

Examination of Milstein Ru-PNN and Rh-Tribi/Tetrabi dual metal catalyst for isomerization-linear-hydroformylation of C4 raffinate and internal olefins

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ARTICLE INFO

Keywords:

Isomerization-linear-hydroformylation
Ru-PNN
Dual metal catalysis
Raffinate
Internal alkenes

ABSTRACT

Isomerization-linear-hydroformylation is demanding, however, not an addressed issue, for production of value-added linear aldehydes by converting cheap and abundant internal alkenes available from bio- & petrochemical industry. In this paper, a dual metal catalysis system combining a Ru-isomerization catalyst and a Rh-linear-hydroformylation catalyst satisfying the “4S” criterions was reported for isomerization-linear-hydroformylation of C4 raffinate (mixed butenes) and internal olefins. The optimized dual metal catalyst system hydroformylated Raffinate II feed to valuable valeraldehyde in 98% linear selectivity ($n:i = 49$), 80% conversion and high activity of 1069 h^{-1} TOF whereas 96% linear selectivity ($n:i = 24$), 71% conversion and 948 h^{-1} TOF were observed using only the Rh-hydroformylation catalyst. Notably, valeraldehyde are produced in million tons scale annually for making non-toxic plasticizer DPHP. Various 2-olefins were also converted to linear aldehydes in > 98% linear selectivity ($n:i > 49$), 78%–82% conversion and high activity of $802\text{--}851 \text{ h}^{-1}$ TOF.

1. Introduction

Hydroformylation is the largest applied homogenous catalysis transformation where CO and H₂ are added into cheap alkenes feedstock for making high-value aldehydes for pharmaceuticals, commodity and fine chemicals among others [1–4]. Over the past 83 years (discovered by Otto Roelen in 1938) [5–7], phosphorus ligands are found crucial for development of active, selective and applicable hydroformylation catalysts. These efforts leads to successful industrial production of linear aldehydes at over 10 million tons scale *via* linear selective hydroformylation of terminal alkenes, such as propylene and higher olefins. However, as cheap and abundant feeds from petrochemical industry, internal alkenes are less reactive and selective for production of value-added linear aldehydes (Fig. 1a). As such, developing a robust isomerization-linear-hydroformylation sequence for converting internal alkenes is of high academic interests and as well industrial importance.

Modification of the Rh-metal by phosphorus ligands is of great

importance for controlling the challenging selectivity and activity of a hydroformylation reaction. Bisphosphorus ligands (2P) with stronger chelating ability afford higher regioselectivities in terminal alkene hydroformylation than monophosphorus ligands (1P), such as triphenylphosphine (TPP) [8]. Bisbi [9–12] and Xantphos [13–15] ligands are representative 2P ligands yielding high linear selectivity in the hydroformylation of terminal alkenes (Fig. 1b). Upon further increasing the local phosphorus concentration and as such chelating possibility, Zhang *et al.* [8,16] introduced triphosphorus and tetraphosphorus ligands (3P and 4P), such as Tribi and Tetrabi as the start-of-the-art, for linear selective hydroformylation reactions. As electron deficient ligands generally make more active catalysts, modified bisphosphorus ligands, such as Naphos [17,18], pyrrole-based bisphosphoramidites [19–22], spiroketal-based bisphosphorus [23,24], and arylphosphite [25,26] also have been reported. However, despite these progresses, limited catalysts show high linear selectivity and activity in isomerization-linear-hydroformylation of internal alkenes. Importantly,

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<https://doi.org/10.1016/j.gresc.2021.10.010>

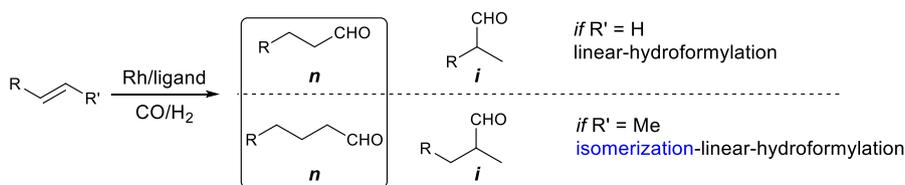
Received 8 September 2021; Received in revised form 27 October 2021; Accepted 28 October 2021

