Efficient and Recyclable RuCl$_3$·3H$_2$O Catalyst Modified with Ionic Diphosphine for the Alkoxycarbonylation of Aryl Halides

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1. Introduction

The transition-metal-catalyzed carbonylation of aryl halides in the presence of nucleophiles is an important methodology for the preparation of aromatic esters and derivatives. Aromatic esters are significant and versatile compounds, known as important ingredients in food, beverages, cosmetics, pharmaceuticals, agrochemicals, detergents and as intermediates for the synthesis of polymers. So far, palladium complexes are the most studied catalytic systems for alkoxycarbonylation of aryl halides. In addition, the other metals such as nickel, cobalt, platinum, rhodium also could be applied as the viable catalysts with the involvement of suitable ligands.

In comparison, RuCl$_3$·3H$_2$O-based complexes have been rarely used to catalyze alkoxycarbonylation of alkenes/aryl halide. As for the high valence state RuCl$_3$·3H$_2$O-based complexes, the existence of the common electron-rich phosphines (as the strong σ-donors) and Ru-ion in +3 valence are incompatible because of the unavoidable redox reaction between them in the course of complexation. Hence, even if RuCl$_3$·3H$_2$O is used as the precursor, the real catalyst is still Ru(II)/Ru(0)-based complex due to the in situ unavoidable reduction of Ru(III)-ion by the involved electron-rich phosphines. Based on this knowledge, it is enlightened that the utilization of RuCl$_3$·3H$_2$O as the viable catalyst absolutely requires a kind of electron-deficient phosphines to guarantee their co-existence and then the expected complexation without redox process.

The typical examples of electron-deficient ligands are phosphinates, phosphonites, phosphites, and fluoroarylphosphines, which are in great concerns in the coordinating chemistry and homogeneous catalysis while providing the essential difference in coordinating nature as well as in catalytic performance. However, the P-O bonds of phosphinates, phosphonites, and phosphites are instable and sensitive to protic cleavage. Although fluoroarylphosphines with inert P-C linkages can be considered as alternatives, their structural diversity is limited. Compared to the functional groups of −F, −CF$_3$, −NO$_2$, −COR etc., the positively charged quaternary ammoniums are the most intensive electron-withdrawing moieties. Hence, the ionic phosphines tailed with the positively charged imidazolium cationic system are potential electron-deficient ligand candidates with the apparent robustness against oxidative degradation and versatile sources. Our group already reported some imidazolium-based phosphines as the electron-deficient ligands for transition metal complex catalyzed carbonylations. However, it should be noted that such electron-deficient ionic phosphine also can serve as the N-heterocyclic carbene precursors upon cleavage of P-C(imidazolium) bonds even by the attack of the weak nucleophiles like Cl$^-$. As for alkoxycarbonylation of aryl halides, the reductive reagents are present universally such as CO, the base of organic amine (as HX scavenger), the involved phosphines, water etc. The use of RuCl$_3$·3H$_2$O was initiated by the sensitive nature of Pd(II) complexes to the ingredients (CO, the base and water) existed this reaction, which often resulted in the deactivation of Pd(II)-catalyst with the precipitation of Pd(0)-black. In

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comparison, RuCl₃·3H₂O is advantageous with apparent robustness against CO, organic amine and water.

Herein a series of ionic phosphines (L₂, L₄, and L₆) as the electron-deficient ligands were applied with RuCl₃·3H₂O together to catalyze alkoxy carbonylation of aryl halides (Scheme 1).

For comparison, their corresponding neutral counterparts (L₁, L₃, and L₅) with structural similarity were investigated in parallel in order to elucidate the electronic and steric effects of the involved phosphines on the catalytic performance of RuCl₃·3H₂O.

