Reaction of Enol Ethers with Alkynes Catalyzed by Transition Metals: 5-*exo-dig* versus 6-*endo-dig* Cyclizations via Cyclopropyl Platinum or Gold Carbene Complexes

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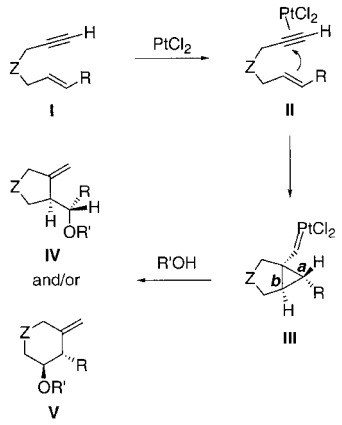
Abstract: The intramolecular reaction of enol ethers with alkynes in methanol is catalyzed by electrophilic Pt^{II}, Pd^{II}, and Au^{III} chlorides and by a Cu^{I} complex to give five- or six-membered rings bearing dimethyl acetals. The reaction takes place by an *anti* addition of the enol ether and the metal to the alkyne. The possible involvement of vinylidene complexes in this reaction is excluded. In addition to the usual 5-*exo-dig* (or 6-*exo-dig*) pathways, a 6-*endo-dig* pathway has also been found to take place with certain enynes. One case of 5-*endo-dig* cyclization has also been found. A general scheme for the alkoxycyclization of enynes catalyzed by transition metals based on DFT calculation of $PtCl_2$ and $AuCl_3$ complexes that includes *exo* and *endo* cyclizations is presented.

Keywords: alkynes · cyclization · density functional calculations · gold · platinum

Introduction

We have recently shown that enynes **I** react with $PtCl_2$ to form complexes **II**, which evolve by an intramolecular reaction of the (η^2-alkyne)$PtCl_2$ with the alkene to form a cyclopropyl Pt–carbene intermediate **III** (Scheme 1).[1] Subsequent attack of the nucleophile (alcohol or water) at the cyclopropyl carbons **a** and **b** of intermediate **III** gives carbo- or heterocycles **IV** or **V**.[1] Similar intermediates might be also involved in the transition metal catalyzed intramolecular attack of allylsilanes and allylstannanes to alkynes,[2] as well as in the skeletal rearrangement of enynes that yield conjugated dienes.[3, 4] DFT calculations also support the formation of intermediates similar to **III** in the first step of the intramolecular reaction of furans with alkynes catalyzed by Pt^{II}.[5]

We found that the reaction proceeds via an attack at carbon **a** with enynes bearing 1,2-disubstiuted or 1,1,2-trisubstituted alkenes. However, by reducing the electronegativity of the substituents at the tether Z, preferential attack at carbon **b** was observed, yielding six-membered ring compounds **V**.[1] Although some of these cyclizations are also catalyzed by Au^{III}, Ru^{II},[1] and Pd^{II},[6] the cyclization with these catalysts is more limited in scope.



Scheme 1. $PtCl_2$-catalyzed cyclization of enynes in the presence of alcohols or water.

The related cyclization of silyl enol ethers with alkynes catalyzed by [W(CO)$_5$L] (L = THF, amine) has been found to proceed with *exo-dig* or *endo-dig* selectivity depending on the reaction conditions.[7] Tungsten vinylidenes have been proposed to be key intermediates in the formation of *endo-dig* products.

We reasoned that the selectivity of the opening of **III** could be controlled by attaching a strong electron-donating substituent at either **a** or **b** (Scheme 2).[8] Thus, attaching an -OR substituent at **a** (**VI**, Scheme 2) would selectively give rise to five-membered ring intermediate **VII**, whereas the alternative

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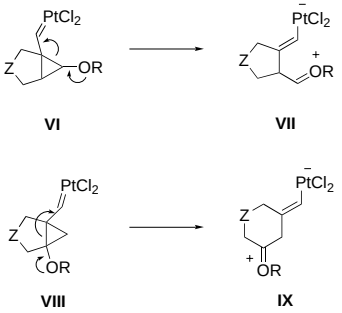
Supporting Information (atomic coordinates for structures of Figures 2, 4, 5, and 7 for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

 DOI: 10.1002/chem.200204646



Scheme 2. Hypothetical openings of alkoxycyclopropyl carbene intermediates.

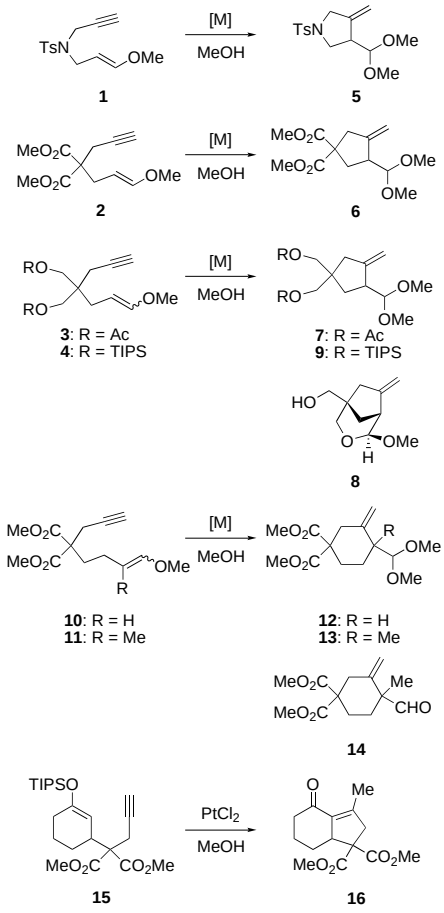
substitution at **b** would favor cleavage to form six-membered ring **VIII**. In the presence of an alcohol or water, these intermediates might evolve to form acetals or carbonyl compounds, respectively.

It is important to note that Dankwardt has recently found that the cyclization of *tert*-butyldimethylsilyl enol ethers of 2-ethynylacetophenones proceeds in a 6-*endo-dig* mode to afford 1-naphthol derivatives.[9] Remarkably, this cyclization can be catalyzed by Rh^{I}, Pt^{II}, Pd^{II}, Au^{III}, Ru^{II}, and Ag^{I}, although more general transformations were found with $[Rh(CO)_2Cl]_2$, $PdCl_2$, and $PtCl_2$. With $[Rh(CO)_2Cl]_2$, Rh^{I}–vinylidene complexes were found to be intermediates in the cyclization. We have found that the reaction of enol ethers, and some trialkylsilyl enol ethers, with alkynes takes place in the presence of a variety of late transition metals to give cyclic compounds by *exo-dig* or *endo-dig* pathways.[10] From these experimental results, as well as from DFT calculations on cyclizations promoted by $PtCl_2$ and $AuCl_3$, a more complete picture of the reaction of alkynes with alkenes emerges.

Results and Discussion

Cyclization of enol ethers with alkynes: Reaction of (*E*)-**1**[11] in methanol under reflux[12] proceeded satisfactorily with $PtCl_2$ (5 mol%), $PdCl_2$ (10 mol%), $[Cu(MeCN)_4]PF_6$ (10 mol%), or $AuCl_3$ (5 mol%) as the catalysts to give exclusively **5** (Table 1, entries 1–4). The clean formation of **5** by an *exo-dig* cyclization is noteworthy, because substrates similar to **1** react anomalously to give cyclopropane derivatives with electrophilic transition metal as the catalysts.[1b, 4f, g] Substrate (*E*)-**2** reacted in methanol similarly to give **6** (entries 5–8). The best results with **1**–**2** were obtained with $PtCl_2$, $PdCl_2$, or $AuCl_3$ as the catalysts (entries 1, 2, 4–6, and 8).

Diacetate **3** (1:0.7 *E*/*Z* mixture) reacted with $PtCl_2$, $PdCl_2$, or $[Cu(MeCN)_4]PF_6$ to give carbocycle **7** in 86–88% yield (entries 9–11). However, the reaction of **3** with $AuCl_3$ gave bicyclic acetal **8** (58%) as a single isomer, as a result of the cleavage of the acetates by $AuCl_3$ in methanol (entry 12).[13] The configuration at the acetal center (C-4) could not be assigned on the basis of the observed vicinal coupling constant of 2.4 Hz, which do not allow to distinguish between a β- or α-configuration (dihedral angle of 56 or 65°, respectively). However, the most stable isomer corresponds to the β-configuration according to semiempirical calculations (PM3 Hamiltonian), which show that **8** is about 2 kcal mol^{-1} more stable than the α anomer. TBS protecting groups were also cleaved by $PtCl_2$ or $AuCl_3$ in methanol. However, TIPS groups were tolerated. Thus, **4** (1:0.8 *E*/*Z*) gave carbocycle **9** in moderate to good yield with the four catalysts examined (entries 13–16).



