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FULL PAPER

Linear-selective hydroformylation of vinyl ether using Rh(acac)(2,2′-bis{(di[1H-indol-1-yl]phosphanyl)oxy}-1,1′-binaphthalene) – Possible way to synthesize 1,3-propanediol

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Three bidentate phosphoramidite ligands were synthesized, characterized, and employed in Rh-catalyzed hydroformylation of vinyl ethers. The complex Rh(acac)(2,2′-bis{(di[1H-indol-1-yl]phosphanyl)oxy}-1,1′-binaphthalene} (acac = acetylacetone) (Rh-**L4**) was also synthesized and characterized. Rh-**L4** showed good regioselectivity for the hydroformylation of vinyl ethers under mild reaction conditions: 2 MPa of syngas, 1:1 (H_2/CO) substrate/catalyst molar ratio 1000:1, and 60 °C. The linear selectivity was up to 98%, and in most cases was about 80%, with no hydrogenation product formation observed, which could be a potential way to synthesize 1,3-propanediol. A mechanism study including density functional theory computational analysis showed that both Rh–H and CO insertion steps in the hydroformylation of vinyl ether were linear-preferred in our catalyst system.

KEYWORDS

linear selectivity, mechanism study, Rh-catalyzed hydroformylation, vinyl ether

1 | INTRODUCTION

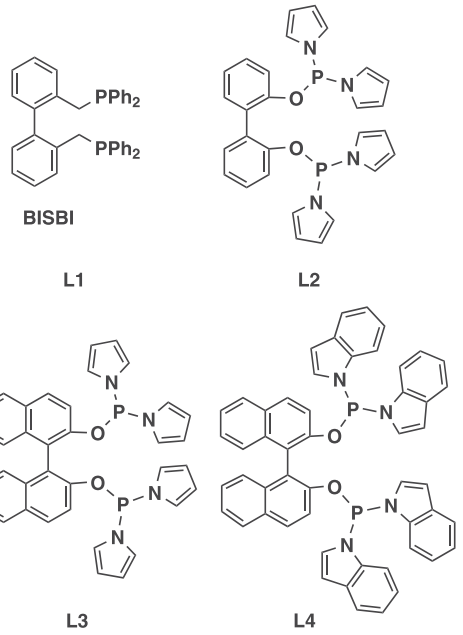
1,3-Propanediol (1,3-PDO) is the raw material for the production of polytrimethylene terephthalate (PTT), a kind of polyester which could be applied in textile and carpet manufacturing owing to its superior properties such as stain resistance, elastic recovery, chromaticity. The production of PTT resin and its downstream products is seriously affected by the synthesis of 1,3-PDO. Although chemical methods,[1] using acrolein or ethylene oxide as starting materials, and biological methods,[2] using glucose or glycerol as starting materials, have been developed to synthesize 1,3-PDO, acrolein is difficult to obtain and quite expensive; besides, high temperature and high pressure are required for the reaction of ethylene oxide with syngas, and the overall efficiency of the biological method needs be increased to meet the industrial requirement. Therefore, identifying a potential

method for the synthesis of 1,3-PDO is quite important to meet the globally increased demand for PTT.

Vinyl acetate is cheap and readily available, and is one of the best candidates for synthesizing 1,3-PDO, because its linear hydroformylation product linear aldehyde could be hydrolyzed and then be hydrogenated to 1,3-PDO. However, preliminary work[3] on the hydroformylation of vinyl acetate is frustrating, with the branched aldehyde dominating the products. Asymmetric hydroformylation focused on branched aldehyde formation from vinyl acetate was widely reported.[4] The best linear-to-branched aldehyde ratio (l/b) achieved so far is 0.8.[5] It is likely that due to the chelation of carbonyl group with rhodium, branched alkyl rhodium complexes might form relatively stable intramolecular five-membered rings (Scheme 1).[6] Therefore, branched aldehydes are the main products in the hydroformylation of vinyl acetate. It is speculated that the ratio of linear to branched aldehyde should be improved if the carbonyl group is removed. With this consideration in mind, vinyl ether was selected as the hydroformylation substrate with the purpose of affording linear aldehyde as the dominant product.

