Synthetic Methods

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Ruthenium/C_5Me_5/Bisphosphine- or Bisphosphite-Based Catalysts for *normal*-Selective Hydroformylation**

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Hydroformylation of alkenes is the most widely industrially applied homogeneous transition-metal-catalyzed reaction.[1] Since the discovery by Roelen that $[HCo(CO)_4]$ can promote this transformation,[2] cobalt complexes have been used extensively as hydroformylation catalysts. However, more recently developed rhodium/phosphine complexes generally afford higher selectivity compared to cobalt catalysts for the production of *normal* aldehydes (*n*-aldehydes), which are utilized as intermediates for the synthesis of plasticizers, solvents, and detergents. Additionally, rhodium complexes typically produce negligible quantities of alkanes from competing alkene hydrogenation unlike cobalt-based hydroformylation catalysts. Thus, rhodium catalysts have come to play a major role in industry.

Intensive studies have been devoted both in industry and in academia to the development of bisphosphine or bisphosphite ligands that promote highly *normal*-selective (*n*-selective) rhodium-catalyzed hydroformylation of 1-alkenes.[3] However, recent global increases in demand for rhodium, particularly in the automotive industry, is increasing the price of this already expensive precious metal.[4] In contrast, more cost-effective cobalt-based systems suffer from concomitant formation of alkane by-products. Considering these factors, the development of hydroformylation catalysts using other transition metals is desirable. In contrast to the extensive studies on cobalt and rhodium systems, other transition metals such as palladium,[5] iridium[6], and ruthenium[7] have received less attention as potential hydroformylation catalysts. We have targeted ruthenium, which is less expensive compared to rhodium. Only two examples of ruthenium-catalyzed hydroformylation with high *n*-selectivity (*normal*/*iso* (n/i) > 30) have been reported.[7d,h]

Our design for ruthenium hydroformylation catalysts is illustrated in Figure 1. In conventional rhodium catalysts for hydroformylation, the hydridorhodium(I) **A** is a key species

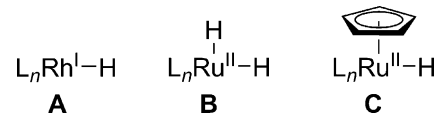

Figure 1. Comparison of conventional rhodium (**A**) and ruthenium (**B**) hydroformylation catalysts with the ruthenium catalyst **C** used in this work.

to which alkenes insert to generate the corresponding alkylrhodium species. In contrast, the dihydrido ruthenium(II) **B** is known as a catalytically active species for hydrogenation of alkenes, which is a problematic side reaction in hydroformylation. By comparing the species **A** and **B**, we envisioned replacing one hydride in **B** with a cyclopentadienyl anion. Through this strategic change, the $[CpRu^{II}]$ complex **C** was expected to be inactive as an alkene hydrogenation catalyst because the ruthenium center lacks one of the requisite hydride ligands present in the active hydrogenation intermediate **B**. Herein, we report a new catalyst system that consists of a $[Cp^*Ru^{II}]$ ($Cp^* = C_5Me_5$) complex ligated by chelating bisphosphines. These complexes effect the hydroformylation of 1-alkenes with the highest level of activity and *n* to *i* selectivity to date for any ruthenium-based catalyst,[7d,h] even though the activity remains well below that of the best rhodium-based catalysts. Additionally, these ruthenium catalysts successfully suppress the rate of competing alkene hydrogenation.

First, hydroformylation of propene was examined using a combination of $[\{Cp^*Ru(acac)\}_2]$ and the bidentate phosphorus ligands A4N3,[3i] Xantphos,[3a] and bisbi[3e] (Figure 2) which were previously developed to promote highly active and *n*-selective rhodium hydroformylation catalysts. The results are summarized in Table 1. The reaction in toluene at 160 °C using a combination of $[\{Cp^*Ru(acac)\}_2]$ and A4N3 as the catalyst proceeded with a turnover frequency (TOF) of

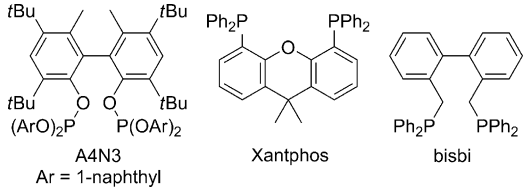

Figure 2. Bidentate bisphosphine and bisphosphite ligands used in this study.