Scheme 3. Transition-metal catalyzed cyclization of enol ethers and silyl enol ether **15** in the presence of MeOH.

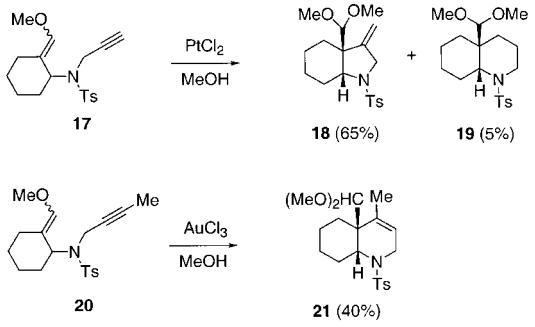
Formation of six-membered rings is also possible with the electrophilic transition metal catalysts. However, the cyclization of **10** (1:1.3 *E*/*Z*) could only be performed with the more reactive $AuCl_3$ as the catalyst, giving rise to carbocycle **12** in 94% yield (entry 17). Substrate **11** (1:1 *E*/*Z*), bearing an additional methyl group at the enol ether, was more reactive than **10** and gave **13** in good or moderate yield by using $PtCl_2$ or $[Cu(MeCN)_4]PF_6$ as the catalysts (entries 18, 19). In this case, cleavage of the acetal took place in the presence of $AuCl_3$ leading to aldehyde **14**, which was isolated in 43% yield (entry 20). The reaction of TIPS enol ether **15**[7b] with $PtCl_2$ in methanol gave α,β-unsaturated bicyclic ketone **16** in 70% yield (entry 21). Cleavage of the intermediate labile acetal and conjugation of the alkene occur under the reaction conditions.

The cyclization of **17** (6.2:1 *E*/*Z*) with $PtCl_2$ gave a 13:1 mixture of acetals **18** and **19** in 70% combined yield (Scheme 4). The *cis* configuration of these heterocycles at the ring fusion was assigned on the basis of NOESY experi-

Table 1. Cyclization of substrates of Scheme 3.[a]

Entry	Enol ether	Catalyst[b]	Product	Yield [%]
1	**1**	$PtCl_2$	**5**	84
2	**1**	$PdCl_2$	**5**	81
3	**1**	$[Cu(MeCN)_4]PF_6$	**5**	77
4	**1**	$AuCl_3$	**5**	97
5	**2**	$PtCl_2$	**6**	97
6	**2**	$PdCl_2$	**6**	97
7	**2**	$[Cu(MeCN)_4]PF_6$	**6**	70
8	**2**	$AuCl_3$	**6**	95
9	**3**	$PtCl_2$	**7**	86
10	**3**	$PdCl_2$	**7**	88
11	**3**	$[Cu(MeCN)_4]PF_6$	**7**	88
12	**3**	$AuCl_3$	**8**	58
13	**4**	$PtCl_2$	**9**	84
14	**4**	$PdCl_2$	**9**	81
15	**4**	$[Cu(MeCN)_4]PF_6$	**9**	57[c]
16	**4**	$AuCl_3$	**9**	90
17	**10**	$AuCl_3$	**12**	94
18	**11**	$PtCl_2$	**13**	90
19	**11**	$[Cu(MeCN)_4]PF_6$	**13**	68[d]
20	**11**	$AuCl_3$	**14**	43
21	**15**	$PtCl_2$	**16**	70

[a] The reactions were carried out under reflux for 17 h. [b] 5 mol% of $PtCl_2$ or $AuCl_3$ and 10 mol% of $PdCl_2$ or $[Cu(MeCN)_4]PF_6$. [c] 81% yield based on unrecovered starting material. [d] 99% yield based on unrecovered starting material.



Scheme 4. *exo*- vs *endo* Cyclization of substrates **17** and **20**.

ments. Interestingly, substrate **20**, with a methyl substituent on the alkyne, led selectively to *endo-dig* cyclization with $PtCl_2$ in methanol giving **21**. In this case, more reproducible results were realized with $AuCl_3$ as the catalyst, which gave **21** as the only product, isolated in 40% yield.

Octahydroquinolines **19** and **21** result from *endo* cyclization,[14] a type of reaction that has been found in the cyclization of ω-acetylenic silyl enol ethers with $[W(CO)_6]$,[7] from which tungsten vinylidene complexes were proposed as intermediates.[15] A rhodium–vinylidene complex was also proposed for the formation of naphthalenes by *endo* cyclization of *tert*-butyldimethylsilyl enol ethers with alkynes.[9]

However, the formation of **21** from methyl substituted **20** clearly excludes the involvement of a similar platinum or gold vinylidene complex in the cyclization. To further secure that conclusion, the reaction of **17** was carried out in $[D_4]$methanol with $PtCl_2$ as the catalyst. Under these conditions, in addition to >95% deuterium incorporation at the alkene, exchange of the acetal with $[D_4]$methanol occurs yielding **[D_7]-18** and **[D_7]-19** (Figure 1). The cyclization of **2** with $PtCl_2$ in $[D_4]$methanol gave **[D_7]-6**, which indicates that exchange

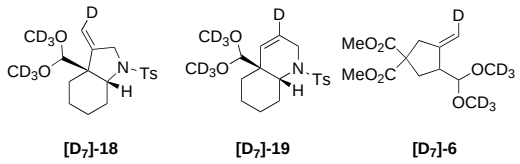
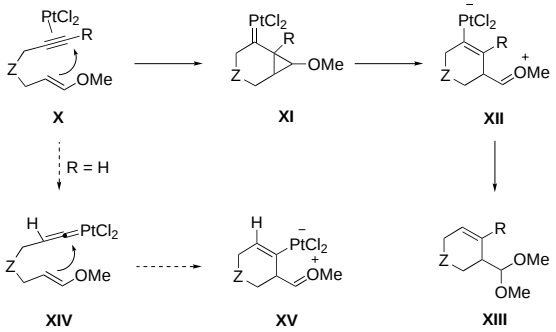


Figure 1. Products of cyclizations on $[D_4]$methanol.

of the dimethyl acetal with the solvent is a facile process under the reaction conditions. However, no transesterification of the ester of **6** was observed. In addition, it is significant that in all cases the cyclizations are faster than the addition of methanol to the enol ether or the alkyne functions of the starting enyne.[16]

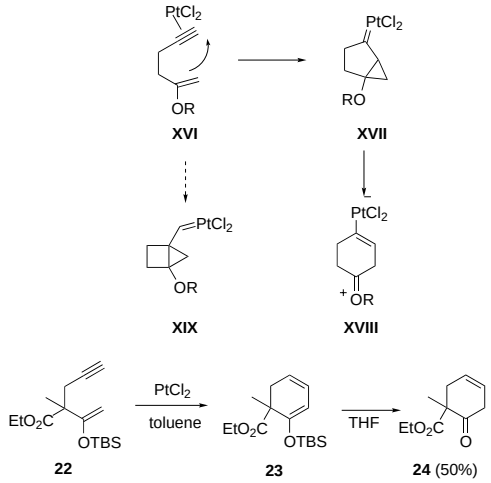
The stereoselective deuteration of **[D_7]-18** and **[D_7]-6** demonstrates that the C–C and the C–M are formed *anti* on the alkyne, which suggests that alkenyl–metal complexes similar to **III** (Scheme 1) are involved as intermediates in the cyclization of the ω-acetylenic enol ethers.[17] On the other hand, formation of **19** and **21** suggests that an *endo-dig* attack of the enol ether to the (η^2-alkyne)platinum complex **X** to give cyclopropyl platinum carbene **XI** is possible (Scheme 5). Opening of the cyclopropane of **XI**, would then give zwitterionic intermediate **XII**, which would finally give **XIII**. Cyclization of a platinum(II) vinylidene complex **XIV**, similar to that proposed for the reactions with $[W(CO)_6]$[7] or Rh^I[9] is ruled out since it would have resulted in deuteration at C-4 of **19** via complex **XV**.



