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Palladium-Catalysed [3+2] Cycloaddition of Alk-5-ynylidenecyclopropanes to Alkynes: A Mechanistic DFT Study

Rebeca García-Fandiño,[b] Moisés Gulías,[b] Luis Castedo,[b] Juan R. Granja,[b] José L. Mascareñas,*[b] and Diego J. Cárdenas*[a]

Abstract: The mechanism of the palladium-catalysed [3+2] intramolecular cycloaddition of alkylidenecyclopropanes to alkynes has been computationally explored at DFT level. The energies of the reaction intermediates and transition states for different possible pathways have been calculated in a model system that involves the use of PH_3 as a ligand. The results obtained suggest that the most favourable reaction pathway involves the initial C–C oxidative addition of the cyclopropane to a Pd^0 complex to give an alkylidenepalladacyclobutane, which isomerises to a methylenepalladacyclobutane intermediate. Subsequent cyclisation by alkyne carbometallation, followed by reductive elimination affords the final product. An alternative mechanism consisting of a palladaene-type rearrangement is less probable in terms of Gibbs energy, but cannot be fully discarded because it is competitive if one considers electronic energies. For substrates that present an ester group at the terminal position of the triple bond we have found an alternative, more favourable mechanistic route that explains why the [3+2] cycloaddition of these types of systems does not lead to the expected cycloadducts.

Keywords: alkynes · carbocycles · density functional calculations · metallacycles · palladium

Introduction

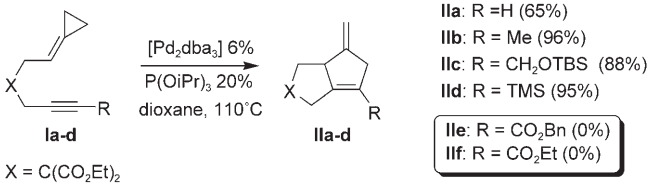
Natural and non-natural polycyclic systems containing cyclopentanoid rings constitute a large class of compounds of great importance in organic chemistry, biology and medicine.[1] The prominent occurrence of these types of systems continues to encourage the development of new strategies for their rapid and efficient synthesis.[2] Among the different approaches thus far described, the metal-catalysed cycloaddition of methylenecyclopropanes (MCPs) to alkenes or alkynes is particularly appealing.[3–5] The intramolecular version of this cycloaddition, mainly studied by Motherwell's and Lautens' groups, provides for the assembly of interesting bicyclic structures from simpler precursors. Apparently, the success of the reaction is dependent on the presence of electron-withdrawing groups in the alkyne, and is particularly effective when the alkyne bears an ester substituent.[5] More recently, our group has demonstrated that alk-5-ynylidenecyclopropanes (**I**), which are much easier to ensemble than the isomeric methylenecyclopropanes, do also undergo an intramolecular [3+2] cycloaddition under palladium catalysis.[6] The reaction proceeds efficiently with a variety of substituted alkynes, even with those containing bulky TMS (TMS = trimethylsilyl) groups, but in contrast to that observed in the cycloaddition of homologous methylenecyclopropanes, failed in substrates containing an ester substituent at the alkyne terminus (Scheme 1). Therefore alkynyl esters **Ie** or **If** were rapidly consumed even when the reaction was carried out at lower temperatures (50 °C), leading to products other than the expected cycloadducts.

The lack of mechanistic information on the above cycloaddition, as well as of an explanation for the different reactivity of the ester-containing substrates, prompted us to in-

[a] Dr. D. J. Cárdenas
Departamento de Química Orgánica
Universidad Autónoma de Madrid, Cantoblanco
28049 Madrid (Spain)
Fax: (+34) 914-973-966
E-mail: diego.cardenas@uam.es

[b] R. García-Fandiño, M. Gulías, Prof. Dr. L. Castedo, Prof. Dr. J. R. Granja, Prof. Dr. J. L. Mascareñas
Departamento de Química Orgánica y Unidad Asociada al CSIC, Facultade de Química
Universidade de Santiago
15706 Santiago de Compostela (Spain)
E-mail: qojoselm@usc.es

Supporting information for this article includes atomic coordinates and energies for all stationary points as well as schemes of the reaction pathways involving substituted alkynes. This information is available on the WWW under http://www.chemeurj.org/ or from the author.



Scheme 1. Pd-catalyzed intramolecular [3+2] cycloaddition between alkylidenecyclopropanes and alkynes.

vestigate the mechanistic course of the process at a theoretical level. Previous computational studies on these types of cycloaddition have been limited to an isolated report of Suzuki and Fujimoto on the DFT exploration of the palladium-catalysed [3+2] intermolecular cycloaddition between methylenecyclopropane and ethylene.[7] The restricted scope of this study precludes the possibility of envisaging a mechanistic course for the cycloaddition of alk-5-ynylidenecyclopropanes. Herein, we report the results of a DFT study of this intramolecular reaction, by using Pd/PH_3 as model catalytic system.