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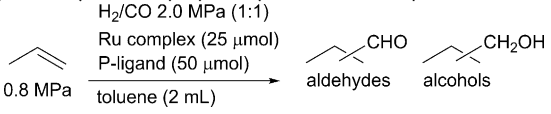
Table 1: Hydroformylation of propene by ruthenium complexes.[a]



Entry	Catalyst	*T* [°C]	*t* [h]	Aldehydes TOF [h^{-1}] (*n*/*i*)	Alcohols TOF [h^{-1}] (*n*/*i*)
1[b]	[{Cp*Ru(acac)}$_2$]/A4N3	160	24	1.3 (17)	0.29 (14)
2[c]	[{Cp*Ru(acac)}$_2$]	160	24	0.92 (1.8)	0.07 (2.5)
3[d]	[$Ru_3(CO)_{12}$]	160	24	8.3 (1.7)	8.5 (1.9)
4[e]	[$Ru_3(CO)_{12}$]/A4N3	160	24	0.03 (8.0)	0.85 (8)
5[f]	[{Cp*Ru(acac)}$_2$]/Xantphos	160	24	1.7 (13)	0.05 (> 100)
6[f]	[{Cp*Ru(acac)}$_2$]/bisbi	160	24	0.6 (14)	0.04 (> 100)
7	[{Cp*Ru(acac)}$_2$]/A4N3	120	24	0.48 (43)	0.06 (> 100)
8[g]	[NEt_4][$HRu_3(CO)_{11}$]	70	66	0.11 (45)	n.d.
9	[{(indenyl)Ru$(CO)_2$}$_2$]/A4N3	120	24	2.2 (32)	0.14 (12)
10	[{(1,2,3-trimethylindenyl)Ru$(CO)_2$}$_2$]/A4N3	120	24	4.3 (41)	0.14 (>100)

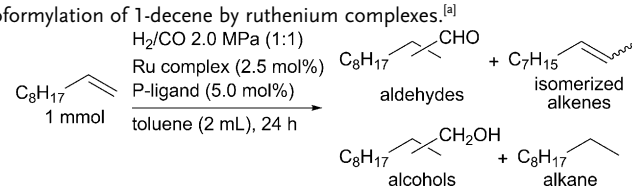
[a] The molar quantity of the ruthenium complexes is based on the total mol of Ru atoms. TOF = (mol of product)/[(mol of Ru) × (reaction time)]. The amounts of charged H_2 and CO were so high that the changes in their partial pressure during the reaction time were negligible. No significant amount of by-product was detected by GC unless otherwise mentioned. [b] Unidentified high-boiling products were observed. The TOF of their formation was roughly estimated to be 0.08 h^{-1}. [c] Unidentified high-boiling products similar to those for entry 1 were observed by GC. The TOF of their formation was was roughly estimated to be 0.07 h^{-1}. [d] Unidentified high-boiling products different from those of entry 1 were observed by GC. The TOF of their formation was roughly estimated to be 3 h^{-1}. [e] Unidentified high-boiling products different from those of entry 1 were observed by GC. The TOF of their formation was roughly estimated to be 0.9 h^{-1}. [f] 1,4-dioxane was used as a solvent. [g] The reaction conditions were the same as the best conditions reported in literature (Ref. [7d]). Ru complex (102 μmol), propene (0.5 MPa), H_2 (0.17 MPa), CO (0.34 MPa) in dimethoxyethane (2 mL), 70 °C, 66 h. acac = acetyl acetonate, n.d. = not determined.

1.3 h^{-1} and *n*/*i* of 17 (Table 1, entry 1). Reduction of some of the desired aldehyde to the alcohol was observed (18%). Without the addition of the A4N3 ligand, the reaction proceeded with poor *n*/*i* selectivity and a slightly lower TOF (Table 1, entry 2). When the ruthenium source was changed to [$Ru_3(CO)_{12}$], which is one of the most active ruthenium catalysts reported, a higher TOF of 8.3 h^{-1} but lower *n*/*i* of 1.7 were observed (Table 1, entry 3). Alcohol formation was also a problem when [$Ru_3(CO)_{12}$] was used without the added ligand; equimolar amounts of alcohol were formed together with the desired aldehyde. Significant amounts of unidentified high-boiling by-products also formed under these reaction conditions. A combination of [$Ru_3(CO)_{12}$] and A4N3 as the catalyst formed a lower fraction of reduced alcohol product compared to the reaction using [$Ru_3(CO)_{12}$] and no additional ligand (Table 1, entry 4). Low *n*/*i* selectivity is also observed, which suggests that the active species in entry 1 is different from that in entry 4. The use of Xantphos and bisbi (Table 1, entries 5 and 6) resulted in TOFs of 1.7 and 0.6 h^{-1}, respectively, and with *n*/*i* selectivity comparable to that observed for A4N3. The *normal* selectivity can be improved (*n*/*i* = 43) by lowering the reaction temperature to 120 °C (Table 1, entry 7). The *n*/*i* value of 43 in entry 7 is comparable to that obtained at 70 °C using [NEt_4][$HRu_3(CO)_{11}$],[7b] which is the ruthenium catalyst reported to have the best *n*-selectivity (Table 1, entry 8).

