Gold-Catalyzed Hydroarylation of Alkynes

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Dedicated to Professor Gernot Boche on the occasion of his 65th birthday

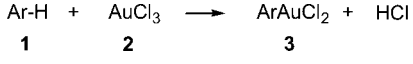
Keywords: Homogeneous catalysis / Gold / Alkynes / Aromatic substitution / C−H Activation

The hydroarylation of aryl-substituted alkynes by substituted electron-rich arenes is catalyzed by $AuCl_3$ activated by such silver salts as $AgSbF_6$. In the case of terminal alkynes, complete regioselectivity in favor of the 1,1-disubstituted olefin is observed. In the case of electron-poor alkynes such as acetylenecarboxylic acid ester, gold(I) complexes such as $[Ph_3PAuCl]$ activated by Ag salts or $BF_3{\cdot}OEt_2$ are the best catalysts, resulting in opposite regioselectivity and high degrees of (Z)-selectivity.

Introduction

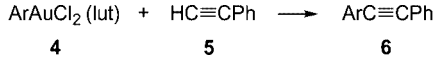
Activation of aromatic C−H bonds followed by C−C bond formation constitutes a conceptionally attractive and potentially environmentally benign methodology because it avoids the otherwise necessary prefunctionalization by means of aromatic halogenation. Although a number of stoichiometric reactions of this kind are known, catalytic systems are rare. Two mechanistically distinct processes have evolved. One is based on chelation-assisted reactions of low-valent metals, prominent examples being Ru^0 or Rh^I insertion into C−H bonds of arenes followed by addition to alkenes.[1] The other type of process is initiated by electrophilic metalation (e.g., palladation) of arenes with formation of arylmetal species which then undergo coupling reactions (e.g., Heck type).[2−4] Moreover, electrophilic metalation may also be involved in some Friedel−Crafts reactions catalyzed by certain metal salts.[5]

We were attracted by old and new reports concerning the ready auration of aromatic compounds **1** by gold(III) salts such as $AuCl_3$ (**2**) with formation of arylgold compounds **3** (Scheme 1).[6]



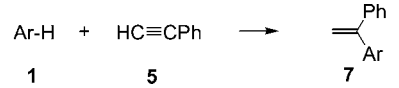
Scheme 1. Auration of arenes by $AuCl_3$

Compounds **3** are actually dimeric in nature and tend to decompose, although isolation in ligand-stabilized monomeric form of the type $[ArAuCl_2(L)]$ (L = PPh_3, SR_2, lutidine, etc.) poses no problems. In what appears to be a potentially useful synthetic transformation, the lutidine adducts **4** were shown to undergo stoichiometric coupling with phenylacetylene (**5**), product **6** being formed in nearly quantitative yield (Scheme 2).[6d]



Scheme 2. The reaction of lutidine-stabilized arylgold complexes **4** with phenylacetylene **5**

Although the mechanism of the reaction was not elucidated, the formation of alkynyl-arylgold(III) intermediates is likely, which then undergo reductive elimination. This would generate Au^I species, which would have to be re-oxidized to Au^{III} in order for a *catalytic* overall process starting from the arene to be possible. Our original goal was to devise such a catalytic cycle by employing appropriate oxidants.[7] However, upon screening several oxidants, appreciable amounts of the desired coupling products were never obtained. Rather, low yields of hydroarylated products **7** were observed in a catalytic reaction (Scheme 3).



Scheme 3. Hydroarylation of phenylacetylene **5**

This type of transformation, which can be viewed as regioselective hydroarylation of alkynes or Friedel−Crafts alkenylation, had previously been reported to be catalyzed by palladium salts,[8] and more recently by Zr, In and Sc triflates.[9] Furthermore, heterogeneous catalysis by zeolites was reported.[10] The yields vary widely according to the

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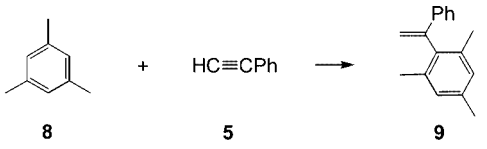
nature of the arene and alkyne. Whereas in the case of Pd^{II}-catalysis arylpalladium species were postulated, the metal triflates were believed to induce a Friedel−Crafts alkenylation. Whatever the mechanism of these reactions may be, a change in valence of the metal is not involved. Therefore, re-oxidation is not relevant.

The aim of the present study was to optimize the Au-catalyzed reaction and to test its scope, which includes the problem of regio- and stereoselectivity as well as the question whether Au^{I} or Au^{III} salts should be used. It should be noted that other types of Au-catalyzed reactions have previously been reported by Ito, Hashmi and others.[11−13] Moreover, Fürstner has described a phenanthrene synthesis by Pt- and Au-catalyzed cycloisomerization reactions.[14a]

Results and Discussion

Terminal Aryl-Substituted Alkynes

Preliminary experiments directed towards optimizing the conditions of the Au^{III}-catalyzed hydroarylation were carried out with mesitylene (**8**) and phenylacetylene (**5**) in nitromethane (Scheme 4). Nitromethane was the solvent of choice because it dissolves $AuCl_3$ and most silver salts.



8 **5** **9**

Scheme 4. Test reaction for the optimization of the hydroarylation of aryl-substituted alkynes

Table 1 shows some remarkable trends. $AuCl_3$ itself leads to poor yields of the desired product **9** (Entry 1). In contrast, activation of $AuCl_3$ via cationization induced by treatment with appropriate silver salts, results in excellent yields. In most cases a small amount of a side product was detected. Although the precise structure was not cleared up, GC-MS analysis showed that the product **9** had undergone a second hydroarylation. Of the four Ag salts tested, $AgSbF_6$ seems to be most efficient. For example, using 5 mol % of $AuCl_3$ in combination with three parts of $AgSbF_6$ at 60 °C for 1 h results in an 88% yield of **9** (Table 1, Entry 8). Further optimization showed that lower amounts of catalyst and co-catalyst can be used, e.g., only 1 mol % of $AuCl_3$ and two parts of $AgSbF_6$ as an activator suffice (Table 1, Entry 12). Interestingly, the use of $AgClO_4$ as a co-catalyst essentially shuts down the reaction (Table 1, Entry 4). Silver salts alone do not catalyze the reaction. In further experiments Au^{I} salts of the type $Ph_3PAuCl/AgBF_4$ turned out to be completely ineffective.

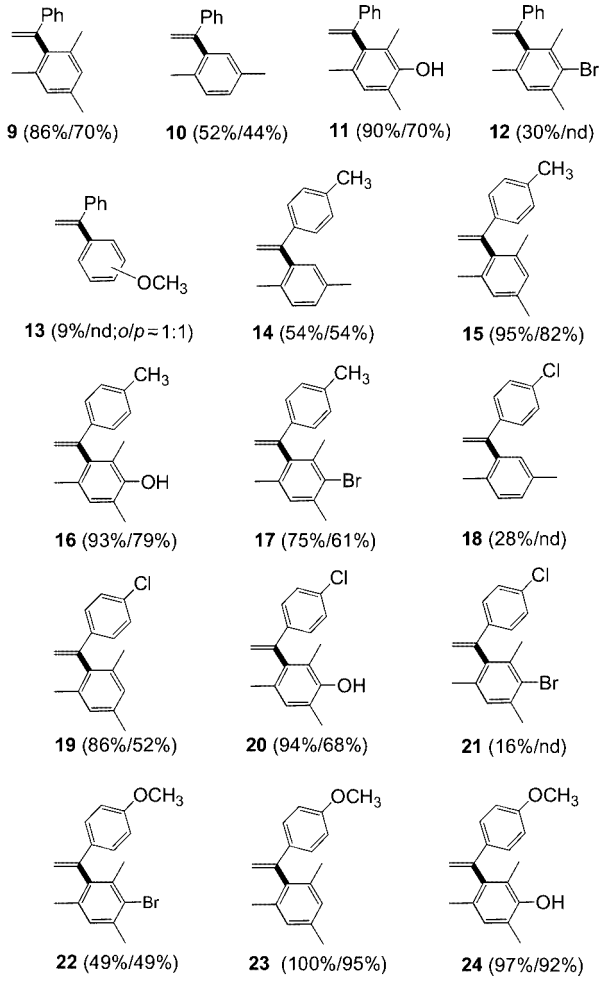
In order to test the scope of the reaction, the arene and alkyne were varied under "standard" conditions employing 1.5 mol % of $AuCl_3$ activated by 3.0 mol % $AgSbF_6$ (10 equiv. arene) at 50 °C for 4 h. Excess arene can be easily recovered after the reaction by distillation or sublimation. The products together with their GC and isolated yields are shown in Scheme 5, the bold-faced bonds indicating the C−C bond formed in the reaction. It can be seen that a variety of arenes react with variously substituted alkynes. The yields appear to be best in the case of alkynes with electron-rich aryl-substituents. In all cases regioselectivity in favor of the 1,1-product was complete.

With electron-rich arenes good to excellent yields are obtained in most cases (e.g., 70% **9** or 95% **23**). Less activated arenes (e.g., bromomesitylene) give acceptable yields in combination with electron rich alkynes (e.g., 61% **17**). Anisole turned out to be a poor substrate (**13**), resulting in the formation of isomer mixtures and low yields. In this case several side products were observed which could not be identified. In most cases small amounts (ca. 5−10%) of a side product were formed, corresponding to compounds containing two alkenyl moieties as indicated by GC-MS analysis. Furthermore, traces (< 5%) of the corresponding acetophenone derivative were observed in most cases due to reaction of the alkyne with traces of water present in the reaction mixture.

Table 1. Au-catalyzed hydroarylation of phenylacetylene **5** by mesitylene **8** in CH_3NO_2

Entry	$AuCl_3$ [mol %]	Co-catalyst (Ag:Au)	Equiv. **8**	Temp. [°C]	Reaction time [h]	Yield **9** [%][a]	Side products [%][a]
1	5	−	2	60	16	20	4
2	5	AgOTf (3)	2	60	16	56	5
3	5	$AgBF_4$ (3)	2	60	16	85	15
4	5	$AgClO_4$ (3)	2	60	16	5	0
5	5	$AgSbF_6$ (3)	2	60	16	85	15
6	5	$AgBF_4$ (3)	4	60	1	84	9
7	5	$AgSbF_6$ (3)	2	60	1	81	16
8	5	$AgSbF_6$ (3)	3	60	1	88	10
9	5	$AgSbF_6$ (3)	4	60	1	88	8
10	1.5	$AgSbF_6$ (2)	10	50	4	86	13
11	1	$AgSbF_6$ (1)	10	50	4	69	19
12	1	$AgSbF_6$ (2)	10	50	4	84	16
13	1.5	$AgBF_4$ (2)	10	50	4	50	<5

[a] Determined by GC using *n*-hexadecane as an internal standard.



Scheme 5. Scope of the hydroarylation reactions with aryl-substituted alkynes. Conditions: 1.5 mol % $AuCl_3$, 3.0 mol % $AgSbF_6$, 10 equiv. arene, CH_3NO_2, 50 °C, 4 h. (GC yield/isolated yield); nd = not determined

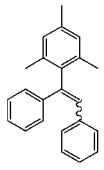
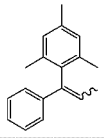
Internal Aryl-Substituted Alkynes

We tested the reaction of mesitylene **8** with diphenylacetylene **25** and 1-phenyl-1-propyne (**26**). The latter alkyne gave the desired product **28** in good yield as a (79:21)-mixture of (*Z*)/(*E*)-isomers (Table 2, Entry 3). Diphenylacetylene **25** showed only very low reactivity, perhaps due to steric hindrance.