In addition, the recyclability of the ionic phosphine based RuCl₃·3H₂O in combination of the room temperature ionic liquid (RTIL) of [B₅ mim]PF₆ (as the reaction medium) was also investigated. The method in combination of transition metal complex coordinated by ionic phosphines and RTIL medium has been accepted as an easy operation and efficient alternative to immobilize a homogeneous transition metal catalyst for recovery and recycling in green chemistry in recent years.[30–33]

![Scheme 1. The neutral and ionic phosphines (L₁–L₆) and related Ru³⁺ complexes (Ru³⁺L₂, Ru³⁺L₄) for alkoxy carbonylation of aryl halides.](image)

2. Results and Discussion

Under the optimal conditions (P/Ru = 0.8 molar ratio, NET₃ as base, CO 2 MPa, NMP as solvent, 120 °C, 16 h; see Table S1 in the Supporting Information), the ligand effect on the performance of RuCl₃·3H₂O catalyst was summarized in Table 1. It was noticed that benzoic acid was universally formed during the reaction, which was derived from the hydrolysis of methyl benzoate or the direct hydrocarboxylation of PhI. Over the neutral phosphines (L₁, L₃ and L₅), the selectivities to benzoic acid were much higher than those over the ionic ones (L₂, L₄ and L₆). The highest conversion of PhI (96 %) along with the best selectivity to methyl benzoate (99 %) was observed on L₄-based RuCl₃·3H₂O system (Entry 4), and the other phosphines just corresponded to the relatively slow transformation of PhI.

| Entry | Ligand | Conv. [%] | Sel. [%] | Sel. [%] |
|-------|--------|-----------|---------|---------|
| 1     | L₁     | 75        | 86      | 14      |
| 2     | L₂     | 87        | 96      | 4       |
| 3     | L₃     | 88        | 93      | 7       |
| 4     | L₄     | 96        | 99      | 1       |
| 5     | L₅     | 78        | 81      | 19      |
| 6     | L₆     | 82        | 95      | 4       |
| 7     | Ru³⁺L₄ | 96        | 98      | 2       |
| 8     | –      | 43        | 95      | 5       |

[a] RuCl₃·3H₂O 0.01 mmol (Ru 0.5 mol %), monophosphine 0.008 mmol, diphosphine 0.004 mmol, (P/Ru = 0.8 molar ratio), iodobenzene 2 mmol, CH₃OH 10 mmol, NET₃ 5 mmol, CO 2 Mpa, N-methyl pyrrolidone (NMP) 3 ml, 120 °C, 16 h. [b] Determined by GC. Sel. represents selectivity to methyl benzoate; Sel. represents selectivity to benzoic acid. [c] The as-synthesized complex of Ru³⁺L₄ (0.005 mmol) was used instead of mixing RuCl₃·3H₂O (0.01 mmol) and L₄ (0.004 mmol).

Even over L₃ with the very structural similarity to L₄, 88 % conversion of PhI was obtained along with the formation of by-product of benzoic acid in selectivity of 7 % (Entry 3). When the complexes of Ru³⁺L₄ was used to replace the mixture of RuCl₃·3H₂O and L₄ as the pre-catalyst, nearly the same yield of methyl benzoate was obtained, indicating the in situ formed complex exhibited the identical activity as the as-synthesized one (Entry 7 vs 4). Without the involvement of any phosphate ligand, RuCl₃·3H₂O itself couldn’t enable the rapid conversion of PhI to the target product as a result of only 43 % conversion (Entry 8).

Table 1. Methoxy carbonylation of PhI catalyzed by RuCl₃·3H₂O with the involvement of different phosphines.[a]

The effect of Ru- and Pd-precursors on this reaction was summarized in Table 2. It was noted that over the different Ru-

| Entry | Precursor | Conv. [%] | Sel. [%] | Sel. [%] |
|-------|-----------|-----------|---------|---------|
| 1     | RuCl₃·3H₂O | 96        | 99      | 1       |
| 2     | Ru(COD)Cl₂ | 84        | 97      | 3       |
| 3     | Ru₃(CO)₁₂ | 86        | 97      | 3       |
| 4     | Pd(OAc)₂ | 89        | 93      | 7       |
| 5     | PdCl₂ | 89        | 94      | 6       |
| 6     | Pd(MeCN)Cl₂ | 77       | 91      | 9       |

[a] M (metal) 0.5 mol %, L₄ 0.004 mmol, P/M = 0.8 molar ratio, iodobenzene 2 mmol, MeOH 10 mmol, NET₃ 5 mmol, CO 2 Mpa, N-methyl pyrrolidone (NMP) 3 ml, 120 °C, 16 h. [b] Determined by GC. Sel. represents selectivity to methyl benzoate; Sel. represents selectivity to benzoic acid; [c] Pd(0)-black precipitated upon reaction. [d] The Pd-black residue was collected after washing by diethyl ether completely to repeat the reaction.