Substitution of Cp* with an indenyl ligand leads to improved activity and selectivity. In entries 9 and 10 in Table 1, Ru–Ru bonded dimers [{(indenyl)-Ru$(CO)_2$}$_2$][8] and [{(1,2,3-trimethyindenyl)-Ru$(CO)_2$}$_2$],[9] respectively, were employed. The TOF for formation of the *n*-aldehyde reached 4.3 and an aldehyde *n*/*i* of 41 by using a combination of [{(1,2,3-trimethylindenyl)Ru$(CO)_2$}$_2$] and A4N3.

Next, we investigated the hydroformylation of 1-decene. The results are summarized in Table 2. High *n*-selectivity (*n*/*i* = 79) was observed using [{Cp*Ru-(acac)}$_2$]/A4N3 as the catalyst system (Table 2, entry 1). [{Cp*Ru(acac)}$_2$]/Xantphos (Table 2, entry 2) also exhibited a high level of selectivity (*n*/*i* = 27). In these experiments, however, reproducibility was problematic, thus resulting in fluctuating amounts of internal alkene products. In fact, the use of [{(1,2,3-trimethylindenyl)Ru$(CO)_2$}$_2$]/A4N3 as the catalyst resulted in significant isomerization to

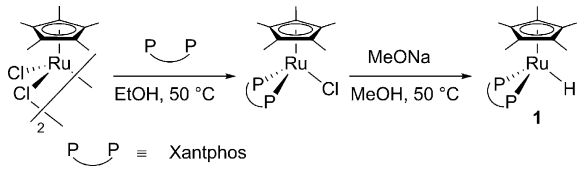
Table 2: Hydroformylation of 1-decene by ruthenium complexes.[a]



Entry	Catalyst	*T* [°C]	*t* [h]	Recovery of starting material [%]	Aldehydes [%] (*n*/*i*)	Alkane [%]	Isomerized alkenes [%]
1	[{Cp*Ru(acac)}$_2$]/A4N3	100	18	13	66 (79)	1.5	19
2	[{Cp*Ru(acac)}$_2$]/Xantphos	160	21	15	56 (27)	2.5	19
3	[{Cp*Ru(acac)}$_2$]	160	12	0	13 (5.5)	10	81
4	**1**/Xantphos[c]	160	24	60	29 (31)	1.2	8.5
5	**1**/Xantphos[c]	160	48	23	60 (28)	3.2	8.4
6	[$Ru_3(CO)_{12}$]/Xantphos	160	18	9	20 (14)	10	56
7[c]	**1**/Xantphos[b]	160	24	86	< 0.1 (–)	1.4	4.6
8[d]	**1**/Xantphos[b]	160	48	23[e]	58[e] (28)	5.6[e]	15[e]

[a] The molar quantity of the ruthenium complexes is based on the total mol of Ru atoms. The amounts of charged H_2 and CO were such that the changes in their partial pressure during the reaction time were negligible. No significant amount of by-product was detected by GC unless otherwise mentioned. In the blank experiment, loss of 1-decene because of its volatility was confirmed. The recovery of 1-decene was 94% in the absence of catalyst under the same reaction conditions.[10] [b] Xantphos 2.5 mol%. [c] (*Z*)-2-decene (purity 95%, containing decane 1.6%, (*E*)-2-decene 2.5%, and other C10 alkenes 0.9%) was used as substrate. [d] 1-eicosene was used as a substrate. [e] Yield determined by ^{1}H NMR analysis using trimethoxybenzene as an internal standard.

