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Novel multi-dentate phosphines for Pd-catalyzed alkoxycarbonylation of alkynes promoted by H₂O additive



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ABSTRACT

A series of novel multi (bi-/tri-/tetra-)-dentate phosphines with good robustness against water and oxygen were synthesized and fully characterized. It was found that the developed ionic tri-dentate phosphine (**L2**') enabled Pd-catalyzed alkoxycarbonylation of alkynes most efficiently while H₂O was used as an additive instead of acid. As for **L2**', its unique steric configuration with two types of potential P-P chelation modes (P...P distance of 4.31 Å and 4.36 Å respectively) to Pd-centre rendered the corresponding Pd-catalyst high activity and good stability for alkoxycarbonylation of alkynes. The *in situ* FT-IR analysis also verified that the formation and stability of Pd–H active species were greatly facilitated with the presence of **L2**' as well as H₂O additive. In addition, as an ionic phosphine, **L2**' based PdCl₂(MeCN)₂ system immobilized in RTIL of [Bmim]NTf₂ could be recycled for 7 runs without obvious activity loss or metal leaching.

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1. Introduction

Alkoxycarbonylation of alkynes is one of 100% atom-economic protocols for the production of α , β -unsaturated esters [1]. Compared to oxidative alkoxycarbonylation of olefins [2], alkoxycarbonylation of alkynes is more environmental benign with the advantages of no risk of a large excess of dangerous oxidants and then the much better selectivity.

The steric and electronic properties of phosphines play important roles for Pd-catalyzed alkoxycarbonylation of alkynes [3–6]. The N,P-containing ligands have been found to be favourable for this reaction [3–6]. It was found that the N,P-chelating effect in such hybrid ligands was responsible for the improved catalytic performance of the corresponding Pd-complexes [7]. Similarly, the bidentate phosphines with dramatic chelating effect also have attracted much attention to tailor the catalytic performance of the transition metal complexes [8,9]. For example, the rigid diphosphine ligands (such as Xantphos and Nixantphos) with the fixed bite angles have been widely applied in Pd-catalyzed methoxycarbonylation [9]. However, the multi-dentate flexible phosphines with the adjusting chelating mode to occupy the preferential position (such as *cis-, trans-*, ee-site, ea-site, or aa-site in a complex) were rarely reported. And the recovery and recycling of

* Corresponding author. E-mail address: yliu@chem.ecnu.edu.cn (Y. Liu). the multi-dentate phosphine-based Pd-catalysts for homogenous alkoxycarbonylation has never been reported in literature.

On the other hand, a (Brønsted/Lewis) acid promoter is required in this protocol universally. However, the excess proton coming from Brønsted acid can induce the alkylation of phosphine [10], and the deactivation Pd-H hydride species by evolution of H₂ [11,12]. As for Lewis acid, only Al(OTf)₃ was reported to be the effective additive in Pd-catalyzed alkoxycarbonylation [8]. This bimetallic system is relative more complicated than monometallic one. Compare to acid additives, water is a low-cost, safe and environmental friendly source. We have reported the successful hydroaminomethylation of olefins with H₂O as the hydrogen source to generate metal hydride species [13]. Accordingly, the use of H₂O as a promoter in place of acids is feasible for alkoxycarbonylation of alkynes if the stable and moisture-insensitive ligand is involved.

To fulfil the efficient alkoxycarbonylation of alkynes with H_2O as promoter, a series of novel bi-/tri-/tetra-dentate phosphines with good robustness against water and oxygen were synthesized and fully characterized herein (Scheme 1). In these developed multi-dentate phosphines, the locations of the incorporated – PPh₂ fragments attached to the parent core of 1-(thiophen-3'-yl)-imidazolyl could be adjusted more flexibly than the ones in the rigid phosphines like Xantphos and Nixantphos due to the rotatable σ -bond linkage between imidazolyl and thiophenyl moieties.





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Scheme 1. Synthesis of the multi-dentate phosphines based on 1-(thiophen-3'-yl)-imidazolyl core.

