Intramolecular Hydroarylation of Alkynes Catalyzed by Platinum or Gold: Mechanism and *endo* Selectivity

Cristina Nevado[b] and Antonio M. Echavarren*[a, b]

Abstract: The cyclization of differently substituted aryl alkynes with Pt^{II} or Au^{I} catalysts proceeds by *endo-dig* pathways. When Ag^{I} was used to generate reactive cationic Au^{I} catalysts, 2*H*-chromenes dimerize to form cyclobutane derivatives by a Ag^{I}-catalyzed process. A DFT study on the cyclization mechanism shows a kinetic and thermodynamic preference for 6-*endo-dig* versus 5-*exo-dig* cyclizations in Pt^{II}-catalyzed processes. Calculations indicate that although Friedel–Crafts and the cyclopropanation processes via metal cyclopropyl carbenes show very similar activation energies, platinum cyclopropyl carbenes are the stationary points with the lowest energy.

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

Introduction

The hydroarylation of alkynes (also known as alkenylation of arenes) catalyzed by electrophilic transition-metal complexes has received much attention as a valuable synthetic alternative to the Heck and cross-coupling processes for the synthesis of alkenyl arenes.[1] Fujiwara et al. have reported the hydroarylation of a wide range of alkynes catalyzed by cationic complexes of Pd^{II} and Pt^{II}.[2] Heteroaromatic compounds, such as pyrroles, indoles, and furans, also react with alkynoates in the presence of $Pd(OAc)_2$.[3] σ-Aryl or σ-heteroaryl-Pd species were proposed as intermediates in this reaction.[2,3] Reetz and Sommer have found that Au^{III} and Au^{I} complexes also catalyze the hydroarylation of alkynes.[4] Related results were reported by He with Au^{III}.[5] In addition, metal trifluoromethanesulfonates ($M(OTf)_n$; M = Sc, Zr, In) catalyze the alkenylation of arenes with internal alkynes to give 1,1-diarylalkenes, probably via alkenyl cation intermediates.[6]

Similarly, aryl-alkynoates and alkynanilides cyclize in the presence of $Pd(OAc)_2$ in trifluoroacetic acid to give coumarins and quinolin-2(1*H*)-ones, respectively.[7] Trost and Toste developed an apparently similar palladium-catalyzed alkenylation of phenols with alkynoates that affords coumarins.[8] However, this reaction is mechanistically different because it is assumed to be catalyzed by Pd^{0} and proceeds via Pd–H intermediates.[9]

Murai, Chatani and co-workers reported the cyclization of electron-rich aromatic rings with alkynes and Ru^{II} and Pt^{II} as catalysts.[10] The scope of this reaction was later extended to substrates in which the arene moiety does not possess strong electron-donating groups by the use of $GaCl_3$ as a catalyst.[11] *exo-dig* Cyclization is preferred when three or four carbon atoms separate the alkyne and the arene. However, the *endo-dig* cyclization mode was observed in substrates with two carbon atoms in the tether. Fürstner et al. reported a similar reaction for the synthesis of phenanthrenes that is catalyzed by $PtCl_2$ or other metal halides, such as $AuCl_3$, $GaCl_3$, and $InCl_3$.[12] Sames et al. developed a $PtCl_4$-catalyzed intramolecular hydroarylation under mild conditions for the synthesis of chromenes, 1,2-dihydroquinolines, and coumarins.[13] Cycloisomerization of ω-aryl-1-alkynes has been performed by Nishizawa et al. at room temperature with Hg^{II} as the catalyst.[14,15]

Substrates of type **1** usually give **2** by a 6-*endo-dig* pathway, instead of **3**, the product of a 5-*exo-dig* cyclization.[16] The simplified mechanism of Scheme 1 shows intermediates representative of those usually proposed[10–14] based on a

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Supporting information for this article is available on the WWW under http://www.chemeurj.org or from the author. This information includes atomic coordinates for structures of stationary points in Figure 1, Figure 3, Figure 5.

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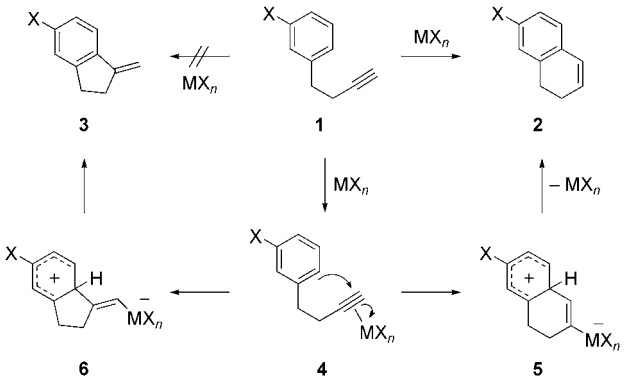


Scheme 1. Proposed Friedel–Crafts mechanism for the metal-catalyzed 6-*endo-dig* cyclization of 4-aryl-1-alkynes.

Friedel–Crafts alkenylation reaction.[17] Thus, η^2-coordination of MX_n to **1** affords **4**, which undergoes an electrophilic aromatic substitution to give the Wheland-type intermediate **5**. Intermediate **5** would then give **2** by a formal 1,3-H shift or alternative pathways.[10] In accordance with this mechanism, electron-donating substituents X facilitate the hydroarylation process. However, the fact that **6** is not formed from **4** remains unsolved when the *exo* cyclization of enynes is the most common pathway followed by substrates bearing terminal alkynes.[18] In fact, it has been pointed out that the slippage of MX_n towards C2 of the alkyne in the transformation of **4** to **5** is unlikely because this would result in a rather unstable primary alkenyl cation (anti-Markovnikov process).[14]

Importantly, metal vinylidene intermediates[19,20] are not involved in these cyclizations, as shown by deuteration experiments[21] and by the fact that internal alkynes are also cyclized with electrophilic metal complexes.[12]

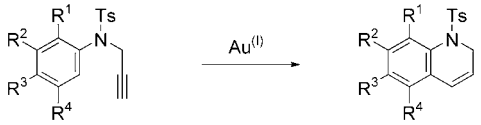
Although the mechanistic hypothesis shown in Scheme 1 is plausible and is inspired by a fundamental mechanism in organic chemistry, an alternative explanation based on the formation of metal cyclopropyl carbenes could also account for the experimental results. Indeed, we have shown that the Pt^{II}-catalyzed reaction of furans with alkynes proceeds via metal cyclopropyl carbenes,[21,22,23] similar to those involved in the alkoxycyclization and skeletal rearrangement of enynes.[18,24,25]

We have reported that $PtCl_2$ catalyzes the cyclization of arenes with alkynes for the synthesis of 1,2-dihydroquinolines and chromenes.[21] In all cases, substrates of type **1** reacted by the 6-*endo-dig* pathway. We set out to test whether this behavior is followed when different catalysts are used. Herein we present different Au^I catalysts[26] for the cyclization of aryl alkynes. The use of Ag^I to generate the reactive cationic Au^I catalyst led to an unexpected dimerization of 2*H*-chromenes promoted by Ag^I. We also report computational work on the mechanism of the cyclization of two model systems with $PtCl_2$ that shows a kinetic and thermodynamic preference for 6-*endo-dig* versus 5-*exo-dig* cyclizations. Significantly, our results suggest that metal cyclopropyl carbenes are probable intermediates in this electrophilic aromatic substitution reaction.

