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A Theoretical Investigation on the Mechanism of the $PtCl_2$-Mediated Cycloisomerization of Heteroatom-Tethered 1,6-Enynes

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A mechanistic study based on DFT theoretical calculations for the $PtCl_2$-catalyzed formation of bicyclic adducts from heteroatom tethered 1,6-enynes is reported. Different reaction pathways have been taken into account and the results are discussed. This analysis clearly reveals that the kinetically preferred pathway involves an initial 6-*endo*-cyclization from a triggered reactant complex by π-complexation of Pt(II) onto the alkyne to form a cyclopropyl platina-carbene intermediate, followed by a [1,2]-hydrogen shift.

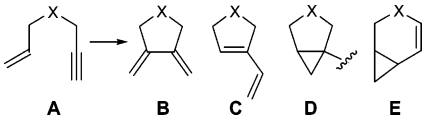
Introduction

Formation of C−C bonds with a high regio-, chemo-, or enantioselectivity is one of the most active areas of research in synthetic organic chemistry. In this context, catalytic organometallic chemistry has emerged as a powerful tool during the past decade.[1] Consequently, transition metal-catalyzed intramolecular cycloisomerization of enynes has been widely reported.[2] Thus, for instance, hept-1,6-enynes (**A**) can give rise, depending on the transition-metal catalyst,[3] to cycloisomerization (**B**), skeletal reorganization (**C**) products, and/or polycyclic systems (**D**, **E**) (Scheme 1).

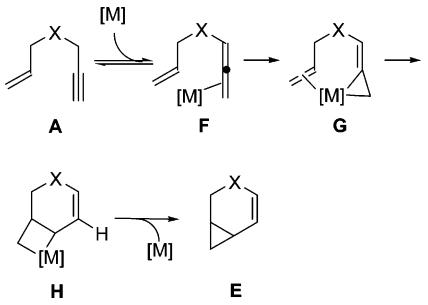
Regarding the heteroatom-tethered 1,6-enynes, one of the first recorded examples was the Pt-catalyzed ($PtCl_4$) enyne cycloisomerization reported by Blum and co-workers.[4] It was shown that allyl propargyl ethers cyclized to 3-oxabicyclo[4.1.0]hept-4-enes in moderate yields. They suggested that the reaction proceeds by tautomerization of the 1,6-enyne to a 1,2,6-triene (**F**), followed by complexation with Pt and intramolecular capture by the allyl group (**G**). A subsequent cycloaddition-prototropy step gives rise to metallacyclobutane intermediate **H**, which, finally, generates the cyclopropyl ring-fused **E** by reductive elimination (Scheme 2).

Analogously, Fürstner has described that allyl propargylamines afforded 3-azabicyclo[4.1.0]hept-4-enes.[5] They observed that Pt(II)-catalyzed cycloisomerization processes of heteroatom-tethered 1,6-enynes are substrate dependent, giving rise to the metathesis product **C** and/

SCHEME 1



SCHEME 2



† Instituto Universitario de Investigación.
‡ Laboratorio de Radicales Libres.

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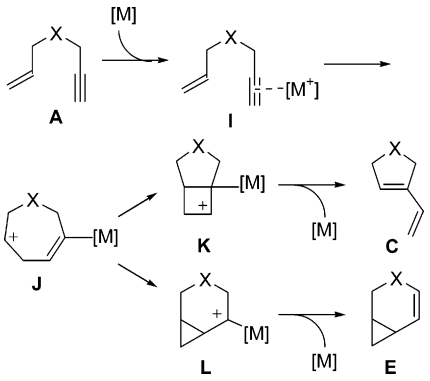
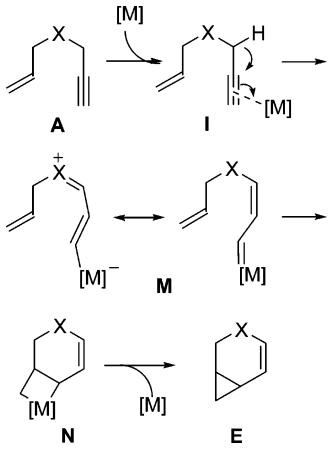
SCHEME 3