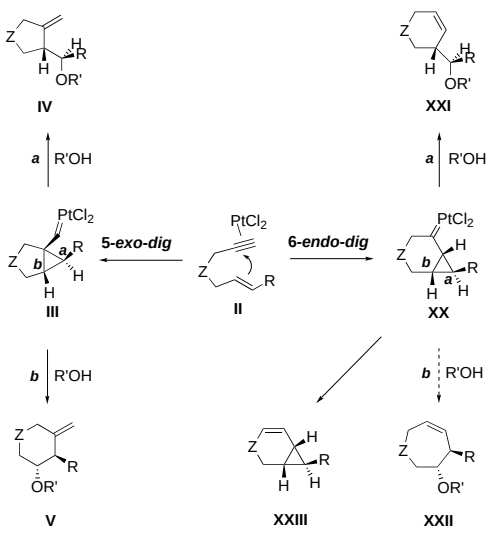
Scheme 5. Mechanism for the 6-*endo-dig* cyclization.

Importantly, the mechanism proposed in Scheme 5 suggests that the *endo-dig* cyclization would be also favored if the alkyne and the alkene were tethered by just two atoms, instead of three. In that case, cyclization of **XVI** (Scheme 6) would proceed through bicyclic system **XVII**, which would open to form **XVIII**. The alternative pathway, leading finally to five-membered rings, would be less favorable since it would proceed through highly strained **XIX**.

In the event, reaction of *tert*-butyldimethylsilyl enol ether **22**[7b] with $PtCl_2$ as the catalyst (5 mol%) in toluene under reflux gave 1-silyloxydiene **23**, which was hydrolyzed to known **24**[7b] (50% overall yield). Formation of **23** can be explained by proton abstraction from an intermediate of type **XVIII**, to form a conjugated diene, followed by cleavage of the C–Pt bond by H^+. This cyclization corresponds formally to a 6-*endo-dig*/*endo-trig* process.



Scheme 6. 6-*endo-dig*/*endo-trig* cyclization.



Scheme 7. General mechanism for the $PtCl_2$-catalyzed cyclization of enynes.

A more general mechanistic scheme for the transition metal-catalyzed alkoxycyclization of enynes: The possible pathways are summarized in Scheme 7 for $PtCl_2$ as the catalyst starting from a complex **II**. In addition to the 5-*exo-dig* cyclization via complex **III**,[1] a 6-*endo-dig* process would give complexes such as **XX**. Attack at center **a** would give compounds of general structure **XXI**. This pathway is that followed by **20** and, in part, **17**. Reaction at center **b** would give seven-membered ring derivatives **XXII**. Such a process has not yet been reduced to practice. Cyclopropanes of structure **XXIII**, which have been observed when Z = O or NTs,[1b, 4b, f–g, 18] are probably derived from intermediates **XX** by a hydrogen-shift.

We decided to analyze the *exo*- and *endo* cyclizations of model enynes with $PtCl_2$ and $AuCl_3$ to obtain a clearer picture of the reactions of enynes promoted by electrophilic metal halides. Three different types of substrates were considered, in order to understand the effect of the presence of a heteroatom in the chain and the dependence of the cyclization mode on the type of alkyne (terminal or internal). The model Pt complexes present water as an additional ligand.[1b]

The results of the cyclization of 6-octen-1-yne are summarized in Figure 2. An important feature of the starting complex **XXIVa** is the polarization induced by $PtCl_2$ on the bonded alkyne. The internal carbon of the asymmetrically bonded alkyne becomes more electrophilic than the terminal one (natural charges being +0.05 and −0.25, respectively), which makes the *exo*-cyclization reaction to give **XXVa** faster than the *endo* process (E = 10.3 and 11.2 kcal mol^{-1}, respectively). Both reactions are exothermic

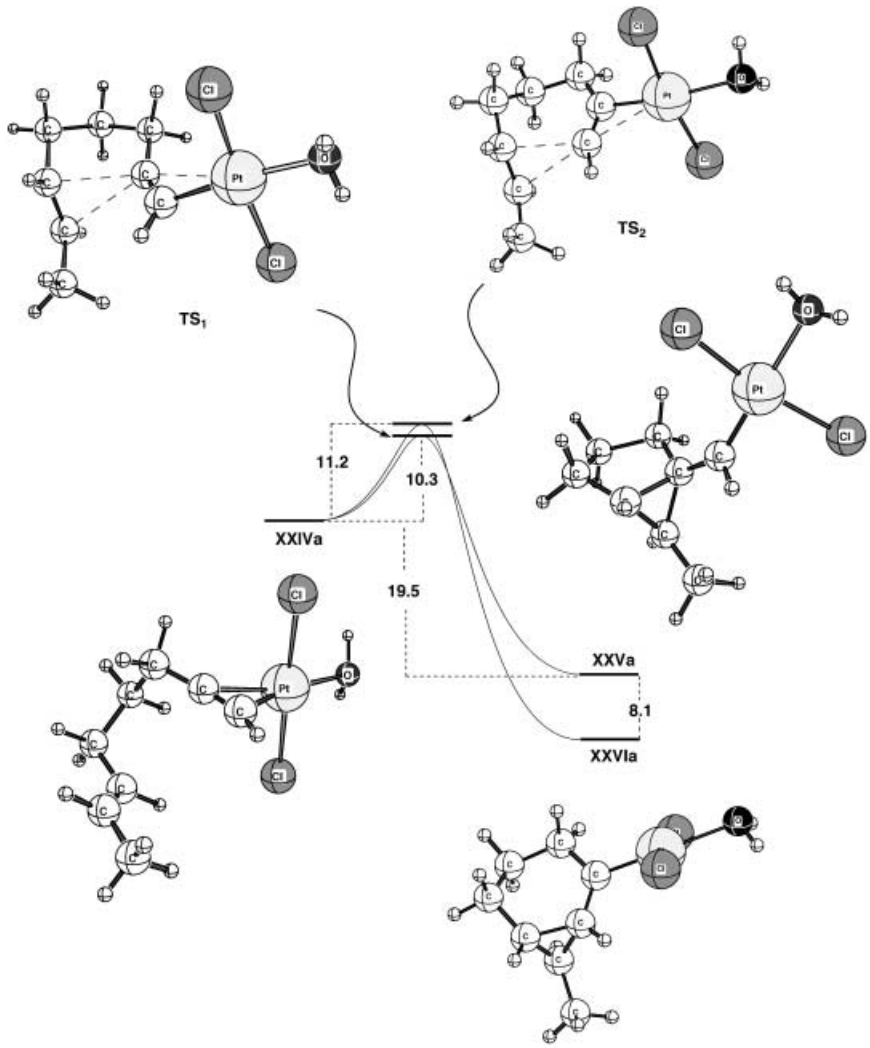


Figure 2. Energy profile for the cyclization of $PtCl_2$-complex **XXIVa** (values in kcal mol^{-1}).

(−19.5 and −27.6 kcal mol^{-1}), the six-membered-ring product **XXVIa** being more stable. These findings perfectly parallel the experimental results.

To obtain information about the effect of an heteroatom in the tether between the alkyne and the alkene, cyclizations of model complex **XXIVb** were studied (Figure 3). Interestingly, the heteroatom does not further polarize the alkyne. The electron deficiency that the electronegative heteroatom could induce on the internal alkyne carbon is compensated by donation from the metal fragment, as shown from the natural charges of carbons (−0.01 and −0.24, for the internal an terminal ones, respectively). In this case, the *exo*-cyclization mode leading to **XXVb** is less favorable both kinetical and thermodynamically than the *endo* cyclization to form six-membered-ring complex **XXVIb**, in spite of the higher electrophilic character of C-2, which contrasts with the results shown in Figure 1. The reason for this preference is that geometrical restrictions are stronger for the formation of **TS$_3$** compared with the formation of **TS$_1$**, due to the shorter C–O distances. As a consequence, the less strained six-membered ring derivative is formed through a lower energy transition state **TS$_4$**, which is 1.5 kcal mol^{-1} more stable than **TS$_3$**.

