DOI: 10.1002/adsc.201000750

Palladium-Catalyzed Hydroesterification of Alkynes Employing Aryl Formates without the Use of External Carbon Monoxide

Yuko Katafuchi,[a] Tetsuaki Fujihara,[a] Tomohiro Iwai,[a] Jun Terao,[a] and Yasushi Tsuji[a,*]

[a] Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan
Fax: (+81)-75-383-2514; phone: (+81)-75-383-2515; e-mail: ytsuji@scl.kyoto-u.ac.jp

Received: October 5, 2010; Published online: February 16, 2011

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000750.

Abstract: A highly efficient hydroesterification of alkynes employing aryl formates has been developed without the use of external carbon monoxide and at ambient pressure. The reaction in the presence of a palladium-xantphos catalyst system selectively affords α,β-unsaturated esters in good to high yields. Use of an aryl formate is crucial and alkyl formates did not react at all. The hydroesterification of norbornene and terminal alkenes also readily proceeded under similar reaction conditions. A mechanistic study showed that conversion of aryl formates to carbon monoxide and phenol derivatives occurred in the hydroesterification. Xantphos is highly effective as a ligand both in the conversion of aryl formates and the hydroesterification reactions.

Keywords: alkynes; aryl formates; homogeneous catalysis; hydroesterification; palladium; phosphane ligands

Introduction

The hydroesterification of alkynes and alkenes is one of the most straightforward reactions affording one-carbon elongated esters. Especially, the reaction of alkynes affords useful α,β-unsaturated esters. The hydroesterification is usually carried out under carbon monoxide pressure with an alcohol in the presence of a transition metal catalyst.[1] However, a transformation without the use of external carbon monoxide is highly desirable.[2]

Formic acid and its esters can be readily derived from carbon monoxide.[3] Thus, formate esters may be regarded as liquid condensates and expedient alternative sources of carbon monoxide and alcohols. Actually, much effort has been made to realize the hydroesterification reaction employing formate esters[4] without the use of external carbon monoxide. However, so far the hydroesterification utilizing formate ester has been suffering from low efficiency: often high reaction temperature ($>180\,^{\circ}C$)[4b–f,k] and/or even carbon monoxide pressure,[4a,c–f,k] or an appropriate directing group[4h–j] were indispensable.

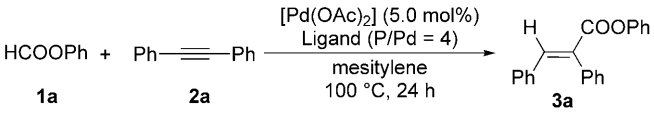
Recently, we have developed the addition of acid chlorides to alkynes catalyzed by an iridium complex[5a] and the addition of formamides to alkynes catalyzed by a palladium complex.[5b] These reactions efficiently afforded the corresponding *syn*-addition products. Herein, we now report the formal *syn*-addition of formate esters to alkynes in the presence of a palladium-xantphos[6] catalyst system. Simply mixing alkynes and readily available aryl formates with the catalyst in a usual flask (no pressure bottle is required) realizes the highly efficient hydroesterification of the alkynes. The reaction can be carried out without the use of external carbon monoxide, and no directing group is required.

Results and Discussion

Optimization

First, the reaction of phenyl formate (**1a**) with diphenylacetylene (**2a**) was carried out in the presence of a catalytic amount of [$Pd(OAc)_2$] using a 10-mL flask equipped with a three-way glass-plug stopcock attached by a standard ground glass joint (Table 1). Without an added ligand, no product was obtained at all (entry 1). With the addition of monodentate phos-

Table 1. Effect of phosphanes on the palladium-catalyzed hydroesterification of diphenylacetylene (**2a**) with phenyl formate (**1a**).[a]



Entry	Ligand	Yield [%][b]	*E*/*Z*[c]
1	none	0	–
2	PPh_3	1	–
3	P(*o*-Tol)$_3$	18	100/0
4	PCy_3	27	100/0
5	dppf	54	100/0
6	dppe	75	100/0
7	dppb	99	84/16
8	dppbz	93	84/16
9	*rac*-binap	99	83/17
10	xantphos	99	100/0
11	xantphos[d]	99 (97)[e]	100/0
12	xantphos[f]	6	100/0