Results and Discussion

Cyclization of arylalkynes with Pt^{II} or Au^I catalysts: The cyclization of *N*-propargyl-*N*-tosyl anilines **7a–c** to form *N*-tosyl-1,2-dihydroquinolines **8a–c** with $PtCl_2$ as catalyst proceeded in toluene under reflux with low-to-moderate yields.[21] The use of a cationic Au^I catalyst formed in situ from $[Au(PPh_3)Me]$ and HBF_4, which presumably forms $[Au(PPh_3)]BF_4$, gave **8a–c** in good yields at 23–50 °C (Table 1, entries 1, 4, and 6).[26] The yields of these reactions were higher in toluene, and an excess of protic acid was required to efficiently generate the cationic Au^I species. We have also found that catalysts formed from $[Au(PPh_3)Cl]$ (3 mol %) and a silver salt (3 mol %) allowed these cyclizations to be performed under protic acid-free conditions in CH_2Cl_2 as the solvent. Generally, the best conversions were obtained with $AgSbF_6$ (Table 1, entries 2, 5, and 7), although in the case of the most reactive substrate, **7c**, $AgBF_4$ also gave satisfactory results (Table 1, entry 8).

Table 1. Cyclization of *N*-propargyl-*N*-tosyl anilines **7a–c** catalyzed by cationic Au^I complexes.



7a $R^1 = R^4 = OMe$, $R^2 = R^3 = H$
7b $R^1 = R^4 = H$, $R^2 = R^3 = OMe$
7c $R^1 = H$, $R^2 = R^3 = R^4 = OMe$

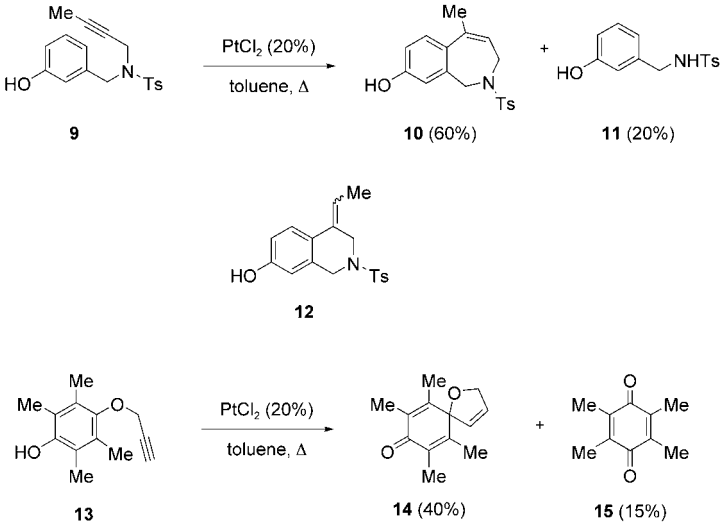
8a–c

Entry	Substrate	Catalyst (mol %)	Solvent	T [°C]	t [h]	Product	Yield [%]
1	**7a**	$[Au(PPh_3)Me]$ (3), HBF_4 (6)	toluene	23	4	**8a**	71
2	**7a**	$[Au(PPh_3)Cl]$ (3), $AgSbF_6$ (3)	CH_2Cl_2	40	2	**8a**	72
3	**7a**	$[Au(PPh_3)Cl]$ (3), $AgBF_4$ (3)	CH_2Cl_2	40	17	**8a**	45[a]
4	**7b**	$[Au(PPh_3)Me]$ (3), HBF_4 (6)	toluene	23	4	**8b**	71
5	**7b**	$[Au(PPh_3)Cl]$ (3), $AgSbF_6$ (3)	CH_2Cl_2	23	2	**8b**	80
6	**7c**	$[Au(PPh_3)Me]$ (3), HBF_4 (6)	toluene	23	4	**8c**	92
7	**7c**	$[Au(PPh_3)Cl]$ (3), $AgSbF_6$ (3)	CH_2Cl_2	23	2	**8c**	76
8	**7c**	$[Au(PPh_3)Cl]$ (3), $AgBF_4$ (3)	CH_2Cl_2	23	2	**8c**	82 (96)[b]

[a] Determined by ^{1}H NMR spectroscopy. [b] Based on 85 % conversion.

The reaction of phenol **9** with the $[Au(PPh_3)Cl]/AgSbF_6$ catalytic system led only to depropargylated derivative **11**.[27] However, $PtCl_2$ as the catalyst gave 2,3-dihydro-1*H*-benzo[*c*]azepine (**10**) in 60 % yield (73 % based on 82 % conver-

sion) (Scheme 2) by an unusual 7-*endo-dig* cyclization of **9**. The 6-*exo-dig* cyclization product **12** was not observed, despite its higher stability (stability: *Z*-**12** > *E*-**12** > **10**; PM3 calculations). Interestingly, the monopropargyl ether of 2,3,5,6-tetramethylhydroquinone (**13**) reacts in the presence of $PtCl_2$ to give spiro derivative **14** in a moderate yield as well as duroquinone (**15**) (Scheme 2). In this case, **14** is formed by attack of the more electron-rich *ipso*-carbon atom by a 5-*endo-dig* process. Quinone **15** arises by depropargylation of **13** to form 2,3,5,6-tetramethylhydroquinone, followed by air oxidation.



Scheme 2.

The regioselectivity in the cyclization of resorcinol propargyl derivatives **16** and **17** was studied with different catalysts and under different conditions (Table 2). Reaction of **16** with $PtCl_2$ led to a mixture of **18** and **19**, in addition to isomerized 4*H*-chromene **20** (Table 2, entry 1). This isomerization was suppressed when the reaction was carried out in wet toluene (Table 2, entry 2). 2*H*-Chromene **18** was isolated as the exclusive cyclization product with $[Au(PPh_3)Me]$ and HBF_4 (Table 2, entry 3), which allowed us to perform the reaction at room temperature. On the other hand, a 2:1 mixture of **18** and **19** was obtained with $[Au(PPh_3)Cl]$ and $AgSbF_6$ (Table 2, entry 4). The reversed regioselectivity was observed in the $PtCl_2$-catalyzed reaction of **17** (Table 2, entry 5).

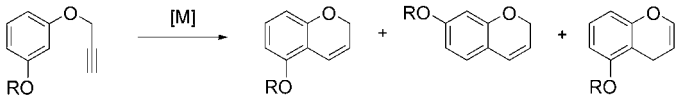
Sesamol propargyl ether (**23**) reacts with a Pt^{II} catalyst to afford 6*H*-[1,3]dioxolo[4,5-*g*]chromene (**24**) in excellent yield.[21] Surprisingly, when cationic Au^I catalysts generated in the presence of Ag^I were used, in addition to 2*H*-chromene **24**, symmetrical dimer **25** was obtained (Scheme 3). The structure of **25** was confirmed by X-ray diffraction. Substrate **26** reacted with $PtCl_2$ as catalyst to give a 1:1 mixture 6,7-dimethoxy-2*H*-chromene (**27**) and 6,7-dimethoxy-4*H*-chromene (**28**) in moderate yields (Scheme 3). In contrast, $[Au(PPh_3)Me]$ and HBF_4 gave **27** selectively. With $[Au(PPh_3)Cl]$ and $AgSbF_6$, **26** gave a mixture of **27** and dimer **29**.

