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Phosphine-ligated Ir(III)-complex as a bi-functional catalyst for one-pot tandem hydroformylation-acetalization

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ABSTRACT

The complexation of $IrCl_3{\cdot}3H_2O$ with the electron-deficient phosphines (**L1**-**L6**) respectively afforded a bi-functional catalyst possessing the dual functions of transition metal complex (Ir^{III}-P) and Ir^{III}-Lewis acid for tandem hydroformylation-acetalization of olefins. The best result was obtained over **L5**-based $IrCl_3{\cdot}3H_2O$ catalytic system which corresponded to 97% conversion of 1-hexene along with 92% selectivity to the target acetals free of any additive. The crystal structure of the novel Ir^{III}-complex of **Ir^{III}-L4** indicated that the electron-deficient nature of the involved phosphine warranted Ir-center in +3 valence state without reduction, which served as the Lewis acid catalyst for the subsequent acetalization of the aldehydes as well. Moreover, as an ionic phosphine, **L6**-based $IrCl_3{\cdot}3H_2O$ system immobilized in RTIL of $[Bmim]PF_6$ could be recycled for 6 runs without the obvious activity loss or metal leaching.

1. Introduction

Hydroformylation, the addition of synthesis gas (CO/H_2) to olefins, is one of the most important homogeneously catalyzed processes for the production of aldehydes in industrial scale [1–4]. In many cases, aldehydes are not the final products and can further convert into alcohols, esters, acetals etc. The one-pot tandem reaction of hydroformylation along with the other transformation is always advantageous over multistep synthesis since it avoids the complex steps for the separation and purification of aldehyde intermediates, which fulfills the principles of atom economy and low energy consumption in green chemistry [5–7]. Examples include tandem hydroformylation–acetalization, hydroformylation–hydrogenation, hydroformylation–aldol condensation etc. [2,8–17], in which tandem hydroformylation–acetalization represent a one-pot synthesis of acetals via formation of aldehydes followed by the acetalization with alcohols. Acetals could be used to protect the sensitive aldehyde group from side reactions in organic synthesis or to further synthesize fine chemicals such as pharmaceutical, fragrances, domestics, and detergents [18–20]. As for tandem hydroformylation–acetalization, two types catalytic systems are required wherein the phosphine-based transition metal catalyst is responsible for hydroformylation of olefins to produce aldehydes [2,12,13], and the Lewis/ Brønsted acid catalyst is in charge of the subsequent acetalization of the aldehydes to produce acetals. In general, the phosphine-based transition metal catalysts and the Lewis/ Brønsted acid catalysts are used in the mode of mechanical mixing [20,22–24]. More recently, the bi-functional phosphines dually containing phosphino-fragments and Lewis acidic moieties (such as phosphonium) has been explored by us for Rh(I)-catalyzed tandem hydroformylation-acetalization of olefins with advantages of the bi-functional synergetic co-catalysis and the simplified manipulation without the function-quenching problem [25,26]. On the other hand, the high valence state transition metal compounds also can serve as the bi-functional catalysts due to their ability to complex with the electron-deficient ligands as well as the inherent Lewis acidic character [11,21,27,28]. For example, $RhCl_3{\cdot}3H_2O$ could directly drive tandem hydroformylation-acetalization of olefins with the involvement of electron-deficient phosphites $[P(OR)_3]$[21]. And the ionic electron-deficient diphosphine based $RuCl_3{\cdot}3H_2O$ system also proved to be catalytically bi-functional for tandem hydroformylation-acetalization-hydrogenolysis in our previous work [11]. The requirement of electron-deficient P-containing ligands like phosphites or the ionic phosphines with intensive π-accepting nature is to warrant the high-valence state of the metal-ion unchanged without redox between metal-ion (like Rh^{3+}/Ru^{3+}) and the involved ligand. Resultantly, the corresponding high-valence metal-catalyst was featured with two functionalities

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in terms of transition metal catalysis and Lewis acid catalysis [11,29]. However, the lability of P–O bonds in phosphites towards hydrolysis has limited their practical applications [30–32].

