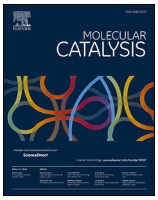
Molecular Catalysis 508 (2021) 111598

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.journals.elsevier.com/molecular-catalysis



Highly regioselective homogeneous isomerization-hydroformylation of 2-butene with water- and air-stable phosphoramidite bidentate ligand

Songbai Tang, Conceptualization; Methodology; Formal analysis; Investigation; Writing - original draft; Visualization [a], Yanxin Jiang, Validation; Visualization [a], Jiwei Yi [a], Xiaoxia Duan [a], Haiyan Fu [a], Ruixiang Li, Methodology; Funding acquisition [a], Maolin Yuan [a], Hua Chen, Project administration; Supervision; Resources; Methodology [a], Chunji Yang [b], Xueli Zheng, Conceptualization; Writing - review & editing; Project administration; Supervision [a,*]

[a] *Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, PR China*
[b] *Petrochemical Research Institute QaQing Petrochemical Research Center, Daqing, 163000, PR China*

ARTICLE INFO

Keywords:
Isomerization-hydroformylation•2-butene
Diphosphoramidite•linear selectivity
Cyclic voltammetry

ABSTRACT

Highly selective isomerization-hydroformylation of 2-butene was achieved with the presence of Rh(acac)$(CO)_2$ and a phosphoramidite bidentate ligand which bearing 2,2′-dihydroxy-1,1′-binaphthyl backbone and N-indolyl substitute. The molar ratio of n- to isovaleraldehyde (217) is distinctly higher than the reported systems. NMR and IR revealed that the five-coordinate HRh(ligand)$(CO)_2$ was an equatorial-equatorial configuration which contributed to the n-selectivity of valeraldehyde. The strong π-acceptor ability of ligand was suggested to play a key role in fast isomerization of 2-butene. Hydrolysis and oxidation experiments demonstrated that the ligand was water- and air-stable. Cyclic voltammetry measurement confirmed that this phosphoramidite ligand is more difficult to be oxidized, compared with the phosphine, phosphinite and phosphite ligands. Inspiringly, recycling experiments showed the catalytic system could work for at least 7 runs with unchanged selectivity.

1. Introduction

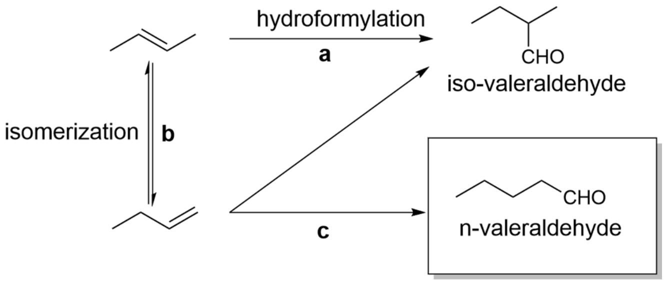
Hydroformylation (oxo) is one of the most important reactions in industrial. Various aldehydes and alcohols, which are important intermediates for the synthesis of bulk chemicals, such as detergents, cosmetics, air fresheners, plasticizers, and food additives, are produced by this highly atom-economical process [1,2]. The most representative rhodium catalyzed plants are the homogeneous low-pressure oxo process (LPO) and the biphasic Ruhrchemie/Rhône-Poulenc process (RCH/RP) based on a water soluble catalyst [3,4]. Compared with biphasic process, rhodium-catalyzed homogeneous hydroformylation has the advantages of high activity and selectivity for aldehydes under mild conditions. Raffinate-2, which consists of 1-butene, most preferentially 2-butene and small amount of butane, is widely used in hydroformylation, not only for the cheap and extensive C4 feedstock [5], but also for the production of n-valeraldehyde. Recently there has been an increasing demand in the production of alternative plasticizer alcohols due to environmental concern about current products. As an important fungible plasticizer alcohol, 2-propylheptanol could be synthesized by the aldol condensation of n-valeraldehyde and the subsequent hydrogenation of the condensation product [6,7]. During the hydroformylation of Raffinate-2, n- and isovaleraldehydes are produced and the production of n-valeraldehyde is more desirable due to better physical properties of the resulting plasticizers. As demonstrated in Scheme 1, direct hydroformylation of 2-butene may yield to isovaleraldehyde product (reaction a). Hoechst Company developed a new method for the hydroformylation of mixed butene, in which two different catalytic systems are combined to produce n-valeraldehyde [8]. The first catalytic system allows 2-butene isomerization to 1-butene and the second one catalyzes the hydroformylation of 1-butene to yield n-valeraldehyde. To obtain n-valeraldehyde from 2-butene in one catalytic system, an ideal catalyst has to catalyze the competitive

---

* Corresponding author.

E-mail addresses: 1451298321@qq.com (S. Tang), 997373774@qq.com (Y. Jiang), 2720673131@qq.com (J. Yi), 1638372111@qq.com (X. Duan), scufhy@scu.edu.cn (H. Fu), liruixiang@scu.edu.cn (R. Li), cdscyml@sina.com (M. Yuan), ycj459@petrochina.com.cn (C. Yang), zhengxueli@scu.edu.cn (X. Zheng).

https://doi.org/10.1016/j.mcat.2021.111598
Received 21 February 2021; Received in revised form 30 March 2021; Accepted 20 April 2021



Scheme 1. Isomerization-hydroformylation of 2-butene to yield n-valeraldehyde.

isomerization of 2-butene to 1-butene (reaction b) and then predominantly convert 1-butene to n-valeraldehyde (reaction c) rather than isovaleraldehyde, which is quite essential to the industrial utilization of Raffinate-2.

Phosphorus ligands modified rhodium catalyst usually allows good activity and selectivity in hydroformylation, and the steric as well as the electronic properties of ligand are always the key issues. Casey et al. examined the steric effects of different ligands and concluded that a wide bite angle between bidentate ligand (i.e., BISBI) and rhodium would improve the n-selectivity through the formation of equatorial-equatorial (ee) coordination in which the ligand occupied the two equatorial positions of the rhodium complex [9,10]. Similar to the backbone of BISBI, 2,2′-dimethyl-1,1′-binaphthalene [11], 2,2′-dihydroxy-1,1′-biphenyl [12] and 2,2′-dihydroxy-1,1′-binaphthyl [13] were proved to be suitable backbone of phosphorus ligands to achieve ee configuration of rhodium-ligand complex. Furthermore, xanthene and it derivatives [14] as well as some spiroketal-based chemicals [15] were also good backbones. Hydroformylation of 2-butene with the presence of spiroketal-based diphosphite ligands could obtain the n/i ratio (n- to iso-valeraldehyde) of 34.5. It is also reported that the rhodium catalysts modified with strong π-acceptor ligands could achieve higher activity and n-selectivity compared to those with σ-donor ligands, since the lower basicity of the ligand could facilitate olefin coordination to rhodium [16–18]. In 2001, Beller group successfully applied electron-deficient NAPHOS-type diphosphines to rhodium-catalyzed homogeneous hydroformylation of 2-butene, the n/i was 95:5 and the TOF was up to 900 h^{-1} [19]. Later, similarly strongly electron-deficient sulfonated ligand BINAS was utilized in a water-organic biphasic system in the isomerization-hydroformylation of internal olefins and the n/i ratio could reach 49 in the hydroformylation of 2-butene [20]. More recently, some new techniques were developed in continuous C4 hydroformylation industrially such as supporting ligands on ionic liquid phase (SILP) [21] or applying porous organic copolymer phosphine ligand [22]. High TOF could be obtained with moderate n-selectivity by these methods.