2. Results and discussion

2.1. Characterization of phosphines (L1, L2, L2', L3 and L3')

Firstly, the ³¹P NMR spectra of the synthesized phosphines are shown in Fig. 1. All the phosphorus atoms correspond to the signals at much higher field ($\delta < -18$ ppm) than that of PPh₃ ($\delta = -5.5$ ppm) [14], indicating the enhanced electron-rich character of these phosphines. As for the multi-dentate phosphines (**L1**-**L3**, **L2**' and **L3**'), each —PPh₂ fragment exhibits anisotropy in terms of the electronic effect. The available positive charge in imidazolium with the strong electron-withdrawing effect can dramatically reduce the electron density of the adjacent $-PPh_2$ fragments in **L2**' and **L3**' respectively, leading to the obvious shifts of the corresponding signals to the much lower field. For example, 2-C positioned $-P^2Ph_2$ in the neutral **L2** corresponding to the signal of -34.4 ppm down-field shifts to -20.6 ppm upon methylation by MeOTf at imidazolyl in **L2**'.

The TG/DTG analyses of **L1-L3**, **L2**' and **L3**' in air flow (Fig. 2) confirm that, the thermal decomposition temperature of ionic



Fig. 1. ³¹P NMR spectra (202 MHz) of the phosphines of L1-L3, L2' and L3'.



Fig. 2. TG/DTG analyses of the phosphine ligands of L1-L3, L2' and L3' in air flow.

phosphines is universally higher than their neutral counterparts (T_{decomp} .: 340 °C for **L2**′ vs 315 °C for **L2**; 315 °C for **L3**′ vs 290 °C for **L3**). And **L2**′ possesses the best stability with the highest T_{decomp} of 340 °C. It is indicated that the involved positive-charged imidazolium with intensive electron-withdrawing effect in **L2**′ and **L3**′ play an important role in stabilizing the electron-rich phosphines against oxygen and water.

The single crystals X-ray diffraction analysis of L1, L2', L3 and L3' are presented in Fig. 3. The configuration of all P-atoms is close to tetrahedral structures and shows no anomalies. In L1, the two -PPh₂ fragments are attached to 2-C of imidazolyl ring and 2'-C of thiophenyl ring respectively. The interplanar dihedral angle (θ) between imidazolyl and thiophenyl is 51.46°, and the two phosphine-fragments are located in distortioned *tans*-position. Due to the rigid thiazolvl and imidazolvl rings, and the remote distance between P atoms (P1...P2 5.44 Å), L1 is impossible to serve as a diphosphine to chelate a transition metal center. In L2', the third introduced -PPh₂ at 5-C of imidazolyl ring results in 2'-C and 5-C positioned –PPh₂ fragments as well as 2'-C and 2-C positioned – PPh₂ ones are both located in distorted *cis*-position with $P \cdots P$ distance of 4.31 Å and 4.36 Å respectively. In this way, the two types of P–P chelation to Pd-centre by L2' is potentially available to accommodate two P-Pd-P linkages (P-Pd bond distance ca. 2.2–2.3 Å [15]) in linearly *trans*-positions [16]. Comparatively, L3 and L3' are hedgehog-like tetra-dentate phosphines. The crowded space upon the forth incorporation of -PPh₂ makes 2'-C and 5-C positioned --PPh₂ fragments as well as 2'-C and 2-C positioned -PPh₂ ones seriously twisted with P···P distances of 4.75 Å and 3.70 Å in L3 (or 4.61 Å and 3.67 Å in L3').

2.2. Alkoxycarbonylation of alkynes over Pd-catalyst with involvement of L1-L3'

Upon the characterizations of the as-synthesized multi-dentate phosphines by ³¹P NMR, TG/DTA and single crystals X-ray diffraction, they were applied with PdCl₂(MeCN)₂ precursor in the model reaction of methoxycarbonylation of phenylacetylene (Table 1). Under the optimal conditions (110 °C, P/Pd ratio of 6, CO 3.0 MPa and 3 h) (Table S1), only the ionic tri-dentate phosphine of **L2**' corresponded to the highest yield of *gem*- α , β -unsaturated ester (86%) with water (instead of any acid) as the additive. In comparison, the others multi-dentate phosphines including its neutral counterpart of **L2** with structure similarity just gave the much lower yields of

