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Tandem Hydroformylation–Hydrogenation of 1-Decene Catalyzed by Rh-Bidentate Bis(trialkylphosphine)s

Takeo Ichihara, Koji Nakano, Masaya Katayama, and Kyoko Nozaki*[a]

Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

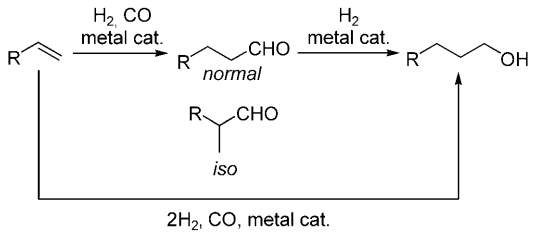
Abstract: A series of 2,2′-bis[(dialkylphosphino)methyl]biphenyls (alkyl-BISBIs) were synthesized and applied to the tandem hydroformylation–hydrogenation of 1-decene. The alkyl-BISBI ligands with "small" primary alkyl groups such as methyl or *n*-hexyl groups on the phosphorus atoms provided 1-alkanols selectively, whereas those with larger alkyl groups such as isopropyl or neopentyl groups showed much lower conversion from alkanals to alkanols. Observation of rhodium complexes of the BISBI-type ligands under H_2/CO atmosphere revealed that the presence of a stable [$RhH(CO)_2$(ligand)] species seems to be less favorable for the second step, the hydrogenation of aldehydes.

Keywords: hydroformylation · hydrogenation · rhodium · trialkylphosphines

Introduction

In industrial production, 1-alkanols are often produced from 1-alkenes via two separate reaction processes: the hydroformylation of 1-alkenes and separation of 1-alkanals from their regioisomers and other byproducts with high boiling points, and the subsequent hydrogenation of the 1-alkanals to 1-alkanols (Scheme 1, upper route). It would be desirable if 1-alkanols were produced directly from 1-alkenes under mild operating conditions with practical selectivities (Scheme 1, bottom route). Cobalt trialkylphosphine catalysts give 1-alkanols as major products, but the competitive alkene hydrogenation is problematic.[1]

A rhodium catalyst is an alternative candidate. The use of ligands such as amines[2] or trialkylphosphines[3] has been reported to give alkanols as well as alkanals. The rhodium/trialkylphoshine system was intensively studied by Cole-Hamilton and co-workers in their successful selective synthesis of alkanols from 1-alkenes using Et_3P as a ligand.[4] A mixture of 1-heptanol (normal isomer) and internal C_7 alcohols (iso isomers) was obtained at a normal/iso (*n*/*i*) ratio of ~3.0 by reaction of 1-hexene with H_2/CO in ethanol at 120 °C. Recently, two new systems were reported to give 1-alkanols selectively starting from 1-alkenes: a silica-gel-supported Rh/xantphos system reported by Reek, van Leeuwen, and colleagues,[5] and a Pd/CF_3SO_3H/trialkylphosphine system reported by Drent et al.[6] Among the reported catalyst systems, the Rh/trialkylphosphine system was most attractive for us because the hydrogenation of 1-alkene is completely suppressed, and the catalyst system is free from the addition of corrosive acids.



Scheme 1. Reaction pathways to normal alcohol.

Hydroformylation of 1-alkenes carried out with Rh/triarylphosphines or Rh/diarylmonoalkylphosphines in aprotic solvents at lower temperature gives alkanals but not alkanols as the main products. The *n*/*i* ratio of the alkanals in the hydroformylation reaction depends heavily on the framework of ligands. Several bidentate phosphorus ligands with large bite angles that occupy the equatorial–equatorial positions of trigonal bipyramidal rhodium have been developed for highly normal-selective hydroformylation of 1-al-

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kenes.[7] A bisphosphine ligand, BISBI, consists of two diarylmonoalkylphosphine units and is one such example.[8] The idea to combine the high *n*/*i* ratio achieved by BISBI and the hydrogenation activity of trialkylphosphines for the selective formation of alcohols prompted us to synthesize a series of alkyl-substituted BISBI analogues **1a**–**1d**.

Results and Discussion

First, the reaction of 1-decene with H_2/CO catalyzed by (n-$C_4H_9)_3$P/Rh (Bu_3P/Rh) in ethanol was monitored in order to determine whether the alcohol production is a one-step or two-step reaction from 1-alkene. In the presence of [Rh(acac)$(CO)_2$] (1 mol%) and Bu_3P (5 mol%), 1-decene was treated at 120°C with H_2/CO (1:1, total pressure of 4.0 MPa). The products were a mixture of *n*-C11 aldehyde (undecanal), *iso*-C11 aldehydes, *n*-C11 alcohol (1-undecanol), and *iso*-C11 alcohols. The isoaldehydes and isoalcohols were mainly 2-methyldecanal and 2-methyldecan-1-ol, respectively, but the other isomers were also present in trace amounts.

The results are summarized in Figure 1. The yield of aldehydes initially increased and then decreased as the yield of alcohols increased. This may mean that at least some of the alcohols are generated by reduction of the aldehydes.[9] The *n*/*i* ratios of both aldehyde and alcohol decreased with time (Figure 2). However, the total *n*/*i*, defined as the (sum of *n*-alcohol and *n*-aldehyde)/(sum of *iso*-alcohols and *iso*-aldehydes) is essentially constant during the whole process. This suggests that the *n*/*i* ratio of the products is essentially determined at the stage of hydroformylation. The *n*/*i* ratios of aldehydes and alcohols varied depending on the conversion of aldehydes into alcohols simply because the *n*-aldehydes are more susceptible to hydrogenation than *iso*-aldehydes. Thus, the *n*-aldehyde decreased more rapidly than the *iso*-aldehydes, and the *n*-alcohol was produced more rapidly than the *iso*-alcohols.