As mentioned above, these catalytic systems have achieved some outstanding developments, there still remain some problems prior to more efficient industrialization, such as the cost and the stability of the ligand in terms of hydrolysis and oxidation, which are quite crucial for their industrial application to the hydroformylation of Raffinate-2. Phosphine ligands show good resistance to hydrolysis but they are sensitive to oxygen. Phosphites with P-O bonds exhibit high resistance to oxidation owing to the absence of P-C bond, however, they are sensitive to moisture. P-N bond might be more stable to moisture than P-O bond. Herein, we reported an efficient and low-cost 2-butene isomerization-hydroformylation system with a readily accessible, water- and air-stable diphosphoramidite ligand bearing 2,2′-dihydroxy-1,1′-binaphthyl skeleton and indolyl substituent. The linear selectivity towards valeraldehyde was up to 99.6% with the aldehyde yield above 93.4%. The stability and the reusability of the catalyst were further explored.

2. Experimental

2.1. General reagents and instruments

2-butene (95%, mixture of cis and trans) and ligand BISBI (L5, Fig. 1) was supplied by Chengdu Xinhuayuan Technology Co., Ltd. Rh(acac)$(CO)_2$ (acac = acetylacetone) [23], ligand L1-L4 and L6-L8 were prepared according to literatures [12,24–29]. H_2O_2 (30%), toluene and xylene were supplied by Chengdu Chron Chemicals Co., Ltd and tetrahydrofuran was purchased from Tianjin Guangfu Fine Chemical Research Institute. The solvents were purified by standard methods. NMR was performed on Bruker AVANCE III HD-400 MHz spectrometer. ^{1}H NMR was reported with TMS as an internal standard. $^{31}P\{^{1}H\}$ NMR was reported with H_3PO_4 as an external reference. High-resolution mass spectra were recorded on a SHIMADZU LCMS-IT-TOF mass spectrometer. FTIR spectra were recorded on an IR Tracer-100 spectrometer. Gas chromatography was analyzed on PANNA A91 (KB-1, 30 m × 0.25 mm × 0.50 μm, FID). Cyclic voltammetry measurements were performed on electrochemical workstation (CHI760E), the working electrode is a Pt plate, counter electrode is a carbon rod and the reference electrode is Ag/AgCl.

2.2. Hydroformylation and recycle procedures

The homogeneous hydroformylation was carried out in a 25 mL stainless steel autoclave with a pressure gage, a magnetic stirrer and a thermocouple. Typically, the precursor Rh(acac)$(CO)_2$ (0.008 g, 0.031 mmol), the ligand (in the P/Rh molar ratio of 5), the internal standard dodecane (100 μL, 0.0753 g) and the solvent toluene or xylene (8 mL) were loaded into the autoclave, and then 2-butene (1.8 g, 32 mmol) was transferred into the autoclave at low temperature using Schlenk technique. After being filled with definite constant pressure of syngas and heated to the desired temperature, the autoclave was vigorously stirred. When the reaction completed, the autoclave was cooled down and carefully vented. The reaction mixture was analyzed by GC immediately using internal standard method.

The recycling runs were similar to typical hydroformylation procedure. After each run completed, the reaction mixture was collected and analyzed by GC. Then the liquid mixture was removed by a rotary evaporator, and the solid residue, including the catalyst and ligand, was dissolved by another portion of solvent and transferred into the same autoclave for the next run.

2.3. Stability test of ligands

The hydrolysis and oxidation experiments were performed in a 15 mL flask. For hydrolysis, ligand L2 (0.1 mmol, 81 mg) was dissolved in toluene (2 mL) and then H_2O (1 mL) was added and stirred at 80 °C for 24 h. For oxidation experiments, L2 (0.1 mmol, 81 mg) was stirred with toluene (2 mL) at 80 °C for 24 h under O_2 balloon, or L2 was stirred with toluene and 30% H_2O_2 (1 mL) at 80 °C for 2 h. After hydrolysis and oxidation reactions, the solvents were removed and the residue was analyzed by ^{31}P NMR and HRMS. In addition, cyclic voltammetry measurements were also used to analyze the ligand stability.

3. Result and discussion

3.1. Influence of different ligands

Due to the goal of achieving more linear valeraldehyde, different types of diphosphorus ligands (Fig. 1) based on 2,2′-dihydroxy-1,1′-biphenyl or 2,2′-dihydroxy-1,1′-(±)binaphthyl backbone, which the phosphorus atoms linked to can bear moderate bite angle with rhodium, were explored in the isomerization-hydroformylation of 2-butene with the presence of catalyst precursor Rh(acac)$(CO)_2$, and the results were shown in Table 1. It can be seen that except phosphine ligand BISBI (L5)

