Pure Appl. Chem., Vol. 82, No. 4, pp. 801–820, 2010.
doi:10.1351/PAC-CON-09-10-06

Synthesis of arenes and heteroarenes by hydroarylation reactions catalyzed by electrophilic metal complexes*

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Abstract: The hydroarylation of alkynes (also known as arylation of alkynes or alkenylation of arenes) catalyzed by gold or other electrophilic metal salts or complexes is reviewed from synthetic and mechanistic perspectives.

Keywords: alkynes; arenes; gold; hydroarylation; platinum.

INTRODUCTION

The hydroarylation of alkynes is the addition of an aromatic compound to an alkyne, a reaction that usually takes place in the presence of electrophilic metal salts or complexes. This reaction is also known as the alkenylation of arenes. In general, hydroarylation of alkynes catalyzed by transition metals proceed by two major reaction pathways. In one pathway, electrophilic metal salts or complexes activate the alkyne in complexes **1** toward nucleophiles to form product **3** by *anti*-addition via intermediates **2** [1,2] (Scheme 1). In the case of water, the nucleophilic addition forms an enol with the expected Markovnikov regiochemistry, which undergoes tautomerization to give the corresponding methyl ketone [3]. Similarly, the reaction of alkynes with electron-rich arenes and heteroarenes results in the electrophilic aromatic substitution of the arene (NuH = ArH) by a formal Friedel–Crafts process [4]. Electrophilic platinum and gold complexes generally promote reactions by this pathway. On the other hand, reactions of terminal alkynes with $[M(CO)_6]$ (M = Cr, Mo, W) and certain Ru(II) complexes may proceed via vinylidene metal complexes **4**, by a 1,2-H migration [5,6] or via intermediates **5** formed by oxidative addition of the C–H bond to the metal center [7]. Similar transformations can occur with alkynes substituted with groups (SiR_3, SR, I) that can undergo 1,2-migration. Pd-catalyzed hydroarylation can also take place by insertion of alkynes into the Pd–C bond of $ArPdXL_2$, formed by oxidative addition of ArX to $Pd(0)L_n$ [8].

Here, we review recent synthetic and mechanistic developments on the hydroarylation reaction for the synthesis of aromatic and heteroaromatic compounds using gold, platinum, and other electrophilic catalysts. For the sake of conciseness, somewhat related processes initiated by iodination of the alkyne or Brønsted-acid catalyzed reactions [2,9–11] are not reviewed.

Pure Appl. Chem.* **82, 757–1063 (2010). An issue of reviews and research papers based on lectures presented at the 13th International Symposium on Novel Aromatic Compounds (ISNA-13), 19–24 July 2009, Luxembourg City, Luxembourg on the theme of aromaticity.

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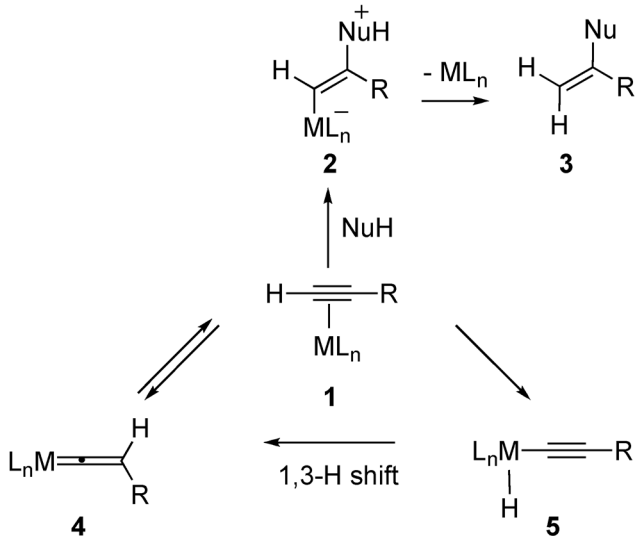


Scheme 1 Alternative pathways in metal-promoted activation of alkynes.

PLATINUM AND GOLD CATALYSTS

In addition to common salts $PtCl_2$, $PtCl_4$, neutral $[Pt(MeCN)_2Cl_2]$ [12] or cationic complexes **6** [13], **7**, and **8** [14] have been used as catalysts for the activation of alkynes (Fig. 1). A carbonyl Pt(II) complex, formed in situ from $PtCl_2$ and carbon monoxide, has also been used as an active catalyst in reactions of enynes and other substrates [15]. Cationic Au(I) complexes and simple salts such as AuCl and $AuCl_3$

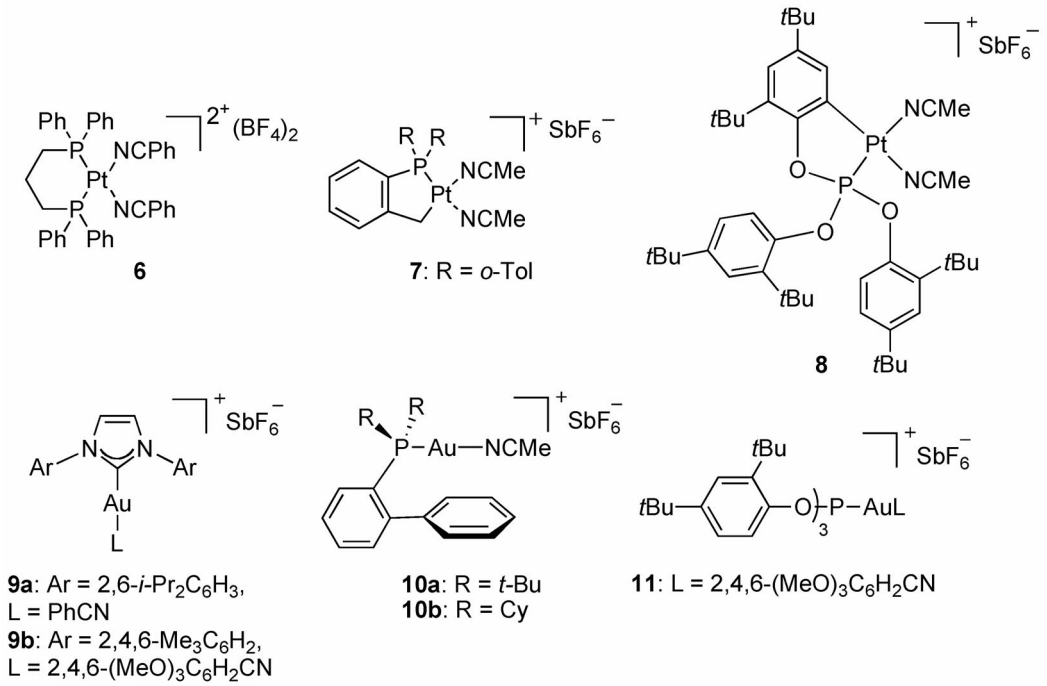
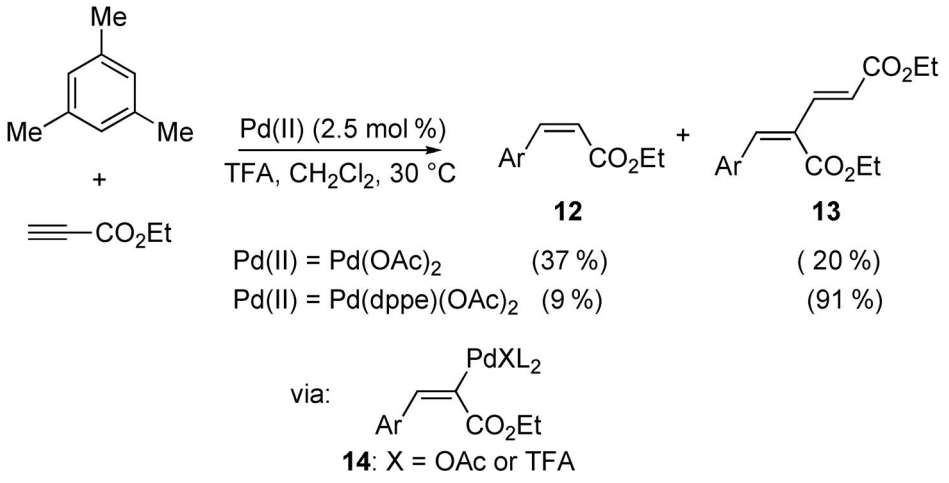