Available online 1 November 2021

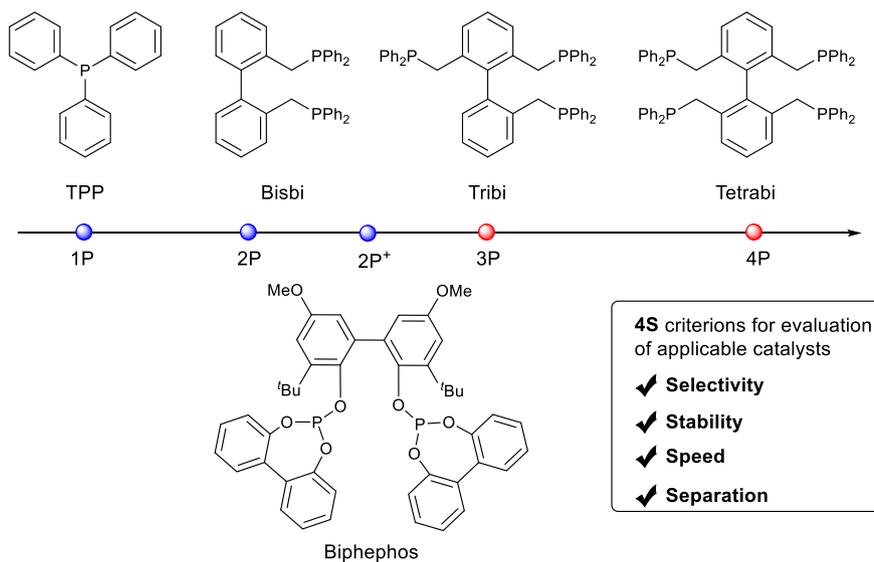
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a. Challenges in linear selective hydroformylation reactions



b. Concept of ligand development for linear selective hydroformylation reactions and the '4S' criteria



c. Concept of dual metal catalysis for challenging isomerization-linear-hydroformylation reactions

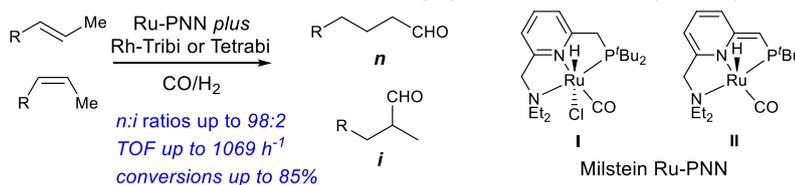


Fig. 1. Dual metal catalysis concept based on our multidentate phosphorus ligands for isomerization-linear-hydroformylation of internal alkenes.

Biphephos [27,28], a bis(triarylphosphite) ligand reported by Union Carbide Corp (abbrev. UCC) in the mid-1980s was successfully commercialized in Raffinate II & III hydroformylation with $n:i$ ratios up to 96/4. The resulting valuable valeraldehyde are used to make a new non-toxic plasticizer bis(2-propylheptyl)phthalate (DPHP), which is a C10 phthalate plasticizer produced from 2-propylheptanol (2-PH) and an ideal replacement for toxic plasticizer DEHP. The annual global production of plasticizer is estimated at 5.5 million tons in 2011, and about 90% of the plasticizer market is dedicated for PVC industry [29,30]. Driven by the huge economic benefits, many similar ligands are developed by groups of DSM [31], Mitsubishi Kasei [32], Evonik [33], BASF [34] and Celanese [35]. However, despite useful selectivity and activity (high speed) obtained at small laboratory scale (< millimolar) conditions, bisphosphite type ligands suffer from less stability due to easy hydrolysis and acidolysis and as well separation issues under the operation conditions. Also, the phosphonic acid formed upon catalyst decomposition can further accelerate the dissociation of P–O bonds, resulting in ligand losses and plugging in the pipelines and as such in separation problems.