the branched methyl 2-phenylacrylate (Entry 3 vs 1, 2 and 4, 5). The decrease of P/Pd molar ratio led to the much slower conversions of phenylacetylene towards the target esters (Entry 3 vs 6 and 7). This relationship indicates that the excess of the involved phosphines was essentially required to prevent the Pd-catalyst from deactivation. Notably, the presence of water dramatically promoted the reaction rate. The conversion of phenylacetylene dropped to 12% if water was absent (Entry 8). The obtained result positively supported that water indeed could serve as an effective promoter to replace Brønsted acid for the generation of Pd-H active species responsible for the catalytic methoxycarbonylation. Without the presence of any phosphine ligand, the reaction did not happen at all (Entry 9). By using BINAP with P...P distance of 4.21 Å [17] to repeat the reaction, in which the two PPh₂-attached phenyl rings were also linked by a rotatable σ -bond, the competitive results in terms of the conversion of phenylacetylene (96%) and B/L ratio (95/5) were obtained in comparison to those over L2' (Entry 10 vs 3). In contrast, the use of Xantphos with $P \cdots P$ distance of 4.08 Å [18] as a rigid bidentate diphosphine led to 99% conversion of phenylacetylene, but the selectivity of the branched gem- α,β -unsaturated ester decreased to 54% (Entry 11).

Correlated to the structural analysis in Fig. 3, L1 can't serve as a diphosphine to chelate Pd-center to guarantee the activity and stability of the corresponding Pd-catalyst, due to remote distance between the two P atoms (P1...P2 5.44 Å). And in the tetradentate phosphines of L3 and L3', the very crowed -PPh₂ fragments with bulky steric hindrance also go against the desired chelation to Pd-center due to the improper P...P distances (4.75 Å and 3.70 Å in L3; 4.61 Å and 3.67 Å in L3'). Hence, L1-, L3- and L3'-based Pd-catalytic systems universally exhibited the relatively worse performance towards the methoxycarbonylation (Table 1, entries 1, 4 and 5). In comparison, only in L2', the availability of 2'-C and 5-C positioned -PPh2 fragments as well as 2'-C and 2-C positioned –PPh₂ ones with P···P distances of 4.31 Å and 4.36 Å respectively facilitated the potential development of two types of P-Pd-P chelation to give rise to stabilization of Pdcomplex intermediate, which corresponded to the high catalytic activity for the reaction (Table 1, entry 3). Although L2 and L2' have the structural similarity, their difference in the electronic nature for $-P^2Ph_2$ with indication of the varied ³¹P NMR signals (Fig. 1) could account for their distinct performance for the methoxycarbonylation (Table 1, entry 2 vs 3). Obviously, $-P^2Ph_2$ linked to positive charged imidazolium in L2' is a more-intensive π -accepting



Fig. 3. The single crystal structures of L1, L2', L3 and L3' [L1: 5.4424(12) Å; L2': P1…P2 4.3662(12) Å, P2…P3 4.3133(11) Å; L3: P1…P3 4.7545(8) Å, P2…P3 3.7048(9) Å; L3': P2…P4 4.6132(19) Å, P3…P4 3.6687(20) Å].

ligand fragment with the ³¹P NMR signal of –20.6 ppm than that in **L2** (δ = –34.4 ppm), due to the much stronger electronwithdrawing effect of imidazolium than that of imidazlyl. Resultantly, over **L2**′, the developed Pd—P bond was consolidated due to the intensive π -backdonation interaction, which facilitated the dissociation of the CO ligand to form the corresponding Pd–acyl complex as the driving force for Pd-catalyzed carbonylation. In addition, **L2**′ possesses the best stability (T_{decomp} = 345 °C, Fig. 2) with less sensitivity to oxygen and moisture, which could warrant the use of water as a promoter without possibility of degradation of **L2**′ self.

The remarkable performance of **L2**'-based Pd-catalyst with H₂O as promoter for methoxycarbonylation provoked us to explore the formation and stability of the active Pd—H species in this process via the high pressure *in situ* FT-IR spectroscopy techinque[19]. As demonstrated in Fig. 4, over **L2**'-PdCl₂(MeCN)₂ system, when the temperature increased from 30 °C to 100 °C gradually, a weak absorption peak at 1944 cm⁻¹ appeared at 100 °C and then reached its maximum intensity at 120 °C, which was identified as the active Pd–H (palladium–hydride) species[9]. The intensive characteristic peak at 1724 cm⁻¹ assigned to the product methyl 2-

phenylacrylate (its standard FT-IR spectrum is given in Fig. S1 in ESI) was observed concurrently. However, over L2-PdCl₂(MeCN)₂ system, the characteristic peak of Pd-H species couldn't be observed under the same conditions (Fig. S2). The *in situ* high-pressure FT-IR characterization further confirmed that the formation of Pd-H species (v 1944 cm⁻¹) with better stability and longevity was greatly facilitated by the presence of L2' with H₂O as promoter, which inherently corresponded to more efficient methoxycarbonylation.