Electron-Poor Terminal Alkynes

The results obtained with the terminal aryl-substituted alkynes suggest that electron-donating groups in the *para* position of the phenylalkyne exert a positive effect, the yields being consistently higher in these cases. On this basis we expected acetylenecarboxylic acid ester **29** to be a poor substrate. However, in an initial experiment using mesitylene **8** as the arene and 5 mol % of $AuCl_3/3AgBF_4$ at 60 °C (16 h), product **30** was obtained in 60% yield (GC) as a 3.6:1 *Z*/*E* mixture (Table 3, Entry 1). Under these conditions small amounts of a second alkyne addition product **31** was observed (Scheme 6).

Table 2. Hydroarylation of internal aryl-substituted alkynes with mesitylene **8**[a].

Entry	Alkyne	Time [h]	Product	Yield [%][b] (*Z*:*E*)
1	Ph-C≡C-Ph **25**	4	 **27**	(5) (one isomer, double bond structure not determined)
2	Ph-C≡C-CH_3 **26**	16	 **28**	(81) (70:30)[d]
3[c]	Ph-C≡C-CH_3 **26**	4		79 (79:21)[d]
4[c]	Ph-C≡C-CH_3 **26**	8		(94) (76:24)[d]

[a] Conditions (unless otherwise stated): 1.5 mol % $AuCl_3$, 3.0 mol % $AgSbF_6$, 50 °C, CH_3NO_2, 10 equiv. mesitylene **8**. [b] Isolated yield. Values in parentheses refer to GC-yields, determined with n-hexadecane as an internal standard. [c] 4.5 mol % $AgSbF_6$ employed. [d] Determinded by GC and/or NMR spectroscopy. Isomers were assigned by comparison with literature NMR spectroscopic data.[25]

Obviously regioselectivity of hydroarylation has been completely reversed. The same was observed by Fujiwara using Pd^{II}-catalysts.[8] Since this reaction appeared to be different from the previous ones, we studied it more closely using a variety of gold catalysts under different conditions. It soon became apparent that Au^I salts complexed with appropriate ligands are in fact superior to the use of Au^{III} salts. Therefore, optimization focused on Au^I-catalysts (Table 3).

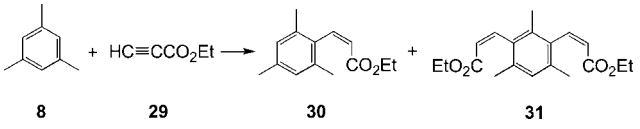
Table 3 shows that several Au^I complexes are effective in catalyzing the regioselective hydroarylation of **29** by mesitylene **8**. Typically, Et_3PAuCl and Ph_3PAuCl function well, nitromethane and 1,2-dichloroethane being the best solvents (Table 3, Entries 3, 4 and 7). In all cases activation by a co-catalyst such as $AgSbF_6$ or the cheaper $BF_3{\cdot}OEt_2$ is necessary. High degrees of (*Z*)-selectivity are observed in almost all cases. Remarkably, the gold(I) complex can be prepared in situ simply by mixing AuCl and equimolar amounts of a phosphorus ligand in nitromethane (Table 3, Entries 15−18). 2-(Dicyclohexylphosphanyl)biphenyl turned out to be the best ligand (Table 3, Entry 17), whereas phosphane ligands with electron-withdrawing groups resulted in low yields (Table 3, Entry 16). Phosphite ligands were also employed successfully (Table 3, Entry 18). Under such conditions product yields of 60−70% are achieved, (*Z*)-selectivity again being the rule. If a large excess of mesitylene **8** is used, yields of 84−95% are reached (Table 3, Entries 19−22). The amount of the gold catalyst can then be lowered to 1 mol %, but $BF_3{\cdot}OEt_2$ must be used in excess (a BF_3:Au ratio of 5:1 turned out to be best). However, due to the low price of $BF_3{\cdot}OEt_2$ this is no significant disadvantage. Control experiments have shown that $BF_3{\cdot}OEt_2$ itself does not catalyze the hydroarylation of **29** by **8**. This observation makes proton catalysis under our reaction conditions unlikely.

On the basis of these promising results other arenes were also tested, although complete optimization was not strived

Table 3. Regioselective hydroarylation of **29** by **8** catalyzed by various gold catalysts

Entry	Au cat. (mol %)	Co cat. (mol %)	Equiv. **8**	Solvent	Temp. [°C]	Time [h]	Yield **30** [%][a] (*Z*:*E*)	Yield **31** [%][a][b]
1	$AuCl_3$ (5)	$AgBF_4$ (15)	3	CH_3NO_2	60	16	60 (78:22)	10
2	Ph_3PAuCl (5)	$AgBF_4$ (5)	3	CH_3NO_2	60	16	57 (>99:1)	17
3	Ph_3PAuCl (5)	$AgBF_4$ (5)	3	CH_3NO_2	60	4	57 (100:0)	16
4	Ph_3PAuCl (5)	$AgBF_4$ (5)	3	1,2-DCE	60	4	56 (100:0)	25
5	Ph_3PAuCl (5)	$AgBF_4$ (5)	3	THF	60	4	0	0
6	Ph_3PAuCl (5)	$AgBF_4$ (5)	3	CH_3CN	60	4	0	0
7	Et_3PAuCl (5)	$AgBF_4$ (5)	3	CH_3NO_2	room temp.	16	65 (100:0)	20
8	Et_3PAuCl (5)	$AgSbF_6$ (5)	3	CH_3NO_2	room temp.	16	67 (>99:1)	20
9	Et_3PAuCl (5)	$AgClO_4$ (5)	3	CH_3NO_2	room temp.	16	27 (100:0)	3
10	Et_3PAuCl (5)	AgOTf (5)	3	CH_3NO_2	room temp.	16	67 (>99:1)	22
11	Et_3PAuCl (5)	$BF_3{\cdot}OEt_2$ (5)	3	CH_3NO_2	room temp.	16	69 (100:0)	21
12	Et_3PAuCl (3)	$BF_3{\cdot}OEt_2$ (3)	3	CH_3NO_2	50	14	66 (100:0)	18
13	Ph_3PAuCl (3)	$BF_3{\cdot}OEt_2$ (3)	3	CH_3NO_2	50	14	62 (100:0)	19
14	AuCl (3)	$BF_3{\cdot}OEt_2$ (3)	3	CH_3NO_2	50	14	14 (100:0)	0
15	AuCl (3)/TPMP[c] (3)[d]	$BF_3{\cdot}OEt_2$ (3)	3	CH_3NO_2	50	14	57 (100:0)	16
16	AuCl (3)/TPTP[e] (3)[d]	$BF_3{\cdot}OEt_2$ (3)	3	CH_3NO_2	50	14	10 (100:0)	0
17	AuCl (3)/DCPB[f] (3)[d]	$BF_3{\cdot}OEt_2$ (3)	3	CH_3NO_2	50	14	71 (100:0)	20
18	AuCl (3)/$(MeO)_3P$ (3)[d]	$BF_3{\cdot}OEt_2$ (3)	3	CH_3NO_2	50	14	62 (99:1)	19
19	Ph_3PAuCl (1)	$BF_3{\cdot}OEt_2$ (5)	10	CH_3NO_2	50	14	84 (100:0)	12
20	Et_3PAuCl (1)	$BF_3{\cdot}OEt_2$ (5)	10	CH_3NO_2	50	14	90 (100:0)	9
21	AuCl (1)/DCPB[f] (1)[d]	$BF_3{\cdot}OEt_2$ (5)	10	CH_3NO_2	50	14	88 (100:0)	9
22	Ph_3PAuCl (1)	$BF_3{\cdot}OEt_2$ (5)	30	CH_3NO_2	50	14	95 (100:0)	5

[a] Determined by GC using *n*-hexadecane as an internal standard. [b] In some cases small amounts (≤ 5%) of a second side product which according to GC-MS analysis contains *three* alkenyl moieties were formed. [c] TPMP = tris(*p*-methoxyphenyl)phosphane. [d] The gold complex was prepared in situ by mixing AuCl and equimolar amounts of the phosphorus ligand. [e] TPTP = tris(*p*-trifluoromethylphenyl)phosphane. [f] DCPB = 2-(dicyclohexylphosphanyl)biphenyl.



Scheme 6. Test reaction for the optimization of the hydroarylation of electron poor alkynes

for in each case. In all cases an excess of the arene was used. Excess arene can be easily recovered after the reaction. Table 4 shows that the best results are obtained in the case of electron-rich arenes, which are highly substituted. In contrast such substrates as toluene or phenol hardly participate in the hydroarylation reaction (Table 4, Entries 4 and 6). Noteworthy are the smooth reactions of furan and 2-methylfuran (Table 4, Entries 7 and 8). Alternative reactions (e.g., Wittig type) give the product **37** mainly as the (*E*)-isomer.[15] The reaction of 2-methylfuran and acetylenecarboxylic acid ester **29** was reported previously to proceed predominantly in a Diels−Alder like manner when using $AlCl_3$ as the Lewis acid.[16] Unfortunately, an inseparable mixture of isomers was obtained with our catalyst system. As a final example of a terminal electron-poor alkyne, 3-butyne-2-one (**39**) was reacted with various arenes using $Ph_3PAuCl/BF_3{\cdot}OEt_2$ as the catalyst system (Scheme 7). Surprisingly, (*E*)-selectivity was observed in all cases (Table 5).

The opposite (*E*)/(*Z*)-selectivity is not due to a change in mechanism. Rather, it is likely that the primary products are in fact (*Z*)-configured but undergo isomerization to the (*E*)-form under the reaction conditions. This was supported by the observation that the (*E*):(*Z*) ratio of product **40** changed from 83:17 to 97:3 upon subjecting the isolated product mixture to the reaction conditions (1 mol % Ph_3PAuCl/5 mol % $BF_3{\cdot}OEt_2$/50 °C/14 h).

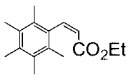
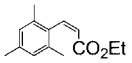
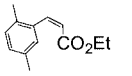
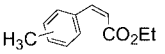
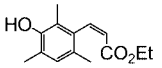
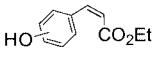
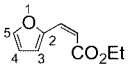
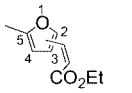
Internal Electron-Poor Alkynes

Unfortunately, internal electron-poor alkynes show essentially no reactivity with the described catalyst system (1 mol % Ph_3PAuCl/5 mol % $BF_3{\cdot}OEt_2$). For example, the reaction of mesitylene (**8**) with acetylene dicarboxylic acid dimethyl ester failed to provide the desired product.

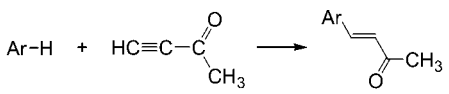
Mechanism

The synthetic results regarding the hydroarylation described herein need to be viewed within the context of other gold-catalyzed nucleophilic addition reactions of alkynes.[17,18] Although cationization of $AuCl_3$ or AuCl complexes by Ag^+ or other Lewis acids is required, auration of the arene as part of the hydroarylation seems unlikely in view of the known stoichiometric reaction of aryl-gold compounds with alkynes, which yields diarylacetylenes.[6d] Thus, we believe that activation of the alkyne by Au-π complexation is involved, as has been postulated for other nucleophilic addition reactions.[17,18] In the case of phenylacetylene (**5**), the π complex undergoes a type of electrophilic aromatic substitution with the electron-rich arene to form an intermediate vinyl-Au species. The simultaneously released H^+ protonates this intermediate, setting free the product **7** as well as re-generating the catalyst (Scheme 8). Regioselectivity is determined by electronic factors.

