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# Heterogeneous Au and Rh catalysts for cycloisomerization reactions of γ-acetylenic carboxylic acids\*

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Abstract: Au- and Rh-based heterogeneized catalytic systems have been prepared and analyzed. Their efficiency has been evaluated for the cycloisomerization of  $\gamma$ -acetylenic carboxylic acids leading to valuable  $\gamma$ -alkylidene  $\gamma$ -butyrolactones. Bulk AuO<sub>3</sub> was found to be a valuable and easy-to-handle catalyst for selective transformations, whereas [C<sub>6</sub>mim][AuCl<sub>4</sub>] presented a high activity and Au/ $\beta$ -zeolite was recyclable.

Keywords: catalysis; cycloisomerization; gold; particle synthesis; rhodium.

## INTRODUCTION

Addition of hydrogen-heteroatom nucleophiles across the C–C triple bond of an alkyne function represents a major entry to heteroatom-substituted alkenes and as such has been the subject of a large variety of investigations. Among other methodologies, transition-metal-catalyzed processes have attracted constant interest due to their superior ability to control the stereoselectivity of the addition process [1].

The intramolecular reaction (the heteroannulation reaction) has been extensively studied as it represents one of the best and straightforward ways to obtain N- and O-containing heterocycles. From the synthetic point of view, these cycloisomerization reactions can be performed with 100 % atom efficiency, in agreement with the 12 principle of green chemistry [2]. Among O-containing heterocycles,  $\gamma$ -alkylidene  $\gamma$ -butyrolactones represent an important family of enol esters due to the presence of this moiety in a number of natural products of biological relevance [3–5] and in synthetic intermediates with applications in pharmaceuticals [6]. Earlier on, Ag [5a,5b,7], Hg [5c,8], Pd [4,5c,9], Ru [10], and Rh [11] complexes have demonstrated interesting catalytic activities. Recently, Pd- and Ni-containing clusters [12] have also been reported to exhibit high catalytic activities. However, most reported catalytic systems developed so far suffer from low activities, toxicity concerns, poor selectivities, and poor functionality compatibility. Consequently, the search for new efficient catalysts constitutes an area of active investigations.

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### Au- AND Rh-CATALYZED CYCLOISOMERIZATION REACTIONS

During the last decade, homogeneous Au catalysis has appeared as a new class of carbophilic Lewis acids [13,14]. The ability of these species to coordinate C–C multiple bond in an  $\eta^2$ -fashion allows a high level of activation of the unsaturation toward *anti* attack of a variety of C- and heteroatom-based nucleophiles [14]. Following our initial investigation regarding the intramolecular addition of diols to alkynes to form cyclic acetals [15], we introduced Au(I) chloride and Au(II) chloride [16] as an active catalyst for the cyclization of functionalized 4-alkynoic acids to  $\gamma$ -alkylidene  $\gamma$ -butyrolactones. Later on, Pale et al. proposed a modified system based on a combination of AuCl and an inorganic base (K<sub>2</sub>CO<sub>3</sub>) to promote the cyclization of unfunctionalized acetylenic acids [17]. Besides the extremely mild reaction conditions and the use of commercially available Au sources, these methodologies suffer from some drawbacks: (1) hydration resulting from the intermolecular addition of water becomes competitive for unsubstituted substrates [18], (2) the employment of a base is not compatible with the use of base-sensitive functionalities, and (3) low levels of regioselectivities are observed for internal alkynes (5-*exo* vs. 6-*endo* modes of cyclization observed).

These drawbacks along with the low metal-to-substrate ratio observed for the AuCl and AuCl/K<sub>2</sub>CO<sub>3</sub> systems (i.e., TON = 8–10) still do not fit the 12 principles of green chemistry [2]. All these considerations induced us to find new catalysts offering higher activities, higher selectivities, and better substrate scope. As a consequence, we embarked on a study of a variety of commercially available Lewis acid salts (Table 1) [19]. In order to develop an efficient system, we have first tested several transition-metal salts in cyclization of phenyl-substituted substrate **1a** (Table 1) under homogeneous conditions.

//	Ph _ CO <sub>2</sub> H CH	mol % [cat] → → →		Ph CO <sub>2</sub> H
	1a		2a	3a
Entry	Catalyst (cat)	Conversion (%)	Ratio <b>2a/3a</b> <sup>b</sup> (%)	Yield <sup>c</sup> (%)
1	None	0	_	_
2	AuCl	100	60/40	n.i.
3	AuCl <sub>3</sub>	100 <sup>d</sup>	n.d.	_
4	IrCl <sub>3</sub>	0	_	_
5	RuČl <sub>3</sub>	3	100/0	n.i.
6	RhCl <sub>3</sub>	3	100/0	n.i.
7	InCl <sub>3</sub>	7	100/0	n.i.
8	$PtCl_2$	100	100/0	81
9 <sup>e</sup>	[Ir(COD)Cl] <sub>2</sub>	100	100/0	92
10	KAuCl <sub>4</sub>	100	0/100	98
11	$Sc(OTf)_3$	4	100/0	n.i.
12	HCl	0	-	-

Table 1 Homogeneous catalysts screening for the cyclization of 1a.<sup>a</sup>

<sup>a</sup>Reaction conditions: Substrate **1a** stirred at room temperature for 3 h in the presence of 5 mol % catalyst in CH<sub>3</sub>CN (1 mol/l).