The room temperature ionic liquid (RTIL) has been regarded as the efficient alternative to immobilize the homogenous catalysts [20–24]. As for L2', in consideration of its advantages of the good stability and the high polarity as an ionic compound, L2' was applied together with RTIL solvent to immobilize the corresponding Pd catalyst for recovery and recycling. Due to the mass transfer limitation in the biphasic system, the reaction time was prolonged to 5 h to achieve the acceptable transformation. The results by using the RTILs of [Bmim]BF₄ and [Bmim]NTf₂ respectively as the solvents were summarized in Table 2. It was found that, in [Bmim]BF₄, L2'-based PdCl₂(MeCN)₂ system with presence of H₂O could be recycled 5 runs. In the 6th run, the conversion of



Table 1 Influence of the phosphines on Pd-catalyzed methoxycarbonylation of phenylacetylene.^a

	LI	LZ		LJ	LJ	
Entry	Ligand	P/Pd	H ₂ O (mmol)	Conv. (%) ^b	Sel. _{α,β-esters} (%) ^b	B/L ^b
1	L1	6	2	21	100	93/7
2	L2	6	2	43	100	93/7
3	L2′	6	2	90	100	95/5
4	L3	6	2	47	100	94/6
5	L3′	6	2	66	100	87/13
6	L2′	1	2	38	100	90/10
7	L2′	3	2	58	100	91/9
8	L2′	6	-	12	100	95/5
9	-	6	2	-	-	- '
10	BINAP	6	2	96	100	95/5
11	Xantphos	6	2	99	100	63/37

^a PdCl₂(MeCN)₂ 0.05 mmol (Pd 2 mol%), phenylacetylene 2.5 mmol, H₂O 2 mmol, MeOH 1 mL, toluene 2 mL (dried by sodium before use), temp. 110 °C, reaction time 3 h, CO 3 MPa.

^b Determined by GC and GC-Mass analysis. Sel._{2,6-esters} represents the selectivity to the products of the linear and branched unsaturated esters.

phenylacetylene decreased to 73%. Since [Bmim]BF₄ was not stable enough against water at high temperature. The hydrolysis of [Bmim]BF₄ might occur to generate HF, which poisoned the phosphine ligand, then diminished the catalytic activity. Comparatively, in [Bmim]NTf₂, **L2**'-based PdCl₂(MeCN)₂ system with presence of H₂O could be recycled 7 runs always with well-maintained activity. The ICP-OES analysis indicated that the leaching of Pd in the combined organic phase in each system was non-detectable (below the detection limit of 0.1 µg/g).

The scope of alkoxycarbonylation catalysed by L2'-PdCl₂(MeCN)₂ system was explored (Table 3). As for phenylacetylene, when EtOH was applied instead of MeOH, the alkoxycarbonylation performed smoothly with 89% conversion and 95% selectivity to the branched product (Entry 1). The increased



Fig. 4. In situ high-pressure FT-IR spectra obtained from 30 to 120 °C after mixing PdCl₂(MeCN)₂, **L2**′, MeOH, toluene, water and phenylacetylene under CO (1.0 MPa).

steric hindrance in *i*-PrOH and cyclohexanol slightly slowed down the reaction rate (Entries 2 and 3, conv. 81% - 85%). The substituents such as methyl, tertiary butyl, cyano group and halides at *para*-position had some influence on the reaction rate along with the varied yields for the branched products in the range of 70–86% (Entries 4–9). Comparatively, the substituent such as methyl at *ortho*-position obviously decelerated the reaction rate with 58% yield of the branched product (Entry 10 vs 4). However, methyl at *meta*-position hardly influenced the reaction rate (Entry 11 vs 4). As for the non-conjugated alkynes, the yields of target esters could reach 77–82% upon the prolonged reaction time up to 8 h (Entries 12–14). However, the intramolecular alkoxycarbonylation of 3butyn-1-ol towards lactone didn't perform well (Entry 15).