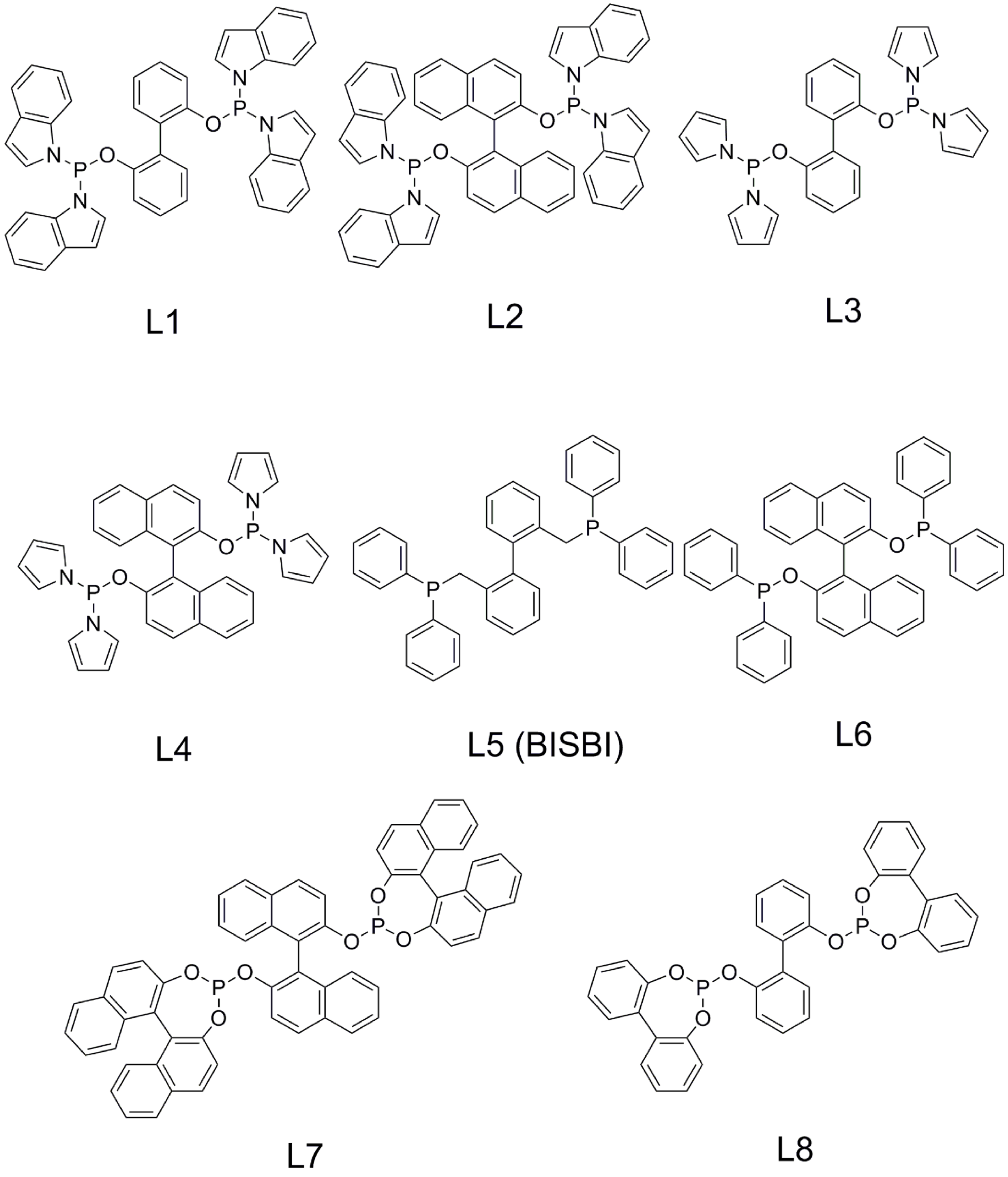


Fig 1. Structure of ligands L1-L8.

and phosphinite L6, the other ligands (including phosphoramidite and phosphite) with strong electron-withdrawing groups achieved good selectivity to n-valeraldehyde (Table 1, entry 1–4 and entry 7–8), and the highest molar ratio of n- to isovaleraldehyde (n/i) was obtained as 40.9 with a good valeraldehyde yield of 61.6% (Table 1, entry 2) when phosphoramidite ligand L2 was used. The phosphite ligands L7 and L8 achieved moderate activity of 23.3% and 31.0%. The regioselectivity follows the trend L2 > L7 > L6 > L5, which correlates to the π-acceptor properties of these ligands [30]. Because ligand with strong π-acceptor property would facilitate the isomerization of 2-butene to 1-butene. Ligand L2 showed excellent results in terms of activity and regioselectivity, therefore, it was selected for the following reaction conditions exploration.

3.2. *Optimization of hydroformylation conditions with L2*

Since the hydroformylation results highly rely on the reaction conditions, the influence of P/Rh ratio, temperature, reaction time and pressure were evaluated. As demonstrated in Table 2, in the absence of ligand, the non-modified rhodium catalyst yielded only 4.7% of aldehydes and the n/i ratio was only 0.61 (Table 2, entry 1). This situation was greatly improved when L2 was added. However, increasing the P/Rh ratio from 5 to 15, the yield slightly decreased (entry 2–4) and sharply dropped to 17.6% when the P/Rh ratio came to 20. The

Table 1
Rh-catalyzed hydroformylation of 2-butene with different ligands[a].

Entry	Ligand	n/i[b]	Aldehyde (%)[c]
1	L1	14.7	51.5
2	L2	40.9	61.6
3	L3	16.5	54.1
4	L4	21.3	38.2
5	L5	0.5	22.9
6	L6	1.1	14.8
7	L7	17.0	23.3
8	L8	20.1	31.0

[a] Reaction conditions: [Rh] = 410 ppm, 2-butene (1.8 g), P/Rh = 5, S/C (Molar ratio of substrate to catalyst) = 1040, 10 bar syngas constant pressure, P_{H2}/P_{CO} = 1/1, 70 °C, 2 h, xylene (8.0 mL) as the solvent, dodecane (100 uL, 0.0753 g) as the internal standard.

[b] Molar ratio of n- to iso-valeraldehyde, determined by GC.

[c] The yield of all aldehydes, determined by GC.

Table 2
Rh/L2 catalyzed isomerization-hydroformylation of 2-butene under different conditions.[a]

Entry	P/Rh	*T* (°C)	*P* (bar)	*t*(h)	n/i[b]	Yield (%)[c]
1	0	70	10	2	0.61	4.7
2	5	70	10	2	40.9	61.6
3	10	70	10	2	42.8	54.9
4	15	70	10	2	35.5	46.9
5	20	70	10	2	35.5	17.6
6	5	50	10	2	33.2	10.8
7	5	60	10	2	38.4	13.0
8	5	80	10	2	38.2	68.1
9	5	90	10	2	21.9	89.5
10	5	100	10	2	5.8	80.1
11	5	70	10	4	43.2	64.7
12	5	70	10	6	44.8	92.7
13	5	70	2.5	2	34.5	45.4
14	5	70	5	2	50.6	49.8
15	5	70	7.5	2	57.0	46.0
16	5	70	10	2	40.9	61.6
17	5	70	15	2	35.5	42.9
18	5	70	20	2	31.4	29.5
19	5	70	25	2	18.8	26.0

[a] [Rh] = 410 ppm, 2-butene (1.8 g), *S*/*C* = 1040, P_{H2}/P_{CO} = 1/1, xylene (8.0 mL), dodecane (100 uL, 0.0753 g).

[b,c] see Table 1.

selectivity did not change too much. It can be explained by that the high concentration of ligand around the metal would inhibit the coordination of olefin to metal and led to low activity. The temperature had a significant impact on the selectivity and the activity. The yield of aldehyde increased from 10.8% to 89.5% when the temperature varied from 50 to 90 °C (entry 2, 6–9), but decreased to 80.1% at 100 °C (entry 10). The selectivity slightly changed from 50 to 80 °C but had a great decline over 90 °C, which indicated that the isomerization-hydroformylation of 2-butene could get better results under 70–80 °C with the presence of ligand L2 and Rh(acac)$(CO)_2$. Compared with ligand L2, NAPHOS [19], Ding's spiroketal-based diphosphite ligands [15] and our previous work [31] could also achieve good n-selectivity but require higher temperature at 100–120 °C. Probably because a certain high temperature would favor the β-H elimination of branched Rh-alkyl species [32] which leads to the isomerization of 2-butene to 1-butene. Upon heating at 70 °C for 6 h, an excellent valeraldehyde yield of 92.7% with the n/i ratio of 44.8 could be obtained (entry 12).

The total syngas pressure was also a key parameter in the hydroformylation of 2-butene. Under low pressure (below 7.5 bar), the regioselectivity was slightly improved as the pressure increased from 2.5 to 7.5 bar (Table 2, entry 13–15), and the best one was found at 7.5 bar, where the n/i ratio was 57.0. However, the n/i ratio and the yield of aldehyde decreased as the pressure increased from 10 to 25 bar (entry 16–19).