Fig. 1 Selected Pt(II) and Au(I) complexes.

are the most active catalysts for the electrophilic activation of alkynes toward a variety of nucleophiles under very mild conditions [16–19]. The neutral donating ligand in cationic complexes can play a very significant role in gold catalysis [16,20–22]. Gold complexes with N-heterocyclic carbene ligands, such as **9a,b** [21,23] (Fig. 1), have been shown to be selective catalysts in the activation of alkynes as well as allenes and alkenes [21,24–27]. Related complexes with bulky cyclic amino carbene [28] and open carbene [29] ligands have also been reported. Gold complexes with bulky dialkylbiarylphosphine ligands such as **10a,b** [24,30] are highly active in many reactions of enynes [12,21,30–33], and other reactions [16,34–37]. These complexes are stable white crystalline salts that can be stored under ordinary conditions. Related complexes with a weakly coordinated bis(trifluoromethanesulfonyl)amide ligand have also been used as catalysts in enyne cyclizations [38,39]. The reactivity of cationic complexes **10a,b** is only surpassed by highly electrophilic cationic complex **11** bearing a bulky phosphite ligand [21].

INTERMOLECULAR HYDROARYLATION

The hydroarylation of alkynes can be catalyzed using metal trifluoromethanesulfonates (metal triflates) [$M(OTf)_n$; M = Sc, Zr, In] [40,41] or other reactive Lewis acids [42,43] to give 1,1-diarylalkenes. Electrophilic Pd(II) and Pt(II) cationic complexes also catalyze the hydroarylation reaction [44–49]. It was initially suggested, that in the presence of alkynes, metal cationic species enhance the metalation of the arenes through electrophilic substitution to give σ-aryl metal species, followed by an unusual *trans*-insertion of the alkyne into the Csp^2-M bond [44]. However, a mechanistic study based on the study of isotope effects was consistent with a reaction proceeding by electrophilic aromatic substitution [50]. This is also in accord with that observed in the hydroarylation of alkynes with arenes catalyzed by palladium complexes with bidentate phosphines (Scheme 2) [51]. In this reaction, dienes **13** were obtained as the major products, in addition to *cis*-cinnamate derivatives **12**. Presumably, in this case, alkenyl-palladium intermediate **14** is intercepted by a second equivalent of the alkyne.

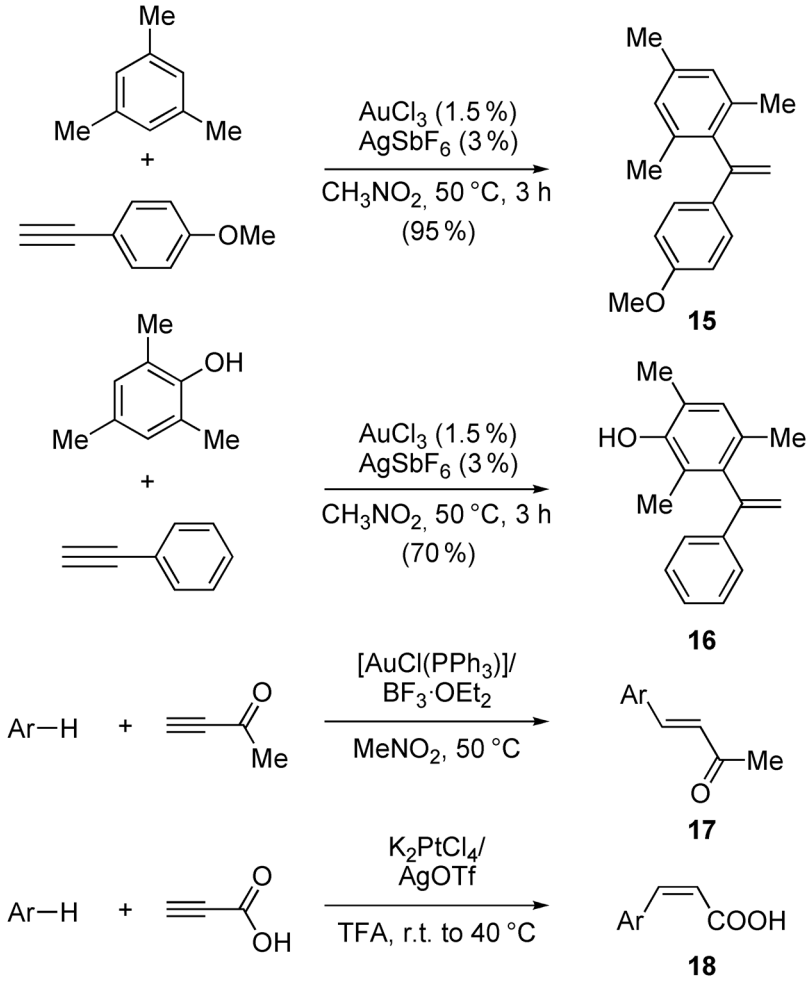


Scheme 2 Intermolecular Pd(II)-catalyzed hydroarylation.