<sup>b</sup>Product ratio **2a/3a** determined on the basis of <sup>1</sup>H NMR spectra.

<sup>c</sup>Isolated yields correspond to analytically pure samples upon filtration on a pad of silica gel and evaporation of the solvents,

<sup>d</sup>Decomposition.

e2.5 mol %. n.d.: not determined. n.i.: not isolated.

It is noteworthy that the best results in terms of conversion were obtained with late carbophilic transition metals such as Au, Ir, Pt (entries 2, 8, 9). Competition between intermolecular addition of water leading to product **3a** and intramolecular addition of the carboxylic acid function leading to lactone **2a** is observed for AuCl catalyst (Table 1, entry 2), while the use of KAuCl<sub>4</sub> led selectively to product **3a** (Table 1, entry 10). It must be outlined that three of the best catalysts {[Ir(cod)Cl]<sub>2</sub>, PtCl<sub>2</sub>, and AuCl<sub>3</sub>} have the same electronic structure [ $6s^25d^6$ ]. An interesting behavior is given by Ir chlorides; IrCl<sub>3</sub> is inactive for this reaction, while [Ir(cod)Cl]<sub>2</sub> presents excellent results in terms of conversion and selectivity (Table 1, entries 4, 9). An oxygen nucleophile-compatible early Lewis acid [Sc(OTf)<sub>3</sub>] and a Brønsted acid (HCl) gave equally poor results (Table 1, entries 11, 12).

To upgrade the activity of late transition-metal catalysts, we made the hypothesis that metal oxides exhibiting both Lewis acid and Lewis base character should provide an interesting combination in view of previous observations regarding Au catalysis [20]. Up-to-date reports of heterogeneous systems have been limited to bulk HgO [7a,7h,8b,9a,11b]. All heterogeneous catalysts tested showed a high level of chemo- and regioselectivity (Table 2).

Ph - CO <sub>2</sub> H C	5 mol % [cat]	Ph 0 + $0$	Ph CO <sub>2</sub> H
1a		2a	3a
Catalyst (cat)	Conversion (%)	Ratio <b>2a/3a</b> <sup>b</sup> (%)	Yield <sup>c</sup> (%)
Au <sub>2</sub> O <sub>3</sub>	100	100/0	95
$Pt\tilde{O_2}$	15	100/0	n.i.
$Ag_2O$	80	100/0	n.i.
HgÕ	100	100/0	89
Au <sub>2</sub> O <sub>3</sub>	100	100/0	92
	$\begin{array}{c} \begin{array}{c} Ph \\ CO_2H \\ \end{array} \\ \hline \\ \hline$	$\begin{array}{c} \begin{array}{c} & \begin{array}{c} 5 \text{ mol } \% \text{ [cat]} \\ \hline \\ CO_2 H \end{array} & \begin{array}{c} \hline \\ CH_3 CN, RT, 2h \end{array} \end{array}$	$\begin{array}{c} \begin{array}{c} & \begin{array}{c} 5 \text{ mol } \% \text{ [cat]} \\ \hline CO_2H \end{array} & \begin{array}{c} 5 \text{ mol } \% \text{ [cat]} \\ \hline CH_3CN, \text{ RT, 2h} \end{array} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} Ph \\ \hline \\ \hline \\ \end{array} & \begin{array}{c} \end{array} & \begin{array}{c} \end{array} \\ \hline \end{array} \\ \hline \begin{array}{c} 1a \end{array} & \begin{array}{c} 2a \end{array} \\ \hline \end{array} \\ \hline \end{array} \\ \hline \begin{array}{c} 1a \end{array} & \begin{array}{c} 2a \end{array} \\ \hline \end{array} \\ \hline \begin{array}{c} Catalyst (cat) \end{array} & \begin{array}{c} Conversion (\%) \\ Ratio \\ 2a/3a^b (\%) \end{array} \\ \hline \begin{array}{c} Au_2O_3 \\ PtO_2 \\ PtO_2 \\ Ag_2O \\ Ag_2O \\ HgO \\ HgO \\ Au_2O_3 \end{array} & \begin{array}{c} 100 \\ 100/0 \\ 100/0 \\ HgO \\ Au_2O_3 \end{array} & \begin{array}{c} 100 \\ 100 \end{array} \\ \hline \end{array} $

Table 2 Heterogeneous catalysts screening for the cyclization of 1a.<sup>a</sup>

<sup>a</sup>Reaction conditions: Substrate **1a** stirred at room temperature for 3 h in the presence of 5 mol % catalyst in CH<sub>3</sub>CN (1 mol/l).

