Green Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Y. Li, P. Wang, H. Liu, Y. Lu, X. zhao and Y. Liu, *Green Chem.*, 2015, DOI: 10.1039/C5GC02127H.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

View Article Online
DOI: 10.1039/C5GC02127H

Journal Name

ARTICLE

Co-catalysis of a bi-functional ligand containing phosphine and Lewis acidic phosphonium for hydroformylation-acetalization of olefins

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yong-Qi Li[a], Peng Wang[a], Huan Liu[a], Yong Lu[a], Xiao-Li Zhao[a] and Ye Liu[a]†

A novel ionic bi-functional ligand of **L2** containing the phosphine and the Lewis acidic phosphonium with I^- as the counter-anion was prepared and fully characterized. The molecular structure indicated that the bi-functionalities in **L2** were well retained without incompatibility problem for the quenching of the acidity of phosphonium cation by the Lewis basic phosphine fragment or the anionic I^- when the incorporated phosphine fragment and the Lewis acidic phosphonium were strictly located in the confined *cis*-positions. The co-catalysis over **L2**-Rh(acac)$(CO)_2$ in the ways of synergetic catalysis and sequential catalysis was successfully fulfilled for one-pot hydroformylation-acetalization, which proved not to be the result of the simple mixture of the mono-phosphine (**L4**) and the phosphonium salt (**L4'**). In **L2**, the phosphonium not only acted as a Lewis acid organocatalyst to drive the sequential acetalization of aldehydes, but also contributed to the synergetic catalysis for the preceding hydroformylation through stabilizing the Rh-acyl intermediate with the phosphine cooperatively. **L2**-Rh(acac)$(CO)_2$ system was also generally applied to hydroformylation-acetalization of a wide range of olefins in the different alcohols. Advantageously, as an ionic phosphonium-based ligand, **L2** could be recycled for 7 runs with Rh(acac)$(CO)_2$ together in RTIL of [Bmim]BF_4 without obvious activity loss or metal leaching.

Introduction

Rh-catalyzed hydroformylation is one of the most important methods for the production of aldehydes from olefins. In practice, aldehydes are needed to be further transformed into alcohols, acetals, esters, amines, and many more[1]. Based on the principles of atom economy and low energy consumption in green chemistry, hydroformylation of olefins are required to be combined with other organic reactions (such as hydrogenation, Aldol reaction, acetalization, Mannich reaction etc.) to form tandem reaction sequences that can be achieved under hydroformylation conditions[2,3]. Hydroformylation followed by acetalization in the presence of alcohols is an important one-pot process for the formation of acetals, which can be used to protect sensitive aldehyde group against side reactions or as ingredients in fragrances, domestics, and detergents[3,4]. The formation of acetals under hydroformylation conditions can be promoted by the presence of the auxiliaries such as zeolites support that can provide the acidic sites[2a,5]. The tandem hydroformylation-acetalization is usually regarded as a sequential catalysis, which means that phosphine-ligated Rh-catalyst activate the substrates of olefins producing aldehydes, the latter as the intermediates are sequentially activated by Lewis acid or Brønsted acid catalysts to produce acetals[2,3,6-9].

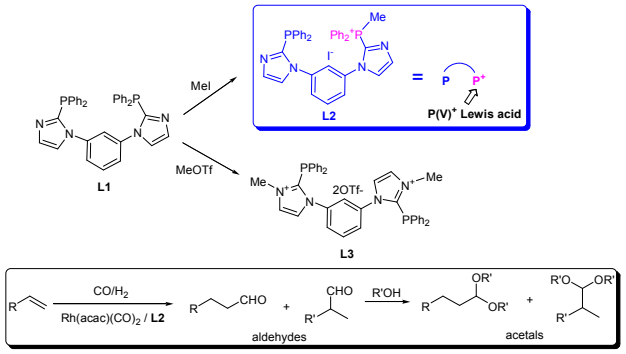
Co-catalysis in combination of transition metal catalysis with organocatalysis in the different ways of synergetic catalysis, cooperative catalysis, and sequential catalysis has been emerged as a powerful strategy to promote organic transformations that cannot be achieved by each individual one independently[10d]. Various organocatalysts such as Lewis/Brønsted acid catalysts, amine/enamine catalysts, phase transfer catalysts and N-heterocyclic carbene catalysts have been exploited in physical combination with transition metal catalysts[2,10]. In this field, bi-functional ligands in compatible combination of phosphines with organocatalysts by intramolecular stable chemical bonds have unique advantages because of the inherent coordination ability of phosphines to transition metals (which corresponds to transition metal catalysis) and the synergetic effect coming from the intramolecular organocatalysts[11-14].

In practice, many examples have proved that phosphonium [$P(V)^+$] cations are typical Lewis acid organocatalysts[15] which can catalyze many reactions such as isomerization of olefins, cationic polymerization, and hydrosilation of olefins and acetylene without involvement of any metal[16], as well to exhibit activities towards C=O bond activation, such as in cyanosilylation of ketones[17], Baylis-Hillman reaction[18], and Aldol and Micheal reactions of carbonyl compounds[19].

[a] Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, P.R. China.
† Correspondence author. Email: yliu@chem.ecnu.edu.cn

View Article Online
DOI: 10.1039/C5GC02127H

Highlighted by the significant role of phosphines [P(III)] to modulate the efficiency of Rh-catalyzed hydroformylation, as well as the character of phosphoniums [$P(V)^+$] as the Lewis acidic organocatalysts to activate C=O bond, it was believed that co-catalysis over bi-functional ligands in combination of phosphines with Lewis acidic phosphoniums would be a promising method for CO-participated hydroformylation and the tandem acetalization if the elegant strategy is applied to avoid incompatibility problem for the quenching of the Lewis acidity of the phosphoniums by the Lewis bases of phosphines. Hence, an ionic bi-functional ligand of **L2** was synthesized herein for the first time, in which the incorporated phosphine fragment and phosphonium cation were linked by the stable chemical bonds without interference. For comparison, the phosphonium-free phosphines of **L1**, **L3** and **L4** were prepared in parallel according to our previously reported method[20,21]. The present protocol provides a novel methodology for co-catalysis of hydrformylation-acetalization in the ways of synergetic catalysis and sequential catalysis, which means that, in bi-functional ligand **L2**, the incorporated Lewis acidic phosphonium contributes to the synergetic catalysis for hydroformylation through stabilizing the Rh-acyl intermediate with the phosphine cooperatively, as well as to sequential catalysis for acetalization of aldehydes.