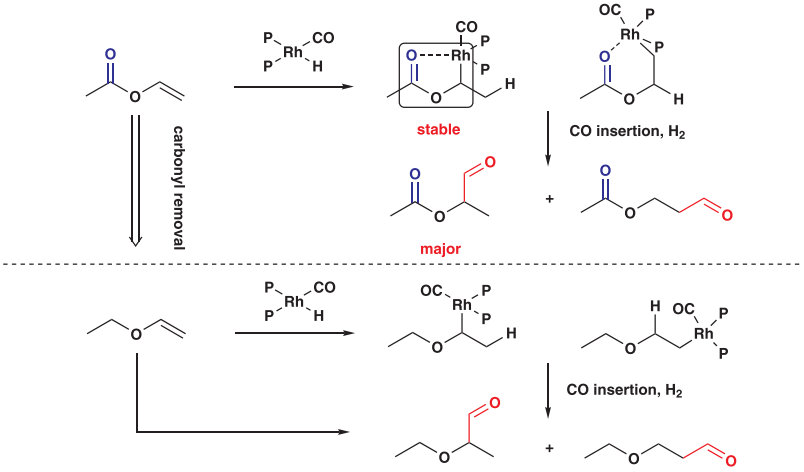
Recently, functionalized olefins such as styrene, acrylate, vinyl acetate, and other vinyl and allyl derivatives have been widely studied in hydroformylation to produce linear or branched aldehydes, because the aldehyde itself and its derivatives are versatile building blocks in organic synthesis and industries.[7] So far, there are only a few systematic reports about hydroformylation of vinyl ether to linear aldehyde.[8]

To guarantee the hydroformylation of vinyl ether in terms of both reactivity and regioselectivity, satisfactory phosphorus ligands are required. Phosphorus ligands usually play a vital role in controlling Rh-catalyzed hydroformylation. It is believed that phosphorus ligands possessing strong π-acceptors were able to make rhodium more electron deficient so that rhodium would readily coordinate to alkene, thus enhancing the



SCHEME 2 Phosphine ligands applied in hydroformylation

reactivity[9]; additionally, the Rh–diphosphorus ligand complex with a large bite angle could promote the formation of rhodium complexes with equatorial–equatorial (ee) configuration, which is the linear aldehyde-preferred configuration, compared with its apical–equatorial (ea) isomer, in hydroformylation.[10] We applied the typical linear aldehyde-preferred diphosphorus ligand BISBI (**L1**) in hydroformylation as a model ligand[11] and on this basis, a pyrrolyl substituent was applied to enhance the π-acceptor properties of phosphorus atom and indolyl substituents to enhance both π-acceptor properties and steric hindrance of the ligand. According to the literature, the dihedral angle between the two moieties of binaphthol is about 104° in the steady state.[12] We wonder whether the binaphthol



SCHEME 1 Hydroformylation of vinyl acetate and ethyl vinyl ether

backbone will be beneficial to the Rh–phosphorus complex with a large bite angle to achieve high linear-aldehyde ratio. Ligands BISBI (**L1**), **L2**, **L3** based on biphenol, and **L4** (Scheme 2) based on the binaphthol skeleton were synthesized and used in the Rh-catalyzed hydroformylation of vinyl ether.[13]

2 | EXPERIMENTAL

2.1 | General

All solvents were purified by standard methods. Reagents were purchased from commercial suppliers and used as received, and moisture-sensitive compounds were stored in a glovebox. ^{1}H, ^{13}C, and $^{31}P\{^{1}H\}$ nuclear magnetic resonance (NMR) spectra were recorded on the Bruker AVANCE III HD-400 MHz in $CDCl_3$ or toluene-d_8 (Bruker, Beijing, P.R. China). GC analysis was performed with Agilent 7890B (KB-1; 30 m × 0.32 mm × 0.25 μm) (Agilent, Shanghai, P. R. China). High-resolution mass spectroscopy was measured on SHIMADZU LCMS-IT-TOF mass spectrometer (SHIMADZU, Kyoto, Japan).