Computational Methods

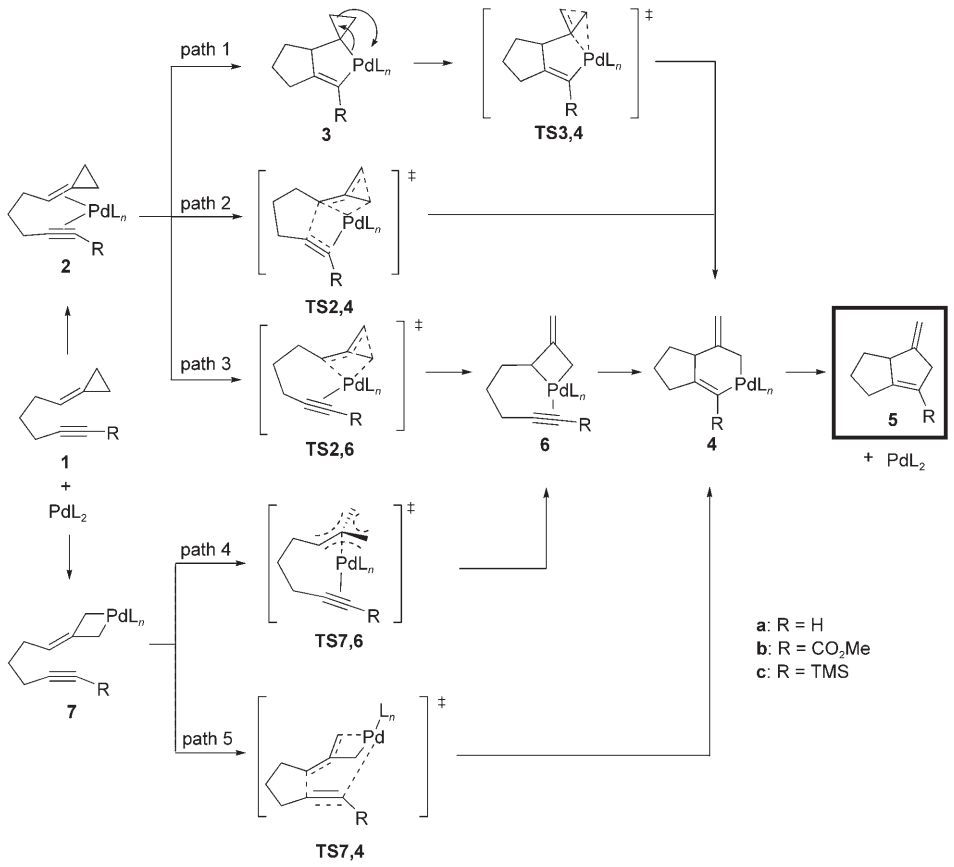
Calculations were performed with Gaussian 98[8] and Gaussian 03[9] at DFT level. The geometries of all complexes here reported were optimised by using the B3LYP hybrid functional.[10] Optimisations were carried out by using the standard 6–31G(d) basis set for C, H, O, Si and P. The LANL2DZ basis set, which includes the relativistic effective core potential (ECP) of Hay and Wadt and employs a split-valence (double-zeta) basis set, was used for Pd.[11] Harmonic frequencies were calculated at the same level to characterize the stationary points and to determine the zero-point energies (ZPE). The starting approximate geometries for the transition states (TS) were located graphically. Intrinsic reaction coordinate (IRC) studies were performed in ambiguous cases to confirm the relation of the transition states with the corresponding minima. Single-point calculations were performed by using the 6–311+G(2df,2p) basis set for C, H, Si, O and P. For Pd, the Stuttgart RSC ECP was utilised. The (8s7p6d) primitive set was contracted to [6s5p3d], and was supplemented with two f and one g polarisation functions ($\zeta_f = 0.6122$, 2.1857; $\zeta_g = 1.3751$).[12] Electronic energy values calculated with the smaller basis set have been corrected by using the residual energy at the zero-point vibrational energy (ZPE). The evaluation of enthalpy (H) and Gibbs free energy $(G)_B$ implies the use of the harmonic-oscillator/rigid-rotor approximation, which introduces some uncertainty in the calculation of the vibrational entropy. Unless otherwise stated, the energy values included in the main text refer to the single-point calculations performed with the higher quality base on the previously optimised structures.

Nomenclature and general format of the energetic profile graphics: Intermediates obtained from the computational study are named with the numbers **1**–**14**. Letters **a**, **b** or **c** refer to the substituent group at the terminal position of the triple bond in the alk-5-ynylidenecyclopropane systems (R = H, CO_2Me or TMS, respectively). The "prime" symbol refers to the number of ligands coordinated to palladium, in such a way that the "primed" intermediate indicates that only one PH_3 is present in the coordination sphere of the metal. Energy values are given in kcal mol^{-1}. Values in brackets appearing in the scheme correspond to single point calculations using the higher quality basis set.

Results and Discussion

Calculations for the alk-5-ynylidenecyclopropane systems have been performed on substrates that do not include the malonate functionality in the tether connecting the reaction partners ($X = CH_2$, Scheme 1). These substrates are valid reaction models because it has been shown that precursors containing an ether tether ($X = O$) also undergo the cycloaddition reaction.[6] Furthermore, recent experiments with substrates in which $X = CH_2$ further demonstrate that the malonate group is not a requisite for a successful cycloaddition.[13] PH_3 has been used instead of $P(OiPr)_3$ because it allowed us to save computation time whilst keeping the rough electronic properties of the system. The intrinsic reactivity of the complexes is expected to be accurately modelled, although the steric effects exhibited by the larger ligands are neglected.

For the [3+2] reaction of substrates **1**, a general alk-5-ynylidenecyclopropane system, two initial processes have been considered (Scheme 2). Coordination of both unsaturated carbon ligands to Pd^0 would afford complex **2** which could evolve through different pathways (paths 1–3, Scheme 2). Alternatively, direct oxidative distal addition of the cyclopropane C–C bond to Pd^0 would give palladacyclobutane **7**, which could in turn evolve to the products through paths 4 or 5 (Scheme 2). Depending on the evolution of complex **2**, at least three pathways can be proposed. In path 1, complex **2** reacts through oxidative cyclometallation, leading to tricyclic intermediate **3**, which after rearrangement could be converted into bicyclic system **4**. Final C–C reductive elimination would afford the final desired cycloaduct **5** and regenerate the active Pd^0 complex. Paths 2 and 3 entail two different rearrangements to transform complex **2** either directly to the palladacyclohexane intermediate **4** (path 2), or to methylenepalladacyclobutane **6** (path 3). This latter intermediate could then evolve to **4** by an alkyne carbometallation process, as has been proposed by Lautens[5] and computationally supported by Fujimoto for the intermolecular reaction with ethylene.[7] In the second alternative (paths 4–5), intermediate **7** may undergo isomerisation to a methylidenecyclopropane **6** via a TMM-type transition state (path 4) or undergo a metalloene reaction to directly provide complex **4** (path 5).