Scheme 1 A bi-functional ligand of **L2** in combination of phosphine with phosphonium for co-catalysis of hydroformylation-acetalization

Results and discussion

It was found that the quaternization of **L1** by MeI could selectively afford **L2** due to the compatibility of the soft electrophile of MeI to the soft nucleophile of phosphine fragment[22], whereas the quaternization of **L1** by hard electrophile of MeOTf could selectively afford **L3**[21]. And **L4** was prepared in parallel according to the procedures reported by us before[21].

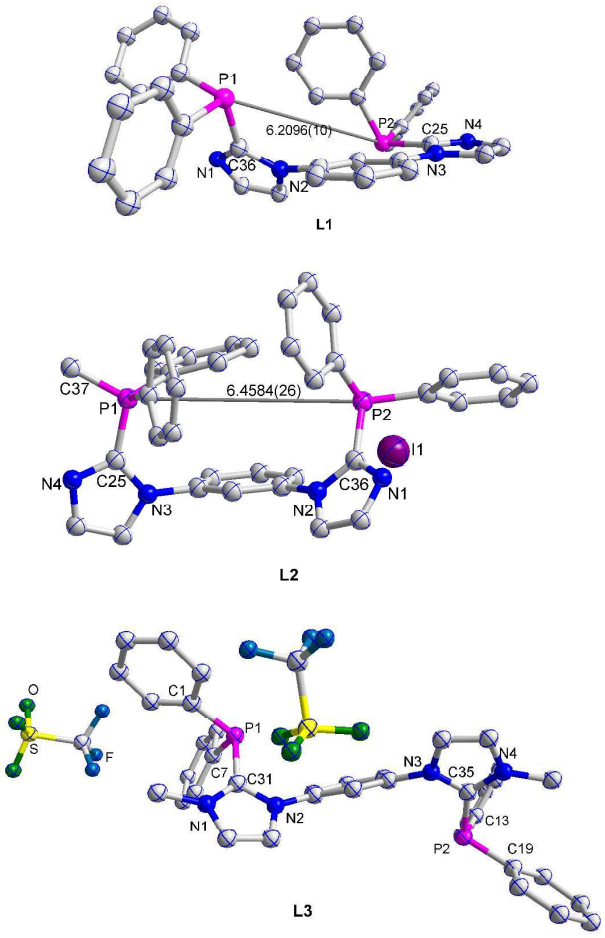


Fig. 1 The single crystal structures of **L1-L3** (The hydrogen atoms are omitted for clarity)

The molecular structures of **L1**[21], **L2** and **L3**[21] determined by the single crystals X-ray diffraction are depicted in Fig. 1. The environment of the P(III)-atoms is close to tetrahedral structures and shows no anomalies. In **L2**, the phosphine-fragment and phosphonium-fragment are properly located in *cis*-position relative to 1,3-diimidazolylphenyl backbone, whereas in **L2** the two phosphine-fragments are located in distortioned *cis*-position with θ of 4.3 ° between phenyl-planar and imidazolyl-planar, and in **L3** the two phosphine-fragments are reversely located in *trans*-position due to the repulsive interaction of the two positive-charged imidazolium rings. Although the P(III)-atom in **L2** is projecting inward towards the $P(V)^+$-atom, their distance [P(2)-P(1): 6.4584(26) Å] is significantly longer than the sum of the van der Waals radii of P-atoms (3.80~4.44 Å), indicating the negligible intramolecular acid-base pair interaction between the Lewis basic phosphine-fragment and the Lewis acidic phosphonium due to their separation from each other by a bulky and rigid 1,3-diimidazolylphenyl backbone. On the other hand, the counter-anion of I^- with relatively large atom radii is located far away from phosphonium site, further indicating the negligible acid-

View Article Online
DOI: 10.1039/C5GC02127H

base pair interaction between $P(V)^+$ and I^-. This structural information demonstrates that our strategy to develop the bi-functional ligand of **L2** in combination of phosphine with Lewis Lewis acidic phosphonium is successful without incompatibility problem for the quenching of the acidity of the phosphonium by the Lewis basic phosphine fragment or the anionic I^-. It was noted that in **L2** the bond distances in $P(V)^+$-C linkages (1.770~1.789 Å) are universally shorter than those of P(III)-C ones, indicating the improved stability of **L2** tailed with phosphonium cation. Consistently, the ^{31}P NMR spectra of **L2** show two types of resonances at 11.7 (singlet) and -28.5 (singlet) ppm, which are attributed to the phosphonium (-P^+Ph_2Me) and phosphine-fragment (-PPh_2) respectively.

Table 1 The selected bond distances, bond angles, θ, and ^{31}P NMR signals for **L1-L3**

Ligand	Bond distance/Å		^{31}P NMR /ppm
	C_{imi}-P	C_{Ph}-P	
L1[21]	1.826(3)	1.834(3), 1.830(3)	−22.4
	1.837(2)	1.835(3), 1.838(3)	
L2	1.827(6)	1.820(6), 1.838(6)	-28.5 (-*P*Ph_2),
	1.770(6) (P^+)	1.774 (6) (P^+), 1.784(6) (P^+),	11.7 (-*P*$^+Ph_2Me$)
		1.789(6) (P^+)	
L3[21]	1.829(3)	1.821(4), 1.829(3)	−20.6
	1.836(3)	1.824(3), 1.824(3)	

[a] θ is the interplanar dihedral angle.

It is believed that the involved positive-charge with strong electron-withdrawing effect would dramatically influence the coordination ability of the peripheral phosphine fragments. Hence, the π-acceptor ability of **L1-L4** was evaluated by measuring the magnitude of $^1J_{P\text{-}Se}$ in the ^{77}Se isotopomer of the corresponding phosphine-selenide in ^{31}P NMR spectra (202 MHz) according to the method reported by Taylor et al., because an increase of $^1J_{P\text{-}Se}$ indicates an increase in the character of π-acceptor ability (i.e., less σ-donor ability)[23]. In order to measure $^1J_{P\text{-}Se}$, the selenide of the phosphine was prepared by reacting the elemental selenium (with 7.63% ^{77}Se) with the corresponding phosphine in deuterated solvent under the appointed conditions, which was then analyzed by a Bruker Avance 500 spectrometer. As shown in Fig. 2, **L3** is the strongest π-acceptor with $^1J_{P\text{-}Se}$ of 782 Hz due to the most intensive electron-withdrawing effect of the positive-charged imidazoliums on the neighbored P(III)-atoms, whereas **L1**, **L2** and **L4** possess less and similar π-donor ability with $^1J_{P\text{-}Se}$ of ~750 Hz which are much higher than that of PPh_3 ($^1J_{P\text{-}Se}$ =729 Hz).

