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Article

Ionic palladium complex as an efficient and recyclable catalyst for the carbonylative Sonogashira reaction

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ABSTRACT

The neutral palladium(II) complex bis-[1-(5'-diphenylphosphinothiazol-2'-yl)-imidazolyl] dichloropalladium(II) (**1A**) ligated by thiazolyimidazolyl-based phosphine (**L1**) in which thiazolyimidazolyl acted as an S- and N-donor provider with weak coordinating nature, and the ionic complex bis-[1-(5'-diphenylphosphinothiazol-2'-yl)-3-methylimidazolium] dichloropalladium(II) trifluoromethanesulfonate (**2A**) ligated by thiazolyimidazolium-based phosphine (**L2**) after quaternization of **L1** using methyl trifluoromethanesulphonate were synthesized. It was found that the introduced positive charges and strong electron-withdrawing effect in **2A** not only led to changes in the configuration and structural stability of the complex, but also lowered its catalytic performance in carbonylative Sonogashira reactions. These effects reveal the important role of the N-donor in **1A**. In addition, as an ionic palladium complex, **2A** combined with the room-temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate could be recycled eight times as the catalyst in carbonylative Sonogashira reactions without detectable metal leaching.

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1. Introduction

Among aromatic carbonyl compounds, α,β -alkynones are important structural motifs in many bioactive molecules and intermediates for the synthesis of natural products and pharmaceuticals [1–4]. In general, α,β -alkynones have been prepared by the coupling of alkyne organometallic reagents with acid chlorides in the presence of transition metal reagents [5–9]. Unfortunately, this methodology is limited with respect to functional group tolerance, substrate stability, reaction conditions (dry solvent under an inert atmosphere), atom economy, and environmental friendliness. Since they were first reported by Tanaka's group [10] in 1981, palladium (Pd)-catalyzed carbonylative Sonogashira reactions have become an

alternative approach to synthesize α,β -alkynones. In carbonylative Sonogashira reactions, CO acts as an important C1 building block to introduce carbonyl group into the parent molecules. Many researchers have modified and improved this methodology, including Wu et al. [11] for homogeneous carbonylative Sonogashira reactions and other groups [12–14] for heterogeneous ones. It is widely accepted that the involved ligands can greatly tailor the catalytic performance of homogeneous Pd complex catalysts through electronic and steric effects [15–19]. However, these catalysts still suffer from the problems of difficult product separation, rapid activity loss, and non-recyclability [11,20,21].

Non-volatile ionic liquids (ILs) have been recognized as promising alternative solvents to immobilize homogenous pal-

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ladium catalysts, preventing their leaching and deactivation [22]. ILs can be functionalized with phosphine ligands, and the resulting phosphine-functionalized ILs have been investigated as ionic complexes (catalysts) and used in combination with room-temperature ionic liquids (RTILs) to immobilize homogeneous catalysts [23–27]. Because the melting points of phosphine-functionalized ILs are usually higher than 100 °C, they are typically defined as ionic phosphines. It has also been found that when phosphines are introduced into ILs to obtain ionic phosphines, the positive charges of ILs with strong electron-withdrawing character dramatically influence the coordinating ability of the involved phosphines and in turn the properties of the corresponding transition metal complexes in terms of structure and catalytic activity [27,28].

Herein, the neutral monophosphine **L1** (1-(5'-diphenylphosphinothiazol-2'-yl)-imidazolyl) and its ionic counterpart **L2** (1-(5'-diphenylphosphinothiazol-2'-yl)-3-methylimidazolium trifluoromethanesulfonate) reported by us previously [29] were complexed with $\text{PdCl}_2(\text{MeCN})_2$ to afford the neutral Pd(II) complex bis-[1-(5'-diphenylphosphinothiazol-2'-yl)-imidazolyl] dichloropalladium(II) (**1A**) and an ionic complex bis-[1-(5'-diphenylphosphinothiazol-2'-yl)-3-methylimidazolium] dichloropalladium(II) trifluoromethanesulfonate (**2A**) (Scheme 1). The effects of the positive charge in **L2** on the coordination ability of the involved phosphine, the structure of the corresponding Pd complex, and the catalytic performance of the complexes in the carbonylative Sonogashira reaction are discussed (Scheme 2). In addition, **2A** can be regarded as an ionic Pd complex that is compatible with RTILs, so its recyclability in 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim] PF_6) is investigated.