Some researches demonstrated that the partial pressure of hydrogen (P_{H2}) and carbon monoxide (P_{CO}) had a prominent impact, not only on the β-H elimination but also on the carbonyl insertion [33–35]. Fig. 2 showed the n/i ratio and the yields of aldehydes when the ratio of P_{H2}/P_{CO} varied from 1/4 to 4/1 with the presence of Rh(acac)$(CO)_2$ and ligand L2 (Rh/L2 for short). It is not difficult to figure out that the isomerization-hydroformylation of 2-butene had poor regioselectivity and activity when P_{H2}/P_{CO} was 1/4 (Fig. 2a, 2b). On the contrary, when the P_{H2}/P_{CO} ratio ascended to 4/1, the regioselectivity increased dramatically (Fig. 2c, 2d). Representatively, n/i ratio was up to 217 as the partial pressure of hydrogen and CO was 10 bar and 2.5 bar, respectively, which was higher than the reported catalytic systems. Landis demonstrated that regioselectivity of styrene hydroformylation might depend on CO pressure at very low pressure [33,35,36], while for the isomerization-hydroformylation of 2-butene, the tendency was that the partial pressure of hydrogen made more contribution to the regioselectivity. Hydroformylation of internal olefin is slower than isomerization and hydroformylation of terminal olefin [37], it is reasonable to infer that the partial pressure of hydrogen would influence the regioselectivity via the isomerization of 2-butene. Under high syngas pressure or high partial pressure of CO, low regioselectivity was probably caused by that carbonyl insertion was more competitive than β-H elimination [19], and low yield of aldehydes was likely due to that the excess CO would somehow inhibit the coordination of olefin to Rh center.

3.3. Catalyst characterization studies

The coordination mode of phosphorus ligands to the rhodium center is quite important to the regioselectivity of hydroformylation. A bidentate ligand can coordinate with rhodium in equatorial-equatorial (ee) or equatorial-axial (ea) configuration at the resting state of five-coordinate HRh(L)$(CO)_2$. In this study, to clarify the configuration of HRh(L2)$(CO)_2$, Rh(acac)$(CO)_2$ and L2 were mixed in the molar ratio of 1/1 and stirred in tol-d_8 under 10 bar of syngas (P_{H2}/P_{CO} = 1/1) for 1 h at 80 °C, and after the syngas was released, the mixture was analyzed by NMR and IR characterization immediately. $^{31}P\{^1H\}$ NMR showed a broad doublet at 137.0 ppm and the corresponding hydride resonance was observed as a broad peak at −10.6 ppm in ^1H NMR (Fig. 3b), the J_{RhP} (226.8 Hz) coupling constant and the chemical shifts of P and H are close to those for the ee configuration of its analogue HRh(L4)$(CO)_2$ [32]. While it is unable to determine J_{HP} and J_{HRh} coupling constants since the resonance is a broad signal, and the J_{PP} is undetected which probably hints that the two phosphorus atoms are equivalent. IR spectrum could give complementary evidence for the coordination of HRh(L2)$(CO)_2$, where the CO vibration were observed at 2068 and 2018 cm^{-1} (Fig. 4), which were quite close to the signals in ee configuration (2075–1970 cm^{-1}) [32,38]. Combining with the NMR results above, it is believed that the two phosphorus atom of L2 is dominantly coordinated with Rh at ee configuration, which is the preferred isomer to achieve linear product. When increasing P_{H2}/P_{CO} to 4/1, the major configuration was also in an ee fashion.

3.4. Stability testing of ligand L2

Excellent catalysis results were gained with the presence of Rh/L2, in order to probe if the Rh/L2 catalyst could be long-time used to catalyze the isomerization-hydroformylation of 2-butene in industrial, the recycling of catalyst was performed. Mild reaction conditions such as 80 °C

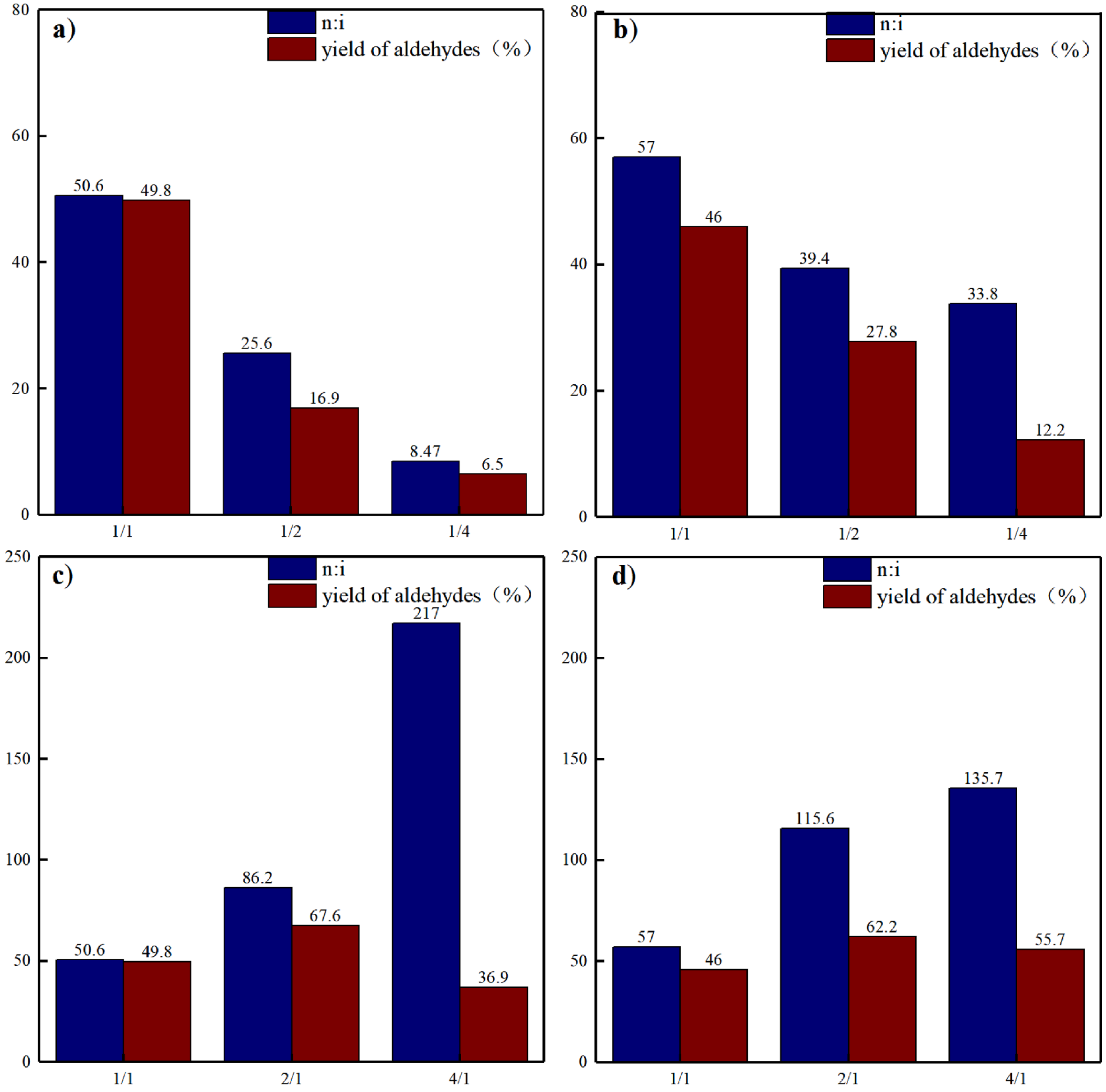


Fig. 2. Rh/L2 catalyzed isomerization-hydroformylation of 2-butene at different P_{H2}/P_{CO}. a) P_{H2} = 2.5 bar, b) P_{H2} = 3.75 bar, c) P_{CO} = 2.5 bar, d) P_{CO} = 3.75 bar. Other reaction conditions: see Table 1.

