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Co-catalysis over bi-functional ligand based Pd-catalyst for tandem bis-alkoxycarbonylation of terminal alkynes

Da Yang,^a Huan Liu,^a Dong-Liang Wang,^a Zhoujie Luo,^a Yong Lu,^a Fei Xia^{ab}* and Ye Liu^a*

The bi-functional ligand (L1) containing diphopshino-fragment and sulfonic acid group (-SO₃H) enabled PdCl₂(MeCN)₂ to efficiently catalyze the tandem bis-alkoxycarbonylation of terminal alkynes to produce aryl-/alkyl-substituted succinate (α , ω -diesters). It was found that the incorporated -SO₃H in L1 indispensably assisted Pd-catalyst to accomplish this tandem reaction via intramolecular synergic effect. The co-catalysis over L1-based Pd-catalyst was not a result of the physical mixture of Xantphos and MeSO₃H. The *in situ* FT-IR analysis verified that the formation and stability of Pd-H active species was facilitated with the presence of L1. The formation of stabilized diacylpalladium intermediate (**F**) was the critical driving force for the second-step methoxycarbonylation. The DFT calculation was carried out to optimize the geometric structure of **F**, which indicated that the developed intramolecular O···H hydrogen bonds were the important structural feature to stabilize **F**. In addition, the L1-based Pd-catalyst could be recycled successfully for at least 3 runs in the ionic liquid of [Bmim]NTf₂ without the obvious activity loss and the detectable metal leaching.

Introduction

The one-pot tandem bis-alkoxycarbonylation of alkynes is a useful protocol to produce aryl-/alkyl-substituted succinate with advantages of 100% atom economy, simplified process operation, and the utilization of cheap CO as building block¹. It has been well known that aryl-/alkyl-substituted succinate are particularly important chemicals in material science such as for the syntheses of dendrimers and polyester/polyamides²⁻⁴, as well used as lubricants⁵, matrix metalloproteinase inhibitor⁶, and active intermediates with pharmaceutical interest'. Unfortunately, the one-pot tandem bis-alkoxycarbonylation of alkynes to produce saturated diesters with apparent simplicity is still a significant challenge up to date. The bisalkoxycarbonylated product of dimethyl 2-phenylsuccinate was only observed as the by-product by Cole-Hamilton⁸ and Williams⁹ respectively. In order to obtain the saturated diesters, the oxidative bis-alkoxycarbonylation of alkenes has been extensively explored but with the disadvantages of low selectivity due to many side reactions and risk of using dangerous oxidants^{10–13}.

Although Pd-catalyzed alkoxycarbonylation of alkynes has commonly allowed for the production of $\alpha,\beta\text{-unsaturated}$

esters in an easy one-step synthesis^{14–17}, the subsequent alkoxycarbonylation of deactivated α , β -unsaturated esters (as the electron-deficient functional alkenes) was found not to continue under the same applied catalytic conditions. Instead, alkoxycarbonylation of simple alkenes was widely reported in the same manner to generate saturated esters¹⁸⁻²⁰. Anyway, the alkoxycarbonylations of several functional alkenes have been successfully reported over Pd-catalysts under the acidic condition²¹⁻²³. It was found that with the presence of methanesulfonic acid (MSA), 1,2-bis(di-tertbutylphosphinomethyl)benzene-based Pd-catalvst could efficiently promote methoxycarbonylation of acrylates to produce succinate derivatives²¹. And the functional alkene of methacrylamide could also be carbonylated to give 3methylsuccinimide over the acidic phosphine-modified Pdcatalytic system²³. These facts highlighted us that the alkoxycarbonylation of electron-deficient functional alkenes has to be initiated by the bi-functional catalysts containing sulfonic acid (-SO₃H) and phosphine-modified Pd-complexes.

Based on our continuous interest in co-catalysis to drive up one-pot tandem carbonylations for the production of high valued compounds, we applied a bi-functional ligand (L1²⁴) based Pd-catalyst which enabled co-catalysis for one-pot tandem bis-alkoxycarbonylation of alkynes to produce aryl-/alkyl-substituted succinates (Scheme 1). Such one-pot tandem reaction catalyzed by the bi-functional ligand-based Pdcomplex has never been reported before. Moreover, in order to explain the unique performance of L1-based Pd-catalyst for bis-alkoxycarbonylation of alkynes, the technique of *in situ* high pressure FT-IR spectroscopy and the density functional theory (DFT) calculation were carried out to study the formation of the critical Pd-complex intermediates. In addition,

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as an ionic ligand, the bi-functional ligand of **L1** was used with the room temperature ionic liquid (RTIL) solvent to fulfill the recovery and recycling of the Pd-catalyst, which has been regarded as an efficient alternative to immobilize the homogenous catalysts^{25,26}.