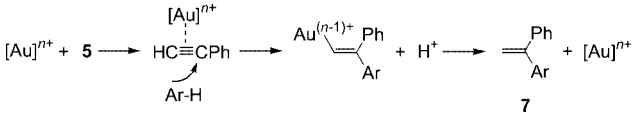
Table 4. Hydroarylation of acetylenecarboxylic acid ester **29** by various arenes[a]

Entry	Arene (equiv.)	Co-catalyst	Time [h]	Temp. [°C]	Product		Yield [%][b] (*Z*:*E*)[c]
1	Pentamethyl-benzene (3)	$BF_3{\cdot}OEt_2$	14	50		**32**	98 (100:0)
2	Mesitylene (30)	$BF_3{\cdot}OEt_2$	14	50		**30**	90 (100:0)
3	*p*-Xylene (15)	$BF_3{\cdot}OEt_2$	14	50		**33**	55 (95:5)
4	Toluene (15)	$BF_3{\cdot}OEt_2$	14	50		**34**	(15) (100:0) *o*:*p* = 60:40
5	2,4,6-Tri-methylphenol (10)	$BF_3{\cdot}OEt_2$	14	50		**35**	83 (100:0)
6	Phenol (3)	$BF_3{\cdot}OEt_2$	14	50		**36**	(0)
7	Furan (20)	$AgSbF_6$	3	40		**37**	82 (>99:1)[d]
8	2-Methylfuran (20)	$AgSbF_6$	4	r.t.		**38a-c**	(80) (*Z*, traces of the *E*-2-isomer are formed) 3 isomers (82:15:3)[c]

[a] Conditions: 1 mol % Ph_3PAuCl, 1 mol % $AgSbF_6$ **or** 5 mol % $BF_3{\cdot}OEt_2$, CH_3NO_2, excess arene. [b] Isolated yields of purified products. GC Yields (determined with *n*-hexadecane as an internal standard) in parentheses[c] Determined by GC or NMR spectroscopy. [d] GC of the crudes product shows minor amounts of two other isomers and side products (according to GC-MS analysis hydroarylation products containing two furyl moieties or (analog to **31**) two alkenyl moieties, respectively). [e] The product consists of 82% (*Z*)-2-isomer **38a**, 15% (*Z*)-4-isomer **38b**, and 3% of a third isomer **38c**, probably the (*Z*)-3-isomer (this isomer was characterized only by GC-MS). Traces of a side product which according to GC-MS analysis contains two methylfuryl moieties are formed.

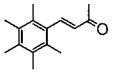
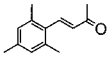
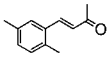
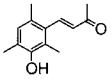


Scheme 7. Hydroarylation of 3-butyn-2-one **39**



Scheme 8. Proposed mechanism for the hydroarylation of phenylacetylene **5**

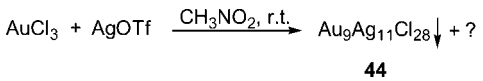
Table 5. Hydroarylation of 3-butyne-2-one **39** by various arenes[a]

Entry	Arene (equiv.)	Time [h]	Product		Yield [%][b] (*Z*:*E*)[c]
1	Pentamethylbenzene (3)	14		**40**	91 (4:96)
2	Pentamethylbenzene (3)	24			(96) (2:98)
3	Mesitylene (3)	14		**41**	78 (3:97)
4	Mesitylene (3)	24			(84) (>2:98)
5	*p*-Xylene (15)	14		**42**	(6) (*E*, traces of the *Z*-isomer are formed)
6	2,4,6-Trimethylphenol (10)	14		**43**	84 (2:98)
7	2,4,6-Trimethylphenol (10)	14			77[d] (>1:99)

[a] Conditions: 1 mol % Ph_3PAuCl, 5 mol % $BF_3{\cdot}OEt_2$, CH_3NO_2, 50 °C, excess arene. [b] Isolated yields of purified products. GC yields (determined with *n*-hexadecane as an internal standard) in parentheses. Side products analog to **31** were not formed (due to the stronger electron-withdrawing effect of a keto- compared to an ester group a second alkenylation of the product does not occur). [c] Determined by GC. [d] After recrystallization

In the case of $AuCl_3$ as the gold compound the exact nature of the catalytic active species is not clear, although it is obviously cationic. However, the reaction of $AuCl_3$ with two equivalents of AgX does not necessarily lead to the formation of "$[AuCl]^{2+}$ $2X^-$" as one might expect. For example, upon reacting $AuCl_3$ with three equivalents of AgOTf, the desired $Au(OTf)_3$ was not formed. It needs to be pointed out that $Au(OTf)_3$ was prepared previously by a different route.[19] Since this procedure is rather complicated (the required starting material $Au(O_3SF)_3$ is prepared in a two step synthesis starting from F_2 and SO_3), we did not test $Au(OTf)_3$ in our reaction. Our own attempts to prepare $Au(OTf)_3$ by reacting $AuCl_3$ with AgOTf failed. Therefore, we examined the precipitate which formed during the reaction more closely (Scheme 9). Instead of the expected formation of AgCl, an orange precipitate was observed, the composition of which was shown by elemental analysis to be "$Au_9Ag_{11}Cl_{28}$" (**44**). Formally, this is a mixture of Au^I and Au^{III} ("$4AuCl_3{\cdot}5AuCl{\cdot}11AgCl$"). In the filtrate triflate ions could be detected by means of IR spectroscopy. In the case of $AgSbF_6$ as the silver compound an orange precipitate was also observed, so that similar processes as in the

triflate case may be involved. Thus, the oxidation state of the active catalyst is not clear. Further attempts to characterize the catalyst failed. However, we do not believe the precipitate formed to be responsible for the catalysis. Rather, cationic gold species $[Au]^{n+}$ in solution are likely to be the catalytically active species.[20]



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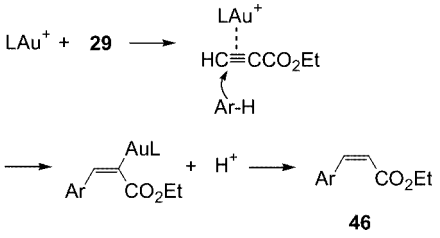
Scheme 9. The reaction of $AuCl_3$ with AgOTf

The described mechanism should lead to the preferential formation of the (*Z*)-isomer in the case of **28**, which is in fact observed. The formation of a mixture of isomers can be explained by isomerization of the initially formed (*Z*)-compound just as it was observed with **40**. An alternative explanation involves the formation of a vinyl-Au cation as an intermediate which could be attacked by an arene from both sides and would thus lead to the formation of a mixture of isomers. However, due to the low stability of vinyl cations this seems rather unlikely.

In the case of the gold(I)-catalyzed reactions of electron-poor alkynes such as **29**, we believe the catalytic active species to be a cationic ligand-stabilized gold(I) complex L-Au^+ **45** as in the previously reported[18] additions of oxygen nucleophiles to alkynes. Gold catalysts are very soft and thus *carbophilic* rather than *oxophilic*. On the basis of this assumption a plausible mechanism for the reaction of acetylenecarboxylic acid ester **29** with arenes can be formulated as shown in Scheme 10.



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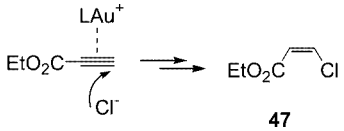
Scheme 10. Proposed mechanism for the hydroarylation of acetylenecarboxylic acid ester **29**

The cationic gold complex coordinates to the alkyne, and nucleophilic attack of the arene from the opposite side leads to the formation of a vinylgold intermediate which is stereospecifically protonated with final formation of the (*Z*)-olefin. Regioselectivity is dominated by electronic factors in a type of gold-catalyzed Michael addition. As mentioned above, the formation of (*E*)-double bonds in case of the ketone is due to isomerization of the initially produced (*Z*)-isomer.

Several NMR experiments were conducted to test these mechanistic assumptions. The ^{31}P NMR spectrum of a sample of Ph_3PAuCl and five equivalents of $BF_3{\cdot}OEt_2$ in CD_3NO_2 shows at 50 °C a sharp signal at $\delta = 32.4$ ppm which is essentially identical to the ^{31}P NMR shift of the pure gold complex. $BF_3{\cdot}OEt_2$ alone thus seems to be not reactive enough to remove the chloride ligand in amounts sufficient to be detected. The situation changes in the presence of acetylenecarboxylic acid ester **29**, which as a soft nucleophile is able to displace the hard chloride in the presence of $BF_3{\cdot}OEt_2$: A sample of Ph_3PAuCl, five equivalents of $BF_3{\cdot}OEt_2$ and five equivalents of **29** in CD_3NO_2 shows at 50 °C a broad signal at $\delta = 31.4$ ppm, probably due to the formation of $[Ph_3P\text{-}Au\text{-}(\mathbf{29})]^+ [ClBF_3]^-$.[21] In the corresponding ^1H NMR spectrum, the slow formation of ethyl (*Z*)-3-chloroprop-2-enoate (**47**) is observed. The proton which is necessary for the formation of this product originates probably from traces of water that are present in the reaction mixture. Unfortunately, we were not able to detect the intermediate vinyl-Au species by NMR spectroscopy. Obviously, when no other nucleophile is present, the gold-alkyne-π complex reacts with a chloride ion, which originates either from $[Cl-BF_3]^-$ or unchanged $Ph_3PAu-Cl$ (Scheme 11).



47

Scheme 11. The formation of **47** in absence of arenes **1**

Activation by silver salts was also examined by means of NMR spectroscopy: A sample of Ph_3PAuCl and one equivalent of $AgSbF_6$ in CD_3NO_2 shows at room temperature a broad peak at $\delta = 29.8$ ppm in the ^{31}P NMR spectrum (Ph_3PAuCl: sharp signal at $\delta = 32.4$ ppm). When five equivalents of the alkyne **29** are added to the same sample, one observes a very small and extremely broad peak at 30−40 ppm, probably due to the formation of $[Ph_3P\text{-}Au\text{-}(\mathbf{29})]^+ [SbF_6]^-$. After addition of 15 equivalents of mesitylene (**8**), a broad peak at $\delta = 31.3$ ppm is observed. In the corresponding ^1H NMR spectrum the signals of the hydroarylation product **30** are visible. These results are fully consistent with our proposed mechanism.

Conclusions

The present study shows that cationic forms of Au^{III}- and Au^{I} complexes catalyze the hydroarylation of aryl-substituted terminal alkynes[22] and of electron-poor alkynes of the type acetylenecarboxylic acid ester, respectively. With electron rich arenes good to excellent yields are obtained in most cases at low catalyst loadings under mild conditions. Previous work[8,9] has shown that other metal catalysts such as Pd-, Pt-, Zr- and Sc salts are also active and in some cases more effective. For example, $Sc(OTf)_3$ catalyzes the addition of benzene to phenylacetylene **5**,[9] whereas Au-catalysis gives a lower yield even with *p*-xylene. However, it should be noted that in the case of the Sc-catalysis much higher catalyst loadings (10 mol %) are necessary. Diphenylacetylene **25** shows almost no reactivity with our catalyst system. In this case, Pd-catalysis is superior.[8a] In the case of the electron-poor alkynes **29** and **39** our results are simi-

lar to or better than the corresponding Pd-/Pt-catalysis. For example, product **32** was obtained in similar yield as in the case of the Pt-catalysis,[8a] but at lower catalyst loadings (1 mol % Au vs. 5 mol % Pt). Moreover, the Pd- and Pt-catalysis needs to be conducted in trifluoroacetic acid, whereas the Au-catalyzed reactions occur under neutral conditions. Aqueous workup and neutralization are not necessary in our protocols. In the case of product **33**, Au-catalysis leads to much better selectivities (*Z*):(*E*) = 95:5 [Au] vs. 67:33 [Pd][8a]). The fact that internal electron poor alkynes such as dimethyl acetylenedicarboxylate fail to give the desired product is a disadvantage of our protocol. In this case, Pd-catalysis is superior, albeit higher catalyst loadings (5 mol %) are necessary.[8a]

Our study shows that cationic gold complexes are extremely useful *soft* and thus *carbophilic* Lewis acids, whereas most "classical" Lewis acids such as $AlCl_3$ or $TiCl_4$ are *hard* (and thus *oxophilic*) electrophiles.[5] This interesting property of gold complexes should lead to new and useful applications in catalysis, which is currently under investigation.