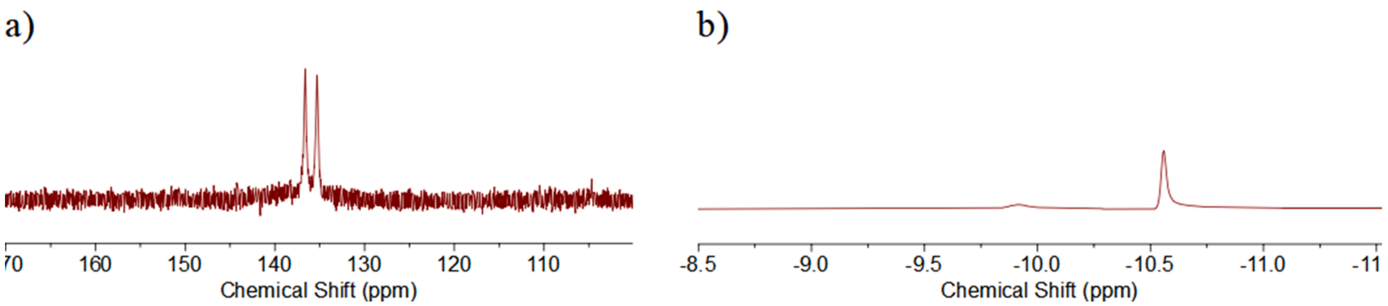


Fig. 3. $^{31}P\{^1H\}$ and ^1H NMR of $HRh(L2)(CO)_2$.

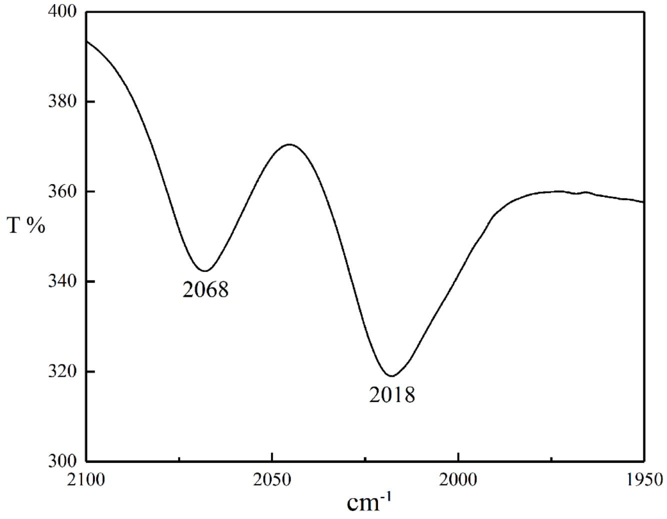


Fig. 4. Carbonyl stretching absorption of HRh(L2)$(CO)_2$.

and 10 bar constant pressure (P_{H2}/P_{CO} = 1/1) were chosen. To our delight, extremely high selectivity of n-valeraldyhyde was obtained (more than 99%) and it could be almost maintained for 7 runs, in other words, the Rh/L2 catalyst could work well for beyond 40 h (Fig. 5). Yields of the aldehydes slightly decreased during the 1–6 runs and maintained about 80% while dropped to 62.7% at the 7th run. However, dramatic changes appeared at the 8th run, in which the yield of aldehydes increased from 62.7% to 98.8% and kept steady in the latter 9th and 10th run, while the selectivity definitely dropped to 59.0% and kept going down at the following runs.

Considering that the ligand L2 has the risk of oxidation, decomposition or hydrolysis during the recycling operation, which might be responsible for the decline of the selectivity and aldehyde yield. In order to probe the exact reason, hydrolysis and oxidation experiments were performed on ligand L2, and the reaction mixture along with the hydroformylation residue after 1st, 7th, 8th and 10th runs were collected for $^{31}P\{^1H\}$ NMR and HRMS characterization. In $CDCl_3$, ligand L2 showed a singlet at 104.6 ppm (Fig. 6a). After stirring with H_2O at 80 °C for 24 h (Fig. 6b), the chemical shift was not changed compared with L2 which revealed that ligand L2 may be water-stable. For oxidation experiments, oxygen and hydrogen peroxide were selected as the oxidants. After heating L2 at 80 °C under O_2 balloon for 24 h, the chemical shift was maintained at 104.6 ppm (Fig. 6c), which hinted that phosphoramidite (III) L2, (L2 (III) for short) was hardly oxidized in O_2 at 80 °C. However, heating L2 in H_2O_2 at the same temperature within 2 h, the singlet signal at 104.6 ppm (Fig. 6d) disappeared while another resonance at −11.9 ppm was observed, which could be assigned to phosphoramide (V) species (L2 (V) for short), and this assumption was proved via mass spectra (SI). In the hydroformylation recycling runs, ligand L2 was not oxidized after 1st run since only the chemical shift of 104.6 ppm was observed (Fig. 6e). As mentioned in Fig. 5, the selectivity was extremely high and was kept for 7 runs, but the activity was gradually falling during the former 7 runs. The resonances were found at 104.6 ppm and −11.9 ppm after the 7 runs, which revealed that L2 (III) partially transformed into L2 (V) species during the recycling process, probably due to the products separation via distillation at high temperature for more than 110 °C. Due to the oxidation of L2 (III), there was a large decrease from 6th run to 7th run and when L2 (III) was completely oxidized, the yield increased from 7th run to 8th run.

As a matter of fact, the coordination ability of L2 (III) is stronger than that of L2 (V). During the former 7 runs, L2 (III) chelating to Rh was dominant and was favorable for the formation of n-valeraldehyde. The selectivity to n-valeraldyhyde fell sharply during 8th -10th runs, since L2 (III) completely transformed to L2 (V) after 8th run (Fig. 6g-6h). But

