Catalysis Communications 12 (2011) 403–407

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Selective hydroformylation of 1-hexene to branched aldehydes using rhodium complex of modified bulky phosphine and phosphite ligands

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ARTICLE INFO

Article history:
Received 23 September 2010
Received in revised form 14 October 2010
Accepted 27 October 2010
Available online 4 November 2010

Keywords:
Hydroformylation
1-Hexene
Monodentate bulky phosphine
Phosphite
Selectivity to branched aldehydes

ABSTRACT

The selective hydroformylation of 1-hexene to branched aldehydes was investigated using rhodium complex of tri-1-naphthylphosphine PNp_3 and tri-1-naphthylphosphite $P(ONp)_3$. The PNp_3 and $P(ONp)_3$ ligands having more steric nature than PPh_3 enhanced the formation of branched aldehydes at 110 °C and 4.0 MPa syngas pressure. The branched aldehyde selectivity increased remarkably (82%) by adding $P(ONp)_3$ as auxiliary ligand in Rh/PNp_3 catalyzed hydroformylation of 1-hexene. The high selectivity for the branched aldehydes is due to rapid alkene isomerization producing internal alkenes followed by hydroformylation to yield branched aldehydes.

1. Introduction

Hydroformylation of olefins is an important industrial process for obtaining aldehydes via C–C formation catalyzed by cobalt or rhodium complex modified with ligand [1–3]. Chemoselectivity to aldehydes and regioselectivity to linear or branched aldehyde is one of the important issues in the hydroformylation. The catalytic systems which give high activity and selectivity (chemo- as well as regio-) are more attractive. Homogeneous catalysts are a tool of choice as they display high activity and selectivity and their properties can be tailored using specially designed ligands. The ligands play a significant role in hydroformylation reactions for achieving good activity, selectivity and regioselectivity. Varieties of modified monodentate and bidentate phosphine/phosphite ligands are synthesized by fine tuning their electronic and steric properties to address the aldehyde regioselectivity [4–9]. The branched aldehyde is mainly obtained by Rh catalyzed hydroformylation of styrene and relates substrates, due to electronic reasons [10–12]. In the case of long chain alkenes hydroformylation, the linear aldehyde is desired while in hydroformylation of functionalized olefins such as styrene and vinyl acetate, the branched aldehydes are the desirable products. However, interests in selective formation of the branched aldehydes in the case of linear alkene have increased recently due to their use in the preparation of polyols and plasticizers. [13–15]. The production of branched aldehydes already represents 9% of the world consumption of oxo chemicals and is expected to increase steadily in the near future [16].

The catalytic systems which give branched aldehydes regioselectivity in linear alkene are limited. The influence of *o*-alkyl substituted triphenylphosphine ligands on the activity and regioselectivity in hydroformylation of propene and 1-hexene was investigated by Riihimaki and co-workers [13–15]. The results indicated that *o*-alkyl substituted triphenylphosphine ligands enhance the branched aldehydes selectivity. However, initial activity decreases as cone angle of ligand increases. It has been suggested that bulky phosphine/phosphite ligands prefer lower coordination number complexes and favors the branched aldehydes [13–17]. Moreover, in the hydroformylation of 2-butene catalyzed by $PtCl_2(cod)/SnCl_2$, the addition of *o*-methyl phenyl diphenyl phosphine enhanced the branched aldehyde selectivity [18].

Herein, we are reporting a protocol for the rhodium catalyzed selective hydroformylation of 1-hexene to branched aldehydes using bulky phosphine, PNp_3 and phosphite, $P(ONp)_3$ as ligands. The bulky PNp_3 and $P(ONp)_3$ ligands increased the selectivity to branched aldehydes under optimum condition. The high selectivity to branched aldehydes (82%) was obtained with high conversion and high aldehyde chemo selectivity.