Knowingly, compared to the electron-withdrawing groups like —CF_3, —NO_2 and —COR, the positive-charged quaternary ammoniums (such as imidazolium) are one of the most intensive electron-withdrawing moieties. Hence, the linkage of imidazolium moiety to P-atom can greatly decrease the electron-density of the resultant phosphines [11,33–35]. On the other hand, the replacement of phenyl ring of PPh_3 by N-containing heteroaryl ring (such as imidazolyl) also renders the corresponding phosphine the electron-deficiency to some extent [25,36,37]. Herein, for the first time, a series of imidazolyl- and imidazolium-tailed phosphines (**L1-L6**) were applied, which were featured with the electron-deficient character, in order to warrant the bi-functionalities of the high-valence Ir^{III}-catalyst to fulfill co-catalysis for one-pot tandem hydroformylation-acetalization of olefins. Since Ir^{III}-ion is a much stronger Lewis acid in comparison to Ir^{I}-ion, it is believed that the electron-deficient phosphine modified Ir(III)-complex is able to serve as a bi-functional catalyst merging transition metal catalyst (Ir^{III}-P) and Lewis acid catalyst (Ir^{3+}). In addition, as for the imidazolium tailed phosphines (**L2**, **L4** and **L6**), they are typical ionic compounds with high polarity and improved stability against water and oxygen, which can be used with the room temperature ionic liquid (RTIL) solvent to fulfill the recovery and recycling of the homogenous Ir-catalyst expectantly [38,39] (see Scheme 1).

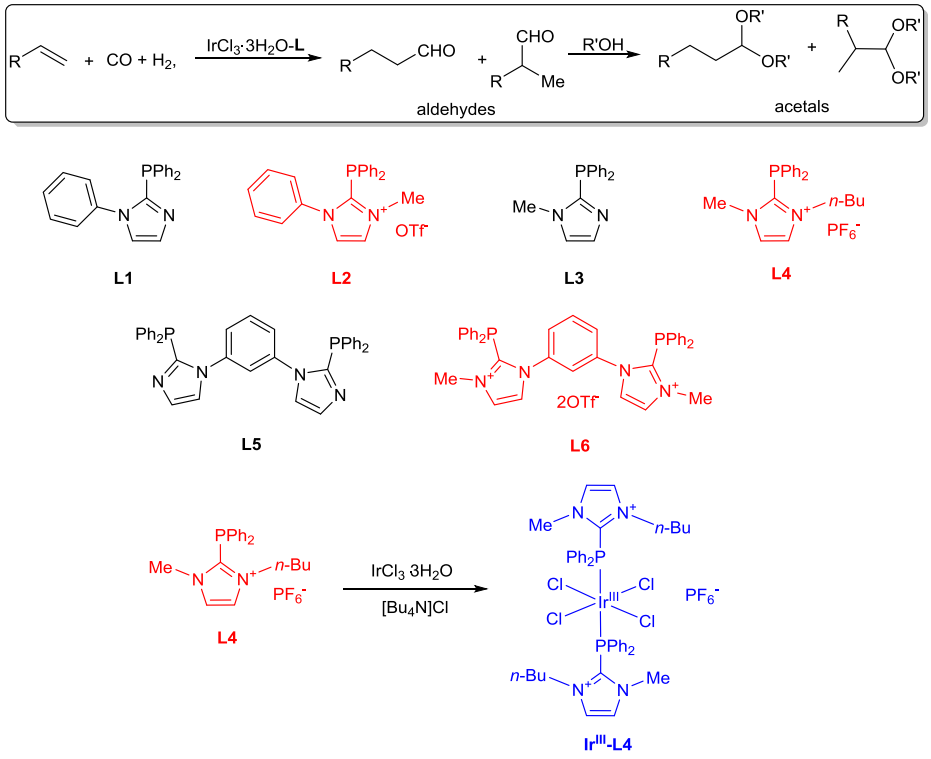
2. Results and discussion

The one-pot tandem hydroformalytion-acetalization of 1-hexene over the different catalyst precursors was initially investigated with the involvement of **L1** as summarized in Table 1.

Under the optimal conditions [see S. Table 1 in ESI for screening the reaction conditions], over **L1**-based $[Ir^{I}(COD)Cl]_2$ system, only hydroformylation occurred smoothly resulting in 82% conversion of 1-hexene to heptanals with selectivity of 90% and L/B of 76/24 (Entry 1). And the additional introduction of anhydrous $FeCl_3$ as a Lewis acid co-catalyst under the same conditions successfully led to the subsequent conversion of heptanals to the corresponding acetals, resulting in 95% conversion of 1-hexene with 78% selectivity to acetals as well as 17% selectivity to hexane (Entry 2). However, the addition of H_2O (10 mol%) into anhydrous $FeCl_3$ (2.0 mol%) led to the decreased conversion of 1-hexene accompanied by the boosted side-reaction of hydrogenation towards n-hexane (Entries 3 *vs* 2), probably due to the hydrolysis of $FeCl_3$ with the release of HCl. This comparison data indicated that the low-valence Ir(I)-catalyst didn't exhibit any activity toward the acetalization of the aldehydes, which only transformed into the acetals over the additional Lewis acid catalyst ($FeCl_3$). Interestingly, over **L1**-based $IrCl_3{\cdot}3H_2O$ system, the conversion of 1-hexene reached 96% along with 89% selectivity to the acetals (Entry 4). Accordingly, **L1**-based $IrCl_3{\cdot}3H_2O$ system served as an ideal bi-functional catalyst not only catalyzing the hydroformylation of olefin to produce aldehyde, but also effectively spurring the subsequent acetalization of the aldehydes with MeOH. It was also noted that over **L1**-based $IrCl_3{\cdot}3H_2O$ the conversion of 1-hexene was even much higher than that over **L1**-based $RhCl_3{\cdot}3H_2O$ catalyst (Entry 5 *vs* 4) [40,41].