[a] Diphenylacetylene (**2a**, 0.50 mmol), phenyl formate (**1a**, 2.0 mmol), [Pd(OAc)$_2$] (0.025 mmol, 5.0 mol%), phosphane (0.050 mmol or 0.10 mmol, P/Pd = 4), mesitylene (0.50 mL) at 100 °C for 20 h.
[b] Yield based on the GC internal standard technique.
[c] Determined by GC analysis.
[d] 0.0375 mmol (P/Pd = 3).
[e] Isolated yield of **2a**.
[f] 0.030 mmol (P/Pd = 2.4).

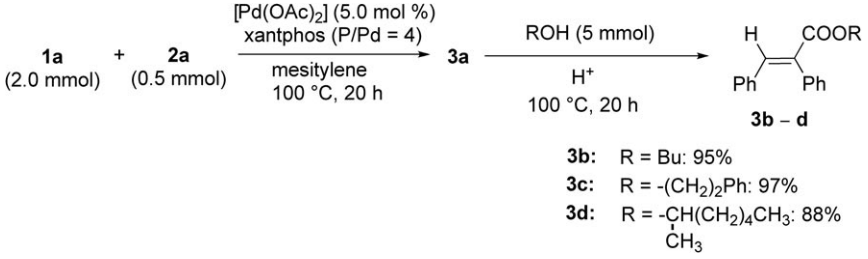
phanes such as PPh_3, P(*o*-Tol)$_3$ and PCy_3[6] **3a** was afforded in only low yields (entries 2–4). In contrast, the use of bidentate phosphanes such as dppf, dppe, dppb, dppbz and *rac*-binap[6] improved the catalytic activity (entries 5–9), although yields (entries 5 and 6) or stereoselectivities (entries 7–9) of the product were not satisfactory. Among the ligands examined, xantphos gave the best result affording **3a** in 99% yield with perfect (*E*)-stereoselectivity as confirmed by X-ray crystallography (Supporting Information) (entry 10). No *E*-*Z* isomerization occurred during the reaction. Evidently, the P/Pd ratio affected the catalytic activity. While the yields at P/Pd = 4 and 3 were 99% (entries 10 and 11), the yield decreased dramatically to 6% at P/Pd = 2.4 (entry 12).

Other Pd precursors such as [$PdCl_2$(PhCN)$_2$] and [Pd_2(dba)$_3$] were not so effective.

Under the same reaction conditions as in entry 10, alkyl formates such as butyl formate (**1b**), 2-phenylethyl formate (**1c**), and benzyl formate (**1d**) did not convert at all and the corresponding alkyl ester products (**3**) could not be obtained. Thus, uniquely phenyl formate (**1a**) can be a good substrate in the present hydroesterification. Notably, the resulting phenyl ester (**3a**) is very reactive in the acid-catalyzed transesterification reaction. Indeed, the resulting **3a** readily reacted with various alcohols and the corresponding alkyl esters **3b**–**d** were isolated in high yields in a one-pot reaction from **1a** and **2a** (Scheme 1). This is another benefit in employing phenyl formate as the substrate.