<sup>b</sup>Product ratio 2a/3a determined on the basis of <sup>1</sup>H NMR spectra.

<sup>c</sup>Isolated yields correspond to analytically pure samples upon filtration on a pad of

silica gel and evaporation of the solvents.

<sup>d</sup>2.5 mol %.

<sup>e</sup>CH<sub>3</sub>CN/H<sub>2</sub>O 6/1 as solvent. n.i.: not isolated.

The best activities are obtained for HgO and  $Au_2O_3$  (Table 2, entries 1, 4), Au oxide being obviously preferred due to toxicity constraint. The only product observed was butyrolactone **2a** in 92 % isolated yield [19]. No competition resulting from the intermolecular addition of water is observed with this catalyst. A test experiment conducted in an acetonitrile/water (6/1) mixture highlighted the complete absence of reactivity of  $Au_2O_3$  for alkyne hydration reaction (Table 2, entry 5). Several substrates (some examples, **1b–h**, are presented in Scheme 1) have been tested in the presence of the  $Au_2O_3$  catalyst and have been obtained in excellent yields (79–99 %). In sharp contrast with AuCl reacting under homogeneous conditions,  $Au_2O_3$  is allowing the cyclization of both substituted and unsubstituted acetylenic acids under heterogeneous conditions and exclusive 5-*exo* mode of cyclization was observed for internal alkynes [19]. Au oxide catalyst  $Au_2O_3$  also showed high activities and high substrate-to-catalyst ratios (up to 1000 on a specific substrate under neat conditions [19]).



Scheme 1 Cyclization of various  $\gamma$ -acetylenic carboxylic acids.

In the meantime, we also decided to focus our attention on other heterogeneous systems, which would be suitable for recycling purpose. In a first step, we investigated the synthesis of a recyclable basic Rh heterogeneous catalyst, designed as an immobilized Rh(TPPTS)<sub>3</sub>Cl complex (TPPTS-3,3',3"-phosphanetriyl benzenesulfonic acid) onto two Zn<sub>2</sub>Al and Zn<sub>2</sub>Ga basic layered double hydroxides (LDHs). The immobilization of the Rh complex by ionic exchange was accomplished with success for both LDHs [21]. The catalyst structures and the chemical composition were confirmed by X-ray diffraction (XRD) analysis, X-ray photoelectron spectroscopy (XPS), diffuse reflectance Fourier transform (DRIFT), and inductively coupled plasma-atomic electron spectroscopy (ICP-AES). The ionic exchange with the Rh-TPPTS complex results in partial insertion of the complex (only TPPTS) between the LDH layers and does not affect the high crystallinity of both LDHs, as confirmed by XRD analysis. Both catalysts were tested in the cyclization of 4-alkynoic acids and afforded the desired lactones in good yield and selectivity. For example, the 4-alkynoic acids bearing alkyl or alkenyl side chains (1b-e,j) were cleanly cyclized to afford the lactones in good isolated yield (up to 80 %). The heterogeneous Rh-TPPTS/LDH catalysts also permit the cyclization of unsubstituted acetylenic acids [2-phenylpent-4-ynoic acid 1a, and 2-(methoxycarbonyl)hex-5-ynoic acid 1i] in very good yields. In all cases, similar results were observed for both LDH supports. This behavior compared to other Rh-based



Scheme 2 Catalytic performances of the Rh/TPPTS/LDH catalysts.

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systems [11] may be due to the modified electronic properties of Rh(I) complex in intimate interaction with the basic support and not that directly to the basicity considered from LDH.

The heterogeneous system Rh/TPPTS/LDH was the first heterogeneous catalyst for the cycloisomerization of acetylenic carboxylic acids able to be recycled. Even though these catalytic results are not competing with the homogeneous approach, this early study validated the postulate that catalyst reactivity could be carefully modulated when heterogenized on a specific inorganic support and encouraged us to continue the research of more efficient heterogeneous catalysts [22–24].