2. Experimental

2.1. Reagents and analysis

L1 and **L2** were first prepared according to our previously published method [29]. Other chemical reagents were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd. and Shanghai Alfa Aesar, China, and used as received. Diethyl ether was distilled from sodium. DMF was dried over CaSO_4 and distilled before use. Both diethyl ether and DMF were stored over 4 Å molecular sieves under N_2 . ^1H , ^{31}P , and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer (400 MHz) at room temperature. ^{31}P NMR spectra were referenced to 85% H_3PO_4 sealed in a capillary tube as an internal standard. CHN elemental analysis was performed on a Vario EL III Elemental Analyzer. The amount of Pd in the organic phase was quantified by inductively coupled plasma atomic emission spectrometry

Scheme 1. Formation of complexes **1A** and **2A** from ligands **L1** and **L2**, respectively.

(ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). 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) was recorded on an Agilent 6890 spectrometer equipped with an Agilent 5973 mass selective detector. Purification of the compounds was carried out by flash chromatography on silica gel.

2.2. Synthesis of catalysts

2.2.1. Synthesis of complex **1A**

Under N_2 atmosphere, **L1** (0.13 g, 0.4 mmol) dissolved in dry CH_2Cl_2 (4 mL) was added to a solution of $\text{PdCl}_2(\text{MeCN})_2$ (0.05 g, 0.2 mmol) in dry CH_2Cl_2 (8 mL). The mixture was stirred vigorously at room temperature for 3 h. The solvent was removed under vacuum using a rotary evaporator. The obtained yellow solid residue was washed with diethyl ether and dried under vacuum to give the product **1A** in 97% yield. A sample suitable for single-crystal X-ray diffraction (XRD) analysis was obtained by slow volatilization of a CH_2Cl_2 solution containing **1A**. ^1H NMR (δ , CD_2Cl_2): 8.23 (s, 2H, NCHN), 7.55–7.75 (m, 24H), 7.21 (s, 2H); ^{13}C NMR (δ , CD_2Cl_2): 164.43 (s, NCN), 151.17 (s), 135.69 (s), 134.25 (s), 131.70 (s), 131.05 (s), 128.67 (s), 128.23 (s), 121.70 (s), 117.62 (s); ^{31}P NMR (δ , CD_2Cl_2): 10.80 (s, PPh_2). CHN (%) elemental analysis for **1A** ($\text{C}_{36}\text{H}_{28}\text{Cl}_2\text{N}_6\text{P}_2\text{Pd}_1\text{S}_2$, 848.0): C 50.82, H 3.43, N 9.96 (Calcd. C 50.99, H 3.33, N 9.91).

2.2.2. Synthesis of complex **2A**

Under N_2 atmosphere, **L2** (0.250 g, 0.50 mmol) dissolved in dry CH_2Cl_2 (3 mL) was added to a solution of $\text{PdCl}_2(\text{MeCN})_2$ (0.065 g, 0.25 mmol) in dry CH_2Cl_2 (7 mL). The mixture was

Scheme 2. Carbonylative Sonogashira reaction of iodobenzene with phenylacetylene catalyzed by **1A** and **2A**.

stirred vigorously at room temperature for 3 h. The collected yellow solid precipitate was washed with diethyl ether and dried under vacuum to give the product **2A** with a yield of 86%. A sample suitable for single-crystal XRD analysis was obtained by slow volatilization of a CH_2Cl_2 solution containing **2A**. ^1H NMR (δ , CD_2Cl_2): 9.93 (s, 2H, NCHN), 8.39 (t, 2H, $J = 2$ Hz), 8.04 (t, 2H, $J = 2$ Hz), 7.77–7.83 (m, 10H), 7.65–7.69 (m, 4H), 7.58–7.63 (m, 8H), 4.23 (s, 6H, 2CH₃); ^{13}C NMR (δ , CD_3CN): 160.80 (s, NCN), 150.61 (s), 135.80 (s), 134.33 (t, $J = 27$ Hz), 132.54 (s), 132.19 (s), 128.99 (t, $J = 22.5$ Hz), 127.60 (q, $J = 117.5$ Hz, CF₃), 125.22 (s), 122.40 (s), 120.73 (s), 36.77 (s, CH₃); ^{31}P NMR (δ , CD_2Cl_2): 11.8 (s, PPh₂). CHN (%) elemental analysis of **2A** ($\text{C}_{40}\text{H}_{34}\text{Cl}_2\text{F}_6\text{N}_6\text{O}_6\text{P}_2\text{Pd}_1\text{S}_4$, 1176.2): C 40.76, H 2.97, N 7.19 (Calcd. C 40.84, H 2.91, N 7.14).