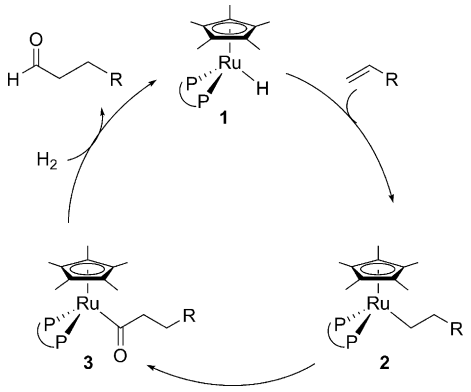
internal alkenes.[10] The rapid alkene isomerization that occurred in the absence of phosphorus ligands (Table 2, entry 3) suggests that a trace amount of a non-phosphine-coordinated ruthenium species is present and acts as an isomerization catalyst. To avoid this problem, we examined an isolated phosphine-coordinated Ru–H complex. We successfully isolated the [Cp*Ru(Xantphos)H] complex (**1**) as shown in Scheme 1. The reaction of dimeric of [{Cp*Ru(Cl)(μ-Cl)}$_2$]



Scheme 1. Synthesis and isolation of [Cp*Ru(Xantphos)H] (**1**).

with Xantphos first formed [Cp*Ru(Xantphos)Cl], which was then converted into [Cp*Ru(Xantphos)H] (**1**) upon treatment with sodium methoxide in methanol at 50 °C. Complex **1** was fully characterized by ^{1}H, ^{13}C, ^{31}P NMR spectroscopy and HRMS/ESI.[10] The *n*-selective hydroformylation with suppressed alkene isomerization and good reproducibility was achieved by using complex **1** and one additional equivalent of Xantphos (aldehyde 29 %, $n/i = 31$; Table 2, entry 4)). When the reaction time was prolonged to 48 hours, the aldehyde yield increased to 60 % with an *n*/*i* of 28 (Table 2, entry 5), thus suggesting the absence of an induction period and slow catalyst deactivation. Longer reaction times did not change the amount of isomerized alkenes (8.5 % for 24 h, 8.4 % for 48 h), thereby suggesting that their formation occurs predominantly during the initial stage of the reaction. In contrast, the use of an in situ generated catalyst from the combination of [$Ru_3(CO)_{12}$]/Xantphos resulted in significant alkene isomerization (Table 2, entry 6). When (*Z*)-2-decene was used as a substrate, no hydroformylation was observed over 24 hours at 160 °C (Table 2, entry 7). Using 1-eicosene, a less volatile substrate, a similar result to that with 1-octene was accomplished with complete mass recovery (Table 2, compare entry 8 to entry 5). The use of other phosphorus ligands such as P*t*Bu$_3$, P(*o*-tol)$_3$, and DPPP resulted in low selectivity and activity.[10]

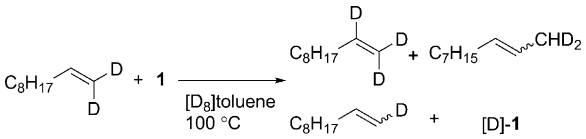
We also conducted a series of mechanistic studies related to hydroformylation catalyzed by [Cp*Ru(Xantphos)H]/Xantphos complexes (Scheme 2). First, reversible 1-alkene insertion into **1** was studied. When **1** was treated with a stoichiometric amount of 1-decene at 100 °C, the Ru/alkyl complex **2** was not detected, but the isomerization of 1-decene to (*E*)- and (*Z*)-2-decene ($E/Z = 85:15$) did occur over the same period of time. No further isomerization to 3- or 4-decenes was detected.[10] The production of 2-decenes is explained by 2,1-insertion of 1-decene into the Ru–H and subsequent β-hydride elimination from the C3-position. These data suggest the insertion of 1-decene into the Ru–H bond in **1** is reversible while the insertion reaction of internal alkenes to **1** is slow under these reaction conditions. The almost quantitative recovery of (*Z*)-2-decene as shown in



Scheme 2. A possible reaction mechanism for the [Cp*Ru]-catalyzed hydroformylation of alkenes.

entry 7 of Table 2 provides further evidence for the slow insertion reaction of internal alkenes with **1**.