The [2+2] cycloaddition of cinnamic acids to form truxillic or truxinic acids is not promoted by Ag_2O.[28,29] However, the dimerization of 2*H*-chromenes is catalyzed by Ag^I. Thus, heating 2*H*-chromene **27** with $AgSbF_6$ in CH_2Cl_2 led to **29** in 40% yield (Scheme 4). This reaction takes place in the dark, which excludes a photocycloaddition similar to that catalyzed by Cu^I.[30] A greater yield (58%) was obtained from $[Au(PPh_3)Cl]$ and $AgSbF_6$ (3 mol% each) in CH_2Cl_2 at 35°C for 4 h. However, **27** was recovered unchanged after being heated with $[Au(PPh_3)Cl]$ in CH_2Cl_2 at 23–40°C, in the presence or absence of sunlight.

Mechanism for the electrophilic aromatic substitution with (η^2-alkyne)metal complexes: We decided to carry out a computational study of the arene cyclizations with alkynes by means of density functional calculations (DFT) on the 5-*exo-dig* and 6-*endo-dig* cyclizations of 4-(butyn-3-yl)phenol and 3-(butyn-3-yl)phenol as model compounds with $PtCl_2$. We have previously reported that qualitatively similar results are obtained with Pt^{II}, Au^I, or Au^{III} in the calculations performed for the cyclization of enynes.[26,31]

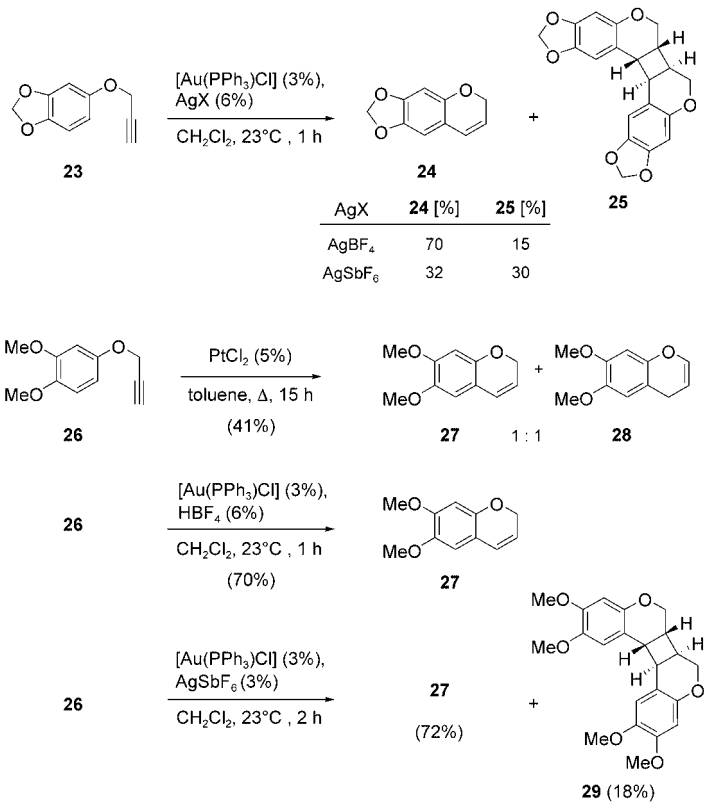
The first step involves coordination of the alkyne to the metal to form **30** and **31**, respectively (Scheme 5). A 5-*exo-dig* cyclization from **30** would give platinum cyclopropyl carbene **32**. Alternatively, **33** could be involved as an intermediate in this reaction by a simple electrophilic aromatic substitution. Similarly, in the 6-*endo-dig*

Table 2. Cyclization of resorcinol derivatives **16** and **17** catalyzed by Pt^{II} or cationic Au^I complexes.

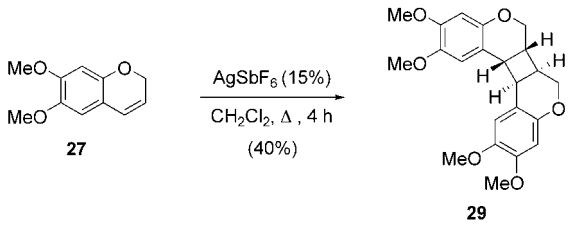


Entry	Substrate	Catalyst (mol%)	Solvent	T[°C]	t[h]	Yield[%]	Product ratio
1	**16**	$PtCl_2$ (5)	toluene	100	17	63	**18** + **19** + **20** (3:3:2)
2	**16**	$PtCl_2$ (5)	10:1 toluene-H_2O	100	15	72	**18** + **19** (2:1)
3	**16**	$[Au(PPh_3)Me]$ (3), HBF_4 (6)	toluene	23	5	56	**18**
4	**16**	$[Au(PPh_3)Cl]$ (3), $AgSbF_6$ (3)	CH_2Cl_2	23	2	40	**18** + **19** (2:1)
5[a]	**17**	$PtCl_2$ (5)	toluene	100	15	76	**21** + **22** (1:2)

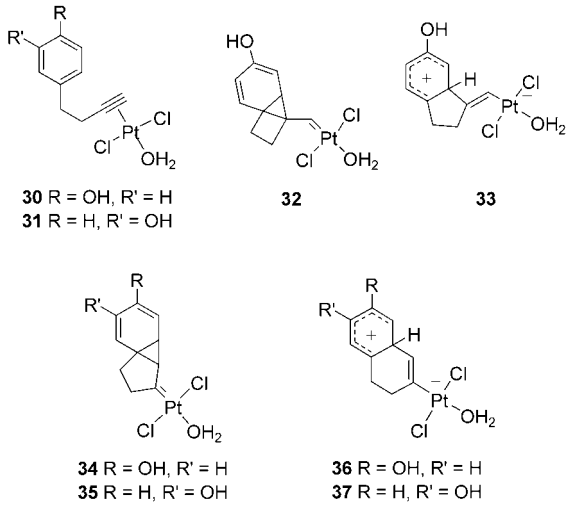
[a] Yields after hydrogenation (H_2, Pd/C) of the crude reaction mixture.



Scheme 3.



Scheme 4.



Scheme 5. Starting complexes **30** and **31** and hypothetical intermediates for the 5-*exo-dig and* 6-*endo-dig* cyclization.

cyclization pathway, platinum cyclopropyl carbenes **34** and **35** or Friedel–Crafts intermediates **36** and **37** were considered.

A minimum structure for **32** could not be obtained. The only minimum located in the 5-*exo-dig* cyclization of **30** was the zwitterionic intermediate **33**. However, formation of **33** from **30** is a highly endothermic process (+21.7 kcal mol^{-1}). The transition state (**TS$_1$**) lies 22.3 kcal mol^{-1} above **30**. These calculations are in agreement with the experimental results, which show that 5-*exo-dig* cyclization products are not formed in the cyclization of 4-aryl-1-ynes. (Figure 1).

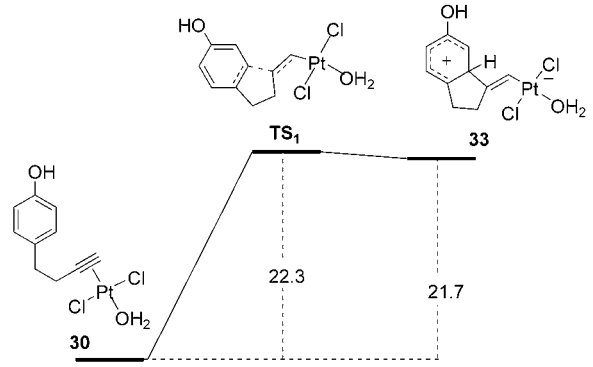


Figure 1. Reaction coordinate for the 5-*exo*-dig cyclization of 4-(butyn-3-yl)phenol. Calculations at the B3LYP/6-31G(d) level (ZPE-corrected energies are given in kcal mol^{-1}).