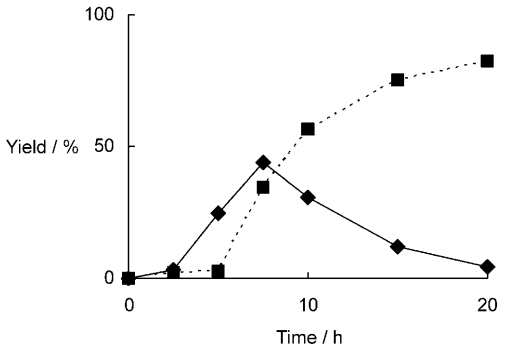


Figure 1. The total yields of C11 aldehydes (◆) and C11 alcohols (■) as a function of time.

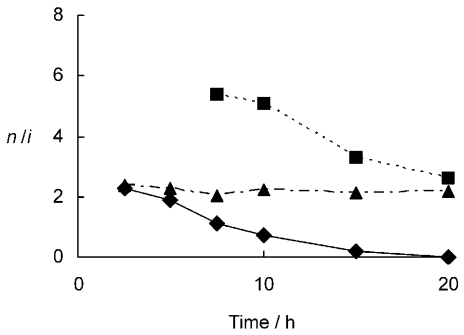


Figure 2. The *n*/*i* ratios of aldehyde (◆) and alcohol (■), and the sum of aldehyde and alcohol (▲) as a function of time.

Based on the above observation, we synthesized a series of bidentate bis(alkylphosphine)s with the BISBI-type framework (Figure 3), expecting that the unique backbone would perform the highly *n*/*i*-selective hydroformylation while the trialkylphosphines would be active for the hydrogenation of the resulting aldehydes to alcohols. Thus, the methyl-substituted BISBI ligand (Me-BISBI, **1a**) was synthesized as shown in Scheme 2. Reaction of potassium dimethylphosphide[10] with 2,2′-bis(chloromethyl)biphenyl[11] gave **1a**. Attempts to synthesize ligands **1b**–**1d** with the same process resulted in partial oxidation of the phosphorus atom. Accordingly, we used the procedure with borane protection. Borane-protected lithium phosphides were prepared

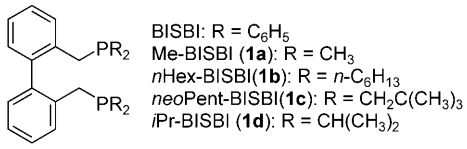
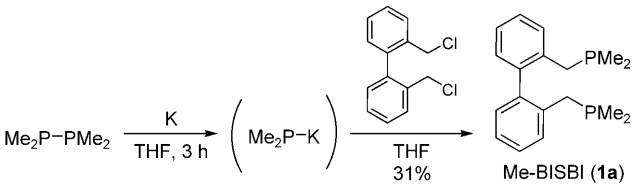


Figure 3. A series of BISBI-type ligands synthesized in the study reported herein.

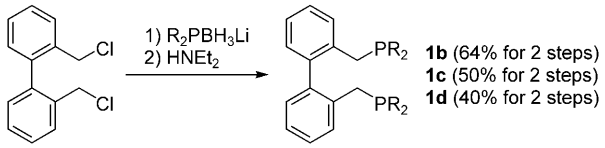


Scheme 2. Synthesis of Me-BISBI (**1a**).

Abstract in Japanese:

ビフェニル-2,2'-イレンジメタンジイル骨格をもつビストリアルキルホスフィン配位子を合成し，それらをもちいて1-デセンのタンデムヒドロホルミル化－水素化をおこなつた．リン原子上に1級アルキル基が置換した配位子をもちいると，1-アルカノールが選択的に得られた．一方，リン原子上のアルキル基が嵩高いと，アルカナールからアルコールへの転化率が低かつた．水素／一酸化炭素下でこれら二座配位子とロジウムから形成される錯体を観察し，安定なRhH$(CO)_2$(配位子)が観測されると，第二ステップのアルデヒドの水素化が不利であることが示唆された．

according to published methods.[12] Their reaction with 2,2′-bis(chloromethyl)biphenyl and deprotection by heating with amine provided ligands **1b**–**1d** in good yields (Scheme 3).



Scheme 3. Synthesis of R-BISBI (**1b**–**1d**).

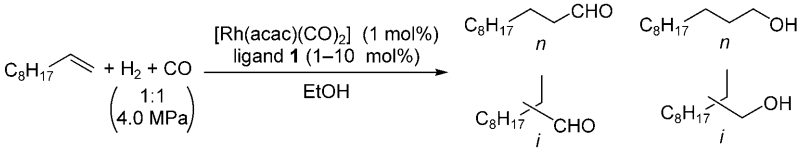
In the presence of [Rh(acac)(CO)$_2$] and ligand **1**, the reaction of 1-decene with hydrogen and carbon monoxide was carried out under various conditions. The results are summarized in Table 1. Because the reaction is a two-step process that consists of hydroformylation of decene and hydrogenation of the resulting aldehydes, the total *n*/*i* values are also described in Table 1.