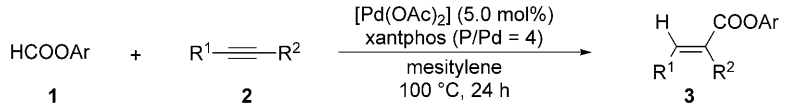
Scope of Substrates

Various internal alkynes **2b**–**j** reacted with **1a** under the standard reaction conditions (Table 2). Bis(4-acetylphenyl)acetylene (**2b**) and bis(4-methylphenyl)acetylene (**2c**) afforded the corresponding products **3e** and **3f** stereoselectively in high yields (entries 1 and 2). Aliphatic alkynes such as 5-decyne (**2d**) and 4-octyne (**2e**) also gave the corresponding products, **3g** and **3h**, stereoselectively in high yields (entries 3 and 4). As for unsymmetrical alkynes, 1-phenyl-1-propyne (**2f**) provided two regioisomers **3i** and **3i′**, but each product was isolated in pure form in 64% and 29% yields, respectively (entry 5). Alkynes with ester and amide functionalities (**2g** and **2h**) successfully gave the hydroesterification products and each product was isolated in pure form (entries 6 and 7). Although it was difficult to determine the structure of the product bearing an amide functionality, the structure of **3k** was confirmed by X-ray crystallography (Supporting Information). With 1-cyclohexyl-1-propyne (**2i**) the regioselectivity was improved and **3l** and **3l′** were isolated in 79% and 7% yields, respectively (entry 8). Gratifyingly, 1-phenyl-2-(trimethylsilyl)ethyne (**2j**) afforded a single regioisomer **3m** in 96% yield selectively (entry 9). Aryl formates bearing both electron-rich (entries 10 and 11) and electron-poor (entries 13 and



Scheme 1. One-pot transesterification reaction of **3a**.

Table 2. Hydroesterification of internal alkynes **2** with aryl formates **1**.[a]



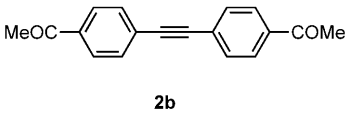
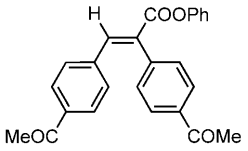
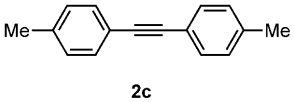
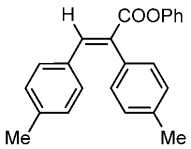
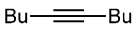
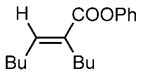
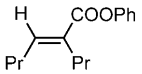
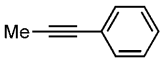
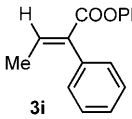
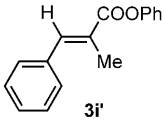
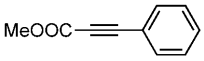
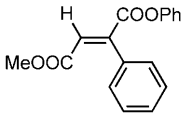
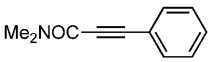
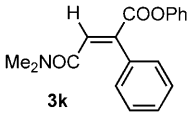
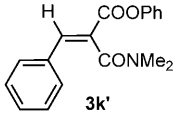
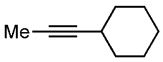
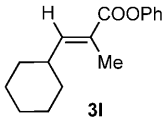
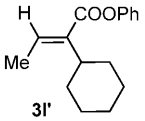
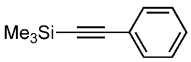
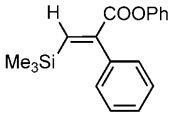
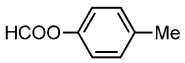
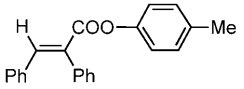
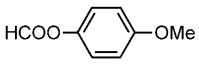
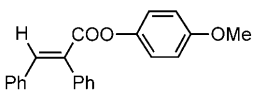
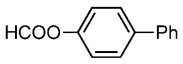
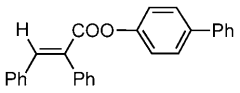
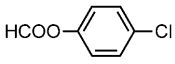
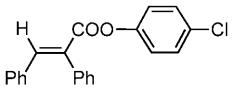
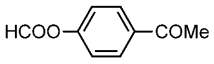
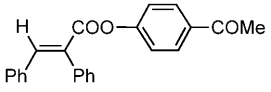
Entry	1	2	Product	Yield [%][b] (*E*/*Z*)[c]
1	**1a**	 **2b**	 **3e**	83 (100/0)
2[d]	**1a**	 **2c**	 **3f**	78 (100/0)
3[e]	**1a**	 **2d**	 **3g**	88 (99/1)
4[f]	**1a**	**2e**	 **3h**	78 (100/0)
5	**1a**	 **2f**	 **3i** and  **3i'**	64 (100/0) and 29 (100/0)
6[g]	**1a**	 **2g**	 **3j**	64 (100/0)
7[g]	**1a**	 **2h**	 **3k** and  **3k'**	55 (100/0) and 30 (100/0)
8	**1a**	 **2i**	 **3l** and  **3l'**	79 (100/0) and 7 (100/0)
9	**1a**	 **2j**	 **3m**	96 (99/1)
10[g]	 **1e**	**2a**	 **3n**	94 (99/1)
11	 **1f**	**2a**	 **3o**	98 (99/1)