The structure of transition state **TS$_1$** is shown in Figure 2a, in which the closest interaction between the electrophilic part of the molecule and the arene ring occurs with C6 (C2–C6 distance of 1.956 Å). The C2–C5 distance is considerably longer (2.139 Å). Intermediate **33** (Figure 2b) shows a highly distorted structure, in which the angles around C6 are very far from the tetrahedral bond angles of sp^3-hybridized carbon atoms. This strain may explain the high energy of this intermediate and, in consequence, the improbability of the 5-*exo-dig* pathway.

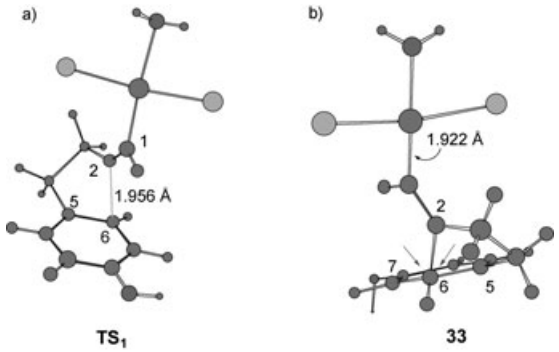


Figure 2. a) Structure of transition state **TS$_1$** showing the closest interaction between the electrophile and the arene ring. The C2–C5 distance is 2.139 Å. b) A view of intermediate **33** showing the highly distorted structure around C6, with very different C2-C6-C5 angles (82.6°) and C2-C6-C7 (118.5°).

In the 6-*endo-dig* cyclization pathway, the formation of the platinum cyclopropyl carbene **34** is an almost thermoneutral process: 14.7 kcal mol^{-1} are required to reach the corresponding transition state (**TS$_2$**) (Figure 3). Interestingly,

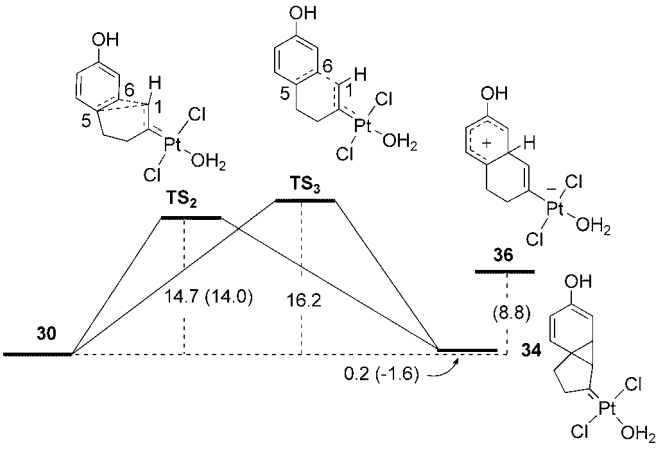


Figure 3. Reaction coordinates for the 6-*endo-dig* cyclization of 4-(butyn-3-yl)phenol with $PtCl_2$. Calculations at the B3LYP/6-31G(d) level (ZPE-corrected energies are given in kcal mol^{-1}). Values in parentheses take solvent effects into consideration.

a Friedel–Crafts mechanism is also possible. Another transition state (**TS$_3$**), which lies 16.2 kcal mol^{-1} above the corresponding metal-coordinated aryl-alkyne, was found. Surprisingly, analysis of the energy gradient profile showed a remarkable and rapid decrease from **TS$_3$** that finally led to **34** as the unique minimum structure. Zwitterionic intermediate **36** could only be found when solvent effects were considered.[32]

Formation of platinum cyclopropyl carbene **34** from **30** is an asynchronous process. Although **TS$_2$** and **TS$_3$** are very similar in energy, they show remarkable structural differences (Figure 4). In **TS$_2$**, formation of the C1–C5 bond precedes that of the C1–C6 bond owing to the donor effect of the hydroxy group. The C–C distances to the forming cyclopropane ring are 2.188 Å (C1–C5) and 2.565 Å (C1–C6), respectively. On the other hand, the closest distance in **TS$_3$** is C1–C6 (2.050 Å), whereas the C1–C5 distance is 2.478 Å.

In the case of Pt^{II} complex of 3-(butyn-3-yl)phenol (**31**), formation of **35** is almost thermoneutral with an activation energy of 14.7 kcal mol^{-1} via **TS$_4$** (Figure 5). A Friedel–Crafts mechanism is also possible in the cyclization of **31**. This transformation is kinetically

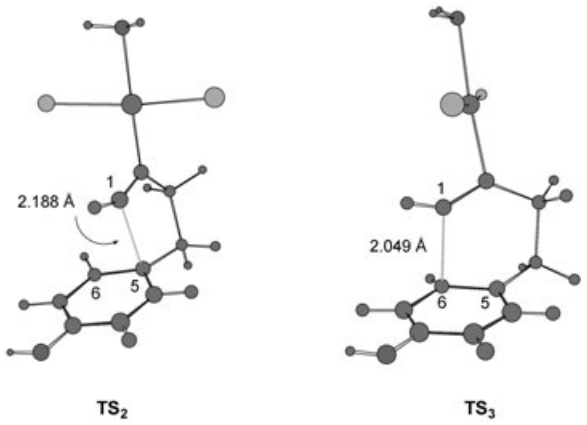


Figure 4. Structures of transitions states **TS$_2$** and **TS$_3$** that highlight the closest interaction between the electrophile and the arene ring. The C1–C6 distance in **TS$_2$** is 2.565 Å and for **TS$_3$** the C1–C5 distance is 2.478 Å.

slightly more facile: transition state **TS$_5$** lies 13.2 kcal mol^{-1} above **31**. However, formation of zwitterionic intermediates **37** is more endothermic (4.9 versus 0.4 kcal mol^{-1}). In contrast to **TS$_2$**, the closest C–C bond lengths in **TS$_4$** between the electrophile and the arene occurs with C6 (2.214 Å), the position *para* to the donor hydroxyl group (Figure 6). In **TS$_5$**, the C1–C6 distance is even shorter (2.179 Å).

Intermediates **36** and **37** show structures resembling the Wheland cations that have been characterized structurally in typical electrophilic aromatic substitution reactions (Figure 7).[33] In contrast to **33** (Figure 2), which shows very different C2-C6-C5 angles (82.6°) and C2-C6-C7 (118.5°), the angles around C6 in **36** and **37** are closer to sp^3 hybridization. In **36**, the C2-C6-C5 angle is 100.3°, while the C2-C6-C7 angle is 106.4°. In intermediate **37** these angles are 103.6° and 106.3°, respectively. The Pt–C bond lengths of 1.960–1.965 Å are longer that those found for the carbene complexes (see Figure 7).[34]

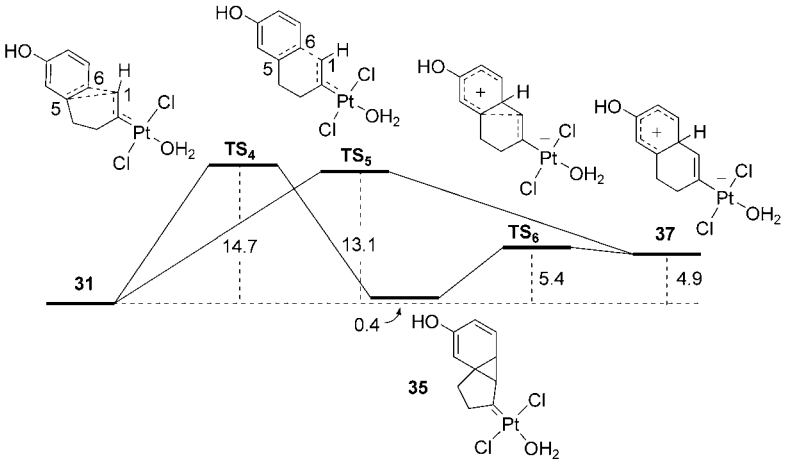


Figure 5. Reaction coordinates for the 6-*endo-dig* cyclization of 3-(butyn-3-yl)phenol with $PtCl_2$. Calculations at the B3LYP/6-31G(d) level (ZPE-corrected energies are given in kcal mol^{-1}).

