuji, H.; Suginome, M.; Murakami, M.; Ito, Y. *Organometallics* **2008**, *27*, 1736–1742. (g) Macgregor, S. A.; Roe, D. C.; Marshall, W. J.; Bloch, K. M.; Bakhmutov, V. I.; Grushin, V. V. *J. Am. Chem. Soc.* **2005**, *127*, 15304–15321.
(21) Woska, D.; Prock, A.; Giering, W. P. *Organometallics* **2000**, *19*, 4629–4638.
(22) Rahman, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1–7.
(23) Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, *16*, 655–660.

and the intramolecular [2+2+2] cyclotrimerization in the 15-membered azamacrocyclic triyne **1** ($n = m = 1$ in Scheme 2), both catalyzed with the same model catalyst, $[RhCl(PH_3)_3]$.

2. Method of Calculation

The geometries of the reactants, intermediates, transition states (TSs), and products were optimized using the DFT B3LYP hybrid exchange−correlation functional with the Gaussian03[24] program package. All the geometry optimizations were performed without symmetry constraints. 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.[25] These two latter terms were computed at 298.15 K and 1 atm to provide the reported relative Gibbs free energies (ΔG_{298}). Furthermore, the connectivity between stationary points was unambiguously established by intrinsic reaction path[26] calculations. The all-electron cc-pVDZ basis set[27] was employed for the nonmetal atoms, and the cc-pVDZ-PP basis set containing an effective core relativistic pseudopotential was used for Rh.[28] The solvent effects were not included in the present calculations since the reaction is usually carried out in rather nonpolar solvents. Previous results have shown that solvent effects are unimportant in this reaction.[7] Finally, some earlier theoretical studies suggested the presence of paramagnetic intermediates in the mechanism.[8,11,19,29] For this reason, we computed three possible electronic states for all intermediates and TSs, namely, the singlet closed shell, singlet open shell, and triplet open shell states. The results obtained showed that the singlet closed shell state is the ground state for all stationary points located. For this reason, we report here only the results corresponding to the singlet closed shell potential energy surface. The *xyz* Cartesian coordinates of all minima and transition states (TSs) located can be found in the Supporting Information.

3. Results and Discussion

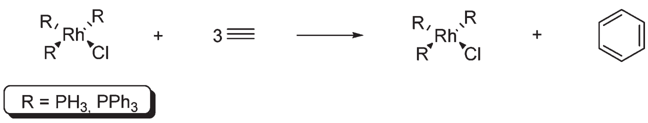
This section is organized as follows. First, we briefly discuss the optimized geometries of the $[RhCl(PR_3)_3]$ species (R = H and Ph) and compare them with experimental X-ray data for the $[RhCl(PPh_3)_3]$ complex. Second, we discuss the computed energy profile of the cyclotrimerization of three acetylenes catalyzed by Wilkinson's catalyst (Scheme 3, R = Ph). Third, the reaction mechanism of the same process catalyzed by a model of Wilkinson's catalyst in which the phenyl groups are substituted by H atoms, $[RhCl(PH_3)_3]$, is presented and compared with the results obtained in the previous subsection. Finally, we make a comparison between the intramolecular [2+2+2] cyclotrimerization in the 15-membered azamacrocycle triyne **1** ($n = m = 1$ in Scheme 2)[12] and the intermolecular [2+2+2] cyclotrimerization of three acetylene molecules, both catalyzed by the same model of Wilkinson's catalyst, $[RhCl(PH_3)_3]$.

Table 1. Experimental and Computed Most Important Geometrical Parameters for the $[RhCl(PR_3)_3]$ Species (R = H and Ph) (distances in Å and angles in deg)

	$RhCl(PPh_3)_3$[a]	$RhCl(PPh_3)_3$	$RhCl(PH_3)_3$
Rh−Cl	2.376	2.420	2.391
Rh−P(1)	2.334	2.411	2.304
Rh−P(2) *trans*	2.214	2.301	2.244
Rh−P(3)	2.322	2.375	2.313
∠P(1)RhP(2)	97.9	100.4	96.0
∠P(1)RhP(3)	152.8	151.7	168.6
∠P(2)RhP(3)	100.4	99.9	95.5
∠ClRhP(1)	85.2	84.7	84.4
∠ClRhP(3)	100.4	84.6	84.2
∠ClRhP(2)	156.2	156.2	179.7

[a] X-ray data for the red form of $[RhCl(PPh_3)_3]$ from ref 23.