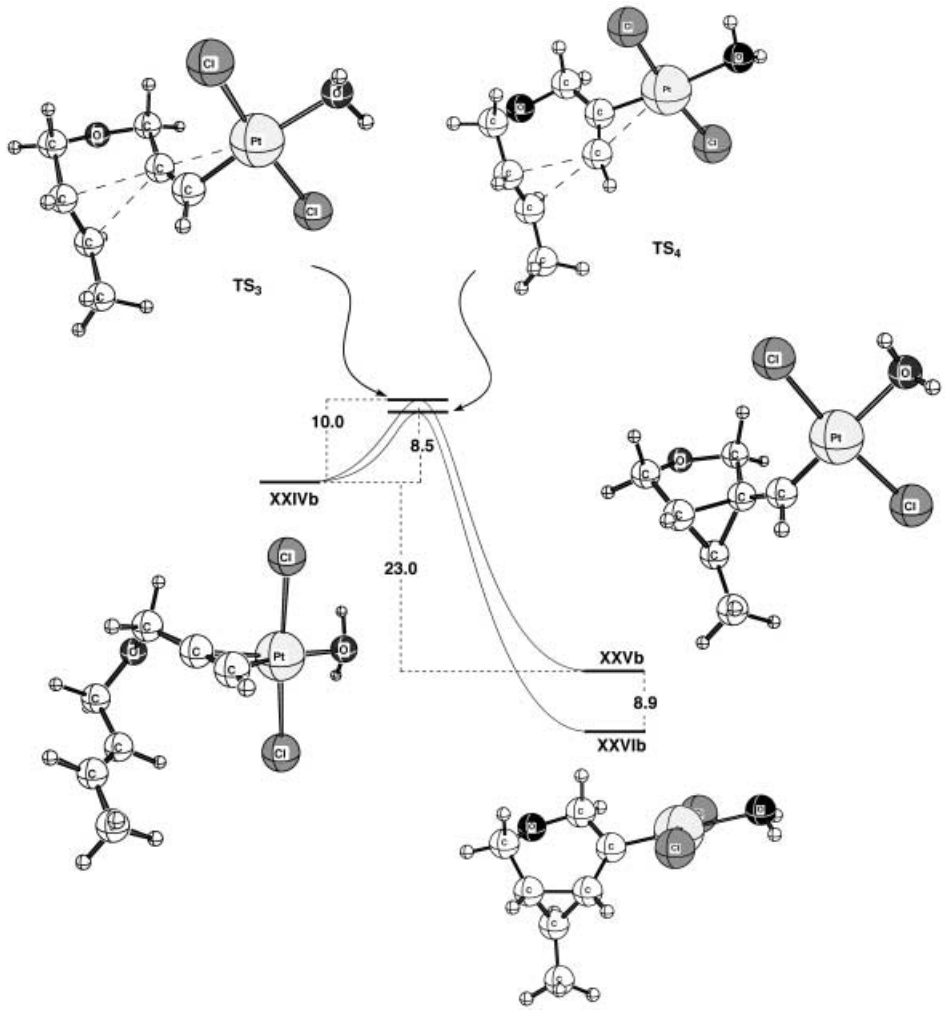


Figure 3. Energy profile for the cyclization of $PtCl_2$ complex **XXIVb** (values in kcal mol^{-1}).

This hypothesis was confirmed by studying the intermolecular reaction between propargyl alcohol coordinated to $Pt(H_2O)Cl_2$ and *trans*-2-butene, which showed that, in fact, the preferred pathway leads to formation of the C–C bond with C-2 of the alkyne (*exo*-type cyclization) through a transition state which is 2.3 kcal mol^{-1} more stable than the alternative *endo*-type transition state (Figure 4).

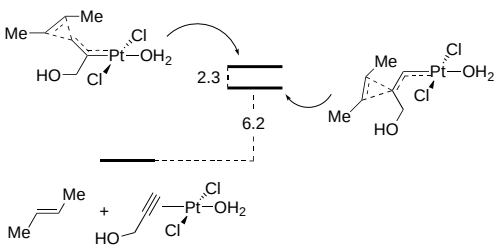


Figure 4. Activation energies [kcal mol^{-1}] for the model intermolecular reaction of propargyl alcohol with *trans*-2-butene.

Internal alkynes containing an electronegative heteroatom within the chain suffer *endo* cyclization to six-membered rings preferentially. In this case, the theoretical model also accounts for the observed results (Figure 5). Starting from **XXIVc**, the preferred cyclization for both kinetic and thermodynamic reasons leads to **XXVIc**. These reactions show higher activation barriers (12.5 and 14.2 kcal mol^{-1} for the *endo* and *exo* cyclizations, respectively) and are less exothermic (−21.8 and −17.0 kcal mol^{-1}, respectively) than those of **XXIVa** and **XXIVb** (Figures 2 and 3) probably due to steric hindrance imposed by the methyl group. In the cases of **XXVc** and **XXVIc**, the dihedral angles between the coordination and the carbene planes are 20–25° higher than those of **XXVb** and **XXVIb**. The alkyne of **XXIVc** is only slightly polarized and in the opposite sense (natural charges are −0.04 and +0.02 for C-3 and C-2, respectively), in spite of the presence of the electronegative O atom.

Bader analysis of the starting alkyne–$PtCl_2$ complexes of terminal alkynes (**XXIVa** and **XXIVb**) show a single bond critical point located between the terminal carbon and the metal, the internal alkyne carbon being not coordinated. Thus, it can be said that a hypothetical resonance structure containing a vinyl cation has a considerable contribution in these complexes (Figure 6). Therefore, terminal alkynes

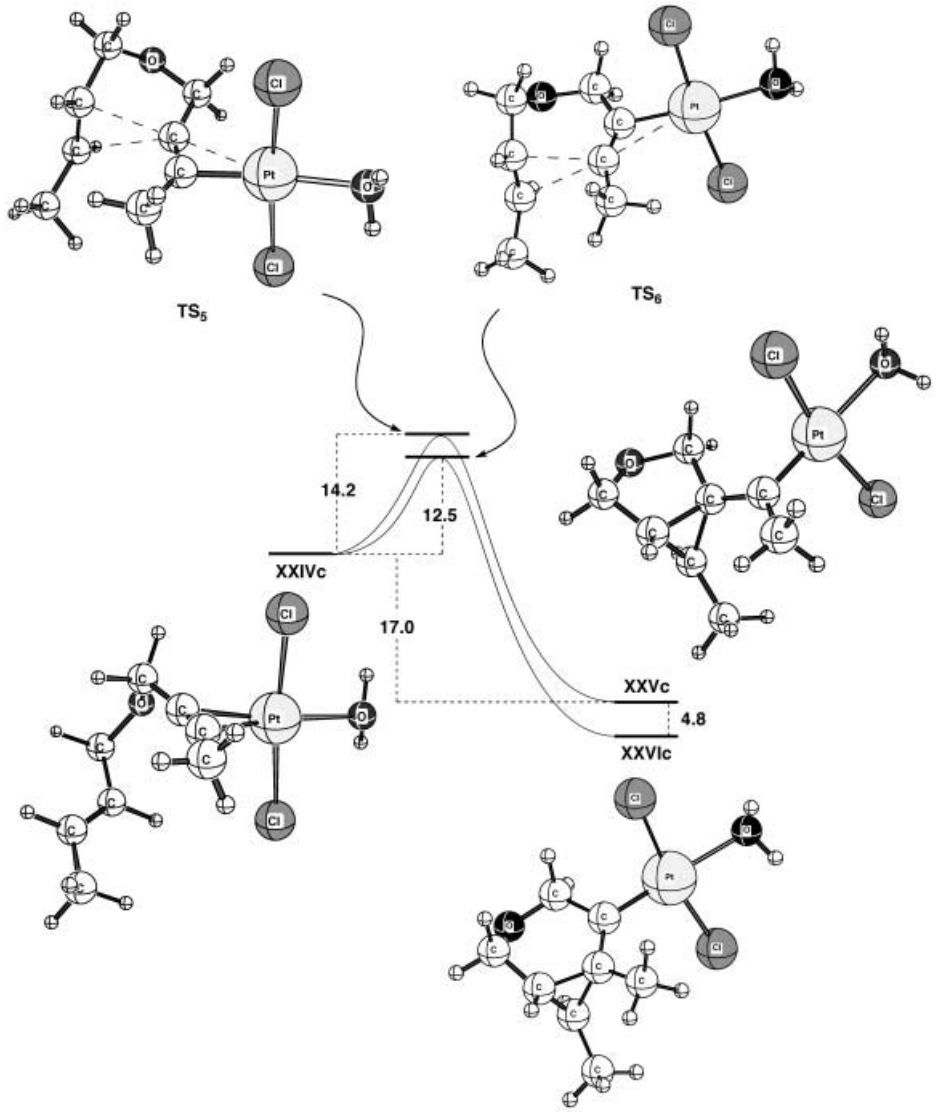


Figure 5. Energy profile for the cyclization of $PtCl_2$-complex **XXIVc** (values in kcal mol^{-1}).

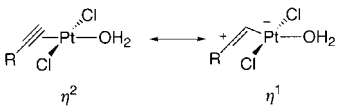


Figure 6. Bonding of terminal alkynes to Pt^{II} in Pt(alkyne)$(H_2O)Cl_2$ complexes.

complexes of $PtCl_2$ are better described as η^1 species. On the other hand, a single bond critical point involving both carbons is found for complex **XXIVc**, which corresponds to a η^2-alkyne complex.