Experimental Section

General Remarks: All gold and silver compounds are commercially available (Aldrich, Lancaster) and were handled under argon but used without further purification. Liquid arenes were distilled from CaH_2 prior to use. Commercially available alkynes (Aldrich, ACROS, Lancaster) were dried (CaH_2 or molecular sieves) and distilled. *p*-Chlorophenylacetylene[23] and *p*-methoxyphenylacetylene[24] were prepared according to literature procedures. All phosphorus ligands are commercially available (Aldrich, STREM) and were used as received. Borontrifluoride−diethyl ether (Aldrich) was distilled in vacuo. Nitromethane (Aldrich, H_2O < 0.03%) was handled under argon but used without further purification. All reactions were conducted in an atmosphere of dry argon. Experiments on a small scale (typically 0.90 mmol) were conducted in rapid parallel screening reactors, and yields were determined by GC using the internal standard method (usually *n*-hexadecane was employed as standard). Larger scale experiments (5.0 or 10 mmol) were conducted in Schlenk flasks, and isolated yields were determined. Isolated compounds were fully characterized (NMR, IR, MS, HRMS and in the cases of new compounds also by elemental analysis).

An inert atmosphere is advisable in order to minimize ketone formation which was observed in the cases of aryl-substituted alkynes.[7] Furthermore, $AuCl_3$ and silver salts are hygroscopic and therefore should be handled under exclusion of moisture. Ph_3PAuCl is perfectly air-stable. However, several experiments showed that an increasing amount of water diminishes the yield in the case of the catalyst system $Ph_3PAuCl/BF_3{\cdot}OEt_2$, probably due to the hydrolysis of the $BF_3{\cdot}OEt_2$. The influence of oxygen was not systematically investigated, but oxygen does not appear to cause any harm. If the reactions are conducted with exposure to air, the yields may be slightly lower due to the above mentioned issues.

General Procedure for the Hydroarylation of Aryl-Substituted Alkynes (Small Scale Experiments). Liquid Arenes: Stock solutions of $AuCl_3$ (c = 0.015 M) and $AgSbF_6$ (c = 0.030 M) in nitromethane were prepared. 0.90 mL of each solution was added to a reaction flask under argon. An orange precipitate was observed. 9.0 mmol arene and 0.90 mmol alkyne (solid alkynes as a concentrated solution in nitromethane) were then added using syringes. The reaction mixture was stirred for 4 h at 50 °C. After cooling, 100 μL of *n*-hexadecane and 2 mL of ethyl acetate were added. An aliquot (ca. 0.5 mL) was taken and filtered through a small plug of silica gel (elution with ethyl acetate). The yield of hydroarylation product was determined by GC. The double bond structure was determined by ^{1}H NMR of the crude product after all volatiles were removed in vacuo.

Solid Arenes: Solid arenes (9.0 mmol) were weighed into the reaction flask with exposure to air. The flask was then evacuated for several minutes and charged with argon (3 ×). 2 mL of nitromethane was added. The Au and Ag solutions and the alkyne (0.90 mmol) were added rapidly, and the reaction mixture was stirred at 50 °C for 4 h. Workup was conducted as described above.

General Procedure for the Hydroarylation of Aryl-Substituted Alkynes (Large-Scale Experiments). Liquid Arenes: 45.5 mg $AuCl_3$ (0.150 mmol) and 103 mg $AgSbF_6$ (0.300 mmol) were weighed into a 100-mL Schlenk flask under argon. 20 mL of nitromethane was added. The arene (100 mmol) and the alkyne (10 mmol; solid alkynes as a concentrated solution in nitromethane) were added, and the reaction mixture was stirred for 4 h at 50 °C. After cooling, the solvent and excess arene were removed in vacuo. The residue was purified by column chromatography (silica gel, hexanes/ethyl acetate). After all volatiles were removed, an oil remained which was further purified by distillation in diffusion pump vacuum (< 10^{-3} mbar).

Solid Arenes (2,4,6-Trimethylphenol): 2,4,6-Trimethylphenol (13.62 g, 100.0 mmol) was weighed into a 100-mL Schlenk flask with exposure to air. The flask was then evacuated for several minutes and charged with argon (3 ×). 20 mL of nitromethane was added. Solutions of 45.5 mg $AuCl_3$ (0.150 mmol) and 103 mg $AgSbF_6$ (0.300 mmol) in 8.0 mL of nitromethane and the alkyne (10 mmol, solid alkynes as a concentrated solution in nitromethane) were added rapidly. The reaction mixture was stirred at 50 °C for 4 h. After cooling, the solvent was removed in vacuo. Excess 2,4,6-trimethylphenol was removed by sublimation in vacuo (ca. 10^{-2} mbar) at 80 °C. The further workup procedure was the same as described above.

Analytical Data: Yields are given in Scheme 5 and Table 2.

1-Mesityl-1-phenylethene (9): Slightly yellow oil; b.p. 66 °C (diffusion pump). NMR ($CDCl_3$, TMS as internal standard): ^{1}H NMR (300.13 MHz): δ = 7.28 −7.19 (m, 5 H, Ph), 6.90 (s, 2 H, mesityl-H), 5.95 (d, J = 1.4 Hz, 1 H, vinyl-H), 5.09 (d, J = 1.4 Hz, vinyl-H), 2.31 (s, 3 H, Me), 2.11 (s, 6 H, 2 × Me) ppm. ^{13}C NMR (75.48 MHz): δ = 146.9, 139.6, 138.2, 136.4, 136.1, 128.4, 128.1, 127.5, 125.8, 114.5, 21.1, 20.1 ppm. IR [vs = very strong; s = strong; m = medium; w = weak]: $\tilde{\nu}$ = 3081 (s), 3056 (s), 3022 (s), 2948 (s), 2917 (s), 1614 (s), 1574 (m), 1493 (vs), 1482 (s), 1445 (vs), 1377 (m), 1028 (s), 902 (vs), 851 (vs), 782 (vs), 710 (vs), 691 (m), 597 (s) 535 (w) cm^{-1}. MS: *m*/*z* (rel. int.) = 222 (48), 207 (100), 192 (59). $C_{17}H_{18}$ (222.33): calcd. 222.140850; found 222.140771 (HRMS).

1-(2,5-Dimethylphenyl)-1-phenylethene (10): Slightly yellow oil; b.p. 55 °C (diffusion pump). NMR ($CDCl_3$, TMS as internal standard): ^{1}H NMR (300.13 MHz): δ = 7.28−7.23 (m, 5 H, Ph), 7.09−7.05 (m, 2 H, *p*-xylyl-H), 7.05−7.02 (m, 1 H, *p*-xylyl-H), 5.75 (d, J = 1.4 Hz, 1 H, vinyl-H), 5.18 (d, J = 1.4 Hz, 1 H, vinyl-H), 2.33 (s, 3 H, Me), 2.01 (s, 3 H, Me) ppm. ^{13}C NMR (75.48 MHz): δ =

149.6, 141.5, 140.7, 135.1, 133.0, 130.7, 130.0, 128.3, 128.1, 127.5, 126.5, 114.7, 20.9, 19.6 ppm. IR: $\tilde{\nu}$ = 3082 (s), 3018 (s), 2971 (s), 2948 (s), 2921 (s), 2864 (m), 1613 (s), 1574 (m), 1493 (vs), 1445 (vs), 1379 (m), 1322 (m), 1028 (s), 900 (vs), 813 (vs), 780 (vs), 703 (vs), 606 (m), 495 (m), 470 (w) cm^{-1}. MS: *m*/*z* (rel. int.) = 208 (44), 193 (100), 178 (51). $C_{16}H_{16}$ (208.30): calcd. 208.125200; found 208.125370 (HRMS).

1-(3-Hydroxy-2,4,6-trimethylphenyl)-1-phenylethene (11): New compound. Yellow oil; b.p. 93 °C (diffusion pump). NMR ($CDCl_3$, TMS as standard): ^1H NMR (300.13 MHz): δ = 7.29−7.22 (m, 5 H, Ph), 6.88 (s, 1 H, Ar-H), 5.97 (d, *J* = 1.5 Hz, vinyl-H), 5.08 (d, *J* = 1.5 Hz, 1 H, vinyl-H), 4.50 (s, 1 H, OH), 2.62 (s, 3 H, Me), 2.06 (s, 3 H, Me), 2.04 (s, 3 H, Me) ppm. ^{13}C NMR (75.48 MHz): δ = 150.1, 147.0, 139.8, 139.5, 129.4, 128.4, 127.8, 127.6, 125.9, 121.6, 121.5, 114.6, 19.5, 15.9, 13.0 ppm. IR: $\tilde{\nu}$ = 3576 (br.,vs), 3082 (s), 3056 (s), 2921 (vs), 2860 (s), 1614 (s), 1599 (m), 1574 (s), 1492 (vs), 1480 (vs), 1462 (vs), 1444 (vs), 1414 (s), 1379 (s), 1296 (s), 1240 (vs), 1187 (vs), 1108 (s), 1077 (w), 1040 (s), 1026 (vs), 904 (vs), 869 (m), 843 (m), 787 (vs), 710 (vs), 689 (s), 664 (m), 568 (m), 536 (w) cm^{-1}. MS: *m*/*z* (rel. int.) = 238 (81), 223 (100), 208 (55). HRMS: calcd. 238.135765; found 238.135648. $C_{17}H_{18}O$ (238.33): calcd. C 85.67, H 7.61; found C 85.75, H 7.69.

1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenylethene (12, not isolated): [Not all products were isolated in pure form. In the cases where only GC yields were determined, the structure of the double bond was determined by ^1H NMR of the crude product. Only the vinyl-H resonances are given.] ^1H NMR of the crude product (300.13 MHz, $CDCl_3$, TMS as standard) [p = pseudo]: δ(vinyl-H) = 5.93 (pd, *J* = 1.2 Hz), 5.02 (pd, 1.2 Hz) ppm. MS (GC/MS): *m*/*z* (rel. int.) = 302 (12), 300 (15), 287 (18), 285 (20), 220 (10), 206 (100). $C_{17}H_{17}Br$ (301.23).

1-(4-Methoxyphenyl)-1-phenylethene and 1-(2-Methoxyphenyl)-1-phenylethene (13a,b not isolated): ^1H NMR of the crude product (300.13 MHz, $CDCl_3$, TMS as standard): δ(vinyl-H) = 5.69 (d, *J* = 1.5 Hz), 5.36 (d, 1.5 Hz), 5.32 (d, 1.5 Hz), 5.29 (d, 1.5 Hz) ppm. MS (GC/MS): *ortho*-Isomer: *m*/*z* (rel. int.) = 210 (17), 195 (100), 167 (67), 165 (33), 152 (18). *para*-Isomer: *m*/*z* (rel. int.) = 210 (100), 195 (69), 167 (19), 165 (22), 152 (17). $C_{15}H_{14}O$ (210.28).