Table 2. (Continued)

Entry	1	2	Product	Yield [%][b] (*E*/*Z*)[c]
12	 **1g**	**2a**	 **3p**	94 (99/1)
13	 **1h**	**2a**	 **3q**	92 (100/0)
14	 **1i**	**2a**	 **3r**	93 (100/0)

[a] Internal alkyne (**2**: 0.5 mmol), formate (**1**: 2.0 mmol), [$Pd(OAc)_2$] (0.025 mmol, 5.0 mol%), xantphos (0.050 mmol, P/Pd = 4), mesitylene (0.50 mL) at 100 °C for 20 h.
[b] Yield of the isolated product.
[c] Determined by GC analysis.
[d] At 130 °C.
[e] Xantphos (0.0375 mmol, P/Pd = 3), at 90 °C.
[f] At 90 °C.
[g] At 120 °C.

14) phenyl moieties gave the corresponding products (**3n**–**r**) in high yields.

Terminal alkynes were also successfully utilized in the hydroesterification. In Table 3, various terminal alkynes **2k**–**r** afforded the adducts in high yields with an excess **1a** in the presence of [$Pd_2(dba)_3$]-xantphos catalyst system. The reaction of phenylacetylene (**2k**) with **1a** proceeded regioselectively, giving a single regioisomer **3s** in 93% yield (entry 1). 4-Ethynyltoluene (**2l**) also afforded a single adduct **3t** regioselectively (entry 2). 1-Ethynyl-4-methoxybenzene (**2m**) and 1-chloro-4-ethynylbenzene (**2n**) provided the corresponding products with high regioselectivity (entries 3 and 4). Other terminal alkynes **2o**–**r** having alkyls or a silyl substituents on the sp carbon also afforded the corresponding products in high yields with high regioselectivities (entries 5–8). It is noteworthy that the silyl substituent reversed the regioselectivity (entry 8 *vs.* entries 1–7).

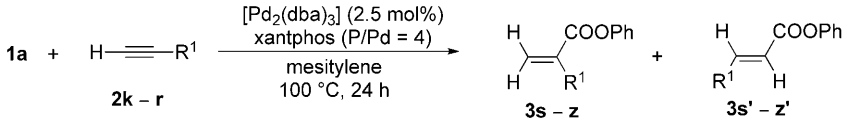
Besides alkynes, the reaction could be applied to alkenes (Scheme 2). The reaction of 2-norbornene (**4a**) with **1a** proceeded smoothly to afford **5a** in 91% yield *exo*-selectively [Scheme 2 (A)]. In the reaction of styrene (**4b**) with **1a**, two regioisomers **5b** and **5b′** were isolated in pure form in 66% and 28% yields, respectively. 1-Dodecene (**4c**) also afforded a mixture of **5c** and **5c′** in 70% total yield with high regioselectivity [8/92, Scheme 2 (B)].

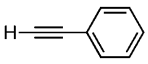
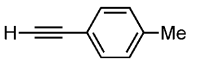
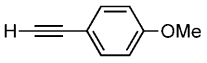
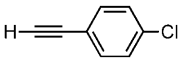
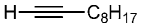
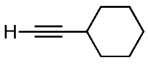
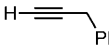
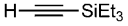
Reaction Mechanisms

During the course of the catalytic reaction, the facile conversion of aryl formates to the corresponding phenols and carbon monoxide was observed. Therefore, the hydroesterification could proceed *via* the very efficient formation of carbon monoxide and phenols from aryl formates. Actually, the reaction of **2a** with phenol in the presence of the [$Pd(OAc)_2$]-xantphos catalyst system under carbon monoxide atmosphere (1 atm) afforded the corresponding product **3a** in 99% yield [Scheme 3 (A)]. Furthermore, the reaction of **1a** with **2a** in the presence of *p*-cresol afforded products **3a** and **3n** in 49% and 30% yields, respectively [Scheme 3 (B)]. These results clearly indicate that with xantphos as the ligand the reaction proceeds *via* conversion of aryl formates to phenols and carbon monoxide, not *via* direct addition of aryl formates to alkynes. Usually, the reactivity of phenol in the hydroesterification and related Reppe carbonylations is quite low due to its low nucleophilicity. In these former reactions, the established general reactivity order is as follows: aliphatic alcohol > water > phenol.[1b] Thus, the present catalyst system (Pd-xantphos, P/Pd > 3) is uniquely active to utilize phenols and aryl formates very efficiently in the hydroesterification.[7]