We also studied the reaction of the oxygen-containing internal alkyne promoted by $AuCl_3$ (Figure 7). In this case, the cyclizations are not as exothermic as in the case of the Pt^{II}-catalyzed reactions, but have considerable lower activation energies, still favoring the *endo* process (4.4 vs 6.9 kcal mol^{-1}). The structures of the resulting cyclopropyl gold carbenes **XXVIII** and **XXIX** are very similar to those of the platinum analogues **XXVc** and **XXVIc**, respectively, although the gold carbenes present longer Au–C bonds (2.0–2.1 vs 1.8–1.9 Å for platinum carbenes).

Conclusion

Unlike other cyclizations of enynes that give 1,3- or 1,4-dienes as a result of cycloisomerization, the cyclization of ω-acetylenic enol ethers provides carbo- and heterocycles bearing two different functionalities that could be later transformed selectively. Since enol ethers are readily synthesized by a variety of methods,[19] this experimentally simple catalytic cyclization could be applied for the ready access to complex organic molecules.

These results support the proposal that the cyclization of enynes with electrophilic Pt^{II}, Pd^{II},[6, 20] Au^{III}, Cu^{I}, take place by a common mechanism. This conclusion is also supported by the similar profile of the reaction of enynes with $PtCl_2$ or $AuCl_3$ as the electrophiles (Figures 2, 4, 5, and 7) and by the results of Dankwardt in the cyclization of *tert*-butyldimethylsilyl enol ethers of 2-ethynylacetophenones.[9] The observed regioselectivity is a result of both the electronic effect of the coordination of the alkyne to the metal and the geometrical constraints of an intramolecular process. In the absence of ring strain, coordinated terminal alkynes are attacked by the alkene at the internal carbon.

A more complete picture of the cyclization of enynes initiated by the η^2-coordination to electrophilic metal fragments such as $PtCl_2$ or $AuCl_3$ includes both *exo-dig* and *endo-dig* cyclization modes. The corresponding transition states differ little in energy, which suggests that substituents positioned at strategic positions could highly influence the cyclization pathways.

Experimental Section

General procedure for the synthesis of enol ethers by Wittig reaction: *n*BuLi (1.2 equiv) was slowly added at $-40\,^{\circ}C$ to suspension of (methoxymethyl)triphenylphosphonium chloride (1.2 equiv) in THF and the resulting mixture was stirred at $-40\,^{\circ}C$ for 40 min. Then a solution of the corresponding aldehyde (1.0 equiv) was added and the mixture was stirred at $23\,^{\circ}C$ for 30 min. Treatment with NH_4Cl (pH 8), extractive workup (Et_2O), and chromatography on deactivated silica gel (packed with 5%

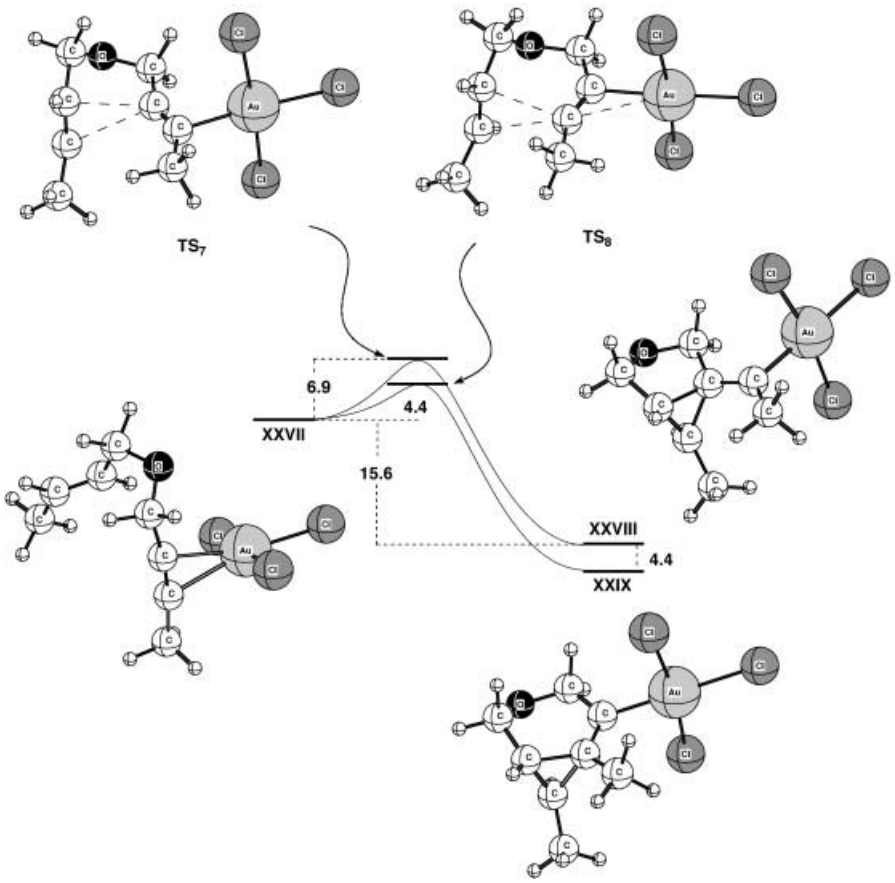


Figure 7. Energy profile for the cyclization of the $AuCl_3$ complex **XXVII** (values in kcal mol^{-1}).

Et_3N in hexane) provided substrates **1**–**4**, **10**, **11**, and **17** in 16–48% (non optimized) yields. Substrate **22** has been described before.[7b]

Compound 1: yellow oil, *E* isomer; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.72$ (d, $J = 8.3$ Hz, 2H), 7.28 (d, $J = 8.3$ Hz, 2H), 6.48 (d, $J = 12.5$ Hz, 1H), 4.63 (dt, $J = 12.5$, 7.7 Hz, 1H), 4.10 (d, $J = 2.4$ Hz, 2H), 3.75 (d, $J = 7.7$ Hz, 2H), 3.52 (s, 3H), 2.42 (s, 3H), 1.99 (t, $J = 2.4$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 152.66$ (CH), 144.10 (C), 136.82 (C), 130.10 (CH), 128.40 (CH), 96.41 (CH), 78.10 (C), 74.24 (C), 56.70 (CH_3), 45.49 (CH_2), 35.61 (CH_2), 22.21 (CH_3); EI-HRMS: calcd for $C_{14}H_{17}NO_3S$: 279.0929; found: 279.0919.

Compound 2: colorless oil, *E* isomer; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.33$ (d, $J = 12.5$ Hz, 1H), 4.41 (dt, $J = 12.5$, 8.1 Hz, 1H), 4.37 (s, 6H), 3.44 (s, 3H), 2.73 (d, $J = 2.8$ Hz, 2H), 2.62 (dd, $J = 8.1$, 1.2 Hz, 2H), 1.98 (t, $J = 2.8$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 170.90$ (C), 151.10 (CH), 95.59 (CH), 79.48 (CH), 72.12 (C), 58.09 (C), 56.56 (CH_3), 53.41 (CH_3), 31.40 (CH_2), 23.03 (CH_2); FAB-HMRS: calcd for $C_{12}H_{17}O_5$: 241.1076; found: 241.1079.

Compound 3: pale yellow oil, 1:0.7 *E*/*Z*; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 6.33 (dt, $J = 11.9$, 0.8 Hz, 1H, *E*), 6.00 (dt, $J = 6.7$, 1.2 Hz, 1H, *Z*), 4.60 (dt, $J = 11.9$, 8.1 Hz, 1H, *E*), 4.27 (dt, $J = 8.1$, 6.7 Hz, 1H, *Z*), 4.01 (s, 3H, *E*), 2.27 (d, $J = 2.8$ Hz, 2H, *Z*), 2.24 (d, $J = 2.8$ Hz, 2H, *E*), 2.22 (dd, $J = 8.1$, 1.2 Hz, 2H, *Z*), 2.08 (dd, $J = 8.1$, 0.8 Hz, 2H, *E*), 2.06 (s, 6H), 2.05 (s, 6H), 2.01 (t, $J = 2.8$ Hz, 1H), 1.99 (t, $J = 2.8$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 170.83$ (C), 170.74 (C), 150.15 (CH), 149.18 (CH), 99.84 (CH), 95.85 (CH), 79.71 (CH), 79.61 (CH), 71.27 (C), 70.96 (C), 66.26 (CH_2), 65.99 (CH_2), 60.24 (CH_3), 59.57(CH_3), 40.39 (C), 40.13 (C), 30.40 (CH_2), 26.64 (CH_2), 22.87 (CH_2), 22.53 (CH_2), 20.80 ($2 \times CH_3$); elemental analysis calcd (%) for $C_{14}H_{20}O_5$: C 62.67, H 7.51; found: C 62.48, H 7.74.

