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Efficient and Recyclable $RuCl_3 \cdot 3H_2O$ Catalyst Modified with Ionic Diphosphine for the Alkoxycarbonylation of Aryl Halides

Qing Zhou, Lei Liu, Wen-Di Guo, Wen-Yu Liang, Yong Lu, and Ye Liu*[a]

A series of ionic (mono-/di-)phosphines (**L2**, **L4**, and **L6**) with structural similarity and their corresponding neutral counterparts (**L1**, **L3**, and **L5**) were applied to modulate the catalytic performance of $RuCl_3 \cdot 3H_2O$. With the involvement of the ionic diphosphine (**L4**), in which the two phosphino-fragments were linked by butylene group, $RuCl_3 \cdot 3H_2O$ with advantages of low cost, robustness, and good availability was found to be an efficient and recyclable catalyst for the alkoxycarbonylation of aryl halides. The **L4**-based $RuCl_3 \cdot 3H_2O$ system corresponded 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. The electronic and steric effects of the applied phosphines, which were analyzed by the ^{31}P NMR for $^{1}J^{31}{}_{P-}{}^{77}{}_{Se}{}^{1}J$ measurement and single-crystal X-ray diffraction, were carefully co-related to the performance $RuCl_3 \cdot 3H_2O$ catalyst. In addition, the **L4**-based $RuCl_3 \cdot 3H_2O$ system could be recycled successfully for at least eight runs in the ionic liquid $[Bmim]PF_6$.

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.[1,2] 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.[2–4] So far, palladium complexes are the most studied catalytic systems for alkoxycarbonylation of aryl halides.[5] In addition, the other metals such as nickel,[6,7] cobalt,[8] platinum,[9] rhodium[10] also could be applied as the viable catalysts with the involvement of suitable ligands.

In comparison, $RuCl_3 \cdot 3H_2O$-based complexes have been rarely used to catalyze alkoxcarbonylation of alkenes/aryl halide. As for the high valence state $RuCl_3 \cdot 3H_2O$-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.[11] Hence, even if $RuCl_3 \cdot 3H_2O$ 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 $RuCl_3 \cdot 3H_2O$ 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 phosphinites, phosphonites, phosphites,[12] and fluoroarylphosphines,[13] 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 phosphinites, phosphonites, and phosphites are instable and sensitive to protic cleavage.[14,15] Although fluoroarylphosphines with inert P–C linkages can be considered as alternatives, their structural diversity is limited.[16] 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 vicinal to the P(III) atom are the alternative electron-deficient ligand candidates[17–21] 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.[22–25] 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^-.[26]

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 $RuCl_3 \cdot 3H_2O$ 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.[27–29] In

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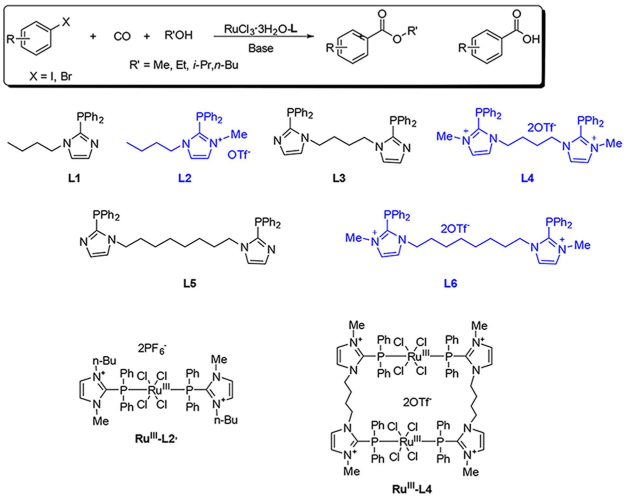
comparison, $RuCl_3 \cdot 3H_2O$ is advantageous with apparent robustness against CO, organic amine and water.

Herein a series of ionic phosphines (**L2**, **L4**, and **L6**) as the electron-deficient ligands were applied with $RuCl_3 \cdot 3H_2O$ together to catalyze alkoxycarbonylation of aryl halides (Scheme 1).