1-(2,5-Dimethylphenyl)-1-(*p*-tolyl)ethene (14): New compound. Slightly yellow oil; b.p. 58 °C (diffusion pump). NMR ($CDCl_3$, TMS as standard): ^1H NMR (300.13 MHz): δ = 7.19−7.14 (m, 2 H, Ar-H), 7.10−7.02 (m, 5 H, Ar-H), 5.71 (pd, *J* = 1.5 Hz, 1 H, vinyl-H), 5.11 (pd, *J* = 1.5 Hz, 1 H, vinyl-H), 2.32 (s, 6 H, 2 × Me), 2.01 (s, 3 H, Me) ppm. ^{13}C NMR (75.48 MHz): δ = 149.3, 141.6, 137.8, 137.3, 135.0, 132.9, 130.6, 129.9, 129.0, 128.1, 126.4, 113.7, 21.1, 20.9, 19.6 ppm. IR: $\tilde{\nu}$ = 3085 (m), 3022 (s), 2921 (vs), 1612 (s), 1567 (w), 1511 (vs), 1498 (s), 1450 (s), 1322 (m), 1305 (m), 1185 (m), 1119 (m), 1039 (m), 1019 (m), 896 (vs), 827 (vs), 811 (vs), 736 (m), 604 (m): 482 (s) cm^{-1}. MS: *m*/*z* (rel. int.) = 222 (39), 207 (100), 192 (66). HRMS: calcd. 222.14085; found 222.140697. $C_{17}H_{18}$ (222.23): calcd. C 91.84, H 8.16; found C 91.69, H 8.24.

1-Mesityl-1-(*p*-tolyl)ethene (15): New compound. Slightly yellow oil; b.p. 79 °C (diffusion pump). NMR ($CDCl_3$, TMS as standard): ^1H NMR (300.13 MHz): δ = 7.16 (d, *J* = 8.2 Hz, 2 H, *p*-tolyl-H), 7.06 (d, *J* = 8.2 Hz, 2 H, *p*-tolyl-H), 6.90 (s, 2 H, mesityl-H), 5.91 (d, *J* = 1.4 Hz, 1 H, vinyl-H), 5.03 (d, *J* = 1.4 Hz, 1 H, vinyl-H), 2.31 (s, 6 H, 2 × Me), 2.11 (s, 6 H, 2 × Me) ppm. ^{13}C NMR (75.48 MHz): δ = 146.6, 138.3, 137.3, 136.7, 136.3, 136.1, 135.8, 129.1, 128.1, 125.7, 21.1, 21.0, 20.1 ppm. IR: $\tilde{\nu}$ = 3083 (m), 3028 (s), 2947 (s), 2918 (vs), 2859 (m), 1619 (s), 1611 (s), 1568 (m), 1511 (vs), 1482 (s), 1439 (s), 1377 (s), 1303 (m), 1176 (m), 1068 (m), 1018 (m), 899 (s), 851 (vs), 826 (vs), 754 (w), 736 (m), 587 (m) cm^{-1}. MS: *m*/*z* (rel. int.) = 236 (42), 221 (100), 206 (65). HRMS: calcd. 236.156500; found 236.156732. $C_{18}H_{20}$ (236.36): calcd. C 91.47, H 8.53; found C 91.35, H 8.47.

1-(3-Hydroxy-2,4,6-trimethylphenyl)-1-(*p*-tolyl)ethene (16): New compound. Highly viscous orange oil; b.p. 110 °C (diffusion pump). NMR ($CDCl_3$, TMS as standard): ^1H NMR (300.13 MHz): δ = 7.17 (pd, *J* = 8.3 Hz, 2 H, *p*-tolyl-H), 7.07 (pd, *J* = 8.3 Hz, 2 H, *p*-tolyl-H), 6.87 (s, 1 H, Ar-H), 5.93 (d, *J* = 1.2 Hz, 1 H, vinyl-H), 5.01 (d, *J* = 1.2 Hz, 1 H, vinyl-H), 4.51 (br. s, 1 H, OH), 2.32 (s, 3 H, Me); 2.26 (s, 3 H, Me), 2.05 (s, 3 H, Me), 2.04 (s, 3 H, Me) ppm. ^{13}C NMR (75.48 MHz): δ = 150.0, 146.7, 140.0, 137.4, 136.6, 129.4, 129.2, 127.8, 125.8, 121.5, 121.4, 113.6, 21.1, 19.5, 15.9, 13.0 ppm. IR: $\tilde{\nu}$ = 3575 (vs, br), 3083 (s), 3008 (s), 2920 (vs), 1618 (s), 1568 (m), 1511 (vs), 1479 (vs), 1461 (vs), 1416 (s), 1378 (s), 1319 (s), 1295 (vs), 1240 (vs), 1190 (vs), 1120 (m), 1103 (s), 1040 (vs), 1018 (vs), 938 (w), 901 (vs), 866 (m), 847 (m), 828 (vs), 737 (m), 656 (m), 558 (m), 455 (w) cm^{-1}. MS: *m*/*z* (rel. int.) = 252 (64), 237 (100), 222 (67). HRMS: calcd. 252.151415; found 252.151676. $C_{18}H_{20}O$ (252.36): calcd. C 85.67, H 7.99; found C 85.70, H 8.10.

1-(3-Bromo-2,4,6-trimethylphenyl)-1-(*p*-tolyl)ethene (17): New compound. Yellow oil; b.p. 104 °C (diffusion pump). NMR ($CDCl_3$, TMS as standard): ^1H NMR (300.13 MHz): δ = 7.15 (d, *J* = 8.4 Hz, 2 H, *p*-tolyl-H), 7.07 (d, *J* = 8.4 Hz, 2 H, *p*-tolyl-H), 6.99 (s, 1 H, Ar-H), 5.93 (d, *J* = 1.2 Hz, 1 H, vinyl-H), 5.00 (d, *J* = 1.2 Hz, 1 H, vinyl-H), 2.42 (s, 3 H, Me); 2.32 (s, 3 H, Me), 2.26 (s, 3 H, Me), 2.01 (s, 3 H, Me) ppm. ^{13}C NMR (75.48 MHz): δ = 146.9, 140.2, 137.7, 136.7, 136.1, 134.9, 129.6, 129.2, 125.7, 125.4, 113.8, 24.0, 21.4, 21.1, 19.9 ppm. In $CDCl_3$ one signal could not be resolved. Therefore, a ^{13}C NMR in [D_6]acetone was measured, too: ^{13}C NMR (75.48 MHz) in [D_6]acetone (δ[(CD_3)$_2$CO] = 29.3): δ = 147.3, 140.7, 138.0, 136.9, 136.3, 135.9, 135.2, 130.1, 129.6, 125.9, 125.4, 113.8, 23.5, 21.1, 20.6, 19.5 ppm. IR: $\tilde{\nu}$ = 3084 (w), 3023 (s), 2949 (s), 2921 (vs), 2859 (m), 1621 (w), 1608 (w), 1566 (w), 1512 (vs), 1451 (vs), 1379 (s), 1316 (w), 1291 (w), 1215 (w), 1186 (m), 1131 (m), 1120 (w), 1071 (m), 1018 (s), 975 (vs), 901 (s), 864 (m), 826 (vs), 736 (w), 563 (w) cm^{-1}. MS: *m*/*z* (rel. int.) = 316 (24), 314 (24), 301 (35), 299 (36), 220 (100). HRMS: calcd. 314.067025; found 314.067310. $C_{18}H_{19}Br$ (315.25): calcd. C 68.58, H 6.08; found C 68.78, H 6.15.

1-(4-Chlorophenyl)-1-(2,5-dimethylphenyl)ethene (18, not isolated): ^1H NMR of the crude product (300.13 MHz, $CDCl_3$, TMS as standard): δ(vinyl-H) = 5.69, (d, *J* = 1.5 Hz), 5.17 (d, 1.5 Hz) ppm. MS (GC-MS): *m*/*z* (rel. int.) = 242 (15), 227 (25), 207 (45), 192 (100). $C_{16}H_{15}Cl$ (242.75).

1-(4-Chlorophenyl)-1-mesitylethene (19): New compound. Slightly yellow oil; b.p. 82 °C (diffusion pump). NMR ($CDCl_3$, TMS as standard): ^1H NMR (300.13 MHz): δ = 7.24−7.17 (m, 4 H, Ar_{Cl}-H), 6.90 (s, 2 H, mesityl-H), 5.93 (d, *J* = 1.2 Hz, 1 H, vinyl-H), 5.10 (d, *J* = 1.2 Hz, 1 H, vinyl-H), 2.31 (s, 3 H, Me), 2.09 (s, 6 H, 2 × Me) ppm. ^{13}C NMR (75.48 MHz): δ = 145.8, 138.0, 137.6, 136.7, 136.0, 133.4, 128.6, 128.2, 127.1, 115.0, 21.0, 20.0 ppm. IR: $\tilde{\nu}$ = 3084 (m), 2948 (vs), 2918 (vs), 2857 (s), 1615 (vs), 1590 (m), 1665 (m), 1490 (vs), 1438 (s), 1395 (s), 1377 (s), 1311 (m), 1291 (m), 1177 (m), 1112 (m), 1093 (vs), 1066 (m), 1032 (w), 1012 (vs), 905 (vs), 852 (vs), 838 (vs), 823 (vs), 755 (m), 738 (m), 721 (m), 615 (w), 564 (m), 460 (m) cm^{-1}. MS: *m*/*z* (rel. int.) = 258 (13), 256 (38), 243 (17), 241 (50), 221 (37), 206 (100). HRMS: calcd. 256.101878; found 256.101935. $C_{17}H_{17}Cl$ (256.77): calcd. C 79.52, H 6.67; found C 79.39, H 6.78.

1-(4-Chlorophenyl)-1-(3-hydroxy-2,4,6-trimethylphenyl)ethene (20): New compound. Viscous orange oil; b.p. 114 °C (diffusion pump).

NMR ($CDCl_3$, TMS as standard): ^1H NMR (300.13 MHz): δ = 7.25−6.87 (m, 4 H, Ar_{Cl}-H), 6.87 (s, 1 H, Ar-H), 5.95 (d, *J* = 1.2 Hz, 1 H, vinyl-H), 5.09 (d, *J* = 1.2 Hz, 1 H, vinyl-H), 4.52 (s, 1 H, OH), 2.26 (s, 3 H, Me), 2.04 (s, 3 H, Me), 2.02 (s, 3 H, Me) ppm. ^{13}C NMR (75.48 MHz): δ = 150.2, 145.9, 139.3, 138.0, 133.4, 129.5, 128.6, 127.7, 127.2, 121.8, 121.4, 115.1, 19.5, 15.9, 13.0 ppm. IR: ṽ = 3588 (vs, br), 3084 (m), 2920 (s), 2860 (m), 1615 (m), 1588 (m), 1490 (vs), 1461 (s), 1396 (s), 1379 (s), 1292 (s), 1243 (s), 1186 (vs), 1114 (s), 1089 (vs), 1040 (s), 1011 (s), 907 (s), 870 (m), 837 (vs), 755 (m), 739 (m), 711 (m), 652 (w), 546 (w), 524 (w), 460 (m) cm^{-1}. MS (DE): *m*/*z* (rel. int.) = 274 (23), 272 (66), 259 (17), 257 (48), 424 (17), 237 (35), 222 (100). HRMS: calcd. 272.096793; found 272.097012. $C_{17}H_{17}ClO$ (272.77): calcd. C 74.86, H 6.28; found C 74.68, H 6.35.