Compound 4: colorless oil, 1:0.8 *E*/*Z*; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.32$ (d, $J = 12.5$ Hz, 1H, *E*), 6.28 (dt, $J = 6.3$, 1.2 Hz, 1H, *Z*), 4.71 (dt, $J = 12.5$, 8.1 Hz, 1H, *E*), 4.37 (dt, $J = 7.8$, 6.3 Hz, 1H, *Z*), 3.60 (s, 4H, *Z*), 3.57 (s, 4H, *E*), 3.53 (s, 3H, *Z*), 3.49 (s, 3H, *E*), 2.25 (d, $J = 2.8$ Hz, 2H), 2.21 (dd, $J = 7.8$, 1.2 Hz, 2H, *Z*), 2.03 (dd, $J = 8.1$, 1.0 Hz, 2H, *E*), 1.91–1.88 (t, $J = 2.8$ Hz, 1H, *E* and *Z*), 1.11–0.98 (m, 42H, *E* and *Z*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.62$, 148.34, 102.63, 98.50, 83.08, 82.83, 70.72, 70.44, 65.70, 65.20, 59.99, 56.64, 44.73, 29.95, 26.41, 22.34, 22.09, 18.74, 18.41, 12.66; elemental analysis calcd (%) for $C_{28}H_{56}O_3Si_2$: C 67.68, H 11.36; found: C 67.83, H 11.42.

Compound 10: colorless oil, 1:1.3 *E*/*Z*; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.28$ (dt, $J = 12.5$, 1.2 Hz, 1H, *E*), 5.84 (dt, $J = 6.1$, 1.6 Hz, 1H, *Z*), 4.64 (dt, $J = 12.5$, 7.2 Hz, 1H, *E*), 4.26 (dt, $J = 6.1$, 6.7 Hz, 1H, *Z*), 3.71 (s, 12H, *E* and *Z*), 3.54 (s, 3H, *E*), 3.46 (s, 3H, *Z*), 2.83 (d, $J = 2.4$ Hz, 2H, *E*), 2.81 (d, $J = 2.8$ Hz, 2H, *Z*), 2.13–1.79 (m, 8H, *E* and *Z*); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 170.66$ (C), 170.64 (C), 147.70 (CH), 146.78 (CH), 104.96 (CH), 101.40 (CH), 78.97 (C), 78.74 (C), 71.35 (C), 71.17 (C), 59.50 (CH_2), 56.75 (CH or CH_3), 56.60 (CH or CH_3), 55.82 (CH or CH_3), 53.44 (CH or CH_3), 53.37 (CH or CH_3), 33.17 (CH_2), 31.86 (CH_2), 22.91 (CH_2), 22.67 (CH_2), 22.57 (CH_2), 18.64 (CH_2); elemental analysis calcd (%) for $C_{13}H_{18}O_5$: C 61.40, H 7.14; found: C 61.69, H 7.48.

Compound 11: yellow oil, 1:1 *E*/*Z*; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.77$ (m, 1H), 5.70 (m, 1H), 3.73 (s, 6H), 3.72 (s, 6H), 3.53 (s, 3H), 3.49 (s, 3H), 2.86 (d, $J = 3.8$ Hz, 2H), 2.82 (d, $J = 3.8$ Hz, 2H), 2.15–2.08 (m, 4H), 2.03–1.90 (m, 4H), 1.80–1.72 (m, 4H), 1.57 (d, $J = 1.6$ Hz, 3H), 1.51 (d, $J = 1.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 171.30$ (C), 171.29 (C), 143.09 (CH), 142.87 (CH), 113.28 (C), 113.00 (C), 79.65 (CH), 79.37 (CH), 72.03 (C), 71.78 (C), 59.90 (CH_3), 59.82 (CH_3), 53.38 (CH_3), 53.27 (CH_3), 31.29 (CH_2), 30.23 (CH_2), 29.09 (CH_2), 24.04 (CH_2), 23.43 (CH_2), 23.15 (CH_2), 17.54 (CH_3), 13.33 (CH_3); FAB-HMRS: calcd for $C_{14}H_{20}O_5$: 268.1311; found: 268.1319.

Compound 17: white vitreous solid, 6.2:1 *E*/*Z*; m.p. 65–67 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.80$ (d, $J = 8.5$ Hz, 2H, *E* and *Z*), 7.25 (d, $J = 8.5$ Hz, 2H, *E* and *Z*), 5.74 (m, 1H, *E*), 5.72 (m, 1H, *Z*), 4.40 (m, 1H, *E* and *Z*), 4.27 (dd, $J = 18.2$, 2.4 Hz, 1H, *Z*), 4.25 (dd, $J = 18.6$, 2.4 Hz, 1H, *E*), 3.87 (dd, $J =$ 18.2, 2.4 Hz, 1H, *Z*), 3.85 (dd, $J = 18.6$, 2.4 Hz, 1H, *E*), 3.49 (s, 3H, *Z*), 3.33 (s, 3H, *E*), 2.43 (m, 2H, *E* and *Z*), 2.15 (t, $J = 2.4$ Hz, 1H, *Z* and *E*), 2.19–1.36 (m, 6H, *E* and *Z*); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 170.83$ (C), 170.74 (C), 150.15 (CH), 149.18 (CH), 99.84 (CH), 95.85 (CH), 79.71 (CH), 79.61 (CH), 71.27 (C), 70.96 (C), 66.26 (CH_2), 65.99 (CH_2), 60.24 (CH), 59.57 (CH), 40.39 (C), 40.13 (C), 30.40 (CH_2), 26.64 (CH_2), 22.87 (CH_2), 22.53 (CH_2), 20.80 (CH_3); elemental analysis calcd (%) for $C_{19}H_{27}NO_4S$: C 64.84, H 6.95, N 4.20; found: C 64.93, H 6.73, N 4.12.

Compound 20: yellow oil, 1: 1.8 *Z*:*E*; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.82$ (d, $J = 8.5$ Hz, 2H, *Z* isomer), 7.81 (d, $J = 8.5$ Hz, 2H, *E* isomer), 7.27 (d, $J =$ 8.5 Hz, 2H, *Z* isomer), 7.24 (d, $J = 8.5$ Hz, 2H, *E* isomer), 5.76 (m, 1H, *Z* isomer), 5.74 (m, 1H, *E* isomer), 4.41 (dd, $J = 7.1$, 4.2 Hz, 1H, *E* isomer), 4.29 (m, 1H, *Z* isomer), 4.22 (dc, $J = 18.20$, 2.2 Hz, 1H, *Z* isomer), 4.18 (dc, $J = 18.6$, 2.2 Hz, 1H, *E* isomer), 3.86 (dc, $J = 18.20$, 2.2 Hz, 1H, *Z* isomer), 3.82 (dc, $J = 18.6$, 2.2 Hz, *E* isomer), 3.50 (s, 3H, *Z* isomer), 3.35 (s, 3H, *E* isomer), 2.42 (s, 3H, *Z* isomer), 2.40 (s, 3H, *E* isomer), 2.04–1.8 (m, 2H, *Z* and *E* isomers), 1.68 (t, $J = 2.2$ Hz, 3H, *E* isomer), 1.65 (t, $J = 2.2$ Hz, 3H, *Z* isomer), 1.57–0.82 (m, 6H, *Z* and *E* isomer); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT): $\delta = 143.54$ (C), 143.07 (C), 143.02 (CH, *E* isomer), 142.15 (CH, *Z* isomer), 138.81 (C), 138.52 (C), 129.73 ($2 \times$ CH, *Z* isomer), 129.48 ($2 \times$ CH, *E* isomer), 128.52 ($2 \times$ CH, *E* isomer), 128.24 ($2 \times$ CH, *Z* isomer), 114.68 (C), 114.60 (C), 80.78 (C), 80.28 (C), 76.41 (C), 75.93 (C), 60.32, 60.09, 59.13, 55.40, 36.81 (CH_2), 34.74 (CH_2), 33.09 (CH_2), 32.55 (CH_2), 29.67 (CH_2), 27.68 (CH_2), 26.22 (CH_2), 25.98 (CH_2), 25.34 (CH_2), 23.76 (CH_2), 22.14 (CH_3), 22.10 (CH_3), 4.15 ($2 \times CH_3$); EI-MS: *m*/*z*: 347 (1) $[M]^+$, 316

(23), 302 (21), 242 (18), 192 (100); elemental analysis calcd (%) for $C_{19}H_{25}NO_3S$: C 65.68, H 7.25, N 4.03; found: C 65.63, H 7.14, N 4.25; EI-HRMS: calcd for $C_{19}H_{25}NO_3S$: 347.1555; found: 347.1569.