SCHEME 4



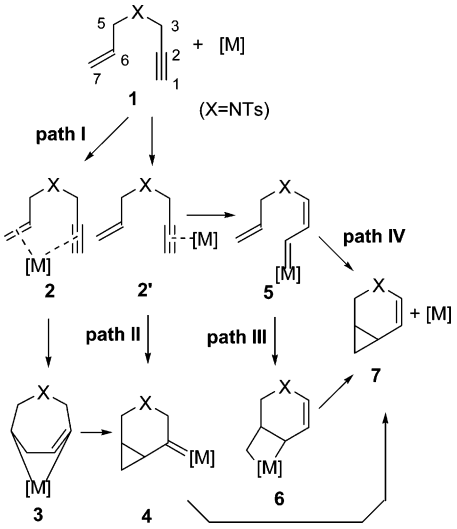
or the vinylcyclopropane **E** (Scheme 3). So, they suggested that, although both catalytic processes produce significantly different structural motifs, they share a common mechanism comprising a nonclassical carbocation manifold.

On the other hand, Echavarren et al. have studied the Pt-catalyzed cycloisomerization of enynes in polar, nonnucleophilic solvents.[6] They observed that, if the 1,6-enyne contains a heteroatom as a tether between propargylic and allylic units, the reaction affords oxa- or azabicyclo[4.1.0]hept-4-enes, whereas if it lacks it the conventional Alder-ene type products are obtained. Consequently, it seems that the heteroatom is crucial and they proposed that the lone pair at the heteroatom promotes a [1,2]-shift of H from the propargylic position to generate an alkenyl platinum carbene (**M**) stabilized by the heteroatom. Then, this intermediate might suffer an intramolecular [2+2] cycloaddition with the alkene group to form a metalla(IV)cyclobutane structure (**N**) that could evolve to the final bicyclic adduct by reductive elimination of catalyst (Scheme 4).

Since the knowledge of the detailed molecular mechanism can be of great importance to develop new synthetic strategies and design selectively novel or specific compounds, in past years many mechanistic investigations have been performed from spectroscopic, kinetic, or isotopic labeling studies, and accordingly the distinct pathways outlined above have been derived. However,

(6) Méndez, M.; Muñoz, M. P.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2001**, *123*, 10511−10520.

SCHEME 5



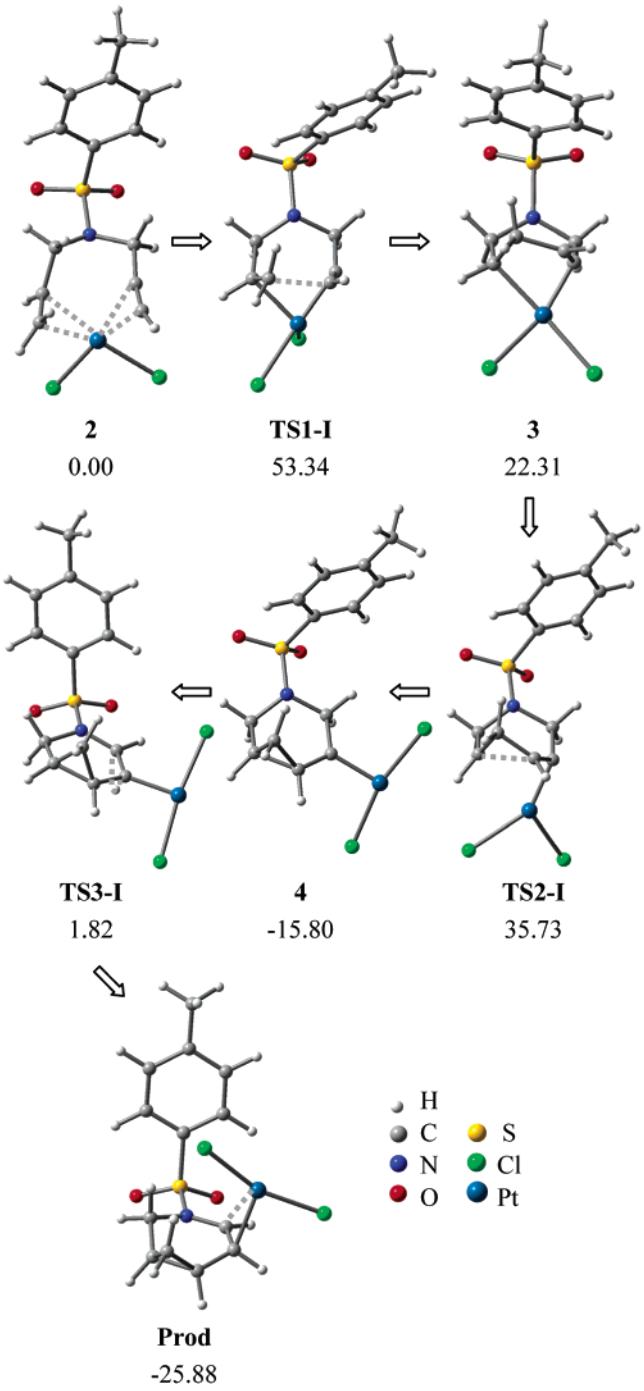
some aspects about the true nature of the intermediates involved remain controversial and other details of this process are not well known. Theoretical mechanistic investigations at ab initio or DFT levels can make important contributions to (1) understand how reactants progress to different cycloisomerization products, (2) know if alternative pathways involve a common intermediate structure, and (3) elucidate the factors which control the evolution to the potential isomers. The determination of intermediate and transition state structures and the understanding of the possible reaction pathways would allow us to carry out more efficient and selective cycloisomerization reactions.