1-(3-Bromo-2,4,6-trimethylphenyl)-1-(4-chlorophenyl)ethene (21, not isolated): ^1H NMR of the crude product (300.13 MHz, $CDCl_3$, TMS as standard): δ(vinyl-H) = 5.86 (br. s), 5.00 (br. s) ppm. MS (GC/MS): *m*/*z* (rel. int.) = 336 (25), 334 (20), 286 (25), 284 (25), 242 (30), 240 (100), 220 (70). $C_{17}H_{16}BrCl$ (335.67).

1-(3-Bromo-2,4,6-trimethylphenyl)-1-(4-methoxyphenyl)ethene (22): New compound. Yellow oil (this product was pure after column chromatography; distillation was not necessary). NMR ($CDCl_3$, TMS as standard): ^1H NMR (300.13 MHz): δ = 7.18 (m, 2 H, Ar_{OMe}-H), 6.99 (s, 1 H, Ar_{Br}-H), 6.80 (m, 2 H, Ar_{OMe}-H), 5.85 (d, *J* = 1.1 Hz, 1 H, vinyl-H), 4.94 (d, *J* = 1.1 Hz, 1 H, vinyl-H), 3.78 (s, 3 H, OMe), 2.42 (s, 3 H, Me), 2.67 (s, 3 H, Me), 2.07 (s, 3 H, Me) ppm. ^{13}C NMR (75.48 MHz): δ = 159.4, 146.4, 140.2, 136.7, 136.1, 134.9, 131.6, 129.6, 127.0, 125.4, 113.8, 112.7, 55.2, 24.0, 21.4, 19.9 ppm. IR: ṽ = 3083 (m), 2999 (s), 2952 (s), 2922 (s), 2834 (s), 1605 (vs), 1573 (m), 1511 (vs), 1462 (vs), 1453 (vs), 1441 (vs), 1379 (m), 1301 (s), 1250 (vs), 1179 (vs), 1132 (m), 1117 (m), 1035 (vs), 975 (s), 897 (m), 83 (vs), 778 (m), 565 (m) cm^{-1}. MS: *m*/*z* (rel. int.) = 332 (29), 330 (29), 317 (44), 315 (45), 236 (100), 220 (14), 193 (16), 118 (21). HRMS: calcd. 330.061940; found 330.061640. $C_{18}H_{19}OBr$ (331.25): calcd. C 65.27, H 5.78; found C 65.76, H 5.85.

1-Mesityl-1-(4-methoxyphenyl)ethene (23): New compound. Yellow oil (this product was pure after column chromatography; distillation was not necessary). NMR ($CDCl_3$, TMS as standard): ^1H NMR (300.13 MHz): δ = 7.22−7.20 (m, 2 H, Ar-H), 6.89 (br. s, 2 H, mesityl-H), 6.81−6.77 (m, 2 H, Ar-H), 5.83 (d, *J* = 1.4 Hz, 1 H, vinyl-H), 4.97 (d, *J* = 1.4 Hz, 1 H, vinyl-H), 3.76 (s, 3 H, MeO), 2.31 (s, 3 H, Me), 2.11 (s, 6 H, 2 × Me) ppm. ^{13}C NMR (75.48 MHz): δ = 159.2, 146.2, 138.4, 136.3, 136.1, 132.2, 128.2, 127.0, 114.2, 112.4, 55.2, 21.0, 20.0 ppm. IR: ṽ = 3082 (m), 2998 (s), 2952 (vs), 2917 (vs), 2857 (m), 2835 (s), 1605 (vs), 1573 (s), 1510 (vs), 1460 (s), 1441 (s), 1376 (s), 1319 (s), 1298 (s), 1287 (s), 1249 (vs), 1183 (s), 1174 (vs), 1128 (m), 1117 (m), 1068 (w), 1035 (vs), 865 (s), 851 (s), 837 (vs), 771 (w), 652 (w), 588 (s), 537 (w) cm^{-1}. MS: *m*/*z* (rel. int.) = 252 (49), 237 (100), 222 (38), 206 (21). HRMS: calcd. 252.151415; found 252.151643 . $C_{18}H_{20}O$ (252.36): calcd. C 85.67, H 7.99; found C 85.52, H 7.84.

1-(3-Hydroxy-2,4,6-trimethylphenyl)-1-(4-methoxyphenyl)ethene (24): New compound. Viscous orange oil (this product was pure after column chromatography; distillation was not necessary). NMR ($CDCl_3$, TMS as standard): ^1H NMR (300.13 MHz): δ = 7.22−7.19 (m, 2 H, Ar_{OMe}-H), 6.87 (br. s, 1 H, Ar-H), 6.82−6.78 (m, 2 H, Ar_{OMe}-H), 5.85 (d, *J* = 1.3 Hz, 1 H, vinyl-H), 4.96 (d, *J* = 1.3 Hz, 1 H, vinyl-H), 4.51 (br. s, 1 H, OH), 3.78 (s, 3 H, OMe), 2.26 (s, 3 H, Me), 2.06 (s, 3 H, Me), 2.04 (s, 3 H, Me) ppm. ^{13}C NMR (75.48 MHz): δ = 159.2, 150.1, 146.3, 140.1, 132.1, 129.4, 127.7, 127.1, 121.5, 121.4, 113.8, 112.5, 55.2, 19.4, 15.9, 12.9 ppm. IR: ṽ = 3504 (s, br), 3003 (s), 2921 (s), 2836 (m),1605 (vs), 1574 (s), 1510 (vs), 1479 (vs), 1462 (vs), 1442 (vs), 1419 (s), 1378 (m), 1300 (vs), 1278 (vs), 1248 (vs), 1177 (vs), 1118 (m), 1104 (s), 1033 (vs), 897 (s), 837 (vs), 810 (s), 762 (m), 749 (m), 643 (m), 563 (m), 535 (m) cm^{-1}. MS: *m*/*z* (rel. int.) = 268 (58), 253 (100), 238 (41), 222 (18). HRMS: calcd. 268.146330; found 268.146394. $C_{18}H_{20}O_2$ (268.36): calcd. C 80.56, H 7.51; found C 80.66, H 7.60.

1-Mesityl-1,2-diphenylethene (27, not isolated): Due to the very low yield, the structure of the double bond was not determined. MS (GC-MS): *m*/*z* (rel. int.) = 298 (100), 283 (30), 268 (15), 207 (45), 192 (50). $C_{23}H_{22}$ (298.43).

(*Z*)- and (*E*)-1-Mesityl-1-phenyl-1-propene (28a,b): Colourless oil. This product was pure after column chromatography; distillation was not necessary. NMR ($CDCl_3$, TMS as standard, *Z*:*E* mixture, 3.7:1).^1H NMR (300.13 MHz; integral intensities are given relative to the (*E*)-vinyl-H (= 1 H); isomers were assigned by comparison with literature NMR spectroscopic data):[25] δ = 7.15 −7.26 [m, 24 H, (*E*,*Z*)-Ph], 6.91 [s, 7.4 H, (*Z*)-mes-H], 6.85 [s, 2 H, (*E*)-mes-H], 6.35 [q, *J* = 6.8 Hz, 3.7 H, (*Z*)-vinyl-H], 5.62 [q, *J* = 7.2 Hz, 1 H, (*E*)-vinyl-H], 2.31 [s, 11 H, mes-Me, (*Z*)-isomer], 2.27 [s, 3 H, mes-Me, (*E*)-isomer], 2.15 [s, 6 H, 2 × mes-Me, (*E*)-isomer], 2.04 [s, 22 H, 2 × mes-Me, (*Z*)-isomer], 1.97 [d, *J* = 7.2 Hz, 3 H, (*E*)-vinylic-Me], 1.52 [d, *J* = 6.8 Hz, 11 H, (*Z*)-vinylic-Me] ppm. ^{13}C NMR (100.61 MHz): δ = 140.9, 140.5, 139.9, 139.5, 139.4, 136.4, 136.3, 136.2, 136.0, 135.6, 129.1, 128.3, 128.2, 128.1, 127.8, 126.6, 126.4, 126.2, 125.5, 123.3, 21.1, 21.0, 20.5, 19.7, 15.4, 15.0 ppm. IR: ṽ = 3021 (s), 2969 (s), 2915 (vs), 2855 (s), 1611 (m), 1597 (m), 1493 (s), 1442 (vs), 1376 (s), 1179 (w), 1077 (w), 1031 (m), 966 (w), 881 (m), 850 (s), 759 (vs), 695 (vs), 618 (m) cm^{-1}. MS (GC-MS): *m*/*z* (rel. int.) = 236 (60), 207 (100), 192 (63), 115 (15). [(*Z*)-isomer; the MS of the (*E*)-isomer is virtually identical.]. $C_{18}H_{20}$ (236.36): calcd. 236.15650; found 236.156389 (HRMS).

General Procedure for the Hydroarylation of 29 by 8 with in situ Prepared Gold Complexes: 6.28 mg AuCl (0.027 mmol) and 0.027 mmol of a (solid) phosphorus ligand were weighed into a reaction flask in air. The flask was evacuated several minutes and charged with argon (3 ×). 2 mL of nitromethane were added. Liquid phosphorus ligands (0.027 mmol) were now added (either with microliter syringes or as stock solutions in nitromethane). Yellow suspensions were obtained which became clear colourless solutions within a few minutes of stirring. 1.0 mL of a stock solution of $BF_3{\cdot}OEt_2$ in nitromethane (*c* = 0.027 M) were added. Finally, 0.38 mL (2.7 mmol) mesitylene **8** and 92 μL (0.90 mmol) acetylenecarboxylic acid ester **29** were added rapidly. The reaction mixture was stirred for 14 h at 50 °C. After cooling, 100 μL of *n*-hexadecane and 2 mL ethyl acetate were added. An aliquot (ca. 0.5 mL) was taken and filtered through a small plug of silica gel (elution with ethyl acetate). The yields of **30** and **31** were determined by GC.

General Procedure for the Hydroarylation of Alkynes 29 and 39 by various Arenes with Ph_3PAuCl under Optimized Conditions (Small-Scale Experiments). Liquid Arenes: 4.45 mg (0.00900 mmol) Ph_3PAuCl were weighed into a reaction flask in air. The flask was then evacuated for several minutes and charged with argon (3 ×). 2.0 mL of nitromethane were added. Now the co-catalyst (either 1.5 mL of a 0.030 M solution of $BF_3{\cdot}OEt_2$ in nitromethane or 0.90 mL of a 0.010 M solution of $AgSbF_6$ in the same solvent) was added. Finally, the flask was charged with the arene (excess) and the alkyne (0.90 mmol). The reaction mixture was stirred at the temperature and for the time given in Table 4 and 5. Workup was conducted as described above.

Solid Arenes: Solid arenes were weighed into the flask in air as well as the gold catalyst. The flask was then evacuated for several minutes and charged with argon (3 ×). 2.0 mL of nitromethane were added. A solution of the co-catalyst and the alkyne was then added. The further procedure was the same as described above for liquid arenes.

General Procedure for the Hydroarylation of Alkynes 29 and 39 by various Arenes with Ph_3PAuCl under Optimized Conditions (Large-Scale Experiments). Liquid Arenes: 24.7 mg Ph_3PAuCl (0.0500 mmol) and (where applicable, see Table 4) 17.2 mg $AgSbF_6$ (0.0500 mmol) were weighed in a 100-mL Schlenk flask under argon. 5.0 mL of nitromethane and (where applicable, see Table 4) 32 μL (0.25 mmol) $BF_3{\cdot}OEt_2$ were added. Now the arene (excess) and alkyne (5.0 mmol) were added rapidly. The reaction mixture was stirred for the time and at the temperature given in the Table 4 and 5. After cooling, the solvent was removed at reduced pressure, and the remaining residue was purified by column chromatography (silica gel, hexanes/ethyl acetate).