Highlighted by the co-catalysis of **L1**-based $IrCl_3{\cdot}3H_2O$ for tandem hydroformylation-acetalization of 1-hexene, the ligand effect on the catalytic performance of $IrCl_3{\cdot}3H_2O$ precursor were carefully investigated in Table 2.

L1-**L4** were obtained respectively via the replacement of one phenyl ring of PPh_3 by imidazolyl- or imidazolium-group. And the diphosphine analogues of **L5** and **L6** were also studied in parallel. The electronic nature of the phosphines of **L1**-**L6** was evaluated by the magnitude of $^{1}J^{31}P–^{77}Se$ coupling constant of the corresponding phosphine selenide [42,43] recorded by ^{31}P NMR spectroscopy (see ESI). An increase value of $^{1}J^{31}P–^{77}Se$ indicates a decrease of electron-density of P-atom and then an increase in the character of π-acceptor ability of the phosphine. In comparison, **L1**-**L6** are definitely more electron-deficient featured with more



Scheme 1. The phosphines (**L1**-**L6**) with electron-deficient character applied in $IrCl_3{\cdot}3H_2O$ catalyzed hydroformylation-acetalization.

Table 1
The one-pot tandem hydroformylation-acetalization of 1-hexene over different catalyst precursors with involvement of **L1**.[a]

Entry	Precursor	Co-catalyst	Conv. (%)[b]	Sel. (%)[b]				L/B[b]
				Aldehydes	Acetals	n-Hexane	Isomer	
1	$[Ir^{I}(COD)Cl]_2$	–	82	90	–	9	<1	76/24
2[c]	$[Ir^{I}(COD)Cl]_2$	$FeCl_3$	95	<1	78	17	4	78/22
3[d]	$[Ir^{I}(COD)Cl]_2$	$FeCl_3 + H_2O$	82	<1	70	23	7	74/26
4	$Ir^{III}Cl_3{\cdot}3H_2O$	–	96	<1	89	10	<1	78/22
5	$Rh^{III}Cl_3{\cdot}3H_2O$	–	63	7	92	<1	<1	62/38

[a] Ir 0.01 mmol (0.2 mol%), **L1** 0.01 mmol (P/Ir = 1 M ratio), 1-hexene 5.0 mmol, methanol 5 mL, *N*-methyl pyrrolidone (NMP) 2 mL, CO/H_2 (v_{CO}:v_{H2} = 5:1) 4.0 MPa, temperature 110 °C, time 8 h.
[b] Determined by GC and GC-Mass; L/B, the ratio of linear aldehydes and acetals to branched aldehydes and acetals.
[c] Anhydrous $FeCl_3$ 0.1 mmol (2.0 mol%).
[d] Anhydrous $FeCl_3$ 0.1 mmol (2.0 mol%) and H_2O 10 μL (10 mol%).

Table 2
$IrCl_3{\cdot}3H_2O$-catalyzed tandem hydroformylation-acetalization of 1-hexene in the presence of different phosphines.[a]

Entry	ligand	$^1J^{31}P–^{77}Se$	Time (h)	Conv. (%)[b]	Sel. (%)[b]				L/B[b]	TON[c]
					Aldehydes	Acetals	n-Hexane	Isomer		
1	–	–	8	66	<1	73	26	<1	78/22	241
2	**L1**	753[41]	8	96	<1	89	10	<1	78/22	427
3	**L2**	780[41]	8	81	<1	86	13	<1	78/22	348
4	**L3**	750	8	94	<1	88	11	<1	78/22	413
5	**L4**	789	8	79	<1	87	12	<1	78/22	344
6	**L5**	751[41]	8	97	<1	92	7	<1	78/22	446
7	**L6**	782[41]	8	82	<1	87	12	<1	79/21	356
8	**L6**	782[41]	10	95	<1	87	12	<1	79/21	413
9	PPh_3	729[41]	8	78	<1	79	20	<1	80/20	253
10[d]	**L4**	789	8	79	<1	85	14	<1	79/21	344
11[e]	**Ir^{III}-L4**	--	8	80	<1	86	13	<1	80/20	344