Results and Discussion

To determine the preferred reaction pathway involved in the $PtCl_2$-catalyzed intramolecular cyclization of heteroatom-tethered 1,6-enynes, we have explored the mechanistic proposals summarized in Scheme 5.

Initially, we have analyzed the mechanism suggested by Fürstner (Scheme 5, path I) involving a nonclassical carbocation as the key intermediate[5] (structure **J**, Scheme 3) that could stabilize along different pathways (**K** for metathesis reaction, or via **L** affording bicyclo[4.1.0]-heptene systems). Importantly, we have noted that the type-**J** intermediate cannot be located and characterized as a minimum energy structure on the potential energy surface, but our calculations provided instead the organometallic species **3** (Schemes 5 and 6) as the intermediate structure. In addition, the metallabicyclo[3.2.1]octene **3** is formed via the oxidative cyclometalation step from the initial η^4-reactant complex **2**, where both alkene and alkyne units coordinate to the metal center. The associated transition state, **TS1-I** shows the initial formation of the C_1-C_7 bond (1.990 Å) and strengthening of $Pt-C_2$ (2.046 Å) and $Pt-C_6$ (2.076 Å) interactions from reactant complex **2** (2.207 and 2.268 Å, respectively). This endothermic step (by 22.31 kcal/mol, Table 1) proceeds with a very high activation energy (53.34 kcal/mol). Although our calculations confirmed the involvement of structures consistent with the mechanistic proposal path **I** advanced in Scheme 5 (see Scheme 6), these unfavorable results led us to analyze alternative pathways.

SCHEME 6. Optimized Structures for the $PtCl_2$-Mediated Cycloisomerization According to Path I (Scheme 5)[a]



[a] Corrected free energies are given in kcal mol^{-1} relative to reactant complex.