2.2 | Procedure for the catalytic experiments

Hydroformylation studies were conducted in a 25-mL autoclave. In a typical experiment, the reactor was charged with toluene (2 mL), ethyl vinyl ether (10 mmol) and $Rh(acac)(CO)_2$ (0.01 mmol), biphosphorus ligand (0.02 mmol), and monophosphorus ligand (0.04 mmol). The reactor was purged with syngas ($H_2/CO = 1/1$) three times and pressurized to 2 MPa. The mixture was then heated up to the appropriate temperature. Samples were analyzed after 2 hr by GC or ^{1}H NMR with dibromomethane (700 μL) as the internal standard.

2.3 | Preparation of 2,2′-bis{(di[1H-pyrrol-1-yl]phosphanyl)oxy}-1,1′biphenyl (L2)

Under an argon atmosphere, a solution of 2,2′-dihydroxy-1,1′-biphenyl (1.7 g, 9.0 mmol) in 25 mL of tetrahydrofuran (THF) was added dropwise to a solution of chlorodipyrrolylphosphine (3 mL, 18.0 mmol) and triethylamine (6.0 mL, 43.0 mmol) in 30 mL of THF at 0 °C. The $Et_3N{\cdot}HCl$ salt was filtered off after 12 hr of stirring at room temperature and the solvent was removed under vacuum to obtain a yellow oily crude product, which was recrystallized in ethanol to give the desired product as a white solid in 62.4% yield.

2.4 | Preparation of 2,2′-bis{(di[1H-pyrrol-1-yl]phosphanyl)oxy}-1,1′binaphthalene (L3)

Under an argon atmosphere, a solution of 2,2′-dihydroxy-1,1′-(±)binaphthyl (1.4 g, 4.6 mmol) and triethylamine (1.6 mL, 12.0 mmol) in 30 mL THF was added dropwise to a solution of chlorodipyrrolylphosphine (2.3 g, 11.4 mmol) in 20 mL THF at 0 °C. The $Et_3N{\cdot}HCl$ salt was filtered off after 12 hr of stirring at room temperature and the solvent was removed under vacuum to obtain a yellow oily product. The crude product was recrystallized with ethyl alcohol to obtain a white solid (yield: 45.7%).

2.5 | Preparation of 2,2′-bis{(di[1H-indol-1-yl]phosphanyl)oxy}-1,1′binaphthalene (L4)

Under an argon atmosphere, a solution of 2,2′-dihydroxy-1,1′-(±)binaphthyl (1.4 g, 4.6 mmol) and triethylamine (1.6 mL, 12.0 mmol) in 30 mL THF was added dropwise to a solution of chlorodiindolylphosphine (3.45 g, 11.4 mmol) in 20 mL THF at 0 °C. The $Et_3N{\cdot}HCl$ salt was filtered off after 12 hr of stirring at room temperature and the solvent was removed under vacuum to obtain a yellow oily product. The crude product was separated by flash column chromatography with CH_2Cl_2:PE = 3:1 (yield: 35.7%).

2.6 | Preparation of Rh(acac)(2,2′-bis{(di[1H-indol-1-yl]phosphanyl)oxy}-1,1′-binaphthalene) (Rh [acac][L4])

$Rh(acac)(CO)_2$ (25.8 mg, 0.1 mmol) and **L4** (89 mg, 0.11 mmol) were added into 20 mL toluene, stirred in room temperature for 10 min. Many bubbles are produced in this process. Then, the solvent was removed under vacuum and the bright yellow complex was dried at 60 °C. The yield was 99%.

3 | RESULTS AND DISCUSSION

3.1 | Ligand effect on the hydroformylation of ethyl vinyl ether

Ethyl vinyl ether was selected as a model substrate for the hydroformylation. In the presence of rhodium dicarbonyl-2,4-pentanedionate ($Rh[acac][CO]_2$) (0.1 mol%) and diphosphorus ligand (0.2 mol%) or monophosphorus ligand (0.4 mol%), 2 MPa syngas ($H_2/CO = 1/1$) was added

TABLE 1 Ligand effect on the hydroformylation of ethyl vinyl ether

Entry	Ligand	Conversion (%)	l. (%)[a]	b. (%)[b]	Hydrogenation product (%)
1	PPh_3	41	29	71	–
2	P(*N*-pyrrolyl)$_3$	98	26	74	–
3	P (OPh)$_3$	83	33	66	–
4	P(*N*-indolyl)$_3$	19	9	91	–
5	DIPHOS	39	43	57	–
6	**L1**	36	52	48	–
7	**L2**	96	60	40	–
8	**L3**	70	73	27	–
9	**L4**	41	82	18	–