2. Experimental

2.1. General remarks

The ligand synthesis was performed using standard Schlenk technique under nitrogen atmosphere. THF was distilled from

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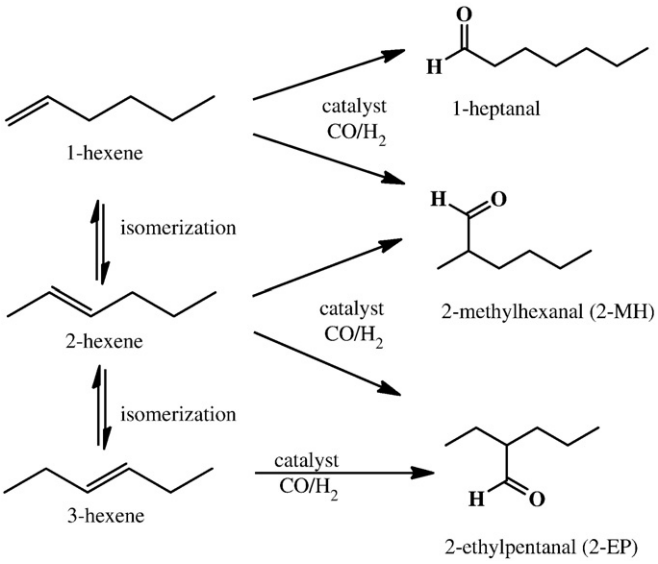
doi:10.1016/j.catcom.2010.10.026



Scheme 1. Hydroformylation of 1-hexene.

sodium/benzophenone prior to use. PCl_3 and 1-bromonaphthalene were obtained from S.D. Fine Chemicals, India, and used as received. Anhydrous toluene, $[Rh(CO)_2acac]$, 1-hexene, triphenylphosphine PPh_3, tricyclohexylphosphine PCy_3, tris(2,4,6-trimethoxyphenyl) phosphine $(2,4,6\text{-}MeO\text{-}C_6H_2)_3P$ and triphenylphosphite $P(OPh)_3$ were purchased from Sigma-Aldrich Chemicals, USA and were used as received. The syngas (99.9%) was procured from Hydro Gas India Pvt. Ltd., India. PNp_3 was synthesized according to reported procedure [13] (see supporting information). The $P(ONp)_3$ was synthesized as per reported procedure [19]. The steric parameter of the ligand can be determined by cone angle. Crystallographic data for PNp_3 (see supporting information) and $P(ONp)_3$ [19] have been used for the cone angle calculation. Crystallographic cone angles for PNp_3 and $P(ONp)_3$ were 196° and 166° respectively.

The hydroformylation reactions were performed in 100 mL stainless steel autoclave (Autoclave Engineers, EZE-Seal Reactor, USA). In a typical hydroformylation experiment, required amount of $[Rh(CO)_2acac]$, ligand, substrate and solvent were charged into the reactor. The stirrer was adjusted to 1000 rpm. The reactor was flushed three times with nitrogen followed by flushing syngas twice at room temperature. The reactor was brought to the desire reaction temperature within 30 min; and pressurized with the desired syngas pressure. The reaction was initiated by stirring. After preset reaction time, the stirring was stopped, reactor was cooled down to room temperature, depressurized, flushed with N_2 and opened to collect final sample for a GC analysis. The reaction products were analyzed on Shimadzu GC-17A gas chromatograph equipped with a flame ionization detector having 5% diphenyl- and 95% dimethyl siloxane capillary column (60 m length, 0.25 mm diameter).

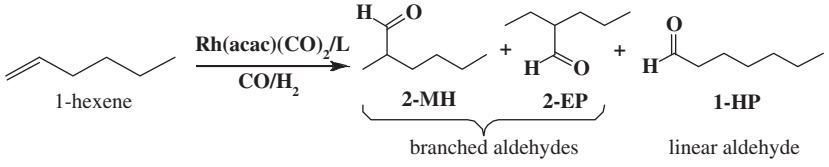
3. Results and discussion

The isomerization–hydroformylation of 1-hexene was studied first using $[Rh(CO)_2acac]$ as the catalyst precursor and PNp_3 as ligand. The reaction products were 1-heptanal (1-HP), 2-methylhexanal (2-MH) and 2-ethylpentenal (2-EP) along with 2-hexene and 3-hexene, the isomerization of 1-hexene as side products (Scheme 1). Branched to linear aldehyde ratio was calculated by considering both the branched aldehydes; 2-methylhexanal (2-MH), 2-ethylpentanal (2-EP) and the linear aldehyde 1-heptanal (1-HP).