Scheme 1 Bi-functional ligand (L1) containing diphosphino-fragment and - SO_3H group for Pd-catalyzed bis-alkoxycarbonylation of alkynes to produce aryl-/alkyl-substituted succinate succinates

Results and discussion

the Firstly. tandem bis-methoxycarbonylation of phenylacetylene was studied as a model reaction over L1based PdCl₂(MeCN)₂ catalyst. As shown in Table 1, without any auxiliary additive, under the selected conditions (100 °C, P/Pd = 2 molar ratio, CO 1.0 MPa and 20 h), L1-based Pd-complex exhibited high activity towards the tandem bismethoxycarbonylation of phenylacetylene along with 80% vield of dimethyl 2-phenylsuccinate (Entry 1, see Fig. S1 in ESI for its structural characterization). Increasing P/Pd molar ratio up to 4 led to a further increased yield up to 90% (Entry 2). An increase of CO pressure from 1.0 MPa to 4.0 MPa led to the decreased selectivity to dimethyl 2-phenylsuccinate (Entry 3,

Sel._{diester} 75%), along with the increased selectivity to the linear product of methyl cinnamate (Entry 3, Sel. L-ester 18%). Comparatively, under the same conditions, the use of Xantphos in place of L1 just resulted in 36% yield of the diester along with the presence of linear and branched mono-esters as the main products (Entry 4). The mechanical mixture of Xantphos (0.05 mmol) and MeSO₃H (0.1 mmol) in the stoichiometric amount could improve the yield of dimethyl 2phenylsuccinate to some extent (Sel.diester 54%), but it was still much lower than that obtained over L1-based Pd-catalyst (Entry 5 vs 1). The use of sodium salt of L1 (i.e. L2) also led to a dramatic drop in selectivity to the diester (Entry 6, Sel.diester 40%). The mixing of the stoichiometric amount of MeSO₃H (0.1 mmol) and L2 (0.05 mmol) was still uncompetitive to that over L1 (Entry 6 vs 1). These results proved that the presence of -SO₃H was prerequisite for promoting the second-step methoxycarbonylation of α , β -unsaturated esters. Particularly, as a bi-functional ligand, L1 intramolecularly incorporated with diphosphino-fragment and -SO₃H group corresponded to much better performance than the mechanical mixture of L2 (or Xantphos) and MeSO₃H towards this tandem bismethoxycarbonylation. In addition, over L1, the left amount of methyl 2-phenylacrylate, which was the branched product of the first-step methoxylcarbonylation of phenylacetylene, was universally less than those over Xantphos and L2 (Entry 1-3 vs 4-7). At the same time, a scaled-up experiment was performed (Entry 8), the product of dimethyl 2-phenylsuccinate was obtained by the yield of 88%. It was indicated that this tandem bis-alkoxycarbonylation of phenylacetylene to diester had an excellent scalability and potential application in industry.

Table 1 Pd-catalyzed bis-methoxycarbonylation of phenylacetylene with MeOH under different conditions^a

	CO + MeOH Cat.: PdC⊵(MeCl	N)2 ^L methyl cinnamate	• OMe <u>CO + MeC</u> methyl 2-phenylacrylate	MeO dimethyl 2-phenyls	OMe Me	Antphos	SO3H VIE VIE SO3H PPh2 PPh2 SO3H L1	SO3Na Me Me SO3Na L2
Entry	Ligand	Solvent	Amount of MeSO ₃ H	Temp. (°C)	Conv. (%) ^b	Sel. _{L-ester} (%)	^b Sel. _{B-ester} (%)	^b Sel. _{diester} (%) ^b
1	L1	MeOH		100	100	12	8	80
2 ^c	L1	MeOH		100	100	10	-	90
3 ^d	L1	MeOH		100	100	18	7	75
4	Xantphos	MeOH		100	100	41	23	36
5	Xantphos	MeOH	6.5 μL (0.1 mmol)	100	100	29	17	54
6	L2	MeOH		100	100	24	36	40
7	L2	MeOH	6.5 μL (0.1 mmol)	100	100	16	30	54
8 ^e	L1	MeOH		120	100	12	-	88