First, the reaction was examined by varying the ligand/Rh ratio using **1a** (Table 1, Entries 1–5). The highest alcohol yield was observed with a **1a**/Rh ratio of 5 (Entry 4). The H_2/CO ratio hardly affected the result (Entries 4 and 6). A slight improvement in the *n*/*i* ratio was observed by changing the solvent from EtOH to *i*PrOH (Entries 4 and 7). The use of protic solvent seems essential to convert aldehydes to alcohols (Entry 8).[4e] Notably, despite the bite angle realized by the biphenyl-2,2′-ylene dimethane diyl framework, the *n*/*i* ratio is much lower than the parent BISBI for hydroformylation itself (*n*/*i* = 25.1).[8] At the lower temperature of 120 °C, the alcohol yield was only 36 %, with alkene consumption of 71 % in 6 h (Entry 9). The alcohol yield reached 97 % by elevation of the reaction temperature to 170 °C (Entry 10). The use of alkyl-BISBI derivatives **1b–d** with larger alkyl substituents on the phosphorus atoms resulted in lowering the yield of alcohols (Entries 11–13). Steric effects seem more significant than electronic effects because the electron-donating nature of the ligand increases in the order of $Me_3P < nHex_3P \approx neoPen_3P < iPr_3P$,[13] whereas the steric bulk increases in the order of $Me_3P < nHex_3P < iPr_3P < neoPen_3P$.[14] Notably, 1-decene was completely consumed in all cases except for those listed in Entries 6 and 7 (Table 1). The low yields of alcohols reported in Entries 7 and 11–13 originate from the high-boiling-point byproducts, which were derived from aldol condensation of the aldehydes or subsequent dehydration from the aldols. In these cases, the hydrogenation of aldehydes was slow, and as a result, the aldehydes underwent side reaction under the harsh reaction conditions. Because the *n*-aldehydes are more reactive for aldol condensation than *iso*-aldehydes, the *n*/*i* ratio of the remaining aldehydes is low.

In their studies on monodentate Rh/trialkylphosphine catalysts, Cole-Hamilton and colleagues suggested that the aldehyde hydrogenation activity being lower with iPr_3P than with Et_3P might result from the dissociation of iPr_3P from [Rh(iPr_3P)$_2$] species during the reaction process due to steric repulsion.[4e,f] Because such ligand dissociation was anticipated for **1d**, the following NMR studies were carried out for ligands **1a** and **1d**.

A mixture of [Rh(acac)(CO)$_2$] and **1d** (Rh/**1d** = 1:1) was treated with H_2/CO (1:1, 2.0 MPa total) in C_6D_6 at 70 °C for 16 h. After releasing the pressure, ^{1}H NMR analysis of the product under Ar at ambient pressure exhibited a hydride peak at $\delta = -11.0$ ppm, which is assignable to Rh-H species (Figure 4a). ^{31}P NMR data showed one doublet at $\delta =$ 61.5 ppm ($J_{Rh-P} = 144$ Hz), which corresponds to a structure with two equivalent phosphorus atoms coordinated to Rh

Table 1. Tandem hydroformylation–hydrogenation of 1-decene with Rh/R-BISBI.



Entry	Ligand	Ligand/Rh	*T* [°C]	*t* [h]	Aldehyde yield [%]	Aldehyde *n*/*i*	Alcohol yield [%]	Alcohol *n*/*i*	Total *n*/*i*
1	**1a**	1	150	6	85	1.4	<1	–	1.4
2	**1a**	2	150	6	20	0.94	62	3.8	2.1
3	**1a**	3	150	6	5	0.07	65	5.1	3.4
4	**1a**	5	150	6	<1	–	77	4.1	4.1
5	**1a**	10	150	6	7	0.72	64	6.0	4.5
6[a]	**1a**	5	150	6	2.5	1.6	74	4.1	4.0
7[b]	**1a**	5	150	6	<1	–	83	5.3	5.3
8[c]	**1a**	5	120	6	96	1.2	<1	–	1.2
9[d]	**1a**	5	120	6	8	1.6	36	9.2	4.4
10	**1a**	5	170	6	<1	–	97	4.1	4.1
11	**1b**	5	150	20	22	1.4	53	5.4	3.3
12	**1c**	5	150	20	28	0.48	17	0.84	0.6
13	**1d**	5	150	30	13	0.24	25	1.0	0.4

[a] The reaction was carried out with H_2/CO: 2.7 MPa/1.3 MPa; the conversion of 1-decene was 98%. [b] *i*PrOH was used as a solvent in place of EtOH. [c] THF was used as a solvent in place of EtOH. [d] Total conversion was 71%.