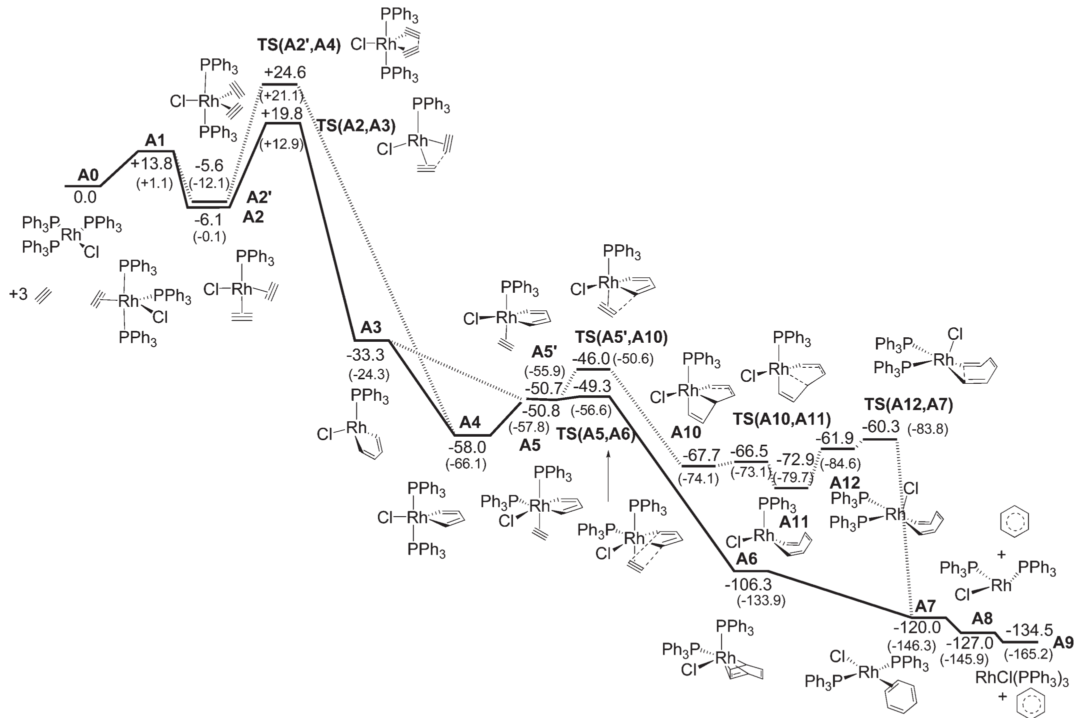
Scheme 3. [2+2+2] Cyclotrimerization Reaction Catalyzed by Wilkinson's Complex



3.1. Molecular Structure of Wilkinson's Catalyst. Before starting the study of the reaction mechanism, let us compare the experimental and calculated geometrical parameters for the $[RhCl(PR_3)_3]$ species (R = H and Ph) listed in Table 1. From the values of this table it can be seen that the two mutually *trans* Rh−P bonds are significantly longer than the other Rh−P bond *trans* to the Rh−Cl one as a result of the smaller *trans* effect exerted by the chlorine.[30] In comparison with the experimental values, the bond lengths of the $[RhCl(PH_3)_3]$ model are somewhat better than those of the $[RhCl(PPh_3)_3]$ species, which are slightly overestimated. The Rh−P bond distances are shorter for $[RhCl(PH_3)_3]$ as compared to $[RhCl(PPh_3)_3]$, indicating stronger Rh−P bonds in the former complex. Indeed, the dissociation *enthalpy* energies corresponding to the process $[RhCl(PR_3)_3] \rightarrow [RhCl(PR_3)_2] + PR_3$ are 19.40 and 27.47 kcal·mol^{-1} for R = Ph and H, respectively. Rather than to electronic effects, the smaller dissociation enthalpy for R = Ph is attributed to the larger steric repulsion between the ligands in the $[RhCl(PPh_3)_3]$ catalyst, which is partially avoided by increasing the Rh−P bond lengths and, consequently, the separation between the phosphine ligands. The bulkier PPh_3 ligands therefore facilitate exchange.[31] As we will discuss later, this results in important differences between $[RhCl(PPh_3)_3]$ and $[RhCl(PH_3)_3]$ catalysts for the initial part of the reaction corresponding to the exchange of one or two PR_3 groups by two alkyne molecules. On the other hand, the