3.1. Effect of temperature on Rh/PNp_3 catalyzed hydroformylation of 1-hexene

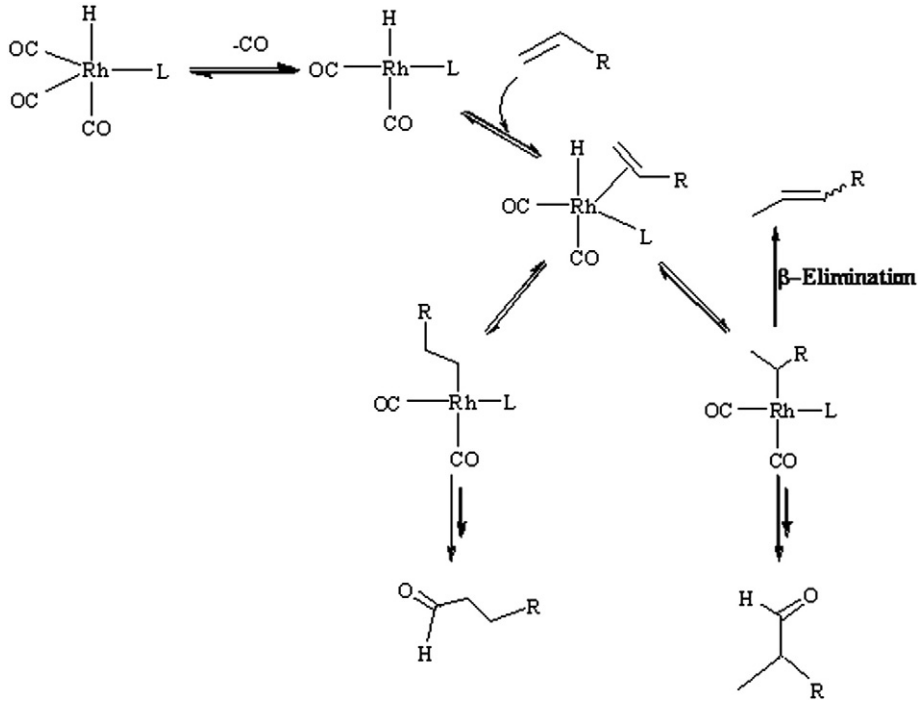
The reaction temperature plays a significant role in isomerization–hydroformylation. The conversion and selectivity data for Rh/PNp_3 catalyzed hydroformylation of 1-hexene performed at different temperatures (70–120 °C), under 4.0 MPa syngas pressure, are summarized in Table 1. With an increasing in temperature, the conversion and isomerization of 1-hexene increased. However, chemoselectivity toward aldehyde decreased with an increase in reaction temperature. The decrease in aldehydes selectivity at higher temperature is mainly due to increase in the isomerized product. The hydroformylation activity of internal alkenes is less as compare to 1-alkene [20]. The degree of isomerization depends on the reaction conditions. The alkene coordination with rhodium forms primary and secondary alkyl-rhodium species (Scheme 2). At higher temperature secondary alkyl-rhodium species gives back to isomeric alkenes by β-elimination as it has higher tendency to undergo β-elimination than the primary one [21]. As a result the amount of isomerization product increased from 19 to 31% as the temperature increases from 70 to 120 °C (Table 1). Interestingly, selectivity to branch aldehydes increased from 55 to 78% with an increase in temperature (70–120 °C). The best agreement between the branched aldehydes

Table 1
Effect of temperature on Rh/tri-1-naphthyl phosphine catalyzed hydroformylation of 1-hexene.