Table 2. Comparison of methoxy carbonylation of PhI catalyzed by different Ru- and Pd complex precursors with involvement of L₄.[a]

Even over L₃ with the very structural similarity to L₄, 88 % conversion of PhI was obtained along with the formation of by-product of benzoic acid in selectivity of 7 % (Entry 3). When the complexes of Ru³⁺L₄ was used to replace the mixture of RuCl₃·3H₂O and L₄ as the pre-catalyst, nearly the same yield of methyl benzoate was obtained, indicating the in situ formed complex exhibited the identical activity as the as-synthesized one (Entry 7 vs 4). Without the involvement of any phosphate ligand, RuCl₃·3H₂O itself couldn’t enable the rapid conversion of PhI to the target product as a result of only 43 % conversion (Entry 8).

The effect of Ru- and Pd-precursors on this reaction was summarized in Table 2. It was noted that over the different Ru-
Supporting Information). When the precipitated Pd(0)-black (Entry 4) was collected after washing by diethyl ether completely to repeat the reaction under the same condition, it was found that Pd(0)-black exhibited the poor activity towards methoxycarbonylation of iodobenzene with 7% yield of methyl benzoate. Based on this experiment, we could rule out the catalytic activity of Pd-black for this reaction. These obtained results further confirmed the much better tolerance of Ru-based catalyst against reduction to atom state in the reductive environment than that of Pd-based ones.

It has been reported that the magnitude of $^{1}J_{P}^{\text{P}-\text{Se}}$ coupling constant in the $^{77}$Se isotopomer of the corresponding phosphine-selenide in $^{31}$P NMR spectra can evaluate the $\pi$-acceptor ability of different phosphines. An increase of $^{1}J_{P}^{\text{P}-\text{Se}}$ indicates an increase in the character of the $\pi$-acceptor ability (i.e., less $\sigma$-donor ability). In this work, the measurement of $^{1}J_{P}^{\text{P}-\text{Se}}$ of the phosphines of L1–L6 upon reacting with elemental selenium by $^{31}$P NMR spectroscopy was given in Figure 1. It was demonstrated that that the values of $^{1}J_{P}^{\text{P}-\text{Se}}$ of the ionic phosphines universally higher than their neutral analogues, which means a dramatic increase in the character of the $\pi$-acceptor ability for the ionic phosphines due to the intensive electron-withdrawing effect from the positive-charged imidazolium. Although the ionic phosphines of L2, L4$^{[37]}$ and L6 all possessed the very similar magnitude of $^{1}J_{P}^{\text{P}-\text{Se}}$ they demonstrated quite different promoting effect on the performance of RuCl$_3$·3H$_2$O. Evidently, only L4 enabled RuCl$_3$·3H$_2$O to exhibit the best activity for methoxycarbonylation of PhI (Entry 4 of Table 1), which implied that the steric effect of these phosphines played more predominant role in tailoring the behavior of RuCl$_3$·3H$_2$O over their electronic effect.

The molecular structures of the complexes of Ru$^{II}$-L2 and Ru$^{II}$-L4 reported in our previously published work$^{[22,38]}$ can help us understand the steric effect of L2 and L4 on the performance of RuCl$_3$·3H$_2$O (Table 3). Undoubtedly, the redox between the ionic phosphine (L2 or L4) and the high valence state Ru$^{IV}$ was avoided completely as expected. As shown in Table 3, Ru(III) (d$^3$)-center of Ru$^{II}$-L2$^{[38]}$ and Ru$^{IV}$-L4$^{[22]}$ is in six-coordinated octahedral configuration with paramagnetism. In Ru$^{II}$-L2, the tailed butylimidazolium moieties are located in trans-positions. Ru$^{II}$-L4 is a dimer analogue of Ru$^{II}$-L2 in which the two butylidyln-linked imidazolium moieties are reversed to cis-positions to form a quadrilateral ring dinuclear Ru(III) complex. It was found in Ru$^{II}$-L4 that the distance of the four Ru–Cl bonds was in the range of 2.36–2.38 Å, and the two Ru–Cl bonds inside the quadrilateral ring were dramatically lengthened due to the additional developed hydrogen bonding of Cl–