The one-pot hydroformylation-acetalization of 1-octene in MeOH was selected as a model reaction to investigate the co-catalysis over **L2** in comparison to those over the phosphine ligands of **L1**, **L3**, and **L4** (Table 2). In Table 2, Conv. (conversion of 1-octene) and S_{oxo} [selectivity to the total oxo-products including nonanals and dimethoxynonanes (acetals)] were defined to evaluate the hydroformylation efficiency of the Rh-L catalytic system, while $P_{acetals}$ (percentage of acetals in the total oxo-products) was defined to evaluate the acetalization efficiency of the acidic phosphonium site in **L2**.

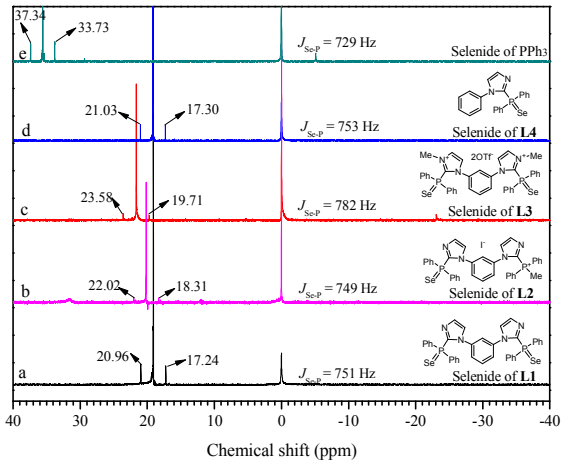
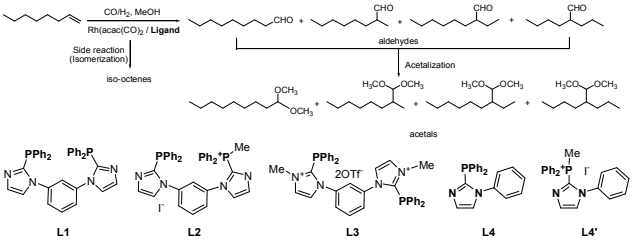


Fig. 2 ^{31}P NMR spectra (202 MHz) of the selenides of **L1-L4**: a) reacting elemental selenium with **L1** in $CDCl_3$ at 70 °C for 10 h; b) reacting elemental selenium with **L2** in $CDCl_3$ at 70 °C for 10 h; c) reacting elemental selenium with **L3** in DMSO-d_6 at 70 °C for 10 h: d) reacting elemental selenium with **L4** in $CDCl_3$ at 70 °C for 10 h; e) reacting elemental selenium with PPh_3 in $CDCl_3$ at 70 °C for 10 h.

Table 2 The homogeneous hydroformylation-acetalization of 1-octene with $Rh(acac)(CO)_2$ as the catalyst precursor in the presence of different ligands [a]



Entry	Additive	Conv. (%)[b]	S_{oxo} (%)[b,c]	$P_{acetals}$ (%)[b,c]	$S_{iso\text{-}octenes}$ (%)[b,c]	L/B[d]	TON_{oxo}[e]
1	--	41	83	--	17	2.0	680
2	**L1**	64	88	2	12	2.1	1130
3	**L2**	91	94	62	6	1.9	1710
4	**L3**	86	90	28	10	2.4	1550
5	**L4**	78	89	2	11	1.9	1400
6	PPh_3	44	89	1	11	1.7	780
7[f]	**L4/L4'**	53	86	3	14	2.1	910
8[g]	**L2**/TBAF	88	90	2	10	1.9	1570

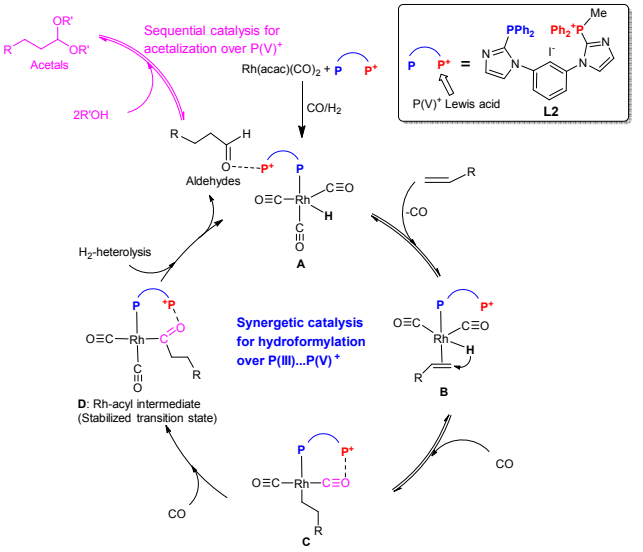
[a] $Rh(acac)(CO)_2$ 0.0025 mmol, 1-octene 5.0 mmol (S/C=2000, Rh 0.05 mol%), P/Rh=6:1 molar ratio (**L1** or **L3** 0.0075 mmol; **L2** or **L4** 0.015 mmol), CO/H_2 (1:1) 4.0 MPa, MeOH 3 mL, 80 °C, reaction time 6 h; [b] Determined by GC; [c] S_{oxo}=(aldehydes+acetals)/(aldehydes+acetals+iso-octenes), $P_{acetals}$ =acetals/(aldehydes+acetals), percentage of acetals in the total oxo-products; $S_{iso\text{-}octenes}$=iso-octenes/(aldehydes+acetals+iso-octenes); [d] L/B, the ratio of linear nonanals and acetals to branched nonanals and acetals; [e] TON_{oxo} (turnover number)=mol of oxo products·(mol of Rh)$^{-1}$; [f] 0.015 mmol of **L4** and 0.015 of mmol **L4'** were mixed mechanically; [g] 0.015 mmol of TBAF was added additionally.

Under the mild reaction conditions (P/Rh=6, syngas 4.0 MPa, 6 h, 80 °C), the catalyst precursor of $Rh(acac)(CO)_2$ itself