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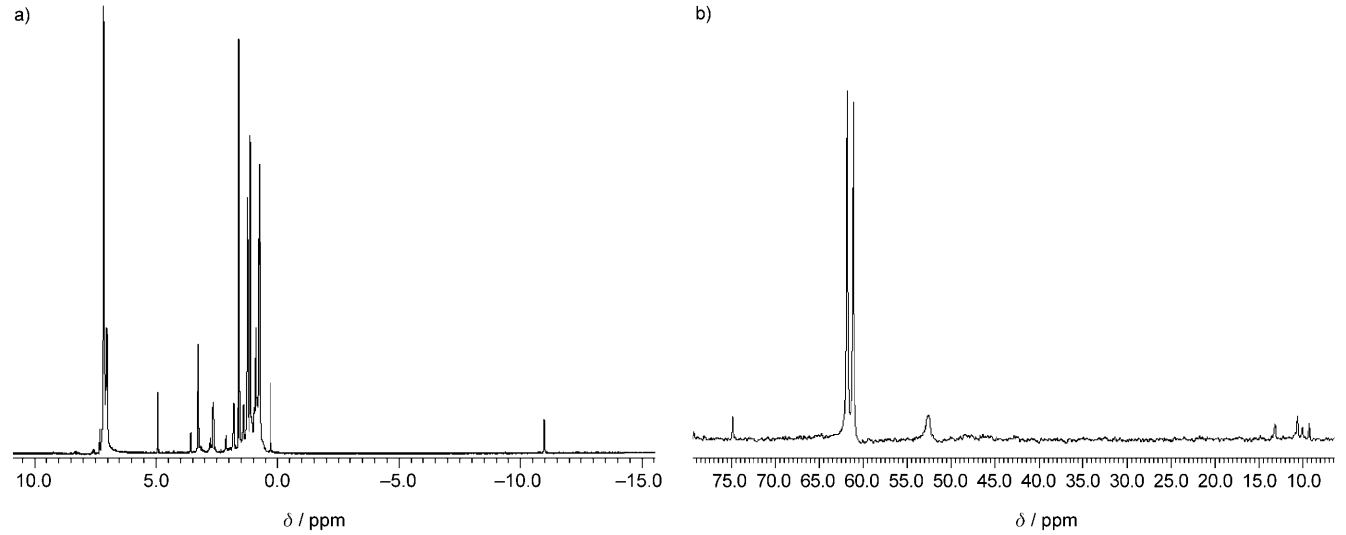

Figure 4. a) ^{1}H and b) $^{31}P\{^{1}H\}$ NMR spectra of a mixture of **1d** and [Rh(acac)(CO)$_2$] (Rh/**1d** = 1:1) under Ar (1 atm) in C_6D_6 after treatment with H_2/CO (1.0 MPa/1.0 MPa) at 70 °C for 16 h.

(Figure 4b). Judging from the reported data for [RhH(CO)$_2$(BISBI)],[8] the formation of the [RhH(CO)$_2$(**1d**)] species is suggested. Thus, in contrast to what we anticipated, the two phosphorus atoms stayed on the Rh center at least at the stage of resting state for hydroformylation, that is, the rhodium hydride species. The same species is generated with treatment of a mixture of [Rh(acac)(CO)$_2$] and **1d** (Rh/**1d** = 1:5) under the same conditions (Figure 5). The peak around $\delta = 46$ ppm in the ^{31}P NMR spectrum (Figure 5b), which is shifted lower relative to a free ligand, is unidentified at this moment. One of the possible species is tricoordinated Rh, realized by one bidentate coordination by **1d** plus coordination by half of the bidentate **1d**, leaving the other coordination site free. Another possible species is a ligand-bridged dimer.

In contrast, such clear presence of a Rh-H species was not observed for **1a**. No peak assignable for a hydride was detected by ^{1}H NMR conducted for the same reaction procedure as that for **1d**.[15] Because the loss of hydrogen is a possible decomposition pathway for Rh-H species in the absence of additional H_2, high-pressure NMR studies were further carried out as follows: A mixture of [Rh(acac)(CO)$_2$] and **1a** (Rh/**1a** = 1:5) was treated with H_2/CO (1:1, 2.0 MPa total) in a high-pressure NMR tube, and again no peak was assignable to metal hydride. By ^{31}P NMR, only the peak of free ligand was assignable. Because there were a few broad peaks, the mixture was heated at 100 °C. However, all of the peaks remained as they were, and still no peak was observed for a Rh−H bond (^{1}H NMR) or for a Rh−P bond (^{31}P NMR), even after 16 h at 100 °C (Figure 6). The peaks of the ^{31}P NMR spectrum were not sharpened at 25 °C.

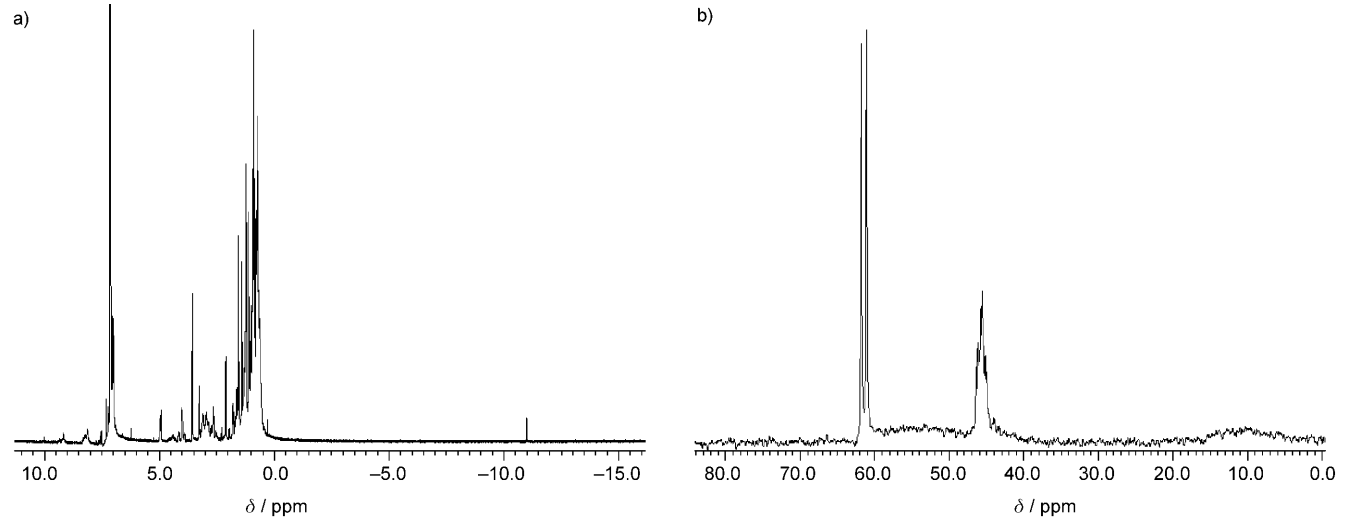

Figure 5. a) ^{1}H and b) $^{31}P\{^{1}H\}$ NMR spectra of a mixture of **1d** and [Rh(acac)(CO)$_2$] (Rh/**1d** = 1:5) under Ar (1 atm) in C_6D_6 after treatment with H_2/CO (1.0 MPa/1.0 MPa) at 70 °C for 16 h.