Scheme 1. The neutral and ionic phosphines (**L1**–**L6**) and related Ru^{III} complexes (**Ru^{III}-L2′**, **Ru^{III}-L4**) for alkoxycarbonylation of aryl halides.

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 $RuCl_3 \cdot 3H_2O$.

In addition, the recyclability of the ionic phosphine based $RuCl_3 \cdot 3H_2O$ in combination of the room temperature ionic liquid (RTIL) of $[Bmim]PF_6$ (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]

2. Results and Discussion

Under the optimal conditions (P/Ru = 0.8 molar ratio, NEt_3 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 $RuCl_3 \cdot 3H_2O$ 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 $RuCl_3 \cdot 3H_2O$ system (Entry 4), and the other phosphines just corresponded to the relatively slow transformation of PhI.

Table 1. Methoxycarbonylation of PhI catalyzed by $RuCl_3 \cdot 3H_2O$ with the involvement of different phosphines.[a]

Entry	Ligand	Conv.[b] [%]	$Sel._{ester}$[b] [%]	$Sel._{acid}$[b] [%]
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	96	4
7[c]	**Ru^{III}-L4**	96	98	2
8	–	43	95	5

[a] $RuCl_3 \cdot 3H_2O$ 0.01 mmol (Ru 0.5 mol %), monophosphine 0.008 mmol, diphosphine 0.004 mmol, (P/Ru = 0.8 molar ratio), iodobenzene 2 mmol, CH_3OH 10 mmol, NEt_3 5 mmol, CO 2 Mpa, *N*-methyl pyrrolidone (NMP) 3 mL, 120 °C, 16 h. [b] Determined by GC. $Sel._{ester}$ represents selectivity to methyl benzoate; $Sel._{acid}$ represents selectivity to benzoic acid. [c] The as-synthesized complex of **Ru^{III}-L4** (0.005 mmol) was used instead of mixing $RuCl_3 \cdot 3H_2O$ (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 **Ru^{III}-L4** was used to replace the mixture of $RuCl_3 \cdot 3H_2O$ 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 phosphine ligand, $RuCl_3 \cdot 3H_2O$ 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-based precursors such as $RuCl_3 \cdot 3H_2O$, $Ru(COD)Cl_2$ and $Ru_3(CO)_{12}$, only $RuCl_3 \cdot 3H_2O$ exhibited the best activity towards methoxycarbonylation of PhI with the involvement of **L4** (Entries 1 *vs* 2 and 3). When the Pd-based precursors were used instead, not only the relatively lower yield of methyl benzoate was observed, but the Pd(0)-black was seriously precipitated upon the reaction which indicated the rapid deactivation of these Pd-catalysts even with the presence of **L4** (Entries 4–6; pictures of the slurry mixture upon reaction were provided in the

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

Entry	Precursor	Conv.[b] [%]	Sel_{ester}[b] [%]	$Sel._{acid}$[b] [%]
1	$RuCl_3 \cdot 3H_2O$	96	99	1
2	$Ru(COD)Cl_2$	84	97	3
3	$Ru_3(CO)_{12}$	86	97	3
4*c	$Pd(OAc)_2$	89	93	7
5*	$PdCl_2$	89	94	6
6*	$Pd(MeCN)_2Cl_2$	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, NEt_3 5 mmol, CO 2 MPa, *N*-methyl pyrrolidone (NMP) 3 mL, 120 °C, 16 h. [b] Determined by GC. $Sel._{ester}$ represents selectivity to methyl benzoate; $Sel._{acid}$ represents selectivity to benzoic acid; * Pd(0)-black precipitated upon reaction. [c] The Pd-black residue was collected after washing by diethyl ether completely to repeat the reaction.