OTf⁻

3. Experimental

3.1. Reagents and analysis

The chemical reagents were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd. and Alfa Aesar China, and used as received. The solvents were dried and distilled before use. The ¹H/¹³C NMR and ³¹P NMR spectra (85% H₃PO₄ sealed in a capillary tube as an internal standard) were recorded on a Bruker Avance 500 spectrometer. CHN-elemental analysis was performed on a Vario EL III Element Analyzer. Gas chromatography (GC) was performed on a SHIMADZU-2014 equipped with a DM-Wax capillary column (30 m \times 0.25 mm \times 0.25 µm). GC-mass spectrometry (GC-MS) which equipped with a DB-Wax capillary column $(30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m})$ was recorded on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector. TG/DTG analysese was performed on Thermo Gravimetric Analyzer (TGA/SDTA/SF/1100/851e). FT-IR spectra were obtained using a Nicolet NEXUS 670 spectrometer. The amount of Pd and P in the sample was quantified by using an inductively coupled plasma

Table 2

The recycling uses of the PdCl2(MeCN)2-L2'	catalytic system in	[Bmim]BF4 and	[Bmim]NTf2	respectively	for methoxycarbony-
lation of phenylacetylene. ^a					



	RTIL: [Bmim]BF ₄			RTIL: [Bmim]NTf ₂			
Run	Conv. (%) ^b	Sel. $_{\alpha,\beta\text{-esters}}$ (%) ^b	B/L ^c	Conv. (%) ^b	Sel. $_{\alpha,\beta\text{-esters}}$ (%) ^b	B/L ^c	
1	90	100	95/5	93	100	95/5	
2	89	100	95/5	92	100	95/5	
3	89	100	91/9	93	100	93/7	
4	85	100	90/10	91	100	91/9	
5	84	100	91/9	90	100	93/7	
6	73	100	90/10	91	100	91/9	
7	Undone	-	-	88	100	90/10	

^a PdCl₂(MeCN)₂ 0.05 mmol (Pd 2 mol%), P/Pd = 6 M ratio, phenylacetylene 2.5 mmol, H₂O 2 mmol, CO 3.0 MPa, MeOH 1 mL, RTIL 3.0 mL, temp. 110 °C, reaction time 5 h.

^b Determined by GC and GC-Mass.

^c B/L = the ratio of branched methyl 2-phenylacrylate to the linear methyl cinnamate.

optical emission spectrometer (ICP-OES) on an Optima 8300 instrument (PE Corporation).

3.2. Synthesis

2-(Diphenylphosphanyl)-1-(2-(diphenylphosphanyl)thiophen-3'-yl)-1H-imidazole (**L1**)

L1 was prepared according to the procedures reported by us [25] with some modifications.

Under N₂ atmosphere, a solution of 1-(thiophen-3'-yl)-1Himidazole (1.50 g, 10 mmol) in dry CH₂Cl₂ (100 mL) was cooled to -78 °C, then N, N, N', N'-tetramethylethylenediamine (TMEDA, 3.0 mL, 20 mmol) and *n*-BuLi (2.5 M in hexane, 8.8 mL, 22 mmol) were added dropwise. After stirring vigorously for 1 h, the obtained reaction mixture was added with chlorodiphenylphosphine (PPh₂-Cl, 4.60 g, 22 mmol) dropwise. The resultant mixture was stirred for another 1 h then warmed up to room temperature. After quenching the excess *n*-BuLi with deionized water (100 mL), the mixture was extracted with ethyl acetate (3 \times 80 mL) and the combined organic phase was concentrated by vacuum. The residue was purified by column chromatography on silica gel, using pure dichloromethane as eluant, to give product of L1 as a yellow solid (2.38 g, yield of 48%). The sample suitable for X-ray diffraction analysis was obtained by slow volatilization of an ethyl acetate solution containing L1. ¹H NMR (δ , ppm, CD₃COCD₃): 7.68 (s, 1H, SCH), 7.44 (s, 1H, SCCH), 7.42-7.32 (m, 20H, 4C₆H₅), 7.29 (s, 1H, 2NCH), 6.99 (s, 1H, NCCH). ³¹P NMR (δ, ppm, CD₃COCD₃): -29.12 (d, J = 9.78 Hz, $P^{1}Ph_{2}$), -29.82 (d, J = 8.15 Hz, $P^{2}Ph_{2}$). CHNelemental analysis (%, found): C 70.96, H 5.65, N 5.36 (calcd., C 71.80, H 4.67, N 5.40).