Previously our group reported triphosphorus and tetraphosphorus ligands that demonstrated high linear selectivity and activity in the hydroformylation of terminal and some internal alkenes [8,16,36–39]. In

this paper, we reported a dual metal catalysis concept by combining a Ru-PNN-isomerization catalyst and a Rh-Trib/Tetrabi-hydroformylation catalyst satisfying the “4S” criteria (High Linear Selectivity, High Reaction Speed, Longer Term Catalytic Stability, Easy Separation) for isomerization-linear-hydroformylation of mixed butenes (Raffinate II feed) and other internal alkenes as well ($n:i$ ratios up to 98:2, TOF up to 1069 h⁻¹, conversions up to 85%, Fig. 1c). The Milstein Ru-PNN [40,41] complex (PNN:2-di-*tert*-butylphosphino-methyl-6-diethylaminomethylpyridine) was used for internal alkenes isomerization. Tribi and Tetrabi ligands were used for the linear selective hydroformylation of the terminal alkenes obtained upon isomerization. It is important to emphasize that the Rh-multidentate catalysts fulfill “4S” criterion that are important for industrial production of linear aldehydes. Note that a Ru₃(CO)₁₂/Rh-Binaphos dual metal catalysis system initially reported by Beller and co-workers [42] gave rather poor selectivity ($n:i$ ratio 56/44). A Rh/bisphosphite and Shvo's catalyst dual metal catalysis system later reported by Nozaki and co-workers displayed high selectivity of $n:i$ ratio up to 27 for (*Z,E*)-2-octene although alcohols obtained instead of versatile aldehydes [43]. Vorholt [44] and Reek [45] also have reported palladium and rhodium dual metal catalysis system for isomerization-linear-hydroformylation reactions.

2. Results and discussion

Palladium, cobalt and ruthenium based catalysts have been examined in isomerization-hydroformylation process [46–50]. Milstein Ru-PNN complex (I or II) was demonstrated in efficient alkene isomerization whereas it was seldom explored under hydroformylation conditions [51]. As such, we set out to examine the compatibility and potential of this Ru-PNN complex combined with rhodium-Tribi/Tetrabi catalyst in isomerization-linear-hydroformylation of mixed butenes using a self-design batch oxo synthesis unit. The mixed butenes consist of 1-butene (25 mol%), (*Z*)-2-butene (40 mol%) and (*E*)-2-butene (35 mol %) and the hydroformylation reaction was performed at grams scale of 2.25 g (40 mmol). The oxo synthesis unit and the detailed experimental procedures are illustrated in Figs. S5 and S6 (Supporting information). The correction factor (*K*) between mixed butene and decane (internal standard) is given in Fig. S1 (Supporting information). The effects of different ligands, solvents, L/Rh ratios, temperatures, and pressures on *n*:*i* ratio and activity were evaluated, and the results are summarized in Table 1 and details are seen in Table S9 (Supporting information).

Rh-Tribi and Rh-Tetrabi catalysts gave 96% linear selectivity (*n*:*i* 23.4–24.1), activity of 940–973 h⁻¹ TOF and conversions of 70.5%–74.9% (Table 1, entries 1, 2, 4 and 5). In contrast, when 0.025 mol% Ru-PNN (II) was added, both linear selectivity and activity were improved by 2% and >100 h⁻¹ TOF, respectively (Table 1, entries 3 and 6). The results suggest that Ru-PNN isomerization catalyst is compatible with the rhodium hydroformylation catalysis conditions. In particular, Ru-PNN significantly promotes the isomerization of both (*Z*)- and (*E*)-2-butenes to 1-butene for linear selective hydroformylation by Rh-Tribi/Tetrabi catalysts, which also showed interesting results in the isomerization-linear-hydroformylation reactions. The linear selectivity and activity of Rh-Tetrabi are not improved compared to Rh-Tribi in the presence of Ru-PNN catalyst (97.6% vs. 98.0%, 1069 h⁻¹ vs. 1067 h⁻¹, Table 1, entries 3 and 6).

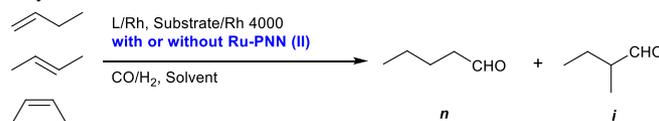
Importantly, the bisphosphorus ligand Bisbi even with higher L/Rh ratio displayed inferior linear selectivity and activity in the absence or presence of even higher amounts of Ru-PNN isomerization catalyst (95.2%–96.2% linear aldehydes, 968 h⁻¹–1033 h⁻¹, Table 1, entries 9–11). The monophosphorus ligand TPP at extremely high L/Rh ratio of 200 yielded an even lowered linear selectivity (63.2% linear aldehyde, *n*:*i* ratio of 1.7, Table 1 entry 10). Industrial applied electron deficient bisphosphorus ligand Biphephos gave inferior linear selectivity although

slightly higher activity thanks to accelerated dissociation of CO and insertion of alkene in the catalytic cycle (96.1% linear aldehyde, *n*:*i* 25.6, 1116 h⁻¹, Table 1, entry 11). This suggests that the stable multidentate ligands are robust for linear selective hydroformylation reactions.