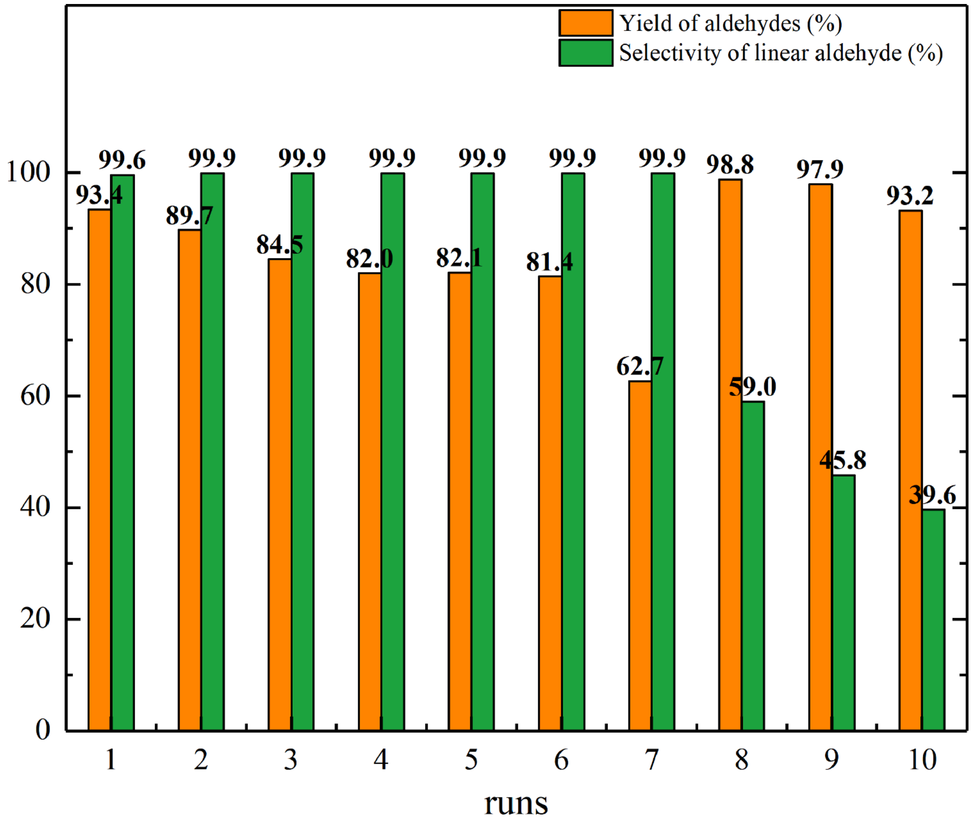


Fig. 5. Recycling tests: [Rh] = 328 ppm, P/Rh = 5, toluene (30 mL) as the solvent, 80 °C, 6 h, 10 bar constant pressure (P_{H2}/P_{CO} = 1/1), dodecane as internal standard. Mass of 2-butene for each run: 1) 6.0 g, 2) 5.4 g, 3) 4.8 g, 4) 4.5 g, 5) 6.0 g, 6) 4.8 g, 7) 4.8 g, 8) 7.2 g, 9) 6.3 g, 4 h,10) 6.0 g, 4 h.

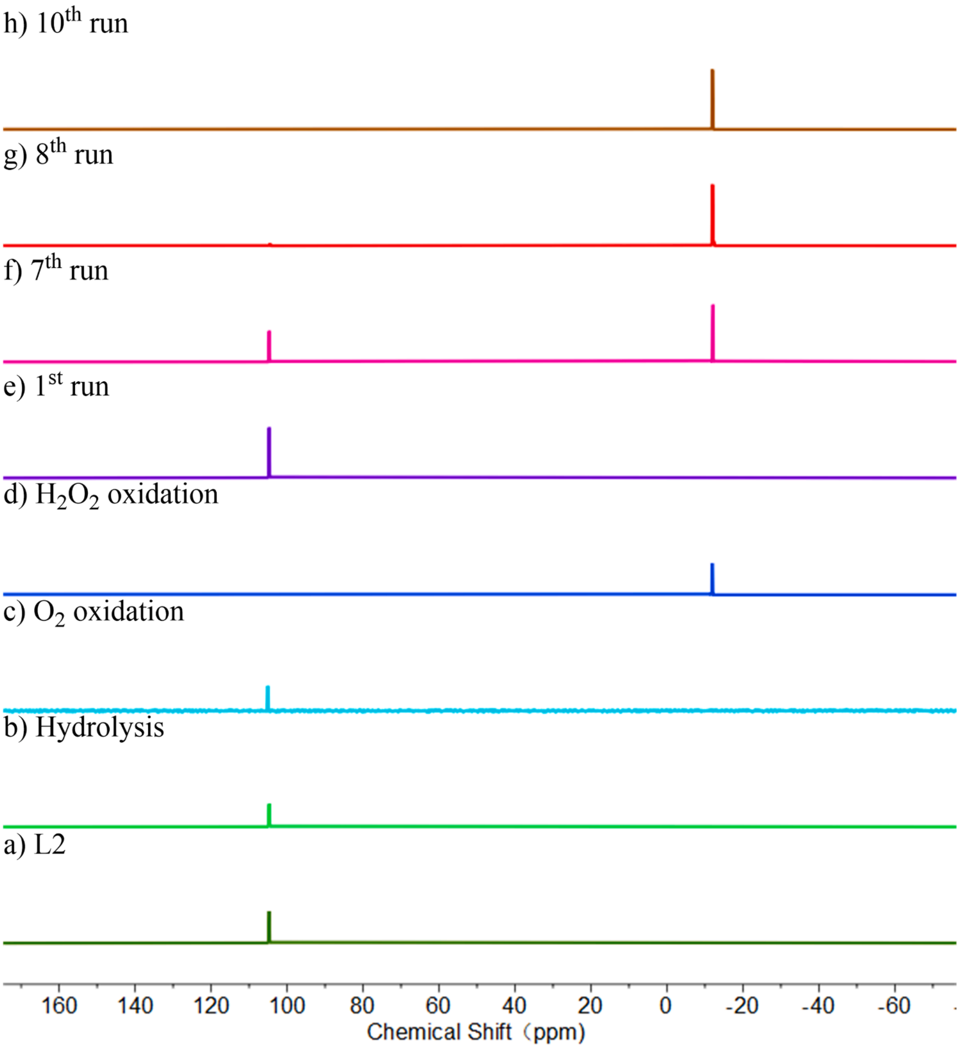


Fig. 6. Stacked ^{31}P{^{1}H}NMR spectra of L2, and the reaction residue after hydrolysis, oxidation experiments and the 1st, 7th, 8th and 10th hydroformylation runs.

much to our surprise, high activity could also be obtained after the 8th run which was probably due to the coordination of L2 (V) to rhodium via oxygen [39,40]. To understand the different catalytic performance of Rh/L2 (III) and Rh/L2 (V), their hydroformylation samples were continuously taken out from the autoclave at different time and analyzed by GC. The results revealed that in the presence of Rh/L2 (III), the n/i ratio was high all the time and 2-butene conversion to n-valeraldehyde was the major process (Fig. 7a). It is probably that the strong π-accepting bidentate ligand L2 (III) coordinates with Rh in an ee HRh(L2)(CO)$_2$ configuration, which allows fast isomerization of 2-butene to 1-butene and facilitates the hydroformylation of 1-butene to proceed immediately once 1-butene is formed [26]. Interestingly, in Rh/L2 (V) system, the n/i ratio was rather low in all time and remained constant and the n- and i-aldehyde formation rate was close (Fig. 7b). The yield of all aldehydes was beyond 90% in 4 h, which was in consistent with the good aldehyde yields at 8th -10th runs when L2 (III) has changed into L2 (V).

To further confirm the stability of phosphoramidite ligand L2, cyclic voltammetry measurement was performed in tetrahydrofuran at room temperature, with 0.1 M t-Bu$_4$NBF$_4$ as the supporting electrolyte. For comparison, the profiles of L5, L6 and L7 were also recorded which represent phosphine, phosphinite, and phosphite respectively. According to the electricity peaks in Fig. 8, the oxidation potential of L5, L6 and L7 located at around 1.07 V, 1.28 V and 1.65 V, respectively. The oxidation potential of L2 was not observed from -1.4 V to $+2.62$ V versus Ag/AgCl. It may be explained that ligand L2 is hard to be oxidized under this condition. The oxidation possibility might follow the tendency L5 > L6 > L7 > L2, which is consistent with the σ-donor ability [30]. Combined with the above NMR analyses (Fig. 6), it is shown that the phosphoramidite ligand L2 exhibits good resistance to water and oxygen and has better stability than other ligands.