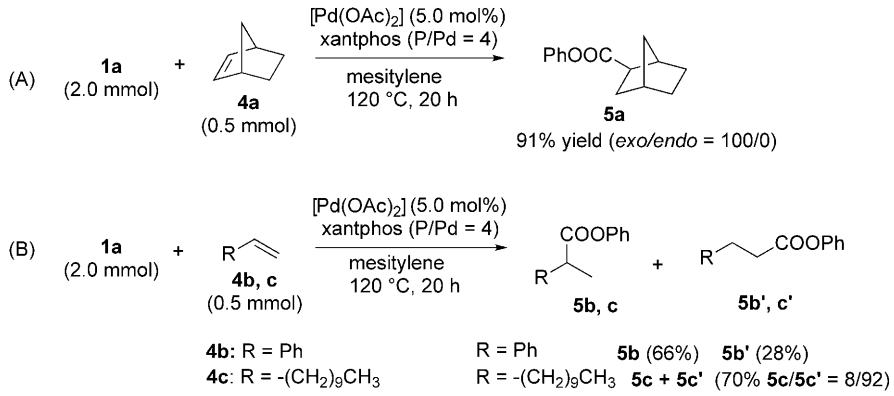
The conversion of aryl formates to phenols and carbon monoxide is crucial in the present hydroesterification. Therefore, this step was examined in detail with **1a**. The conversion showed a zero-order depend-

Table 3. Hydroesterification of terminal alkynes with **1a**.[a]



Entry	Alkyne **2k–r**		Total yield of **3**+**3′** [%][b]	Selectivity (**3**/**3′**)[c]
1		**2k**	**3s**: 93	**3s**/**3s′** = 100/0
2		**2l**	**3t**: 83	**3t**/**3t′** = 100/0
3		**2m**	**3u**: 74	**3u**/**3u′** = 100/0
4		**2n**	**3v**+**3v′**: 50	**3v**/**3v′** = 93/7
5		**2o**	**3w**+**3w′**: 94	**3w**/**3w′** = 90/10
6		**2p**	**3x**+**3x′**: 97	**3x**/**3x′** = 96/4
7		**2q**	**3y**: 77	**3y**/**3y′** = 100/0
8		**2r**	**3z′**: 90	**3z**/**3z′** = 0/100

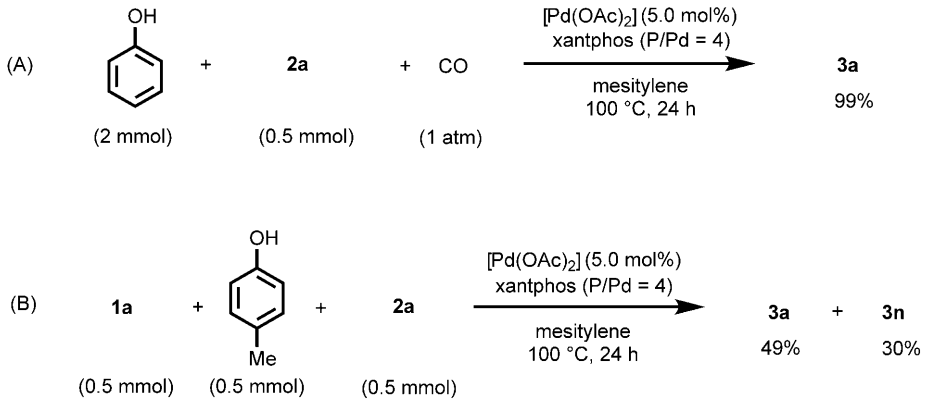
[a] Terminal alkyne (0.50 mmol), **1a** (5.0 mmol), $[Pd_2(dba)_3]$ (0.0125 mmol, 5.0 mol%), xantphos (0.050 mmol, P/Pd = 4), mesitylene (1.5 mL) at 100 °C for 20 h.
[b] Yield of the isolated product.
[c] Determined by GC analysis.