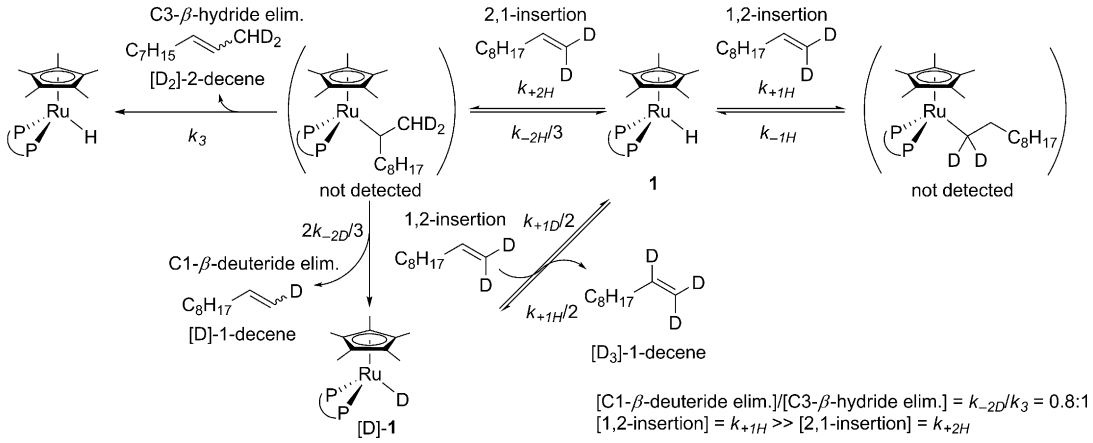
The stoichiometric reaction of the bisdeuterated (C1) 1-decene ([D$_2$]-1-decene, D content 96 %) and **1** was conducted (Scheme 3) to determine the relative rate of 1,2- and 2,1-alkene insertion and β-hydride elimination. Following 2,1-



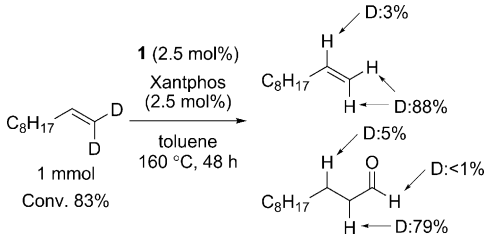
Scheme 3. Control study for the isomerization of 1-decene.

insertion of [D$_2$]-1-decene into **1**, there are two potential β-hydride elimination pathways (Scheme 4). One is β-hydride elimination from C1 to reform 1-decene. The other is β-hydride elimination from C3 to give 2-decene. From the increase of C1–H and the increase of 2-decenes, the ratio of k_{-2D}/k_3 was estimated to be 0.8:1. Taking into account the reported kinetic isotope effect for β-hydride elimination as 1.0–3.3, k_{-2H}/k_3 could be estimated to be 0.8:1–2.6:1, thus showing that the two pathways are comparable to each other.[11] In contrast, the ratio of [D$_3$]-1-decene to [D]-**1** remained constant at 1:1 during the reaction. These data imply that 1,2-insertion and subsequent β-hydride elimination is much faster than the 2,1-insertion and subsequent β-hydride elimination ($k_{+1H} \gg k_{+2H}$) such that there exists a rapid equilibrium between [D$_2$]-1-decene plus [D]-**1** and [D$_3$]-1-decene plus **1**; otherwise the ratio of [D$_3$]-1-decene/[D]-**1** would have increased as the reaction proceeded.[12]

Reversible 1,2-insertion and nearly reversible 2,1-insertion of the 1-alkene were suggested under the hydroformylation conditions. The hydroformylation of [D$_2$]-1-decene catalyzed by **1**/Xantphos afforded the product *n*-aldehyde with the deuterium content, as well as recovered 1-decene (Scheme 5). In the recovered 1-decene, the deuterium content was 88 % at C1 and 3 % at C2. In the obtained *n*-aldehyde, it was less than 1 % at C1, 79 % at C2, and 5 % at C3. Thus, the decrease of the terminal D content in [D$_2$]-1-decene indicates that 2,1-insertion/C1-β-deuteride elimination took place to



Scheme 4. Possible reaction in the initial stage of the stoichiometric reaction of [D_2]-1-decene and **1**.



Scheme 5. Deuterium distributions in the reaction mixture of hydroformylation using [D_2]-1-decene.[13]

some extent. Since 1,2-insertion was estimated to be much faster than 2,1-insertion as mentioned in the previous paragraph, the 1,2-insertion step should occur reversibly at a rate much faster than that of 2,1-insertion.