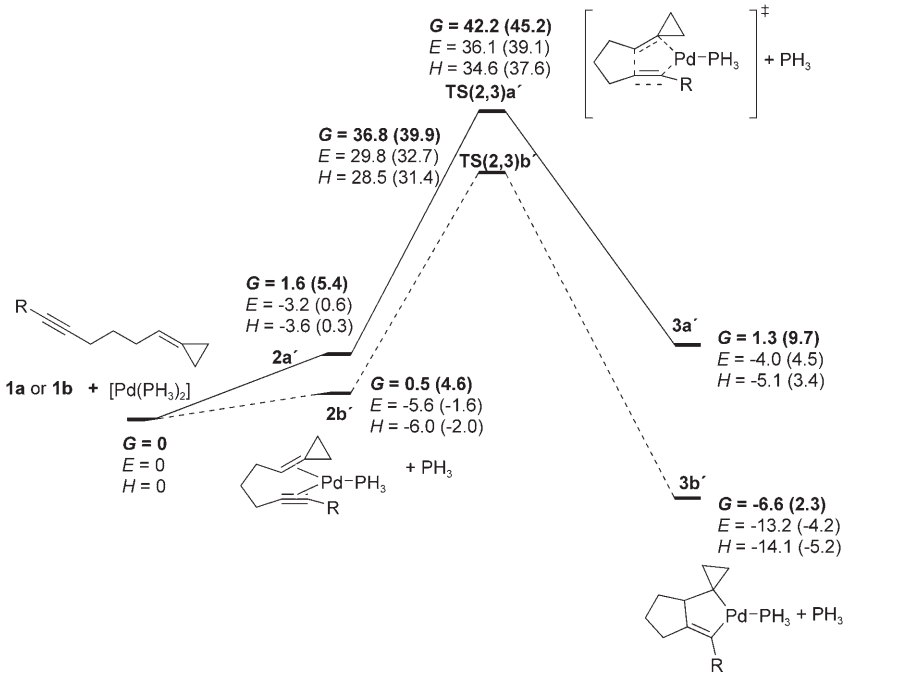


Scheme 2. Proposed reaction pathways for the [3+2] cycloaddition between alkylidenecyclopropanes and alkynes.

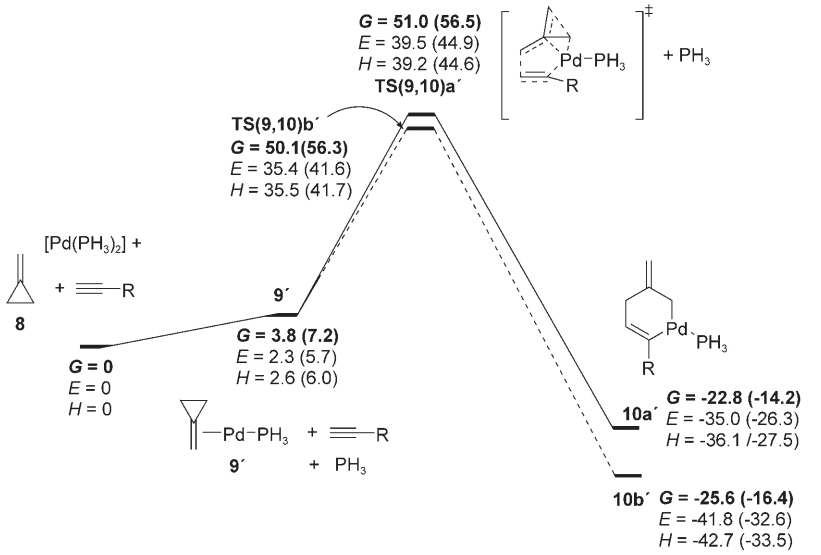
These five possible pathways (paths 1–5) were explored computationally at DFT level, for different substituents at the terminal position of the alkyne (substrates **1a–c**, R = H, CO_2Me or TMS, respectively). As shown in Scheme 3, the activation energy for the oxidative cyclometallation step in path 1 for the substrate containing a terminal alkyne (**1a**) is quite high (**TS(2,3)a′**, $\Delta G^{\ddagger} = 45.2\ kcal\,mol^{-1}$). The presence of a carbonyl group at the terminal position of the alkyne (**1b**) leads to lower values for the electronic energy, enthalpy and Gibbs free energy. However, even these values are rather higher than those obtained for the steps involved in paths 4–5, as will be shown below.

Path 2 involves a skeletal rearrangement from complex **2** directly to the bicyclic intermediate **4** (Scheme 2). The corresponding transition state could not be found for the intramolecular system. The extremely high energy values presented by the transition state **TS-(9,10)a′** corresponding to the intermolecular related transformation (Scheme 4) strongly suggest that this alternative is clearly disfavoured, regardless of the substitution at the alkyne.

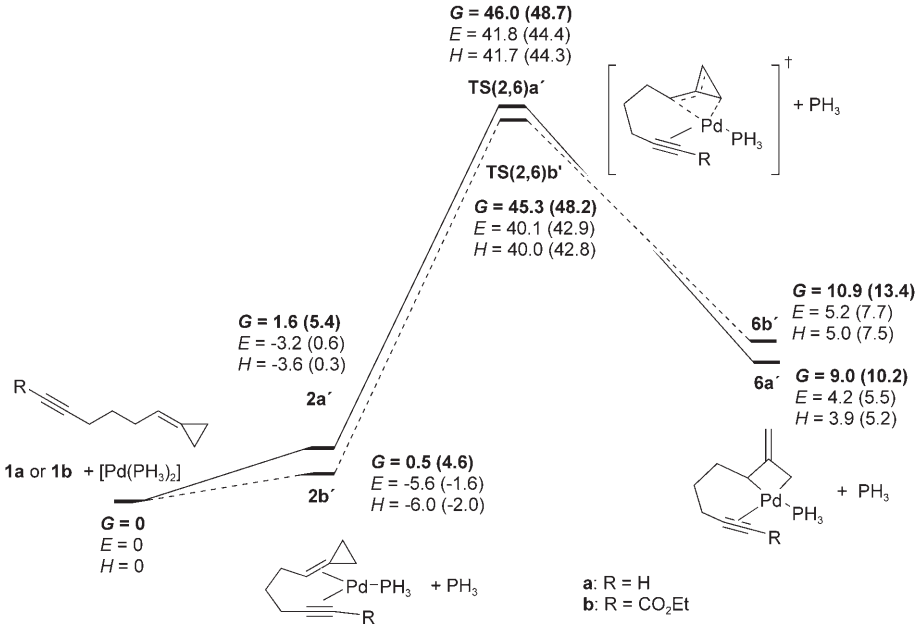
Path 3, which involves a direct rearrangement from complex **2** to the methylenepalladacyclobutane complex **6** was also studied (Scheme 5). The corresponding transition states for the terminal alkyne or the internal alkyne holding an electron-withdrawing group (**TS-(2,6)a′** and **TS(2,6)b′**, respectively) showed high energy values. We also studied an analogous transformation on complexes containing an unco-



Scheme 3. Relative electronic energy, enthalpy and Gibbs free energy (bold; kcal mol^{-1}) calculated for intermediates involved in path 1 for system **1a** (R = H, ——) and **1b** (R = CO_2Me, -----). Values are referred to systems **1a** or **1b** + [Pd(PH$_3$)$_2$], respectively.



Scheme 4. Relative electronic energy, enthalpy and Gibbs free energy (bold; kcal mol^{-1}) calculated for intermediates involved in path 2 (intermolecular reaction) for different substituents at the alkyne (R = H, ——; R = CO_2Me, -----). Values are referred to the system (**8** + HC≡CR + [$Pd(PH_3)_2$]).



