

# High *iso* aldehyde selectivity in the hydroformylation of short-chain alkenes

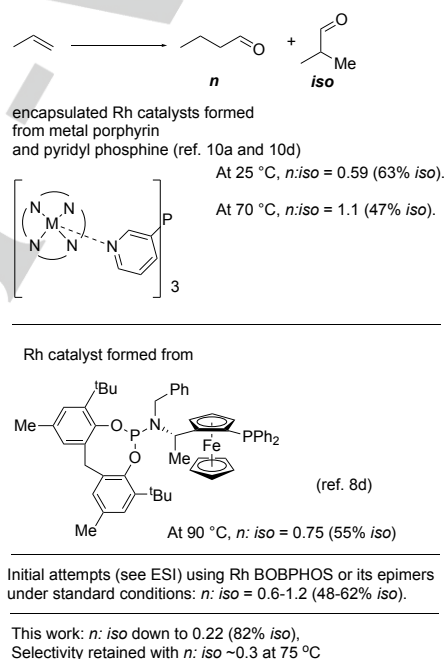
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**Abstract:** The hydroformylation of propene to give predominantly *iso*-butanal has been achieved; class-leading selectivity is possible even at higher temperatures that deliver fast rates. Racemic Rh complexes of bidentate phospholane phosphites derived from *tropos*-biphenols and unusual solvent systems are the key to the selectivity observed.

Rh-catalysed hydroformylation is a reaction of high importance in the production of a variety of chemicals. Millions of tonnes of aldehydes are produced in this way each year.<sup>[1]</sup> Hydroformylation of terminal 'alkyl' alkenes shows a preference towards linear aldehyde formation and with the correct ligands near-perfect linear selectivity can be obtained.<sup>[1-5]</sup> This is used at large scale and in organic synthesis. There are also some very significant chemicals that require a branched-aldehyde selective hydroformylation of a terminal alkene for an efficient synthesis. Sometimes this can be achieved by substrate control.<sup>[6,7]</sup> However, arguably the most industrially important branched aldehyde is *iso*-butanal, which requires the very challenging (branched) *iso*-selective hydroformylation of an unbiased alkyl alkene, propene.<sup>[8-10]</sup> Global demand for *iso*-butanal can be estimated to be over half a million tonnes in 2014.<sup>[11]</sup> Rhodium catalysts derived from ligand (*R*<sub>ax</sub>,*R*,*R*)-1, (nicknamed BOBPHOS and illustrated in Scheme 2), are extremely unusual in being able to transform simple terminal alkenes into branched aldehydes with good regioselectivity and up to 93% e.e.; the smallest terminal alkene reported was hex-1-ene.<sup>[9]</sup> Unfortunately, using either the typical published conditions for operating this catalyst, or the typical temperatures and pressures used in propene hydroformylation, Rh/ BOBPHOS catalysts do not give satisfactory results in the hydroformylation of propene (see supporting information, Table S1).

The small size of propene renders it less influenced by steric barriers, and possibly reduces attractive interactions as well. A review of the patent and open literature reveals that despite research over decades, *iso*-selective hydroformylation is very much an unsolved problem, especially at typical reaction temperatures employed in industry. The best selectivity obtained

is 63% (*n*: *iso* = 0.59); however, this was observed at 19 °C where rates are not sufficiently high for commodity chemicals production.<sup>[10a]</sup> The same catalyst at higher temperatures (80 °C) delivers lower *iso* selectivity below 50%.<sup>[10a,d]</sup> An alternative benchmark is 57% (*n*:*iso* = 0.75) observed at more typical industrial reaction temperatures (Scheme 1).<sup>[8c,d]</sup> Surprisingly, we have now found a combination of reaction conditions and more economic racemic Rh / phospholane-phosphite catalysts that can deliver unprecedented *iso*-butanal selectivity from propene and report this discovery here.