2.2.3. Preparation of phosphine selenides

Phosphine selenides were prepared by the reactions of phosphines **L1**, **L2**, and PPh₃ with 30 mg selenium (7.63% ^{77}Se) with a molar ratio of 1:1 in CDCl_3 at 50 °C for 24 h. The selenides were directly analyzed without isolation by a Bruker Avance 500 spectrometer at ambient temperature.

2.3. X-ray crystallography

Intensity data for **1A** and **2A** were collected at 25 °C on a Bruker SMART APEX II diffractometer using graphite-monochromated Mo- K_α radiation ($\lambda = 0.071073$ nm). Data reduction included absorption correction by the multi-scan method. 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. The crystal data and refinement details are given in Table 1.

2.4. General procedure for carbonylative Sonogashira reaction

In a typical experiment, the isolated crystalline precatalyst **1A** (or **2A**, 0.005 mmol) was sequentially mixed with 3 mL of solvent (DMF or [Bmim]PF₆ if required), iodobenzene (5 mmol), phenylacetylene (6 mmol), and Et₃N (7.5 mmol). The obtained mixture was placed in a sealed Teflon-lined stainless steel autoclave, purged with syngas (CO, 1.0 MPa) and then stirred vigorously at the required temperature for the appointed time. Upon completion of the reaction, the mixture was cooled to room temperature and the pressure was carefully released. The reaction mixture was extracted with diethyl ether (5 mL $\times$ 3). The ether fractions were combined and then analyzed by GC to determine the conversion of PhI (1-dodecane as an internal standard) and the selectivity for the carbonylative products (normalization method). The structures of the carbonylative products were further confirmed by GC-MS.

In the recycling experiments, the remaining slurry containing **2A**, [Bmim]PF₆, and the formed ammonium salt (Et₃N-HI) after ether extraction was used directly without further treatment for the next run unless otherwise specified. In specified cases, the formed ammonium salt (Et₃N-HI) was removed by

Table 1
Crystal data and structure refinement for **1A** and **2A**.

Item	1A	2A
Empirical formula	$\text{C}_{36}\text{H}_{28}\text{Cl}_2\text{N}_6\text{P}_2\text{Pd}_1\text{S}_2$	$\text{C}_{38}\text{H}_{34}\text{Cl}_2\text{N}_6\text{P}_2\text{Pd}_1\text{S}_2 \cdot 2(\text{C}_3\text{F}_7\text{SO}_3)$
Formula mass	848.00	1176.21
Crystal system	Triclinic	Monoclinic
Space group	$P-1$	$P2_1/c$
<i>a</i> (nm)	1.02543(13)	1.4322(2)
<i>b</i> (nm)	1.16366(15)	1.9177(3)
<i>c</i> (nm)	1.6126(2)	0.90143(13)
α (°)	81.525(4)	90
β (°)	74.388(4)	100.888(5)
γ (°)	83.266(4)	90
<i>V</i> (nm ³)	1.8269(4)	2.4313(6)
<i>Z</i>	2	2
<i>d</i> _{calc} (Mg/m ³)	1.542	1.607
μ (Mo- K_α) (mm)	0.892	0.803
<i>T</i> (°C)	23(2)	23(2)
λ (nm)	0.071073	0.071073
Total reflections	20959	28184
Unique reflections (<i>R</i> _{int})	6400 (0.0911)	4288 (0.0821)
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0603	0.0417
<i>wR</i> ₂ (all data)	0.1815	0.0973
<i>F</i> (000)	856	1184
Goodness-of-fit on <i>F</i> ²	0.995	1.038

washing the slurry with water (3 mL). The remaining IL phase was then collected for reuse. Because of the stoichiometric consumption of the base, Et₃N (7.5 mmol) was added to each reaction. All manipulations were conducted in air.