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revison C.01; Gaussian, Inc.: Pittsburgh, PA, 2003.
(25) Atkins, P.; De Paula, J. *Physical Chemistry*; Oxford University Press: Oxford, 2006.
(26) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154–2161.
(27) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007–1023. (b) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358–1371.
(28) Peterson, K. A.; Figgen, D.; Dolg, M.; Stoll, H. *J. Chem. Phys.* **2007**, *126*, 124101.
(29) Koga, N.; Morokuma, K. *J. Phys. Chem.* **1990**, *94*, 5454–5462.
(30) Hartley, F. R. *Chem. Soc. Rev.* **1973**, *2*, 163–179.
(31) Goodman, J.; Grushin, V. V.; Larichev, R. B.; Macgregor, S. A.; Marshall, W. J.; Roe, D. C. *J. Am. Chem. Soc.* **2009**, *131*, 4236–4238.

Scheme 4. Gibbs Free Energy Profile at 298 K (electronic energies in parentheses) for the [2+2+2] Cyclotrimerization Catalyzed by $[RhCl(PPh_3)_3]$[a]



[a] The lowest Gibbs free energy path has been marked with a thick black line. Energies are in kcal·mol^{-1}.

angles are better predicted by the real Wilkinson's catalyst. This is clearly seen for instance in the ∠P(1)RhP(3) angle, which is clearly larger for the $[RhCl(PH_3)_3]$ species. The discrepancy in the angles found in the $[RhCl(PH_3)_3]$ model is not unexpected because of the stronger steric hindrance introduced by the PPh_3 ligands as compared to the PH_3 ones. These results indicate that our computational method provides reasonable molecular geometries for the species studied here and that the $[RhCl(PH_3)_3]$ model leads to acceptable geometries. The Mulliken charges on the Rh atom are −0.15 and −0.36 e for the $[RhCl(PPh_3)_3]$ and $[RhCl(PH_3)_3]$ species, respectively. These values are somewhat unexpected given the larger σ-donation and smaller π-back-donation of PPh_3 as compared to PH_3 and is the result of the larger Rh−P bonds in $[RhCl(PPh_3)_3]$, which make the σ-donation of the bulky PPh_3 ligands less efficient than that of the PH_3 species in $[RhCl(PH_3)_3]$.

3.2. Cyclotrimerization of Acetylene Catalyzed by Wilkinson's Complex. Scheme 4 draws the Gibbs free energy profile of the cyclotrimerization of three acetylene molecules catalyzed by Wilkinson's complex. Initially, there is the exchange of PPh_3 ligands by acetylene molecules that coordinate to the metal. The substitution of two PPh_3 ligands by two acetylene molecules leads to complex **A2**. Alternatively, the two incoming acetylene molecules may displace a single PPh_3 ligand, forming either complex **A2′**, with two equatorial acetylene ligands, or **A2″**, with one axial and one equatorial acetylene ligand. The formation of the latter is endothermic by 3.9 kcal·mol^{-1}, and for this reason it has not been considered in the study. On the other hand, the substitution process of phosphines by acetylenes to yield **A2** and **A2′** is exothermic by 6.1 and 5.6 kcal·mol^{-1}, respectively.

In the next step the oxidative coupling of two alkynes takes place. At this stage, two possible TSs (**TS(A2,A3)** and **TS(A2′,A4)**), depending on whether the coupling occurs in **A2** or **A2′**, are found. **TS(A2,A3)**, which is depicted in Figure 1, has the lowest Gibbs free energy barrier (19.8 kcal·mol^{-1} with respect to isolated reactants **A0**) and an imaginary frequency of 461.8i cm^{-1}. On the other hand, the Gibbs free energy barrier of **TS(A2′,A4)** is 30.2 or 24.6 kcal·mol^{-1} measured with respect to intermediate **A2′** or isolated reactants **A0**, respectively. Thus, the reaction proceeds essentially from **A2** through **TS(A2,A3)** to yield intermediate **A3**. The **A2** → **A3** process is exergonic by 27.2 kcal·mol^{-1}. The formation of a similar metallacyclopentadiene intermediate in the case of the CpRuCl-, RhCp-, and CpCo-catalyzed cyclotrimerization was reported to have similar barriers but to be somewhat less exothermic.[4,5,7] It is worth emphasizing that the Gibbs free energy barrier for this process is the highest along the reaction coordinate, and therefore, this step is rate-determining, as found in previous works using other catalysts. The barrier and the geometry of **TS(A2,A3)** found are similar to those obtained for the same process catalyzed by the $[CoCp(L)_2]$ (L = CO, PR_3, THF, and olefin),[2,5,8,10,13] [CpRuCl],[4,6,9,10] and LRh (L = Cp and indene)[4,7] complexes. In particular, the molecular structure of **TS(A2,A3)** is almost the same as that found by us in an intramolecular cyclotrimerization catalyzed by $[RhCl(PH_3)_3]$.[12] As reported in related cases,[5,7,12] intermediate **A3** is a nonaromatic species since it presents a clear π-localization with C_α−C_β and C_β−$C_{\beta'}$ bond lengths of 1.354 and 1.475 Å, respectively.