Time courses of butene isomers composition, aldehyde yield and isomerization with the dual catalyst system are shown in Table S3 and Fig. S7 (Supporting information). The apparent isomerization and hydroformylation rates are calculated using linear fitting of butene composition vs. time and aldehyde yield vs. time respectively (fitting results given in Tables S4–S8 in Supporting information). For 1-butene, the most unstable α -olefin is easily isomerized to its (*Z*)-, (*E*)-isomers from 0 to 60 min. The composition versus time shows a decreasing exponential form. The maximum isomerization rate is recorded at 0.65 s⁻¹ from 0 to 30 min, then flatten out at 0.03 s⁻¹ from 30 min to 180 min. For the less stable (*Z*)-2-butene, the rate of forming the *cis*-isomer is larger than its consumption rate for the first 30 min, at 0.41 s⁻¹. Then it keeps isomerizing at 0.10 s⁻¹ until reaction ceased. In contrast to 1-butene and (*Z*)-2-butene, the isomerization rate for the most stable (*E*)-2-butene shows an increasing linear correlation of 0.16 s⁻¹, meaning that the rate of forming (*E*)-2-butene is much bigger than its isomerization rate. Hydroformylation rate (aldehyde yield) for mixed butene shows a linear behaviour of 0.38 s⁻¹. The percentage of isomerization increases sharply from 0 to 14.7% at the first 30 min, then plateau to around 12%–15%. For experiments without the second Ru catalyst, time courses of butene isomers composition are similar. However, the hydroformylation rate and isomerization percentage are relatively lower than the dual-metal catalyst, affording 0.33 s⁻¹ and 10.6%–13.2% respectively. Also, an inferior linear aldehyde selectivity and conversion was observed upon analysing the final reaction mixtures.

Isomerization-linear-hydroformylation of C4 raffinate providing valeraldehyde is industrially applied for making a new non-toxic plasticizer DPHP. Besides, isomerization-linear-hydroformylation of linear chain internal alkenes provides important aldehydes for detergent industry. Thus, we further investigated the dual metal catalysis system in converting other 2-alkenes to value-added linear aldehydes using the Ru-PNN isomerization catalyst. The correction factors are given in Figs. S2–S4 (Supporting information). Long chain internal alkenes are more challenge than mixed butenes and as such reaction conditions (ligand/metal ratio, temperature, syngas pressure, reaction time and solvent) were reoptimized in the hydroformylation of 2-octene using Ru-PNN and Rh-Tribi catalysts (Table S10 in Supporting information).

Table 1
Dual metal catalyzed isomerization/hydroformylation of mixed butene^a.



Entry	Ligand	L/Rh	Ru. (mol%)	Conv.(%)	<i>n</i> : <i>i</i>	Linear (%)	TOF(h ⁻¹) ^b
1	Tribi	3	N/A	70.5	24.0	96.0	940
2	Tribi	3	N/A	71.1	24.1	96.0	948
3	Tribi	3	0.025	80.0	49.1	98.0	1067
4	Tetrabi	3	N/A	74.5	23.4	95.9	973
5	Tetrabi	3	N/A	74.9	19.0	95.0	999
6	Tetrabi	3	0.025	81.6	39.9	97.6	1069
7	Bisbi	6	N/A	73.4	19.9	95.2	979
8	Bisbi	6	N/A	72.6	23.0	95.8	968
9	Bisbi	6	0.05	77.5	25.4	96.2	1033
10 ^c	TPP	200	N/A	61.6	1.7	63.2	821
11 ^d	Biphephos	4	N/A	83.7	25.6	96.1	1116

^a S/C = 4000 (Rh = 159 ppm in reacting solution), C4 raffinate = 40 mmol (3.57 mL), 110 °C, CO/H₂ = 4.25/4.25 bar, reaction time = 3 h, solvent = 4.3 mL, decane as internal standard (0.64 mL), entries 1, 4, 7, 10 and 11, toluene as solvent, entries 2, 3, 5, 6, 8 and 9, 0.5 mL toluene and 3.8 mL 1-butanol were used as solvent.