Conditions: ethyl vinyl ether, 1 mL (10 mmol); $Rh(acac)(CO)_2$, 2.6 mg (0.01 mmol);
Toluene, 2 mL. Selectivity was determined by ^1H NMR (supporting information, part VI).
[a]l represents linear aldehyde.
[b]b represents branched aldehyde.

to the solution of ethyl vinyl ether in toluene at 60 °C for 2 hr. Two products were detected by ^1H NMR: 3-ethoxypropanal (l) and 2-ethoxypropanal (b); no diethyl ether was detected. As shown in Table 1, for monophosphorus ligands (Entries 1–4), the excellent and good π-accepting phosphorus ligand P(*N*-pyrrolyl)$_3$, P(OPh)$_3$, achieved high conversion under this mild condition as expected. PPh_3 was a σ-donor ligand, compared with O- and N-substituted phosphorus ligands, which are π-accepting phosphorus ligand, as mentioned previously,[9] and therefore its activity was poor. In the case of P(*N*-indolyl)$_3$, the conversion was determined to be 19% and only 9% linear aldehyde could be detected, which may be caused by significant steric hindrance of the indole substituent. Although the conversion was not satisfactory with the diphosphorus ligand DIPHOS, an increase of regioselectivity was observed (43%). Possessing a larger bite angle than DIPHOS (85°), **L1** (113°) further improved the regioselectivity (Table 1, Entry 6). Subsequently, the diphosphorus ligand **L2** with a structure similar to **L1** was

TABLE 2 Optimizations of the reaction conditions based on **L4**

Entry	P/Rh	T (°C)	P (MPa)	Conversion (%)	l (%)	b (%)	Hydrogenation product (%)
1	0	60	2	Trace	n.d.	/	/
2	1	60	2	60	33	66	–
3	2	60	2	39	80	20	–
4	4	60	2	41	82	18	–
5	6	60	2	35	81	19	–
6	10	60	2	13	70	30	–
7	20	60	2	Trace	n.d.	/	/
8	4	60	8	29	67	33	–
9	4	60	4	39	73	27	–
10	4	60	1	25	75	25	–
11	4	60	0.5	16	70	30	–
12	4	40	2	15	65	35	–
13	4	80	2	80	72	28	4
14	4	100	2	98	52	48	14

Conditions: ethyl vinyl ether, 1 mL (10 mmol); toluene, 2 mL; t = 2 hr. Dibromomethane (700 μL) was added after the reaction as internal standard. Selectivity was determined by GC.
[a]l represents linear aldehyde.
[b]b represents branched aldehyde.

TABLE 3 Substrates scope for the hydroformylation of vinyl ethers using Rh/**L4**

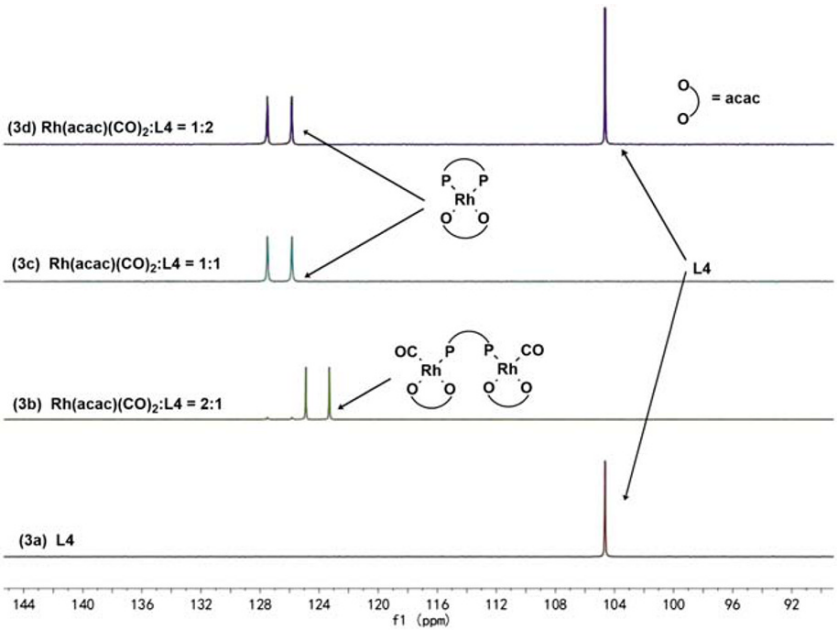
Entry	Substrate	Conversion (%)	l (%)	b (%)	Hydrogenation product (%)
3a	Ethyl vinyl ether	74	82	18	–
3b	2-Chloroethyl vinyl ether	89	68	32	–
3c	Butyl vinyl ether	77	82	18	–
3d	Iso-butyl vinyl ether	78	82	18	–
3e	Tertiary-butyl vinyl ether	75	98	2	–
3f	Cyclohexyl vinyl ether	90	90	10	–
3g	Phenyl vinyl ether	83	50	50	–