Entry	Temp. (°C)	Conv.[a](%)	Iso.[b](%)	Ald.[c](%)	Selectivity (%) [d]			B/l [e]
					2-EP	2-MH	1-HP	
1	70	88	19	81	5	50	45	55/45
2	80	98	21	79	7	52	41	59/41
3	90	98	24	76	12	53	35	65/35
4	100	98	25	75	15	55	30	70/30
5	110	99	29	71	20	58	22	78/22
6	120	99	31	69	21	56	22	77/22

Reaction conditions: Sub/cat. = 2000, $[Rh(CO)_2acac]$ = 0.23 mmol/L, P/Rh = 6.0, Syngas pressure (1:1) = 4.0 MPa, solvent (toluene) = 50 mL, reaction time = 60 min.
[a] Conversion of 1-hexene.
[b] Selectivity to isomerization.
[c] Selectivity to aldehydes.
[d] Regioselectivity to aldehydes.
[e] Branched aldehydes (2-MH and 2-EP) to linear aldehyde ratio.



Scheme 2. Mechanism for the hydroformylation of 1-alkene with possible pathways.

selectivity and aldehyde chemoselectivity was achieved at 110 °C and selected for further optimization.

3.2. Effect of syngas pressure on Rh/PNp_3 catalyzed hydroformylation of 1-hexene

The 1-hexene hydroformylation catalyzed by Rh/PNp_3 system was studied at 110 °C at different syngas pressure (1.0–6.0 MPa). The total syngas pressure was found to affect the isomerization and selectivity to branched aldehydes (Table 2). The selectivity to the branched aldehydes was comparatively low at low syngas pressure and increased with an increase in the syngas pressure, whereas the isomerization decreased gradually with increase in the syngas pressure. At low pressure (1.0 MPa), isomerization of 1-hexene was high (96%). The internal olefins (2-hexene and 3-hexene) are less reactive than terminal alkenes; and require comparatively high syngas pressure for hydroformylation [20]. As a result only 4% aldehyde selectivity was obtained with low regioselectivity (50/50) at 1.0 MPa syngas pressure. The increase in the syngas pressure considerably enhanced the selectivity to branched aldehydes. The hydroformylation of internal olefins (2-hexene and 3-hexene) occurred with an increase in syngas pressure (1.0–6.0 MPa) [22]. Thus, selectivity to branched aldehydes (2-methylhexanal and 2-ethylpentanal) increased from 50 to 78% (Table 2). The marked increase in branched aldehydes selectivity may be due to the rapid 1-hexene isomerization concurrently producing 2- and 3-hexenes which yielded branched aldehydes. It is also evident from the relative rates of 1-hexene isomerization and hydroformylation (Table 2) at different syngas pressure. In contrast to this, Klein et al. reported the excellent selectivity to linear aldehyde in the hydroformylation of olefin using NAPHOS-type ligands through isomerization of internal olefin [23].

3.3. Effect of ligands on hydroformylation of 1-hexene

For comparison, a number of selected monodentate phosphorous ligands having different steric and electronic character were screened for the rhodium catalyzed isomerization–hydroformylation of 1-hexene under the identical reaction conditions (temp. 110 °C, 4.0 MPa syngas pressure). The hydroformylation of 1-hexene is also studied using [Rh$(CO)_2$acac] as catalyst. The steric character of ligands remarkably

Table 2
Effect of syngas pressure on Rh/tri-1-naphthyl phosphine catalyzed hydroformylation of 1-hexene.