^{*a*} PdCl₂(MeCN)₂ 0.05 mmol (Pd 1 mol%), P/Pd = 2 molar ratio, phenylacetylene 5 mmol, CO 1.0 MPa, MeOH 3 mL, temp. 100 ^oC, reaction time 20 h; ^{*b*} Determined by GC and GC-Mass. Sel._{L-ester} represents selectivity to linear methyl cinnamate. Sel._{B-ester} represents selectivity to branched methyl 2-phenylacrylate. Sel._{diester} represents selectivity to dimethyl 2-phenylacrylate. Sel._{diester} selectivity selectivity to dimethyl 2-phenylacrylate. Sel._{diester} selectivity select

The reaction evolution profiles (Fig. 1) of bismethoxycarbonylation of phenylacetylene over L1-based $PdCl_2(MeCN)_2$ system indicated that, in the initial 30 min, the first-step methoxycarbonylation had completed, while the second-step methoxycarbonylation was just initiated. It was noted that only the branched methyl 2-phenylacrylate with C=C bond in *gem*-position was able to gradually convert to the corresponding diester until it depleted completely in 20 h. In

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contrast, the linear methyl cinnamate barely proceeded the subsequent methoxycarbonylation. Evidently, the use of **L1** absolutely preferred the formation of the branched unsaturated ester to the linear one in the first-step transformation.



Figure 1 The evolution profiles of phenylacetylene conversion and product selectivity distribution vs reaction time catalyzed by $L1-PdCl_2(MeCN)_2$ (phenylacetylene 5 mmol, MeOH 3 mL, 1.0 MPa, 100 °C, P/Pd = 4 molar ratio, Pd 1 mol%)



Figure 2 The ³¹P NMR spectra (202 MHz) of the selenides of Xantphos, L1, and L2: (a) reacting elemental selenium with L1 in CD₃OD at 70 °C for 10 h; (b) reacting elemental selenium with L2 in CD₃OD at 70 °C for 10 h; (c) reacting elemental selenium with Xantphos in CDCl₃ at 70 °C for 10 h.

The key role of the bi-functional ligand of **L1** for Pd-catalyst catalyzed bis-methoxycarbonylation of phenylacetylene impelled us to understand its inherent nature. It is believed that a decrease of ${}^{1}J_{^{\rm H}P.^{^{\rm T}Se}}$ detected by ${}^{31}P$ NMR spectroscopy indicates an increase in the character of σ -donor ability (*i.e.*, less π -acceptor) of the phosphine^{27–29}. The values of ${}^{1}J_{^{\rm H}P.^{^{\rm T}Se}}$ for **L1**, **L2** and Xantphos were measured in the order of **L2** (${}^{1}J_{^{\rm H}P.^{^{\rm T}Se}}$ = 758 Hz) ~ Xantphos (${}^{1}J_{^{\rm H}P.^{^{\rm T}Se}}$ = 758 Hz) > **L1** (${}^{1}J_{^{\rm H}P.^{^{\rm T}Se}}$ = 743 Hz)

(Fig. 2). It was indicated that **L1** was featured with relatively stronger σ -donor character than **L2** or Xantphos. The stronger σ -donor ligand **L1** tailed with SO₃H group might facilitate the formation and stability of the active Pd-H species, which was the real catalyst in charge of alkoxycarbonylation. In order to confirm this conjecture, the *in situ* high pressure FT-IR spectroscopic technique was applied for an in-depth understanding of the catalytic mechanism over **L1**-based Pd catalyst³⁰.