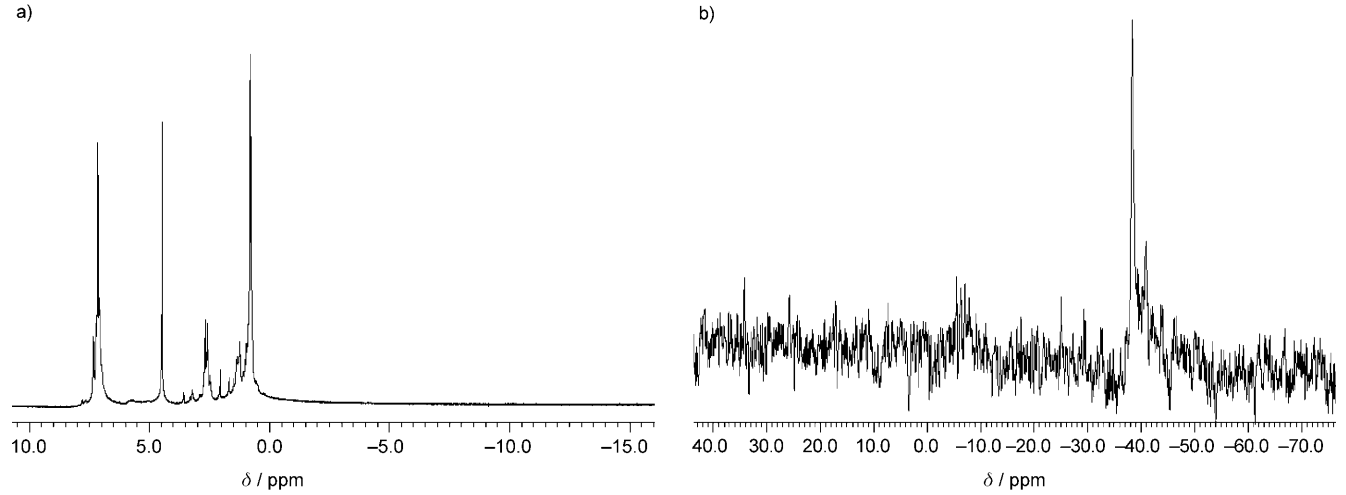

Figure 6. a) ^{1}H and b) $^{31}P\{^{1}H\}$ NMR spectra of a mixture of **1a** and $[Rh(acac)(CO)_2]$ (Rh/**1a** = 1:5) under H_2/CO (1.0 MPa/1.0 MPa) in C_6D_6 after treatment with H_2/CO (1.0 MPa/1.0 MPa) at 100 °C for 16 h.

In their studies on the silica-gel-supported Rh/xantphos system, Reek, van Leeuwen, and co-workers[5] proposed that the neutral Rh-H species is inactive for hydroformylation, and that cationic rhodium species or neutral Rh-Cl species are active for aldehyde hydrogenation. The lack of clear evidence for the stable Rh-H species with **1a** might be related to its much higher hydrogenation activity than that with **1d**, but details for this are still unknown.

Conclusions

Using bidentate trialkylphosphine **1a**, tandem hydroformylation–hydrogenation of 1-decene was achieved with an *n*/*i* ratio of up to 4.5. The more bulky bidentate ligand **1d** resulted in lower conversion of the aldehydes to alcohols. Although the dissociation of one of the two phosphorus atoms was anticipated for **1d**, rather stable $[RhH(CO)_2(ligand)]$ species was detected for **1d** rather than for **1a**.

Experimental Section

General: All operations involving air- or moisture-sensitive compounds were carried out with standard Schlenk techniques under an argon atmosphere purified by passing through a hot column packed with BASF R3-11 catalyst or in an argon-filled glove box, except where CO was used as indicated. NMR spectra were recorded on a JEOL JNM-ECP500 spectrometer (500 MHz for ^{1}H, 202 MHz for ^{31}P, and 125 MHz for ^{13}C). GC data were collected on a Shimadzu-GC-14B instrument with an Agilent J&W GC Column HP-1. MS data were measured on a JEOL JMS-700 mass spectrometer. Compound 2,2′-bis(chloromethyl)biphenyl,[11] Me_2PPMe_2,[10c] and $iPr_2PH\text{-}BH_3$,[16] were synthesized according to published procedures. *neo*$Pent_2PH\text{-}BH_3$ and $nHex_2PH\text{-}BH_3$ were prepared by reduction of *neo*$Pent_2PCl$[17] or $nHex_2PCl$[18] with $LiAlH_4$ and following protection with BH_3–THF complex.