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 $^{1}J^{31}{}_{\text{P-}}{}^{77}{}_{\text{Se}}$ coupling constant in the ^{77}Se isotopomer of the corresponding phosphine-selenide in ^{31}P NMR spectra can evaluate the π-acceptor ability of different phosphines. An increase of $^{1}J^{31}{}_{\text{P-}}{}^{77}{}_{\text{Se}}$ indicates an increase in the character of the π-acceptor ability (i.e., less σ-donor ability).[34–36] In this work, the measurement of $^{1}J^{31}{}_{\text{P-}}{}^{77}{}_{\text{Se}}$ 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 $^{1}J^{31}{}_{\text{P-}}{}^{77}{}_{\text{Se}}$ of the ionic phosphines universally higher than their neutral analogues, which means a dramatic increase in the character of π-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 $^{1}J^{31}{}_{\text{P-}}{}^{77}{}_{\text{Se}}$, they demonstrated quite different promoting effect on the performance of $RuCl_3 \cdot 3H_2O$. Evidently, only **L4** enabled $RuCl_3 \cdot 3H_2O$ to exhibit the best activity for methoxcarbonylation 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 $RuCl_3 \cdot 3H_2O$ over their electronic effect.

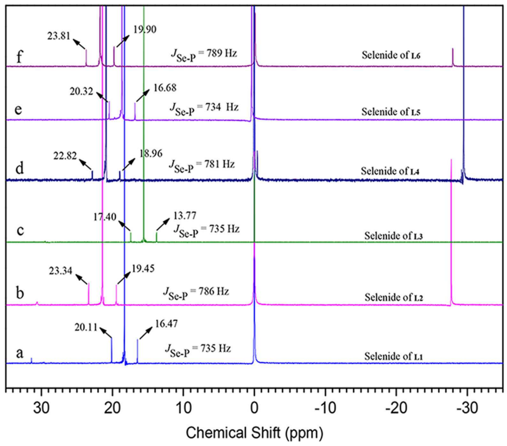
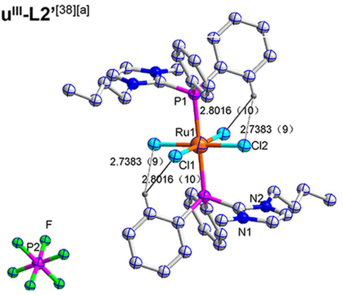
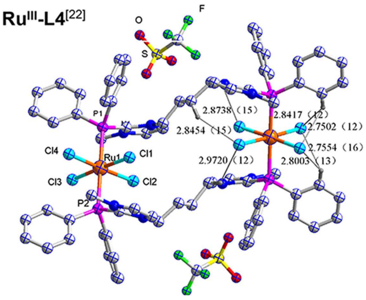
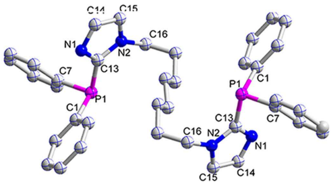
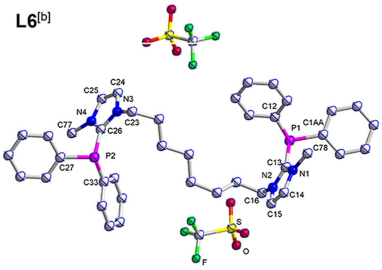


Figure 1. ^{31}P NMR spectra (202 MHz) of the selenides of **L1**–**L6**:[37] reacting elemental selenium with a) **L1** in $CDCl_3$ at 70 °C for 12 h; b) **L2** in $CDCl_3$ at 70 °C for 12 h; c) **L3** in $CDCl_3$ at 70 °C for 12 h; d) **L4** in $CDCl_3$ at 70 °C for 12 h; e) **L5** in $CDCl_3$ at 70 °C for 12 h; f) **L6** in CD_3COCD_3 at 70 °C for 24 h.

The molecular structures of the complexes of **Ru^{III}-L2′** and **Ru^{III}-L4** reported in our previously published work [22,38] can help us understand the steric effect of **L2** and **L4** on the performance of $RuCl_3 \cdot 3H_2O$ (Table 3). Undoubtedly, the redox between the ionic phosphine (**L2** or **L4**) and the high valence state Ru^{3+} was avoided completely as expected. As shown in Table 3, Ru(III) (d^5)-center of **Ru^{III}-L2′**[38] and **Ru^{III}-L4**[22] is in six-coordinated octahedral configuration with paramagnetism. In **Ru^{III}-L2′**, the tailed butylimidazolium moieties are located in *trans*-positions. **Ru^{III}-L4** is a dimer analogue of **Ru^{III}-L2′** in which the two butylenyl-linked imidazolium moieties are reversed to *cis*-positions to form a quadrilateral ring dinuclear Ru(III) complex. It was found in **Ru^{III}-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⁻