^b Turnover frequency, number of moles of substrate consumed/(reaction time × moles of catalyst).

^c TPP: Triphenylphosphine.

^d CO/H₂ = 5/5 bar, T = 90 °C.

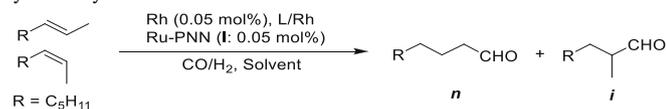
Importantly, under optimized reaction condition of L/Rh = 4, 4 h, 120 °C and CO/H₂ = 2.0/2.0 bar, a significant solvent effect on the selectivity and conversion was observed (Table 2). In general, non-polar and polar aprotic solvents, such as toluene, 1,4-dioxane, and acetonitrile, resulted in inferior activity and linear selectivity (Table 2, entries 1–7). In contrast, high activity and selectivity were achieved in polar protic solvents (Table 2, entries 8–10, 12). Notably, significantly enhanced selectivity and activity were observed (97.9% vs. 94.5% linear selectivity) upon using Ru-PNN/Rh-Tribi dual catalyst compared to Rh-Tribi catalyst (Table 2, entries 11, 13).

Table 3 summarized the results using dual metal catalysis coming the Ru-PNN isomerization catalyst and Rh-catalyst with multidentate or bidentate phosphorus ligands under optimized reaction conditions. In the isomerization-linear-hydroformylation of (*Z*)-2-hexene, (*Z,E*)-2-octene and (*Z,E*)-2-nonene, Ru-PNN/Rh-Tribi and Ru-PNN/Rh-Tribi dual catalyst gave superior linear selectivity and activity than Ru-PNN/Rh-Bisbi dual catalyst where the linear selectivity and activity were increased by 2.3%–3.7% and 74–331 h⁻¹ TOF, respectively. The significantly improved selectivity and activity for the long chain substrates is likely originated from faster isomerization of internal alkenes to terminal position than its hydroformylation by the dual metal catalyst as isomerization of long chain substrate to terminal alkenes is more complex and difficult than shorter ones.

To gain insights in the Ru-PNN/Rh-Tribi and Ru-PNN/Rh-Tribi dual catalyst for isomerization-linear-hydroformylation reactions, control experiments were conducted. The results are summarized in Table 4. Isomerization conversion of various 2-alkenes were observed under syngas conditions, indicating the isomerization reaction by Ru-PNN catalyst. From 35.9% to 33.4% conversions were observed from short (*E*)-2-butene to longer (*Z,E*)-2-octene (Table 4, entries 1, 3, 5, 7). Thus, an increase of substrate and as such the steric hindrance at the double bond deactivates the isomerization by Ru-PNN. Rh-Tetrabi catalyst gave

Table 2

Solvent effects for dual catalyst system in the isomerization-linear-hydroformylation of 2-octenes^a.



Entry	Solvent	Conv. (%)	Isomer. (%) ^b	<i>n</i> : <i>i</i>	Linear (%)	TON ^c
1	PhMe	54.5	22.3	17.2	94.5	1090
2	CH ₂ Cl ₂	59.5	11.4	17.9	94.7	1190
3	EtOAc	33.2	15.3	14.8	93.7	664
4	1,4-Dioxane	39.6	15.6	15.4	93.9	792
5	MeCN	45.2	21.6	20.5	95.3	904
6	THF	62.1	24.3	16.3	94.2	1242
7	C ₂ H ₄ Cl ₂	19.7	4.6	14.3	93.5	394
8	EtOH	62.8	29.5	19.4	97.1	1256
9	<i>i</i> PrOH	64.7	28.4	20.5	95.3	1294
10 ^d	MeOH	85.9	41.8	46.5	97.9	1718
11 ^e	MeOH	76.2	35.8	17.1	94.5	1524
12 ^f	TFE	81.1	57.5	54.6	98.2	1632
13 ^f	TFE	75.2	44.2	19.7	95.2	1504

^a Reaction conditions: S/C = 2000, Rh(acac)(CO)₂ = 1.0 mmol/L, Tribi as ligand, L/Rh = 4, CO/H₂ = 2.0/2.0 bar, 120 °C (140 °C oil bath), reaction time = 4 h, *i*PrOH/substrate, 1/1 M ratio, decane as internal standard. A mixture of 19.5% *cis*-2-octene and 80.5% *trans*-2-octene, determined by GC. Results determined by GC, average of 2 repeated runs.