Scheme 2. Hydroesterificaion of alkenes with **1a**.

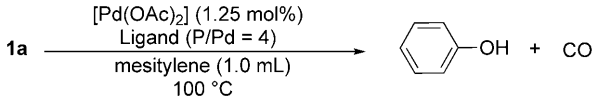
ence on the concentration of aryl formates up to 80% conversion. Furthermore, the nature of the ligand strongly affected the rate constant with **1a** (Table 4). Without phosphane ligands, no conversion of **1a** was observed. Bidentate ligands such as xantphos and dppf showed high efficiency as the ligand (entries 1 and 2), while dppf was not a suitable ligand and xantphos was the best one in the hydroesterification reaction (entries 5 and 10 in Table 1). The reaction using xantphos as a ligand (entry 1 in Table 4) was carried out at 80 °C, 100 °C, and 110 °C, and the Eyring plot provided the activation parameters: $\Delta H^{\neq} = 13.4$ kcal mol^{-1} and $\Delta S^{\neq} = -38.9$ cal mol^{-1} K^{-1}. Further, the effect of a substituent on the phenyl ring of the formates (**1e**, **1f**, **1h** and 3-methoxyphenyl formate **1j**) was examined. The Hammett plot of these rate constants with the corresponding σ values[8] showed a straight line with the slope $\rho = 3.46$ (Figure 1), indicating that more electron-withdrawing substituents accelerate the conversion.

Under these reaction conditions, the reactivity of alkyl formates such as **1b**, **1c**, and **1d** was quite low



Scheme 3. Hydroesterification of **2a** with phenol derivatives.

Table 4. Effect of phosphane on the conversion of phenyl formate (**1a**) to phenol and carbon monoxide.[a]



Entry	Ligand	k_{obs} (mol L^{-1} min^{-1})[b]
1	xantphos	1.95×10^{-2}
2	dppf	3.29×10^{-2}
3	PPh_3	3.5×10^{-3}
4	PCy_3	7×10^{-4}

[a] **1a** (2.0 mmol), $[Pd(OAc)_2]$ (0.025 mmol), phosphane (0.050 mmol or 0.10 mmol, P/Pd = 4), mesitylene (1.0 mL) at 100 °C.

[b] $-d[\mathbf{1a}]/dt = k_{obs}[\mathbf{1a}]^0$.

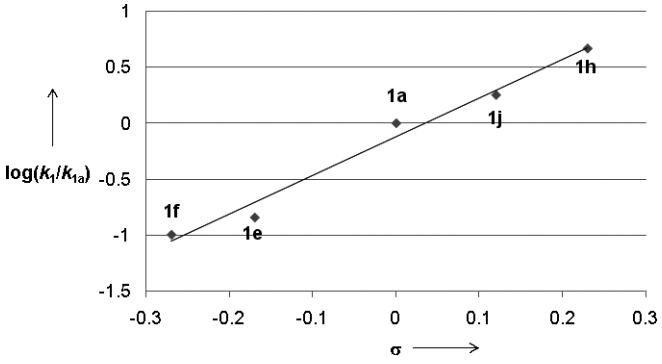
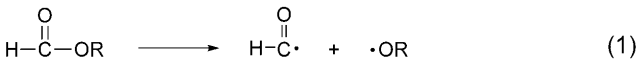


Figure 1. The Hammett plot for the palladium-catalyzed conversion of **1**. *Reaction conditions:* **1** (2.0 mmol), $[Pd(OAc)_2]$ (0.025 mmol), xantphos (0.050 mmol, P/Pd = 4), mesitylene (1.0 mL) at 100 °C.