Syntheses of ligands: Me-BISBI (**1a**): A potassium block (2.0 g, 51 mmol) was added to a solution of Me_2PPMe_2 (300 mg, 2.4 mmol) in THF (20 mL) and stirred for 15 h at room temperature. The resulting orange solution of $KPMe_2$ was added dropwise to a solution of 2,2′-bis(-chloromethyl)biphenyl (500 mg, 2.0 mmol) in THF (20 mL) at −35 °C. After warming to room temperature and stirring for 6 h, volatiles were removed. The residue was dissolved in THF and passed through a short path of silica gel. The resulting solution was concentrated under reduced pressure. The crude product was purified by preparative TLC (hexane/THF = 100:1) to afford Me-BISBI as a colorless oil (190 mg, 0.63 mmol, 31 %). ^{1}H NMR ($CDCl_3$): $\delta = 0.79$ (broad, 6H, CH_3), 0.88 (broad, 6H, CH_3), 2.44 (broad d, $J_{H,H} = 12.2$ Hz, 2H, CH_2), 2.53 (broad d, $J_{H,H} = 12.2$ Hz, 2H, CH_2), 7.07–7.26 ppm (m, 8H, ArH); ^{13}C NMR ($CDCl_3$): $\delta =$ 14.3 (d, $J_{P,C} = 14.3$ Hz), 14.5 (d, $J_{P,C} = 14.3$ Hz), 36.6 (d, $J_{P,C} = 14.3$ Hz), 125.5 (s), 127.4 (s), 129.6 (d, $J_{P,C} = 8.6$ Hz), 131.0 (s), 136.7 (s), 140.8 ppm (d, $J_{P,C} = 2.9$ Hz); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): $\delta = -41.8$ ppm (s); HRMS (FAB): *m*/*z* calcd for $C_{18}H_{25}O_2P_2$: 335.1330 $[M+2O+H]^+$, found: 335.1331.

*n*Hex-BISBI (**1b**): *n*BuLi (0.60 mL, 1.6 M solution in hexane, 0.94 mmol) was added to a solution of $nHex_2PH\text{-}BH_3$ (200 mg, 0.92 mmol) in THF (5.0 mL) at 0 °C. The resulting pale yellow solution was allowed to warm to room temperature and stirred for 2 h. The solution was then cooled to 0 °C, and 2,2′-bis(chloromethyl)biphenyl (100 mg, 0.40 mmol) was added as a solid. After warming to room temperature and stirring for overnight, the reaction mixture was quenched with water. The product was extracted with CH_2Cl_2, and the combined layers were dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure, and the resulting residue was purified by preparative TLC (hexane/EtOAc = 20:1) to afford *n*Hex-BISBI-BH_3 (200 mg, 82 %). ^{1}H NMR ($CDCl_3$): $\delta = 0.35$ (broad d, $J_{B,H} = 113$ Hz, 6H, BH_3), 0.86 (t, $J_{H,H} = 7.2$ Hz, 6H, CH_3), 0.87 (t, $J_{H,H} = 7.1$ Hz, 6H, CH_3), 1.03–1.42 (m, 40H, $(CH_2)_5Me$), 2.78 (dd, $J_{P,H} = 13.9$ Hz, $J_{H,H} = 13.9$ Hz, 2H, CH_2Ar), 2.94 (dd, $J_{P,H} = 10.2$ Hz, $J_{HH} =$ 13.9 Hz, 2H, CH_2), 7.18–7.20 (m, 2H, Ar*H*), 7.30–7.34 (m, 2H, Ar*H*), 7.35–7.38 (m, 2H, Ar*H*), 7.45–7.48 ppm (m, 2H, Ar*H*); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): $\delta = 20.8$ ppm (m). A part of the obtained *n*Hex-BISBI-BH_3 (100 mg, 0.16 mmol) was dissolved in $HNEt_2$ (1.0 mL) and THF (1.0 mL) and stirred for 4 days at 50 °C. The volatiles were removed under reduced pressure, and the residue was dissolved in Et_2O and passed through a short path of silica gel. The resulting solution was concentrated under reduced pressure. The obtained crude product was purified by preparative TLC (hexane/THF = 50:1) to afford *n*Hex-BISBI as a colorless oil (74 mg, 0.13 mmol, 78 %). ^{1}H NMR ($CDCl_3$): $\delta = 0.86$ (t, $J_{H,H} = 7.0$ Hz, 6H, CH_3), 0.88 (t, $J_{H,H} = 6.9$ Hz, 6H, CH_3), 1.13–1.40 (m, 40H, $(CH_2)_5Me$), 2.47 (dd, $J_{P,H} = 2.4$ Hz, $J_{H,H} = 13.5$ Hz, 2H, CH_2Ar), 2.57 (d, $J_{H,H} = 13.5$ Hz, 2H, CH_2Ar), 7.15–7.35 ppm (m, 8H, ArH);^{13}C NMR ($CDCl_3$): $\delta = 14.3$ (s), 22.7 (s), 25.7 (d, $J_{P,C} = 12.5$ Hz), 26.0 (d, $J_{P,C} =$ 13.4 Hz), 27.6 (d, $J_{P,C} = 14.4$ Hz), 27.9 (d, $J_{P,C} = 14.4$ Hz), 31.2 (d, $J_{P,C} =$ 10.5 Hz), 31.3 (d, $J_{P,C} = 11.5$ Hz), 31.7 (d, $J_{P,C} = 5.7$ Hz), 32.7 (d, $J_{P,C} =$ 16.3 Hz), 125.4 (s), 127.3 (s), 129.6 (d, $J_{P,C} = 9.6$ Hz), 130.9 (s), 137.4 (d,

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$J_{P,C}$=5.7 Hz), 140.9 ppm (d, $J_{P,C}$=2.9 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=−20.8 ppm (s); HRMS (FAB): *m*/*z* calcd for $C_{38}H_{65}O_2P_2$: 615.4460 [*M*+2O+H]$^+$, found: 615.4460.