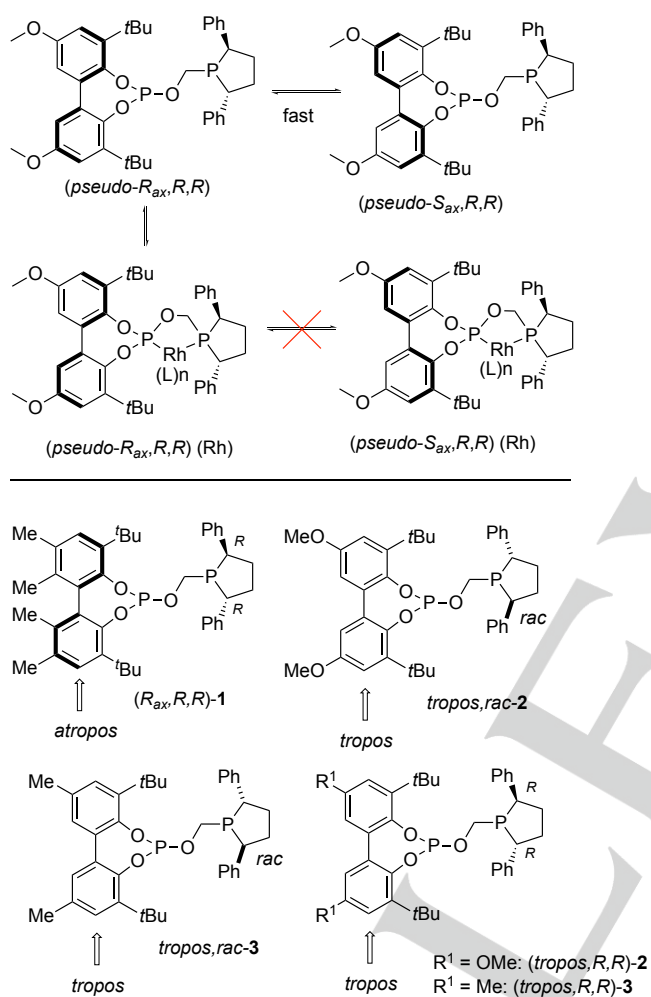
**Scheme 1.** *iso*-selective hydroformylation of propene is highly desired but an extreme challenge.

The unusual regioselectivity observed for Rh catalysts derived from (*R*<sub>ax</sub>,*R*,*R*)-1 in the hydroformylation of allyl benzene utilises subtle interactions that prevent the linear Rh-alkyl intermediate being formed; an attractive interaction between the phospholane Ph substituents and the substrate stabilises an unproductive C-H forming process, on the wrong side of a steric barrier between the transition state and linear Rh-alkyl.<sup>[9d]</sup> Even subtle changes to the ligand structure might reduce branched selectivity, yet a racemic ligand would be preferable, since it reduces ligand cost very significantly. We speculated that swapping the enantiomerically pure *atropos* diol for a configurationally unstable *tropos* diol could deliver a phosphite unit that while interconverting freely as a ligand would set itself in a single preferred conformation upon coordination to rhodium (Scheme 2,

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top).<sup>[12]</sup> We hoped that this would be an analogous conformation to that observed with ( $R_{ax},R,R$ )-**1**, rather than its diastereomer, ( $S_{ax},R,R$ )-**1**, (although this could not be predicted in advance). If the *tropos*- $R,R$  system were to behave more like ( $R_{ax},R,R$ )-**1**, it can also be envisaged that utilising a *racemic, trans* diastereomer of phospholane to partner the *tropos* diol would lead to two species forming upon coordination that had a similar ligand shape to ( $S_{ax},S,S$ )-**1** and ( $R_{ax},R,R$ )-**1**, but not its diastereomers.



**Scheme 2.** (top): proposed interconversion of *tropos* phosphite in free ligands and formation of one *atropos* isomer on coordination to rhodium; (bottom) ligands used in this study.

In order to test this hypothesis, ligands **2** and **3** were synthesised (see supporting information). Relative to the parent BOBPHOS ligand, **1** these new derivatives reduce the cost of synthesis as neither the resolution of the racemic phospholane ring, nor the resolution of the diol to produce a single *atropisomer* is required.