In the presence of palladium acetate and silver acetate, electron-rich arenes react with diphenylacetylene and related disubstituted alkynes to form highly substituted naphthalenes [52]. Electron-rich heteroaromatic compounds, such as pyrroles, indoles, and furans, readily undergo addition to alkynoates at room temperature with catalytic amounts of $Pd(OAc)_2$ to give *Z*-alkenes in most cases

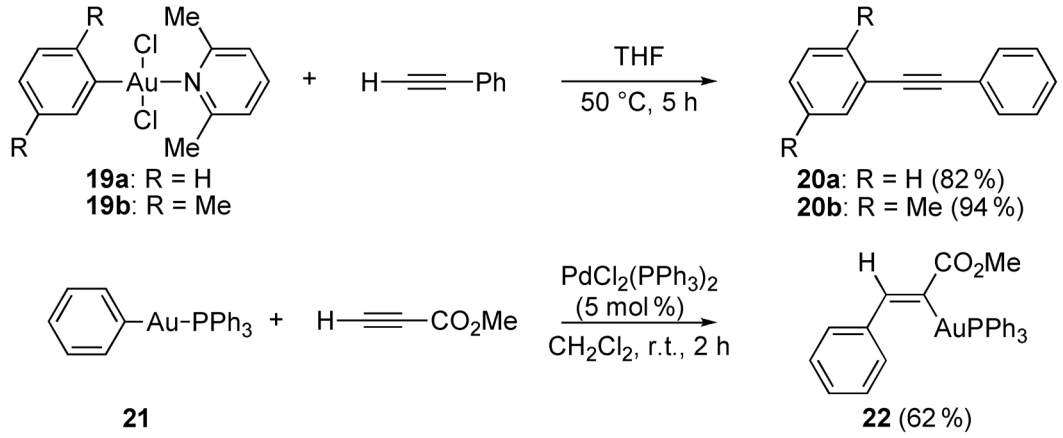
[53]. Methoxyarenes also react with allenes under mild conditions in the presence of a Au(I) catalyst to give products of allylation [54].

The gold-catalyzed intermolecular hydroarylation of alkynes leads to 1,1-disubstituted alkenes such as **15** and **16** [55–58] (Scheme 3) as a result of an addition proceeding with a Markovnikov regiochemistry. However, alkynes with electron-withdrawing groups afford 1,2-disubstituted derivatives **17** [55]. Interestingly, reaction of arenes with propiolic acid leads to *cis*-cinnamic acids **18** in good to high yields by using a catalyst generated in situ from K_2PtCl_4/AgOTf [59].



Scheme 3 Intermolecular Au(I)- and Au(III)-catalyzed hydroarylation.

It is important to recall that the direct metalation (auration) of electron-rich arenes and heteroarenes by Au(I) [60] and Au(III) are well known reactions [61–63]. However, treatment of complexes $ArAuX_2L$ (**19a,b**) with terminal alkynes such as phenylacetylene results in the formation of diarylalkynes **20a,b** [62b] instead of products of hydroarylation (Scheme 4). On the other hand, reaction of aryl-Au(I) complexes **21** with alkynes only occurs in the presence of a Pd(0) catalyst, or a Pd(II) precatalyst, to form products of carboauration **22** [64].



Scheme 4 Stoichiometric and Pd-catalyzed reactions of aryl-gold complexes.

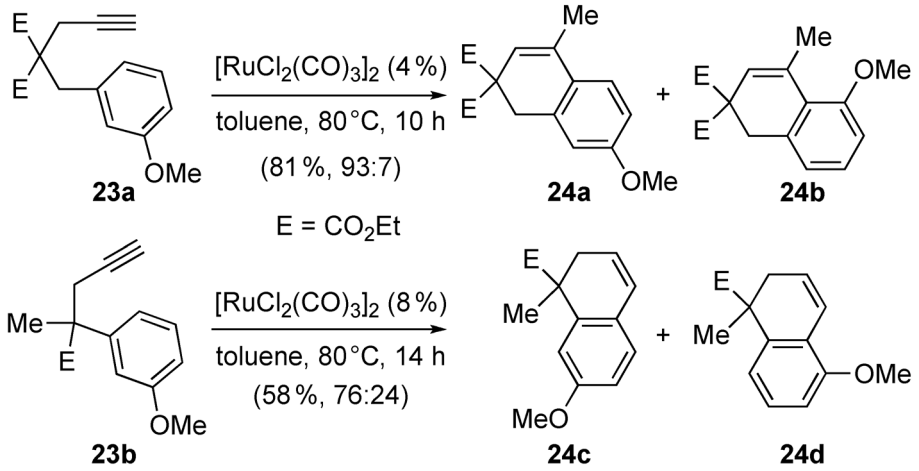
INTRAMOLECULAR HYDROARYLATION

Intramolecular reactions of arenes with alkynes

The catalytic system based on $Pd(OAc)_2$ and TFA [44] has been also applied in the intramolecular hydroarylation of alkynes. This process is faster than the intermolecular one, suggesting that the electrophilic substitution of arenes by Pd(II) cationic species is assisted by alkyne coordination. Thus, arylalkynoates and alkynanilides cyclize in the presence of catalytic amounts of $Pd(OAc)_2$ in TFA, yielding coumarins and quinolin-2(1*H*)-ones, respectively, in good to excellent yields [65]. *N*-Arylpropiolamides undergo 5-*exo-dig* hydroarylation reaction to form 3-methyleneoxindoles with Pd(II) catalysts [66].

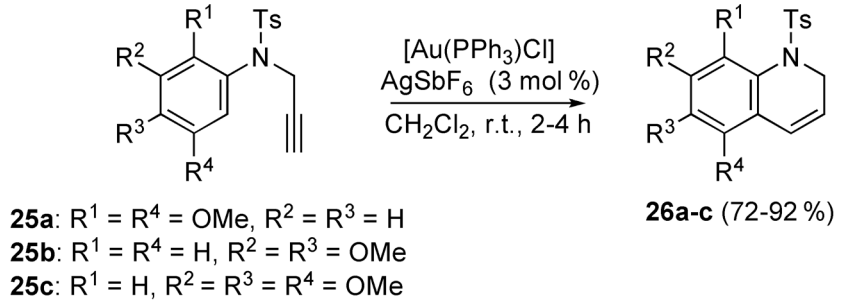
Similar cyclizations have also been carried out with other Pd(II) catalytic systems [67,68] and Au(III) catalysts [62]. The addition of phenols to alkynoates catalyzed by Pd(0) leads to coumarins via an overall aryl C–H insertion [69]. This coumarin synthesis was used in the context of an enantioselective synthesis of (+)-aflatoxins B_1 and B_{2a} [70]. This reaction can also be carried out using stoichiometric amounts of a Ag(I) salt [70].

Ru(II) complexes catalyzed the cycloisomerization of ω-aryl-1-alkynes **23** by an intramolecular hydroarylation reaction in which aromatic rings act as nucleophiles toward π-alkyne-transition metal complexes, in a reaction in which metalation of the arene moiety does not take place [71] (Scheme 5). Similar results were obtained with $PtCl_2$ as catalyst. In this process, dihydronaphthalenes are obtained by *exo*- (**24a,b**) or *endo-dig* (**24c,d**) cyclizations depending on the length of the tether. Dihydrobenzocycloheptenes could also be obtained by this process. The scope of the reaction was extended to substrates where the arene moiety does not possess strong electron-donating groups by using $GaCl_3$ [72] or $FeCl_3$ [42,73] as catalysts.