*neo*Pent-BISBI (**1c**): *n*BuLi (0.86 mL, 1.6 M solution in hexane, 1.4 mmol) was added to a solution of *neo*Pent$_2$PH-BH_3 (250 mg, 1.4 mmol) in THF (3 mL) at 0 °C. The resulting pale yellow solution was allowed to warm to room temperature and stirred for 2 h. The solution was then cooled to 0 °C, and 2,2′-bis(chloromethyl)biphenyl (170 mg, 0.67 mmol) was added as a solid. After warming to room temperature and stirring for 24 h, the reaction mixture was quenched with water. The product was extracted with CH_2Cl_2, and the combined organic layers were dried over anhydrous $MgSO_4$. After the solvent was evaporated under reduced pressure, *neo*Pr-BISBI-BH_3 was recrystallized from hexane/$CHCl_3$ (231 mg, 62 %). ^1H NMR($CDCl_3$): δ=0.40 (broad, 6H, B*H*$_3$), 0.94 (s, 18H, C*H*$_3$), 0.99 (s, 18H, C*H*$_3$), 1.09–1.26 (m, 6H, C*H*$_2$*t*Bu), 1.50–1.56 (m, 2H, C*H*$_2$*t*Bu), 2.77 (dd, $J_{P,H}$=13.5 Hz, $J_{H,H}$=13.5 Hz, C*H*$_2$Ar), 3.06 (dd, $J_{P,H}$=8.8 Hz, $J_{H,H}$=13.5 Hz, 2H, C*H*$_2$Ar), 7.20–7.22 (m, 2H, Ar*H*), 7.33–7.40 (m, 4H, Ar*H*), 7.53–7.55 ppm (m, 2H, Ar*H*); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=15.8 ppm (m). A part of the obtained *neo*Pr-BISBI-BH_3 (185 mg, 0.33 mmol) was dissolved in $HNEt_2$ (5.0 mL) and THF (5.0 mL) and stirred for 3 days at 50 °C. The volatiles were removed under reduced pressure. The residue was dissolved in Et_2O and passed through a short path of silica gel. The resulting solution was concentrated under reduced pressure. The resulting crude product was purified by preparative TLC (hexane/THF=100:1) to afford *neo*Pent-BISBI as a white powder (140 mg, 0.27 mmol, 80 %). ^1H NMR ($CDCl_3$): δ=0.75 (s, 18H, C*H*$_3$), 0.86 (s, 18H, C*H*$_3$), 1.13 (dd, $J_{P,H}$=4.2 Hz, $J_{H,H}$=14.1 Hz, 2H, C*H*$_2$*t*Bu), 1.21–1.26 (m, 4H, C*H*$_2$*t*Bu), 1.36 (dd, $J_{P,H}$=4.2 Hz, $J_{H,H}$=14.1 Hz, 2H, C*H*$_2$*t*Bu), 2.43 (d, $J_{H,H}$=13.5 Hz, 2H, C*H*$_2$Ar), 2.58 (d, $J_{H,H}$=13.5 Hz, 2H, C*H*$_2$Ar), 7.13–7.20 (m, 4H, ArH), 7.22–7.25 (m, 2H, ArH), 7.37–7.39 ppm (m, 2H, ArH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=30.8 (d, $J_{P,C}$=8.6 Hz), 30.9 (d, $J_{P,C}$=9.6 Hz), 31.3 (d, $J_{P,C}$=14.4 Hz), 31.5 (d, $J_{P,C}$=14.4 Hz), 36.2 (d, $J_{P,C}$=16.3 Hz), 45.1 (d, $J_{P,C}$=17.3 Hz), 45.8 (d, $J_{P,C}$=18.2 Hz), 125.4 (d, d, $J_{P,C}$=1.9 Hz), 127.1 (s), 130.0 (d, $J_{P,C}$=10.6 Hz), 131.1 (s), 137.6 (d, $J_{P,C}$=6.7 Hz), 141.4 ppm (d, $J_{P,C}$=2.9 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=−37.9 ppm (s); HRMS (FAB): *m*/*z* calcd for $C_{34}H_{57}O_2P_2$: 559.3834 [M+2O+H]$^+$, found: 559.3840.