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

Structures	Bond distances [Å]	
Ru^{III}-L2′[38][a]  	Ru(1)-Cl(1) Ru(1)-Cl(2) Ru(1)-Cl(1a) Ru(1)-Cl(2a) Ru(1)-P(1) Ru(1)-P(1a)	2.3441(10) 2.3614(9) 2.3441(10) 2.3614(9) 2.4056(9) 2.4056(9)
Ru^{III}-L4[22]  	Ru(1)-Cl(1) Ru(1)-Cl(2) Ru(1)-Cl(3) Ru(1)-Cl(4) Ru(1)-P(1) Ru(1)-P(2)	2.3755(12) 2.3806(14) 2.3599(12) 2.3571(14) 2.4109(15) 2.4119(15)
L5[b]  	P(1)-C(1) P(1)-C(7) P(1)-C(13)	1.8290(16) 1.8398(17) 1.8279(16)
L6[b]  	P(1)-C(1) P(1)-C(12) P(1)-C(13) P(2)-C(26) P(2)-C(27) P(2)-C(33)	1.8261(2) 1.8406(2) 1.8329(18) 1.8365(19) 1.8340(2) 1.8324(19)

[a] **Ru^{III}-L2′** with counter-anion of PF_6^- possesses the same cation as **Ru^{III}-L2**. [b] The related structural data were provided in the Supporting Information.

with H-butylenyl group. In contrast, in **Ru$^{\text{III}}$-L2′**, the distances of the four Ru–Cl bonds are much shorter in the range of 2.34~2.36 Å. Hence, when **Ru$^{\text{III}}$-L4** or **L4**-based $RuCl_3\cdot 3H_2O$ (in situ formation of **Ru$^{\text{III}}$-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*-octylenyl, the expected dinuclear complex with structural similarity to **Ru$^{\text{III}}$-L4** was not obtained successfully while reacting $RuCl_3\cdot 3H_2O$ 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_6 was selected as the most suitable medium after comparing to [Bmim]BF_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**-$RuCl_3\cdot 3H_2O$ 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_6 and the formed $Et_3N\cdot HI$ salt. Subsequently, the slurry was washed by water to remove $Et_3N\cdot HI$ and then the hydrophobic [Bmim]PF_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_6) in the combined organic phase was 1.6 % and 6.2 % respectively, indicating that the catalyst could be locked in [Bmim]PF_6 medium tightly only with very low leaching into the organic phase.

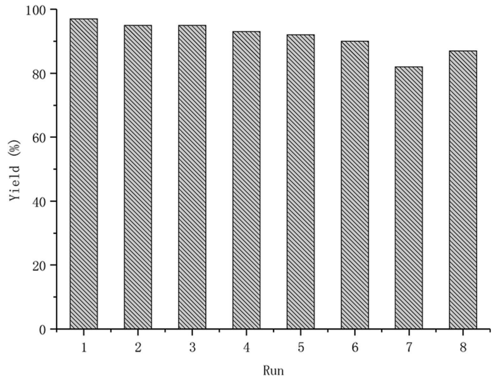
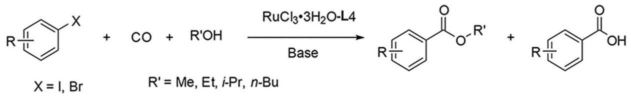
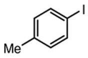
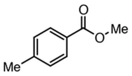
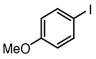
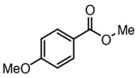
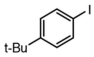
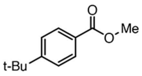
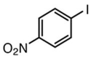
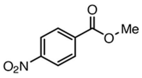
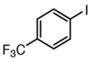
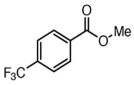
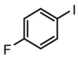
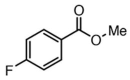
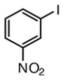
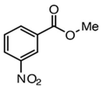
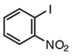
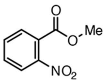
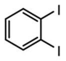
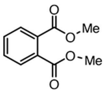
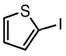
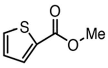
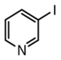
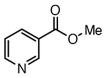
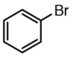
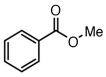
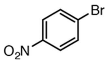
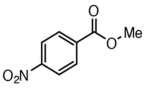
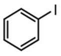
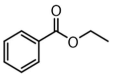
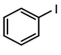
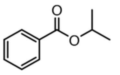
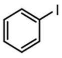
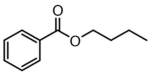