Depending on the borane-protected phospholane used, the ( $R,R$ ) and *tropos,rac* analogues of the *tropos* ligands **2** and **3** were synthesised. With the new ligands in hand, a range of variables such as pressure, temperature and solvents were examined. The key finding was the use of the rather unusual

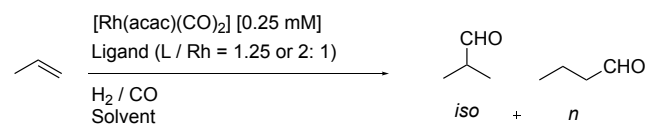
solvent octafluorotoluene, which we previously had observed to offer very marginal gains (1–3%) in branched selectivity,<sup>[8d]</sup> actually leads to very significantly higher selectivity for this industrially important reaction relative to the state of the art (Table 1). This effect is observed using the new *tropos* ligands and ( $R_{ax},R,R$ )-BOBPHOS itself. In a variety of studies using these types of catalysts, we have observed that while using L:Rh ratios of 1.25:1 can work well, larger L:Rh ratios are sometimes needed under certain conditions and a ligand to Rh ratio of 2:1 is recommended here (Table 1, entries 1 and 2 and supporting information Table S1).

The use of fluorinated solvents has attracted interest for a variety of reasons.<sup>[13]</sup> Lattanzi *et al* examined the use of hexafluorobenzene as additive in catalytic asymmetric Michael addition reactions and discovered that only 5–10 equivalents of hexafluorobenzene relative to the substrates were required to achieve comparable results to those using hexafluorobenzene as the solvent.<sup>[13d]</sup> The equivalents needed were substrate-dependent, suggesting the presence of interactions between the substrate and hexafluorobenzene. In this case an experiment using a mixture of toluene and 2205 equivalents of octafluorotoluene w.r.t Rh does not maintain the high selectivity, and hence we believe this is a solvent effect on these reactions (Table 1, Entry 6 and 7).

Commercial production of butanal isomers does not make use of volatile organic solvents, since they would be too expensive; non-volatile solvents that dissolve the catalyst and enable the products to be distilled away, while catalyst and solvent are recycled again and again are preferred. An alternative to the use of volatile octafluorotoluene is therefore likely to be needed for large-scale application. We therefore decided to produce a new solvent that maintains the properties of octafluorotoluene in this reaction, but is no longer volatile.

Pentafluorophenyl *n*-octyl ether (PFPOE), which has never been used as a synthesis solvent before<sup>[14]</sup> was chosen since it could be made in one step from two simple chemicals and would have a high enough boiling point to not be stripped away from the catalyst. We were delighted to find that using this new solvent, even after increasing reaction temperature to 75 °C, enabled the desired high proportion of *iso*-butanal, but this time with the improved turnover frequencies (TOF) possible at 75 °C. (Table 1, entries 12 and 13, and further results in supporting information). We note also that *n*:*iso* ratios below 0.5 are possible even at 90 °C in PFPOE (see supporting information). The protio analogue phenyl octyl ether, while giving lower selectivity than the fluorinated variant still enables an impressive *iso*-butanal yield (see the supporting information).

A promising solution to the long-standing and commercially important problem of obtaining significantly higher proportions of *iso*-butanal than *n*-butanal in propene hydroformylation is now in place. The new ligands are cheaper to make than the ligand that inspired them, which is also desirable for such relatively low value-high volume commodity chemicals. Both catalyst and solvents will need long term stability to be viable in a commercial process, and these studies and other elements of process development are now underway.

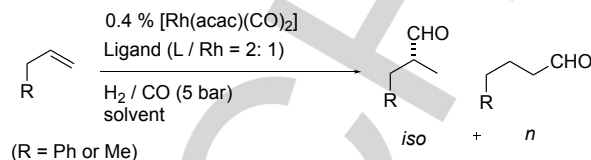
**Table 1.** Hydroformylation of propene in fluorinated solvents.