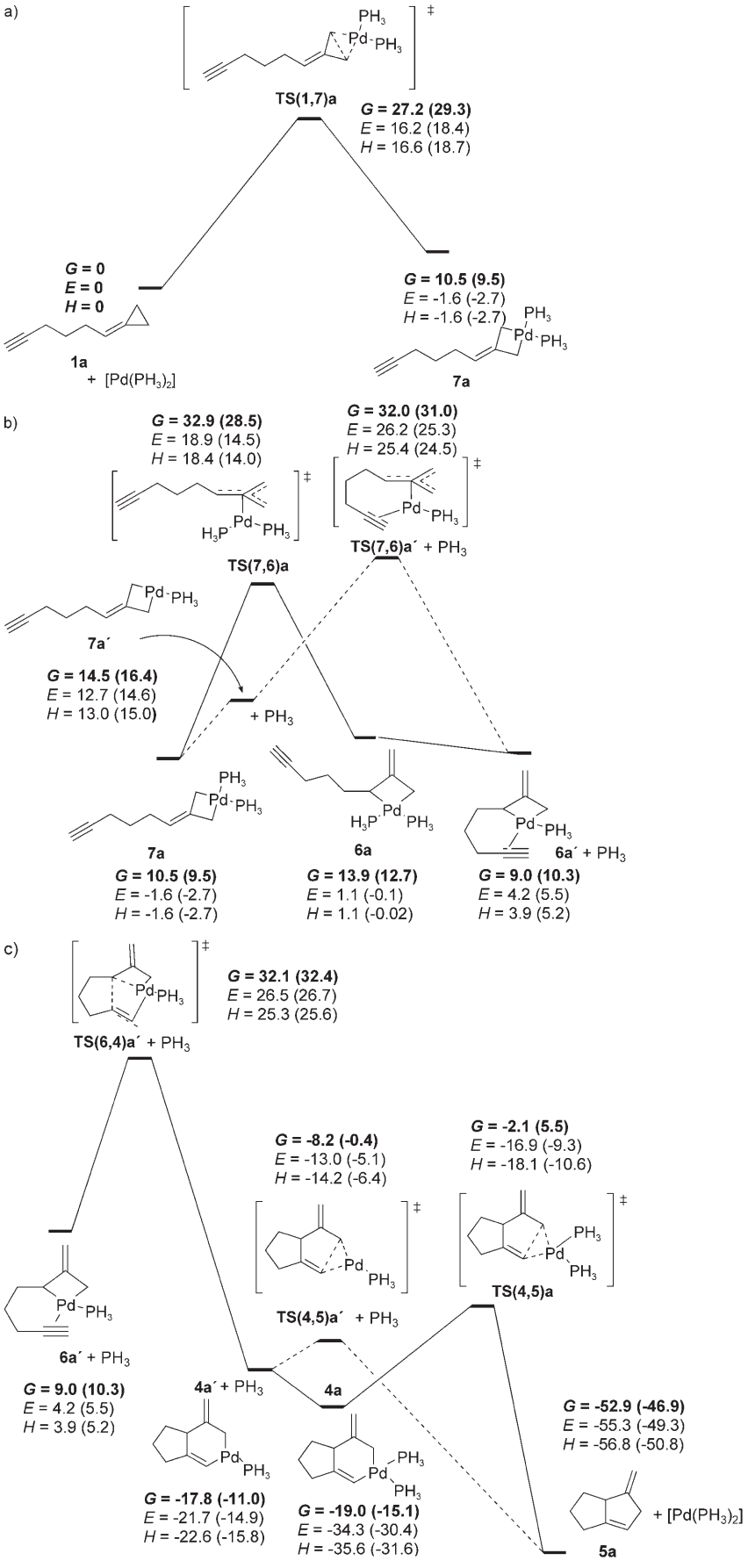
Scheme 5. Relative electronic energy, enthalpy and Gibbs free energy (bold; kcal mol^{-1}) calculated for intermediates involved in path 3 for system **1a** (R = H, ——) and **1b** (R = CO_2Me, -----). Values are referred to systems **1a** or **1b** + [$Pd(PH_3)_2$], respectively.

ordinated alkyne but with the metal centre coordinated to two phosphine ligands (**TS(1,6)a** and **TS(1,6)b**, see the Supporting Information) and, although we have obtained slightly lower energetic values for the intermediates involved in the same step, they are still very high.

The second mechanistic alternative consists of assuming the initial formation of palladacyclobutane **7** by oxidative addition of the palladium complex to the distal position of the cyclopropane (paths 4–5, Scheme 2).[14] The activation barrier for the formation of the intermediate **7a** (containing a terminal alkyne) is 18.4 kcal mol^{-1} in terms of electronic energy (Scheme 6). The activation free energy of the process is considerably higher (29.3 kcal mol^{-1}), and accounts for an endoergonic transformation. Depending on the evolution of the alkylidenecyclopropane complex, **7a**, two pathways can be proposed (paths 4 and 5). Path 4 involves isomerisation of **7a** to a methylenepalladacyclobutane **6a** via a Pd-trimethylenmethane-type of transition state (**TS(7,6)a**). This isomerisation could also take place from a complex containing the alkyne intramolecularly coordinated to the Pd (**TS-(7,6)a′**); however, the activation energy is slightly higher than in the previous case.

In both cases, the structure of the transition states (**TS-(7,6a)**) takes the shape of an umbrella, in which the metal is coordinated to the four carbon atoms of the trimethylenmethane unit (TMM), albeit not at the same distance (Figure 1). It should be mentioned, however, that **7a′** is not a realistic system as the formation of tricoordinated Pd^{II} complexes by ligand dissociation is not a favourable process.[15]

Intermediate **6a′**, which is the complex formed by rearrangement through the Pd-TMM-type transition state, is the kind of complex that could be formed by C–C oxidative addition to methylenecyclopropanes systems like those studied by Lautens.[5] Therefore, the next steps of the mechanism (carbometallation and reductive elimination) would be similar to those proposed for these types of substrates. Carbometallation through the transition state **TS(6,4)a′** would lead to the bicyclic intermediate **4a′** (Scheme 6). Subsequent C–C reductive elimination of the palladium complex (coordinated to one **TS(4,5)a′** or two phosphines, **TS(4,5)a**) would provide the final cycloadduct **5a**. Energy data indicate that the rate-limiting step of path 4 is the carbometallation process (**TS(6,4)a′**).