^b Percentage of isomerized alkene in the total product.

^c Turnover number (TON), determined on the basis of alkene conversion by GC analysis.

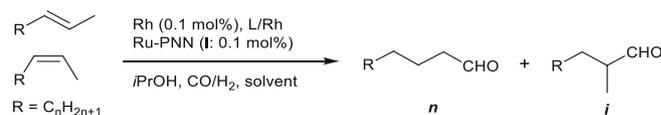
^d Ru-PNN/Rh-Tribi dual catalyst complex was used for reaction.

^e Rh-Tribi single catalyst complex was used for reaction.

^f Entries 12 and 13: same condition as entry 10 and entry 11, except 2,2,2-trifluoroethanol was used as solvent.

Table 3

Dual metal catalyzed isomerization-linear-hydroformylation of challenging long chain 2-alkenes^a.



Entry	Olefin	Ligand	Conv. (%)	Isomer (%)	<i>n</i> : <i>i</i>	Linear (%)	TON
1	(<i>Z</i>)-2-hexene	Bisbi	77.7	37.5	23.4	95.9	777
2	(<i>Z</i>)-2-hexene	Tribi	81.9	34.1	49.0	98.0	819
3	(<i>Z</i>)-2-hexene	Tetrabi	85.1	39.9	68.5	98.5	851
4	(<i>Z,E</i>)-2-octene	Bisbi	63.8	31.7	26.8	96.4	638
5	(<i>Z,E</i>)-2-octene	Tribi	77.6	34.8	67.9	98.6	776
6	(<i>Z,E</i>)-2-octene	Tetrabi	80.2	34.7	74.4	98.7	802
7 ^b	(<i>Z,E</i>)-2-nonene	Bisbi	49.3	24.9	16.9	94.4	493
8 ^b	(<i>Z,E</i>)-2-nonene	Tribi	61.1	20.5	31.3	96.9	611
9 ^b	(<i>Z,E</i>)-2-nonene	Tetrabi	82.4	33.1	50.7	98.1	824

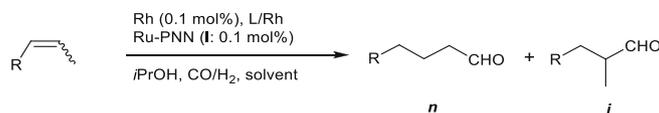
^a S/C = 1000, L/Rh = 6 for Bisbi, L/Rh = 4 for Tribi and Tetrabi, CO/H₂ = 2.0/2.0 bar, reaction time = 2 h, 120 °C (140 °C oil bath), *i*PrOH/substrate, 1/1 M ratio, decane as internal standard. Results determined by GC.

^b A mixture of 36.8% (*Z*)-2-nonene and 63.2% (*E*)-2-nonene is used in entries 7–9.

high conversions thanks to the isomerization-linear-hydroformylation process that depletes the thermodynamically stable internal alkenes upon the terminal alkenes converting to linear aldehydes (from 64.4% to 76.4% conversions, Table 4, entries 2, 4, 6, 8). However, the linear selectivity was much lower than the experiments performed with dual metal catalyst (from 92.1% to 97.0% linear selectivity, Table 4, entries 2, 4, 6, 8). Importantly, α -olefin percentage is higher for Ru-PNN catalyst than Rh-Tetrabi catalyst for unknown reason and the highest isomerization to α -olefin is 5.4% for (*Z,E*)-2-octene albeit with the lowest TOF value of 33 h⁻¹, 4.3% for (*E*)-2-butene, follow by 3.4% for (*Z*)-2-butene and 2.7% for (*Z*)-2-hexene (Table 4, entries 7, 1, 3 and 5). Also, as expected, the Rh-Tetrabi catalyst displayed a lower activity for all the internal alkenes studied in Table 4 compare to the dual metal catalysis results presented in Tables 2 and 3. On the basis of the catalysis experiments and control experiments and the alkene isomerization mechanism reported [51], we proposed dual metal Ru-PNN and Rh-Tribi/Tetrabi catalytic isomerization-linear-hydroformylation (Fig. 2). In the isomerization cycle, **II** reacts with alcohol to form **A**, upon simultaneously dissociation of the hemilabile N(Et)₂ group. This allows the formation of a vacant coordination site to the hydride. Alkene binding results in **B**. The ruthenium-alkyl complex **C** is formed upon hydride-insertion. The following β -hydride elimination and alkene dissociation from **D** to **E** lead to formation of isomerized alkenes, including terminal alkene entering the linear hydroformylation cycle, leading to the production of linear aldehydes.