A3 can either add a PPh_3 ligand to form **A4** or add an acetylene molecule to yield **A5′**, and therefore, there is a bifurcation of the reaction path at this point. The two generated routes merge at intermediate **A7**. In the former pathway, complex **A4** is formed first in a quite exergonic process that releases 24.7 kcal·mol^{-1}. This species then adds an acetylene molecule to form the distorted octahedral complex **A5** in a process that is endergonic by 7.2 kcal·mol^{-1}. The next step

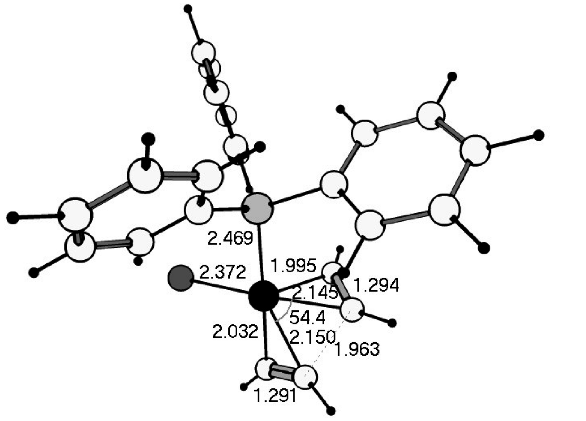


Figure 1. Optimized structure (B3LYP/cc-pVDZ-PP) for **TS-(A2,A3)** with the most relevant bond lengths [Å] and angles [deg].

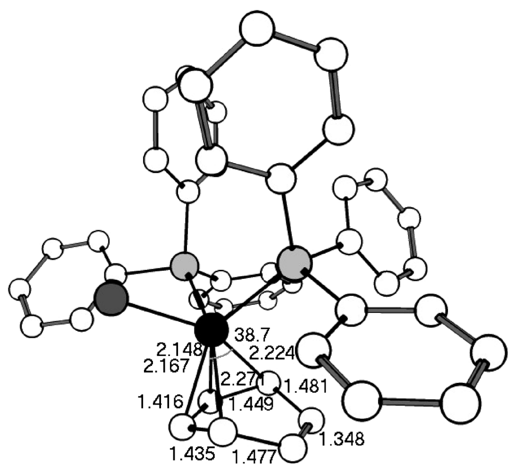


Figure 2. Structure of complex **A6** with selected interatomic distances [Å] and angles [deg]. For the sake of clarity nonrelevant H atoms have been omitted.

that converts **A5** into **A6** is an intramolecular [4+2] cycloaddition reaction of the coordinated acetylene to the rhodacyclopentadiene. In accordance with previous studies,[5,7,12] the Gibbs free energy barrier for this process is very low (1.5 kcal·mol^{-1}), and the exergonicity is as large as 56.5 kcal·mol^{-1}. Although this 18-electron **A6** complex could be regarded as a rhodanorbornadiene intermediate, we consider that it is better represented as a complex in which the formed benzene ring is η^4-coordinated to Rh(I) since the four shorter Rh−C distances are quite similar (see Figure 2). The uncoordinated portion of the benzene molecule displays significant short−long bond alternation (Figure 2), indicating that the aromaticity of the benzene ring in **A6** is partially lost. This is reinforced by the fact that this ring shows a hinge angle of 38°, not far from the 37° found in the BLYP/TZ2P-optimized geometry of the [Rh(η^4-benzene)Cp] complex[7] or the 42° measured in the X-ray structure of [Rh(η^5-$C_5(CH_3)_5$)(η^4-$C_6(CH_3)_6$)] species.[32] Ring slippage in **A6** leads to **A7**, in which the two pathways join. This is an exergonic process by 13.7 kcal·mol^{-1}, despite the change from a saturated 18-electron species to a 16-electron system. Stabilization of **A7** comes from a gain in the aromaticity of the