Solid Arenes: Solid arenes were weighed into a 100-mL Schlenk flask in air as well as 24.7 mg (0.0500 mmol) of Ph_3PAuCl. The flask was then evacuated for several minutes and charged with argon (3 ×). 20−35 mL nitromethane were added. Finally, 32 μL (0.25 mmol) $BF_3{\cdot}OEt_2$ and the alkyne (5.0 mmol) were added. The reaction mixture was stirred for the time and at the temperature given in the Table 4 and 5. The workup procedure was the same as described above for liquid arenes.

Analytical Data: Yields are given in Table 4 and 5.

Ethyl (*Z*)-3-Mesitylprop-2-enoate (30): Colourless liquid. NMR ($CDCl_3$, TMS as standard): ^{1}H NMR (300.13 MHz): δ = 7.00 (d, *J* = 11.9 Hz, 1 H, vinyl-H), 6.83 (s, 2 H, Ar-H), 6.10 (d, *J* = 11.9 Hz, 1 H, vinyl-H), 4.01 (q, *J* = 7.1 Hz, 2 H, OCH_2), 2.25 (s, 3 H, CH_3), 2.15 (s, 6 H, 2 × CH_3), 1.08 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.48 MHz): δ = 165.4, 144.1, 136.7, 134.5, 133.1, 127.8, 122.8, 59.9; 21.0, 20.1, 14.0 ppm. IR: ṽ = 2980 (m), 1919 (m), 1729 (s), 1715 (vs), 1636 (w), 1612 (w), 1479 (w), 1445 (w), 1384 (w), 1287 (m), 1196 (s), 1172 (s), 1130 (w), 1032 (m), 851 (m), 595 (w) cm^{-1}. MS: *m*/*z* (rel. int.) = 218 (40), 203 (15), 173 (100), 144 (60), 129 (55), 115 (25), 105 (9), 91 (10), 29 (10). $C_{14}H_{18}O_2$ (218.30): calcd. 218.130680; found 218.130913 (HRMS).

Diethyl (*Z*)-3,3′-(2,3,6-Trimethyl-1,3-phenylene)bis(prop-2-enoate) (31): ^{1}H NMR (300.13 MHz): δ = 7.01 (d, *J* = 11.9 Hz, 2 H, vinyl-H), 6.88 (s, 1 H, Ar-H), 6.10 (d, *J* = 11.9 Hz, 2 H, vinyl-H), 4.03 (q, *J* = 7.2 Hz, 4 H, 2 × OCH_2), 2.15 (s, 6 H, 2 × Ar-CH_3), 2.05 (s, 3 H, Ar-CH_3), 1.12 (t, *J* = 7.2 Hz, 6 H, 2 × OCH_2CH_3) ppm. ^{13}C NMR (75.48 MHz): δ = 165.4, 144.4, 133.5, 133.0, 131.0, 128.4, 122.7, 59.9, 20.2, 17.7, 14.0 ppm. MS (GC-MS): *m*/*z* (rel. int.) = 316 (7), 301 (14), 298 (14), 271 (29), 225 (62), 197 (100), 169 (28), 153 (34), 128 (19). $C_{19}H_{24}O_4$ (316.40).

Ethyl (*Z*)-3-(Pentamethylphenyl)propenoate (32): White powder. NMR ($CDCl_3$, TMS as standard): ^{1}H NMR (300.13 MHz): δ = 7.13 (d, *J* = 11.9 Hz, 1 H, vinyl-H), 6.13 (d, 1 H *J* = 11.9 Hz, vinyl-H), 4.02 (q, *J* = 7.1 Hz, 2 H, OCH_2), 2.23 (s, 3 H, CH_3), 2.20 (s, 6 H, 2 × CH_3), 2.14 (s, 6 H, 2 × CH_3), 1.10 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.48 MHz): δ = 165.4, 146.5, 134.0, 133.2, 131.9, 129.8, 122.1, 59.8, 17.6, 16.8, 16.4, 14.0 ppm. IR: ṽ = 2981 (m), 2920 (m), 2870 (m), 1721 (vs), 1632 (s), 1458 (m), 1445 (m), 1383 (m), 1297 (w), 1226 (s), 1184 (vs), 1093 (m), 1059 (w), 1021 (m), 935 (w), 847 (m), 828 (w), 812 (m), 762 (w), 718 (w), 626 (w) cm^{-1}. MS: *m*/*z* (rel. int.) = 246 (88), 231 (69), 203 (57), 201 (100), 186 (23), 172 (70), 157 (64), 143 (31), 128 (19), 115 (12), 105 (5), 91 (8), 77 (8), 29 (10). $C_{16}H_{22}O_2$ (246.35): calcd. 246.161980; found 246.162055 (HRMS).

Ethyl (*Z*)-3-(2,5-Dimethylphenyl)propenoate (33): Colourless oil. NMR ($CDCl_3$, TMS as standard, (17:1)-*Z*:*E* mixture): ^{1}H NMR (400.13 MHz; integral intensities are given relative to (*E*)-vinyl-H (= 1 H]): δ = 7.95 [d, *J* = 15.6 Hz, 1 H, (*E*)-vinyl-H], 7.36 [s, 1 H, (*E*)-Ar−H], 7.12 [s, 17 H, (*Z*)-Ar−H], 6.98−7.10 [m, 53 H, (*E*,*Z*)-Ar-H + (*Z*)-vinyl-H], 7.07 [d, *J* = 12.3 Hz, 17 H, (*Z*)-vinyl-H], 6.35 [d, *J* = 15.6 Hz, 1 H, (*E*)-vinyl-H], 5.99 [d, *J* = 12.3 Hz, 17 H, (*Z*)-vinyl-H], 4.26 [q, *J* = 7.1 Hz, 2 H, (*E*)-OCH_2] 4.08 [q, *J* = 7.1 Hz, 34 H, (*Z*)-OCH_2], 2.38 [s, 3 H, (*E*)-Me], 2.31 [s, 3 H, (*E*)-Me], 2.29 [s, 51 H, (*Z*)-Me], 2.22 [s, 51 H, (*Z*)-Me], 1.33 [t, *J* = 7.1 Hz, 3 H, (*E*)-OCH_2CH_3] 1.13 [t, *J* = 7.1 Hz, 51 H, (*Z*)-OCH_2CH_3] ppm. ^{13}C NMR (100.61 MHz): δ = 167.1, 166.0, 142.9, 142.4, 135.7, 134.9, 134.6, 134.5, 133.2, 132.6, 130.8, 130.7, 129.6, 129.3, 129.1, 127.0, 121.0, 119.0, 60.4, 60.1, 20.9 (br., 2 × Me), 19.4, 19.3, 14.3, 14.0 ppm. IR: ṽ = 2980 (s), 2923 (m), 1227 (vs), 1716 (vs), 1633 (m), 1496 (m), 1446 (m), 1384 (m), 1274 (m), 1177 (vs), 1108 (m), 1240 (m), 1033 (s), 830 (s), 811 (m) cm^{-1}. MS (GC-MS): *m*/*z* (rel. int.) = 204 (27), 189 (13), 161 (21), 160 (12), 159 (100), 131 (44), 130 (60), 115 (40), 91 (22), 29 (9). [(*Z*)-isomer; the MS of the (*E*)-compound is virtually identical]. $C_{13}H_{16}O_2$ (204.27): calcd. 204.115030; found 204.115336 (HRMS).

Ethyl (*Z*)-3-(4-Tolyl)propenoate and Ethyl (*Z*)-3-(2-Tolyl)propenoate (34a,b, not isolated): ^{1}H NMR of the crude product, *ortho*/*para* mixture (1.5:1) [300.13 MHz, $CDCl_3$, TMS as standard, integral intensities are given relative to *para* vinyl-H (= 1 H)]: δ = 7.51 (d, *J* = 7.7 Hz, 2 H, Ar-H *para*-isomer), 7.30 (d, *J* = 7.7 Hz, 2 H, Ar-H *para*-isomer), 7.14−7.24 (m, 6 H, Ar-H *ortho*-isomer), 7.11 (d, *J* = 12.6 Hz, 1.5 H, vinyl-H *ortho*-isomer), 6.88 (d, *J* = 12.9 Hz, 1 H, vinyl-H *para*-isomer), 6.02 (d, *J* = 12.6 Hz, 1.5 H, vinyl-H *ortho*-isomer); 5.88 (d, *J* = 12.9 Hz, 1 H, vinyl-H *para*-isomer), 4.12 (q, *J* = 7.2 Hz, 2 H, OCH_2 *para*-isomer), 4.07 (q, *J* = 7.2 Hz, 3 H, OCH_2 *ortho*-isomer), 2.34 (s, 3 H, Me *para*-isomer), 2.27 (s, 4.5 H, Me *ortho*-isomer), 1.30 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3 *para*-isomer), 1.14 (t, *J* = 7.2 Hz, 4.5 H, OCH_2CH_3 *ortho*-isomer) ppm. MS (GC-MS): *ortho*-Isomer: *m*/*z* (rel. int.) = 190 (10), 175 (10), 145 (100), 115 (95), 91 (30), 65 (20), 29 (15). *para*-Isomer: *m*/*z* (rel. int.) = 190 (50), 175 (5), 162 (15), 145 (100), 115 (65), 91 (25), 65 (20), 29 (10). $C_{12}H_{14}O_2$ (190.24).

Ethyl (*Z*)-3-(3-Hydroxy-2,4,6-trimethylphenyl)propenoate (35): Slightly yellow powder. NMR ($CDCl_3$, TMS as standard): ^{1}H NMR (300.13 MHz): δ = 7.00 (d, *J* = 11.9 Hz, 1 H, vinyl-H), 6.80 (s, 1 H, Ar-H), 6.13 (d, *J* = 11.9 Hz, 1 H, vinyl-H), 4.54 (s, 1 H, OH), 4.04 (q, *J* = 7.1 Hz, 2 H, OCH_2), 2.20 (s, 3 H, CH_3); 2.09 (s, br., 6 H, 2 × CH_3), 1.11 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.48 MHz): δ = 165.4, 149.8, 144.0, 134.3, 129.2, 126.1, 122.8, 121.9, 120.2, 60.0, 19.6, 15.9, 14.0, 13.0 ppm. IR: ṽ = 3480 (s), 2980 (m), 2924 (m), 2867 (w), 1713 (vs), 1636 (m), 1479 (m), 1384 (m), 1299 (m), 1203 (s), 1181 (vs), 1082 (m), 1028 (m), 866 (w), 831 (w) cm^{-1}. MS (DE): *m*/*z* (rel. int.) = 234 (96), 189 (100), 160 (91), 145 (48), 115 (16), 91 (16). $C_{14}H_{18}O_3$ (234.30): calcd. 234.125595; found 234.125419 (HRMS).