Another idea was to evaluate the stabilization of gold in the form of nanoparticles in ionic liquids. The cycloisomerization reactions were first performed in the presence of Au/ $\beta$ -zeolite in different ionic liquids. Besides the problems of separation of the different ionic liquids from the reaction products (Table 3), the obtained results were similar to those obtained in organic classical solvents. [25]

1	CO <sub>2</sub> H 4 % Au/beta Ph IL, 40 °C, 16 h	Ph
1a		2a
Entry	Solvent	Conversion <sup>a</sup> (Yield) (%)
1	BIL	75 <sup>b</sup>
2	[P <sub>66614</sub> ][HSO <sub>4</sub> ]	70 <sup>b</sup>
3	$[P_{66614}][NTf_2]$	70 <sup>b</sup>
4	[C <sub>4</sub> mim][NTf <sub>2</sub> ]	80 <sup>b</sup>
5	[C <sub>6</sub> mim]Cl	83 (79)

**Table 3** Cyclization of functionalized acetylenic substrate over Au/ $\beta$  in a range of ionic liquids.

<sup>a</sup>Determined by <sup>1</sup>H NMR,

<sup>b</sup>IL unseparable from the system;

trihexyltetradecylphosphonium hydrogen sulfate

([P<sub>66614</sub>][HSO<sub>4</sub>]); trihexyltetradecylphosphonium

 $bis{(trifluoromethyl)sulfonyl}imide ([P_{66614}][NTf_2]);$ 

1-hexyl-3-methylimidazolium chlorine ([C<sub>6</sub>mim]Cl);

(1-butyl-3-methylimidazolium

bis{(trifluoromethyl)sulfonyl}imide ([C<sub>4</sub>mim][NTf<sub>2</sub>]);

5-diisopropylamino-3-oxapentyl)

dimethylethylammonium

bis{(trifluoromethyl)sulfonyl}imide (BIL).

We have therefore investigated the behavior of exchanged tetrachloroaurate-based ionic liquids such as  $[C_6 mim][AuCl_4]$ , a solid at room temperature, in  $[C_6 mim]Cl$  as solvent. All the  $\gamma$ -acetylenic carboxylic acids examined were cleanly transformed to the corresponding  $\gamma$ -alkylidene  $\gamma$ -butyrolactones. Moreover, similar activity and selectivity were found for the ionic liquid catalyst compared with the homogeneous AuCl catalysts system in acetonitrile [16]. Irrespective of the alkenyl side chain length, the lactones were isolated in 85–96 % yields even at room temperature. In all cases, the catalytic amount of Au ionic liquid used in these reactions was equivalent to the amount used under heterogeneous conditions. It is noteworthy that the cyclizations were conducted at room temperature, and high turnover frequencies (TOFs) were observed for Au ionic liquid catalyst compared to other heterogeneous systems (Table 4). This high activity may be a consequence of the ionic liquid medium, which prevents nanoparticle formation via stabilization of the Au in the form of isolated species by chlorine coordination. The ionic liquid may also allow activation of the carboxylic acid.

		$R^1$ $R^2$ $CO_2$	H [C <sub>6</sub> mim][AuCl <sub>4</sub> [C <sub>6</sub> mim]Cl, R1		$R^1$ $R^2$ O	
	1a 1b 1d	$R^1 = Ph, R^2 = H$ $R^1 = CO_2Et, R^2$ $R^1 = CO_2Me, F$	H <b>1e</b> $R^{1} =$ $R^{2} = n$ -Bu <b>1i</b> $R^{1} = C$ $R^{2} = allyl$ <b>1j</b> $R^{1} =$	$CO_2Me$ , $R^2 = CO_2Me$ , $R^2 = H$ $CO_2Et$ , $R^2 = H$	cinnamyl H 3n	
Entry	Catalyst	Product	Solvent	T [°C]	TOF $(h^{-1})$	Yield <sup>a</sup> (Conversion) (%)
1	4 % Au/β	2a	[C <sub>6</sub> mim]Cl	40	1.71	79 (83)
2	4 % Au/β	2b	[C <sub>6</sub> mim]Cl	40	1.25	58 (91)
3	4 % Au/β	2b	CH <sub>3</sub> CN	40	1.30	60 (90)
4	$[C_6 mim][AuCl_4]$	2b	[C <sub>6</sub> mim]Cl	RT	19.81	96 (100)
5	$[C_6 mim][AuCl_4]$	2e	[C <sub>6</sub> mim]Cl	40	9.28	90 (100)
6	$[C_6 mim][AuCl_4]$	2d	[C <sub>6</sub> mim]Cl	RT	9.38	91 (100)
7	$[C_6 mim][AuCl_4]$	2.j	[C <sub>6</sub> mim]Cl	RT	17.53	85 (100)
8	$[C_6 mim][AuCl_4]$	2i	[C <sub>6</sub> mim]Cl	RT	17.33	84 (100)
9	$[C_6^{mim}][AuCl_4^{-}]$	2a	[C <sub>6</sub> mim]Cl	RT	19.80	96 (100)

Table 4 Comparative results in term of TOF between Au/ $\beta$ -zeolite and Au ionic liquid catalyst.

<sup>a</sup>Isolated yield.