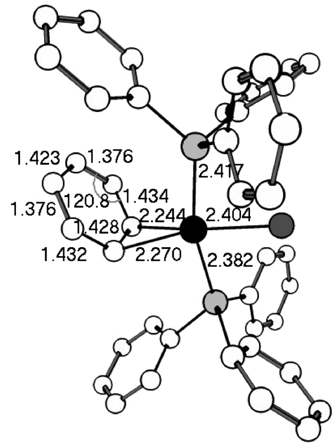


Figure 3. Structure of complex **A7** with selected interatomic distances [Å] and angles [deg]. For the sake of clarity nonrelevant H atoms have been omitted.

benzene ring that is more planar and suffers less bond length alternation (see Figure 3). Despite several attempts, no TS connecting **A6** to **A7** was found. However, on the basis of previous findings[12] and also taking into account the results of the next subsection (*vide infra*), the energy barrier of this step is expected to be relatively low (about 5 kcal·mol^{-1}).

Alternatively, intermediate **A3** can add an acetylene molecule, forming **A5′**. The molecular structure of the resulting complex is similar to the only reported example of a metallacyclopentadiene(alkyne) species.[33] Interestingly, in this case, the addition of the new coordinated acetylene molecule to the rhodacyclopentadiene occurs through an intramolecular [2+2] cycloaddition leading to the five- and four-membered bicyclic ring intermediate **A10** (Figure 4), which is similar to that found in previous works.[4,6,7,12] The transformation of **A5′** into **A10** is exergonic by 17.0 kcal·mol^{-1} and takes place via **TS(A5′,A10)** (Figure 5) with a Gibbs free energy barrier of 4.7 kcal·mol^{-1}.

Subsequent scission of the central Rh−C single bond in **A10** leads to the rhodacycloheptatriene intermediate **A11** (Schore's mechanism[16]) through an almost barrierless **TS-(A10,A11)** (1.2 kcal·mol^{-1}) and slightly exergonic process by 5.2 kcal·mol^{-1}. Addition of a new PPh_3 ligand leads to **A12** and increases the Gibbs free energy by 11 kcal·mol^{-1}. Finally, complex **A7** is formed through a very exergonic reductive elimination step (58.1 kcal·mol^{-1}) via **TS(A12, A7)**, which has a barrier of only 1.6 kcal·mol^{-1}.

The two routes (**A3** → **A4** → **A5** → **A6** → **A7** and **A3** → **A5′** → **A10** → **A11** → **A12** → **A7**) have similar energy requirements, so it is likely that both pathways are operative for the [RhCl(PPh_3)$_3$] catalyst. The first pathway (**A3** → **A4** → **A5** → **A6** → **A7**) is similar to that found for the [CoCp(L)$_2$] (L = CO, PR_3, THF, and olefin)[5,8] (although it has been reported that the mechanism can change with strongly dienophilic alkynes[8]) and RhCp catalysts,[7] while the second route (**A3** → **A5′** → **A10** → **A11** → **A12** → **A7**) has been previously found for the RuCpCl catalyst.[6] Once **A7** is formed, the exchange of benzene by a PPh_3 molecule that releases the final product and recovers the catalyst is an exergonic (14.5 kcal·mol^{-1}) and almost barrierless process. The whole reaction is thermodynamically very favorable. Our results at the B3LYP/cc-pVDZ-PP level show

(32) Bowyer, W. J.; Merkert, J. W.; Geiger, W. E.; Rheingold, A. L. *Organometallics* **1989**, *8*, 191–198.

(33) Dosa, P. I.; Whitener, G. D.; Vollhardt, P. C.; Bond, A. D.; Teat, S. J. *Org. Lett.* **2002**, *4*, 2075–2078.

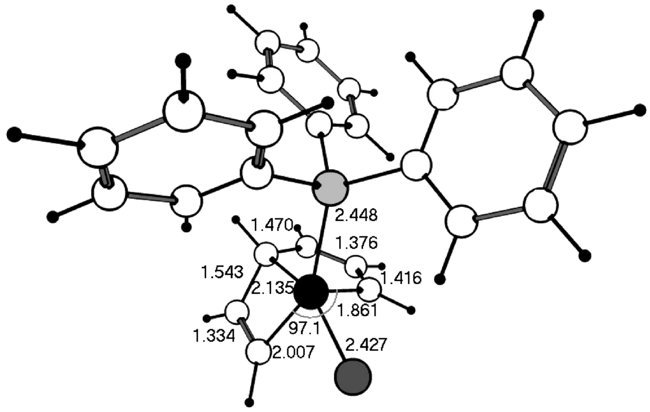


Figure 4. Optimized structure (B3LYP/cc-pVDZ-PP) for bicyclic intermediate **A10** with the most relevant bond lengths [Å] and angles [deg].