2.5. ^1H and ^{13}C NMR data for the products listed in Table 3

1,3-Diphenylprop-2-yn-1-one (Table 3, entry 1). ^1H NMR (δ , CDCl_3): 8.23 (d, 2H, $J = 7.2$ Hz), 7.65–7.68 (m, 2H), 7.59–7.63 (m, 1H), 7.45–7.52 (m, 3H), 7.38–7.42 (m, 2H); ^{13}C NMR (δ , CDCl_3): 178.08 (s, C=O), 136.89 (s), 134.18 (s), 133.12 (s), 130.85 (s), 129.62 (s), 128.73 (s), 128.67 (s), 120.14 (s), 93.16 (s), 86.91 (s).

3-Phenyl-1-(*o*-tolyl)prop-2-yn-1-one (Table 3, entry 2). ^1H NMR (δ , CDCl_3): 8.31 (d, 2H, $J = 8.8$ Hz), 7.65–7.67 (m, 2H), 7.35–7.49 (m, 5H), 7.28 (d, 1H, $J = 7.2$ Hz), 2.68 (s, 3H, CH₃); ^{13}C NMR (δ , CDCl_3): 179.78 (s, C=O), 140.54 (s), 140.54 (s), 135.70 (s), 133.24 (s), 132.96 (s), 132.21 (s), 130.63 (s), 128.67 (s), 125.92 (s), 120.35 (s), 91.87 (s), 88.38 (s), 22.02 (s, CH₃).

3-Phenyl-1-(*m*-tolyl)prop-2-yn-1-one (Table 3, entry 3). ^1H NMR (δ , CDCl_3): 8.04 (t, 2H, $J = 6.8$ Hz), 7.68–7.70 (m, 2H), 7.39–7.51 (m, 5H), 2.45 (s, 3H, CH₃); ^{13}C NMR (δ , CDCl_3): 178.28 (s, C=O), 138.53 (s), 136.91 (s), 135.03 (s), 133.09 (s), 130.79 (s), 129.81 (s), 128.71 (s), 128.55 (s), 127.16 (s), 120.22 (s), 92.91 (s), 87.03 (s), 21.38 (s, CH₃).

3-Phenyl-1-(*p*-tolyl)prop-2-yn-1-one (Table 3, entry 4). ^1H NMR (δ , CDCl_3): 8.12 (d, 2H, $J = 8$ Hz), 7.67–7.70 (m, 2H), 7.47–7.51 (m, 1H), 7.40–7.44 (m, 2H), 7.32 (d, 1H, $J = 8$ Hz), 2.45 (s, 3H, CH₃); ^{13}C NMR (δ , CDCl_3): 177.78 (s, C=O), 145.26 (s), 134.61 (s), 133.07 (s), 130.72 (s), 129.75 (s), 129.38 (s),

Fig. 1. ^{31}P NMR spectra (162 MHz) of the selenides of **L1**, **L2**, and PPh_3 .

128.69 (s), 120.27 (s), 92.64 (s), 86.94 (s), 21.89 (s, CH_3).

1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one (Table 3, entry 5). ^1H NMR (δ , CDCl_3): 8.18–8.22 (m, 2H), 7.67–7.69 (m, 2H), 7.40–7.52 (m, 3H), 6.97–7.01 (m, 2H), 3.91 (s, 3H, CH_3); ^{13}C NMR (δ , CDCl_3): 176.63 (s, $\text{C}=\text{O}$), 164.50 (s), 132.99 (s), 131.93 (s), 130.62 (s), 130.22 (s), 128.68 (s), 120.36 (s), 113.91 (s), 92.24 (s), 86.93 (s), 55.64 (s, CH_3).

1-(2-Methoxyphenyl)-3-phenylprop-2-yn-1-one (Table 3, entry 6). ^1H NMR (δ , CDCl_3): 8.10 (dd, 1H, $J_1 = 2$ Hz, $J_2 = 7.6$ Hz), 7.62–7.65 (m, 2H), 7.53–7.57 (m, 1H), 7.38–7.48 (m, 3H), 7.01–7.08 (m, 2H), 3.97 (s, 3H, CH_3); ^{13}C NMR (δ , CDCl_3): 176.81 (s, $\text{C}=\text{O}$), 159.84 (s), 135.11 (s), 133.00 (s), 132.74 (s), 130.51 (s), 128.63 (s), 126.66 (s), 120.67 (s), 120.33 (s), 112.20 (s), 91.65 (s), 89.19 (s), 55.96 (s, CH_3).