Accordingly, we located the reactant complex **2′** (Scheme 5) formed by π-complexation onto the catalyst of the alkyne moiety, which became susceptible to nucleophilic attack by the tethered alkene (NPA charges: −0.211 for C_1 and +0.013 for C_2). Pt−C_1 (2.066 Å) and Pt−C_2 (2.106 Å) bond lengths and Wiberg bond index matrix analysis (Pt−C_1 = 0.59 and Pt−C_2 = 0.55) confirms that this structure can be described as a η^2-complex rather than a slipped η^1-coordinated alkyne. This η^2-complex evolves to the cyclopropyl platinum-carbene[7] **4** (Scheme 5, path II) by the anti attack of the alkene moiety to the activated alkyne via the early transition structure **TS1-II** (Scheme 7), which shows that C_1−C_6 (2.585 Å) and C_1−C_7 (2.488 Å) are being formed in a concerted and slightly asynchronous mode. Interestingly, this 6-*endo*-cyclization step is very exothermic (−34.98 kcal/mol) and the activation energy to reach the transition state is moderately low (7.96 kcal/mol). The Pt-carbene **4** (Pt−C_2 = 1.867 Å) drives to the final product (**Prod**) by a [1,2]-hydrogen shift via **TS2-II** (Scheme 7), a transition state 26.21 kcal/mol more stable than **TS1-II**. This transition structure displays the H migration from the propargylic center C_3 (C_3−H= 1.331 Å) to C_2 (C_2−H = 1.377 Å), which, in turn, implies the expected shortening of the C_2−C_3 bond (1.418 Å, vs 1.497 Å in **4**). The natural charge for H in **TS2-II** (0.359) suggests a proton-transfer rather than a hydrogen transfer step. Despite the Pt−C_3 distance not being too long (2.340 Å), the strong Pt−C_2 bond (2.093 Å) and Wiberg bond index analysis (Pt−C_2 = 0.64 and Pt−C_3 = 0.34) suggest that the final bicyclic product **Prod** should be better described as a η^1-species rather than as a η^2-species. In addition, a partial C_3−N double bond character is also observed (1.342 Å in **Prod** vs 1.467 Å in **4**) suggesting an effective stabilization by heteroatom donor. These results reveal that the strong Pt−C_2 back-bonding interaction induces the nonplanarity of the olefin group (C_2 shifts 0.304 Å from the substituents plane), whereas the electronic effects of −NTs reduces the back-donation to C_3 (C_3 only deviates 0.093 Å). This second step is exothermic (by 10.07 kcal/mol) and takes place with an energy barrier of 17.62 kcal/mol (−17.36 kcal/mol relative to **2′**). The overall two-step mechanism is highly exothermic (−45.05 kcal/mol) and the key step is the formation of cyclopropyl platinum-carbene **4**.

Alternatively, we have also analyzed the inverse sequence of steps, that is, an initial [1,2]-hydrogen migration to C_3 aided by heteroatom, followed by intramolecular cyclization (Scheme 5, paths III and IV). The ground structure **2′** (cis chloride arrangement)[8] may lead to the vinyl Pt-carbene[9] **5** via the cyclic transition structure **TS1-III** (C_2−H = 1.442 Å and C_3−H = 1.276 Å) (see Scheme 8). This exothermic migration step (−30.54 kcal/mol) proceeds with a moderately high activation energy (15.06 kcal/mol), and remarkably **TS1-III** lies 6.59 kcal/mol above **TS1-II**. Then, two different pathways for the evolution of the vinyl carbene intermediate have been considered. First, Echavarren[6] proposed a stepwise mechanistic scheme based on a [2+2] cycloaddition between alkene and Pt-carbene to form a Pt(IV)-

(7) A recent work suggesting the involvement of cyclopropylmetallacarbene in the formation of bicyclo[4.1.0]hept-4-enes: Nevado, C.; Cárdenas, D. J.; Echavarren, A. *Chem. Eur. J.* **2003**, *9*, 2627−2635.

(8) Reactant complex with a cis chloride arrangement should favor this step over the trans chloride arrangement because one of the halide ligands lies trans to the alkyne ligand, increasing the π-back-donation to C_1 and C_2, which then could facilitate the H-shift. The computed natural charge confirms this proposal: for *cis*-chloride disposition, −0.301 for C_1 and −0.055 for C_2; for *trans*-chloride arrangement, −0.211 for C_1 and +0.013 for C_2.