Figure 1. $^{31}$P NMR spectra (202 MHz) of the selenides of L1–L6$^{[37]}$ reacting elemental selenium with a) L1 in CDCl$_3$ at 70 °C for 12 h; b) L2 in CDCl$_3$ at 70 °C for 12 h; c) L3 in CDCl$_3$ at 70 °C for 12 h; d) L4 in CDCl$_3$ at 70 °C for 12 h; e) L5 in CDCl$_3$ at 70 °C for 12 h; f) L6 in CD$_2$COCD$_2$ in CDCl$_3$ at 70 °C for 24 h.

Table 3. The structures and the selected bond distance of Ru$^{II}$-L2, Ru$^{II}$-L4, L5, L6.

| Structures | Bond distances [Å] |
|------------|--------------------|
| Ru$^{II}$-L2$^{[38]}$ | |
| Ru(1)-Cl(1) | 2.3441(10) |
| Ru(1)-Cl(2) | 2.3614(9) |
| Ru(1)-Cl(1a) | 2.3441(10) |
| Ru(1)-Cl(2a) | 2.3614(9) |
| Ru(1)-P(1) | 2.4056(9) |
| Ru(1)-P(1a) | 2.4056(9) |
| Ru$^{II}$-L4$^{[22]}$ | |
| Ru(1)-Cl(1) | 2.3755(12) |
| Ru(1)-Cl(2) | 2.3806(14) |
| Ru(1)-Cl(3) | 2.3599(12) |
| Ru(1)-Cl(4) | 2.3571(14) |
| Ru(1)-P(1) | 2.4109(15) |
| Ru(1)-P(2) | 2.4119(15) |

(a) Ru$^{II}$-L2 with counter-anion of PF$_6$ possesses the same cation as Ru$^{II}$-L2. (b) The related structural data were provided in the Supporting Information.
with H-butylenyyl group. In contrast, in Ru^{ll}L2, the distances of the four Ru–Cl bonds are much shorter in the range of 2.34–2.36 Å. Hence, when Ru^{ll}L4 or L4-based RuCl{sub}3·3H{sub}2O (in situ formation of Ru^{ll}L4) were applied as the catalysts for methoxycarbonylation of PhI in Table 1 (Entries 7 and 4), the weakened Ru–Cl bonds inside the quadrilateral ring were able to be cleaved preferentially to provide unsaturation site for oxidative addition of PhI and coordination of CO for the formation of Ru-acyl intermediate (responsible for the efficient methoxycarbonylation). As for L5 and L6 with long dangling linker of n-octylencyl, the expected dinuclear complex with structural similarity to Ru^{ll}L4 was not obtained successfully while reacting RuCl{sub}3·3H{sub}2O with L5 and L6 respectively. Accordingly, the uncompetitive performance over L5 or L6 based catalyst was observed in comparison to that over L4 (Entries 6 vs 4 of Table 1).

In addition, as an ionic phosphine, L4-based Ru-catalyst could be used with the room temperature ionic liquid (RTIL) solvent to fulfil the recovery and recycling of transition metal catalysts. [Bmim]PF{sub}6 was selected as the most suitable medium after comparing to [Bmim]BF{sub}4 (1-butyl-3-methylimidazolium tetrafluoroborate) and [Bmim]Cl (1-butyl-3-methylimidazolium chloride) (See Table S2). As shown in Figure 2, in the first 6 runs, L4-RuCl{sub}3·3H{sub}2O system could be successfully recycled affording 86–96% yield of methyl benzoate. However, in the 7th run, the conversion of PhI dropped slightly due to the inefficient stirring of the slurry mixtures contain [Bmim]PF{sub}6 and the formed Et3N·HI salt. Subsequently, the slurry was washed by water to remove Et3N·HI and then the hydrophobic [Bmim]PF{sub}6 was refreshed to use in the next run. In the 8th run, the competitive yield (84%) was obtained. The ICP-OES analysis demonstrated that, after 8 runs, the loss of Ru and P (coming from L4 and [Bmim]PF{sub}6) in the combined organic phase was 1.6% and 6.2% respectively, indicating that the catalyst could be locked in [Bmim]PF{sub}6 medium tightly only with very low leaching into the organic phase.