3-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (Table 3, entry 7). ^1H NMR (δ , CDCl_3): 8.33 (d, 2H, $J = 8$ Hz), 7.79 (d, 2H, $J = 8$ Hz), 7.69–7.71 (m, 2H), 7.50–7.54 (m, 1H), 7.42–7.46 (m, 2H); ^{13}C NMR (δ , CDCl_3): 176.76 (s, $\text{C}=\text{O}$), 139.35 (s), 133.17 (q, CF_3 , $J = 130$ Hz), 133.25 (s), 131.25 (s), 128.83 (s), 125.73 (q, $J = 14.8$ Hz), 124.91 (s), 122.20 (s), 119.64 (s), 94.52 (s), 86.58 (s).

1-(3-Nitrophenyl)-3-phenylprop-2-yn-1-one (Table 3, entry 9). ^1H NMR (δ , CDCl_3): 9.06 (t, 1H, $J = 2$ Hz), 8.48–8.54 (m, 2H),

7.72–7.78 (m, 3H), 7.53–7.57 (m, 1H), 7.45–7.49 (m, 2H); ^{13}C NMR (δ , CDCl_3): 175.48 (s, $\text{C}=\text{O}$), 148.48 (s), 138.13 (s), 134.62 (s), 133.38 (s), 131.48 (s), 129.98 (s), 128.89 (s), 128.18 (s), 124.50 (s), 119.39 (s), 95.33 (s), 86.25 (s).

3-Phenyl-1-(thiophen-2-yl)prop-2-yn-1-one (Table 3, entry 10). ^1H NMR (δ , CDCl_3): 8.04 (d, 1H, $J = 3.5$ Hz), 7.75 (d, 1H, $J = 4.5$ Hz), 7.69 (d, 2H, $J = 7$ Hz), 7.51 (t, 1H, $J = 7$ Hz), 7.45 (t, 2H, $J = 7$ Hz), 7.22 (t, 1H, $J = 4.5$ Hz); ^{13}C NMR (δ , CDCl_3): 169.80 (s, $\text{C}=\text{O}$), 144.97 (s), 135.26 (s), 135.10 (s), 133.06 (s), 130.88 (s), 128.73 (s), 128.37 (s), 119.95 (s), 91.75 (s), 86.53 (s).

1-Nitro-4-(phenylethynyl)benzene (Table 3, entry 11). ^1H NMR (δ , CDCl_3): 8.20 (d, 2H, $J = 8.8$ Hz), 7.65 (d, 2H, $J = 8.8$ Hz), 7.54–7.58 (m, 2H), 7.37–7.40 (m, 3H); ^{13}C NMR (δ , CDCl_3): 147.00 (s, $\text{C}=\text{O}$), 132.28 (s), 131.87 (s), 130.27 (s), 129.31 (s), 128.57 (s), 123.65 (s), 122.13 (s), 94.74 (s), 87.59 (s).

3. Results and discussion

It was believed that the introduction of a positive charge with strong electron-withdrawing ability into **L1** to afford **L2** would change the coordination ability of the corresponding phosphines. According to the method reported in Refs. [30–32], the values of $1J_{\text{Se-P}}$ in the ^{77}Se isotopomer of the corresponding phosphine selenides in ^{31}P NMR spectra can be used to evaluate the σ -donor ability of a phosphine. As shown in Fig. 1, after replacement of one phenyl group in PPh_3 ($1J_{\text{Se-P}} = 729$ Hz) with thiazolylimidazolyl, the phosphine obtained using **L1** exhibited an increased value of $1J_{\text{Se-P}}$ (744 Hz). This indicates an increase in the π -acceptor ability (i.e., weaker σ -donor ability) originating from the relatively stronger electron-withdrawing ability of thiazolylimidazolyl than that of a phenyl group. Compared with **L1** and PPh_3 , the highest $1J_{\text{Se-P}}$ value (768 Hz) was observed for **L2** because of the intense electron-withdrawing effect resulting from the positively charged thiazolylimidazolium ring on the phosphine fragment.