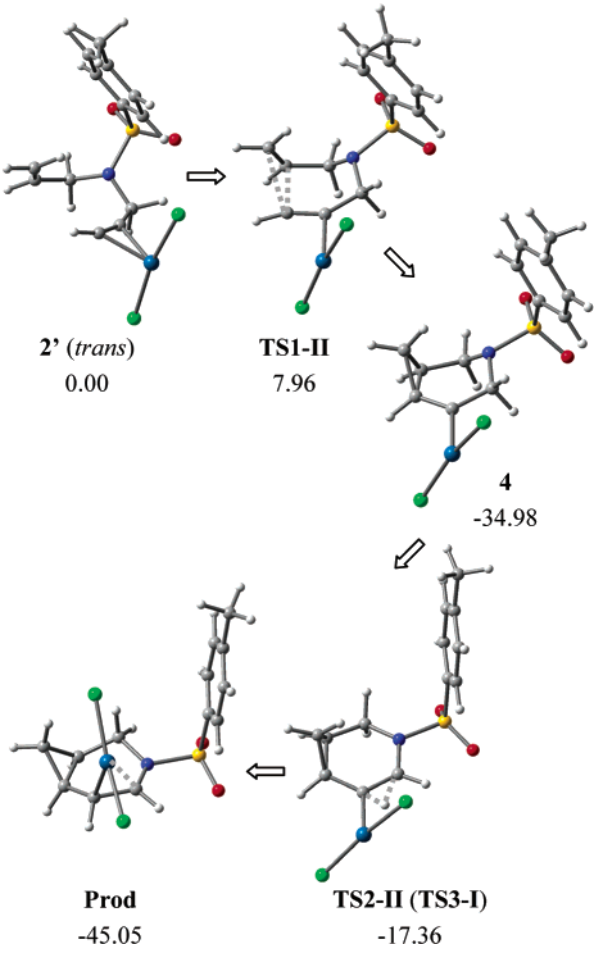
(9) The implication of related metallacarbenes as intermediates for the intramolecular cyclopropanation with alkenes has been previously proposed: (a) For Pt(II)-catalyzed processes: Mainetti, E.; Mouries, V.; Fensterbank, L.; Malacria, M.; Marco-Contelles, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2132−2135. (b) For rhodium salts and ruthenium carbonyl catalysts: Chatani, N.; Kataoka, K.; Murai, S.; Furukawa, N.; Seki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9104−9105.

TABLE 1. Total Free Energies[a] (au) and Relative Free Energies[b] (kcal/mol) Computed at B3LYP Level for Alternative Pathways Analyzed for the $PtCl_2$-Catalyzed Cyclization of Heteroatom-Tethered 1,6-enynes

	path I		path II		path III		path IV	
	$E_{DFT+ZPE}$	ΔG^b	$E_{DFT+ZPE}$	ΔG^b	$E_{DFT+ZPE}$	ΔG^b	$E_{DFT+ZPE}$	ΔG^b
2/2′	−2147.077281	0.00	−2147.046730	0.00	−2147.047537	0.00	−2147.047537	0.00
TS1	−2146.992280	+53.34	−2147.034048	+7.96	−2147.023545	+15.06	−2147.023545	+15.06
3/5	−2147.041735	+22.31			−2147.096211	−30.54	−2147.096211	−30.54
TS2	−2147.020346	+35.73			−2147.058672	−6.99	−2147.020187	+17.16
4/6	−2147.102468	−15.80	−2147.102468	−34.98	−2147.118254	−44.38		
TS3	−2147.074388	+1.82	−2147.074388	−17.36	−2147.099732	−32.75		
Prod	−2147.118520	−25.88	−2147.118520	−45.05	−2147.118520	−44.54	−2147.118520	−44.54

[a] Optimized geometries at the B3LYP/6-31G**/LANL2DZ level. [b] Relative to reactant complex. Thermal corrections (298 K) have been included.

SCHEME 7. Optimized Structures for the $PtCl_2$-Mediated Cycloisomerization According to Path II (Scheme 5)[a]



[a] Corrected free energies are given in kcal mol^{-1} relative to reactant complex.

cyclobutane[10] **6**, which could lead to the final fused cyclopropane[11] (Scheme 5 path III, and Scheme 8). This final route is equivalent to that suggested by Blum for $PtCl_4$-catalyzed cycloisomerization of allyl propargyl ethers to 3-oxabicyclo[4.1.0]heptenes.[4] Both elementary steps are exothermic and take place with moderate energy barrier (23.56 and 11.62 kcal/mol, repectively) through the properly characterized transition structures **TS2-III** (C_1−C_6 = 1.781 Å; C_6−C_7 = 1.495 Å; C_7−Pt = 2.065 Å; Pt−C_1 = 2.053 Å; C_1−C_7 = 2.728 Å) and **TS3-III** (C_1−C_6 = 1.479 Å; C_6−C_7 = 1.507 Å; C_7−Pt = 2.382 Å; Pt−C_1 = 2.107 Å; C_1−C_7 = 1.793 Å).