Scheme 6. Relative electronic energy, enthalpy, and Gibbs free energy (bold; kcal mol^{-1}) calculated for intermediates involved in path 4 for system **1a**. Values are referred to systems **1a**+[$Pd(PH_3)_2$], respectively. ----- connect complexes with only one PH_3 ligand. a) Oxidative addition. b) Isomerisation through Pd–TMM-type transition states. c) Carbometallation reaction and C–C reductive elimination.

Complex **7a** could also directly evolve to palladacyclohexane intermediate **4** by means of a metalloene-type of transformation through transition structures **TS-(7,4)a** or **TS(7,4)a′** (Schemes 7 and 8).[16] We found similar Gibbs energy values for both metalloene transition states (Scheme 8). Considering only electronic and enthalpic energy, there is a higher intrinsic reactivity for the complex containing two PH_3 ligands through **TS(7,4)a** compared to the reaction through **TS(7,4)a′**. The bond length of the new Pd–C and C–C bonds in the former transition state are 2.475 and 2.197 Å, respectively. In **TS-(7,4)a′**, the corresponding distances are 2.323 and 2.377 Å, respectively. Thus, for the fastest process, the C–C bond formation takes place earlier along the reaction coordinate.

Comparison between paths 4 and 5 in terms of electronic and enthalpic energy shows very little differences (about 1 kcal mol^{-1}), suggesting that they could be competitive (Scheme 9a). However, introduction of the entropy parameter and hence considering Gibbs energies (Scheme 9b) shows that the most favourable mechanism is that involving isomerisation through a TMM-type transition state (path 4). Both pathways (paths 4 and 5) are clearly kinetically favoured with respect to previously discussed paths 1–3.

We have also calculated possible reaction pathways for substrates containing substituted alkynes, in particular those contain-

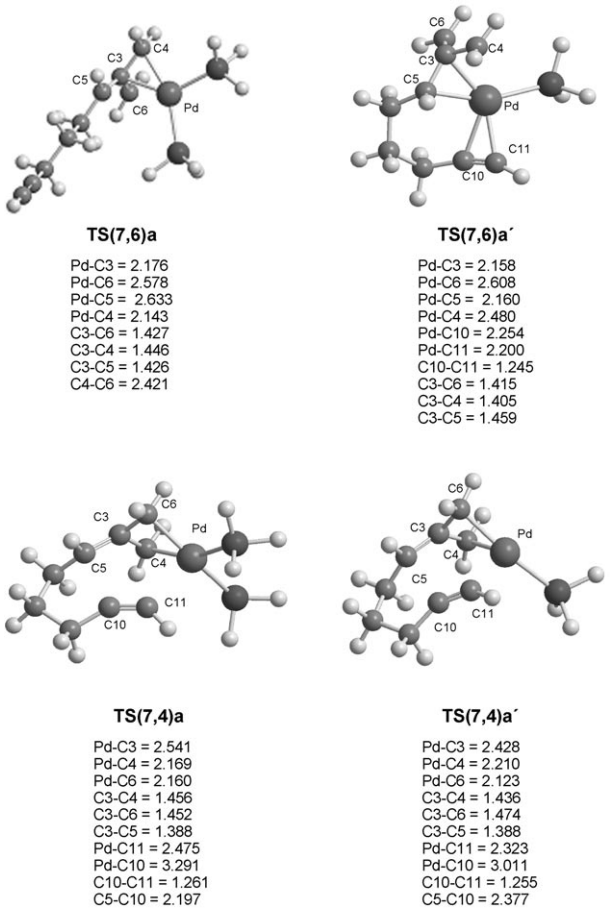
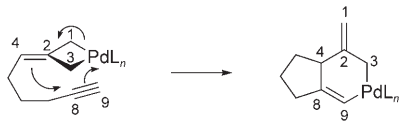


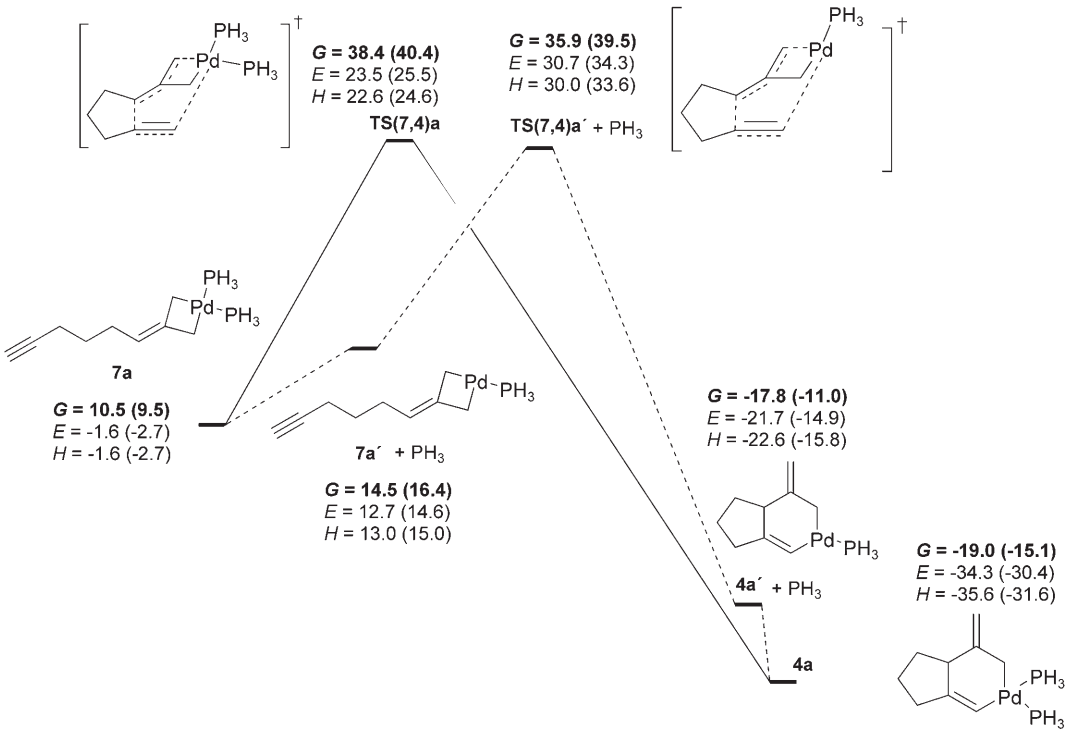
Figure 1. Optimised structures for selected stationary points (bond lengths in Å).