Entry	Press. (MPa)	Conv.[a](%)	Iso.[b](%)	R_1[c] $\times 10^{-3}$(M min^{-1})	Ald.[d](%)	R_2[e] $\times 10^{-3}$(M min^{-1})	Selectivity (%) [f]			B/I [g]
							2-EP	2-MH	1-HP	
1	1.0	97	96	7.21	4	0.30	–	50	50	50/50
2	2.0	97	91	6.84	9	0.67	8	56	36	64/36
3	3.0	98	57	4.33	43	3.26	19	60	21	79/21
4	4.0	99	29	2.23	71	5.45	20	58	22	78/22
5	5.0	99	10	0.77	90	6.90	22	56	22	78/22
6	6.0	99	4	0.31	96	7.34	22	55	23	77/23

Reaction conditions: Sub/cat. = 2000, [Rh$(CO)_2$acac] = 0.23 mmol/L, P/Rh = 6.0, Temperature = 110 °C, solvent (toluene) = 50 mL, reaction time = 60 min.
[a] Conversion of 1-hexene.
[b] Selectivity to isomerization.
[c] Rate of isomerization.
[d] Selectivity to aldehydes.
[e] Rate of hydroformylation.
[f] Regioselectivity to aldehydes.
[g] Branched aldehydes (2-MH and 2-EP) to linear aldehyde ratio.

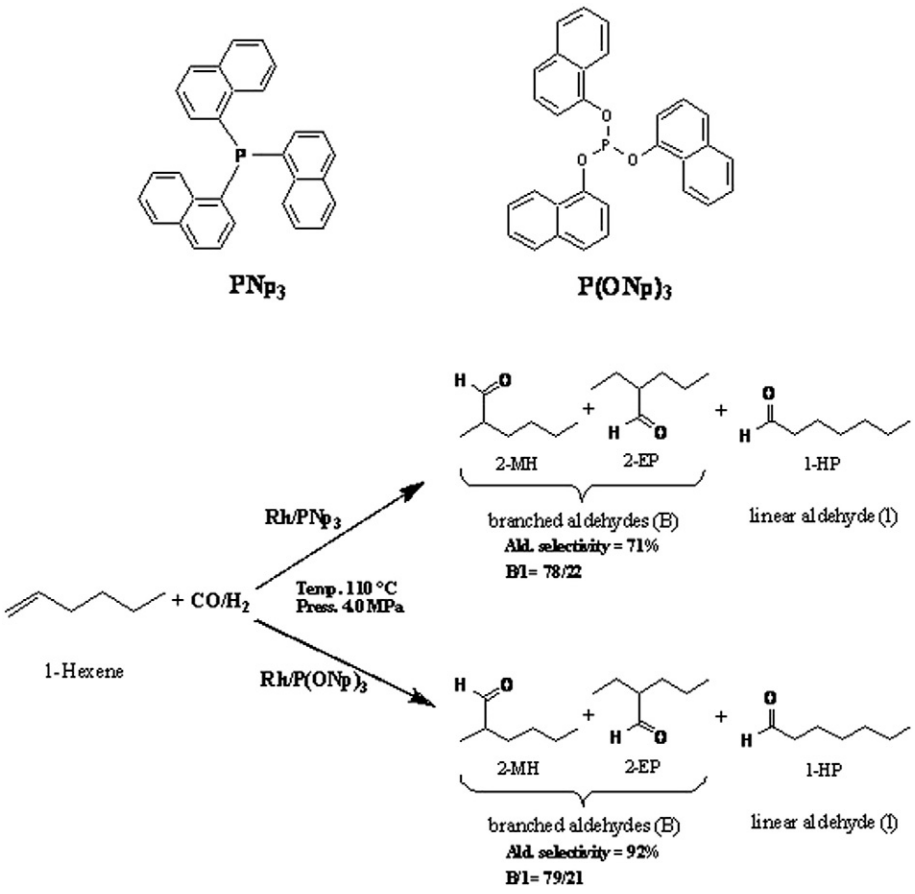
Table 3
Effect of ligands on the hydroformylation of 1-hexene.