Additionally, a direct cyclization by addition of carbene onto the alkene moiety can be envisaged (Scheme 5, path IV, and Scheme 9). This concerted cyclopropanation proceeds through the transition structure **TS2-IV** (C_1−C_6 = 2.254 Å and C_1−C_7 = 1.967 Å) with a very high activation energy, 47.71 kcal/mol (17.16 kcal/mol above that of the reactant complex). Nevertheless, on the basis of the high energy of the **TS1-III** structure, both alternative pathways III and IV can also be ruled out. The alkyne bond is polarized in the initial η^2-reactant complex, being the internal carbon C_2 is an electrophilic center. Consequently, migration of proton at C_2 is an unfavorable process, despite the donor heteroatom at the propargylic position being able to facilitate the [1,2]-H shift, and should imply a higher activation energy than a 6-*endo*-cyclization step.

In view of these results, summarized in Table 1 and Figure 1, we can conclude that nucleophilic addition of alkene on the alkyne terminal carbon, followed by a H-shift step is the more favorable pathway for $PtCl_2$-catalyzed intramolecular cyclization of heteroatom-tethered enynes from a kinetic perspective.

Remarkably, the bicyclic product presents a very stable structure due to the lone pair at the heteroatom being delocalized with the C_2−C_3 double bond, as the short N−C_3 bond distance (1.342 Å), the lengthened N−S bond (1.768 Å), and planarity around N suggest (N deviates 8° from the C_3−S−C_5 plane). This effect is induced by $PtCl_2$ since the electrophilic character increases the weight of zwitterionic resonance form **b** (Figure 2). Accordingly, we found a moderate hyperconjugation effect between the lone-pair electrons at N and the antibonding orbital π^*_{C2-C3}. The calculated hyperconjugation energy was 5.86 kcal/mol, which resulted in the large C_2−C_3 bond length (1.451 Å).

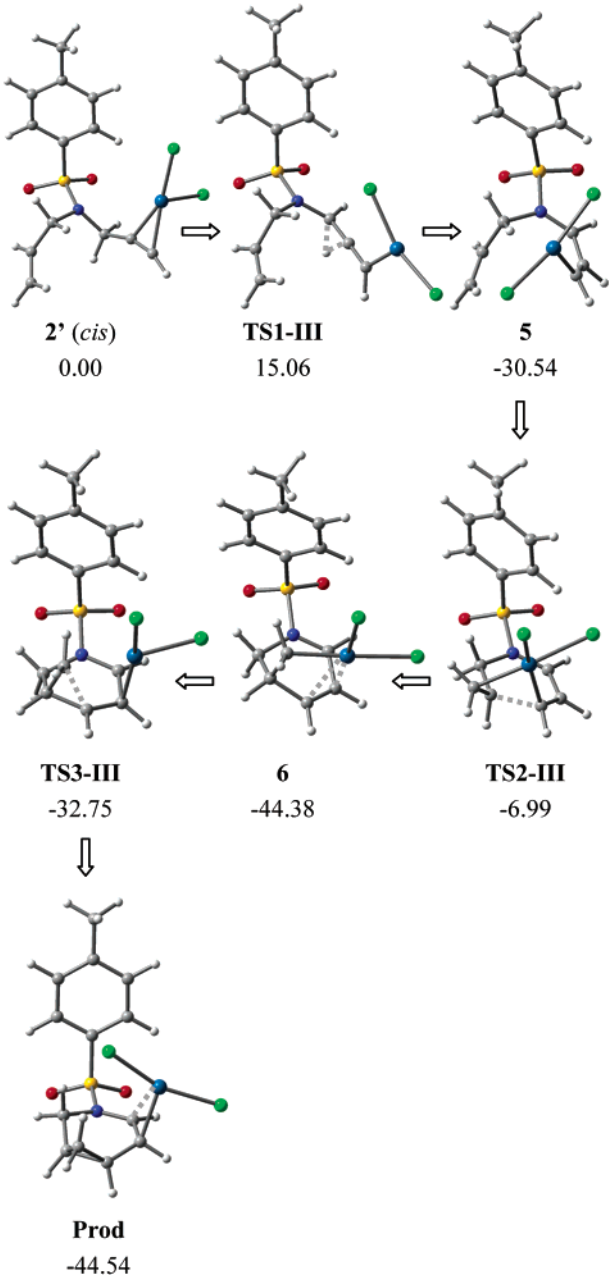
Conclusions

The skeletal rearrangement of 1,6-enynes promoted by electrophilic metal complexes led to interesting products with potential synthetic applications, so the understand-

(10) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241−2290.