Ethyl (*Z*)-3-(2-Furyl)propenoate (37): Colourless liquid which becomes yellow rapidly. NMR ($CDCl_3$, TMS as standard) [The structure of **37** was unequivocally confirmed by COSY and HSQC experiments]: ^{1}H NMR (400.13 MHz): δ = 7.68 (d, $^3J_{3,4}$ = 3.6 Hz, 1 H, furyl-H^3), 7.47 (d, $^3J_{5,4}$ = 1.7 Hz, 1 H, furyl-H^5), 6.78 (d, $^3J_{\beta,\alpha}$ = 12.9 Hz, 1 H, vinyl-H$^\beta$), 6.50 (pdd, 1 H, $^3J_{4,3}$ = 3.6, $^3J_{4,5}$ = 1.7 Hz, furyl-H^4), 5.73 (d, 1 H, $^3J_{\alpha,\beta}$ = 12.9 Hz, vinyl-H$^\alpha$), 4.22 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.31 (t, *J* = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C

(100.62 MHz): δ = 166.0 (*C*O_2Et), 150.9 (furyl-C^2), 143.9 (furyl-C^5), 130.4 (vinyl-C^β), 117.0 (furyl-C^3), 114.4 (vinyl-C^α), 112.6 (furyl-C^4), 60.2 (*C*H_2), 14.3 (*C*H_3) ppm. IR: $\tilde{\nu}$ = 3147 (w), 2982 (w), 1716 (vs), 1626 (s), 1479 (m), 1430 (s), 1374 (m), 1215 (s), 1182 (vs), 1090 (m), 1020 (m), 835 (w), 752 (m), 595 (w) cm^{-1}. MS (GC-MS): *m*/*z* (rel. int.) = 166 (60), 138 (35), 121 (100), 110 (10), 94 (30), 65 (35), 39 (23). $C_9H_{10}O_3$ (166.18): calcd. 166.062995; found 166.062842 (HRMS).

Ethyl (*Z*)-3-[2-(5-Methylfuryl)]propenoate (38a): The different isomers of **38** could not be separated by colomn chromatography, but it was possible to interpret the NMR spectra and thus to assign the different isomers to the GC peaks (except for **38c**). NMR ($CDCl_3$, TMS as standard, assignments were confirmed by means of HSQC): ^{1}H NMR (400.13 MHz): δ = 7.60 (d, *J* = 3.3 Hz, 1 H, furyl-H^3), 6.71 (d, *J* = 12.8 Hz, 1 H, vinyl-H^β), 6.11 (pd, *J* = 3.3 Hz, 1 H, furyl-H^4), 5.64 (d, *J* = 12.8 Hz, 1 H, vinyl-H^α), 4.21 (q, *J* = 7.1 Hz, 2 H, OCH_2), 2.32 (s, 3 H, furyl-CH_3), 1.31 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (100.62 MHz): δ = 166.2 (*C*O_2Et), 154.4 (furyl-C^2 or C^5), 149.6 (furyl-C^5 or C^2), 130.5 (vinyl-C^β), 118.7 (furyl-C^3), 112.6 (vinyl-C^α), 109.3 (furyl-C^4), 60.0 (OCH_2CH_3), 14.3 (OCH_2CH_3), furyl-CH_3) ppm. MS (GC-MS): *m*/*z* (rel. int.) = 180 (57), 152 (23), 135 (100), 108 (19), 77 (24), 43 (53). $C_{10}H_{12}O_3$ (180.20): calcd. 180.078645; found 180.078799 (HRMS).

Ethyl (*Z*)-3-[4-(5-Methylfuryl)]propenoate (38b): ^{1}H NMR (400.13 MHz): δ = 7.24 (d, *J* = 2.0 Hz, 1 H, furyl-H), 7.22 (d, *J* = 2.0 Hz, 1 H, furyl-H), 6.67 (d, *J* = 12.5 Hz, 1 H, vinyl-H^β), 5.71 (d, *J* = 12.5 Hz, 1 H, vinyl-H^α), 4.20 (q, *J* = 7.1 Hz, 2 H, OCH_2), 2.34 (s, 3 H, furyl-CH_3), 1.30 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3) ppm. It was not possible to assign all ^{13}C NMR peaks undoubtedly to certain isomers, thus only the ^{1}H NMR spectroscopic data are given. MS (GC-MS): *m*/*z* (rel. int.) = 180 (93), 151 (31), 135 (100), 77 (66), 43 (85). $C_{10}H_{12}O_3$ (180.20).

Ethyl (*Z*)-3-[3-(5-Methylfuryl)]propenoate (38c): Since only traces of this isomer were formed, we were not able to obtain NMR spectroscopic data for **38c**. Thus, it was not possible to determine the structure of **38c** beyond doubt. However, in view of the structures of **38a** and **38b**, it is likely that this compound is the isomer Ethyl (*Z*)-[3-(5-methylfuryl)]propenoate. MS (GC-MS): *m*/*z* (rel. int.) = 180 (56), 136 (35), 107 (100), 77 (30). $C_{10}H_{12}O_3$ (180.20).

(*E*)-4-(Pentamethylphenyl)-3-buten-2-one (40): Slightly yellow powder. NMR ($CDCl_3$, TMS as standard): ^{1}H NMR (300.13 MHz): δ = 7.73 (d, *J* = 16.6 Hz, 1 H, vinyl-H), 6.15 (d, 1 H *J* = 16.6 Hz, vinyl-H), 2.40 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.28 (s, 6 H, 2 × CH_3), 2.22 (s, 6 H, 2 × CH_3) ppm. ^{13}C NMR (75.48 MHz): δ = 198.4, 145.1, 135.4, 133.9, 132.9, 132.7, 131.1, 27.4, 18.0, 16.9, 16.5 ppm. ^{1}H NMR (300.13 MHz, (*Z*)-Isomer): (The vinyl-H signals are given only): δ = 7.19 (d, *J* = 12.5 Hz, 1 H, vinyl-H), 6.30 (d, *J* = 12.5 Hz, 1 H, vinyl-H) ppm. IR: $\tilde{\nu}$ = 3033 (w), 1297 (w), 2921 (m), 1670 (s), 1617 (s), 1444 (m), 1360 (s), 1253 (s), 1231 (m), 1062 (w), 981 (s), 602 (w), 531 (m) cm^{-1}. MS: *m*/*z* (rel. int.) = 216 (13), 201 (100), 186 (7), 157 (13), 43 (9). $C_{15}H_{20}O$ (216.32): calcd. 216.151415; found 216.151587 (HRMS).

(*E*)-4-(Mesityl)-3-buten-2-one (41): Yellow powder. NMR ($CDCl_3$, TMS as standard): ^{1}H NMR (300.13 MHz): δ = 7.67 (d, *J* = 16.6 Hz, 1 H, vinyl-H), 6.90 (s, 1 H, Ar-H), 6.33 (d, *J* = 16.6 Hz, 1 H, vinyl-H), 2.38 (s, 3 H, CH_3), 2.33 (s, 6 H, 2 × CH_3), 2.29 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.48 MHz): δ = 198.5, 142.0, 138.5, 136.8, 132.4, 130.9, 129.3, 27.4, 21.1, 21.0 ppm. ^{1}H NMR (300.13 MHz, (*Z*)-isomer): δ = 7.05 (d, *J* = 12.5 Hz, 1 H, vinyl-H), 6.27 (d, *J* = 12.5 Hz, 1 H, vinyl-H) ppm. IR: $\tilde{\nu}$ = 3006 (w), 2966 (w), 2918 (w), 2861 (w), 1682 (s), 1661 (w), 1628 (m), 1611 (vs), 1567 (m), 1481 (m), 1458 (m), 1380 (w), 1354 (m), 1313 (m), 1290 (m), 1253 (m), 1178 (m), 1145 (w), 1035 (w), 1003 (m), 974 (m), 906 (w), 858 (m), 722 (w), 600 (m), 577 (m), 514 (w) cm^{-1}. MS: *m*/*z* (rel. int.) = 188 (10), 173 (100), 145 (10), 129 (12). $C_{13}H_{16}O$ (188.27): calcd. 188.120115; found 188.120003 (HRMS).

(*E*)-4-(2,5-Dimethylphenyl)-3-buten-2-one (42, not isolated): ^{1}H NMR of the crude product (300.13 MHz, $CDCl_3$, TMS as standard): δ = 7.78 (d, *J* = 16.2 Hz, 1 H, vinyl-H), 7.06−7.12 (m, 3 H, Ar-H), 6.63 (d, *J* = 16.2 Hz, 1 H, vinyl-H), 2.38 (s, 3 H, Me), 2.35 (s, 3 H, Me), 2.31 (s, 3 H, Me) ppm. MS (GC-MS): *m*/*z* (rel. int.) = 174 (15), 159 (100), 131 (15), 91 (10), 43 (5). $C_{12}H_{14}O$ (174.24).

(*E*)-4-(3-Hydroxy-2,4,6-trimethylphenyl)-3-buten-2-one (43): New compound. Dark yellow needles; m.p. (hexanes/chloroform) 141−142 °C. NMR ($CDCl_3$, TMS as standard): ^{1}H NMR (300.13 MHz): δ = 7.64 (d, *J* = 16.6 Hz, 1 H, vinyl-H), 6.86 (s, 1 H, Ar-H), 6.26 (d, *J* = 16.6 Hz, 1 H, vinyl-H), 4.78 (s, 1 H, OH), 2.39 (s, 3 H, CH_3), 2.24 (s, 9 H, 3 × CH_3) ppm. ^{13}C NMR (75.48 MHz): δ = 198.6, 150.5, 142.5, 133.1, 132.8, 130.1, 128.1, 123.6, 121.8, 27.4, 20.3, 16.0, 13.3 ppm. IR: $\tilde{\nu}$ = 3386 (s), 2964 (w), 2923 (w), 1655 (s), 1634 (s), 1618 (s), 1477 (w), 1458 (w), 1410 (m), 1384 (w), 1366 (m), 1266 (s), 1225 (s), 1203 (m), 1108 (m), 1025 (w), 1009 (m), 994 (m), 867 (w), 742 (w) cm^{-1}. MS: *m*/*z* (rel. int.) = 204 (32), 189 (100), 174 (11), 160 (17), 145 (20). HRMS: calcd. 204.115030; found 204.115259. $C_{13}H_{16}O_2$ (204.27): calcd. C 76.44, H 7.90; found C 76.32, H 7.82.

Reaction of $AuCl_3$ with AgOTf to give "$Au_9Ag_{11}Cl_{28}$" (44): 200 mg $AuCl_3$ (0.659 mmol) were dissolved in 6.0 mL CH_3NO_2 under Ar to give a yellow solution. A solution of 169 mg (0.659 mmol) AgOTf in 14 mL CH_3NO_2 was added all at once. An orange precipitate formed immediately. The suspension was stirred 14 h under exclusion of light. The precipitate was filtered under Ar and washed with 5 mL CH_3NO_2 and 3 × with 5 mL pentane. The product was dried in vacuo (14 h) to give 102.3 mg of an orange powder (**44**). A cloudy filtrate was obtained. All volatiles were removed, and the remaining residue was dried in vacuo (14 h). A light brown oily product was obtained, the IR spectrum of which indicated the presence of triflate, but showed a band structure different from that of AgOTf.

$Ag_{11}Au_9Cl_{28}$ (3951.90): calcd. Au 44.86, Ag 30.03, Cl 25.12; found Au 44.98, Ag 29.72, Cl 25.06.

Ethyl (*Z*)-3-Chloropropenoate (47): An authentic sample of **47** was prepared by esterification of the corresponding carboxylic acid with ethanol according to a standard protocol.[26] The authentic sample showed identical NMR shifts, the same GC retention time and mass spectrum as the compound observed in the described mechanistic experiment. NMR ($CDCl_3$, TMS as standard): ^{1}H NMR (300.13 MHz): δ = 6.71 (d, *J* = 8.2 Hz, 1 H, vinyl-H), 6.19 (d, *J* = 8.2 Hz, 1 H, vinyl-H), 4.24 (q, *J* = 7.1 Hz, 2 H, OCH_2), 1.31 (t, *J* = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.48 MHz): δ = 163.5, 132.4, 121.5, 60.7, 14.2 ppm. MS (GC-MS): *m*/*z* (rel. int.) = 134 (0.1), 119 (2), 109 (2), 99 (42), 91 (35), 89 (100), 61 (16). $C_5H_7ClO_2$ (134.56).

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