[a] $IrCl_3{\cdot}3H_2O$ 0.01 mmol (Ir 0.2 mol%), P/Ir = 1 (molar ratio), 1-hexene 5.0 mmol, methanol 5 mL, NMP 2 mL, CO/H_2 (v_{CO}:v_{H2} = 5:1) 4.0 MPa, temperature 110 °C, time 8 h.
[b] Determined by GC; L/B, the ratio of linear acetals to branched acetals.
[c] TON, turnover number = mol of acetal products (mol of Ir)$^{-1}$.
[d] P/Ir = 2 (molar ratio)f;
[e] The as-synthesized **Ir^{III}-L4** complex was used.

π-accepting character than PPh_3 (Table 2), in which the ionic **L2**, **L4** and **L6** are more electron-deficient than their counterparts. Evidently, the absence of any phosphine led to the sluggish conversion of 1-hexene to heptanals, which could rapidly transform into the corresponding acetals over the unmodified $IrCl_3{\cdot}3H_2O$ (Entry 1). **L1**-**L6** universally corresponded to much higher conversion of 1-henexe and the better selectivity to the acetals than PPh_3 (Entries 2–7 *vs* 9). It was found that the neutral phosphines (**L1**, **L3** and **L5**) universally led to the higher conversion of 1-hexene and the better selectivity to the acetals than their ionic counterparts (**L2**, **L4** and **L6**) (Entries 2 *vs* 3; Entries 4 *vs* 5; Entries 6 *vs* 7). In particular, over the neutral diphosphine of **L5**, the conversion of 1-hexene reached 97% along with 92% selectivity to the acetals, whereas its ionic counterpart of **L6** corresponded to 82% conv. and 87% sel. (Entries 6 *vs* 7). Certainly, the prolonged reaction time to 10 h could increase the conversion of 1-hexene and yield of acetals over **L6**-based $IrCl_3{\cdot}3H_2O$ system (Entry 8). It was found that when the as-synthesized **Ir^{III}-L4** was used to replace the physical mixtures **L4** and $IrCl_3{\cdot}3H_2O$ at P/Ir of 2, nearly the same conversion of 1-hexene along with the identical selectivity to the acetals was observed under the same conditions, indicating the *in situ* formed **Ir^{III}-L4** exhibited the same activity as the as-synthesized one (Entry 11 *vs* 10).

The available molecular structure (Fig. 1) of the complex of Ir^{III}-**L4** obtained upon complexation of $IrCl_3{\cdot}3H_2O$ with **L4** further confirmed that the use of an electron-deficient phosphine indeed kept + 3 valence state of Ir-center unchanged. In Ir^{III}-**L4**, the Ir^{III}-complex cation which is in an ideal octahedral geometry is counteracted by one anionic PF_6^-. The Ir^{III}-center is six-coordinated by four chlorine atoms in the equatorial plane and two imidazolium-tailed phosphines in the axial positions. The

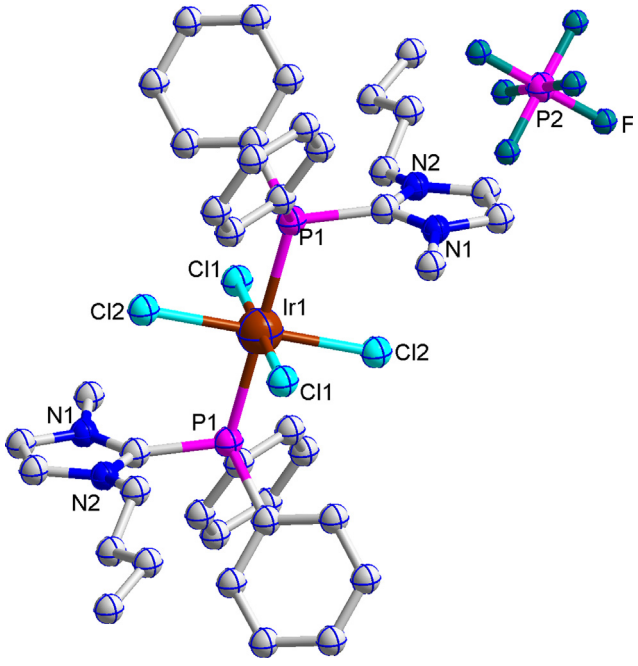


Fig. 1. The single crystal structure of **Ir^{III}-L4** (all H-atoms and solvent molecules have been omitted for clarity). The selected bond distances (Å): Ir-P1 2.3639 (13), Ir-Cl1 2.3602 (13), Ir-Cl2 2.3628 (12).