The generality of RuCl{sub}3·3H{sub}2O-L4 catalytic system for alkoxy-carbonylation of different aryl and heteroaryl halides was summarized in Table 4. It was found that the para-positioned aryl iodides all converted to the corresponding methyl esters in excellent yields (80–92%) without discrimination on the

### Table 4. Generality of L4-based RuCl{sub}3·3H{sub}2O for alkoxy-carbonylation.

| Entry | Substrate | Alcohol | Product | Conv.[%] | Yield [%] |
|-------|-----------|---------|---------|----------|-----------|
| 1     | MeI       | MeOH    | MeOOC-Ph | 93       | 90        |
| 2     | MeO       | MeOH    | MeOOC-Ph | 82       | 80        |
| 3     | i-PrI     | MeOH    | MeOOC-n-Pr | 88       | 84        |
| 4     | O2N       | MeOH    | MeOOC-O2N-Ph | 90       | 86        |
| 5     | NO2       | MeOH    | MeOOC-NO2-Ph | 90       | 83        |
| 6     | F         | MeOH    | MeOOC-F-Ph | 95       | 92        |
| 7     | NO2       | MeOH    | MeOOC-NO2-Ph | 86       | 80        |
| 8     | I         | MeOH    | MeOOC-I-Ph | 67       | 64        |
| 9     | MeI       | MeOH    | MeOOC-Ph | 51       | 43        |
| 10    | MeO       | MeOH    | MeOOC-Ph | 63       | 57        |
| 11    | MeO       | MeOH    | MeOOC-Ph | 70       | 63        |
| 12    | Br        | MeOH    | MeOOC-Ph | 7         | 4         |
| 13    | O2N       | MeOH    | MeOOC-O2N-Ph | 84       | 80        |
| 14    | i-PrI     | EtOH    | EtOOC-Ph | 95       | 90        |
| 15    | i-ProH    | i-ProH  | i-ProOOC-Ph | 91       | 66        |
| 16    | n-BuI     | BuOH    | BuOOC-Ph | 89       | 81        |

[a] RuCl{sub}3·3H{sub}2O 0.5 mol %, L4 0.004 mmol (P/Ru = 0.8 molar ratio), aryl or heteroaryl halides 2 mmol, alcohol 10 mmol, NEt{sub}3 5 mmol, CO 2 MPa, N-methyl pyrroldione (NMP) 3 mL, 120 °C, 16 h. [b] Determined by GC. [c] 140 C.
Unfortunately, L4 could afford the corresponding esters in the moderate yields of dimethyl phthalate at 43% yield (Entry 9). Heteroaryl halides was subjected to the double methoxycarbonylation to produce methyl 2-nitrobenzoate (Entry 8). Notably, 1,2-diiodobenzene was used to afford an arylruthenium complex (Scheme 2). In the catalytic cycle, the available active Ru(I)-based RuCl₃·3H₂O catalytic system exhibited poor activity towards methoxycarbonylation of bromobenzene (Entry 12). However, when 1-bromo-4-nitrobenzene was applied to repeat the reaction, 80% yield of methyl 4-nitrobenzoate was obtained at the temperature of 140 °C (Entry 13), indicating that the conjugated and inductive effects of –NO₂ group dramatically increased the reactivity of the corresponding substrate. In addition to methanol, ethanol, isopropanol and 1-butanol were also suitable for this reaction to give the corresponding esters in good yields (66%–90%, Entries 14–16). Notably, besides the target esters, the corresponding acids were observed universally. For example, the use of i-PrOH in place of MeOH afforded isopropyl benzoate in the yield of 66% along with 25% yield of benzoic acid due to the dramatically increased steric hindrance of i-PrOH (Entry 15).