Conditions: vinyl ether, 10 mmol; $Rh(acac)(CO)_2$, 2.6 mg (0.01 mmol); **L4**, 16 mg (0.02 mmol); toluene, 2 mL; t = 4 hr. Selectivity was determined by ^1H NMR.
[a]l represents linear aldehyde.
[b]b represents branched aldehyde.

used in the hydroformylation. To our delight, this biphenol skeleton with pyrrolyl-substituted diphosphorus ligand showed remarkable reactivity (96%) and slightly improved regioselectivity (60%). Because the reactivity is guaranteed, the regioselectivity was further improved by increasing the rigidity of backbone (**L3)** and replacing pyrrolyl with indolyl which has a larger steric hindrance **(L4**). In particular, **L4** showed the highest regioselectivity for linear aldehyde (82%) at a little expense of reactivity compared with **L2** and **L3** (Entry 9).

3.2 | Optimization of reaction conditions

We applied **L4** as the model diphosphorus ligand to explore how the reaction condition influenced this reaction. The reaction hardly occurred without the ligand (Table 2, Entry 1); however, a big jump in the conversion and regioselectivity was observed once a small amount of ligand was introduced. The selectivity of linear aldehyde was slightly improved when the P/Rh ratio increased from 1/1 to 4/1 (Entries 2 and 4); however, further increasing the P/Rh ratio resulted in a sharp drop in reactivity. An optimal P/Rh ratio of 4 was preferred to achieve high selectivity to linear aldehyde. The syngas (CO/H_2 = 1/1) pressure also influenced the reaction. Relatively low pressure benefited linear aldehyde (Entries 4 and 8), because the CO-insertion of branched Rh-alkyl species was not favored in the low-pressure syngas condition. However, when the syngas pressure was pretty low, the reactivity dropped sharply and the linear selectivity was slightly decreased (Entries 10 and 11). The effect of temperature on selectivity was not obvious. Moderate temperature was in favor of linear aldehyde. The



SCHEME 3 Stacked $^{31}P\{^1H\}$ NMR spectra of $Rh(acac)(CO)_2$ and **L4** mixed in different molar ratios

hydrogenation product can only be detected at high temperature (80–100 °C)