View Article Online
DOI: 10.1039/C5GC02127H

exhibited the poor activity to hydroformylation with 41 % conversion of 1-octene and 83% selectivity to the oxo-products without formation of any acetals (Entry 1). Comparatively, Rh-**L2** system exhibited the best activity towards hydroformylation with TON of 1710 for oxo-products, along with the good acetalization efficiency (62%, Entry 3). In comparison, under the same conditions, Rh-**L1**, Rh-**L3**, Rh-**L4** and Rh-PPh_3 not only resulted in the poor catalytic activities for the acetalization due to the lack of the Lewis acidic phosphonium site, but also unexpectedly corresponded to the relatively lower hydroformylation efficiency (Entries 2, 4-6). Although the π-acceptor ligands involved Rh-catalysts have been reported to be highly active for hydroformylation of olefins even like internal or branched ones[24-28], it was noted herein that **L3** ($^1J_{P\text{-}Se}$=782 Hz) possessing the stronger π-acceptor ability than **L2** ($^1J_{P\text{-}Se}$=751 Hz) contrarily led to the lower hydroformylation efficiency (Entry 3 vs 4). As for **L1** which possessed the similar π-acceptor ability to **L2** for the incorporated phosphine fragments ($^1J_{P\text{-}Se}$~750 Hz), the tight chelation of **L1** as a diphosphine ligand to Rh-center (not facilitating the ligand dissociation to provide the unsaturation site for the substrate insertion) and the lack of Lewis acidic phosphonium site reasonably accounted for the activity drop over **L1** (Entry 2, TON_{oxo}=1130). While **L4**, which could be regarded as the separate phosphine fragment of **L2** with the similar π-acceptor ability ($^1J_{P\text{-}Se}$=753 Hz for **L4**; $^1J_{P\text{-}Se}$=749 Hz for **L2**), was used to repeat the reaction, the efficiency neither for hydroformylation nor acetalization could reach the level over **L2** (Entry 5). In contrast to **L1**-**L4**, the traditional PPh_3 with the strongest σ-donor ability ($^1J_{P\text{-}Se}$=729 Hz) led to the poorest activity in terms of hydroformylation and acetalization (Entry 6, TON_{oxo}= 784). In addition, when **L2** was replace by the mixture of **L4** and **L4'**, which could be regarded as the mechanical adduct of the independent phosphine and phosphonium units in **L2**, the efficiency for hydroformylation-acetalization over **L4/L4'** was found to be decreased dramatically only with 53% conversion of 1-octene and very poor $P_{acetals}$ of 3% (Entry 7). All these results indicated that the combination of the phosphine fragment and phosphonium by chemical bonds in **L2** was not the result of the simple mixture of the mono-phosphine of **L4** and the phosphonium salt of **L4'**. The incorporated phosphonium not only contributed to the sequential acetalization of nonanals, but also synergetically promoted the hydroformylation through working together with the *cis*-positioned phosphine fragment to cooperatively stabilize the Rh-acyl intermediate (**D**) by forming the bonding interaction between $P(V)^+$-atom and O atom (in C=O), which facilitated the expedition of the rate controlling step of H_2-heterolysis from **D** to **A** as proposed in Scheme 2.

It was obvious that in **L2**, there is no incompatibility problem for quenching the acidity of phosphonium site by the Lewis basic phosphine fragment when they are strictly located in the proper *cis*-positions as shown in Fig. 1, whereas in the mechanical mixture of **L4** and **L4'**, the individual properties of the phosphine fragment in **L4** and the phosphonium site in **L4'** could be quenched to some extent through the acid-base pair interaction because of their free mobility. Consequently, the bi-functionalities of **L2** in combination of phosphine and Lewis acidic phosphonium were retained intact to fulfil the synergetic catalysis and sequential catalysis for hydroformylation-acetalization. On the other hand, the remote location of I^- counter-anion to the phosphonium cation in **L2** indeed had no influence on the acidity of phosphonium and then the performance of **L2**. In addition, the use of TABI (tetrabutylammonium iodide) with **L1**, **L3**, or **L4** also confirmed that the involved I^- had no negative effect on the reactions (See the data in S. Table 1 provided in ESI) Anyway, F^- could badly quench the acidity of phosphonium due to the unique nature of fluorophilicity for phosphoniums[29-31]. Hence, when **L2** was encountered with F^- in TABF, the efficiency for acetalization as well as for hydroformylation was both decreased ($P_{acetasl}$=2%), (Entry 8, TON_{oxo}=1570).



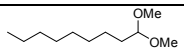
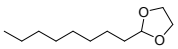
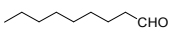
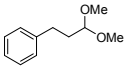
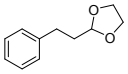
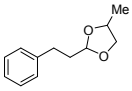
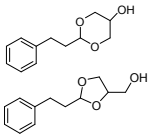
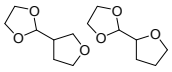
Scheme 2 Co-catalysis of bi-functional ligand of **L2** containing phosphine and Lewis acidic phosphonium [$P(V)^+$] for hydroformylation-acetalization

The generality of **L2**-Rh(acac)$(CO)_2$ as the catalyst for hydroformylation-acetalization in different alcohols was examined on different olefins (Table 3). Under the higher reaction temperature of 120 °C, the system of **L2**-Rh(acac)$(CO)_2$ universally exhibited excellent activities towards hydrofomylation of different olefins and good to excellent performance for acetalization. The applied alcohols had the obvious influence on the reaction rate of acetalization. Glycol indeed gave more rise to acetalization than MeOH due to the formation of thermodynamically stable five-member 1,3-dioxolanyl ring (Entry 2 vs 1). However, the acetalization of nonanals with *t*-BuOH was completely inhibited along with the decreased hydroformylation efficiency due to bulky steric hindrance and the possible solvent effect of *t*-BuOH (Entry 3 vs 1). The repeat of the reaction with styrene instead of 1-octene also produced the desired oxo-products with the high yields of 95~98%, in which acetals were in percentage of 45-89% depending on the structures of alcohols (Entries 4-7). It was noted when styrene was used as the substrate, the

View Article Online
DOI: 10.1039/C5GC02127H

regioselectivity to the branched oxo-products was more favoured due to the formation of a stable benzylic Rh-species induced by the η^2-electron donation from the benzene ring[32,33]. However, the more steric hindrance of propane-1,2-diol in comparison to that glycol reasonably resulted in the sluggish reaction rate for acetalization of phenylpropanal and then the low yields of the corresponding acetals (Entry 6 vs 5). When glycerol was used, the higher $P_{acetals}$ of 89% was obtained because of the predominant formation of the thermodynamically favoured six-member-ring dioxolane [75%; See ESI for the ^{1}H NMR analysis of the mixed acetalized products of 2-phenethyl-1,3-dioxan-5-ol and (2-phenethyl-1,3-dioxolan-4-yl)methanol] as another driving force for acetlization (Entry 7). When the cycloolefin of 2,5-dihydrofuran was applied with glycol, the excellent hydroformylation was performed with 98% yield of oxo-products, in which only 42% was converted to the acetalized products of 2-(tetrahydrofuran-2-yl)-1,3-dioxolane and 2-(tetrahydrofuran-3-yl)-1,3-dioxolane (Entry 8). Rationally, since the electron-richer tetrahydrofuranyl ring rendered the carbonyl group (C=O) less electrophilic, the nucleophilic attack of glycol to C-atom of C=O group was to be badly suppressed, leading to the decreased yields of acetals in comparison to the acetalization of phenylpropanal with glycol ($P_{acetals}$ = 42 %, Entry 8 vs 5). As for the hydroformylation-acetalization of cyclohexene with glycol, the sole acetalized product of 2-cyclohexyl-1,3-dioxolane was obtained with the highest acetalization efficiency (P_{acetal} = 96%) but the relatively low conversion of cyclohexene (Entry 9).