Compound 15: TIPS enol ether **15** was prepared in 80% yield following the procedure described for the corresponding diethyl ester.[7b] ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.82$ (brs, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 3.15 (m, 1H), 2.79 (d, $J = 2.8$ Hz, 2H), 1.97 (t, $J = 2.8$ Hz, 1H), 2.10–1.29 (m, 6H), 1.14–1.04 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 170.25$ (C), 170.17 (C), 152.85 (C), 103.21 (CH), 79.73 (CH), 70.09 (C), 60.60 (C), 52.43 ($2 \times CH_3$), 38.99 (CH), 29.45 (CH_2), 24.12 (CH_2), 22.39 (CH_2), 22.34 (CH_2), 17.93 (CH_3), 12.43 (CH).

General procedure for the cyclization of ω-acetylenic enol ethers: A mixture of the ω-acetylenic enol ethers (0.15 mmol) and the catalyst (0.05–0.1 equiv) was heated in methanol (4 mL) under reflux under Ar for 17 h. After being cooled to room temperature, the solvent was evaporated and the residue was purified by chromatography on silica gel deactivated with 5% Et_3N in hexane. Although the reactions were faster at higher concentrations, substantial amounts of the corresponding aldehydes were observed.

***N*-(*p*-Toluenesulfonyl)-3-dimethoxymethyl-4-methylenepyrrolidine (5)**: pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.70$ (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.1$, 0.8 Hz, 2H), 5.12 (q, $J = 2.3$ Hz, 1H), 5.01 (q, $J = 2.3$ Hz, 1H), 4.13 (d, $J = 7.3$ Hz, 1H), 3.79 (m, 2H), 3.42 (dd, $J = 10.1$, 2.3 Hz, 1H), 3.31 (s, 3H), 3.27 (s, 3H), 3.18 (dd, $J = 10.1$, 6.5 Hz, 1H), 2.90 (m, 1H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 143.66$ (C), 143.10 (C), 132.44 (C), 129.62 (CH), 127.90 (CH), 109.71 (CH_2), 104.72 (CH), 59.19 (CH_3), 53.74 (CH_3), 52.62 (CH_2), 49.61 (CH_2), 45.26 (CH), 21.50 (CH_3); EI-HRMS: calcd for $C_{15}H_{21}NO_4S$: 311.1191; found: 311.1181.

Dimethyl 3-dimethoxymethyl-4-methylenecyclopentane-1,1-dicarboxylate (6): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.05$ (m, 1H), 5.01 (m, 1H), 4.24 (d, $J = 6.5$ Hz, 1H), 3.71 (s, 6H), 3.35 (s, 3H), 3.33 (s, 3H), 2.85–2.93 (m, 3H), 2.52 (m, 1H); 2.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 172.02$ (C), 171.82 (C), 147.11 (CH_2), 109.30 (CH_2), 106.62 (CH), 58.40 (C), 53.96 (CH_3), 53.91 (CH_3), 52.71 (CH_3), 52.65 (CH_3), 44.54 (CH), 41.75 (CH_2), 35.19 (CH_2); EI-HRMS: calcd for $C_{12}H_{17}O_5$: 241.1076; found: 241.1086 $[M - OCH_3)]^+$; elemental analysis calcd (%) for $C_{13}H_{20}O_6$: C 57.34, H 7.40; found: C 57.73, H 7.74.

1,1-Bis(acetoxymethyl)-3-dimethoxymethyl-4-methylenecyclopentane (7): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.05$ (brs, 1H), 5.04 (brs, 1H), 4.23 (d, $J = 6.1$ Hz, 1H), 4.08–3.73 (m, 4H), 3.37 (s, 3H), 3.34 (s, 3H), 2.90–2.80 (m, 1H), 2.26 (brs, 2H), 2.04 (s, 6H), 1.84–1.75 (m, 1H), 1.65–1.55 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 171.79$ (C), 171.71 (C), 149.20 (C), 110.18 (CH_2), 107.82 (CH), 68.23 (CH_2), 66.23 (CH_2), 54.89 (CH_3), 54.78 (CH_3), 44.79 (CH), 44.65 (C), 41.08 (CH_2), 33.41 (CH_2), 21.53 ($2 \times CH_3$); elemental analysis calcd (%) for $C_{15}H_{24}O_6$: C 59.98, H 8.05; found: C 60.30, H 8.16.

1-Hydroxymethyl-4-methoxy-6-methylene-3-oxabicyclo[3.2.1]octane (8): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.96$ (brs, 1H), 4.92 (brs, 1H), 4.43 (d, $J = 2.4$ Hz, 1H), 3.80 (dd, $J = 10.1$, 1.2 Hz, 1H), 3.53–3.48 (m, 3H), 3.39 (s, 3H), 2.65 (m, 1H), 2.47 (m, 1H), 2.19 (m, 1H), 2.03 (dd, $J = 10.9$, 2.8 Hz, 1H), 1.39 (ddd, $J = 10.9$, 4.8, 2.8 Hz, 1H), 1.39 (overlapping signal, OH); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 149.95$ (C), 106.45 (CH_2), 101.99 (C), 77.26 (C), 69.69 (CH_2), 67.29 (CH_2), 54.60 (CH_3), 47.97 (CH), 37.20 (CH_2), 32.30 (CH_2); GC/EI-HRMS: calcd for $C_9H_{13}O_2$: 153.0916 $[M - OMe]^+$; found: 153.0910.

1,1-Bis(triisopropylsilyloxymethyl)-3-dimethoxymethyl-4-methylenecyclopentane (9): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.99$ (m, 1H), 4.91 (m, 1H), 4.19 (d, $J = 6.9$ Hz, 1H), 3.63–3.37 (m, 4H), 3.36 (s, 3H), 3.30 (s, 3H), 2.78 (m, 1H), 2.32–2.16 (m, 2H), 1.74 (dd, $J = 13.5$, 8.5 Hz, 1H), 1.50 (dd, $J = 13.5$, 9.9 Hz, 1H), 1.05–1.01 (m, 42H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 151.68$ (C), 108.79 (CH_2), 107.87 (CH), 67.40 (CH_2), 65.84 (CH_2), 54.74 (CH_3), 53.60 (CH_3), 49.17 (C), 45.09 (CH), 39.88 (CH_2), 32.57 (CH_2), 18.74 (CH_3), 12.63 (CH);eacp;elemental analysis calcd (%) for $C_{29}H_{60}O_4Si_2$: C 65.85, H 11.43; found: C 66.00, H 11.44.

Dimethyl 4-dimethoxymethyl-3-methylenecyclohexane-1,1-dicarboxylate (12): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.90$ (brs, 1H), 4.85 (brs, 1H), 4.47 (d, $J = 8.1$ Hz, 1H), 3.71 (s, 6H), 3.35 (s, 3H), 3.33 (s, 3H), 2.72 (dt, $J = 14.5$, 8.1 Hz, 2H), 2.40 (m, 1H), 2.13 (m, 1H), 2.0 (m, 1H), 1.83 (m, 1H), 1.65(m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 171.53$ (C), 171.41 (C), 142.62 (C), 112.43 (CH_2), 103.91 (CH), 56.81 (C), 53.31 (CH_3), 53.14 (CH_3), 52.61 ($2 \times CH_3$), 43.99 (CH), 39.07 (CH_2), 28.88 (CH_2), 25.21 (CH_2); elemental analysis calcd (%) for $C_{14}H_{22}O_6$: C 58.73, H 7.74; found: C 59.15, H 7.86.

Dimethyl 4-dimethoxymethyl-4-methyl-3-methylenecyclohexane-1,1-dicarboxylate (13): pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.94$ (brs, 1H), 4.86 (brs, 1H), 4.31 (s, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.51 (s, 3H), 3.45 (s, 3H), 2.81 (m, 2H), 1.99 (m, 1H), 1.86 (m, 1H), 1.42–1.31 (m, 2H), 1.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 172.93$ (C), 171.76 (C), 147.30 (C), 113.53 (CH_2), 110.16 (CH), 59.31 (CH_3), 58.95 (CH_3), 57.33 (C), 53.35 (CH_3), 53.10 (CH_3), 45.06 (C), 38.68 (CH_2), 32.18 (CH_2), 28.05 (CH_2), 20.05 (CH_3); EI-HRMS: calcd for $C_{14}H_{21}O_5$: 269.1389; found: 269.1391 $[M - OCH_3]^+$.