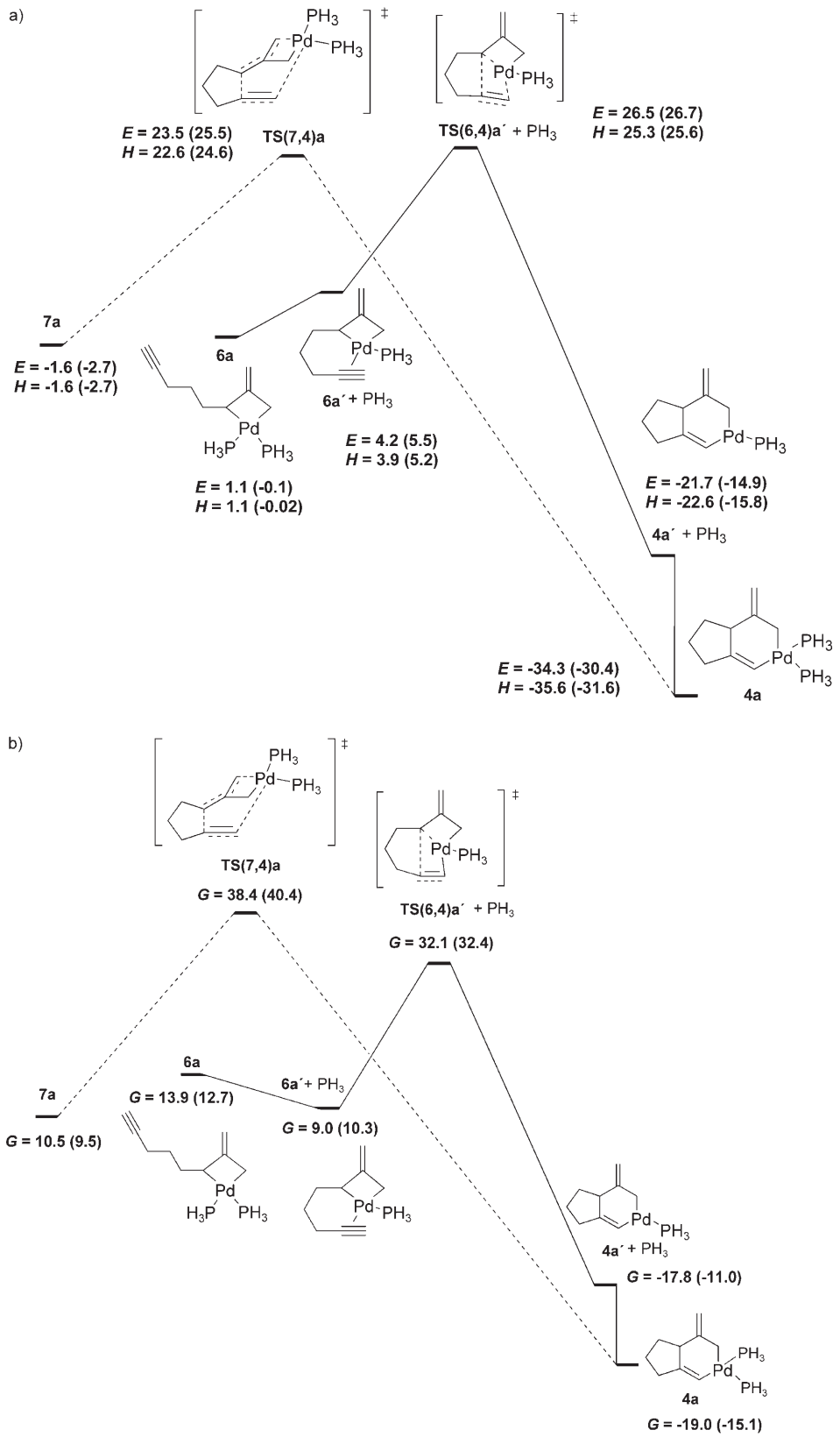
Scheme 7. Intramolecular palladaene-type reaction of an (alkenyliden)-palladacyclobutane and an alkyne.

ing a TMS or a CO_2Me group at the terminal position of the alkyne. The energy values obtained for the TMS-substituted substrate indicate that the barrier of the rate-determining step is slightly higher than that obtained for the systems containing a terminal alkyne (Table 1). The presence of the ester group at the alkyne terminus decreases considerably the energetic barrier of the carbometallation step in path 4, and provides for lowering the Gibbs free energy of the metalloene process by more than 8 kcal mol^{-1} with respect to that for the unsubstituted enyne. With lower energetic barriers it should be expected that the ester-substituted substrates would readily provide the cycloadducts. However experimentally we have observed that such substrates do not lead to the desired adducts, but decompose when heated under the reaction conditions, even at temperatures as low as 50 °C. Calculations do provide an explanation for this observation by suggesting an alternative mechanistic evolution of the palladacyclobutane intermediate **7b** (path 6, Scheme 10).

The presence of the carbonyl group promotes a Michael-type cyclisation of **7b** to give the π-allyl palladium zwiterionic species **11b**. The formation of this intermediate might entail the cleavage of one σ Pd–C bond of the palladacyclo-



Scheme 8. Relative electronic energy, enthalpy and Gibbs free energy (bold; kcal mol^{-1}) calculated for intermediates involved in path 5 for system **1a**. Values are referred to system **1a** + [Pd(PH$_3$)$_2$]. ----- lines connect complexes with only one PH$_3$ ligand.



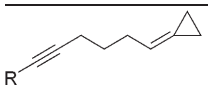
Scheme 9. Relative electronic energy and enthalpy (a) and Gibbs free energy (b) calculated for intermediates involved in paths 4 and 5 for system **1a**. Values are referred to system **1a**+[$Pd(PH_3)_2$]. ----- connect complexes with only one PH_3 ligand.

butane **A**. Cannonical structures for this intermediate are useful to visualize the process (Scheme 10). The calculated structure of intermediate **11b** indicates that the central carbon of the allyl moiety (C3) is the one closer to the metal. The Pd–C3 distances in metallacycle **7b** and complex **11b** are 2.618, and 2.251 Å, respectively (Figure 2). In complex **11b**, the negatively charged oxygen approaches the palladium atom, which remains formally positively charged. Compared with the metalloene-type of reaction, there is no need for the alkyne terminal carbon atom to interact with Pd, as the incipient negative charge gets delocalised on the ester group. Thus, a longer Pd–C11 distance is found in **TS(7,11)b** compared to that of the metalloene transition-state **TS(7,4)b** (3.266 and 3.002 Å, respectively). The distance of the newly formed C–C bond is very similar in both transition states (2.173 and 2.149 Å, respectively).