1-(2,5-Bis(diphenylphosphanyl)thiophen-3'-yl)-2-(diphenylphosphanyl)-1H-imidazole (**L2**)

L2 was obtained with the yield of 39% according to the preparation procedures for **L1**. ¹H NMR (δ , ppm, CD₃COCD₃): 7.67–7.21 (m, 30H, 6C₆H₅), 7.17 (t, 2H, SCHCH, *J* = 10 Hz), 6.90 (s, 1H, NCH). ³¹P NMR (δ , ppm, CD₃COCD₃): -28.80 to -28.97 (ABd, *P*³Ph₂, *J*₁ = 19.56 Hz, *J*₂ = 8.15 Hz), -29.27 (t, *P*¹Ph₂, *J*₁ = 19.56 Hz), -34.35 to -34.50 (ABd, *P*²Ph₂, *J*₁ = 17.93 Hz, *J*₂ = 6.52 Hz). CHN-elemental analysis (%, found): C 73.43, H 5.05, N 3.39 (calcd., C 73.49, H 4.73, N 3.99).

1-(2,5-Bis(diphenylphosphanyl)thiophen-3'-yl)-2-(diphenylphosphanyl)-3-methyl-1H-imidazol-3-ium trifluoromethanesulfonate (**L2**')

A solution of **L2** (0.70 g, 1 mmol) in dry CH₂Cl₂ (30 mL) was cooled to -78 °C, then methyl-trifluoromethanesulfonate (0.18 g, 1.1 mmol) was added dropwise. The solution was stirred overnight with the reaction temperature increasing to ambient. After evaporation of the solvent under vacuum, the residue was recrystallized from CH₂Cl₂/Et₂O to yield **L2**′ as white solids (0.71 g, 82%). ¹H NMR (δ , ppm, CD₂Cl₂): 7.54–7.26 (m, 30H, 6C₆H₅), 7.11 (s, 1H, NCH), 7.02 (t, 2H, SCHCH, *J* = 10 Hz), 3.32 (s, 3H, CH₃). ³¹P NMR (δ , ppm, CD₃-COCD₃): -20.49 to -20.61 (dd, *P*²Ph₂, *J*₁ = 26.08 Hz, *J*₂ = 6.52 Hz), -30.56 to -30.80 (ABd, *P*³Ph₂, *J*₁ = 20.68 Hz, *J*₂ = 6.52 Hz). CHN-elemental analysis (%, found): C 62.47, H 4.65, N 3.26 (calcd., C 62.35, H 4.19 N 3.23).

1-(2,5-Bis(diphenylphosphanyl)thiophen-3'-yl)-2,5-bis (diphenylphosphanyl)-1H-imidazole (**L3**)

L3 was obtained with the yield of 26% according to the preparation procedures for **L2**. ¹H NMR (δ , ppm, CD₃COCD₃): 7.45–7.12 (m, 40H, 6C₆H₅), 7.19–7.15(m, 1H, SCCH), 7.14 ~ 7.11 (m, 1H, 1NCH). ³¹P NMR (δ , ppm, CD₃COCD₃): -17.73 (s, P^4 Ph₂), -27.58 (t, P^1 Ph₂, J = 21.19 Hz), -28.04 to -28.22 (ABd, P^3 Ph₂, $J_1 = 21.19$ Hz, $J_2 = 8.15$ Hz), -33.70 to -33.88 (ABd, P^2 Ph₂, $J_1 = 21.19$ Hz, $J_2 = 8.15$ Hz). CHN-elemental analysis (%, found): C 74.52, H 5.23, N 2.91 (calcd., C 74.48, H 4.77, N 3.16).