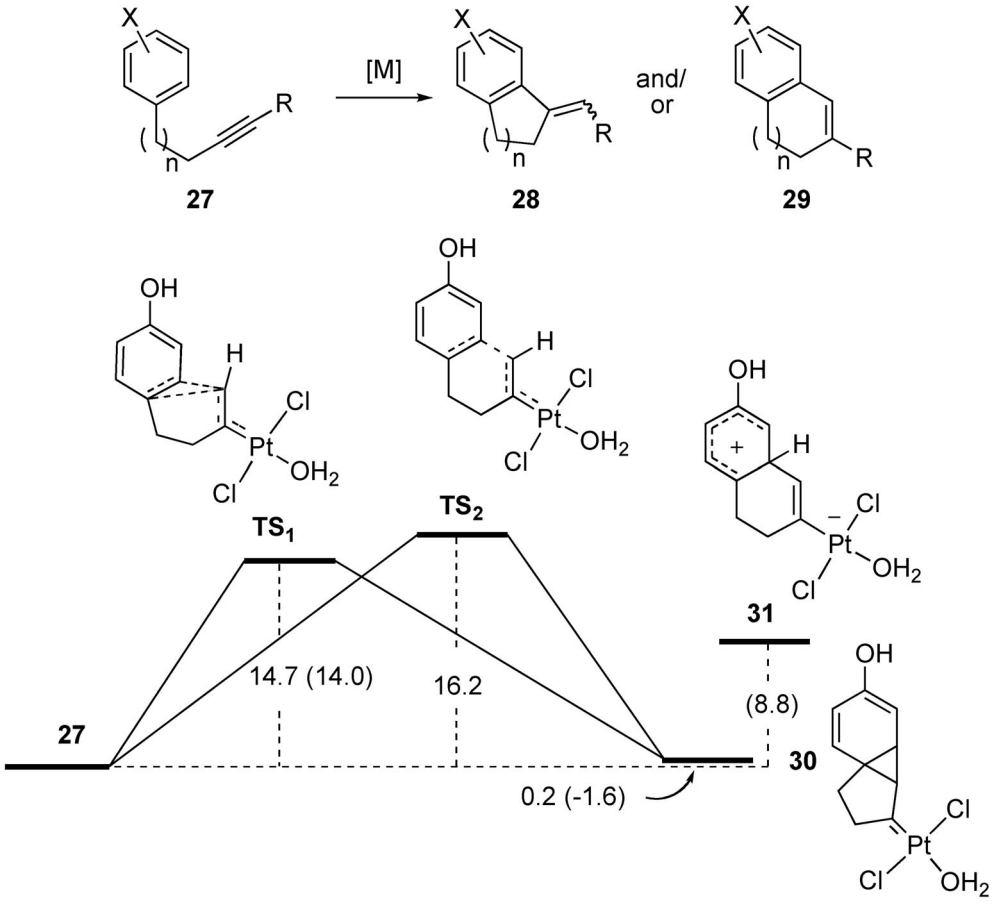
Scheme 5 Ru(II)-catalyzed intramolecular hydroarylation.

2*H*-Chromenes, 1,2-dihydroquinolines, and coumarins can similarly be obtained by intramolecular hydroarylation using $RuCl_3$/AgOTf, $PtCl_2$, $PtCl_4$ as the catalysts [74,75]. Using $PtCl_2$ as the catalyst the cyclization of *N*-propargyl-*N*-tosyl anilines **25a–c** proceeds in toluene under reflux to give *N*-tosyl-1,2-dihydroquinolines **26a–c** [76]. The best yields and milder reaction conditions were obtained using a cationic Au(I) catalyst formed in situ by chloride abstraction from [Au(PPh_3)Cl] with a silver salt [77] (Scheme 6). A general method for the cyclization of aryl propargyl ethers and propargyl tosylamines has been developed recently using as catalyst Au(I) cationic complex **10a** [78].



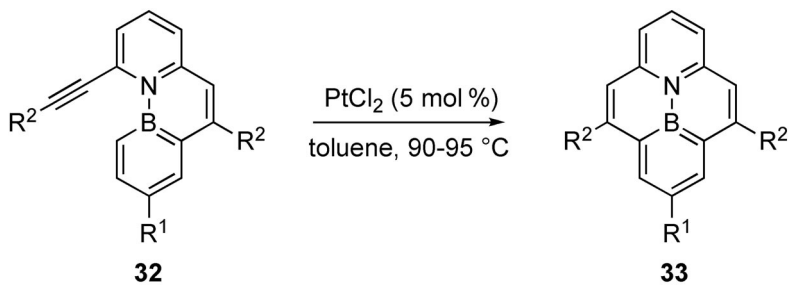
Scheme 6 Synthesis of dihydroquinolines by Au(I)-catalyzed intramolecular hydroarylation.

Experimental results with Ru(II) [71], Pt(II) [71,76,77], Pt(IV) [74a], Ga(III) [72], and Hg(II) [79] as catalysts for systems **27** in which $n = 0, 1$ show that the *endo*-cyclization is strongly favored leading to compounds **29** (Scheme 7). According to theoretical work [77], the *endo*-cyclization of 3- or 4-but-3-ynylphenols **27** (X = OH) catalyzed by Pt(II) is strongly favored and proceeds through transition state $\mathbf{TS_1}$ to form intermediates of type **30**. These intermediates are related to the cyclopropyl carbene metal that have been proposed as the intermediates in metal-catalyzed cyclizations of 1,n-enynes [16f,19,80]. Formation of the final dihydronaphthalenes would proceed by opening of **30** to form intermediate **31**, which corresponds to the intermediate expected for a conventional Friedel–Crafts-type reaction.



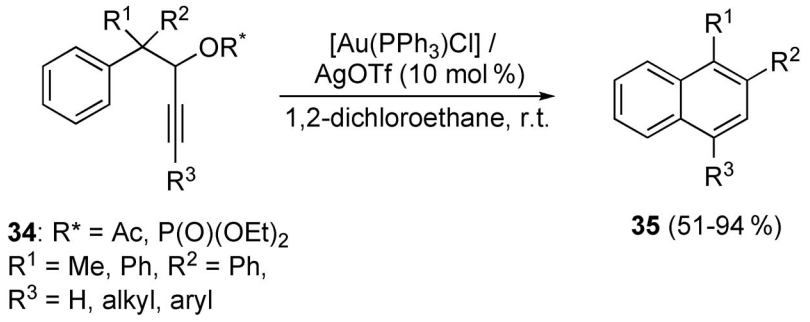
Scheme 7 Mechanism for the Pt(II)-catalyzed intramolecular hydroarylation (energies in kcal mol^{-1}).

Propargyl anilines, which are formed in situ in the presence of the Au(I) catalysts from *N*-(pent-4-ynyl)anilines and terminal alkynes, are cyclized to form pyrrolo[1,2-a]quinolines by a similar intramolecular hydroarylation [81]. Related processes involving hydroamination-hydroarylation of alkynols using Pt(II) have also been described [82]. Allenic anilines and phenols also undergo gold-catalyzed intramolecular hydroarylation to form dihydroquinoline and chromene derivatives [83]. The noteworthy cyclization of substrates **32** using $PtCl_2$ as catalyst to give 10a-aza-10b-borapyrenes (**33**) in a 6-*endo-dig* process illustrates the broad applicability of this reaction [84] (Scheme 8).