Figure 3 provided the in situ high pressure FT-IR analysis for L1-PdCl₂(MeCN)₂ and Xantphos-PdCl₂(MeCN)₂ systems. The characteristic peaks for gaseous CO were clearly observed with the vibrations of 2175 and 2116 cm⁻¹. As for L1-PdCl₂(MeCN)₂ system (Fig. 3-A), while the temperature increased to 100 °C, a weak absorption peak at 1947 cm⁻¹ appeared immediately and then reached the maximum intensity at 120 °C, which was identified as the active Pd-H (palladium-hydride) species³¹. The accompanying peak at 1871 cm⁻¹ was assigned to Pd-CO species which was the result of the complexation of PdCl₂(MeCN)₂ with CO. Along with the appearance of the peak at 1947 cm⁻¹ (Pd-H species), the most characteristic peak at 1730 cm⁻¹ assigned to the product of dimethyl 2phenylsuccinate (its standard FT-IR spectrum was given as Fig. S2-e in ESI) was concurrently observed. In contrast, over Xantphos-PdCl₂(MeCN)₂ system (Fig. 3-B), although Pd-CO and Pd-H species could also be generated during the reaction, their poor stability and short longevity made the corresponding vibrations hard to be observed in the overall monitoring process. Correspondingly, only the characteristic peaks at 1718 cm⁻¹ for the mono-methoxycarbonylated product of methyl cinnamate (its standard FT-IR spectrum was given as Fig. S2-d in ESI) was observed, which implied that the subsequent methoxycarbonylation of the α , β -unsaturated ester was inhibited completely. The in situ high pressure FT-IR characterization confirmatively verified that the formation of Pd-H species (v 1947 cm⁻¹) with better stability and longevity was greatly facilitated by the presence of L1 and then inherently corresponded to the more efficient bismethoxycarbonylation to afford the diester of dimethyl 2phenylsuccinate.

Then a mechanism for the studied tandem reaction over L1-PdCl₂(MeCN)₂ system was proposed in Scheme 2. In the atmosphere of CO under heating condition, Pd(II)-precursor was reduced to generate Pd(0) species in situ, which behaved as the reductant to reduce proton (H⁺) into hydride (H⁻) for the formation of active Pd^{II} -H species (A)^{32,33}. With the presence of L1, the readily formed Pd(II)-H active species (A) was added by terminal alkynes to form а (β-vinyl)palladium intermediate (B) following Markownikoff's rule. The insertion of CO to Pd-C bonds afforded an acylpalladium intermediate complex (C) which proceeded methanolysis to mainly yield the branched α , β -unsaturated ester (D) accompanied by the regeneration of Pd(II)-H species. In the sluggish second-step methoxycarbonylation, the branched α , β unsaturated ester (D) with the exposed terminal C=C double bond in gem-position was preferentially add to Pd-H species (A) again to afford the alkylpalladium intermediate complex (E). The subsequent insertion of another CO to E afforded the diacylpalladium

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intermediate of **F**, whose availability is the driving force of the tandem reactions and irreversibly responsible for the generation of the bis-methoxycarbonylated product of **G**. In this proposed mechanism, both MeOH and Bronsted acid could serve as the proton reservoir. In the first-step methoxycarbonylation, the proton (H⁺) coming from the sluggish deprotonation of MeOH corresponded to the formation of Pd^{II}-H species¹⁷. Hence, even

without the acidic additive, the mono-carbonylated product isomers were also observed in Entries 4 and 6 of Table 1. Anyway, only the proton (H^+) coming from an acid like **L1** with the rapid proton shift was responsible for the formation of the hydride (Pd^{II} -H) which led to the success of the subsequent methoxycarbonylation.



Figure 3 The *in situ* high-pressure FT-IR spectra recorded from 30 to 120 °C after mixing PdCl₂(MeCN)₂, L1 (or Xantphos), MeOH and phenylacetylene in 1.0 MPa CO (A: L1, PdCl₂(MeCN)₂, phenylacetylene and MeOH; B: Xantphos, PdCl₂(MeCN)₂, phenylacetylene and MeOH.



 $[\]label{eq:scheme 2} Scheme \ 2 \ The proposed \ catalytic mechanism \ over \ L1-PdCl_2(MeCN)_2 \ for \ bis-methoxy carbonylation \ of \ terminal \ alkyness \ alkyness \ bis \ bis$