1-(2,5-Bis(diphenylphosphanyl)thiophen-3'-yl)-2,5-bis (diphenylphosphanyl)-3-methyl-1H-imidazol-3-ium trifluoromethanesulfonate (**L3**')

L3′ was obtained with the yield of 79% after the quaternization of **L3** by MeOTf according to the preparation procedures for **L2**′. ¹H NMR (δ , ppm, CD₃COCD₃) 7.54–7.17 (m, 40H, 6C₆H₅), 7.16–7.14 (m, 1H, SCCH), 7.13–7.10 (m, 1H, 1NCH), 3.48 (s, 3H, CH₃). ³¹P NMR (δ , ppm, CD₃COCD₃): –16.77 (s, P^{4} Ph₂), –19.23 to –19.36 (ABd, P^{2} Ph₂, J_1 = 14.67 Hz, J_1 = 6.52 Hz), –28.55 to –28.81 (ABd, P^{3} Ph₂, J_1 = 27.71 Hz, J_2 = 14.67 Hz), –32.48 to –32.74 (dd, P^{1} Ph₂, J_1 = 27.71 Hz, J_2 = 9.78 Hz). CHN-elemental analysis (%, found): C 64.04, H 4.30, N 2.39 (calcd., C 65.14, H 4.32, N 2.67).

Table 3		
Generality of L2 '	'-PdCl ₂ (MeCN) ₂ system for alkoxycarbonylation of the different alkynes with the	alcohols. ^a

Entry	Substrates		Products		Conv. (%) ^b	Sel. _{α,β-esters} (%) ^b	B/L ^b
	Alkyne	Alcohol	Branched ester	Linear ester			
1		EtOH	OEt	ODEt	89	100	95/5
2		i-PrOH	OPr-i	O OPr-i	85	100	90/10
3		ОН			83	100	90/10
4	Me	МеОН	OMe	O OMe	90	100	93/7
5	'Bu	МеОН	Me OMe	Me OMe	90	100	90/10
6	F	МеОН	OMe	'Bu' OMe	88	100	90/10
7		MeOH	F OMe	F' OMe	79	100	89/11
8	Br	MeOH	OMe	CI	90	100	95/5
9	NC	MeOH	Br OMe	Br	86	100	89/11
10	Me	МеОН	OMe	O O Me	64	100	90/10
11	Me	МеОН	Me OMe	Me Me OMe	89	100	93/7
12 ^c		МеОН	OMe	OMe	82	100	89/11
13 ^c	₩3	MeOH	→ → OMe	OMe O	77	100	83/17
14 ^c	W ₅	МеОН	OMe O	→ 5 OMe	79	100	84/16
15	≡он	-			9	100	100

^a PdCl₂(MeCN)₂ 0.05 mmol (Pd 2 mol%), P/Pd = 6 M ratio, phenylacetylene 2.5 mmol, H₂O 2 mmol, CO 3.0 MPa, MeOH 2 mL, toluene 2 mL (dried by sodium before use), temp. 110 °C, reaction time 3 h.

^b Determined by GC and GC-Mass spectrometry. Sel._{32,β-esters} represents the selectivity to the products of the linear and branched unsaturated esters.

^c Reaction time 8 h.

3.3. Single crystal X-ray crystallography

3.4. General procedures for alkoxycarbonylation of alkynes

Intensity data for L1, L2', L3 and L3' were collected 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. The structures were solved by direct methods and refined by full matrix leastsquares using SHELXS-97 (Sheldrick, 1990), with all nonhydrogen atoms refined anisotropically. Hydrogen atoms were added at their geometrically ideal positions and refined isotropically. The crystal data and refinement details are given in Table 4. In a typical experiment, $PdCl_2(MeCN)_2$ (0.05 mmol), **L2'** (0.1 mmol) (or the other ligand), H_2O (2 mmol) were mixed with phenylacetylene (2.5 mmol, or the other alkyne), methanol (1 mL, or the other alcohol) and toluene (2 mL). The mixture was added in a 50 mL sealed Teflon-lined stainless steel autoclave, which was pressured with 3.0 MPa CO. Then the reaction mixture was stirred vigorously at the reaction 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

Table 4				
The crystal data and structure refinement for	or L1	L2′,	L3 and	L3′.