bond distances of P-Ir^{III} is 2.3639 (13) Å identically, which are relatively longer than the classical ones (2.29–2.32 Å) in the typical phosphine-ligated Ir^{I}-complexes [41,44]. It is believed that the

reduction of Ir^{III} to Ir^{I} unavoidably ensues with the presence of the electron-rich donor like PPh_3 as a good reducing reagent, leading to the formation of Ir^{I}-complex finally in the course of complexation of Ir^{III}-ion with PPh_3. Hence, the previous reported PPh_3-ligated Ir^{III}-complexes were prepared with the involvement of risky oxidant like $SnOCl_2$ or liquid bromine [45,46]. In contrast, **L4** is a very electron-deficient phosphine with much weaker electron-donating ability and then the dramatically weakened reductive ability. Consequently, the redox reaction between **L4** and $IrCl_3{\cdot}3H_2O$ in the course of complexation is avoided completely, leading to the availability of trivalence **Ir^{III}-L4**.

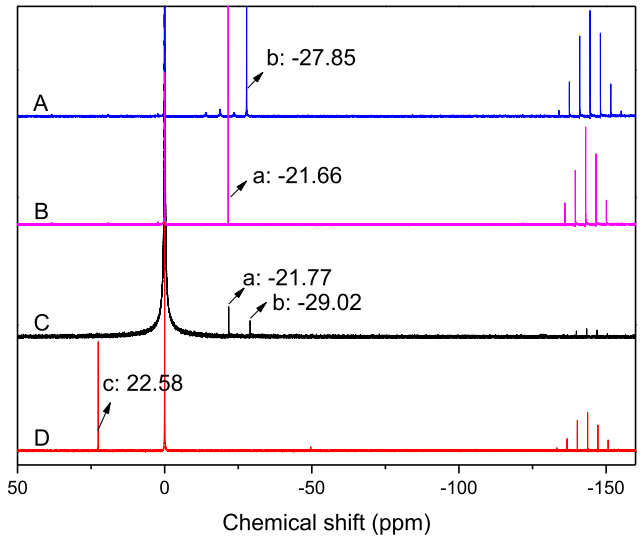
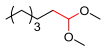
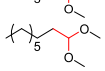
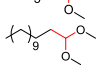
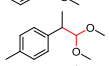
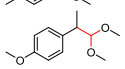
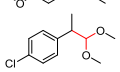
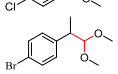
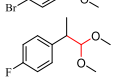
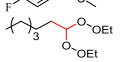
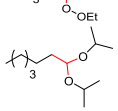
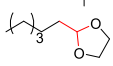


Fig. 2. A: The ^{31}P NMR spectra of **L4** (A), **Ir^{III}-L4** (B), the resultant mixture using **Ir^{III}-L4** as the catalyst (C) and **Ir^{I}-L4** prepared by reacting $[Ir^{I}(COD)Cl]_2$ with **L4** in the presence of CO (D).

In order to prove that Ir(III)-species were not reduced to Ir(I) during the reaction procedures at 110 °C, the obtained reaction mixture by using the as-synthesized **Ir^{III}-L4** as the catalyst was detected by the ^{31}P NMR spectroscopy (500 MHz). The obtained spectra (Fig. 2C) showed that the characteristic peak for **Ir^{III}-L4** was still observed at −21.77 ppm which was consistent to the signal of the fresh sample of **Ir^{III}-L4** (Fig. 2B), whereas the signal at the much lower field (δ = 22.58 ppm) assigned to **Ir^{I}-L4** complex was unobservable completely. In addition, the characteristic peak of the free ligand of **L4** was also present at −29.02 ppm, indicating the partial dissociation of **L4** from **Ir^{III}-L4 t**o make accommodation for the substrate (olefin and CO) insertion.