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To further elucidate the formation and stability of the critical diacylpalladium intermediate of F, the DFT calculation was performed in Gaussian09 software package³⁴ to optimize its geometric structure (see computational data in ESI). As shown in Fig. 4, F is in a distorted square-planar geometry in which Pd(II)(d⁸)-center is coordinated by the diphosphinofragment of L1 in cis-position, and the two carbonyl groups (coming from dimethyl 2-phenylsuccinate moiety). The two Pd-P bond distances are the same as 2.5 Å and the two Pd-C(=O) bond distances are 2.0 Å and 2.9 Å, respectively. Meanwhile, the oxygen atoms from the ester (-COOCH₃) group both can form hydrogen-bonds with the hydrogens from phenyl in L1, with H…O distances of 2.2 \sim 2.4 Å. Hence, the stability of **F** is guaranteed by the factors including: (1) the chelating effect of L1 to Pd-center, (2) the thermodynamically favored fivemember ring structure between Pd-center and the two C=O groups, and (3) the developed hydrogen-binding interactions between the ester group and the phenyl in L1.



Figure 4 The optimized structure and bond lengths of F by DFT calculation (R is phenyl group herein).

On the other hand, as an ionic ligand, **L1** could be used with the room temperature ionic liquid (RTIL) solvent to fulfil the recovery and recycling of the homogeneous Pd-catalyst. As summarized in Table 2, in [Bmim]NTf₂ (1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide), **L1**-based PdCl₂(MeCN)₂ system could be recycled at least 3 runs. The ICP-OES analysis indicated that the leaching of Pd in the combined organic phase was non-detectable (below the

detection limit of 0.1 μ g/g). Anyway, in the fourth run, the selectivity to dimethyl 2-phenylsuccinate dropped to 48% along with the precipitation of Pd-black, indicating the deactivation of the Pd-catalyst.

The scope of bis-alkoxycarbomylation catalysed by L1-PdCl₂(MeCN)₂ was explored in Table 3. It was found that the first-step alkoxycarbonylation all performed smoothly with 100% conversion without discrimination on the steric and electronic effects of the substituents in the applied alkynes. The steric and electronic effects of the substrates only had influence on the reaction rate of the second-step alkoxylcarbonylation of the (gem-)-unsaturated ester. As for phenylacetylene, when EtOH was applied instead of MeOH, the increased steric hindrance slowed down the reaction rate for the second-step alkoxycarbonylation (Entry 2, 78%). The substituents such as methyl, methoxyl, tertiary butyl and halides at para-position had slight influence on the reaction rate of the second-step methoxycarbonylation along with the good diester yields from the range of 76%~85% (Entries 3-8). Comparatively, the substituent such as methyl at orthoposition obviously decelerated the reaction rate of the secondstep methoxycarbonylation with 42% yield of the diester (Entry 9 vs 3). Interestingly, as for the linear aliphatic alkynes such as 1-octyne, the alkyl-substituted succinates (Entry 10, 75%) were obtained as the major products but along with the other α, ω -diesters due to the double-bond shift of the resultant α , β -unsaturated ester before the second-step methoxycarbonylation. When 1-hexyne was applied to repeat the reaction, the targeted dimethyl 2-butylsuccinate was only obtained as a minor product accompanied by the other isomerized diesters.

Table 2 Recycling uses of L1 based $PdCl_2(MeCN)_2$ catalytst for bismethoxycarbonylation of phenylacetylene^a



Run	Conv. (%) ^b	Sel. _{L-ester} (%) ^b	Sel. _{B-ester} (%) ^b	Sel. _{diester} (%) ^b
1st (fresh)	100	12	-	88
2nd	100	16	-	84
3rd	100	12	6	82
4th	100	12	40	48

^a PdCl₂(MeCN)₂ 0.05 mmol (Pd 1 mol%), P/Pd = 4 molar ratio (**L1** 0.1 mmol), phenylacetylene 5.0 mmol, CO 1.0 MPa, MeOH 3 mL, [Bmim]NTf₂ 3 mL, temp. 120 °C, reaction time 15 h; ^b Determined by GC and GC-mass spectrometry. Sel._{L-ester} represents selectivity to linear methyl cinnamate. Sel._{B-ester} represents selectivity to branched methyl 2-phenylacrylate. Sel._{diester} represents selectivity to dimethyl 2-phenylsuccinate.

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 a PdCl₂(MeCN)₂ 0.05 mmol (Pd 1 mol%), P/Pd = 4 molar ratio (**L1** 0.1 mmol), alkyne 5.0 mmol, CO 1.0 MPa, alcohol 3 mL, temp. 100 °C, reaction time 20 h, isolated yields; b GC yield.