3.3 | Hydroformylation of other vinyl ethers

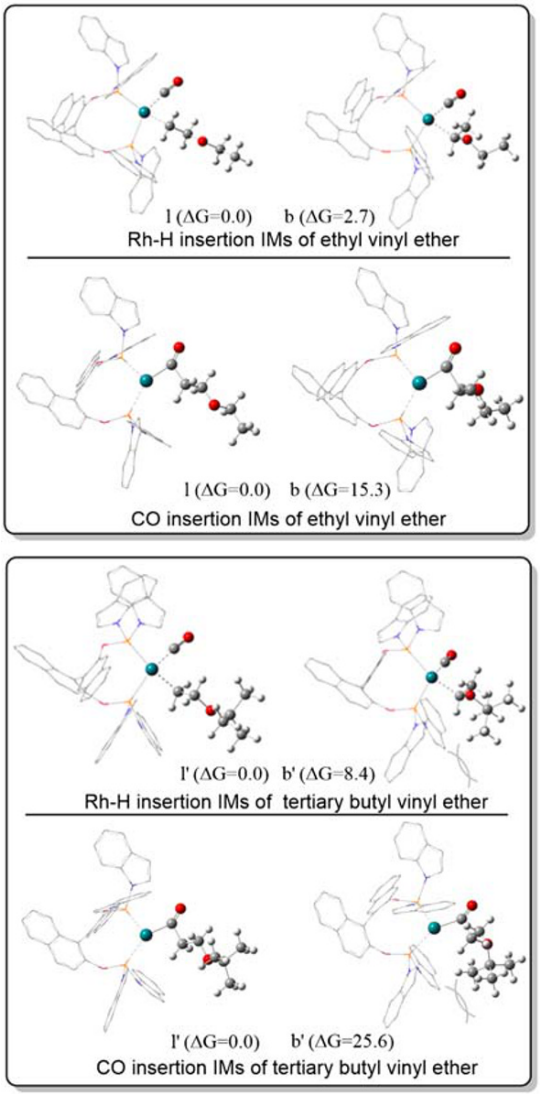
The substrate scope was investigated under the optimized reaction conditions of using 0.1 mol% of $Rh(acac)(CO)_2$ and 0.2 mol% of **L4** (Table 3) and we prolonged the reaction time to 4 hr. In all cases, no hydrogenation product was detected in the hydroformylation of substituted vinyl ethers under 60 °C. The regioselectivity for tertiary butyl-substituted vinyl ether was the highest among all the alkyl-substituted vinyl ethers (3e; l:b ratio of up to 49). This could be attributed to the large steric hindrance between the tertiary butyl group in substrate and the indolyl group in phosphorus ligand, causing branched Rh-alkyl species to be extremely unstable, which will be explained in the "Computational Study" section. Although the reactivity for the phenyl-substituted vinyl ether was comparable with that of cyclohexyl vinyl ether, the regioselectivity for the former (3g) was significantly lower than the latter (3f). We could not figure out the exact reason for this phenomenon, but this might be related to the entire conjugation system involved in the hydroformylation of styrene.[14]

3.4 | Confirmation of catalytic precursor

To understand the origin of the reactivity, diphosphorus ligand **L4** and its complexes with $Rh(acac)(CO)_2$ were characterized by $^{31}P\{^1H\}$ NMR. In toluene-d_8, ligand **L4** showed a singlet at 104.57 ppm (Scheme 3a). Compared with BISBI (at −10 ppm), **L4** was more electron deficient. The rigidity of binaphthol skeleton and the bulky indolyl reduced reactivity compared with **L2** to some extent, but it was still superior to that of BISBI. When $Rh(acac)(CO)_2$ and **L4** were mixed in the molar ratio of 2:1 at ambient temperature, a doublet at 124.88 ppm ($^1J_{P\text{-}Rh}$ = 258.7 Hz) in $^{31}P\{^1H\}$ NMR spectra was observed, which corresponded to the structure $Rh_2(acac)_2(CO)_2$**(L4)** (Scheme 3b). When $Rh(acac)(CO)_2$ and **L4** were mixed in the molar ratio of 1:1, $Rh_2(acac)_2(CO)_2$(**L4**) could not be detected and a new doublet resonance at 127.44 ppm ($^1J_{P\text{-}Rh}$ = 267.5 Hz) appeared (Scheme 3c), which corresponded to Rh(acac)(**L4**). When mixing $Rh(acac)(CO)_2$ and **L4**, many bubbles were generated, so we suspected that it was CO, not acetylacetone, which was replaced by the ligand. Both $Rh_2(acac)_2(CO)_2$(**L4**) and Rh(acac)(**L4**) were further confirmed by high-resolution mass spectroscopy and NMR as expected (characterization can be found in the supporting information, Part IV, Intermediates [IMs] S1 and S2). Further increasing the amount of **L4** to 2 equiv. of $Rh(acac)(CO)_2$ (P/Rh = 4) would not generate new species (Scheme 3d); instead, only Rh(acac)(**L4**) and excess **L4** were observed, indicating that the 1:1 complex was the IM of the reaction.