The scope of tandem hydroformylation-acetalization of olefins with the alcohols catalyzed by **L5**-$IrCl_3{\cdot}3H_2O$ system was explored in Table 3. It was found that, as for the terminal aliphatic olefins, the yields of products decreased with the increase of the carbon chains (Entries 1–3). The internal olefin of 2-octene also gave the high yield of the target acetals (81%) with L/B of 35/65 (Entry 4). Cyclooctene and 2,5-dihydrofuran corresponded to the low yield

Table 3
Generality of **L5**-based $IrCl_3{\cdot}3H_2O$ for tandem hydroformylation-acetalization.[a]

Entry	Olefin	Alcohol	Major product	$Yield_{acetals}$ (%)[b]	L/B[b]
1		MeOH		89	78/22
2		MeOH		84	80/20
3		MeOH		83	77/23
4		MeOH		81	35/65
5		MeOH		62	–
6		MeOH		11	–
7[c]		MeOH		80	31/69
8[c]		MeOH		81	33/67
9[c]		MeOH		81	32/68
10[c]		MeOH		79	31/69
11[c]		MeOH		76	30/70
12[c]		MeOH		73	25/75
13		EtOH		80	80/20
14		*i*-PrOH		78	85/15
15		Ethylene glycol		88	75/25

[a] $IrCl_3{\cdot}3H_2O$ 0.01 mmol (Ir 0.2 mol%), **L5** 0.005 mmol (P/Ir = 1 M ratio), 1-hexene 5.0 mmol, methanol 5 mL, *N*-methyl pyrrolidone (NMP) 2 mL, CO/H_2 (v_{CO}:v_{H2} = 5:1) 4.0 MPa, time 8 h, temperature 110 °C.
[b] Determined by GC and GC–MS; L/B, the ratio of linear acetals to branched acetals.
[c] $IrCl_3{\cdot}3H_2O$ 0.05 mmol (Ir 1 mol%), **L5** 0.025 mmol, 14 h.

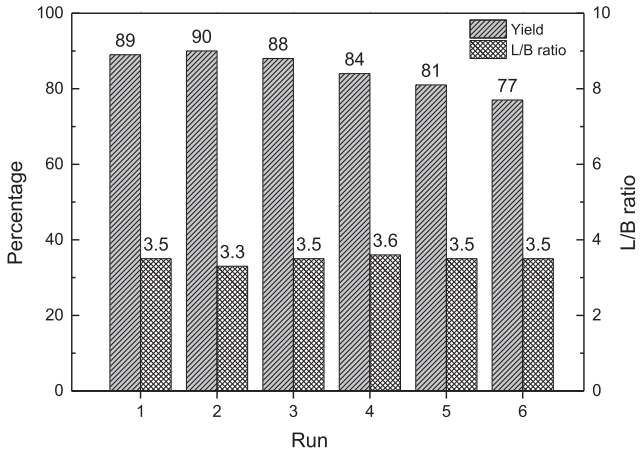


Fig. 3. The recycling uses of the **L6**-$IrCl_3{\cdot}3H_2O$ catalytic system in $[Bmin]PF_6$ for biphasic hydroformylation-acetalization of 1-hexene [$IrCl_3{\cdot}3H_2O$ 0.01 mmol (Ir 0.2 mol%), **L6** 0.005 mmol (P/Ir = 1 M ratio), 1-hexene 5.0 mmol, methanol 5 mL, $[Bmim]PF_6$ 2 mL, CO/H_2 (v_{CO}:v_{H2} = 5:1) 4.0 MPa, time 15 h, temperature 110 °C].

of the acetals due to the bulky steric hindrance (Entries 5 and 6). When styrene and its derivatives were applied to repeat the reactions at the prolonged time of 14 h, the good yields of the corresponding acetals (73–80%) were obtained (Entries 7–12). When EtOH was applied instead of MeOH, the tandem hydroformylation-acetalization of 1-hexene performed smoothly with 80% yield to the acetals (Entry 13). The increased steric hindrance of *i*-PrOH slightly slowed down the reaction rate (Entry 14). Ethylene glycol corresponded to a much higher yield of the acetals (88%) due to the formation of a thermodynamically stable five-membered 1,3-dioxolanyl ring (Entry 15).

In addition, it has been well known that the ionic phosphines which possess the advantages of good stability and high polarity can be applied together with room temperature ionic liquid (RTIL) to immobilize the homogeneous transition metal catalysts for recovery and recycling [10,41,47]. Herein, **L6** and $IrCl_3{\cdot}3H_2O$ were dissolved in the room temperature ionic liquid of $[Bmim]PF_6$ after comparison to that in $[Bmim]BF_4$, $[Bmim]NTf_2$ and $[PEmim]PF_6$ (S. Table 2 in ESI), in order to lock the ionic **L6**-based $IrCl_3{\cdot}3H_2O$ catalyst in the IL phase for the recovery and recycling. It was indicated in Fig. 3, L6-based $IrCl_3{\cdot}3H_2O$ could be recycled 6 runs. The gradual decrease of 1-hexene conversion was mainly due to the physical loss of the catalyst during the transfer process. The precipitation of metal blacks was never observed during the recycling. The ICP-OES analysis revealed that the leaching of Ir and P in the combined organic phase was non-detectable after 6 runs (below the detection limit of <0.1 μg/g). However, the use of $[Bmim]PF_6$ as the solvent led to the biphasic reaction system with mass transfer limitation. So, the reaction time was prolonged to 15 h in comparison to that (8 h) in the homogenous system (Entry 6 of Table 2)."