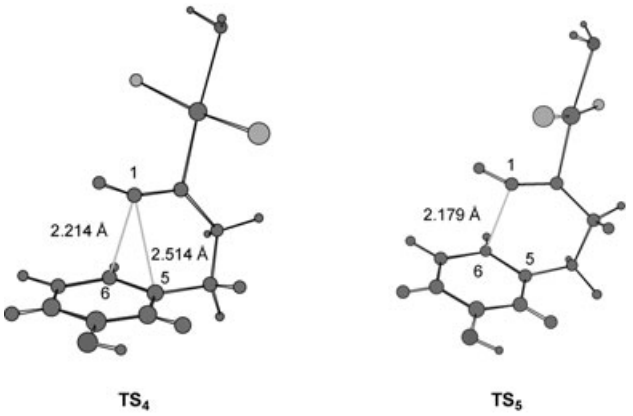


Figure 6. Structures of transition states $\mathbf{TS_4}$ and $\mathbf{TS_5}$ that highlight the closest interactions between the electrophile and the arene ring. The C1–C5 distance in $\mathbf{TS_5}$ is 2.638 Å.

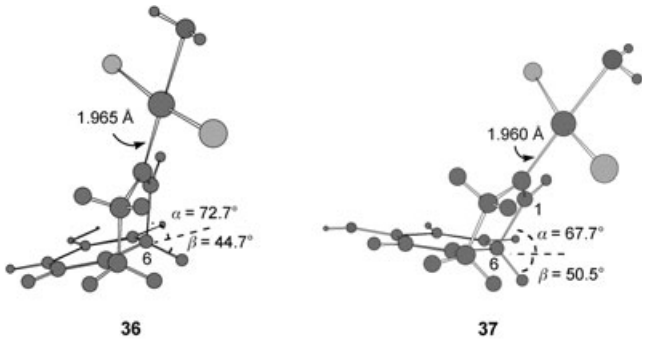


Figure 7. Structures of Friedel–Crafts intermediates **36** and **37** that show the angles between the *ipso*-carbon atom, the plane of the cyclohexadienyl ring, and the electrophile (α) or H6 (β).

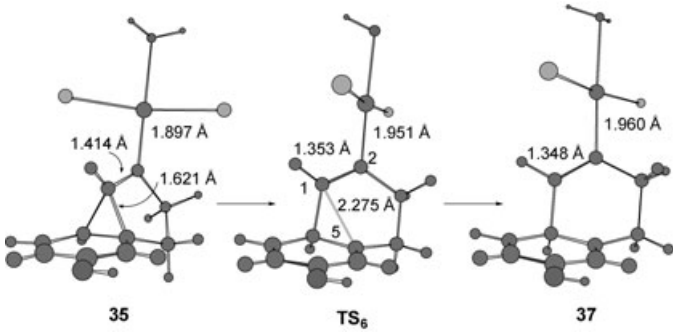


Figure 8. Opening of the cyclopropane in intermediate **35** to form **37** via $\mathbf{TS_6}$ (computed at the B3LYP/6-31G(d) level).

The opening of the C1–C5 cyclopropane bond in intermediate **35** to form Wheland intermediate **37**, proceeds via $\mathbf{TS_6}$ (Figure 5 and Figure 8). This late transition state resembles intermediate **37** and shows an almost fully cleaved C1–C5 bond. In the transformation of **35** to **37**, the C1–C2 bond shortens and the carbene C2–Pt bond lengthens to become an alkenyl–Pt bond.

Platinum cyclopropyl carbenes **34** and **35** show structures similar to that of *endo*-carbene **39**, derived by 6-*endo-dig* cyclization of (*E*)-2-octen-1-yne (Figure 9). Remarkably, the

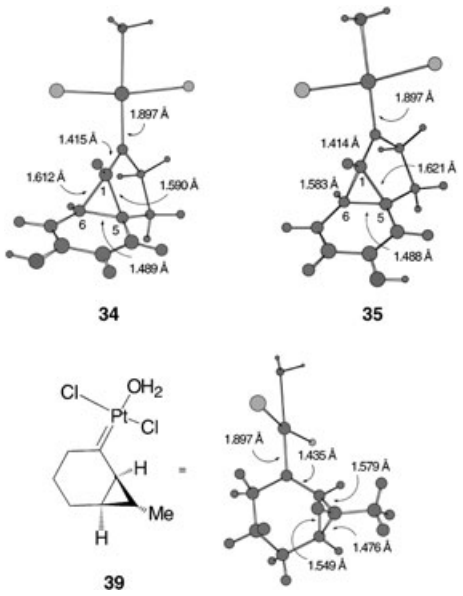


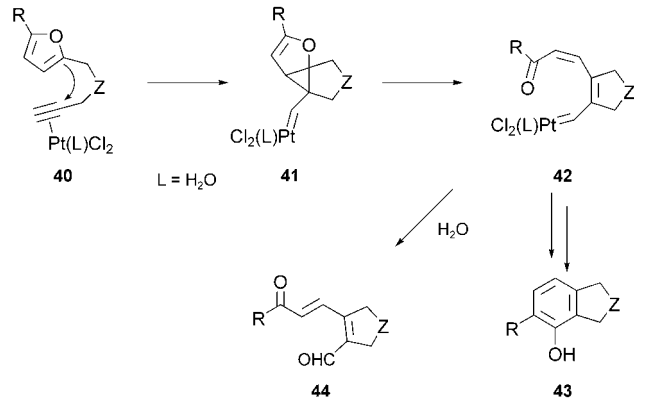
Figure 9. Structure of the cyclopropyl platinum carbenes **34** and **35** compared to **39**, intermediate in the 6-*endo-dig* cyclization of (*E*)-2-octen-1-yne (computed at the B3LYP/6-31G(d) level).[31]

Pt=C bond length is identical in the three complexes. The lengths of the cyclopropane bonds conjugated with the platinum carbene (C1–C5 and C1–C6) in **34** and **35** are distinct, being shorter than the cyclopropane bonds *para* to the hydroxyl (C1–C5 in **34** and C1–C6 in **35**). A very similar structure was found for **34** when solvents effects were considered. Interestingly, platinum carbenes **34** and **35** resemble the products of intramolecular Buchner additions of diazoketones to aryl rings.[35]

Although DFT calculations support the involvement of cyclopropyl metal carbenes as intermediates in, at least, some intramolecular reactions of arenes with alkynes, a more definitive answer to this issue would be provided by the trapping of these intermediates. This has already been demonstrated in the reaction of furans with alkynes.[21,22] In this case, DFT calculations indicated that **40** cyclizes exothermically to form platinum cyclopropyl carbene **41**, which evolves to form **42**, and finally phenols of type **43** (Scheme 6). Isolation of α,β-unsaturated carbonyl compounds, such as **4**, strongly supports the involvement of intermediates **42**, and, consequently, a cyclopropanation pathway for that process.