The catalytic mechanism for alkoxycarbonylation of aryl halides over L4-based RuCl₃·3H₂O was tentatively proposed in Scheme 2. In the catalytic cycle, the available active Ru(I)-intermediate complex (A) upon reduction of the L4-ligated Ru(III) complex (Ru³⁺L4) by CO is oxidatively added by aryl halide to afford an arylruthenium complex (B). Then, the migratory insertion of CO into Ru–Ar bond leads to an acylruthenium intermediate (C) which is attacked by nucleophile of alcohol to give the desired product (ester) along with the regeneration of the active Ru(I)-intermediate complex (A) via reductive elimination.

### 3. Conclusions

The low-cost and robust RuCl₃·3H₂O was successfully applied as an efficient and recyclable catalyst for alkoxycarbonylation of aryl halides with the involvement of the unique ionic diphosphine of L4. Due to the electron-deficient nature of L4, the redox between L4 and the high valence state Ru³⁺ was avoided completely to guarantee the catalysis of Ru(III)-center. On the other hand, the unique steric effect of L4 with ability to form a quadrangular ring dimer of Ru³⁺–L4 along with the differentiated hydrogen bond interaction further facilitated the activity of this Ru(II)-catalyst. As a result, L4-based RuCl₃·3H₂O catalyst led to the best conversion of PhI (96%) along with 99% selectivity to the target product of methyl benzoate as well as the good generality to alkoxycarbonylation of different aryl halides (ArX, X = I and Br) with alcohols (MeOH, EtOH, i-PrOH and n-BuOH). In addition, L4-based RuCl₃·3H₂O system could be recycled successfully at least 8 runs in the hydrophobic ionic liquid of [Bmim]PF₆.

### Experimental Section

#### General Procedures

The chemical reagents used in this work were purchased from Shanghai Aladdin Chemical Reagent Co., Ltd., and TCI Shanghai. Unless otherwise specified, the chemical reagents were used as received. The ¹H and ¹³P NMR spectra for the analyses of the common compounds were recorded on a Bruker ARX 500 spectrometer at ambient temperature. The ³¹P NMR spectra were referenced to 85% H₃PO₄ sealed in a capillary tube as an internal standard. Gas chromatography (GC) analysis was performed on a SHIMADZU-2014 equipped with a DM-Wax capillary column (30 m × 0.25 mm × 0.25 μm). GC-mass spectrometry (GC-MS) which equipped with a DB-Wax capillary column (30 m × 0.25 mm × 0.25 μm) was recorded on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector. TG/DTG analysis was performed on a thermo gravimetric analyzer (TGA/SDTA/SF/1100/851e). The amount of Ru 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 of L1–L4

The phosphine ligands of L1–L4 were prepared according to the procedures reported by our group previously.[22,37]

#### Synthesis of L5 and L6[38]

Under N₂ atmosphere, imidazole (2.86 g, 42 mmol) was added into the distilled DMF (25 mL), then NaH (1.76 g, 60% dispersion in mineral oil, 44 mmol) were added into the mixtures carefully and

Scheme 2. The proposed catalytic mechanism over L4-based Ru(III) complex for alkoxycarbonylation of aryl halides.
slowly. Next, the mixture was stirred vigorously at ice-water bath for 1 h. After the mixtures restored room temperature, 1,8-dibromo-octane (5.44 g, 20 mmol) was added into the mixtures and the mixtures were stirred vigorously at 70°C for 4 h. The excess NaH in reaction mixtures was treated with 100 mL of deionized water. Then the reaction mixture was extracted with dichloromethane (100 mL × 3). After dried with anhydrous sodium sulfate the combined organic phase was concentrated under vacuum to give yellow liquid as the product of 1,1′-(1,8-octanediyl)bis (imidazole) with the yield of 64% (3.15 g).