3. Conclusions

$IrCl_3{\cdot}3H_2O$ with the involvement of the electron-deficient phosphines (**L1**-**L6**) proved to be the efficient bi-functional catalyst to fulfill co-catalysis for one-pot tandem hydroformylation-acetalization, which not only served as a transition metal catalyst responsible for hydroformylation of olefins, but also as an Ir^{III}-Lewis acid catalyst in charge of acetalization of aldehydes. The measurement of $^1J^{31}P–^{77}Se$ indicated that the electron-deficient character of these phosphines were in the ranking of **L2**, **L4**, **L6** > **L1**, **L3**, **L5** > PPh_3. Resultantly, +3 valence state of Ir^{III}-ion could be kept without reduction during the complexation with these phosphines to guarantee the Lewis acidity of Ir^{III}-center, which was verified by the available molecular structure of **Ir^{III}-L4**. It was found that **L5**-based $IrCl_3{\cdot}3H_2O$ exhibited the best performance for this tandem reaction, affording 97% conversion of 1-hexene along with 92% selectivity to the corresponding acetals. In addition, the stable and ionic **L6**-based $IrCl_3{\cdot}3H_2O$ system could be successfully recycled at least 6 times in the IL of $[Bmim]PF_6$.

4. Experimental

4.1. Reagents and analysis

The terminal aliphatic olefins, alcohols, $FeCl_3$ and $[Bmim]PF_6$ were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. The compounds of $[Ir(COD)Cl]_2$, $IrCl_3{\cdot}3H_2O$, and $RhCl_3{\cdot}3H_2O$ were purchased from Shanghai Boka-chem Tech Inc.. Styrene and its derivatives were purchased from Alfa Aesar China. The solvents were distilled and dried before use. The ^1H and ^{31}P NMR spectra were recorded on a Bruker Avance 500 spectroscopy. The ^{31}P NMR spectra were referenced to 85% H_3PO_4 sealed in a capillary tube as an internal standard. CHN-Elemental analyses were obtained using an Elementar Vario EL III instrument. Gas chromatography (GC) was performed on a SHIMADZU-2014 equipped with a DM-Wax capillary column (30 m × 0.25 mm × 0.25 μm). The analyses of GC-Mass (GC–MS) equipped with a DB-Wax capillary column (30 m × 0.25 mm × 0.25 μm) was determined on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector. The amount of Ir and P in the organic phase was quantified by using an inductively coupled plasma optical emission spectrometer (ICP-OES) on an Optima 8300 instrument (PE Corporation).

4.2. Synthesis

The phosphines of **L1**-**L6** were prepared according to the procedures reported by our group previously [41,44,48].

4.2.1. Complex *Ir^{III}-L4*

Under nitrogen atmosphere, **L4** (1.0 mmol) dissolved in 10 mL of dry MeOH was added to the solution containing $IrCl_3{\cdot}3H_2O$ (0.2 mmol) and tetrabutylammonium chloride (Bu_4NCl, 0.17 mmol) in MeOH. The resultant mixture was refluxed for 12 h under vigorous stirring. After cooling to room temperature, the yellow precipitate was collected after washing with methanol and diethyl ether respectively, and then dried under vacuum to give the product of **Ir^{III}-L4** (Yield: 52%). A sample suitable for the single crystal X-ray diffraction analysis was obtained by recrystallization from methanol/ethyl ether. ^1H NMR [δ, ppm, $(CD_3)_2CO$, 298 K]: 8.68 (br, 4H), 8.05 (s, 1H), 7.95 (s, 1H), 7.51(m, 2H), 7.45 (m, 4H), 3.92 (br, 2H), 3.78 (s, 3H), 1.95 (br, 2H), 1.05 (br, 2H), 0.72 (s, 3H). ^{31}P NMR [δ, ppm, $(CD_3)_2CO$, 298 K]: −21.55 (br), −145.08 (PF_6^-, heptet). CHN-Elemental analysis (calculated, %): C 43.09 (42.68), H 4.77 (4.30), N 4.51 (4.98).