Table 3 Generality of Rh(acac)$(CO)_2$-**L2** for hydroformylation-acetalization[a]

Entry	Olefin	Alcohol	Linear acetal	Conv. (%) [b]	S_{oxo} (%) [b,c]	$P_{acetals}$ (%) [b,c]	L/B [d]	TON_{oxo}
1	1-Octene	MeOH		97	98	86	1.9	1900
2	1-Octene	Glycol		96	98	94	1.1	1880
3	1-Octene	*t*-BuOH		82	80	0	2.2	1310
4	Styrene	MeOH		99	99	88	0.2	1960
5	Styrene	Glycol		98	99	83	0.3	1940
6	Styrene	Propane-1,2-diol		98	99	45	0.1	1940
7[e]	Styrene	Glycerol		96	99	89	0.2	1900
8[f]		Glycol		99	99	42	--	1960
9	Cyclohexene	Glycol	 2-cyclohexyl-1,3-dioxolane	62	99	96		1228

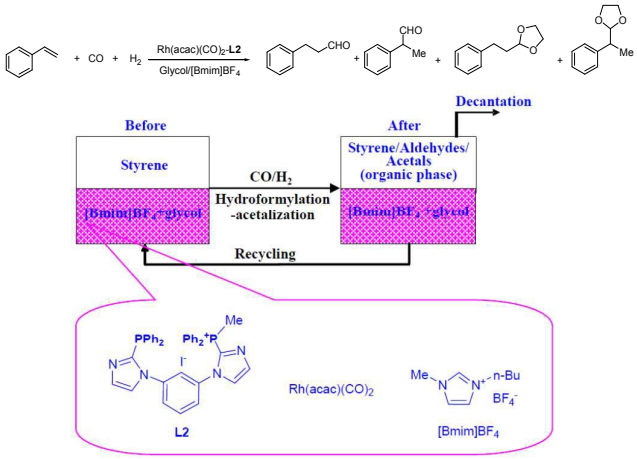
[a] Rh(acac)$(CO)_2$ 0.0025 mmol, olefin 5.0 mmol (S/C=2000), **L2** 0.015 mmol (P/Rh=6:1), CO/H_2 (1:1) 4.0 MPa, temperature 120 °C, alcohol 3 mL, reaction time 2 h; [b] Determined by GC and GC-Mass; [c] S_{oxo}=(aldyhydes+acetals)/(aldyhydes+acetals+*iso*-olefins); $P_{acetals}$=acetals/(aldehydes+acetals); [d] L/B, the ratio of linear aldehydes and acetals to branched aldehydes and acetals; [e] The mixed acetalized products of 2-phenethyl-1,3-dioxan-5-ol and (2-phenethyl-1,3-dioxolan-4-yl)methanol were isolated for ^{1}H NMR analysis (See SEI); [f] The ratio of tetrahydrofuran-3-carbaldehyde and 2-(tetrahydrofuran-3-yl)-1,3-dioxolane to tetrahydrofuran-2-carbaldehyde and 2-(tetrahydrofuran-2-yl)-1,3-dioxolane is 2.5.

Moreover, as the ionic ligand, **L2** could be used with a room temperature ionic liquid (RTIL) solvent as the efficient alternative to immobilize the transition metal catalysts for recovery and recycling[19,34,35]. To demonstrate that issue, the recovery and recycling experiments were investigated over Rh(acac)$(CO)_2$-**L2** system dissolved in [Bmim]BF_4 (1-butyl-3-methylimidazolium tetrafloruoborate) and glycol for hydroforformylation-acetalization. Due to the mass transfer limitation in the biphasic reaction system by using [Bmim]BF_4 as the solvent, the reaction time was prolonged to 7 h. As shown in Table 4, Rh(acac)$(CO)_2$-**L2** could be recycled at least 7 runs along with the slightly decreased conversion of styrene and the unchanged selectivity to the aldehydes (TONs decreased from 1960 to 1700). After the seven-run recycling uses, the total loss of Rh(acac)$(CO)_2$-**L2** system in the combined organic phase was 0.3% for Rh and 0.1% for P (ICP-AES analysis), which revealed that the catalyst could be locked in [Bmim]BF_4 medium with very slight leaching into the organic phase especially for the phosphine of **L2** with the ionic compatibility. Hence, the observed decrease for the

View Article Online
DOI: 10.1039/C5GC02127H

conversion of styrene was mainly attributed to the mechanical loss of Rh-P catalyst during the recycling treatment. However, the reason for the gradually increased L/B value was not clear at present stage.

Table 4 Recycling of $Rh(acac)(CO)_2$-**L2** system in $[Bmim]BF_4$ for biphasic hydroformylation-acetalization of styrene with glycol[a]



Run	Conv. (%)[b]	S_{oxo} (%)[b,c]	$P_{acetals}$ (%)[b,c]	L/B[d]	TON_{oxo}
1	99	99	97	0.2	1960
2[e]	99	99	98	0.3	1940
3	95	99	98	0.3	1880
4	91	99	98	0.4	1800
5	88	99	98	0.5	1740
6	87	99	98	0.6	1720
7	86	99	98	0.7	1700

[a] $Rh(acac)(CO)_2$ 0.0025 mmol, styrene 5.0 mmol (S/C=2000), **L2** 0.015 mmol (P/Rh=6:1), CO/H_2 (1:1) 4.0 MPa, temperature 100 °C, glycol 3 mL, $[Bmim]BF_4$ 3 mL, reaction time 7 h; [b] Determined by GC; S_{oxo}=(aldyhydes+acetals)/(aldyhydes+acetals+*iso*-olefins). $P_{acetals}$=acetals/(aldehydes+acetals); [d] L/B, the ratio of linear aldehydes and acetals to branched aldehydes and acetals; [e] 1.5 mL glycol was added additionally.

Experimental

Reagents and analysis

The chemical reagents were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd. and Alfa Aesar China, and used as received. FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrometer. The ^1H and ^{31}P NMR spectra for the analyses of the common compounds were recorded on a Bruker Avance 400 spectrometer. The ^{31}P NMR spectra for the analyses of the phosphine-selenides (as shown in Fig. 2) were recorded on a Bruker Avance 500 spectrometer. The ^{31}P NMR spectra were referenced to 85% H_3PO_4 sealed in a capillary tube as an internal standard. The amount of Rh in the sample was quantified using an inductive coupled plasma atomic emission spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). Gas chromatography (GC) was performed on a SHIMADZU-2014 equipped with a DM-1 capillary column (30 m × 0.25 mm × 0.25 μm). GC-mass spectrometry (GC-MS) was recorded on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector. Elemental analyses for CHN were obtained using an Elementar Vario EL III instrument.