Under N₂ atmosphere, when a solution of 1,1′-(1,8-octanediyl)bis (imidazole) (1.23 g, 5.5 mmol) in 50 mL of distilled THF was cooled to −78°C, 5 mL of n-BuLi (2.5 M in hexane, 12.5 mmol) was added dropwise in 30 min. After stirring vigorously for 1 h, the obtained reaction mixture was added with chlorodiphenylphosphine (PPh₂Cl₂, 2.32 g, 10.5 mmol) dropwise in 30 min. The reaction mixture was stirred for another 1 h at −78°C and then warmed up to room temperature naturally. After quenching excess n-BuLi with 100 mL deionized water, the mixture was stripped of solvent in vacuo and then extracted with dichloromethane (100 mL × 3). After dried by anhydrous sodium sulfate and concentrated under vacuum, the mixture was further purified by column chromatography on silica gel, using dichloromethane/ethyl acetate (40:1) as an eluent, to give a white solid as the product of L5 with the yield of 55% (1.69 g). H NMR (δ, ppm, CDCl₃/COD): 7.53 (s, 8H, HA), 7.33–7.32 (m, 14H, HA), 7.15 (s, 2H, HA), 4.25 (t, J = 10 Hz, 4H, NCH₂CH₂), 1.64 (m, 4H, NCH₂CH₂), 1.06 (s, 8H, NCH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂N). ¹³P NMR (δ, ppm, CDCl₃/COD): −23.02 (s, PPh₂).

A solution of L5 (1.23 g, 2 mmol) in 30 mL of distilled dichloromethane was cooled to −78°C and then MeOTf (0.67 g, 4.1 mmol) was added dropwise in 30 min. The reaction mixture was stirred at −78°C for another 1 h and then warmed up to room temperature naturally. Upon completion, the mixture was stripped of solvent in vacuo to give a white solid. Then the solid product was washed by diethyl ether completely to give the product L₆ in 90% yield (1.70 g). H NMR (δ, ppm, CDCl₃/COD): 8.08 (s, 2H, N’ CHCHN), 7.96 (s, 2H, N’ CHCHN), 7.59–7.53 (m, 20H, HA), 4.45 (t, J = 10 Hz, 4H, NCH₂CH₂), 3.70 (s, 6H, N’CH₃), 1.63–1.61 (d, J = 10 Hz, 4H, NCH₂CH₂), 1.05 (s, 8H, NCH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂N). ¹³P NMR (δ, ppm, CDCl₃/COD): −28.78 (s, PPh₂).

General Procedures for Alkyloxy-carbonylation of Aryl Halides in Alcohols

In a 50 mL sealed Teflon-lined stainless-steel autoclave, the commercial complex of RuCl₃·3H₂O (0.01 mmol Ru 0.5%) and pure L₄ (0.004 mmol) were mixed with methanol (10 mmol, or the other alcohols), NEt₃ (5 mmol), iodobenzene (2 mmol), or the other aryl iodides and aryl bromides and N-methyl pyrrolidone (NMP) 3 mL (solvent). The autoclave was purged with CO (0.5 MPa) for three times and pressured by CO to 2.0 MPa. The reaction mixture was stirred vigorously at 120°C for 16 h. Upon reaction completion, the reactor was cooled down to room temperature and depressurized carefully. The reactor vessel was washed with anhydrous diethyl ether thoroughly and the reaction solution was analyzed by GC to determine the conversions (normalization method) and the selectivities (normalization method). The products were further identified by GC-Mass to determine the reaction products.

Procedures for the Catalyst Recycling Experiment in [Bmmim]PF₆

In the recycling experiment, the RTIL of [Bmmim]PF₆ was selected as the solvent. In the first run, [Bmmim]PF₆ (3 mL) was mixed with RuCl₃·3H₂O (0.01 mmol), L₄ (0.004 mmol), methanol (10 mmol), NEt₃ (5 mmol), iodobenzene (2 mmol) sequentially to form a homogenous reaction solution. Upon reaction completion, anhydrous diethyl ether (20 mL) was added to the yellow reaction solution. Then the upper transparent phase was decanted from the obtained biphasic mixture. The remaining RTIL phase was washed with anhydrous diethyl ether (3 mL × 3) to extract the reactants and products completely. The yield and selectivity to the target product was analyzed by GC and the remaining RTIL phase was reused without further treatment for the next run. Then the amount of Ru and P in the organic phase was quantified by ICP-OES.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Alkoxycarbonylation · aryl halides · ionic diphosphines · Ru(III) complex · catalyst recyclability

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