Considering the superior reactivity of Au catalysts reported so far, we next considered  $Au_2O_3$  heterogenization. Indeed, we and others have established that the main deactivating path of highly active cationic Au species is their reduction to inactive  $Au^0$  particles under catalysis conditions [26–28]. We postulated that catalyst immobilization on an inorganic material should offer a good balance of basicity and resistance to reduction. Looking at the literature reports on this area, we have found that recently, Corma and Serna reviewed the behavior of gold nanoparticles in catalysis (e.g.,  $Au/TiO_2$  and  $Au/Fe_2O_3$ ) [26], showing that they may act as active redox catalysts for O-containing hydrocarbons and as reduction catalysts for alkenes, alkynes, imines, carbonyls, and nitro compounds. It was also shown [27] that it is possible to modify the reactivity of the Au small particles by supporting them on a nanocrystalline CeO<sub>2</sub>, leading to a very active catalyst for CO oxidation, homocoupling of aryl boronic acids, and Sonogashira's coupling reactions. We have prepared heterogeneous Au catalysts supported on different materials like  $\beta$ -zeolite, CeO<sub>2</sub>, MgO, and TiO<sub>2</sub> via a deposition-precipitation method. The catalytic tests performed for these four catalysts (Table 5) revealed no activity for the CeO<sub>2</sub>, MgO supports, moderate activity for TiO<sub>2</sub> support (50 %), and very good activity and yield for the  $\beta$ -zeolite support (100 % conversion, 99 % isolated yield).

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) `co	D <sub>2</sub> Me CH <sub>3</sub> CN 16	l, 40 °C	0 000
1e		:	2e
Entry	Catalyst	Conversion	Yielda
		(%)	(%)
1	Au/CeO <sub>2</sub>	0	_
2	Au/MgÕ	0	_
3	Au/TiO <sub>2</sub>	50	25
4	Au/β	100	99

**Table 5** Comparative results on gold catalystssupported on different materials.

<sup>a</sup>Isolated yield.

Transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analysis of four catalysts showed very good dispersion of the Au particles on the surface of  $\beta$ -zeolite and quite narrow distribution (3–4 nm) of the Au oxide particles size dimension, while a broad distribution of the particle dimension and structural non-uniformities were observed in the case of CeO<sub>2</sub>, MgO, and TiO<sub>2</sub> supports. Since the latest catalysts were found to be inactive, we could conclude that a narrow size distribution (e.g., 3–4 nm) of the Au particles is a prerequisite for these reactions.

Some functionalized substrates have been engaged in the presence of Au/ $\beta$ -zeolite and their cyclization gave the desired lactones in good isolated yield (up to 88 %, Scheme 3).



Scheme 3 Cyclization of various  $\gamma$ -acetylenic carboxylic acids on Au/ $\beta$  heterogeneous catalyst.

Encouraged by such results, we attempted to transform unsubstituted substrates. The cyclization of 2-(methoxycarbonyl)hex-5-ynoic acid **1i** needed a prolonged reaction time and a temperature of 40 °C to reach complete conversion while the corresponding lactone was isolated in a modest yield of 50 %. In the case of the 2-phenylpent-4-ynoic acid **1a**, the corresponding *exo*-methylene lactone was obtained in 80 % yield.

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One interesting behavior of this catalyst was the low activity presented in inert atmosphere, while an  $O_2$ -containing atmosphere "ignites" the reaction. The in situ XPS experiment revealed that the active species for this reaction was presumably Au(III) and that the oxidized Au was slowly reduced to an inactive species during the reaction. Thus, the role of air was to reoxidize the inactive site Au(I) to the active site Au(III). The recyclability of this catalyst was evaluated during five runs, and catalyst recovery was not hampered by decomposition as the presence of air had no detrimental effect, but on the contrary was a prerequisite to reach high activities [28].

# CONCLUSION

Several heterogeneized catalytic systems based mainly on Au have been prepared and analyzed. Their efficiency has been evaluated for the cycloisomerization of  $\gamma$ -acetylenic carboxylic acids leading to valuable  $\gamma$ -alkylidene  $\gamma$ -butyrolactones. Bulk AuO<sub>3</sub> was found to be a valuable and easy to handle catalyst for selective transformations, whereas [C<sub>6</sub>mim][AuCl<sub>4</sub>] presented a high activity and Au/ $\beta$ -zeolite was recyclable.