Synthesis of L1-L4'

Firstly the diphosphine of **L1** [1,3-bis(2'-diphenylphosphino-3'-imidazole)benzene] was prepared according to the reported methods[20,21]. Then **L1** was quaternized by MeI at one P-position to selectively afford ionic **L2** according to the preparation procedures as described as follows.

At room temperature, the solution of **L1** (1.27 g, 2.2 mmol) in 20 ml of absolute toluene (refluxed with sodium and distilled freshly before use) was treated with iodomethane (0.31 g, 2.2 mmol). The obtained mixture solution was stirred vigorously for 24 h and the white precipitates were formed gradually. The precipitates were collected after filtration and then washed with diethyl ether to give a white solid as the product of **L2** (0.8 g, yield 50 %). ^1H NMR (δ, ppm, $CDCl_3$): 7.78-7.34 (m, 27H, Ar), 7.13 (s, 1H, NCC*H*CN), 2.93-2.90 (d, 3H, $P(V)^+$-C*H*$_3$). ^{31}P NMR (*δ*, ppm, $CDCl_3$): −28.5 (s, *P*Ph_2), 11.7 (Me*P*$^+Ph_2$). CHN-elemental analysis (%, Found): C 61.49, H 4.58, N 7.56 (Calcd: C 61.67, H 4.31, N 7.78). ESI-MS (M^+/z): 593 ($[C_{37}H_{31}N_4P_2]^+$=593).

The quaternization of **L1** by MeOTf (methyl-trifluoromethane sulfonate) at N-positions of two imidazolyl rings selectively could afford the ionic **L3** according to the method reported by us prevoulsy[21]. And **L4** was also prepared in parallel for comparison[21]. On the basis of the preparation of **L4**, its corresponding phosphonium salt of **L4'** was prepared as follows.

The solution of **L4** (0.3 g, 0.9 mmol) in 10 mL of absolute toluene (refluxed with sodium and distilled freshly before use) was treated with iodomethane (0.14 g, 1 mmol). The obtained solution was stirred vigorously at room temperature for 24 h. Then the formed precipitates were collected after filtration and washed with diethyl ether to give a white solid as the product of **L4'** (0.24 g, yield 55 %). ^1H NMR (δ, ppm, $CDCl_3$): 7.79-7.71 (m, 6H, Ar), 7.65-7.62 (m, 5H, Ar), 7.75-7.54 (d, 1H, PhNCNC*H*), 7.43-7.16 (m, 5H, Ar), 2.85-2.82 (d, 3H, $P(V)^+$-C*H*$_3$). ^{31}P NMR (*δ*, ppm, $CDCl_3$): 11.92 (Me*P*$^+Ph_2$).

X-Ray crystallography

Intensity data were collected at 173 K for **L2** on a Bruker SMARTAPEX II diffractometer using graphite monochromated Mo-Kα 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 of **L2** are given in Table 5. The crystal data and refinement details of **L1** and **L3** could be found in Ref. 21.

General procedures for hydroformylation-acetalization of olefin in alcohols

View Article Online
DOI: 10.1039/C5GC02127H

In a typical experiment, the commercial complex of $Rh(acac)(CO)_2$ (0.0025 mmol) and the pure **L2** (0.015 mmol) were added into 1-octene (5 mmol, or the other olefin) and methanol (3 mL, or the other alcohol) sequentially. The obtained mixture in a 50 mL sealed Teflon-lined stainless steel autoclave was pressured by syngas to 4.0 MPa. The reaction mixture was stirred vigorously at the appointed temperature for some time. Upon completion, the autoclave was cooled down to room temperature and depressurized carefully. The reaction solution was analysed by GC to determine the conversions (n-dodecane as internal standard) and the selectivities (normalization method), and the products were further identified by GC-Mass.

When $[Bmim]BF_4$ was used as the solvent for the biphasic hydroformylation-acetalization, in which styrene (5 mmol), glycol (3 mL), $Rh(acac)(CO)_2$ (0.0025 mmol), **L2** (0.015 mmol) were mixed sequentially. Upon reaction, the upper organic phase was decanted from the obtained biphasic reaction mixture, and the left IL phase was washed with n-hexane (3 mL $\times$ 3) to completely extract the reactants and products out of the IL phase. The combined organic phase was analyzed by GC and ICP-AES. The left IL phase was directly used without further treatment for next run (if required glycol was added additionally).

Table 5 Crystal data and structure refinement for **L2**

	L2·CH_2Cl_2
Empirical formula	$[C_{37}H_{31}N_4P_2]\cdot I_1\cdot C_1H_2Cl_2$
Formula weight	805.42
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.5438(7)
b (Å)	39.836(3)
c (Å)	10.6814(11)
α (°)	90
β (°)	116.464(3)
γ (°)	90
V (Å^3)	3635.4(5)
Z	4
d_{calc} (g cm^{-3})	1.472
μ (Mo-K_α) (mm^{-1})	1.149
T (K)	173(2)
λ (A)	0.71073
Total reflections	42503
Unique reflections (R_{int})	6421 (0.1479)
R_1 [I>2σ(I)]	0.0564
wR_2 (all data)	0.1233
F(000)	1624
Goodness-of-fit on F^2	1.049

Conclusions

The ionic bi-functional ligand of **L2** in combination of the phosphine with the Lewis acidic phosphonium by the stable chemical bonds was synthesized and fully characterized. The incorporated phosphonium showed no effect on the coordination ability of the peripheral phosphine fragment with the indication of the same $^1J_{Se\text{-}P}$ of 750 Hz as that of **L1** and **L4**. In co-catalysis for hydroformylation-acetalization, the phosphonium in **L2** not only contributed to the sequential acetalization of nonanals as a typical Lewis acidic organocatalyst, but also synergetically promoted the phosphine-ligated Rh-complex catalyzed hydroformylation through activating C=O by developing the bonding interaction between $P(V)^+$ centre and O atom (in C=O) to cooperatively stabilize the Rh-acyl intermediate. Moreover, the $Rh(acac)(CO)_2$-**L2** system with the wide substrate generality could be applied as a recoverable and recyclable catalyst in RTIL of $[Bmim]BF_4$ without the obvious deactivation.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Nos. 21473058, 21273077, and 21076083), and 973 Program from Ministry of Science and Technology of China (2011CB201403).