Figure 2. The recycling uses of $RuCl_3\cdot 3H_2O$ with the involvement of **L4** in [Bmim]PF_6 for methoxycarbonylation of iodobenzene [Ru 0.01 mmol, **L4** 0.004 mmol, iodobenzene 2 mmol, MeOH 10 mmol, NEt_3 5 mmol, [Bmim]PF_6 3 mL, CO 2 MPa, 120 °C, 16 h; * In the 7th run, the reaction slurry was washed by H_2O to remove the formed ammonium salt of $Et_3N\cdot HI$.

The generality of $RuCl_3\cdot 3H_2O$-**L4** catalytic system for alkoxycarbonylation 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 $RuCl_3\cdot 3H_2O$ for alkoxycarbonylation.[a]

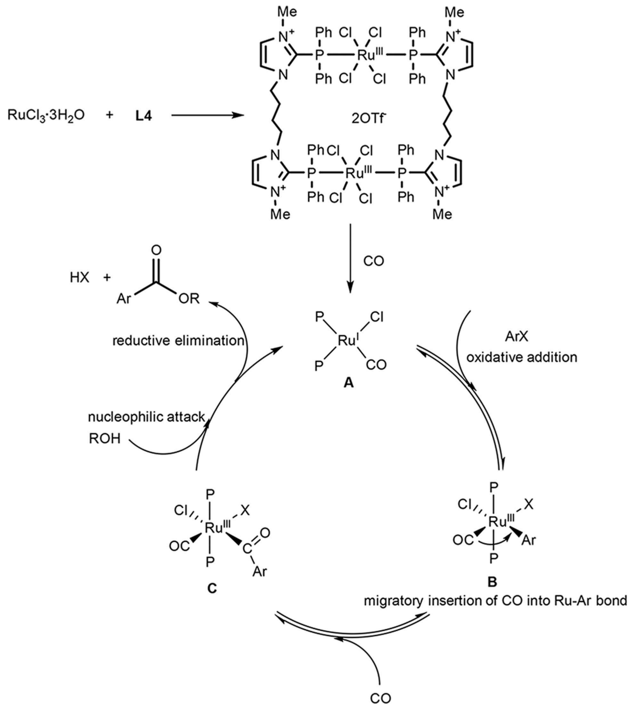


Entry	Substrate	Alcohol	Product	Conv.[b] [%]	Yield[b] [%]
1		MeOH		93	90
2		MeOH		82	80
3		MeOH		88	84
4		MeOH		90	86
5		MeOH		90	83
6		MeOH		95	92
7		MeOH		86	80
8		MeOH		67	64
9		MeOH		51	43
10		MeOH		63	57
11		MeOH		70	63
12		MeOH		7	4
13[c]		MeOH		84	80
14		EtOH		95	90
15		*i*-PrOH		91	66
16		*n*-BuOH		89	81

[a] $RuCl_3\cdot 3H_2O$ 0.5 mol %, **L4** 0.004 mmol (P/Ru = 0.8 molar ratio), aryl or heteroaryl halides 2 mmol, alcohol 10 mmol, NEt_3 5 mmol, CO 2 MPa, *N*-methyl pyrrolidone (NMP) 3 mL, 120 °C, 16 h. [b] Determined by GC. [c] 140 °C.

electronic effect of the substituted groups (Entries 1–6). The steric effect of the substituents at meta- or ortho-position obviously influenced the reaction rate. For example, 1-iodo-3-nitrobenzene corresponded to 80% yield of the product (Entry 7) whereas 1-iodo-2-nitrobenzene gave only 64% yield of methyl 2-nitrobenzoate (Entry 8). Notably, 1,2-diiodobenzene was subjected to the double methoxycarbonylation to produce dimethyl phthalate at 43% yield (Entry 9). Heteroaryl halides could afford the corresponding esters in the moderate yields of 57–63% under the applied conditions (Entries 10 and 11). Unfortunately, **L4**-based $RuCl_3 \cdot 3H_2O$ 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 $-NO_2$ 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 $RuCl_3 \cdot 3H_2O$ 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 (**Ru^{III}-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.