The different coordinating ability of **L1** and **L2** affected the structural parameters of the corresponding Pd complexes **1A** and **2A**, as depicted in Fig. 2. Both **1A** and **2A** possessed typical square-planar geometry, which is structurally similar to $\text{trans-PdCl}_2(\text{PPh}_3)_2$ [33]. The Pd(II) (d^8) center, lying at the

Fig. 2. Single crystal structures of **1A** and **2A**. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond distances (nm) and angles ($^\circ$): **1A**, Pd1–P1 0.2329(2), Pd1–P2 0.2326(2), Pd1–Cl1 0.2281(2), Pd1–Cl2 0.2295(2); P1–Pd1–P2 179.48(9), Cl1–Pd1–Cl2 170.23(1); **2A**, Pd1–P1 0.23316(1), Pd1–Cl1 0.22851(1); P1–Pd1–P2 180.0, Cl1–Pd1–Cl2 180.0. Interplanar dihedral angle (θ , $^\circ$) between thiazolyl and imidazolyl rings: **1A**, 1.671(3), 14.685(3); **2A**, both 13.303(2).

center of inversion, was coordinated by two chloride ions and two phosphines in *trans* positions. However, **1A** possessed distorted square-planar geometry, whereas ideal square-planar geometry with complete anti-symmetry was observed for **2A** because the repulsive force of the two positive charges made the two pendant thiazolylimidazolium groups move apart as far as possible. The bond distances of Pd–P in **1A** (0.2329(2), and 0.2326(2) nm) are slightly shorter than that in **2A** (0.23316(1) nm), indicating the higher structural stability of **1A** compared with **2A**. In **1A**, the interplanar dihedral angles (θ) between the thiazolyl imidazolyl rings are 1.671(3)° and 14.685(3)° in comparison with those in **2A** (both 13.303(2)°), which further indicates the torsional configuration of **1A**.

Because of their different structures, the catalytic performance of the Pd complexes was also varied dramatically. The carbonylative coupling of phenylacetylene with iodobenzene under CuI-free conditions was selected as a model reaction to evaluate the catalytic performance of **1A** and **2A**; the results are summarized in Table 2. DMF was selected as the optimal solvent after screening DMF, THF, toluene, and acetone over **1A**. With the same Pd concentration (0.1 mol%), **1A** exhibited higher activity (turnover frequency (TOF) of 840 h⁻¹) than that of **2A** and PdCl₂(PPh₃)₂ under mild reaction conditions (90 °C, 1 h, and *p*(CO) = 1.0 MPa) (entries 1 vs. 2 and 3). When the reaction temperature was increased from 90 to 120 °C, a very high TOF of 3560 h⁻¹ was obtained over **1A** when Pd concentration was decreased to 0.05 mol% (entry 4). Under the same conditions, a relatively lower TOF of 2960 h⁻¹ was obtained over **2A** (entry 5). As observed in Fig. 1, the phosphine fragments in **L1**, **L2**, and PPh₃ exhibited the σ -donor ability (electron-rich character) in the order of PPh₃ ($1J_{\text{Se-P}} = 729$ Hz) > **L1** ($1J_{\text{Se-P}} = 744$ Hz) > **L2** ($1J_{\text{Se-P}} = 768$ Hz). However, the catalytic efficiency over **A1**, **A2**, and PdCl₂(PPh₃)₂ displayed the order: **A1** (TOF = 840 h⁻¹) > PdCl₂(PPh₃)₂ (TOF = 770 h⁻¹) > **A2** (TOF = 71 h⁻¹), which was not consistently correlated to the σ -donor ability of the involved phosphines. It was noted that, compared with PPh₃, **L1** contains additional coordination sites at S- and N-donor atoms besides that of the common phosphine fragment. Therefore, the available N,S-donors of the weak coordinating ligands in **1A** are believed to be able to temporarily associate with Pd center to provide additional protection for the active Pd catalyst against deactivation and then dissociate to provide an unsaturated site for the subsequent insertion of the reaction substrate, which gave rise to the high activity of **1A**. As for **2A** and PdCl₂(PPh₃)₂,

Table 2

Carbonylative Sonogashira coupling of iodobenzene with phenylacetylene catalyzed by different Pd complexes.