# REFERENCES

- For recent reviews, see: (a) F. Alonso, I. P. Beletskaya, M. Yus. *Chem. Rev.* 104, 3079 (2004); (b) I. Nakamura, Y. Yamamoto. *Chem. Rev.* 104, 2127 (2004); (c) M. Beller, J. Seayad, A. Tillack, H. Jiao. *Angew. Chem., Int. Ed.* 43, 3368 (2004); (d) E. Jimenez-Nunez, A. M. Echavarren. *Chem. Commun.* 333 (2007); for Ru-catalyzed intermolecular reactions, see: (e) C. Bruneau, P. H. Dixneuf. Acc. Chem. Res. 32, 311 (1999).
- (a) M. E. Eissen, J. O. Metzger, E. Schmidt, U. Schneidewind. *Angew. Chem., Int. Ed.* 41, 414 (2002); (b) P. T. Anastas, J. C. Warner. In *Green Chemistry: Theory and Practice*, p. 15, Oxford University Press, New York (1998).
- For a review discussing natural products exhibiting the γ-butyrolactone substructure, see: (a) S. S. C. Koch, A. R. Chamberlin. In *Studies in Natural Products Chemistry*, Vol. 16, Atta-ur-Rahman (Ed.), p. 687, Elsevier Science, Amsterdam (1995); for reviews discussing the synthetic routes to γ-alkylydene-γ-butyrolactones, see: (b) M. Seitz, O. Reiser. *Curr. Opin. Chem. Biol.* 9, 285 (2005); (c) E.-I. Negishi, M. Kotora. *Tetrahedron* 53, 6707 (1997); (d) N. B. Carter, A. E. Nadany, J. B. Sweeny. *J. Chem. Soc., Perkin Trans 1* 2324 (2002); (e) I. Collins. *J. Chem. Soc., Perkin Trans 1* 2845 (2000).
- 4. For representative examples from Pd chemistry, see: (a) G. Balme, N. Monteiro, D. Bouyssi. Handbook of Organopalladium Chemistry for Organic Synthesis, E.-I. Negishi (Ed.), pp. 2245–2265, John Wiley, New York (2002); (b) T. Hosokawa, S.-I. Murahashi. Handbook of Organopalladium Chemistry for Organic Synthesis, E.-I. Negishi (Ed.), pp. 2169–2192, John Wiley, New York (2002); (c) C. Xu, E.-I. Negishi. Handbook of Organopalladium Chemistry for Organic Synthesis, E.-I. Negishi (Ed.), p. 2289, John Wiley, New York (2002).
- For specific cases of natural product synthesis where cyclizations of alkynoic acids constitute a key step, see: (a) M. Algueró, J. Bosch, J. Castañer, J. Castellá, J. Castells, R. Mestres, J. Pascual, F. Serratosa. *Tetrahedron* 18, 1381 (1962); (b) T. T. Jong, P. G. Williard, J. P. Porwoll. *J. Org. Chem.* 49, 735 (1984); (c) H. Imagawa, Y. Fujikawa, A. Tsuchihiro, A. Kinoshita, T. Yoshinaga, H. Takao, N. Nishizawa. *Synlett* 639 (2006).
- (a) A. D. Wright, R. de Nys, C. K. Angerhofer, J. M. Pezzuto, M. Gurrath. J. Nat. Prod. 69, 1180 (2006); (b) C.-H. Chen, W.-L. Lo, Y.-C. Liu, C.-Y. Chen. J. Nat. Prod. 69, 927 (2006).
- Silver catalysis: (a) J. Castaner, J. Pascual. J. Chem. Soc. 3962 (1958); (b) P. Pale, J. Chuche. Tetrahedron Lett. 28, 6447 (1987); (c) V. Dalla, P. Pale. New J. Chem. 23, 803 (1999); (d) V. Dalla, P. Pale. Tetrahedron Lett. 35, 3525 (1994); (e) C. H. Oh, H. J. Yi, J. H. Lee. New J. Chem. 31, 835 (2007).