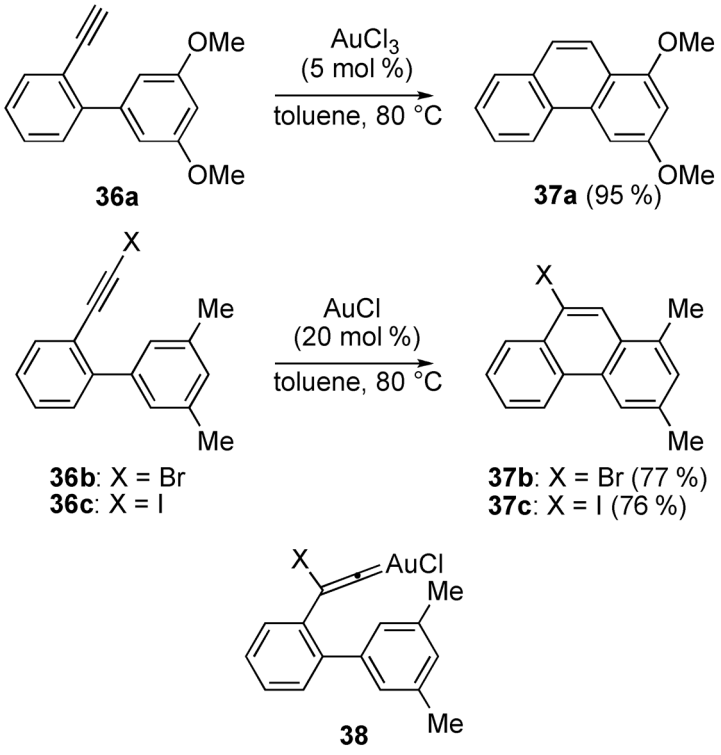
Scheme 8 Synthesis of 10a-aza-10b-borapyrenes by Pt(II)-catalyzed intramolecular hydroarylation.

A remarkable sequence that involves consecutive 1,3- and 1,2-migrations of two different groups in substrates **34** in the presence of Au(I) catalyst leads to substituted naphthalenes **35** [85] (Scheme 9). In this transformation, the initial 1,3-migration of OR* (acetate or phosphate) is followed by a 1,2-migration of R^2. An unusual 1,2-indole migration has also been observed in the gold-catalyzed reaction of indoles propargylated at C-3 [86].



Scheme 9 Synthesis of naphthalenes by Au(I)-catalyzed migration/intramolecular hydroarylation.

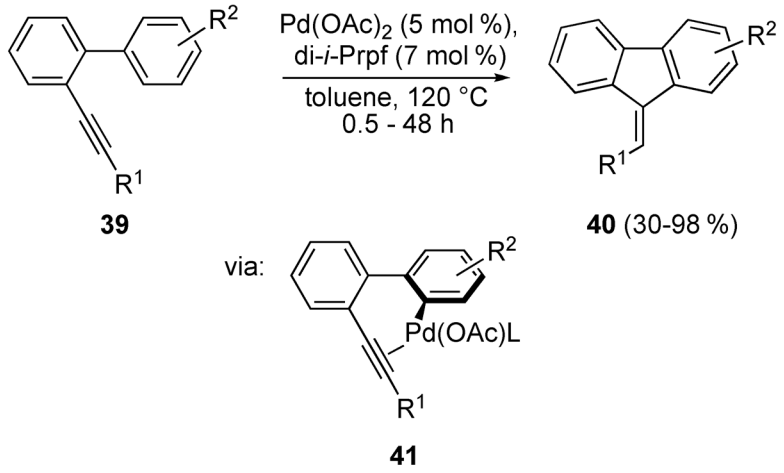
The cyclization of *ortho*-alkynylated biphenyl derivatives **36** with Au(III) and other metal catalysts, such as $PtCl_2$, $GaCl_3$, or $InCl_3$, also proceeds preferentially by the endo pathway leading to phenanthrenes **37** [87] (Scheme 10). Interestingly, haloalkynes **36b,c** react with AuCl to give phenanthrenes **37b,c** in which the halide has suffered a 1,2-shift, whereas using stoichiometric $InCl_3$, the cor-



Scheme 10 Synthesis of phenanthrenes by metal-catalyzed intramolecular hydroarylation.

responding phenanthrenes with halide retention were obtained. The observed 1,2-halogen shift suggests that the Au(I)-catalyzed reaction of **36b,c** proceeds via gold vinylidene species **38**. A similar iodine migration and electrocyclization was reported in cyclizations promoted by $W(CO)_5$ [88]. Gold-vinylidene species have also been proposed as intermediates in Au(I)-catalyzed cyclizations of 1-alkynyl-2-alkenylbenzenes to yield naphthalenes [89,90], as well as in the reaction of 2-(prop-2-ynyl)pyridines with $AuBr_3$ to form indolizines [91]. In this last reaction, Au(III) was proposed to be reduced in situ to form the active Au(I) catalyst. Density functional theory (DFT) calculations support the involvement of vinylidenes of type **38** (X = I) as intermediates in the cyclization catalyzed by AuCl, which then gives the phenanthrene by an electrocyclization process [92].

Although the mechanism proceeding by insertion of the alkyne into the σ-aryl-metal complex has been excluded for the metal-catalyzed hydroarylation reaction, the cyclization of *o*-alkynyl biaryls **39** to form fluorene derivatives **40** was demonstrated to proceed by a mechanism that involves an insertion into a σ-aryl-palladium intermediate [93] (Scheme 11). For this 5-*exo-dig* cyclization, a pathway involving the C–H activation via intermediate **41** was proposed on the basis of the high efficiency of the cyclization of substrates with electron-deficient substituents on the aryl rings, high values of kinetic isotope effects, and the observed exclusive *cis*-selectivity in the insertion step.

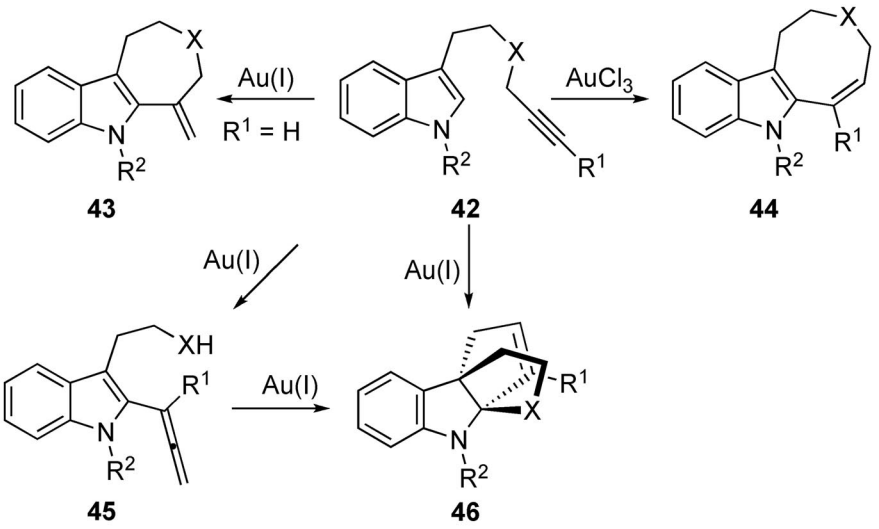


Scheme 11 Synthesis of fluorenes by Pd(II)-catalyzed intramolecular hydroarylation via C–H activation. (Di-*i*-Prpf = 1,1 -bis(diisopropylphosphino)ferrocene).