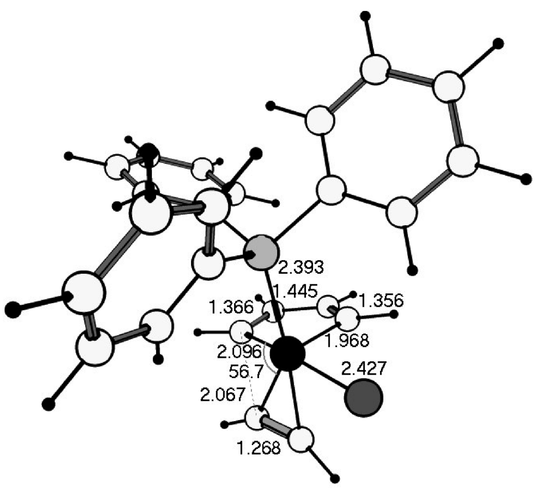


Figure 5. Optimized structure (B3LYP/cc-pVDZ-PP) for **TS-(A5′,A10)** with the most relevant bond lengths [Å] and angles [deg].

that the whole cycloaddition reaction catalyzed by the [RhCl(PPh_3)$_3$] system is exergonic by 134.5 kcal·mol^{-1}.

3.3. Cyclotrimerization of Acetylene Catalyzed by the [RhCl(PH_3)$_3$] Complex. One of our present[12] and future goals is to theoretically analyze the reaction mechanisms of the intramolecular [2+2+2] cyclotrimerizations in relatively large systems, as those depicted in Scheme 2. To make DFT calculations feasible in these systems, the large PPh_3 ligands of the [RhCl(PPh_3)$_3$] catalyst have to be modeled using PH_3 molecules. As stated in the Introduction, there are many theoretical works in which the large PPh_3 ligands of the [RhCl(PPh_3)$_3$] catalyst have to be modeled using PH_3 molecules.[5,12,18−20] Alternatively, one could also use ONIOM[34] or QM/MM[35] methodologies, although our preliminary calculations using these approaches show that the simple substitution offers more reliable and faster results at least for the process analyzed (*vide infra*). Because of the different electronic and steric effects shown by the PPh_3 and PH_3 ligands, it is not clear whether the energy profiles obtained for the real Wilkinson's catalyst and the modeled one are comparable. To answer this question, we decided to explore the Gibbs free energy profile of the simplest of the [2+2+2] cyclotrimerization reaction catalyzed by the [RhCl(PH_3)$_3$] complex and compare the results with those obtained in the preceding section.

The Gibbs free energy profile at 298 K obtained with the [RhCl(PH_3)$_3$] catalyst is depicted in Scheme 5. Full details of this reaction mechanism are discussed in section S1 of the Supporting Information. It is important to note that substitution of PPh_3 by PH_3 in Wilkinson's catalyst reduces the computational cost by 1 order of magnitude or more. As can be seen when comparing the results of Schemes 4 and 5, the thermodynamics of the whole process does not change, the reaction being exergonic in the two cases by exactly the same amount (134.5 kcal·mol^{-1}). On the other hand, the oxidative coupling through **TS(B2,B4)** remains the rate-determining step with an energy barrier of 11.9 kcal·mol^{-1} and a Gibbs free energy barrier of 24.7 kcal·mol^{-1}.

As a whole, the results found indicate that the substitution of the PPh_3 by PH_3 ligands in Wilkinson's catalyst does not produce a significant change in the kinetics (same rate-determining step and similar energy barrier) nor in the thermodynamics of the [2+2+2] cyclotrimerization of three acetylene molecules. Both reaction energies and barriers for the rate-determining step differ by less than 1 kcal·mol^{-1}. Differences in the Gibbs free energy barrier are somewhat larger (4.9 kcal·mol^{-1}). Still the small energy differences found justify the use of the simplified model of the catalyst in theoretical studies of more complex cyclotrimerizations. Finally, it is worth noting that we have found some differences between the two reaction mechanisms. In particular, they differ in the initial step of the reaction and in an alternative pathway for the attack of the third acetylene molecule to the formed rhodacyclopentadiene that is found to be operative for Wilkinson's catalyst only (see Supporting Information, section S1). Therefore, the extrapolation of the excellent performance of the substitution of PPh_3 by PH_3 ligands found in the simplest [2+2+2] cyclotrimerization to any other reaction catalyzed by Wilkinson's catalyst must be made with some caution.