Conclusion

The cyclization of differently substituted substrates with Pt^{II} or Au^{I} catalysts proceeds by *endo-dig* pathways. When Ag^{I} was used to generate reactive cationic Au^{I} catalysts, 2*H*-



Scheme 6.

chromenes were shown to dimerize. This is a Ag^{I}-catalyzed process.

A computational study of the cyclization mechanism of two model systems with $PtCl_2$ shows a kinetic and thermodynamic preference for 6-*endo-dig* versus 5-*exo-dig* cyclizations. For the 5-*exo-dig* pathway, the two atoms tethering the arene and the alkyne are not sufficient to allow the formation of a low-energy Wheland intermediate.

Our results suggest that metal cyclopropyl carbenes are probable intermediates in the 6-*endo-dig* cyclization. Thus, in the cyclization of **30**, with an electron-releasing substituent at the *meta* position with respect to the new C–C bond, both transition states $\mathbf{TS_2}$ and $\mathbf{TS_3}$ converge to give platinum cyclopropyl carbene **34** as the first intermediate in the process. This pathway corresponds to an electrophilic aromatic substitution reaction proceeding by initial formation of two bonds between the electrophile and the arene. This mechanistic picture differs from the generally accepted two-step electrophilic aromatic substitution reaction,[36] in that, instead of the loosely bonded π-complex intermediate, the metal cyclopropyl carbene appears as a well-defined energy minimum in the reaction coordinate very similar to those found in the cyclizations of 1,6-enynes.[25] In the case of substrate **31**, with the electron-releasing substituent at the *para* position with respect the formed C–C bond, a less clear-cut mechanistic picture arises. The Friedel–Crafts and the cyclopropanation processes showed very similar activation energies, although platinum cyclopropyl carbene **35** is the stationary point with the lowest energy.

Experimental Section

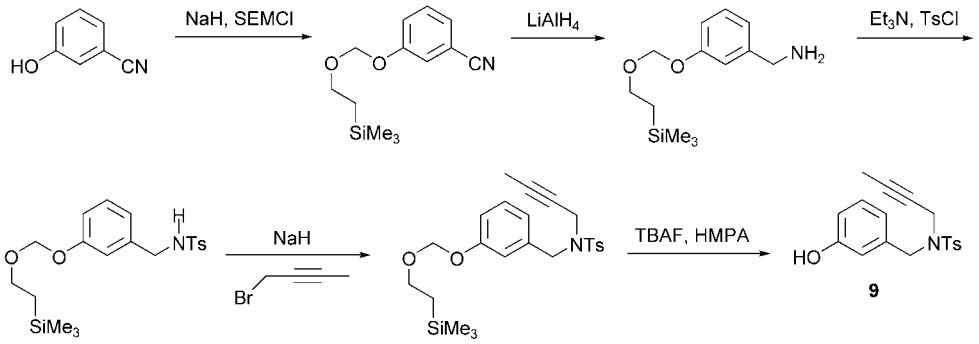
Unless otherwise stated, all reactions were carried out under Ar in dry, freshly distilled solvents under anhydrous conditions. THF was dried by means of 4 Å molecular sieves. Toluene and DMF were distilled from sodium/benzophenone and CaH_2, respectively, and were stored over 4 Å molecular sieves. Chromatography purifications were carried out on flash grade silica gel (SDS Chromatogel 60 ACC, 40–60 μm) with distilled solvents. NMR spectra were recorded at 23 °C on a Bruker AC-300 (300 MHz for ^{1}H, and 75 MHz for ^{13}C) and Bruker AMX-500 (500 MHz for ^{1}H, and 125 MHz for ^{13}C). EI-MS were obtained with a probe temperature of 300 °C, ion source at 300 °C, and 70 eV electron energy. The FAB-MS spectra were obtained with *m*-nitrobenzyl alcohol as the matrix. Both MS (FAB, EI) were recorded on a HP1100 MSD spectrometer. Elemental analyses were performed on a LECO CHNS 932 micro-analyzer. Melting points were determined with a Gallenkamp melting point apparatus.

Compounds **7a–c**,[21] **8a–c**,[21] **16**,[37] **17**,[38] **18**,[39] **23**,[21] and **24**[21] have been previously described.

General procedure for the alkylation of amines and phenols: A solution containing NaH (1.2 equiv, 60 % in mineral oil) in dried DMF (volume of DMF necessary to make the concentration of NaH 1.0 M) was cooled to 0 °C. A solution of the corresponding amine or phenol (1.0 equiv) in DMF (volume of DMF necessary to make the concentration 1.0 M) was added dropwise. The mixture was warmed to room temperature, stirred for 20 min, and the alkylating agent (1.0 equiv) was added. The reaction mixture was stirred at room temperature for 4 h, quenched with 10 % aqueous HCl, and diluted with Et_2O. The organic layer was washed several times with water and then dried over $MgSO_4$. The solvent was evaporated and the residue was purified by chromatography (hexane/EtOAc mixtures) to give the corresponding alkylated products.

Five-step synthesis of 9 (see Scheme 7):

3-[(2-(Trimethylsilyl)ethoxy)methoxy]benzonitrile: To a suspension of NaH (60 % in mineral oil, 880 mg, 22.00 mmol) in THF (10 mL) at 0 °C, was added a solution of 3-hydroxybenzonitrile (2.50 g, 21.0 mmol) in THF (5 mL), followed by trimethylsilylethoxymethyl chloride (SEMCl, 3.9 mL, 22.0 mmol). The mixture was stirred for 2 h at 23 °C and then quenched with H_2O. After extractive workup (Et_2O) and chromatography (hexane/EtOAc 9:1), the title compound was obtained (3.70 g, 70 %) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.28 (m, 4H), 5.27 (d, J = 0.8 Hz, 2H), 3.81–3.75 (m, 2H), 0.99 (ddd, J = 8.1, 8.1, 0.8 Hz, 2H), 0.04 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ = 158.23 (C), 130.94 (CH), 125.99 (CH), 121.79 (CH), 120.16 (CH), 119.27 (CH_2), 113.87 (CH_2), 93.56 (CH_2), 67.28 (CH_2), 18.65 (CH_2), −0.82 ppm (CH_3); FAB-HRMS: $[M+1]^+$: calcd for $C_{13}H_{20}NO_2Si$: 250.1263; found: 250.1269.



Scheme 7. Synthesis of **9**.

[3-((2-(Trimethylsilyl)ethoxy)methoxy)phenyl]methanamine: A solution of 3-[(2-(trimethylsilyl)ethoxy)methoxy]benzonitrile (3.70 g, 14.80 mmol) in THF (10 mL) was added to a suspension of $LiAlH_4$ (850 mg, 22.40 mmol) in THF (10 mL). The mixture was stirred at 35 °C for 4 h, cooled to 0 °C, and quenched with H_2O (1.6 mL, 88.89 mmol). The mixture was diluted with EtOAc and Na_2SO_4 was added. After stirring for 1 h, the reaction mixture was filtered through Celite and dried over $MgSO_4$. The solvent was evaporated to give the crude amine (3.37 g, 90%) as a pale yellow oil. The amine was used without further purification in the following tosylation step. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23 (t, J = 7.8 Hz, 1H), 7.01–6.89 (m, 3H), 5.20 (s, 2H), 3.80 (s, 2H), 3.76–3.56 (m, 2H), 2.37 (s, 2H), 0.98–0.89 (m, 2H), −0.02 ppm (s, 9H).