Conclusions

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The one-pot tandem bis-alkoxycarbonylation of terminal alkynes to produce aryl/alkyl-substituted succinate was efficiently fulfilled over L1-based Pd-catalyst. The applied bi-functional ligand of L1 intramolecularly contained one diphosphino-fragment and two sulfonic acid (-SO₃H) groups. L1-based Pd-catalyst preferentially enabled the transformation of the terminal alkyne into the branched α,β -unsaturated esters, and then continuously converted them into the target diesters (aryl-/alkyl-substituted succinates) under the same catalytic conditions. Co-catalysis of L1-based Pdcatalyst for bis-methoxycarbonylation of alkynes was more efficient than that of the physical mixture of Xantphos (or L2) and MeSO₃H. The in situ FT-IR analysis proved that the formation and stability of Pd-H active species (ν 1947 cm⁻¹), which exclusively spurred the second-step methoxycarbonylation, was greatly facilitated by the involvement of L1. The formation of the stabilized diacylpalladium intermediate of F, whose geometric structure was optimized by the DFT calculation, was the critical driving force for the methoxycarbonylation of the electron-deficient alkenes (α , β unsaturated esters). On the other hand, the ionic nature of L1 could guarantee the coordinated Pd-catalyst to be recycled in the RTIL of [Bmim]NTf₂ at least 3 runs without the obvious activity loss and the detectable leaching of Pd and P elements in the organic phase.

Experimental

Reagents and analysis

The chemical reagents were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd. and Alfa Aesar China, which were used as received. The solvents were distilled and dried before use. The ¹H and ³¹P NMR spectra (85% H₃PO₄ sealed in a capillary tube as an internal standard) were recorded on a Bruker ARX 500 spectrometer at ambient temperature. Gas chromatography (GC) was performed on a SHIMADZU-2014 equipped with a DM-Wax capillary column (30 m × 0.25 mm × 0.25 μ m). GC-mass spectrometry (GC-MS) was recorded on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector. FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrometer. The amount of Pd and P in the sample was quantified by using an inductively coupled plasma optical emission spectrometer (ICP-OES) on an Optima 8300 instrument (PE Corporation).

Synthesis

4,5-bis(diphenylphosphanyl)-9,9-dimethyl-9H-xanthene-2,7disulfonic acid (L1)

L1 was prepared according to the procedures reported by van Leeuwen²⁴ with some modifications.

Under nitrogen atmosphere, to the solution of 9,9dimethyl-4,5-bis(diphenylphosphino)xanthene (Xantphos, 1.0 g, 1.7 mmol) in concentrated sulfuric acid (2.0 mL, 98%) cooled to 0 °C was added dropwise with oleum (3.0 mL, 30% SO₃ in H₂SO₄). The resultant mixture was stirred for 24 h along with the reaction temperature increasing to ambient. Then ice water (20 mL) was added slowly to precipitate the white solid, which was collected and then washed with ethyl acetate (2 × 4 mL). The white solid was obtained as the product of **L1** after drying at 70 °C under vacuum in the yield of 60% (0.75 g). ¹H NMR (500 M, CD₃OD): δ = 8.0 (s, 2H, 2CPPh₂CH), 7.22-7.4 (m, 22H, phenyl, 2C₆H₅ + 2CHCSO₃), 1.7 (s, 6H, 2CH₃); ³¹P NMR (500M, CD₃OD): -17.8 (s, *P*Ph₂).

Sodium 4,5-bis(diphenylphosphanyl)-9,9-dimethyl-9Hxanthene-2,7-disulfonate (L2)

L2 was prepared according to the procedures reported by van Leeuwen²⁴ with some modifications.

Under nitrogen atmosphere, to the solution of 9,9dimethyl-4,5-bis(diphenylphosphino)xanthene (Xantphos, 1.0 g, 1.7 mmol) in concentrated sulfuric acid (2.0 mL, 98%) cooled to 0 °C was added dropwise with oleum (3.0 mL, 30% SO₃ in H₂SO₄). The resultant mixture was stirred for 24 h along with the reaction temperature increasing to ambient. The degassed ice water (20 mL) was added slowly to the solution, which was subsequently poured into a solution of triisooctylamine (54 mmol, 2.3 mL) in toluene (10 mL). The toluene layer was washed with water and then neutralized with NaOH solution (0.5 M). The aqueous phase was concentrated by vacuum to give a white solid, which was washed by alcohol to give the product of **L2** (0.86 g, Yield 65%). ¹H NMR (500M, CD₃OD): 8.0 (s, 2H, 2CPPh₂CH), 7.1-7.4 (m, 22H, 2C₆H₅ + 22CHCSO₃), 1.7 (s, 6H, 2CH₃); ³¹P NMR (500M, CD₃OD): -12.8 (s, PPh₂).