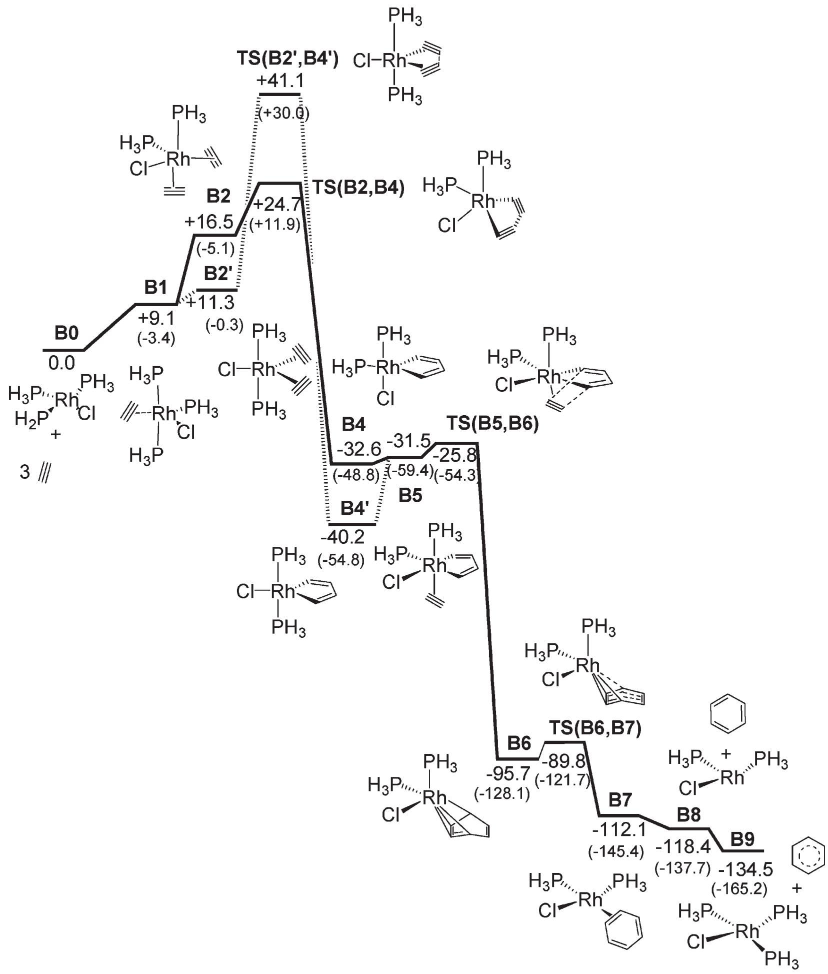
3.4. Intramolecular versus Intermolecular [2+2+2] Cyclotrimerization Reactions Using the Model of Wilkinson's Catalyst, [RhCl(PH_3)$_3$]. In this last section, we briefly compare the thermodynamic and kinetic results of the simplest intermolecular [2+2+2] cyclotrimerization of three acetylene molecules (previous section) with those of one of the simplest intramolecular [2+2+2] cyclotrimerizations in the 15-membered azamacrocycle triyne **1** (Scheme 2 with $n = m = 1$) recently reported by us.[12] Full details of the intramolecular [2+2+2] cyclotrimerizations in the 15-membered macrocycle can be found in ref 12. Here we just make a comparison between the main results obtained for the intra- and intermolecular cyclotrimerizations. Both reactions have been studied at the same level of theory using the same model of Wilkinson's catalyst, [RhCl(PH_3)$_3$].

The intra- and intermolecular reactions are thermodynamically favored and also very exergonic, with estimated Gibbs free reaction energies of 128.4 and 134.5 kcal·mol^{-1}, respectively. In both cases, the rate-determining step of the reaction is the oxidative coupling that takes place through transition states **15-TS(A2,A3)** and **TS(B2,B4)**, for the intra- and intermolecular cyclotrimerizations,

(34) (a) Svensson, M.; Humbel, S.; Froese, R. D. J.; Matsubara, T.; Sieber, S.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 19357–19363. (b) Dapprich, S.; Komáromi, I.; Byu, K. S.; Morokuma, K.; Frisch, M. J. *J. Mol. Struct.* (*THEOCHEM*) **1999**, *461−462*, 1–21.

(35) Maseras, F.; Morokuma, K. *J. Comput. Chem.* **1995**, *16*, 1170–1179.

Scheme 5. Gibbs Free Energy Profile at 298 K (electronic energies in parentheses) for the [2+2+2] Cyclotrimerization Reaction Catalyzed by [RhCl(PH$_3$)$_3$][a]



[a] The lowest Gibbs free energy path has been marked with a thick black line. Energies are given in kcal·mol^{-1}.