4. Conclusion

In conclusion, different types of ligands, including phosphine, phosphinite, phosphite and phosphoramidite were applied to Rh-catalyzed isomerization-hydroformylation of 2-butene. An easily-accessible phosphoramidite ligand L2 demonstrated the best selectivity (beyond 99%) towards n-valeraldehyde as well as superior activity under mild conditions (80 °C, 10 bar). Further investigation of [HRhL2(CO)$_2$] showed that ligand L2 coordinate in an equatorial-equatorial (ee) fashion to the trigonal bipyramidal rhodium, which seems to be the

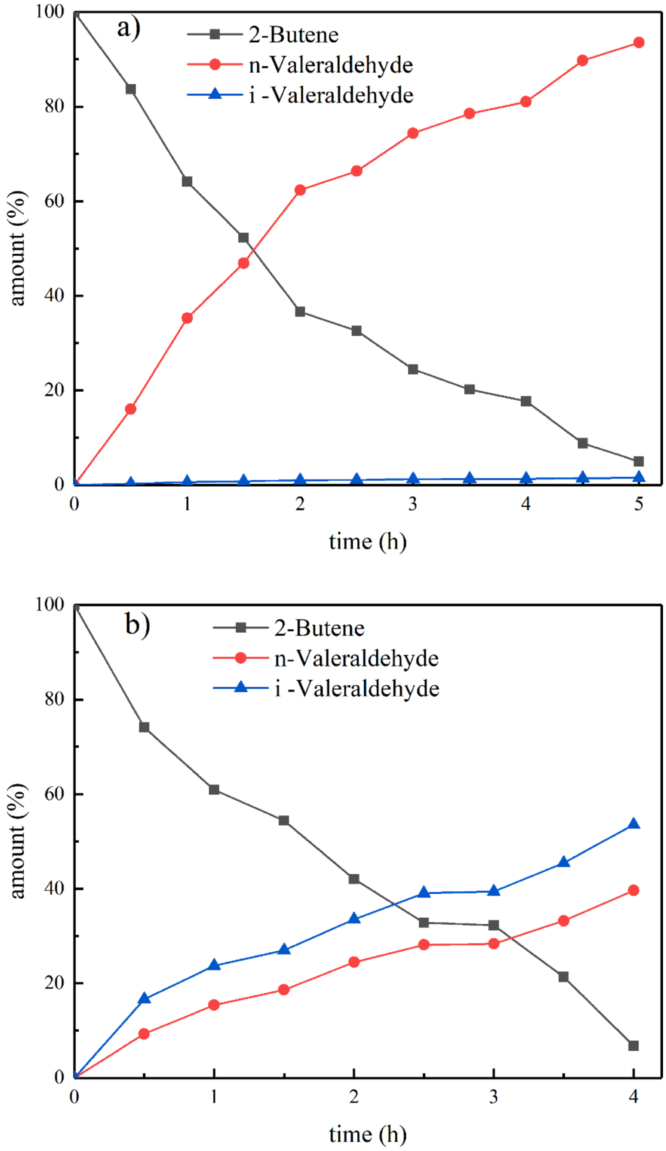


Fig. 7. The distribution of substrate and products with time: a) L2 (III), 2-butene (4.8 g), 5 h; b) L2 (V), 2-butene (6.0 g), 4 h. Reaction conditions: 80 °C, 10 bar, [Rh] = 328 ppm, P/Rh = 5, tol (30 mL) as solvent, dodecane as internal standard.

preferred isomer to achieve high linearity in hydroformylation. Hydrolysis and oxidation experiments as well as electrochemical investigation proved that ligand L2 was stable to water and air but sensitive to strong oxidants. L2 modified rhodium could be recycled for 7 runs and L2 (III) had the risk of transforming into L2 (V) due to distillation separation at high temperature which might be solved in industrial process. Anyhow, these results might offer some references to promising industrialization of Raffinate-2.

CRediT authorship contribution statement

Songbai Tang: . **Yanxin Jiang:** . **Jiwei Yi:** Validation. **Xiaoxia Duan:** Validation. **Haiyan Fu:** Methodology. **Ruixiang Li:** . **Maolin Yuan:** Resources. **Hua Chen:** . **Chunji Yang:** Resources. **Xueli Zheng:** .

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

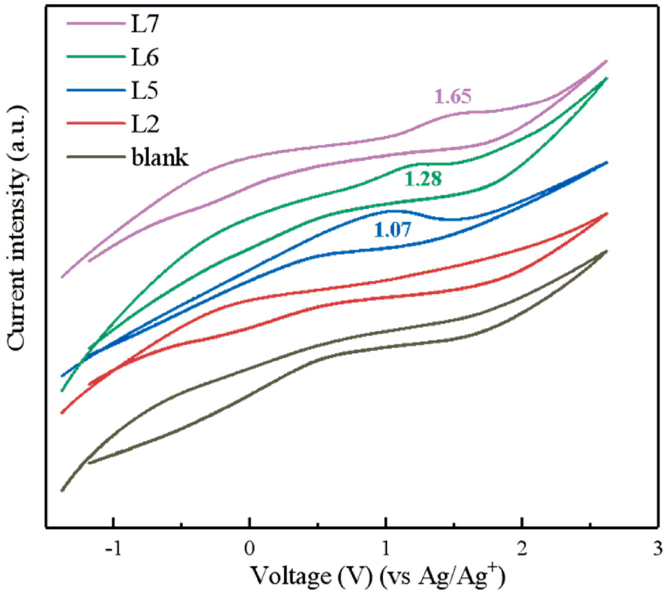


Fig. 8. Cyclic voltammograms of different ligands in tetrahydrofuran, [n-Bu_4NBF_4] = 0.01 M (supporting electrolyte). Working electrode: Pt plate, counter electrode: carbon rod, reference electrode: Ag/AgCl. Scan rate = 100 mV/s.

Acknowledgement

This work was supported by Sichuan Science and Technology program (2019YFG0146) and the Sichuan University Innovation Spark research Project (2018SCUH0079). The authors are grateful to the Centre of Testing & Analysis and the comprehensive training platform of specialized laboratory, College of Chemistry, Sichuan University for the analysis work. And the authors declare that they have no conflict of interest.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2021.111598.

References

[1] R. Franke, D. Selent, A. Börner, Chem. Rev. 112 (2012) 5675–5732, https://doi.org/10.1021/cr3001803.

[2] E.V. Gusevskaya, J. Jiménez-Pinto, A. Börner, Chem. Cat. Chem. 6 (2014) 382–411, https://doi.org/10.1002/cctc.201300474.

[3] C.K. Brown, G. Wilkinson, J. Chem. Soc. A (1970) 2753–2764, https://doi.org/10.1039/J19700002753.

[4] B. Cornils, E.G. Kuntz, J. Organomet. Chem. 502 (1995) 177–186, https://doi.org/10.1016/0022-328X(95)05820-F.

[5] M. Vilches-Herrera, L. Domke, A. Börner, ACS Catal. 4 (2014) 1706–1724, https://doi.org/10.1021/cs500273d.