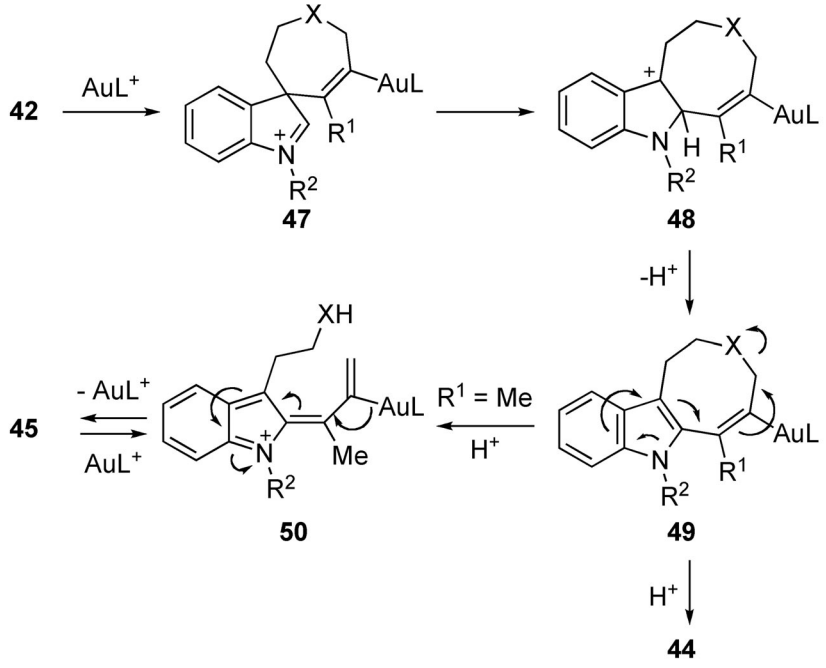
Intramolecular reactions of electron-rich heteroarenes with alkynes

The reaction of substituted indoles **42** with alkynes catalyzed by Au(I) or Au(III) leads to seven- (**43**) and eight-membered rings (**44**), respectively [37] (Scheme 12). Compounds **44** were also obtained in certain cases using Au(I) catalysts. Derivatives **44** are formed in an 8-*endo-dig* process, a type of cyclization that had not been observed before in other hydroarylations of alkynes or cyclizations of enynes. Allenes **45** and tetracyclic compounds **46** were also obtained at longer reactions times by using Au(I)catalysts.

The isolation of a spiro derivative in a gold-catalyzed cyclization [37b] suggests that these reactions of indoles can take place by first forming a C–C bond at C-3 followed by a 1,2-migration to give the final annulated indoles. Thus, the 8-*endo-dig* cyclizations shown in Scheme 12 presumably proceed via spiro derivatives of type **47**, which could be formed directly by a Friedel–Crafts-type reaction or indirectly, by opening of intermediate cyclopropyl gold carbenes (Scheme 13). Proton loss from **48** would give **49**, from which eight-membered ring compounds **44** would be formed. Formation of compounds



Scheme 12 Alternative cyclization in Au(I)- and Au(III)-catalyzed cyclization of alkynes with indoles (X = O, NSO_2R).

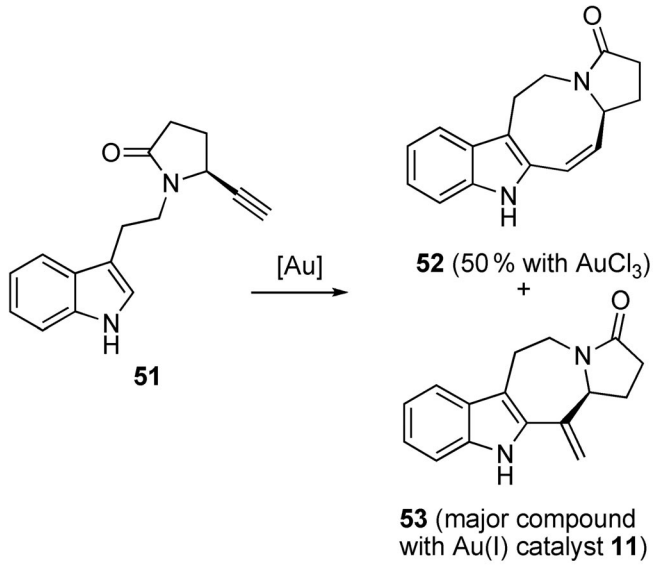


Scheme 13 Mechanism for the Au(I)-catalyzed cyclization of alkynes with indoles.

44 is the major pathway when Au(III) was used as the catalyst. An alternative elimination from **49** would give allenes **45** via cationic intermediate **50**.

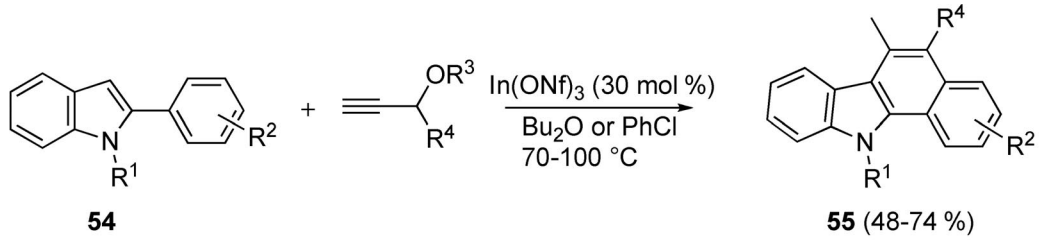
The lundurines are alkaloids with a novel structure characterized by a cyclopropyl moiety embedded within a hexacyclic ring system that includes an 1*H*-azocino[5,4-*b*]indole ring. As part of a project on the synthesis of these alkaloids, the gold-catalyzed cyclization of **51** was studied using different gold catalysts (Scheme 14) [94]. The 8-*endo-dig* cyclization leading to **52** was favored using $AuCl_3$ as

the catalyst, whereas using cationic Au(I) complex **11** (see Fig. 1), the major product formed was **53**, the result of a 7-*exo-dig* process. Related cyclizations of arenes [95] and indoles [96] with allenes catalyzed by gold have also been reported.



Scheme 14 Au(III)-catalyzed cyclization in the synthesis of the tetracyclic core of the lundurines.