General procedures for one-pot tandem bisalkoxycarbonylation of alkynes

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In a typical experiment, $PdCl_2(MeCN)_2$ (0.05 mmol), L1 (0.05 mmol) (or the other ligand) were mixed with phenylacetylene (5 mmol, or the other alkyne) and methanol (3 mL, or the other alcohol). The mixture was added in a 50 mL sealed Teflon-lined stainless steel autoclave which was purged with CO (0.3 MPa) for two times and then pressured by CO to 1.0 MPa. Then the reaction mixture was stirred vigorously at appointed temperature for some time. Upon completion, the autoclave was cooled down to room temperature and slowly depressurized. The solution was analyzed by GC to determine the conversions (*n*-dodecane as internal standard) and the selectivities (normalization method), and the products were further identified by GC-mass spectrometry, ¹H NMR and ¹³C NMR.

When [Bmim]NTf₂ was used as the solvent for the tandem bismethoxycarbonylation, in which phenylacetylene (5 mmol), MeOH (3 mL), PdCl₂(MeCN)₂ (0.05 mmol), and **L1** (0.1 mmol) were mixed sequentially. Upon reaction, the IL phase was washed with *n*hexane (3 mL × 3) to completely extract the reactants and products out of the IL phase. The combined organic phase was analyzed by GC and ICP-OES. The remaining IL phase was directly used without further treatment for the next run (if required MeOH was added additionally).

Computational methods

The DFT calculation was carried out using the Gaussian 09 software package.³⁴ The structural optimization of **F** was performed using the M06 functional^{35,36} combined with the Lanl2dz^{37,38} and 6-31G*³⁹ basis set, denoted as the M06/Lanl2dz+6-31G*method. The Lanl2dz basis set combined with the relativistic effective core potential^{37,38} was used to describe the metal element Pd and the 6-31G* basis set was utilized to describe the nonmetallic elements C, O, P and H. The solvent effect of methanol was evaluated using the SMD⁴⁰ model at the same computational level, with the dielectric constant epsilon of methanol being 31.2. The Cartesian coordinates of optimized structures of **F** can be found in Table S2 of ESI.

In situ high-pressure FT-IR spectral characterization

The *in situ* high pressure FT-IR spectroscopic were recorded on a Nicolet NEXUS 670 spectrometer. The spectral resolution was about 4 cm⁻¹. A mixture of 0.010mmol of **L1** (or Xantphos) with 0.005mmol PdCl₂(MeCN)₂ and 0.1mL of phenylacetylene in methol was added in the specially designed high-pressure IR cell, in which cylindric CaF₂ was used as the sealing sheets. Then 1.0 MPa CO was inflated into the sealed call. Real time monitoring was performed under the different reaction temperatures.

The mixture compositions including $PdCl_2(MeCN)_2$, **L1** (or Xantphos), phenylacetylene and CO were completely the same as those for the real reaction in Table 1, except for the much high concentration of $PdCl_2(MeCN)_2$ and the ligand required for FT-IR spectral detection.

X-ray Crystallography

Intensity data were collected at 296(2) K on a Bruker SMARTAPEX II diffractometer using graphite monochromated Mo-K α radiation (λ = 0.71073 Å). Data reduction included absorption corrections by the multi-scan method (Table S1). The structures were solved by direct methods and refined by full matrix least-squares using SHELXS-97 (Sheldrick, 1990), with all non-hydrogen atoms refined anisotropically. Hydrogen atoms were added at their geometrically ideal positions and refined isotropically.

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Notes and references

‡ CCDC 1573652 contains the supplementary crystallographic data in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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The one-pot tandem bis-alkoxycarbonylation of alkynes was accomplished over a bi-functional ligand based Pd-catalyst with function of co-catalysis.