Notes and references

‡ CCDC-1036473 (**L1**)[21], CCDC-1412745 (**L2**) and CCDC-1036474 (**L3**)[21] contain the supplementary crystallographic data in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1 (*a*) R. Franke, D. Selent and A. Börner, *Chem. Rev.*, 2012, **112**, 5675; (*b*) P.W.N.M. Van Leeuwen and C. Claver, *Rhodium Catalyzed Hydroformylation*, Kluwer Academic Publishers, New York, 2000.

2 (*a*) P. Eilbracht, L. Bärfacker, C. Buss, C. Hollmann, B. E. Kitsos-Rzychon, C. L. Kranemann, T. Rische, R. Roggenbuck and A. Schmidt, *Chem. Rev.*, 1999, **99**, 3329; (*b*) Z. Du and Z. Shao, *Chem. Soc. Rev.*, 2013, **42**, 1337.

3 (*a*) X. Jin, K. Zhao, F. F. Cui, F. F. Kong and Q. Q. Liu, *Green Chem.*, 2013, **15**, 3236; (*b*) Y. Jin, J. Shi, F. Zhang, Y. Zhong and W. Zhu, *J. Mol. Catal. A: Chem.*, 2014, **383-384**, 167; (*c*) J. Balue and J. C. Bayon, *J. Mol. Catal. A: Chem.*, 1999, **137**, 193; (*d*) M. M. Diwakar, R. M. Deshpande and R. V. Chaudhari, *J. Mol. Catal. A: Chem.*, 2005, **232**, 179; (*e*) G. Parrinello and J. K. Stille, *J. Am. Chem. Soc.*, 1987, **109**, 7122; (f) B. E. Ali, J. Tijani and M. Fettouhi, *Appl. Catal. A: Chem.*, 2006, **303**, 213.

4 (*a*) S. R. Khan and B. M. Bhanage, *Tetrahedron Lett.*, 2013, **54**, 5998; (*b*) J. Norinder, C. Rodrigues and A. Börner, *J. Mol. Catal. A: Chem.*, 2014, **391**,139; (*c*) M. C. de Freitas, C. G. Vieira, E. N. dos Santos and E. V. Gusevskaya, *ChemCatChem*, 2013, **5**, 1884.

5 (*a*) V. S. Nair, B. M. Bhanage, R. M. Deshpande and R.V. Choudhari, *Rec. Adv. Basic Appl. Aspects Industr. Catal*. 1998, **113**, 529; (*b*) A. W. S. Currie and J. A. M. Andersen, *Catal. Lett.* 1997, **44**, 109; (*c*) K. Soulantica, S. Sirol, S. Koienis, G. Pneumatikakis and P.Kalck, *J. Organomet. Chem*., 1995, **498**, 10.

6 P. Manjunathan, S. P. Maradur, A.B. Halgeri and G. V. Shanbhag, *J. Mol. Catal. A: Chem.*, 2015, **396**, 47.

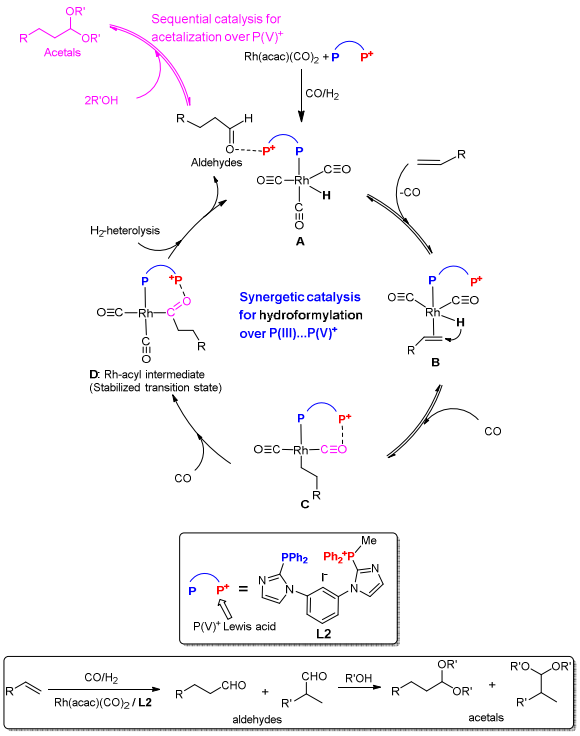
7 A. S. Poyraz, C. H. Kuo, E. Kim, Y. T. Meng, M. S. Seraji and S. L. Suib, *Chem. Mater.*, 2014, **26**, 2803.