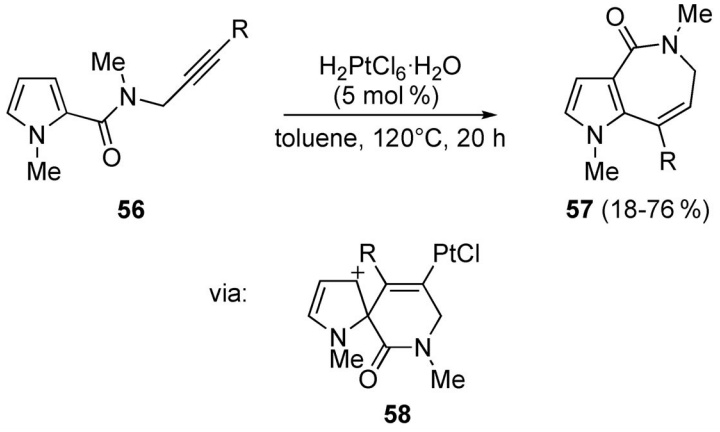
N-propargylindole-2-carboxamides undergo $AuCl_3$-catalyzed cyclization to give β-carbolinones [97]. An annulation 2-arylindoles **54** with propargyl ethers using $In(ONf)_3$ (NfO = nonafluorobutanesulfonate) leads to a concise synthesis of aryl annulated[*a*]carbazoles **55** [98] (Scheme 15). Similar results were obtained using 2-heteroarylindoles as substrates.



Scheme 15 Annulation 2-arylindoles with alkynes catalyzed by In(III).

Cyclization of pyrrole-2-carboxamides **56** with a H_2PtCl_6 give rise to pyrroloazepinones **57** by a 6-*endo-dig* cyclization followed by a rearrangement of the amidocarbonyl group from the 2- to the 3-position of the pyrrole ring [99] (Scheme 16). A similar reaction was observed using $AuCl_3$ as catalyst. The observed rearrangement is consistent with an initial reaction at C-2 to form spiro intermediate **58**, which then expands to form **57**.

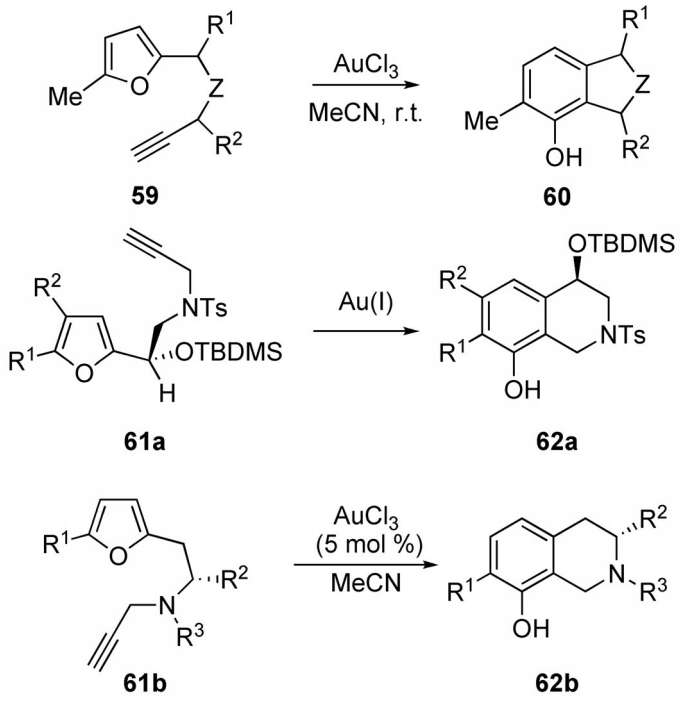
The intermolecular reaction of indoles with alkynes also takes place with Au(I) [37b] or Au(III) catalysts [100]. This reaction can also be carried out with $GaCl_3$ [101] and Pt(II) [102] as catalysts. (*Z*)-Enynols react intermolecularly with indoles in the presence of Au(I) catalysts to form dihydrocyclohepta[*b*]indoles through a Friedel–Crafts/hydroarylation sequence [103]. Homopropargyl alcohols and higher analogs react differently with Au(I) catalysts, forming first a cyclic enol ether, which then



Scheme 16 Platinum-catalyzed cyclization of pyrroles with alkynes.

undergoes a gold-catalyzed addition of indole [104]. Related intermolecular reaction of indoles with alkenes catalyzed by Au(I) have also been described [105]. The intermolecular reaction was also extended to pyrroles [37b]. Interestingly, when the reaction of pyrroles was carried out in the presence of triethylsilane with an In(III) catalyst, products of β-alkylation of the pyrroles were obtained in a regioselective manner [106].

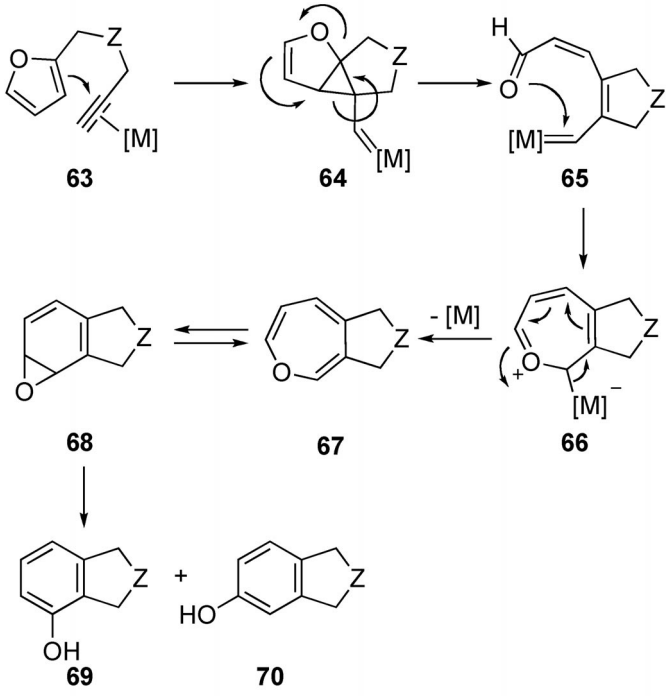
In contrast to the usual Friedel–Crafts-like cyclizations of arenes with alkynes, it was found that alkynyl furans **59** afforded phenols **60** in good to excellent yields by using Au(III) as catalyst [107] (Scheme 17). In addition to Au(III), Au(I), [108], heterogeneous gold [109] and Pt(II) [76,110] can also be used as catalysts for this reaction. Phenols bearing bulky groups at the *ortho* position can also be pre-



Scheme 17 Phenol synthesis by gold-catalyzed cyclization of furans with alkynes.