Entry	Pd complex (mmol)	Pd conc. (mol%)	Time (h)	Conv. ^a (%)	Sel. ^a (%)	TOF (h ⁻¹)
1	1A	0.1	1.0	85	99	840
2	2A	0.1	1.0	75	100	710
3	PdCl ₂ (PPh ₃) ₂	0.1	1.0	78	99	770
4 ^b	1A	0.05	0.5	89	100	3560
5 ^b	2A	0.05	0.5	74	100	2960

Reaction conditions: PhI 5 mmol, phenylacetylene 6 mmol, Et₃N 7.5 mmol, *p*(CO) = 1.0 MPa, DMF 3 mL, 90 °C.

^a Determined by GC analysis. ^b *T* = 120 °C.

the absence of N-donor atoms meant that the active Pd catalyst was unable to be protected effectively, leading to the depressed activity of these catalysts compared with that of **1A**.

The scope of the reaction catalyzed by **1A** was then examined (Table 3). The electronic effect and steric hindrance of the aryl substituents of the aryl iodides obviously affected the reaction rate. Because of the competing Sonogashira reaction, the corresponding side-products of aryl-substituted internal acetylenes were found universally but in very low yields. However, when 1-bromo-4-nitrobenzene was used in parallel, the carbonylative Sonogashira coupling barely proceeded. Conversely, when CO was replaced with N₂, the Sonogashira cross-coupling occurred smoothly under the same reaction conditions. This suggests that the active Pd⁰ species formed in N₂ atmosphere exhibited higher oxidative addition ability than that of the Pd⁰-CO species formed in CO atmosphere toward the substrates, especially aryl bromides with low reactivity.

Ionic complex **2A** could be used as a catalyst with the RTIL

Table 3

Generality of **1A** as a precatalyst for the carbonylative Sonogashira coupling of aryl halides with phenylacetylene in DMF.

Entry	Aryl halide	Product ^a	Conv. ^b (%)	Yield ^b (%)
1			95	99 (1)
2			99	100 (0)
3			96	99 (1)
4			93	99 (1)
5			86	99 (1)
6			79	98 (2)
7			98	97 (3)
8			100	90 (10)
9			100	98 (2)
10			100	99 (1)
11			—	— (—)
12 ^c			100	— (99)

Reaction conditions: **1A** 0.005 mmol, PhI 5 mmol, phenylacetylene 6 mmol, Et₃N 7.5 mmol, CO 1.0 MPa, DMF 3 mL, 90 °C, 1.5 h.

^a The isolated products were characterized by ¹H and ¹³C NMR spectroscopy.

^b Determined by GC and GC-MS and the number in parentheses is the yield of Sonogashira reaction products.

^c 1.0 MPa of N₂ pressure instead of CO.

Table 4

Recyclability of **2A** in [Bmim]PF₆ for carbonylative Sonogashira coupling of iodobenzene with phenylacetylene.

Run	Conv. ^a (%)	Sel. ^a (%)	TOF (h ⁻¹)
1 (fresh)	85	96	544
2	70	99	462
3 ^b	65	99	429
4	71	96	455
5	63	98	412
6 ^b	63	99	416
7	64	95	405
8	62	98	405

Reaction conditions: PhI 5 mmol, phenylacetylene 6 mmol, Et₃N 7.5 mmol, *p*(CO) = 1.0 MPa, [Bmim]PF₆ 3 mL, 90 °C, 1.5 h.

^a Determined by GC analysis.

^b The slurry mixture was washed with water to remove the accumulated ammonium salt from the hydrophobic IL phase.

solvent [Bmim]PF₆, which immobilized the Pd complex catalyst to aid recovery and recycling (Table 4). Because of the mass-transfer limitation in the organic-IL biphasic reaction system, the reaction time was prolonged to 1.5 h during the recycling experiments. Ionic complex **2A** was tightly locked in the IL phase; there was no loss of Pd detected by ICP-AES analysis of the combined organic phase after eight runs. The accumulated slurry of ammonium salts in [Bmim]PF₆ formed after scavenging acid by Et₃N could be removed by water to leave the clear IL phase for the next run because of the hydrophobicity of [Bmim]PF₆ (entries 3 and 6 in Table 4). However, the TOFs of the **2A**-[Bmim]PF₆ system gradually decreased because of the unavoidable deactivation and mechanical loss of the catalyst after multiple reaction cycles.