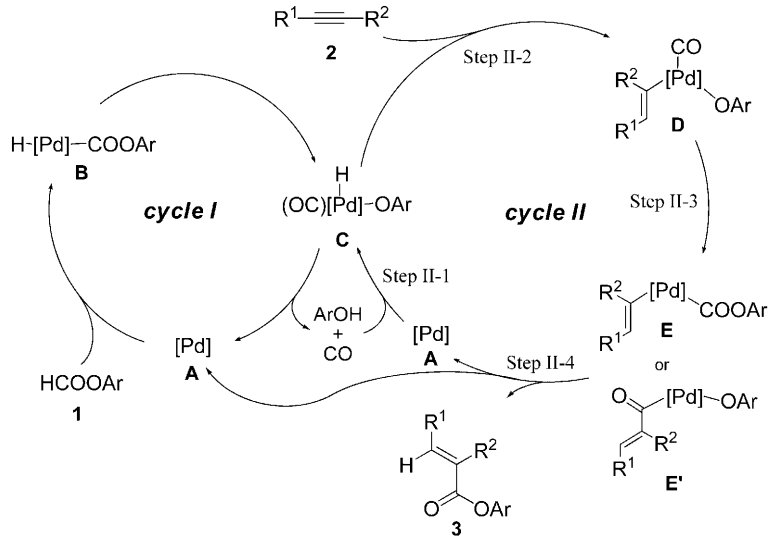
and the hydroesterification did not proceed at all (*vide supra*). To gain some insight into the different reactivity, the bond dissociation energies between the formyl carbons and the alkoxy or aryloxy oxygens were estimated by the MP4(SDQ)/6-31+G(2d,p)//B3LYP/6-31G(d) method[9] for the homolytic cleavage [Eq. (1)].



(1)

The calculated bond energies of the alkyl formate (**1b**: 100.90 kcal mol^{-1}, **1c**: 100.58 kcal mol^{-1}, and **1d**: 100.60 kcal mol^{-1}) are considerably larger than those of the aryl formates (**1a**: 83.91 kcal mol^{-1}, **1e**: 81.69 kcal mol^{-1}, **1f**: 80.16 kcal mol^{-1}, **1h**: 82.93 kcal mol^{-1}, and **1j**: 84.46 kcal mol^{-1}). These stronger bonds of the alkyl formates could cause the much lower reactivity in the hydroesterification.

A possible catalytic cycle is shown in Scheme 4. Aryl formate (**1**) is converted to phenols and carbon monoxide in cycle I. The kinetic measurement of this cycle indicated the rate has a zero-order dependence on the concentration of **1**. Thus, precoordination of **1** to active catalyst species **A** with a large equilibrium constant might be involved. The electron-withdrawing substituents on **1** accelerate the cycle I (Figure 1). These substituents might stabilize the aryloxy intermediate such as **C**. The conversion of **1** in cycle I must be faster than the hydroesterification in cycle II, since phenols and carbon monoxide were accumulated in the reaction system. In the present hydroesterification, phenols of lower nucleophilicity show the higher efficiency. Thus, nucleophilic attack[1] of phenols onto the acryloyl palladium species would be unlikely. The generated phenols might react with the catalyst species **A** to afford **C** (step II-1). Then, insertion of alkyne provides an alkenyl intermediate **D** (step II-2) followed by insertion of CO to provide a carbonyl intermediate **E** or **E′** (step II-3). Finally, reductive elimination could provide the hydroesterification product (**3**) and the active catalyst species (**A**) regenerates (step II-4).



Scheme 4. A plausible catalytic cycle.

Conclusions

The hydroesterification of alkynes employing aryl formates occurred at 100 °C at ambient pressure in the presence of the Pd-xantphos catalyst system to afford α,β-unsaturated esters regio- and stereoselectively. The reaction can be carried out without the use of external carbon monoxide, and no directing group is required. During the reaction aryl formates were converted to carbon monoxide and the corresponding phenols. The reactivity of alkyl formates in the hydroesterification reaction was quite low. The hydroesterification of alkenes also readily proceeded under similar reaction conditions.

Experimental Section

General

All manipulations were performed under an argon atmosphere using standard Schlenk-type glassware on a dual-manifold Schlenk line. All solvents were dried and purified by usual procedures.[10] Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. IR spectra were determined on a Shimadzu FTIR-8300 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a JEOL ECX-400P spectrometer. The ^{1}H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm). The ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm). EI-MS were recorded on a Shimadzu GCMS-QP5050 A with a direct inlet. MALDI-TOF mass spectra were recorded on a Bruker Autoflex. Elemental analysis was carried out at Center for Organic Elemental Microanalysis, Graduate School of Pharmaceutical Science, Kyoto University. GC analysis was carried out using a Shimadzu GC-17 A equipped with an integrator (C-R8 A) with a capillary column (CBP-5, 0.25 mm i.d.× 25 m). Column chromatography was carried out on silica gel (Kanto N60, spherical, neutral, 63–210 μm). TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck Silica gel 60F254.