Entry <sup>[a]</sup>	Ligand	T °C	Solvent	TOF	TON	% iso
1	<i>tropos,rac-3</i>	50	C <sub>7</sub> F <sub>8</sub>	42	670	53.8
2 <sup>[b]</sup>	<i>tropos,rac-3</i>	50	C <sub>7</sub> F <sub>8</sub>	51	820	74.2 <sup>[c]</sup>
3	( <i>tropos,R,R</i> )-3	50	C <sub>7</sub> F <sub>8</sub>	42	670	73.4
4	( <i>tropos,R,R</i> )-2	50	C <sub>7</sub> F <sub>8</sub>	37	590	69.5
5	<i>tropos,rac-2</i>	50	C <sub>7</sub> F <sub>8</sub>	36	570	71.9
6	( <i>R</i> <sub>ax</sub> , <i>R,R</i> )-1	50	C <sub>7</sub> F <sub>8</sub>	49	790	76.7
7	( <i>R</i> <sub>ax</sub> , <i>R,R</i> )-1	50	C <sub>7</sub> F <sub>8</sub> + C <sub>7</sub> H <sub>8</sub> (8:92)	51	810	56.5
8	( <i>R</i> <sub>ax</sub> , <i>R,R</i> )-1	30	C <sub>7</sub> F <sub>8</sub>	12	460	82.0
9 <sup>[b,d]</sup>	( <i>R</i> <sub>ax</sub> , <i>R,R</i> )-1	75	C <sub>7</sub> F <sub>8</sub>	350	350	78.3
10 <sup>[b,d]</sup>	<i>tropos,rac-2</i>	75	C <sub>7</sub> F <sub>8</sub>	340	340	72.2
11 <sup>[b,d]</sup>	<i>tropos,rac-2</i>	75	C <sub>7</sub> F <sub>8</sub>	500	500	60.3
12 <sup>[b,e]</sup>	( <i>R</i> <sub>ax</sub> , <i>R,R</i> )-1	75	PFPOE	670	670	70.3
13 <sup>[b,e]</sup>	( <i>tropos,R,R</i> )-2	75	PFPOE	750	750	67.0

[a] Catalyst preformed from [Rh(acac)(CO)<sub>2</sub>] (5.12 × 10<sup>-3</sup> mmol) and ligand (6.40 × 10<sup>-3</sup> or 10.24 × 10<sup>-3</sup> mmol) by stirring at 8 bar CO/H<sub>2</sub> at reaction temperature for 1 hour in C<sub>7</sub>F<sub>8</sub> (19.35 mL + 0.65 mL toluene) prior to running reaction at 50 °C, for 16 hours using propene/CO/H<sub>2</sub> in 1:4.5:4.5 ratio (8 bar initial pressure). Rh concentration = 2.52 × 10<sup>-4</sup> mol dm<sup>-3</sup>. Product determined by GC using 1-methylnaphthalene as an internal standard. TOF = average TurnOver Frequency in mol prod/mol cat/hr; TON = TurnOver Number in mol prod/mol cat. [b] Ligand / Rh ratio of 2:1. [c] i.e. *n*:*iso* = 0.35. [d] Initial Pressure = 18 bar, reaction time 1 hour. [e] PFPOE = pentafluorophenyl *n*-octyl ether as solvent, 20 bar, reaction time 1 hour.

It seems likely that our hypothesis regarding the dynamic behaviour of the *tropos* ligands was at least partially correct. However, to shed light on this, we also studied the enantioselective hydroformylation of allyl benzene using the *tropos* ligands derived from an (*R,R*)-phospholane (Table 2). It can be seen that the use of the mixture of diastereomers derived from an *atropos* racemic biphenol leads to no enantioselectivity in these reactions, and much lower *iso* selectivity (Table 2, entry 1). If the *tropos* ligands formed two atropisomeric isomers on coordination, similar results to this might be expected. What is observed is a significant contrast; the *tropos* ligands, (*Tropos,R,R*)-2 and (*Tropos,R,R*)-3 selectively form one enantiomer with selectivity towards the *R* enantiomer of 80 to 85% (Table 2, entries 2-4), not quite matching the results obtained using the desired single enantiomer (*R*<sub>ax</sub>,*R,R*)-BOBPBOS/ Rh catalyst, but clearly showing that at least to a significant extent, the *tropos* diol is behaving more like a single

enantiomer during catalysis. NMR analysis of the catalyst resting state [Rh(H)(*R,R*)-2](CO)<sub>2</sub> appears to be a single species in agreement with this (see supporting information for NMR spectra).