[6] G. Leng, H.M. Koch, W. Gries, A. Schutze, A. Langsch, T. Bruning, Otter R, Toxicol. Lett. 231 (2014) 282–288, https://doi.org/10.1016/j.toxlet.2014.06.035.

[7] R.R. Kozlowski, U. Storzum, J. Vinyl Addit. Technol. 11 (2005) 155–159, https://doi.org/10.1002/vnl.20055.

[8] H. Bahrmann, G. Wolfgang, A.G. Abatjoglou, CN Patent 1123289 (A), 1996.

[9] C.P. Casey, G.T. Whiteker, M.G. Melville, L.M. Petrovich, J.A. Gavney, D.R. Powell, J. Am. Chem. Soc. 114 (1992) 5535–5543, https://doi.org/10.1021/ja00040a008.

[10] J.A. Gillespie, D.L. Dodds, P.C.J. Kamer, Dalton Trans 39 (2010) 2751–2764, https://doi.org/10.1039/B913778E.

[11] W.A. Herrmann, R. Schmid, C.W. Kohlpaintner, T. Priermeier, Organometallics 14 (1995) 1961–1968, https://doi.org/10.1021/om00004a057.

[12] M.J. Baker, K.N. Harrison, A.G. Orpen, P.G. Pringle, G. Shaw, J. Chem. Soc., Chem. Commun. (1991) 803–804, https://doi.org/10.1039/C39910000803.

[13] D. Selent, W. Baumann, K.-.D. Wiese, A. Börner, Chem. Commun. (2008) 6203–6205, https://doi.org/10.1039/B814120G.

[14] J.I. van der Vlugt, R. Sablong, P.C.M.M. Magusin, A.M. Mills, A.L. Spek, D. Vogt, Organometallics 23 (2004) 3177–3183, https://doi.org/10.1021/om0498899.

[15] X. Jia, Z. Wang, C. Xia, K. Ding, Chem. Eur. J. 18 (2012) 15288–15295, https://doi.org/10.1002/chem.201203042.

[16] C.P. Casey, E.L. Paulsen, E.W. Beuttenmueller, B.R. Proft, L.M. Petrovich, B. A. Matter, D.R. Powell, J. Am. Chem. Soc. 119 (1997) 11817–11825, https://doi.org/10.1021/ja9719440.

[17] C.P. Casey, E.L. Paulsen, E.W. Beuttenmueller, B.R. Proft, B.A. Matter, D.R. Powell, J. Am. Chem. Soc. 121 (1999) 63–70, https://doi.org/10.1021/ja982117h.

[18] C. Hegedüs, J. Madarász, I. Gergely, Á. Szöllősy, A. Monsees, T. Riermeier, J. Bakos, Tetrahedron 15 (2004) 2507–2513, https://doi.org/10.1016/j.tetasy.2004.07.015.

[19] H. Klein, R. Jackstell, K.D. Wiese, C. Borgmann, M. Beller, Angew. Chem. Int. Ed. 40 (2001) 3408–3411, https://doi.org/10.1002/1521-3773(20010917), 40:18<3408::AID−ANIE3408>3.0.CO;2-A.

[20] H. Klein, R. Jackstell, M. Beller, Chem. Commun. (2005) 2283–2285, https://doi.org/10.1039/B418350A.

[21] M. Jakuttis, A. Schonweiz, S. Werner, R. Franke, K.D. Wiese, M. Haumann, P. Wasserscheid, Angew. Chem. Int. Ed. 50 (2011) 4492–4495, https://doi.org/10.1002/anie.201007164.

[22] Y. Wang, L. Yan, C. Li, M. Jiang, W. Wang, Y. Ding, Appl. Catal. A 551 (2018) 98–105, https://doi.org/10.1016/j.apcata.2017.12.013.

[23] F. Bonati, G. Wilkinson, J. Chem. Soc. (1964) 3156–3160, https://doi.org/10.1039/JR9640003156.

[24] L. Zhang, C. Li, H. Fu, M. Yuan, R. Li, H. Chen, Chin. J. Catal. (Chinese Version) 32 (2011) 299–302.

[25] K. Wan, J. Zhao, S. Qin, X. Zheng, H. Fu, R. Li, H. Chen, J. Yang, C. Yang, Appl. Organomet. Chem. (2020) e5863, https://doi.org/10.1002/aoc.5863.

[26] X. Shu, H. Liang, Q. Wu, F. Zhou, X. Zheng, H. Fu, B. Xu, R. Li, C. Zhang, H. Chen, RSC Adv. 7 (2017) 14816–14823, https://doi.org/10.1039/C7RA01649B.

[27] W. Liu, M. Yuan, H. Fu, H. Chen, R. Li, X. Li, Chem. Lett. 38 (2009) 596–597.

[28] D.S. Clyne, Y.C. Mermet-Bouvier, N. Nomura, T.V. Rajanbabu, J. Org. Chem. 64 (1999) 7601–7611, https://doi.org/10.1021/jo9911387.

[29] M. Yan, L.W. Yang, K.Y. Wong, A.S.C. Chan, Chem. Commun. 30 (1999) 11–12, https://doi.org/10.1039/A807997H.

[30] R. Jackstell, H. Klein, M. Beller, K.D. Wiese, D. Rttger, Eur. J. Org. Chem. (2001) 3871–3877, https://doi.org/10.1002/1099-0690(200110)2001:, 20<3871::AID−EJOC3871>3.0.CO;2-V.

[31] M. Mo, T. Yi, C. Zheng, M. Yuan, H. Fu, R. Li, H. Chen, Catal. Lett. 142 (2012) 238–242, https://doi.org/10.1007/s10562-011-0751-7.

[32] E. Boymans, M. Janssen, C. Müller, M. Lutz, D. Vogt, Dalton Trans. 42 (2013) 137–142, https://doi.org/10.1039/C2DT31738A.

[33] I.A. Tonks, R.D. Froese, C.R. Landis, ACS Catal. 3 (2013) 2905–2909, https://doi.org/10.1021/cs400943s.

[34] E.R. Nelsen, C.R. Landis, J. Am. Chem. Soc 135 (2013) 9636–9639, https://doi.org/10.1021/ja404799m.

[35] A.C. Brezny, C.R. Landis, J. Am. Chem. Soc. 139 (2017) 2778–2785, https://doi.org/10.1021/jacs.6b12533.

[36] A.C. Brezny, C.R. Landis, ACS Catal. 9 (2019) 2501–2513, https://doi.org/10.1021/acscatal.9b00173.

[37] P. Eilbracht, A.M. Schmidt, M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2004, pp. 57–85.

[38] L.A. van der Veen, M.D.K. Boele, F.R. Bregman, P.C.J. Kamer, P.W.N.M. van Leeuwen, K. Goubitz, J. Fraanje, Schenk H, Bo C, J. Am. Chem. Soc. 120 (1998) 11616–11626, https://doi.org/10.1021/ja981969e.

[39] H.J. Clark, R. Wang, H. Alper, J. Org. Chem. 67 (2002) 6224–6225, https://doi.org/10.1021/jo011093l.

[40] V.V. Grushin, Chem. Rev. 104 (2004) 1629–1662, https://doi.org/10.1021/cr030026j.