(11) For the forrmation of cyclopropane from metallacyclobutane structure, see: (a) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908−4916. (b) Van Koppen, P. A. M.; Jacobson, D. B.; Illies, A.; Bowers, M. T.; Hanratty, M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 1991−2001.

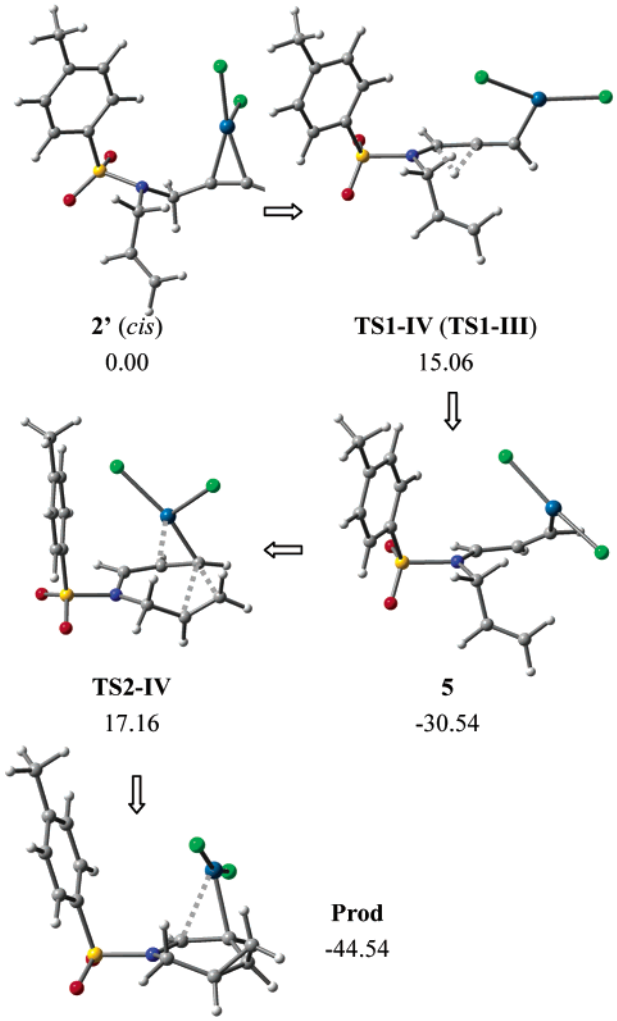
SCHEME 8. Optimized Structures for the $PtCl_2$-Mediated Cycloisomerization According to Path III (Scheme 5)[a]



[a] Corrected free energies are given in kcal mol^{-1} relative to reactant complex.

ing of the mechanisms involved would aid in the development of new synthetic strategies. The computed results for $PtCl_2$-catalyzed cyclization of heteroatom-tethered enynes clearly reveal that the kinetically preferred pathway is a two-step mechanism and involves an initial 6-*endo*-cyclization from a triggered reactant complex by the π-complexation of Pt(II) onto the alkyne to afford a cyclopropyl platina-carbene, followed by a [1,2]-hydrogen shift step (Scheme 5, path II). Additionally, we have observed that the presence of heteroatom induces a stabilization of the final product by delocalization of the lone pair.

SCHEME 9. Optimized Structures for the $PtCl_2$-Mediated Cycloisomerization According to Path IV (Scheme 5)[a]



[a] Corrected free energies are given in kcal mol^{-1} relatives to reactant complex.

Computational Methods

Calculations have been carried out with the Gaussian03[12] package of programs. Initially, the geometries were fully optimized at the Hartree−Fock level with the 6-31G(d) basis set for C, H, N, O, S, and Cl atoms. For Pt we have employed the standard LANL2DZ basis set,[13] where the innermost electrons are replaced by a relativistic ECP and the 18 valence

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; 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.; 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, V. 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, L.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M. P.; Gill, M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.
(13) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283.