[3-((2-(Trimethylsilyl)ethoxy)methoxy)phenyl]-N-tosylmethanamine: To a solution of the corresponding amine (3.40 g, 13.50 mmol) in CH_2Cl_2, was added NEt_3 (2.1 mL, 14.00 mmol) at 0 °C. Then a solution of TsCl (2.50 g, 13.50 mmol) in CH_2Cl_2 was added and the reaction mixture was stirred at 23 °C. The crude mixture was washed with a solution of HCl (10%) and brine. After drying with Na_2SO_4, and evaporation of the solvent, the residue was chromatographed (hexane/EtOAc 10:1) to give the title compound (1.75 g, 32%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 7.17 (t, J = 8.0 Hz, 1H), 6.91 (ddd, J = 8.0, 2.4, 1.0 Hz, 1H), 6.85–6.81 (m, 2H), 5.15 (br s, 2H), 4.08 (d, J = 6.3 Hz, 2H), 3.75–3.69 (m, 2H), 2.43 (s, 3H), 0.96–0.91 (m, 2H), −0.02 ppm (s, 9H) (the NH signal was not observed); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.30, 144.12, 138.46, 137.55, 130.37, 127.88, 127.86, 121.70, 116.34, 116.24, 93.41, 66.94, 47.80, 22.17, 18.67, −0.78 ppm; FAB-HRMS: calcd for $C_{20}H_{30}NO_4SiS$: 408.1665; found: 408.1679.

N-[3-((2-(Trimethylsilyl)ethoxy)methoxy)benzyl]-N-tosylbut-2-yn-1-amine: This compound was obtained following the general procedure for the propargylation after chromatography (hexane/EtOAc 10:1) as a colorless oil (721 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.1 Hz, 1H), 7.00–6.94 (m, 3H), 5.20 (s, 2H), 4.28 (s, 2H), 3.92–3.87 (m, 2H), 3.79–3.70 (m, 2H), 2.44 (s, 3H), 1.53 (t, J = 2.4 Hz, 3H), 0.99–0.91 (m, 2H), −0.01 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.37, 144.26, 137.12, 136.67, 130.37, 130.16, 128.51, 122.62, 117.30, 116.44, 93.50, 82.52, 76.92, 74.77, 66.92, 50.34, 36.24, 22.20, 18.68, −0.77 ppm; FAB-HRMS: $[M+1]^+$: calcd for $C_{24}H_{34}NO_4SiS$: 460.1978; found: 460.1985.

N-[(3-Hydroxy)benzyl]-N-tosylbut-2-yn-1-amine (**9**): TBAF (3.1 mL, 3.12 mmol; 1.0 M in THF) was added to *N*-[3-((2-(trimethylsilyl)ethoxy)-methoxy)benzyl]-*N*-tosylbut-2-yn-1-amine (721 mg, 1.56 mmol) in HMPA (5 mL) and the mixture was stirred at 90 °C for 17 h. The reaction was diluted with EtOAc, washed with brine and water, and the organic phase was dried over Na_2SO_4. The solvent was evaporated and the residue chromatographed (hexane/EtOAc 3.5:1). The product was further purified by trituration with CH_2Cl_2/hexane to give **9** (298 mg, 58%) as a white solid. M.p. 113–114 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.19 (t, J = 7.8 Hz, 1H), 6.90–6.86 (m, 2H), 6.77 (ddd, J = 7.8, 2.4, 0.8 Hz, 1H), 4.26 (s, 2H), 3.90 (d, J = 2.4 Hz, 2H), 2.44 (s, 3H), 1.54 ppm (t, J = 2.4 Hz, 3H) (the OH signal not observed); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.57, 143.98, 137.87, 136.84, 130.48, 129.94, 128.60, 121.67, 116.02, 115.68, 82.54, 72.09, 50.25, 36.89, 22.15, 3.86 ppm; EI-HRMS: calcd for $C_{18}H_{19}NO_3S$: 329.1086; found: 329.1073.

2,3,5,6-Tetramethylhydroquinone: To a suspension of duroquinone (1.0 g, 6.10 mmol) in THF (4 mL) and MeOH (2 mL), was slowly added $NaBH_4$ (300 mg, 8.0 mmol). The reaction mixture was stirred at 23 °C for 30 min and then cooled to 0 °C. Additional MeOH was slowly added until no more gas evolution was observed. A small amount of water was added and a solid precipitated. The solid was filtered off and washed with Et_2O to yield the title compound (1.02 g, quantitative) as a white solid, which was used without further purification in the following propargylation step. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 6H), 1.58 ppm (br s, 2H).

2,3,5,6-Tetramethyl-4-(prop-2-ynyloxy)phenol (13): This compound was obtained following the general procedure for the propargylation from 2,3,5,6-tetramethylhydroquinone and propargyl bromide after chromatography (hexane/EtOAc 20:1 to 8:1) as a pale yellow solid (31%). M.p. 107–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.50 (s, 1H), 4.41 (d, J = 2.4 Hz, 2H), 2.54 (t, J = 2.4 Hz, 1H), 2.28 (s, 6H), 2.19 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.45, 149.00, 128.19 (2C), 120.75 (2C), 80.20, 75.26, 61.09, 13.82 (2C), 12.80 ppm (2C); elemental analysis calcd (%) for $C_{13}H_{16}O_2$: C 76.44, H 7.90; found: C 76.11, H 7.72.

1,2-Dimethoxy-4-(prop-2-ynyloxy)benzene (26): This compound was obtained following the general procedure for the propargylation from 3,4-dimethoxyphenol and propargyl bromide after chromatography (hexane/EtOAc 5:1) as a colorless oil. (2.22 g, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.79 (d, J = 8.7 Hz, 1H), 6.60 (d, J = 2.8 Hz, 1H), 6.49 (dd, J = 8.7, 2.8 Hz, 1H), 4.65 (d, J = 2.4 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 2.52 ppm (t, J = 2.4H, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ = 152.07 (C), 149.81 (C), 144.11 (C), 111.56 (CH), 104.39 (CH), 101.36 (CH), 78.75 (C), 75.29 (CH), 56.40 (CH_2), 56.31 (CH_3), 55.78 ppm (CH_3); EI-HRMS: calcd for $C_{11}H_{12}O_3$: 192.0786; found: 192.0787.

General procedure for the cyclization of arylalkynes with $PtCl_2$: A solution of the 4-aryl-1-alkyne (0.1 mmol) and $PtCl_2$ (0.005 mmol) in toluene (1.5 mL) was stirred at 100 °C for the stated times. The resulting mixture was filtered through a short path of Celite, and the solvent was evaporated. Column chromatography (hexane/EtOAc mixtures) gave the corresponding cyclic compounds.

General procedure for the cyclization of 4-aryl-1-alkynes with [Au(PPh$_3$)Me] and HBF$_4$: A mixture of 4-aryl-1-alkyne (0.1 mmol) and [Au(PPh$_3$)Me] (0.003 mmol) was dissolved in toluene (1.5 mL). HBF_4 (1 μL, 0.006 mmol) was added and the reaction mixture was stirred at 23 °C for the stated times. The mixture was diluted with Et_2O, washed with 5% aqueous $NaHCO_3$, and the organic phases were dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (hexane/EtOAc mixtures) to give the corresponding cyclic compounds.