Entry	Ligand	Aux. ligand	Conv.[a](%)	Iso.[b](%)	Ald.[c](%)	Selectivity (%) [d]			B/l [e]
						2-EP	2-MH	1-HP	
1	–	–	98	56	44	18	52	30	70/30
2 [f]	PPh_3	–	98	8	92	3	37	60	40/60
3	PCy_3	–	98	5	95	4	44	52	48/52
4	TMPP [g]	–	96	87	13	4	42	54	46/54
5 [h]	$P(OPh)_3$	–	98	7	93	17	48	35	65/35
6 [h]	$P(ONp)_3$	–	99	5	95	21	52	27	73/27
7 [h, i]	$P(ONp)_3$		98	71	29	21	54	25	75/25
8[h, j]	$P(ONp)_3$	–	99	8	92	25	54	21	79/21
9	PNp_3	–	99	29	71	20	58	22	78/22
10 [k]	PNp_3	$P(OPh)_3$	99	4	96	23	51	28	72/28
11 [k, l]	PNp_3	$P(ONp)_3$	99	17	83	28	55	17	83/17
12 [k]	PNp_3	$P(ONp)_3$	99	2	98	25	57	18	82/18

Reaction conditions: Sub/cat. = 2000, $[Rh(CO)_2acac]$ = 0.23 mmol/L, P/Rh = 6.0, Temperature = 110 °C, Syngas pressure (1:1) = 4.0 MPa, solvent (toluene) = 50 mL, reaction time = 60 min.

[a] Conversion of 1-hexene.
[b] Selectivity to isomerization.
[c] Selectivity to aldehydes.
[d] Regioselectivity to aldehydes.
[e] Branched aldehydes (2-MH and 2-EP) to linear aldehyde ratio.
[f] Reaction time = 45min.
[g] $(2,4,6\text{-MeO-}C_6H_4)_3P$.
[h] Reaction time = 30 min.
[i] Syngas pressure = 2.0 Mpa.
[j] P/Rh = 3.0.
[k] PNp_3: auxiliary ligand = 3:3, total P/Rh = 6.0.
[l] Syngas pressure (1:1) = 3.0 MPa.

influences the selectivity to branched aldehydes while electronic effect of ligands influences the catalytic activity (Table 3). The PCy_3 and $(2,4,6\text{-MeO-}C_6H_2)_3P$ ligands (Table 3, entries 3 and 4) gave better selectivity toward branched aldehydes. However, $(2,4,6\text{-MeO-}C_6H_2)_3P$ gave low chemoselectivity to aldehydes (13%). The phosphite ligands, $P(OPh)_3$ and $P(ONp)_3$ exhibited high chemoselectivity due to their higher pi-



Scheme 3. Selective hydroformylation to branched aldehydes using PNp_3 and $P(ONp)_3$ ligands.

acceptor ability than phosphine and favored branched aldehydes, particularly $P(ONp)_3$ gave branched aldehydes selectivity comparable to PNp_3. To confirm further whether 1-hexene first isomerized to 2- and 3-hexenes and then hydroformylation occurs to yield branched aldehydes in the case of $P(ONp)_3$ also, a few set of experiments were performed. In the first set of experiment, effect of pressure was studied (entry 7), at 2.0 MPa syngas pressure, 71% isomerized hexene was observed with only 29% aldehyde chemoselectivity. In the second experiment, effect of ligand/Rh ratio was studied (entry 8), at 3.0 ligand/Rh ratio (syngas pressure 4.0 MPa) and 79% selectivity to branched aldehyde with 92% aldehyde chemoselectivity was observed. The results indicated that 1-hexene first isomerized to 2- and 3-hexenes and then yielded branched aldehydes on hydroformylation. The ligand free system (unmodified Rh catalyst) also yielded 70% branched aldehydes with 44% aldehyde chemoselectivity. From the above data it can be concluded that ligands PNp_3 and $P(ONp)_3$ resulted in best (78–79%) branched aldehydes selectivity (Scheme 3).