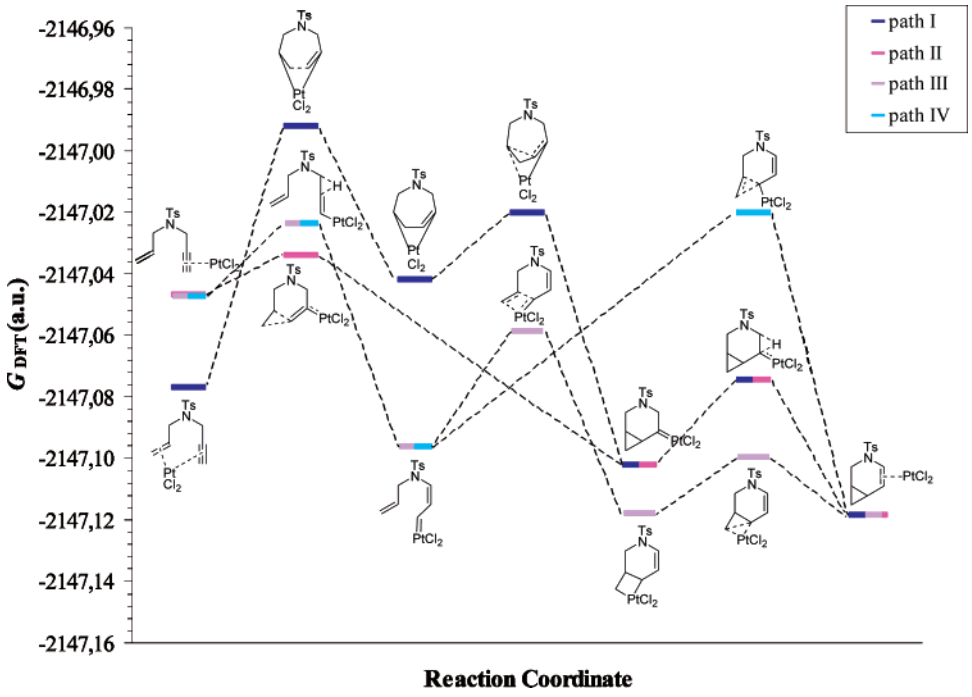


FIGURE 1. Computed energy profiles for the mechanistic proposals in Scheme 5 for the $PtCl_2$-catalyzed cyclization of heteroatom tethered enynes.

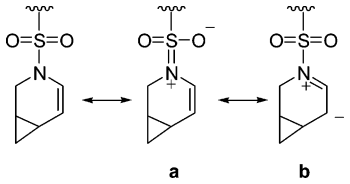


FIGURE 2. Resonance forms of 3-azabicyclo[4.1.0]hept-4-ene.

electrons are explicitly treated by a double-ζ basis set. Then, these computed structures were re-optimized at the DFT level by means of the B3LYP hybrid functional,[14] with the LANL2DZ relativistic pseudopotential for Pt and the standard 6-31G(d,p) basis set for other atoms.

The stationary points have been further characterized by vibrational frequency analysis at the DFT level according to the right number of negative eigenvalues of the Hessian matrix. The intrinsic reaction coordinate (IRC) pathways[15a] from the transition structures have been followed by using a second-order integration method[15b] to verify the expected connections of the first-order saddle points with the correct local minima found on the potential energy surface. Zero-point vibration energy (ZPVE) and thermal corrections (at 298 K) to the energy have been estimated on the basis of the frequency calculations at the optimization level, and scaled by the recommended factor.

Only Gibbs free energies are used for the discussion on the relative stabilities of the chemical structures considered. Relative free energies (including thermal corrections at 298 K) of the structures considered are shown in Table 1. Hard data on total electronic energies and the number of imaginary frequencies to identify stable structures and transition states of all structures considered are available as Supporting Information.

Natural bond orbital (NBO) analyses[16] were performed at the DFT level by the module NBO v.3.1[16a] implemented in Gaussian03 to calculate the NPA atomic charges, hyperconjugation effects, and Wiberg bond index matrix.

Supporting Information Available: Atomic coordinates and computed total energies for optimized structures shown in Schemes 6−9. This material is available free of charge via the Internet at http://pubs.acs.org.

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