**Table 2.** Enantioselective Hydroformylation of allyl benzene and but-1-ene.

Entry <sup>[a]</sup>	Ligand	'R'	Conversion	% iso	e.r. <sup>[b]</sup>
1	( <i>R,S,S,S</i> )-1	Ph	>99	39	50/50
2	( <i>tropos,R,R</i> )-2	Ph	66	71	80/20 (R)
3 <sup>[c]</sup>	( <i>tropos,R,R</i> )-3	Ph	>99	70	80/20 (R)
4	( <i>tropos,R,R</i> )-2	Ph	>99	77	85/15 (R)
5 <sup>[c]</sup>	( <i>R,R,R</i> )-1	Ph	86	72	96/4 (R)
6	( <i>R,R,R</i> )-1	Ph	97	86	96/4 (R)
7 <sup>[d]</sup>	( <i>R,R,R</i> )-1	Me	86	86	96/4

[a] Catalyst preformed from [Rh(acac)(CO)<sub>2</sub>] (4 × 10<sup>-3</sup> mmol) and ligand (8 × 10<sup>-3</sup> mmol) by stirring at 8 bar CO/H<sub>2</sub> at reaction temperature for 1 hour in octafluorotoluene solvent prior to running reaction at 50 °C, for 16 hours using 5 bar CO/H<sub>2</sub>. Conversion and regioselectivity determined by NMR spectroscopy using 1-methylnaphthalene as an internal standard. [b] e.r. determined by HPLC from alcohols obtained after NaBH<sub>4</sub> reduction except entry 7). [c] Toluene used as solvent in place of octafluorotoluene. [d] 2.5 bar, 19 °C, 64h; e.r. determined by conversion into regiochemically pure *N*-(4-chlorobenzyl)-2-methylbutan-1-amine by reductive amination in 57% yield from but-1-ene (see supporting information)

An additional aspect discovered here is the higher branched selectivity in asymmetric hydroformylation in octafluorotoluene, so these conditions are also a synthetically useful improvement for asymmetric hydroformylation using the Rh / BOBPBOS catalyst. For example highly enantioselective hydroformylation of allyl benzene improved from 72% regioselectivity to 86% branched selective under otherwise identical conditions but swapping toluene for octafluorotoluene as solvent (compare Table 2, entries 5 and 6). Unprecedented highly enantioselective and regioselective hydroformylation of but-1-ene was also achieved with 86% *iso*-selectivity (Table 2 entry 7). The conversion of this aldehyde to a chiral secondary amine with e.r. of 96:4 and isolated as a single regioisomer was also achieved.

In summary we have discovered *tropos, racemic* ligands that under specific conditions can deliver unprecedentedly high selectivity for *iso*-butanal in the hydroformylation of propene, with useful rates. The ligands used for this process are more economic to make than the ligand they are inspired from, and hence more suited for development for industrial *iso*-selective hydroformylation in the future. The fact that the (*tropos,rac*)-ligands/Rh catalysts show comparable results to the Rh / BOBPBOS catalyst supports the hypothesis that the *tropos* part

of the ligand settles into a conformation that is very similar to the single enantiomer BOBPBOS ligands (although it cannot quite be definitively ruled out that one conformation is much more reactive than the other). It may be tempting to speculate about the origin of this effect, but for such a subtle effect, with a critical role for the solvent choice, a definitive answer is outside the reach of DFT calculations or other mechanistic techniques, to our knowledge. Evidently, the reasons for *iso*-selectivity studied initially for BOBPBOS are either enhanced in the solvents used, or are actually less attenuated than they are by common solvents like toluene, enlarging the scope of substrate that can be used. Finally, the new conditions were also found to improve enantioselective hydroformylation regioselectivity, with highly enantioselective and regioselective hydroformylation of but-1-ene exemplifying this improvement.

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**Keywords:** Hydroformylation • rhodium • fluorinated solvents • enantioselective catalysis • phosphorus ligands

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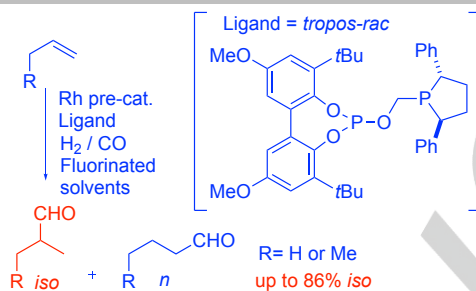


## Entry for the Table of Contents (Please choose one layout)

Layout 1:

## COMMUNICATION

Significant selectivity for the branched or *iso*-aldehydes in the hydroformylation of propene and but-1-ene has been obtained.



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## COMMUNICATION

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