Dimethyl 4-formyl-4-methyl-3-methylenecyclohexane-1,1-dicarboxylate (14): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.32$ (d, $J = 1.22$ Hz, 1H), 5.15 (brs, 1H), 4.95 (brs, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 2.93 (dd, $J = 4.1$, 2.0 Hz, 1H), 2.50 (dt, $J = 4.1$, 1.7 Hz, 1H), 2.27 (dd, $J = 13.2$, 2.0 Hz, 1H), 2.13 (dt, $J = 13.2$, 4.1 Hz, 1H), 2.02–1.90 (m, 1H), 1.57–1.46 (m, 1H), 1.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 202.77$ (C), 171.48 ($2 \times C$), 143.09 (C), 114.48 (CH_2), 56.14 (C), 52.76 (CH_3), 52.54 (CH_3), 51.81 (C), 38.50 (CH_2), 30.22 (CH_2), 27.85 (CH_2), 19.84 (CH_3); elemental analysis calcd (%) for $C_{13}H_{18}O_5$: C 61.40, H 7.14; found: C 61.28, H 7.16.

Dimethyl 3-methyl-4-oxo-2,4,5,6,7,7a-hexahydroindene-1,1-dicarboxylate (16): white vitreous solid; m.p. 106–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.75$ (s, 3H), 3.72 (s, 3H), 3.09 (brd, $J = 18$ Hz, 1H), 2.77 (brd, $J = 18$ Hz, 1H), 2.45 (m, 1H), 2.23–2.10 (m, 2H), 2.09 (s, 3H), 2.07–1.98 (m, 2H), 1.84–1.68 (m, 1H), 1.15 (qd, $J = 12.7$, 2.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 199.23$ (C), 171.67 (C), 170.70 (C), 149.51 (C), 131.88 (C), 61.91 (C), 52.73 (CH_2), 52.29 (CH_3), 51.90 (CH_2), 46.04 (CH_3), 40.57 (CH_3), 27.49, 23.39, 15.66 (CH_2); elemental analysis calcd (%) for $C_{14}H_{18}O_5$: C 63.15, H 6.81; found: C 63.53, H 7.12.

***cis*-3a-Dimethoxymethyl-3-methylene-*N*-(*p*-toluenesulfonyl)octahydroindole (18)**: white vitreous solid; m.p. 84–87 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.74$ (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 5.16 (t, $J = 2.0$ Hz, 1H), 5.04 (m, 1H), 4.11 (dt, $J = 13.9$, 2.6 Hz, 1H), 4.01 (m, 1H), 3.93 (dt, $J = 13.9$, 2.0 Hz, 1H), 3.76 (s, 1H), 2.42 (s, 3H), 1.90–1.81 (m, 2H), 1.69–1.59 (m, 1H), 1.52–1.42 (m, 2H), 1.17–1.05 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 144.46$ (C), 142.96 (C), 137.24 (C), 129.48 (CH), 127.17 (CH), 109.74 (CH_2), 108.15 (CH), 61.21 (CH), 59.68 (CH_3), 57.95 (CH_3), 54.71 (C), 50.02 (CH_2), 28.97 (CH_2), 22.61 (CH_2), 22.53 (CH_2), 21.47 (CH_3), 20.14 (CH_2); elemental analysis calcd (%) for $C_{19}H_{27}NO_4S$: C 62.44, H 7.45, N 3.83; found: C 62.44, H 7.26, N 3.75.

***cis*-4a-Dimethoxymethyl-*N*-(*p*-toluenesulfonyl)-1,2,4a,5,6,7,8,8a-octahydroquinoline (19)**: white vitreous solid; m.p. 137–140 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.72$ (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 5.75 (ddd, $J = 10.2$, 3.8, 2.1 Hz, 1H), 5.50 (m, 1H), 4.33 (s, 1H), 4.10 (m, 3H), 3.62 (s, 3H), 3.48 (s, 3H), 3.30 (dt, $J = 16.9$, 2.1 Hz, 2H), 2.43 (s, 3H), 1.80–1.08 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 143.06$ (C), 137.29 (C), 131.34 (CH), 129.59 (CH), 127.13 (CH), 123.18 (CH), 110.71 (CH), 59.38 (CH_3), 58.44 (CH_3), 53.29 (CH), 45.90 (C), 40.94 (CH_2), 27.75 (CH_2), 24.37 (CH_2), 23.25 (CH_2), 21.44 (CH_3), 20.87 (CH_2); elemental analysis calcd (%) for $C_{19}H_{27}NO_4S$: C 62.44, H 7.45, N 3.83; found: C 62.24, H 7.19, N 3.72.

***cis*-4a-Dimethoxymethyl-4-methyl-*N*-(*p*-toluenesulfonyl)-1,2,4a,5,6,7,8,8a-octahydroquinoline (21)**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.69$ (d, $J = 8.5$ Hz, 2H), 7.27 (d, $J = 8.5$ Hz, 2H), 5.47 (m, 1H), 4.29 (s, 1H), 4.10–4.01 (m, 2H), 3.57 (s, 3H), 3.45 (s, 3H), 3.32 (m, 1H), 2.40 (s, 3H), 1.98–1.93 (m, 1H), 1.76 (m, 3H), 1.63–0.82 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT): $\delta = 136.09$ (C), 130.26 ($2 \times CH$), 129.85 (C), 128.70 (C), 127.89 ($2 \times CH$), 120.87 (CH), 112.08 (CH), 60.24 (CH_3), 58.76 (CH_3), 55.16 (CH), 48.77 (C), 42.44 (CH_2), 37.29 (CH_2), 25.35 (CH_2), 24.46 (CH_2), 22.59 (CH_2), 22.17 (CH_3), 20.80 (CH_3); EI-MS: m/z: 379 (12) $[M]^+$, 348 (42), 304 (17), 260 (32), 192 (100); EI-HRMS: calcd for $C_{20}H_{29}NO_4S$: 379.1817; found: 347.1818.

2-(*tert*-Butyldimethylsilyloxy)-1-methylcyclohexa-2,4-dienecarboxylic ethyl ester (23): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.84–5.77$ (m, 1H), 5.42–5.35 (m, 1H), 5.07 (d, $J = 5.9$ Hz, 1H), 4.19–4.04 (m, 2H), 2.93 (ddd, $J = 17.2$, 3.8, 2.2 Hz, 1H), 2.16 (ddd, $J = 17.2$, 4.8, 1.4 Hz, 1H), 1.28 (s, 6H), 1.24 (t, $J = 7.2$ Hz, 3H), 0.91 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT): $\delta = 175.81$ (C), 154.75 (C), 123.48 (CH), 116.52 (CH), 100.24 (CH), 60.68 (CH_2), 36.03 (CH_2), 25.41 ($3 \times$

CH_3), 20.04 (CH_3), 17.96 (C), 14.13 (CH_3), −0.5 ($2 \times CH_3$). The structure was confirmed by COSY and HMBC experiments.

Computational methods: The calculations were performed with the GAUSSIAN 98 series of programs.[21] The geometries of all complexes were optimized at the DFT level using the B3LYP hybrid functional.[22] The standard 6-31G(d) basis set was used for C, H, O, and Cl and the LANL2DZ relativistic pseudo potential was used for Pt and Au. Harmonic frequencies were calculated at the same level of theory to characterize the stationary points and to determine the zero-point energies (ZPE). Intrinsic reaction coordinate calculations (IRC) were performed to ensure that the transition states actually connect the proposed reagents and products. The bonding characteristics of the different local minima were analyzed by means of two different partition techniques, namely, the atoms in molecules (AIM) theory of Bader[23] and a Natural Bond Orbital (NBO) analysis of Weinhold et al.[24] The first approach is based in a topological analysis of the electron charge density, $\rho(\mathbf{r})$ and its Laplacian $\nabla^2\rho(\mathbf{r})$. More specifically, we have located the so called bond critical points (bcp), i.e., points where $\rho(\mathbf{r})$ is minimum along the bond path and maximum in the other two directions. These points are associated with the positions of the chemical bonds. The NBO technique permits to describe the different bonds of the system in terms of the natural hybrid orbitals centered on each atom and provides also useful information on the charge distribution of the system.

Acknowledgement

We are grateful to the MCyT (Project BQU2001-0193-C02-01) for support of this research and to the CAM for a predoctoral fellowship to C.N. We also acknowledge Johnson Matthey PLC for a generous loan of $PtCl_2$ and $PdCl_2$.

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Received: December 6, 2002 [F4646]