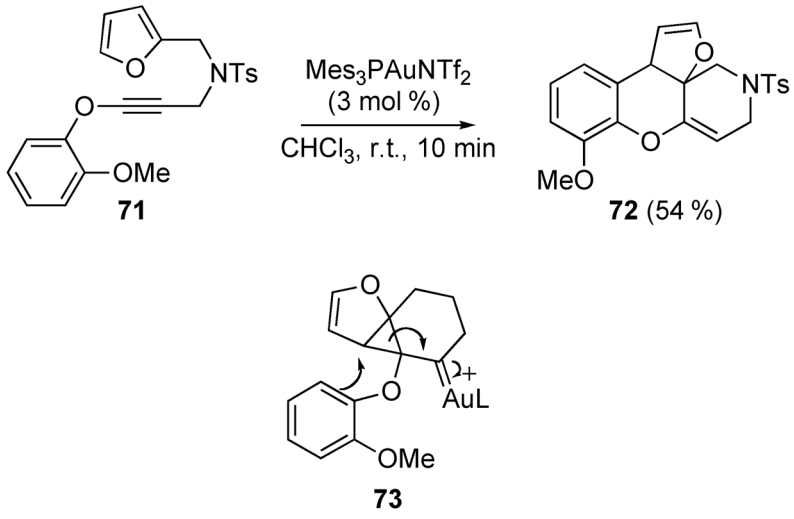
pared by this method [111]. In addition, the gold-catalyzed Michael addition of furans to ethynyl vinyl ketones gives substrates [112–114] that can undergo in situ cyclization leading to hydroxyindanones in a domino process [113]. Enantiomerically enriched substrates **61a,b** bearing a stereocenter in the tether do not suffer racemization during the gold-catalyzed cycloisomerization reaction and provide enantiomerically pure tetrahydroisoquinolines **62a,b** (Scheme 17) [108,115].

Experimental and theoretical studies on the platinum-catalyzed phenol synthesis [76,110], as well as a series of detailed mechanistic studies using gold catalysts [107b,e,f,116,117], suggest that this reaction proceeds by a complex series of reactions summarized in Scheme 18. The reaction starts by the nucleophilic attack of the furan to the (η^2-alkyne)-metal complex **63** to form metal carbene **64**, which is related to the intermediates formed in reactions of enynes with Au(I) or other metal complexes [16f,19,80]. After cleavage of a C–C and C–O bond of the tricyclic intermediate **64**, a second metal carbene **65** is formed, which cyclizes to form **66** and eliminates the metal to give oxepine **67**. Oxepines such **67** are known to be in equilibrium with the corresponding arene oxide **68**. Their opening leads to the formation of phenols **69**, the major compounds of this phenol synthesis, and their regioisomers **70**. Further experimental evidence for this remarkable mechanism was obtained by the NMR detection of both oxepines **67** and arene oxides **68** in the reaction catalyzed by Au(III) complex [107f,g,116,117] and by trapping of the arene oxide intermediate in a Diels–Alder reaction [107f].



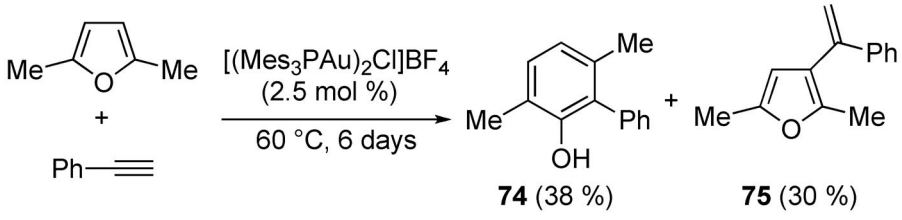
Scheme 18 Mechanism for the gold- or platinum-catalzyed phenol synthesis by cyclization of furans with alkynes.

Furandialkynes lead to the *o*-alkynylphenols that cyclize further in the presence of Au(III) to form benzofurans [118]. Furans containing an ynamide or alkynyl ether moiety in the side chain led to other heterocycles such as chromans, dihydrobenzofurans, dihydroindole, and tetrahydroquinoline derivatives in highly selective reactions [119]. On the other hand, substrates of type **71** with an alkynyl ether moiety undergo furan-yne cyclization to give **72** by a different reaction pathway initiated by an *endo-dig*-cyclization reaction to form **73**, followed by a Friedel–Crafts-type arylation [120] (Scheme 19).



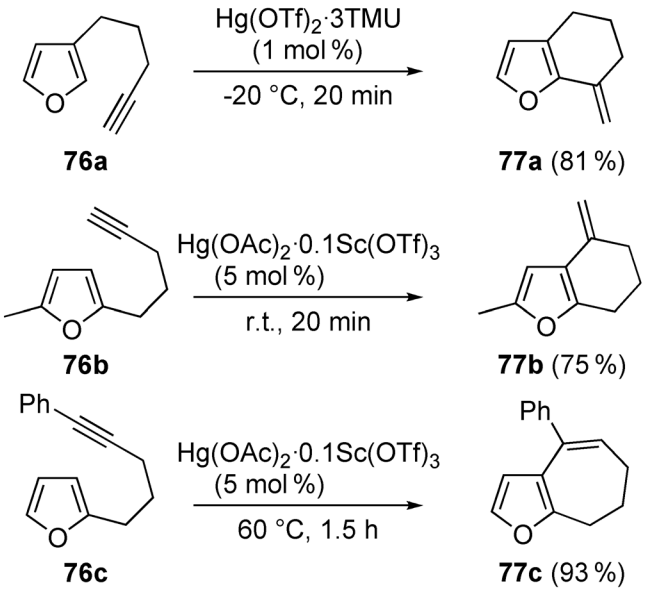
Scheme 19 Gold-catalyzed furan-alkyne-arene cascade cyclization.

Formation of phenol **74** also occurs in the intermolecular reaction of 2,5-dimethylfuran with phenylacetylene [58,121] (Scheme 20). However, this is still not a general process since the reaction is slow, proceeds only in the absence of solvent, and gives **74** in low yield along with furan **75**, the product of a formal Friedel–Crafts-type reaction.



Scheme 20 Gold-catalyzed intermolecular reaction of 2,5-dimethylfuran with phenylacetylene.

In contrast with that observed with gold and platinum in the phenol synthesis, Hg(II) efficiently catalyzes the cyclization of alkynyl furans such as **76a–c** to give products of Friedel–Crafts-type cyclization **77a–c** by 6-*exo*- or 6-*endo-dig* pathways depending on the alkyne substitution [122] (Scheme 21).



Scheme 21 Hg(II)-catalyzed cyclization of furans with alkynes via heterohydroarylation.

SUMMARY AND OUTLOOK

Electrophilic metal-catalyzed reactions of arenes with alkynes follow a Friedel–Crafts-type mechanism leading to the hydroarylation of the alkyne that can also be considered, from another point of view, as an alkenylation of the arene. In general, highly electrophilic gold and platinum complexes have shown the wider applicability in these reactions. In addition, derivatives of Ga(III) and In(III) are also good catalysts for the hydroarylation reaction.

Metal vinylidenes can also be involved as intermediates in certain cases. Interestingly, an intramolecular hydroarylation catalyzed by palladium has been shown to involve a C–H activation, which is similar to that observed for the palladium-catalyzed arylation that gives rise to biaryl systems [123].

Progress on the hydroarylation reaction has led to the development of several methods of broad applicability for the synthesis of rather elaborated molecular architectures in a straightforward manner. Design of more selective electrophilic catalysts based on gold, platinum, or other metals should allow combining this reaction with other C–C bond-forming transformations that could be of broad application in the synthesis of complex molecules.

ACKNOWLEDGMENTS

This work was supported by the MEC (CTQ2007-60745/BQU, Consolider Ingenio 2010, Grant CSD2006-0003), Project PicoInside (FP6-015847), the AGAUR (2009 SGR 47), and the ICIQ Foundation.

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