View Article Online
DOI: 10.1039/C5GC02127H

8 X. Li, Z. Y. Guo, C. X. Xiao, T. W. Goh, D. Tesfagaber and W. Y. Huang, *ACS Catal.*, 2014, **4**, 3490.
9 A. Herbst, A. Khutia and C. Janiak, *Inorg. Chem.*, 2014, **53**, 7319.
10 (*a*) Y. J. Park, J. W. Park and C. H. Jun, *Acc. Chem. Res.*, 2008, **41,** 222; (*b*) C. Zhong and X. Shi, *Eur. J. Org. Chem.*, 2010, 2999; (*c*) J. Meeuwissen and J. N. H. Reek, *Nat. Chem.*, 2010, **2**, 615; (*d*) Y. Deng, S. Kumar and H. Wang, *Chem. Commun.*, 2014, **50**, 4272; (*e*) Z. H. Shao and H. Zhang, *Chem. Soc. Rev.*, 2009, **38**, 2745; (*f*) A. Gualandi, L. Mengozzi, C. M. Wilson and P. G. Cozzi, *Chem. Asian J.*, 2014, **9**, 984.
11 (*a*) M. Rueping, R. M. Koenigs and I. Atodiresei, *Chem. Eur. J.*, 2010, **16**, 9350; (*b*) F. Lv, S. Liu and W. Hu, *Asian J. Org. Chem.* 2013, **2**, 824.
12 (*a*) Q. Zhao, S. Li, K. Huang, R. Wang and X. Zhang, *Org. Lett.*, 2013, **15**, 4014; (b) P. Daka, Z. Xu, A. Alexa and H. Wang, *Chem. Commun.*, 2011, **47**, 224; (*c*) Z. Xu, L. Liu, K. Wheeler and H. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 3484; (d) T. Smejkal, D. Gribkov, J. Geier, M. Keller and B. Breit, *Chem.-Eur. J.*, 2010, **16**, 2470; (*e*) D. Fuchs, G. Rousseau, L. Diab, U. Gellrich and B. Breit, *Angew. Chem., Int. Ed.*, 2012, **51**, 2178; (f) A. D. Worthy, C. L. Joe, T. E. Lightburn and K. L. Tan, *J. Am. Chem. Soc.*, 2010, **132**, 14757; (*g*) C. L. Joe and K. L. Tan, *J. Org. Chem.*, 2011, **76**, 7590; (*h*) K. Ohmatsu, M. Ito, T. Kunieda and T. Ooi, *Nat. Chem.*, 2012, **4**, 473.
13 (*a*) B. F. M. Kimmich, C. R. Landis and D. R. Powell, *Organometallics*, 1996, **15**, 4141; (*b*) N. Tsoureas, G. R. Owen, A. Hamilton and A. G. Orpen, *Dalton Trans.*, 2008, 6039; (*c*) H. Kameo and H. Nakazawa, *Organometallics*, 2012, **31**, 7476; (*d*) G. Bouhadir, A. Amgoune and D. Bourissou, *Adv. Organomet. Chem.*, 2010, **58**, 1; (e) R. Malacea, N. Saffon, M. Gómez and D. Bourissou, *Chem. Commun.*, 2011, **47**, 8163; (*f*) M. W. P. Bebbington, S. Bontemps, G. Bouhadir, M. J. Hanton, R. P. Tooze, H. van Rensburg and D. Bourissou, *New J. Chem.*, 2010, **34**, 1556; (*g*) F. G. Fontaine, J. Boudreau and M. H. Thibault, *Eur. J. Inorg. Chem.*, 2008, 5439; (h) R. Malacea, F. Chahdoura, M. Devillard, N. Saffon, M. Gómez and D. Bourissou, *Adv. Synth. Catal.*, 2013, **355**, 2274.
14 C. Tan, P. Wang, H. Liu, X. L. Zhao, Y. Lu and Y. Liu, *Chem. Commun.*, 2015, **51**, 10871.
15 (*a*) O. Sereda; S. Tabassum and R. Wilhelm, *Top. Curr. Chem.*, 2010, **291**, 349; (*b*) T. Werner, *Adv. Synth. Catal.*, 2009, **351**, 1469; (*c*) M. Selva, A. Perosa, P. Tundo and Davide Brunelli, *J. Org. Chem.*, 2006, **71**, 5770; (d) T. W. Hudnall, Y. M. Kim, M. W. P. Bebbington, D. Bourissou and F. P. Gabbaï, *J. Am. Chem. Soc.,* 2008, **130**, 10890.
16 (*a*) C. B. Caputo, L. J. Hounjet, R. Dobrovetsky and D. W. Stephan, *Science*, 2013, **341**, 1374; (*b*) M. Pérez, L. J. Hounjet, C. B. Caputo, R. Dobrovetsky and D. W. Stephan, *J. Am. Chem. Soc.*, 2013, **135**, 18308.
17 X. Wang and S. K. Tian, *Tetrahedron Lett.*, 2007, **48**, 6010.
18 C. L. Johnson, R. E. Donkor, W. Nawaz and N. Karodia, *Tetrahedron Lett.*, 2004, **45**, 7359.
19 T. Mukaiyama, S. Matsui and K. Kashiwagi, *Chem. Lett.*, 1989, 993.
20 C. Barthes, C. Lepetit, Y. Canac, C. Duhayon, D. Zargarian and R. Chauvin, *Inorg. Chem.,* 2013, **52**, 48.
21 Y. Q. Li, P. Wang, H. Zhang, X. L. Zhao, Y. Lu, Z. Popović and Y. Liu, *J. Mol. Catal. A: Chem.*, 2015, **402**, 37.
22 A. A. Tolmachev, A. A. Yurchenko, A. S. Merculov, M. G. Semenova, E. V. Zarudnitskii, V. V. Ivanov and A. M. Pinchuk, *Heteroatom Chem.*, 1999, **10**, 585.
23 (*a*) D. W. Allen and B. F. Taylor, *Dalton Trans.*, 1982, **1**, 51; (b) A. S. Rrez, M. A. M. Rojas and A. Pizzano, *Organometallics*, 2002, **21**, 4611; (*c*) S. Jeulin, S. D. de Paule, V. R. Vidal, J. P. Genêt, N. Champion and P. Dellis, *Angew. Chem. Int. Ed.*, 2004, **43**, 320.
24 X. F. Wu, X. Fang, L. Wu, R. Jackstell, H. Neumann and M. Beller, *Acc. Chem. Res.*, 2014, **47**, 1041.
25 B. Breit, *J. Mol. Catal. A: Chem.*, 1999, **143**, 143.
26 O. Diebolt, H. Tricas, Z. Freixa and P. W. N. M. van Leeuwen, *ACS Catal.,* 2013, **3**, 128.
27 S. A. Ullate, J. A. Baker, V. G. González, C. Müller, J. D. Hirst and J. J. Carbó, *Catal. Sci. Technol.*, 2014, **4**, 979.
28 H. Tricas, O. Diebolt and P. W. N. M. van Leeuwen, *J. Catal.*, 2013, **298**, 198.
29 S. Jeulin, S. D. de Paule, V. R. Vidal, J. P. Genêt, N. Champion and P. Dellis, *Angew. Chem. Int. Ed.*, 2004, **43**, 320.
30 C. Bolli, J. Gellhaar, C. Jenne, M. Keßler, H. Scherer, H. Seegera and R. Uzunb, *Dalton Trans.*, 2014, **43**, 4326.
31 C. B. Caputo, L. J. Hounjet, R. Dobrovetsky and D. W. Stephan, *Science*, 2013, **341**, 1374.
32 S. C. Yu, Y. M. Chi, Z. H. Guan, Y. P. Zou, W. Li and X. M. Zhang, *Org. Lett.*, 2009, **11**, 241.
33 S. J. Chen, Y. Q. Li, P. Wang, Y. Lu, X. L. Zhao and Y. Liu**,** *J. Mol. Catal. A: Chem.*, 2015, **407**, 212.
34 C. Huo and T. H. Chan, *Chem. Soc. Rev.*, 2010, **39**, 2977.
35 (*a*) B. Ni and A. D. Headley, *Chem.-Eur. J.*, 2010, **16**, 4426; (*b*) R. Sebesta, I. Kmentova and S. Toma, *Green Chem.*, 2008, **10**, 484; (*c*) W. Miao and T. H. Chan, *Acc. Chem. Res.*, 2006, **39**, 897.

View Article Online
DOI: 10.1039/C5GC02127H

A table contents entry:



L2 containing the phosphine and the Lewis acidic phosphonium exhibited synergetic catalysis and sequential catalysis for one-pot hydroformylation-acetalization.