- Mercury catalysis: (a) M. Yamamoto. J. Chem. Soc., Chem. Commun. 649 (1978); (b)
  M. Yamamoto. J. Chem. Soc., Perkin Trans. 1 582 (1981); (c) R. A. Amos, J. A. Katzenellenbogen. J. Org. Chem. 43, 560 (1978); (d) R. A. Amos, J. A. Katzenellenbogen. J. Am. Chem. Soc. 103, 5459 (1981); (e) S. W. Rollinson, R. A. Amos, J. A. Katzenellenbogen. J. Am. Chem. Soc. 103, 4114 (1981); (f) M. J. Sofia, J. A. Katzenellenbogen. J. Org. Chem. 50, 2331 (1984); (g) R. W. Spencer, T. F. Tam, E. Thomas, V. J. Robinson, A. Krantz. J. Am. Chem. Soc. 108, 5589 (1986); (h) A. Jellal, J. Grimaldi, M. Santelli. Tetrahedron Lett. 25, 3179 (1984).
- Palladium catalysis: (a) C. Lambert, K. Utimoto, H. Nozaki. *Tetrahedron Lett.* 25, 5323 (1984);
  (b) N. Yanagihara, C. Lambert, K. Iritari, K. Utimoto, H. Nozaki. *J. Am. Chem. Soc.* 108, 2753 (1986);
  (c) A. Arcadi, A. Burini, S. Cacchi, M. Delmastro, F. Marinelli, B. R. Pietroni. *J. Org. Chem.* 57, 976 (1992);
  (d) M. Cavicchioli, D. Bouyssi, J. Goré, G. Balme. *Tetrahedron Lett.* 37, 1429 (1996);
  (e) X. Wang, X. Lu. *J. Org. Chem.* 61, 2254 (1996);
  (f) Z. Huo, N. T. Patil, T. Jin, N. K. Pahadi, Y. Yamamoto. *Adv. Synth. Catal.* 349, 680 (2007);
  (g) F. Bellina, D. Ciucci, P. Vergamini, R. Rossi. *Tetrahedron* 56, 2533 (2000);
  (h) Z. Ahmed, U. Albrecht, P. Langer. *Eur. J. Org. Chem.* 3469 (2005);
  (i) V. Subramanian, V. R. Batchu, D. Barange, M. Pal. *J. Org. Chem.* 70, 4778 (2005);
  (j) A. Duchêne, J. Thibonnet, J.-L. Parrain, E. Anselmi, M. Abarbri. *Synthesis* 597 (2007).
- Ruthenium catalysis: M. Jimenez-Tenotio, M. C. Puerta, P. Valerga, F. J. Moreno-Dorado, F. M. Guerra, G. M. Massanet. *Chem. Commun.* 2324 (2001).
- Rhodium catalysis: (a) T. B. Marder, D. M. T. Chan, W. C. Fultz, J. C. Calabrese, D. J. Milstein. J. Chem. Soc., Chem Commun. 1885 (1987); (b) D. M. T. Chan, T. B. Marder, D. Milstein, N. J. Taylor. J. Am. Chem. Soc. 109, 6385 (1987); (c) S. Elgafi, L. D. Field, B. A. Messerle. J. Organomet. Chem. 607, 97 (2000).
- Cluster catalysis: (a) T. Wakabayashi, Y. Ishii, K. Ishikawa, M. Hidai. *Angew. Chem., Int. Ed.* 35, 3123 (1996) and refs. cited therein; (b) I. Takei, Y. Wakebe, K. Suzuki, Y. Enta, T. Suzuki, Y. Mizobe, M. Hidai. *Organometallics* 22, 4639 (2003).
- (a) M. Haruta, T. Kobayashi, H. Sano, N. Yamada. *Chem. Lett.* 16, 405 (1987); (b) M. Haruta, H. Kageyama, N. Kamijo, T. Kobayashi, F. Delannay. *Stud. Surf. Sci. Catal.* 44, 33 (1989); (c) M. Haruta, N. Yamada, T. Kobayashi, S. Iijima. *J. Catal.* 115, 301 (1989); (d) B. Chowdhury, J. J. Bravo-Suarez, M. Date, S. Tsubota, M. Haruta. *Angew. Chem., Int. Ed.* 45, 412 (2006).
- For representative examples and seminal references, see: (a) A. Fürstner, P. W. Davies. Angew Chem., Int. Ed. 46, 3410 (2007); (b) D. J. Gorin, D. Toste. Nature 446, 395 (2007); (c) A. S. K. Hashmi, G. J. Hutchings. Angew. Chem., Int. Ed. 45, 7896 (2006); (d) E. Jimenez-Nunez, A. M. Echavarren. Chem. Commun. 333 (2007); (e) S. Ma, S. Yu, Z. Gu. Angew. Chem., Int. Ed. 45, 200 (2006); (f) A. S. K. Hashmi. Angew. Chem., Int. Ed. 44, 6090 (2005); (g) A. Höffmann-Röder, N. Krause. Org. Biomol. Chem. 3, 387 (2005); (h) A. S. K. Hashmi. Gold Bull. 37, 51 (2004); (i) P. Pyykkö. Angew. Chem., Int. Ed. 43, 4412 (2004); (j) A. S. K. Hashmi. Chem. Rev. 107, 3180 (2007); (k) C. Frank Shaw III. Chem. Rev. 99, 2589 (1999); (l) V. Michelet, P. Y. Toullec, J.-P. Genet. Angew. Chem., Int. Ed. 47, 4268 (2008); (m) A. Arcadi. Chem. Rev. 108, 3266 (2008); (n) N. T. Patil, Y. Yamamoto. Chem. Rev. 108, 3395 (2008); (o) Z. Li, C. Brouwer, C. He. Chem. Rev. 108, 3239 (2008); (p) H. C. Shen. Tetrahedron 64, 3885 (2008); (q) R. Skouta, C.-J. Li. Tetrahedron 64, 4917 (2008); (r) A. S. K. Hashmi, M. Rudolph. Chem. Soc. Rev. 37, 1766 (2008); (s) J. Muzart. Tetrahedron 64, 5815 (2008); (t) A. S. K. Hashmi. Chem. Rev. 107, 3180 (2007).
- (a) S. Antoniotti, E. Genin, V. Michelet, J.-P. Genêt. J. Am. Chem. Soc. 127, 9976 (2005); (b)
  E. Genin, S. Antoniotti, V. Michelet, J.-P. Genêt. Angew. Chem., Int. Ed. 44, 4949 (2005).
- (a) E. Genin, P. Y. Toullec, S. Antoniotti, C. Brancour, J.-P. Genêt, V. Michelet. *J. Am. Chem. Soc.* 128, 3112 (2006); (b) E. Genin, P. Y. Toullec, S. Antoniotti, C. Brancour, J.-P. Genêt, V. Michelet. *ARKIVOC* v, 67 (2007).