While the Gibbs energy suggests that both mechanisms (path 4 and path 6) are competitive (Scheme 11), analysis of the electronic energies and enthalpies revealed very low barriers for the formation of the zwiterionic intermediate (**11b**), about 11 kcal mol^{-1} lower than for the carbometallation process (the rate-limiting step of path 4). The energetic difference observed upon introducing the activation entropy term may arise from the highly ordered nature of transition-state **TS(7,11)b**, due to the interaction between Pd and O. In solution, solvation effects would probably contribute to lower the activation entropy and therefore favour the process through path 6.

The zwitterionic species **11b** recalls related allylpalladium

Table 1. Gibbs energy for the transition states involved in the TMM-rearrangement, carbometallation and metalloene-type reaction corresponding to paths 4 and 5 (relative to the corresponding palladacyclobutane complex **7** in each case), for alternatively substituted alkynes.



	Path 4		Path 5
	TMM	carbometallation	metalloene
1a: R = H	19.0	22.9	30.9
1b: R = CO_2Me	18.2	18.9	22.2
1c: R = $SiMe_3$	18.4	25.9	35.8

complexes proposed by Trost and co-workers as intermediates of the Pd-catalysed intramolecular [3+2] cycloaddition between bifunctional Pd-TMM precursors with α,β-unsaturated esters (Scheme 12).[17] In this case, intermediates like **E** can easily evolve to the observed cycloadduct by a nucleophilic attack of the enolate to the allylic system.

In our case, a similar evolution of the 1,2-dienolate intermediate **11b** is not easy due to geometric reasons, and, therefore, it evolves through alternative pathways. When we explored this transformation at DFT level, we found a very favourable pathway involving the formation of the allylidenepalladacyclobutane **13b**, which is much more stable than **11b**, probably due to the presence of a 1,3-diene conjugated to the ester group (Scheme 13). As isomerisation of **11b** to **13b** entails a proton transfer reaction and might be kinetically favourable. We have also found that **13b** can easily undergo a C–C reductive elimination through **TS(13,14)b** to form the allylidenecyclopropane product **14b**. Although experiments carried out in the lab have not allowed us to isolate this product, NMR spectroscopic data of unpurified reaction mixtures are consistent with the presence of this compound, which is probably unstable under the reaction conditions.[13] The calculations indicate that the transformation of **13b** into **14b** is exoergic (-7.1 kcal mol^{-1}), which contrasts with the formation of **7** by oxidative addition (Scheme 6a). Overall the theoretical data support a quite favourable evolution of palladacyclobutane **7b** by pathways other than those that lead to the [3+2] cycloadduct.

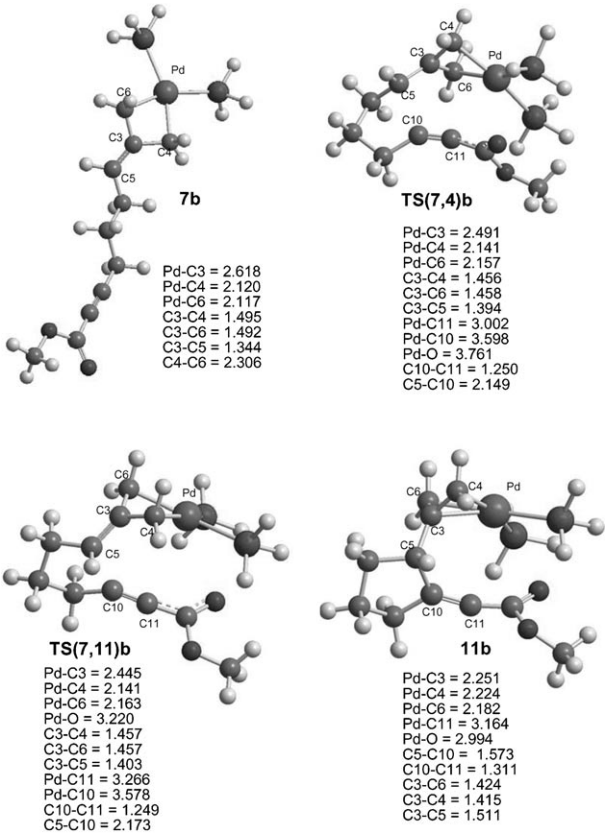
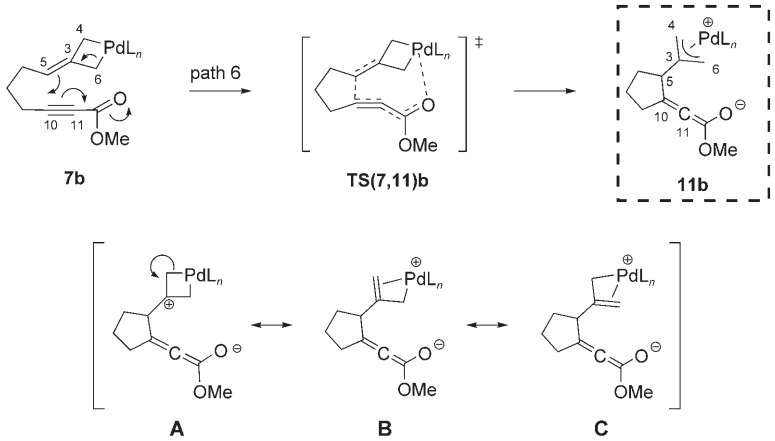