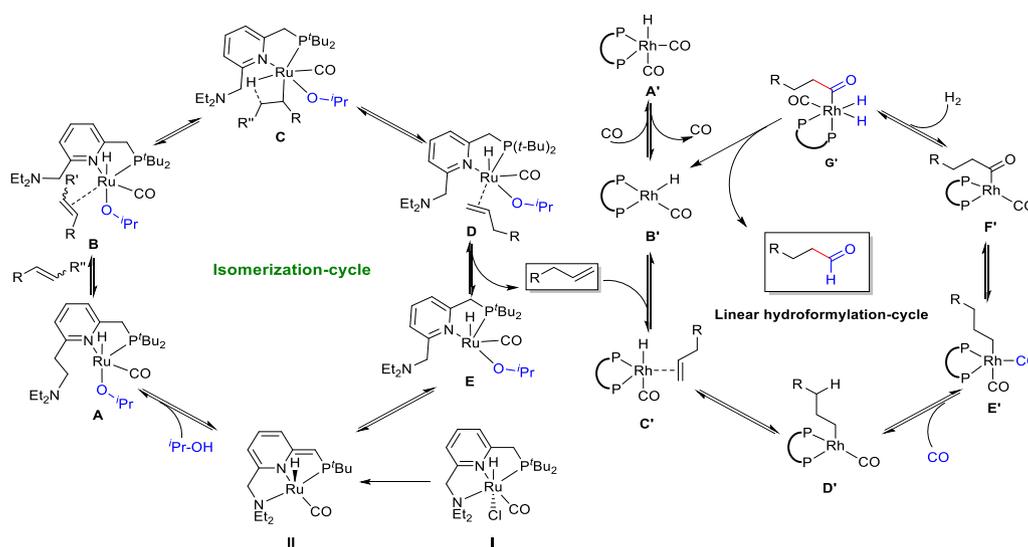
3. Conclusion

Isomerization-linear-hydroformylation is not a well solved issue in converting cheap and abundant internal alkenes available from bio- & petrochemical industry. In this paper, we reported a dual metal catalysis concept for isomerization-linear-hydroformylation of C₄ raffinate and other long chain 2-alkenes feeds with excellent selectivity and activity (*n*:*i* ratios up to 98:2, TOF up to 1069 h⁻¹, and conversions up to 85%).

Table 4Isomerization control experiments for 2-olefins^a.

Entry	Olefin	Catalyst system	Conv.	1-Alkene	(Z)-2-Alkene	(E)-2-Alkene	(Z,E)-3-Alkenes	(Z,E)-4-Alkenes	<i>n</i> : <i>i</i>	linear	TOF (h ⁻¹)
1	(E)-2-butene	Ru-PNN(II)	35.9%	4.3%	17.8%	N/A	N/A	N/A	N/A	N/A	90
2	(E)-2-butene	Rh-Tetrabi	65.4%	1.2%	24.4%	N/A	N/A	N/A	11.6	92.1%	327
3	(Z)-2-butene	Ru-PNN(II)	37.7%	3.4%	N/A	20.4%	N/A	N/A	N/A	N/A	94
4	(Z)-2-butene	Rh-/Tetrabi	64.4%	1.8%	N/A	N/A	N/A	N/A	14.1	93.4%	322
5	(Z)-2-hexene	Ru-PNN(I)	34.0%	2.7%	N/A	30.0%	1.0%	N/A	N/A	N/A	34
6	(Z)-2-hexene	Rh-Tetrabi	76.4%	1.9%	N/A	47.7%	5.9%	N/A	28.0	96.5%	382
7	(Z,E)-2-octene	Ru-PNN(I)	33.4%	5.4%	N/A	N/A	2.6%	N/A	N/A	N/A	33
8	(Z,E)-2-octene	Rh-Tetrabi	73.2%	0.4%	N/A	N/A	6.7%	38.7%	32.5	97.0%	366