Table 2. Gibbs Free Energy Barrier (in kcal·mol^{-1}) for the Rate-Determining Step of the Inter- and Intramolecular Cyclotrimerization at Different Temperatures (K)

	T			
$\Delta G^{\ddagger}$	0	273	298	373
intermolecular	13.2	23.6	24.7	27.9
intramolecular	13.6	20.7	21.7	24.9

respectively. The two reactions have similar Gibbs free energy barriers at 0 K, 13.6 and 13.2 kcal·mol^{-1} for the intra- and intermolecular cyclotrimerizations, respectively. The main structural difference between **15-TS(A2, A3)** and **TS(B2,B4)** is that while the former has a unique PH$_3$ molecule coordinated to Rh, the latter has two. This is attributed to the higher steric hindrance created by the macrocycle. In addition, the C$_{\beta}$−C$_{\beta'}$ distance of 1.948 Å of **15-TS(A2,A3)** is shorter than that found for **TS(B2,B4)** (2.089 Å), indicating that **15-TS(A2,A3)** is closer to the product of the oxidative coupling than **TS(B2,B4)**. This is in agreement with the Hammond postulate[36] since we have a less exothermic intra- than intermolecular oxidative coupling.

(36) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338.

For these two reactions, it is particularly interesting to analyze how the Gibbs free energy barriers change with increasing temperature. Table 2 compares the Gibbs free energy barriers of the rate-determining step of the intra- and intermolecular cyclotrimerization computed at 0, 273, 298, and 373 K. As can be seen, at 0 K the difference between Gibbs free energies barriers of the intra- and intermolecular process is only 0.4 kcal·mol^{-1} in favor of the intermolecular reaction. As temperature rises, the Gibbs free energy barrier of the two processes increases, although the increase is higher for the intermolecular cyclotrimerization, and consequently, the intramolecular process is favored. At 298 K, the Gibbs free energy barrier of the intramolecular process is lower as compared to the intermolecular one by as much as 3.0 kcal·mol^{-1}. Not unexpectedly, this result is due to a more favorable entropic contribution for the intramolecular reaction than the intermolecular one.

4. Conclusions

In this work, we have carried out a study of the mechanism of the [RhCl(PPh$_3$)$_3$]-catalyzed [2+2+2] cyclotrimerization of acetylene to benzene with the B3LYP/cc-pVDZ-PP methodology. The results obtained show that this reaction is thermodynamically very favorable. The process involves the formation of a coordinatively unsaturated 16-electron metallacycle, **A3**, which has been identified as the rate-determining step with a Gibbs free energy barrier of about 12 kcal·mol^{-1} with respect to separated reactants. Next, the barrierless coordination of a third acetylene molecule and its subsequent addition to the π electron system of the rhodacycle leads to an intermediate, which is characterized by a six-membered arene ring coordinated to the metal in η^4 fashion (**A6**).

We have found that modeling PPh_3 by PH_3 in the catalyst results in minor changes in the thermodynamics and kinetics at 0 K. Both the reaction energies and the barriers in the rate-determining step differ by less than 1 kcal·mol^{-1}. This fact can be exploited to reduce the computational cost significantly. However, we should note that there are some differences between the two reaction mechanisms: the initial step of the reaction is not the same and an alternative pathway for the attack of the third acetylene molecule on the formed rhodacyclopentadiene is found to be operative for Wilkinson's catalyst but not in the modeled $[RhCl(PH_3)_3]$ one. In addition, the Gibbs free energy barrier of the rate-determining step at 298 K is somewhat higher (about 5 kcal·mol^{-1}) for the model catalyst, $[RhCl(PH_3)_3]$.

Finally, we have compared the thermodynamic and kinetic results of the simplest intermolecular [2+2+2] cyclotrimerization of three acetylene molecules with those of one of the simplest intramolecular [2+2+2] cyclotrimerizations in a 15-membered azamacrocyclic triyne. By analyzing the Gibbs free energy barrier of the rate-determining step we have found that the entropic term changes the preference for the intermolecular cyclotrimerization at low temperatures to the intramolecular one at high temperatures.

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Supporting Information Available: Details corresponding to the [2+2+2] cyclotrimerization of three acetylene molecules catalyzed by the $[RhCl(PH_3)_3]$ complex. Cartesian *xyz* coordinates and total energies of all stationary points located. This material is available free of charge via the Internet at http://pubs.acs.org.