### F. NEAŢU et al.

- 17. (a) H. Harkat, J.-M. Weibel, P. Pale. *Tetrahedron Lett.* **47**, 6273 (2006); for a recent Au-catalyzed cyclization of  $\gamma$  and  $\delta$ -acetylenic acids, see: (b) E. Marchal, P. Uriac, B. Legoin, L. Toupet, P. van de Weghe. *Tetrahedron* **63**, 9979 (2007).
- For references dealing with the gold-catalyzed hydration of alkynes, see: (a) Y. Fukuda, K. Utimoto. J. Org. Chem. 56, 3729 (1991); (b) J. H. Teles, S. Brode, M. Chabanas. Angew. Chem., Int. Ed. 37, 1415 (1998); (c) E. Mizushima, K. Sato, T. M. Hayashi. Angew. Chem., Int. Ed. 41, 4563 (2002); (d) S. K. Schneider, W. A. Herrmann, E. Herdtweck. Z. Anorg. Allg. Chem. 629, 2363 (2003).
- 19. P. Y. Toullec, E. Genin, S. Antoniotti, J.-P. Genêt, V. Michelet. Synlett 707 (2008).
- (a) M. Uchiyama, H. Ozawa, K. Takuma, Y. Matsumoto, M. Yonehara, K. Hiroya, T. Sakamoto. Org. Lett. 8, 5517 (2006); (b) C. Kanazawa, M. Terada. *Tetrahedron Lett.* 48, 933 (2007).
- F. Neaţu, K. Triantafyllidis, J.-P. Genêt, V. Michelet, V. I. Pârvulescu. Stud. Surf. Sci. Catal. (A. Gedeon, P. Massiani, F. Babonneau, Eds.) 174B, 1057 (2008).
- (a) A. Abad, A. Corma, H. Garcia. *Chem.—Eur. J.* 14, 212 (2008) and refs. therein; (b) A. Corma, H. Garcia. *Chem. Soc. Rev.* 37, 2096 (2008).
- 23. R. J. David. Science 301, 926 (2003) and refs. therein.
- 24. Z.-R. Tang, J. K. Edwards, J. K. Bartley, S. H. Taylor, A. F. Carley, A. A. Herzing, C. J. Kiely, G. J. Hutchings. *J. Catal.* **249**, 208 (2007) and refs. therein.
- 25. F. Neaţu, V. I. Pârvulescu, V. Michelet, J.-P. Gênet, A. Goguet, C. Hardacre. *New J. Chem.* 1, 102 (2009).
- (a) A. Corma, P. Serna. Science 313, 332 (2006) and refs. herein; (b) J. Guzman, S. Carrettin, J. C. Fierro-Gonzalez, Y. Hao, B. C. Gates, A. Corma. Angew. Chem., Int. Ed. 44, 4778 (2005); (c) S. Carrettin, P. Concepción, A. Corma, J. M. López-Nieto, V. F. Puntes. Angew. Chem., Int. Ed. 43, 2538 (2004).
- (a) S. Carrettin, J. Guzman, A. Corma. Angew. Chem., Int. Ed. 44, 2242 (2005); (b) S. Carrettin, A. Corma, M. Iglesias, F. Sanchez. Appl. Catal., A 291, 247 (2005); (c) C. Gonzales-Arellano, A. Abad, A. Corma, H. Garcia, M. Iglesias, F. Sanchez. Angew. Chem., Int. Ed. 46, 1536 (2007); (d) A. Corma, E. Gutierrez-Puebla, M. Iglesias, A. Monge, S. Perez-Ferreras, F. Sanchez. Adv. Synth. Catal. 348, 1899 (2006); (e) S. Carrettin, M. C. Blanco, A. Corma, A. S. K. Hashmi. Adv. Synth. Catal. 348, 1283 (2006).
- 28. F. Neaţu, Z. Li, R. Richards, P. Y. Toullec, J.-P. Genêt, K. Dumbuya, J. M. Gottfried, H.-P. Steinrück, V. I. Pârvulescu, V. Michelet. *Chem.—Eur. J.* 14, 9412 (2008).