*i*Pr-BISBI (**1d**): *n*BuLi (5.0 mL, 1.6 M solution in hexane, 8.0 mmol) was added to a solution of *i*Pr$_2$PH-BH_3 (1.06 g, 8.0 mmol) in THF (10 mL) at 0 °C. The resulting pale yellow solution was allowed to warm to room temperature and stirred for 2 h. The solution was then cooled to 0 °C, and 2,2′-bis(chloromethyl)biphenyl (1.0 g, 4.0 mmol) was added as a solid. After warming to room temperature and stirring overnight, the reaction mixture was quenched with water. The product was extracted with CH_2Cl_2, and the combined organic layers were dried over anhydrous $MgSO_4$. After the solvent was evaporated under reduced pressure, *i*Pr-BISBI-BH_3 was recrystallized from toluene/hexane (1.1 g, 62 %). ^1H NMR ($CDCl_3$): δ=0.40 (broad d, $J_{B,H}$=111 Hz, 6H, B*H*$_3$), 0.71–0.78 (m, 12H, C*H*$_3$), 0.92 (dd, $J_{P,H}$=13.5 Hz, $J_{H,H}$=7.1 Hz, 6H, C*H*$_3$), 1.07 (dd, $J_{P,H}$=14.2 Hz, $J_{H,H}$=7.1 Hz, 6H, C*H*$_3$), 1.59–1.70 (m, 2H, C*H*), 1.76–1.87 (m, 2H, C*H*), 2.79 (dd, $J_{P,H}$=14.2 Hz, $J_{H,H}$=14.2 Hz, 2H, C*H*$_2$), 2.92 (dd, $J_{P,H}$=10.3 Hz, $J_{H,H}$=14.2 Hz, 2H, C*H*$_2$), 7.19–7.21 (m, 2H, Ar*H*), 7.30–7.37 (m, 4H, Ar*H*), 7.66–7.68 ppm (m, 2H, Ar*H*); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=38.0 ppm (m). A part of the obtained *i*Pr-BISBI-BH_3 (300 mg, 0.68 mmol) was dissolved in $HNEt_2$ (5.0 mL) and THF (2.0 mL) and stirred for 4 days at 50 °C. The volatiles were removed under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane/THF=30:1) to afford *i*Pr-BISBI as a colorless oil (180 mg, 64 %). ^1H NMR ($CDCl_3$): δ=0.72–0.80 (m, 6H, C*H*$_3$), 0.95–1.02 (m, 6H, C*H*$_3$), 1.41–1.54 (m, 2H, C*H*), 1.59–1.60 (m, 2H, C*H*), 2.51 (dd, $J_{P,H}$=4.0 Hz, $J_{H,H}$=14.0 Hz, 2H, C*H*$_2$), 2.61 (d, $J_{H,H}$=14.0 Hz, 2H, C*H*$_2$), 7.15–7.35 (m, 6H, ArH), 7.47 ppm (d, $J_{P,H}$=7.3 Hz,2H, ArH); ^{13}C NMR ($CDCl_3$): δ=19.3 (d, $J_{P,C}$=12.5 Hz), 19.5 (d, $J_{P,C}$=12.5 Hz), 19.57 (d, $J_{P,C}$=10.5 Hz), 19.64 (d, $J_{P,C}$=13.4 Hz), 23.3 (d, $J_{P,C}$=14.4 Hz), 27.0 (d, $J_{P,C}$=20.1 Hz), 125.4 (s), 127.3 (s), 123.0 (d, $J_{P,C}$=11.5 Hz), 130.9 (s), 138.2 (d, $J_{P,C}$=8.6 Hz), 141.2 ppm (d, $J_{P,C}$=2.9 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=11.4 ppm (s); HRMS (FAB): *m*/*z* calcd for $C_{26}H_{41}O_2P_2$: 447.2572 [*M*+2O+H]$^+$, found: 447.2578.

Tandem hydroformylation–hydrogenation with Rh-Bu$_3$P (Figures 1 and 2). A mixture of Bu_3P (10.1 mg, 0.050 mmol), [Rh(acac)(CO)$_2$] (2.8 mg, 0.010 mmol), and 1-decene (0.20 mL, 1.0 mmol) in ethanol (1.0 mL) was degassed by three freeze–thaw cycles in a Schlenk tube. The solution was transferred into a 50-mL autoclave under Ar, and then H_2/CO (1:1, 4.0 MPa) was introduced. The mixture was stirred at 120 °C for the appropriate time and then cooled to room temperature. After the H_2/CO pressure was released, dodecane was added, and the mixture was stirred for a few minutes. The conversion and the yields of products were determined by GC (Agilent J&W GC Column HP-1; 50 °C 2 min, then heated to 270 °C at a rate of 10 °C min^{-1}) using dodecane as an internal standard.

Tandem hydroformylation–hydrogenation with Rh-alkyl-BISBIs (Table 1). A mixture of alkyl-BISBI, [Rh(acac)(CO)$_2$] (2.8 mg, 0.010 mmol), and 1-decene (0.20 mL, 1.0 mmol) in ethanol (1.0 mL) was degassed by three freeze–thaw cycles in a Schlenk tube. The solution was transferred into a 50-mL autoclave under Ar, and then H_2/CO (1:1, 4.0 MPa) was introduced. The mixture was stirred at 150 °C for the appropriate time and then cooled to room temperature. The conversion and yields of the products were analyzed as mentioned above.

Analysis of the reaction mixture by ^{31}P NMR spectroscopy. The reaction was carried out by using Me-BISBI (**1a**) according to the procedure described above (Rh/**1a**=1:5, H_2/CO=1:1 (4.0 MPa), 135 °C, 4 h). An aliquot of the reaction mixture was drawn up by syringe under argon and dissolved in $CDCl_3$. The ^{31}P NMR spectrum of the sample showed that the parent compound **1a** (~60 %) and Rh-bound **1a** (~20 %) were present while oxidized **1a** (~20 %) also formed.

NMR studies of the Rh complexes. A mixture of alkyl-BISBI (0.050 mmol) and [Rh(acac)(CO)$_2$] (2.8 mg, 0.010 mmol) in C_6D_6 (1.0 mL) was put into a high-pressure NMR sample tube. The tube was filled with H_2/CO (1:1, 2.0MPa) and heated in an oil bath (Me-BISBI, 100 °C; *i*Pr-BISBI, 70 °C) for 16 h. ^1H and $^{31}P\{^1H\}$ NMR spectra were then taken at 100 °C.

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