4.2.2. Complex *Ir^{I}-L4*

Under nitrogen atmosphere, a solution of $[Ir(COD)Cl]_2$ [dimer of dichloro(1,5-cyclooctadiene)iridium(I), 0.05 mmol] in absolute dichloromethane (10 mL, refluxed with calcium hydride and distilled freshly before use) was stirred vigorously at room temperature for 10 min, and then the atmospheric CO (in a balloon) was introduced into the reaction mixture for 50 min. The obtained mixture was treated with a solution of **L4** (0.05 mmol) in acetonitrile (5 mL) and stirred vigorously for 12 h. Then diethyl ether was added to afford the yellow precipitates, which were collected after drying under vacuum with the yield of 22%. ^1H NMR (500 MHz, δ,

ppm, CD_3CN): 8.03 (m, 8H), 7.86 (m, 4H), 7.68 (m, 8H), 7.58 (m, 4H), 3.80 (t, 4H), 3.57 (s, 6H), 1.51 (m, 4H), 0.96 (m, 4H), 0.72 (t, 6H). ^{31}P NMR (202 MHz, δ, ppm, CD_3CN): 22.58 (s, PPh_2), −143.72 (PF_6^-, heptet). CHN-Elemental analysis (calculated, %): C 42.23 (41.30), H 4.36 (4.06), N 4.32 (4.70).

4.3. X-ray crystallography

The intensity data for **Ir^{III}-L4** was collected on a Bruker SMART APEX 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 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 4.

4.4. General procedures for tandem hydroformylation-acetalization of olefins

The following general procedure was considered for 1-hexene adopted as a model substrate. A mixture of *N*-methyl pyrrolidone (NMP) 2 mL (solvent), $IrCl_3{\cdot}3H_2O$ (0.01 mmol Ir 0.2 mol %), the phosphine (P/Ir = 1 M ratio), 1-hexene (or the other olefin, 5.0 mmol) and MeOH (5 mL, or other alcohol) were added sequentially in a 50 mL sealed Teflon-lined stainless steel autoclave. The autoclave was purged with H_2 (0.5 MPa) for three times, and then pressured by H_2 (0.7 MPa) and CO (3.3 MPa) respectively. The reaction mixture was stirred vigorously at the appointed temperature for some time. Upon completion, the autoclave was cooled down to room temperature and slowly depressurized. The solution was analyzed by GC to determine the conversion (*n*-dodecane as internal standard) and the selectivity (normalization method). And the products were further identified by GC-Mass analysis.

As for the catalyst recycling experiments, $IrCl_3{\cdot}3H_2O$ (0.01 mmol Ir 0.2 mol %), **L6** (0.005 mmol, P/Ir = 1 M ratio), 1-hexene (5.0 mmol), MeOH (5 mL), and $[Bmim]PF_6$ (2 mL) were sequentially added in a 50 mL sealed Teflon-lined stainless steel autoclave which was purged with H_2 (0.5 MPa) for three times, and then pressured by H_2 (0.7 MPa) and CO (3.3 MPa) respectively. The mixture was stirred at 110 °C for 15 h in the sealed autoclave.

Table 4
The crystal data and structure refinement for **Ir^{III}-L4.**

	Ir^{III}-L4
Empirical formula	$C_{40}H_{48}Cl_4Ir_1N_4P_2{\cdot}(P_1F_6){\cdot}2(C_3H_6O_1)$
Formula weight	1241.88
Crystal system	Monoclinic
Space group	*C 2/c*
a (Å)	25.2852(12)
b (Å)	9.7142(5)
c (Å)	22.8565(11)
α (°)	90
β (°)	104.2900(10)
γ (°)	90
V (Å^3)	5440.4(5)
Z	4
d_{calc} (g cm^{-3})	1.516
μ (Mo-K_α) (mm^{-1})	2.789
T (K)	296(2)
λ (A)	0.71073
Total reflections	30,517
Unique reflections (R_{int})	4769(0.0408)
R_1 [I > 2σ(*I*)]	0.0323
wR_2 (all data)	0.0846
F(0 0 0)	2496.0
Goodness-of-fit on F^2	1.072

Upon completion, the reaction solution was added with *n*-hexane (20 mL). Then the upper organic phase was decanted from the obtained biphasic reaction mixture, and the remaining IL phase was washed with *n*-hexane (3 mL × 3) to completely extract the reactants and products. The combined organic phase was analyzed by GC and ICP-OES. The IL phase containing the catalyst after the dryness under vacuum was reused for the next run.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.04.004.

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