The mechanism of coordination of one of the substrates (alkene, CO or H_2) to the 18e, coordinatively saturated ruthenium center of **1** was also considered. One may expect either slippage of the η^5-cyclopentadienyl ligand to give an η^3 coordination, or dissociation of one phosphorus atoms of the bidentate ligand to κ^1 coordination (Figure 3). An η^3-Cp*

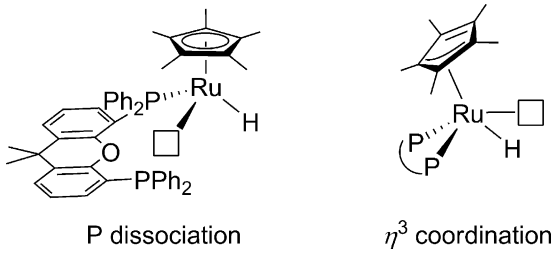


Figure 3. Possible 16e intermediates.

intermediate is consistent with the accelerating effect observed by substitution of an indenyl ligand for Cp* (Table 1, entries 7, 9, and 10), although the effect is small.[14] Dissociation of one phosphorus atom is still possible, but this mechanism seems unlikely considering the lower yields of the aldehyde product obtained when using monophosphines instead of bisphosphines.[10]

The catalytic cycle based on our mechanistic studies is as follows (Scheme 2): First, 1-alkene coordination to the ruthenium complex **1** and successive insertion takes place initially through generation of an open coordination site by either slippage of Cp* from an η^5 coordination to η^3 coordination or by dissociation of one phosphorus atom of the diphosphorus ligand. This step (**1**→**2**) is nearly reversible. The CO coordination to **2** again requires the ring slippage of Cp* or P dissociation. Migratory insertion of CO to form **3** and subsequent hydrogenolysis will release product aldehyde to complete the cycle.

Coordination and insertion of CO (**2**→**3**) or hydrogenolysis (**2**→**1**) seems to be the rate-determining step for the production of *n*-aldehyde since 1,2-insertion of the alkene was determined to be reversible. Furthermore, the reaction rate in the **1**/Xantphos system exhibited a first-order dependence on the 1-alkene concentration.[10] A higher concentration of 1-alkene accelerates the reaction by changing the ratio of the pre-equilibrium complexes (**1** + 1-alkene versus **2** or **3**) to favor either the intermediate **2** or **3**. Finally, the higher *n*-selectivity obtained when using bulky bidentate phosphorus ligands may be attributed to the destabilization of any ruthenium/branched alkyl or acyl intermediates by creating a sterically hindered environment around the ruthenium center.

In conclusion, we have developed a new class of ruthenium catalyst that is effective for the *n*-selective hydroformylation of terminal alkenes. The active species [Cp*Ru(Xantphos)H] (**1**) was isolated and the reaction mechanism was investigated. The reaction rate is still far below that of the industrially applied rhodium systems (about 3–4 orders of magnitude), and future improvement of catalyst activity (TOF) is desirable. Nevertheless, the obtained *n*/*i* ratios are similar to what is typically obtained in commercial processes, and [Cp*Ru] complexes may offer a new direction to further catalyst development for selective hydroformylation reactions and could obviate the use of expensive rhodium complexes in the future.

Experimental Section

General procedure for the hydroformylation of propene: The Ru complex (25 μmol) and bisphosphine (50 μmol) were charged with 2 mL of solvent in a 50 mL stainless steel autoclave with a magnetic stirring bar. The autoclave was pressurized with 0.8 MPa of propene (ca. 16 mmol). Soon after that, it was additionally pressurized with 2 MPa of H_2/CO. After completion of the reaction under the conditions indicated in the tables, the autoclave was cooled to 0 °C with a water/ice bath and the temperature maintained for 30 min. The gas pressure was released and then, to the the resulting solution, dodecane (75 mg, 0.44 mmol) was added as an internal standard for GC analysis. Judging from the propene conversion into aldehydes, the initial charges of H_2 and CO were high enough that the drops in partial pressures were negligible.

General procedure for the hydroformylation of 1-decene: The Ru complex and bisphosphine were charged with 2 mL of solvent in a 50 mL stainless steel autoclave with a magnetic stirring bar. A mixture of 1-decene and dodecane (2:1 molar ratio, 300 μL, ca. 1-decene 1 mmol) was then added and the autoclave was pressurized with appropriate pressure of H_2/CO. After completion of the reaction under the conditions indicated in the tables, the autoclave was cooled to 0 °C with a water/ice bath. The gas pressure was released and the resulting solution was analyzed by GC. The initial charges of H_2 and CO was high enough that the drops of their partial pressures were negligible.

Detailed procedures and results of all the control experiments can be found in the Supporting Information.

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