^a S/C = 1000, L/Rh = 3, CO/H₂ = 4.25/4.25 bar and 110 °C for entries 1–4, CO/H₂ = 2.0/2.0 bar and 120 °C (140 °C oil bath) for entries 5–8, iPrOH/substrate, 1/1 ratio, decane as internal standard. Results were determined by GC.

**Fig. 2.** Proposed isomerization-linear-hydroformylation mechanism of the Ru-PNN and Rh-Tribi/Tetrabi dual metal catalysis system.

The dual metal catalysis system consists of a Milstein Ru-PNN catalyst and an Rh-multidentate-ligand catalyst, *i.e.* Rh-Tribi or Rh-Tetrabi, for isomerization of internal alkenes to terminal alkenes and linear selective hydroformylation of the *in-situ* formed terminal alkenes, respectively. Compared to only Rh-catalyst and bench-reference Bisbi and Biphephos rhodium catalysts, significantly improved linear selectivity and activity were shown. The multidentate phosphorus ligands Tribi or Tetrabi are excellent “4S” catalyst regarding industrial applications. Further work and insights in this research line will be reported in due course.

4. Experimental

4.1. Standard procedure for regioselective isomerization-linear-hydroformylation of C₄ raffinate with Tribi

For dual metal catalysis experiment, a stainless steel (150 mL) autoclave equipped with a magnetic stirring bar was loaded with ligand Tribi (30 μmol, 22.5 mg) and Rh(acac)(CO)₂ (10 μmol, 2.6 mg). 0.5 mL toluene and 3.8 mL 1-butanol were added subsequently to dissolve the catalyst (Rh concentration: 247 ppm). The mixture was stirred for 30 min. Then isomerization catalyst II (10 μmol, 4.9 mg) was added to the Rh-Tribi complex solution and stirred for another 10 min. Decane (0.64 mL) was added as internal standard and the autoclave was sealed under argon. The whole system was purged with argon three times. A syringe pump

transferred pressurized C₄ raffinate (40 mmol) through an electric injection valve to the autoclave. The autoclave was charged with CO (4.25 bar) and H₂ (4.25 bar) and heated to 110 °C. After 3 h, the autoclave was cooled in icy water. Reaction sample was taken carefully *in situ* through a 1/8-inch tube connected to a sampling needle valve without evacuating the autoclave. The sample was immediately analyzed by GC-MS and GC.

4.2. Standard procedure for regioselective isomerization-linear-hydroformylation of 2-olefins with Tribi

For dual metal catalyst experiment, a vial (5 mL) with a magnetic stirring bar was loaded with ligand Tribi (4 μmol, 3.0 mg) and Rh(acac)(CO)₂ (1 μmol, 0.26 mg, 0.1 mL of 10 mm solution in DCM). The Rh-Tribi mixture was stirred for 30 min. Then isomerization catalyst I (1 μmol, 0.49 mg) was added to the Rh-Tribi complex solution and stirred for another 10 min. Decane (0.1 mL) was added as internal standard followed by iPrOH (1 mmol), 2-olefins (1 mmol) and MeOH to bring up the total volume to 1 mL. The reaction mixture was transferred to a 50 mL autoclave under argon atmosphere. The autoclave was purged with argon three times, charged with CO/H₂ (1/1, 4 bar) and stirred at 120 °C (140 °C oil bath). After 2 h, the autoclave was cooled in icy water, and the pressure are carefully released in a well-ventilated hood. By passing the reaction mixture through a short silica column, the purified sample was analyzed by GC-MS and GC.

Declaration of competing interest

The authors declare no conflict of interest.

Acknowledgments

R. Zhang gratefully acknowledges the Free Exploration Fund from the Science and Technology Innovation Committee of Shenzhen (No. JCYJ20170817104824122). We are grateful for the financial support from National Natural Science Foundation of China (No. 22001113) and Guangdong Provincial Key Laboratory of Catalysis (No. 2020B121201002).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gresc.2021.10.010>.

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