	L1	L2′	L3	L3′
Empirical formula	$C_{31}H_{24}N_2P_2S_1$	$C_{44}H_{36}N_2P_3S_1\cdot C_1F_3O_3S_1$	$C_{55}H_{42}N_2P_4S_1$	$C_{56}H_{45}N_2P_4S_1 \cdot C_1F_3O_3S_1$
Formula weight	518.52	866.79	886.84	1050.95
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group	P212121	P-1	P-1	P-1
a (Å)	8.0529(5)	9.1678(5)	10.9933(2)	13.222(3)
b (Å)	12.4032(8)	11.9079(4)	15.4708(6)	13.571(3)
c (Å)	26.2708(17)	20.1097(5)	15.9021(5)	16.709(4)
α (°)	90	81.670(2)	106.376(3)	109.267(8)
β (°)	90	86.101(3)	100.250(2)	92.232(8)
γ (°)	90	79.035(4)	90.377(2)	92.331(8)
$V(Å^3)$	2624.0(3)	2130.69(15)	2548.80(14)	2823.5(12)
Z	4	2	2	2
d_{calc} (g cm ⁻³)	1.313	1.351	1.156	1.236
μ (Mo-K _{α}) (mm ⁻¹)	0.269	2.666	2.025	0.261
Т (К)	296(2)	293(2)	293(2)	296(2)
λ (Α)	0.71073	1.54184	1.54184	0.71073
Total reflections	30,946	22,394	26,645	33,181
Unique reflections (R_{int})	4629 (0.1042)	7533 (0.0582)	9025 (0.0644)	9896 (0.0885)
$R_1 [I > 2\sigma(I)]$	0.0447	0.0731	0.0558	0.0720
wR_2 (all data)	0.0853	0.2068	0.1612	0.2097
F(0 0 0)	1080	896	924	1088
Goodness-of-fit on F^2	1.028	1.027	1.042	0.959

the selectivities (normalization method), and the products were further identified by GC-mass spectrometry. The structures of the some obtained products were further confirmed by ¹H NMR and ¹³C NMR.

When [Bmim]NTf₂ was used as the solvent for the methoxycarbonylation, in which phenylacetylene (2.5 mmol), MeOH (1 mL), PdCl₂(MeCN)₂ (0.05 mmol), **L2**' (0.1 mmol) and H₂O (2 mmol) were added sequentially. Upon reaction, the IL phase was washed with diethyl ether (3 mL × 3) to extract the reactants and products out of the IL phase completely. 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 and water were added additionally).

3.5. In situ high-pressure FT-IR spectral characterization

In situ high-pressure FT-IR spectra were obtained using a Nicolet NEXUS 670 spectrometer. The spectral resolution was about 4 cm^{-1} . A mixture of 0.030 mmol of **L2**' (or **L2**) with 0.005 mmol PdCl₂(MeCN)₂ and 0.1 mL of phenylacetylene in methanol and toluene was added in a specially designed high-pressure IR cell, in which cylindric CaF₂ was used as sealing sheets. Then, 1.0 MPa CO was inflated into the sealed cell. Real-time monitoring was performed at different reaction temperatures. The mixture compositions including PdCl₂(MeCN)₂, **L2**' (or **L2**), phenylacetylene, and CO were completely the same as those for the real reaction in Table 1, except for the much higher concentrations of PdCl₂(MeCN)₂ and the ligand required for FTIR spectral detection.

4. Conclusions

A series of novel multi-dentate phosphines (**L1-L3, L2**' and **L3**') were successfully synthesized and fully characterized. In **L2**', 2'-C and 5-C positioned —PPh₂ fragments as well as 2'-C and 2-C positioned —PPh₂ ones with P...P distance of 4.31 Å and 4.36 Å respectively could potentially develop the two types of P-P chelation modes to Pd center, which could render the corresponding Pd-catalyst high activity and good stability for alkoxycarbonylation of alkynes with H₂O as the promoter. In addition, the ionic tridentate phosphine of **L2**' was featured with more intensive π -acceptor ability in comparison to its analogue of **L2**, due to the much stronger electron-withdrawing effect of imidazolium than

that of imidazlyl. Consequently, **L2**'-based PdCl₂(MeCN)₂ catalytic system corresponded to the highest activity towards alkoxycarbonylation of alkynes and available recyclability in RTILof [Bmim]NTf₂ as well as the good generality to different substrates. The *in situ* FT-IR analysis also proved that water could serve as an effective promoter of **L2**'-based PdCl₂(MeCN)₂ system for alkoxycarbonylation of alkynes through facilitating the formation and stability of Pd-H species.

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Appendix A. Supplementary material

The Supplementary Information (SI) associated with this article can be found online. CCDC-1853296 (L1), 1853297 (L2'), 1853298 (L3) and 1853299 (L3') contain 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. Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.01.031.

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