3.5 | Computational study

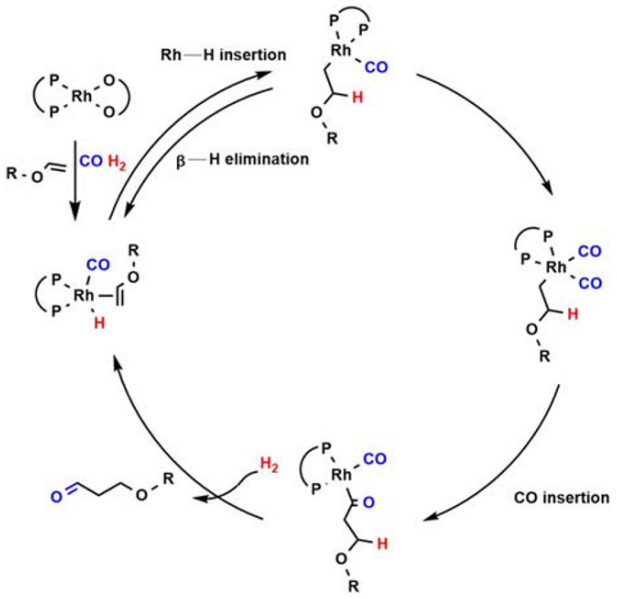
As the entire hydroformylation involves the addition of alkene to rhodium hydride (Rh–H insertion) and CO-insertion steps, hydroformylation **IMs** are produced with certain configuration. Therefore, the formation and evolution of Rh–alkyl IMs in these two steps remain vital to



SCHEME 4 3D model and the energies of Rh-alkyl species; the energies are in kJ/mol. Upper figure corresponds to the ethyl vinyl ether system and the lower figure corresponds to the tertiary butyl vinyl ether system. IM, intermediate

the regioselectivity, based on the density function theory method applied on the Rh/**L4** system at the B3LYP/6-31G(d), LANL2DZ level (the computational details and the optimized structures are available in supplementary information, Part VII). This part focused on the structures and the relative energies of these IMs (Scheme 4). The upper figure in Scheme 4 displays the Rh–H insertion and CO-insertion **IMs** for the ethyl vinyl ethyl system, and the lower figure displays these for the tertiary butyl vinyl ether system.

As shown in Scheme 4, the calculation places the linear **IMs** lower than branched **IMs** in relative energies when ethyl or *t*-butyl vinyl ether was used as substrates. The energy gap between l and b is predicted to be 2.7 and 15.3 kJ/mol for Rh–H and CO-insertion **IMs**, respectively, indicating that the linear **IMs** of ethyl vinyl ether should be more thermodynamically stable in both Rh–H insertion and CO-insertion steps. It should be noted that the calculation predicts that the branched **IMs** suffer from the distinguished steric hindrance between the alkyl group of the substrate and the indole moiety of the ligand. Such a steric hindrance is even more pronounced in the tertiary butyl vinyl ether system. As expected, the energy gap between l′ and b′ is calculated to be 8.4 and 25.6 kJ/mol for Rh–H and CO-insertion IMs, which is remarkably larger than that in the ethyl vinyl ether system. Therefore, the high selectivity could be achieved in tertiary butyl vinyl ether, which is consistent with the experimental observation. Rh/**L4** achieved higher regioselectivity than **L1**, **L2**, and **L3**, which could be attributed to the increase in the steric hindrance effect of branched Rh-alkyl species as a result of the structure rigidity of binaphthol backbone and the large steric hindrance of indolyl substituent on **L4**. Besides, to some extent, the CO insertion of the branched Rh-alkyl was more difficult to occur in comparison with the linear one. This was also confirmed by the result that linear aldehyde was the main product under relatively low syngas pressure.



SCHEME 5 Linear circulation of hydroformylation of vinyl ether

4 | CONCLUSION

In conclusion, we have presented the hydroformylation of vinyl ether with high regioselectivity (up to 98% linear selectivity) through Rh-**L4**, with branched aldehyde as the only by-product. The π-accepting diphosphorus ligand showed significantly improved reactivity (**L1** to **L2**) due to the N and O atoms. Study on the reaction mechanism revealed that the rigidity of backbone and substituent made the linear IM more thermodynamically stable in the Rh/**L4** system. Corresponding to the circulation (Scheme 5), both Rh–H insertion and CO-insertion steps are dominant than those of branched circulation in most cases, especially for tertiary butyl vinyl ether. Further investigation on more effective ligands and the conversion of linear aldehyde to 1,3-PDO is ongoing. This strategy may provide a new idea for the production of 1,3-PDO.

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SUPPORTING INFORMATION

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