General Procedure for Palladium-Catalyzed Hydroesterification of Internal Alkynes (2a–2j) with Aryl Formates (1) (Table 1 and Table 2)

$[Pd(OAc)_2]$ (5.6 mg, 0.025 mmol) and phosphane (0.050 mmol or 0.10 mmol, P/Pd = 4) were added to a 10-mL flask equipped with a three-way glass-plug stopcock attached by a standard ground glass joint. The flask was evacuated and backfilled with argon three times. Then, aryl formate (**1a**, **1e–i**, 2.0 mmol) and mesitylene (0.50 mL) were added to the flask under flowing Ar, and the resulting solution was stirred at room temperature for 15 min. Internal alkyne (**2a–j**, 0.50 mmol) was added to the flask under Ar and the mixture was stirred for additional 10 min. The reaction was carried out at 100 °C (bath temperature). After cooling to room temperature, the mixture was evaporated and the product was isolated by silica gel chromatography using hexane-AcOEt as an eluent. The GC yields were obtained using tridecane as an internal standard.

General Procedure for Palladium-Catalyzed Hydroesterification of Terminal Alkynes (2k–r) with Phenyl Formate (1a) (Table 3)

$[Pd_2(dba)_3]$ (11.5 mg, 0.0125 mmol) and xantphos (29 mg, 0.050 mmol) were added to a 10-mL flask equipped with a three-way glass-plug stopcock attached by a standard ground glass joint. The flask was evacuated and backfilled with argon three times. Then, **1a** (565 μL, 5.0 mmol) and mesitylene (1.5 mL) were added to the flask under flowing Ar, and the resulting solution was stirred at room temperature for 15 min. Then, terminal alkyne (**2k–r**, 0.50 mmol) was added to the flask under Ar, and the mixture was stirred for additional 10 min. The reaction was carried out at 100 °C

(bath temperature) for 24 h. After cooling to room temperature, the mixture was evaporated and the product was isolated by silica gel chromatography using hexane-AcOEt as an eluent.

General Procedure for Palladium-Catalyzed Conversion of Phenyl Formate (1a) (Table 4)

$[Pd(OAc)_2]$ (5.6 mg, 0.025 mmol) and a phosphane (0.050 mmol or 0.10 mmol, P/Pd = 4) were added to a 10-mL flask equipped with a three-way glass-plug stopcock attached by a standard ground glass joint. The flask was evacuated and backfilled with argon three times. Then **1a** (226 μL, 2.0 mmol), tridecane (98 μL, 0.40 mmol, internal standard) and mesitylene (1.0 mL) were added to the flask under flowing Ar, and the resulting solution was stirred at room temperature for 15 min. The reaction was carried out at 100 °C (bath temperature). A small aliquot (40 μL) was taken out from the reaction mixture at a suitable interval and a conversion of **1a** was analyzed by GC. A time-course profile for the conversion of **1a** using dppf as a ligand is shown in the Supporting Information, Figure S1. From the slope of the linear plot, a zero-order rate constant k_{obs} in $-d[\mathbf{1a}]/dt = k_{obs}[\mathbf{1a}]^0$ was determined.

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research on Priority Areas ("Synergy of Elements" and "Chemistry of Concerto Catalysis") from Ministry of Education, Culture, Sports, Science and Technology, Japan.

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[6] Abbreviations: xantphos: 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, *o*-Tol = 2-methylphenyl, Cy = cyclohexyl, dppe = 1,2-bis(diphenylphosphino)ethane, dppb = 1,2-bis(diphenylphosphino)butane, dppbz = 1,2-bis(diphenylphosphino)benzene, *rac*-BINAP = bis(diphenylphosphino)-1,1′-binaphthyl, dppf = 1,2-bis(diphenylphosphino)ferrocene.

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