4. Conclusions

After the introduction of positive charges, Pd complex **2A** exhibited not only changes in complex configuration and

structural stability, but also relatively lower catalytic efficiency toward the carbonylative Sonogashira reaction (TOF = 2960 h⁻¹). Compared with PdCl₂(PPh₃)₂ and **2A** with structural similarity, **1A** ligated by **L1** containing three types of the coordinating sites (P, N, and S donor atoms) exhibited the highest catalytic performance (TOF = 3560 h⁻¹), indicating the importance of the weak, reversible N- and S-ligation to the Pd center through intermolecular coordination in protecting the active Pd catalyst. It was also found that **2A** in [Bmim]PF₆ could be recycled eight times without detectable metal leaching.

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Graphical Abstract

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Ionic palladium complex as an efficient and recyclable catalyst for the carbonylative Sonogashira reaction

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An ionic palladium complex was prepared through complexation of bis(acetonitrile)palladium(II) chloride with an ionic phosphine as an efficient and recyclable catalyst for the carbonylative Sonogashira reaction.

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高效可循环离子型钯配合物催化羰化Sonogashira反应

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摘要: 炔酮类化合物作为一类具有生物活性的分子, 是天然产物全合成中构建杂环类化合物的重要中间体. 炔酮类化合物的传统合成方法是通过过渡金属催化金属有机炔烃和酰氯的交叉偶联, 但存在酰氯本身稳定性和底物官能团耐受性较差的缺点. 近年来, 钯催化的羰化Sonogashira反应(末端炔烃和芳基卤化物与CO的偶联反应)成为合成炔酮类化合物更为直接和有效的方法, 其中与钯中心原子配位的配体的电子效应和空间效应可显著调控钯配合物的催化性能. 但均相钯催化的羰化Sonogashira反应体系存在在催化剂流失、分离困难和难以循环使用的问题.

我们以2-(1-咪唑基)噻唑为母体分子, 合成了具有P,S,N杂合配体特征的配体**L1**, 同时将配体**L1**通过与MeOTf的季铵化反应得到相应的离子型膦配体**L2**. 在此基础上, 利用**L1**和**L2**与过渡金属中心的配位作用合成相应的钯配合物**1A**和**2A**. 由于**L1**和**L2**中含有多种不同配位能力的配体(P-配体, S-配体和/或N-配体), 故通过N/S杂原子对Pd-中心原子的协同弱配位作用, 可以调变相应钯配合物对羰化Sonogashira反应的催化性能. 另外, **2A**中具有强吸电子效应的正电荷的存在, 使其结构和催化性能也必然不同于中性配合物**1A**.

实验结果表明, 在温和的反应条件(90 °C, 1 h, CO压强1.0 MPa)下, 对于碘苯和苯乙炔的羰化Sonogashira偶联反应, **1A**体现出优于**2A**的催化性能, TOF值达到840 h⁻¹; 但反应温度提高到120 °C时, **1A**的TOF高达3560 h⁻¹, **2A**的TOF为2960 h⁻¹. 与**L1**的²J_{P-Se} = 744 Hz相比, **L2**的²J_{P-Se} = 768 Hz, 说明**L2**中具有吸电子效应的正电荷的存在降低了相应P原子的σ给电子能力(²J_{P-Se}数值越大, 相应膦配体的σ给电子能力越弱); 同时, **1A**中具有弱配位能力的N配体的缺失削弱了配体对Pd活性中心的稳定作用. 在底物普适性研究中发现, 4-硝基溴苯在相同反应条件下几乎得不到羰化Sonogashira偶联产物. 而将反应体系中的CO换为同样压强下的N₂, 却可以顺利实现Sonogashira偶联反应. 我们推测, 在CO氛围下形成的Pd⁰-CO活性物种(与N₂氛围下形成的Pd⁰活性物种相比)具有相对较低的对底物的氧化加成能力.

离子型钯配合物**2A**的优势在于, 当将其与室温离子液体[Bmim]PF₆(溶剂)结合使用, 在**2A**催化碘苯与苯乙炔的羰化Sonogashira偶联反应过程中, 循环使用8次催化性能没有明显下降.

关键词: 离子型膦配体; 钯配合物; 羰化Sonogashira反应; 离子液体

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