Scheme 2. The proposed catalytic mechanism over **L4**-based Ru(III) complex for alkoxycarbonylation of aryl halides

3. Conclusions

The low-cost and robust $RuCl_3 \cdot 3H_2O$ 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 Ru^{3+} 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 quadrilateral ring dimer of **Ru^{III}-L4** along with the differentiated hydrogen bond interaction further facilitated the activity of this Ru(III)-catalyst. As a result, **L4**-based $RuCl_3 \cdot 3H_2O$ 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 $RuCl_3 \cdot 3H_2O$ system could be recycled successfully at least 8 runs in the hydrophobic ionic liquid of $[Bmim]PF_6$.

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 ^{31}P NMR spectra for the analyses of the common compounds were recorded on a Bruker ARX 500 spectrometer at ambient temperature. The ^{31}P NMR spectra were referenced to 85% H_3PO_4 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[39]

Under N_2 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 slowly. Next, the mixture was stirred vigorously at ice-water bath for 1 h. After the mixtures restored room temperature, 1,8-dibromooctane (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 N_2 atmosphere, when a solution of 1,1′-(1,8-octanediyl)bis(imidazole) (1.23 g, 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 (PPh_2Cl, 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). ^{1}H NMR (δ, ppm, CD_3COCD_3): 7.53 (s, 8H, *H*Ar), 7.33-7.32 (m, 14H, *H*Ar), 7.15 (s, 2H, *H*Ar), 4.25 (t, $J = 10$ Hz, 4H, NCH_2CH_2), 1.64 (m, 4H, $NCH_2CH_2CH_2$), 1.06 (s, 8H, $NCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2N$). ^{31}P NMR ($\delta$, ppm, CD_3COCD_3): −23.02 (s, PPh_2).

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 white solid product was washed by diethyl ether completely to give the product **L6** in 90 % yield (1.70 g). ^{1}H NMR (δ, ppm, CD_3COCD_3): 8.08 (s, 2H, N^+CHCHN), 7.96 (s, 2H, N^+CHCHN), 7.59–7.53 (m, 20H, *H*Ar), 4.45 (t, $J = 10$ Hz, 4H, NCH_2CH_2), 3.70 (s, 6H, N^+CH_3), 1.63-1.61 (d, $J = 10$ Hz, 4H, $NCH_2CH_2CH_2$), 1.05 (s, 8H, $NCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2N$). ^{31}P NMR ($\delta$, ppm, CD_3COCD_3): −28.78 (s, PPh_2).

General Procedures for Alkoxycarbonylation of Aryl Halides in Alcohols

In a 50 mL sealed Teflon-lined stainless-steel autoclave, the commercial complex of $RuCl_3 \cdot 3H_2O$ (0.01 mmol Ru 0.5 %) and pure **L4** (0.004 mmol) were mixed with methanol (10 mmol, or the other alcohols), NEt_3 (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 then the reaction solution was analyzed by GC to determine the conversions (*n*-dodecane as internal standard) 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 [Bmim]PF_6

In the recycling experiment, the RTIL of [Bmim]PF_6 was selected as the solvent. In the first run, [Bmim]PF_6 (3 mL) was mixed with $RuCl_3 \cdot 3H_2O$ (0.01 mmol), **L4** (0.004 mmol), methanol (10 mmol), NEt_3 (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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[39] https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/open.201800266. CCDC. 1878304 (**L5**) and 1878305 (**L6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from http://www.ccdc.cam.ac.uk/, The Cambridge Crystallographic Data Centre.

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