General procedure for the cyclization of 4-aryl-1-alkynes with [Au(PPh$_3$)Cl] and AgX (X = SbF$_6$, BF$_4$): A mixture of [Au(PPh$_3$)Cl] (0.003 mmol) and AgX (0.003 mmol) was dissolved in toluene (1.5 mL). 4-Aryl-1-alkyne (0.1 mmol) was added and the reaction mixture was stirred at room temperature for the stated times. The mixture was filtered through a short path of Celite, and solvent was evaporated. The residue was purified by column chromatography (hexane/EtOAc mixtures) to yield the corresponding cyclic compounds.

(*Z*)-2,3-Dihydro-5-methyl-2-tosyl-1*H*-benzo[*c*]azepin-8-ol (10): Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.4 Hz, 1H), 6.83 (dd, J = 8.4, 2.7 Hz, 1H), 6.71 (d, J = 2.7 Hz, 1H), 5.67 (td, J = 7.0, 1.5 Hz, 1H), 4.96 (s, 1H, -OH), 4.14 (s, 2H), 3.60 (d, J = 7.0 Hz, 2H), 2.46 (s, 3H), 2.06 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ = 154.99 (C), 143.32 (C), 141.56 (C), 136.12 (C), 135.08 (C), 133.48 (C), 129.62 (CH), 127.67 (CH), 127.52 (CH), 119.30 (CH), 116.62 (CH), 115.12 (CH), 49.75 (CH_2), 44.18 (CH_2), 22.29 (CH_3), 21.54 ppm (CH_3); FAB-HRMS: $[M+1]^+$: calcd for $C_{18}H_{20}NO_3S$: 330.1164; found: 330.1165.

14: Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.25 (dt, J = 3.2, 1.6 Hz, 1H), 5.30 (dt, J = 6.1, 2.4 Hz, 1H), 4.96 (dd, J = 2.4, 1.6 Hz, 2H), 1.92 (dd, J = 2.0, 1.2 Hz, 6H), 1.88 ppm (dd, J = 2.0, 1.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ = 185.63 (C), 152.68 (2C), 132.02 (CH), 131.17 (2C), 129.87 (CH), 91.50 (C), 78.96 (CH_2), 15.14 (2CH_3), 12.17 ppm (2CH_3); EI-HRMS: calcd for $C_{13}H_{16}O_2$: 204.1150; found: 204.1156.

2*H*-Chromen-7-ol (19): Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82 (d, J = 8.1 Hz, 1H), 6.38–6.27 (m, 3H), 5.62 (dt, J = 9.7, 3.4 Hz, 1H), 5.62 (dt, J = 9.7, 3.4 Hz, 1H), 4.79 ppm (dd, J = 3.4, 1.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.24, 151.35, 127.50, 124.23, 118.84, 111.26, 108.17, 103.28, 65.63 ppm; EI: m/z: 147.1 $[M-1]^+$.

4*H*-Chromen-5-ol (20): Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82 (d, J = 8.1 Hz, 1H), 6.38–6.27 (m, 3H), 5.62 (dt, J = 9.7, 3.4 Hz, 1H), 5.62 (dt, J = 9.7, 3.4 Hz, 1H), 4.79 ppm (dd, J = 3.4, 1.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.24, 151.35, 127.50, 124.23, 118.84, 111.26, 108.17, 103.28, 65.63 ppm.

5-Methoxy-2*H*-chromene (21) and 7-methoxy-2*H*-chromene (22): These compounds were hydrogenated in situ (toluene solution) with Pd/C

(10%) at room temperature for 2 h to give a 1:2 mixture of 3,4-dihydro-5-methoxy-2*H*-chromene (**21′**) and 3,4-dihydro-7-methoxy-2*H*-chromene (**22′**): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09 (t, J = 8.5 Hz, 1H, **21′**), 6.97 (ddd, J = 8.5, 1.2, 0.8 Hz, 1H, **22′**), 6.53–6.44 (m, 2H **21′**, 1H **22′**), 6.40 (d, J = 2.8 Hz, 1H, **22′**), 4.23–4.17 (m, 2H **21′**, 2H **22′**), 3.86 (s, 3H, **21′**), 3.80 (s, 3H, **22′**), 2.76 (t, J = 6.5 Hz, 2H, **22′**), 2.70 (t, J = 6.5 Hz, 2H, **21′**), 2.07–1.98 ppm (m, 4H, 2H **22′**, 2H **21′**); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.63, 158.65, 156.38, 156.20, 130.86, 127.41, 115.00, 112.00, 110.18, 107.65, 102.35, 102.17, 67.16, 66.71, 56.07, 55.93, 24.82, 23.16, 22.50, 19.85 ppm; EI-HRMS: calcd for $C_{10}H_{12}O_2$: 164.0837; found: 164.0830.

25: White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.56 (s, 1H), 6.51 (s, 1H), 5.91 (m, 2H), 4.09 (d, J = 11.6 Hz, 1H), 3.73 (d, J = 11.6 Hz, 1H), 3.01–2.91 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 149.61 (C), 146.50 (C), 142.51 (C), 118.73 (C), 107.76 (CH), 100.91 (CH_2), 99.58 (CH), 66.29 (CH_2), 41.06 (CH), 33.38 ppm (CH). The structure was confirmed by NOESY, COSY, HMBC, HMQC experiments and X-ray diffraction.

6,7-Dimethoxy-2*H*-chromene (27): Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.52 (s, 1H), 6.41 (s, 1H), 6.35 (dt, J = 9.4, 1.0 Hz, 1H), 5.65 (dt, J = 9.4, 3.7 Hz, 1H), 4.74 (dd, J = 3.7, 1.0 Hz, 2H), 3.84 (s, 3H), 3.83 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ = 149.52 (C), 148.49 (C), 143.48 (C), 124.38 (CH), 119.19 (CH), 114.34 (C), 109.95 (CH), 100.54 (CH), 65.36 (CH_2), 55.48 (CH_3), 55.92 ppm (CH_3); EI-HRMS: calcd for $C_{11}H_{12}O_3$: 192.0786; found: 192.0787.

6,7-Dimethoxy-4*H*-chromene (28): Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.47 (s, 1H), 6.45 (dt, J = 6.4, 2.0 Hz, 1H), 4.90 (dt, J = 6.4, 3.5 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.32 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ = 149.08 (C), 147.54 (C), 143.67 (C), 140.50 (C), 111.42 (CH), 100.64 (CH), 99.82 (CH), 56.24 (CH_3), 55.90 (CH_3), 22.79 ppm (CH_2) (one C signal is missing owing to overlapping); EI-HRMS: calcd for $C_{11}H_{12}O_3$: 192.0786; found: 192.0789.

29: White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.69 (s, 1H), 6.68 (s, 1H), 3.80 (d, J = 11.4 Hz, 1H), 3.55 (s, 3H), 3.50 (d, J = 11.4 Hz, 1H), 3.38 (s, 3H), 3.00 (d, J = 8.0 Hz, 1H), 2.73 ppm (d, J = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ = 149.87 (C), 149.62 (C), 145.37 (C), 117.89 (C), 114.02 (CH), 102.75 (CH), 65.72 (CH_2), 56.66 (CH_3), 55.19 (CH_3), 40.75 (CH), 33.69 ppm (CH); EI-HRMS: calcd for $C_{22}H_{24}O_6$: 384.1573; found: 384.1578. The structure was confirmed by NOESY, COSY, HMBC, HMQC experiments.

Computational methods: Calculations were performed with the GAUSSIAN 98 series of programs.[40] The geometries of all complexes were optimized at the DFT level with the B3LYP hybrid functional.[41] The standard 6-31G(d) basis set was used for C, H, O, and Cl and the LANL2DZ relativistic pseudopotential was used for Pt. 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.

Acknowledgements

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