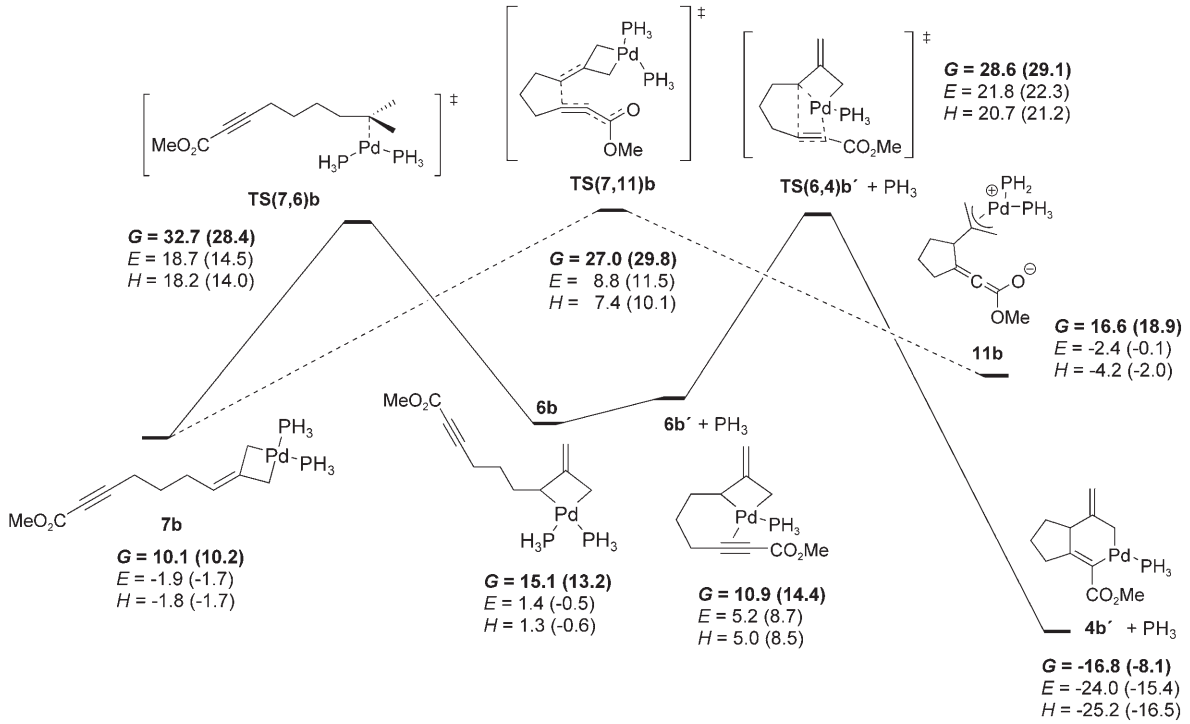
Figure 2. Optimised structures for selected stationary points (bond lengths in Å).

Conclusion

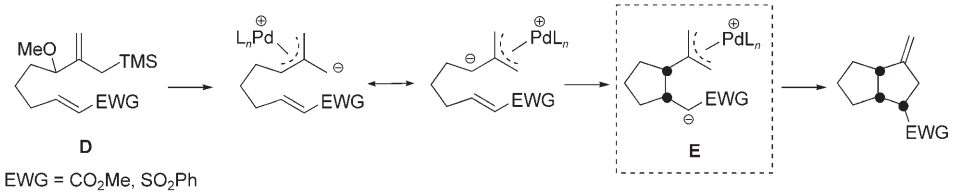
We have studied at DFT level the Pd-catalysed intramolecular [3+2] cycloaddition of alkylidenedencyclopropanes to alkynes equipped with different substituents at the terminal position. We have explored different pathways involving either the initial formation of Pd–enyne complex (paths 1–3) or an alkylidenepalladacyclobutane species (paths 4–5). We have found that the mechanistic pathways derived from the evolution of the first type of complexes are clearly disfavoured in comparison to the possibilities provided by the alkynylidenepalladacyclobutanes. The study of the evolution of these intermediates suggests that for substrates in which the alkyne does not contain an electron-withdrawing group, the most favoured mechanism in terms of Gibbs energy is path 4, consisting of a rearrangement to a methylenepalladacyclobutane followed by carbometallation and final C–C reductive elimination. If



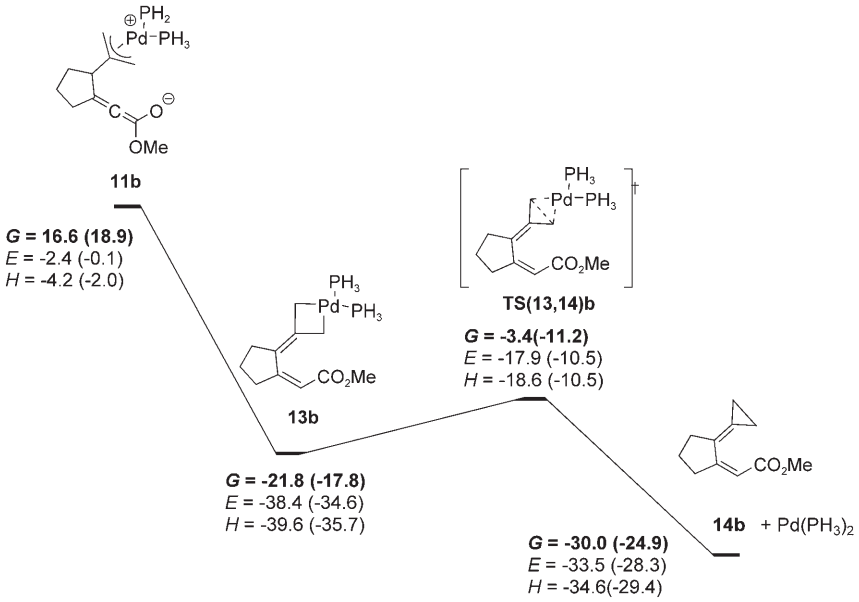
Scheme 10. Intramolecular Michael-type addition of the alkene onto the alkyne to give a (π-allyl)palladium complex (**11b**).



Scheme 11. Relative electronic energy, enthalpy and Gibbs free energy (bold; kcal mol^{-1}) calculated for intermediates involved in paths 4 and 6 for system **1b**. Values are referred to system **1b** + [Pd(PH$_3$)$_2$].



Scheme 12. Pd-catalysed intramolecular cycloaddition of Pd-trimethylenmethane precursors with activated alkenes. EWG = electron-withdrawing group.



Scheme 13. Relative electronic energy, enthalpy and Gibbs free energy (bold; kcal mol^{-1}) calculated for intermediates involved in the evolution of zwiterionic intermediate **11b**. Values are referred to system **1b** + [Pd(PH$_3$)$_2$].

one considers only electronic or enthalpic energies, the alternative palladaene mechanism is competitive, and, therefore, cannot be fully discarded. In the case of substrates in which the alkynes contain an ester substituent, the calculations have allowed us to uncover a different pathway that accounts for the failure of this substrates to undergo the cycloaddition reaction. This pathway consists of an initial Michael-type intramolecular attack of the C–C double bond of the alkylidenepalladacyclobutane to the alkyne to give a (η^3-allyl)palladium alleneolate zwitterionic intermediate. A prototropic reaction, consisting of formal deprotonation of the α-position of the carbon chain bound to the central C atom of the η^3-allyl ligand, followed by C-protonation of the 1,2-dienolate, which is extremely exergonic, leads to an alkenylidenepalladacyclobutane which might easily evolve to a allylidenecyclopro-

pane type of product. In conclusion, our computational studies are consistent with the observed experimental tendencies and provide important mechanistic insights for the Pd-catalysed intramolecular [3+2] cycloaddition of alk-5-ynylidenecyclopropanes. This knowledge may be very useful for designing future experiments, optimising ligands and envisaging asymmetric variants.

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