The PNp_3 gave considerably high branched aldehydes selectivity than PPh_3. However, aldehyde chemoselectivity was low as compared to PPh_3 at 110 °C and 4.0 MPa syngas pressure (Table 3, entries 2 and 9). As reported the appropriate combination of two different monodentate phosphine ligands can greatly influence the regioselectivity as compared to pure ligand [24,25]. Bulky monodentate phosphite ligands are known to show high activity toward the hydroformylation of olefins [26,27]. Moreover phosphites as auxiliary ligands have been employed in several reports [28–30]. Here, we utilized the appropriate ratio of monodentate bulky phosphine and phosphite ligand and studied their influence on regioselectivity. The combination of bulky phosphine and bulky phosphite ligands led to improve the chemo as well as regioselectivity to branched aldehydes (Table 3, entries 11 and 12). The chemoselectivity to aldehyde was increased (71 to 96%) while branched aldehyde selectivity decreased (78 to 72%) using $P(OPh)_3$ as auxiliary ligand (Table 3, entry 10). Interestingly, bulky monodentate phosphite $P(ONp)_3$, as auxiliary ligand increased the aldehyde chemo- (71 to 98%) as well as branched aldehyde (78 to 82%) selectivity (Table 3, entry 12). On the other hand, the individual ligands PNp_3 and $P(ONp)_3$ resulted in ~78% branched aldehydes selectivity with 71% and 92% aldehyde chemoselctivity respectively (Table 3, entries 8 and 9). From the above results, it is evident that proper combination of steric and electronic effect of ligands led to increased overall selectivity (regio as well as chemo selectivity). The addition of $P(OPh)_3$ as auxiliary ligand (entry 10) increased only aldehyde chemoselectivty while use of bulky monodentate phosphite $P(ONp)_3$ as auxiliary ligand (entry 12) increased the aldehyde chemo- (98%) as well as branched aldehydes (82%) selectivity. These results clearly demonstrated the potential of ligands combination for obtaining high branched aldehydes with high aldehyde chemoselectivity compared to the individual ligands as well as the conventional Rh/PPh_3 system.

The high selectivity to branched aldehydes in the case of bulky phosphine/phosphite ligand may be due to the formation of monoligated rhodium complex, $HRh(CO)_3L$ (confirmed by *in situ* IR and NMR) due to their large cone angle [31]. As a result, dissociation of CO from $HRh(CO)_3L$ (L = bulky phosphite /phosphine) generates a 16 electron sterically less hindered complex as compared to $HRh(CO)_2L_2$ (L = PPh_3) species. The 16 electron sterically less hindered complex favors the formation of secondary alkyl-rhodium species which enhances the isomerization and regioselectivity to branched aldehydes (Scheme 2). The sterically demanding PNp_3 ligand exhibited comparatively low catalytic activity due to the lower π-acceptor ability than bulkier phosphite ligand $P(ONp)_3$. Thus, addition of bulky phosphite ligand as auxiliary ligand greatly enhanced the catalytic activity as well as selectivity.

4. Conclusions

The hydroformylation of 1-hexene catalyzed by rhodium complex modified by PPh_3 favors generally linear aldehyde. The rhodium complexes modified with PNp_3 and $P(ONp)_3$ were found to be an effective catalytic system to produce branched aldehydes in the hydroformylation of 1-hexene. The ligands PNp_3 and $P(ONp)_3$ having more steric nature than PPh_3 favored formation of branched aldehydes (110 °C and 4.0 MPa syngas pressure) ensuing in up to 78–79% branched aldehydes. The aldehyde selectivity was 71% in the case of PNp_3. The chemo– as well as regioselectivity were remarkably increased by the addition of $P(ONp)_3$ as auxiliary ligand in Rh/PNp_3 catalyzed hydroformylation of 1-hexene. Such permutation represents a potential catalytic system without synthesizing complicated ligands with an increased formation of branched aldehydes in case of linear alkene like 1-hexene.

Acknowledgements

Authors are thankful to analytical division of the institute for assistance with analyses and CSIR for financial support under CSIR Network Project. Authors are also thankful to Dr E. Suresh for single crystal X-ray data. AAD thanks CSIR, New Delhi, for the award of Senior Research Fellowship.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2010.10.026.

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