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Synthesis and Application of Tetraphosphane Ligands in Rhodium-Catalyzed Hydroformylation of Terminal Olefins: High Regioselectivity at High Temperature

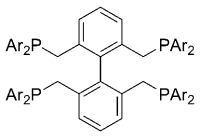
Shichao Yu,[a] Xiaowei Zhang,[a] Yongjun Yan,[a] Chaoxian Cai,[a] Liyan Dai,*[a, b] and Xumu Zhang*[a]

Abstract: A new class of substituted tetraphosphane ligands has been developed and applied in the rhodium-catalyzed regioselective hydroformylation of terminal olefins. The high regioselectivity (linear selectivity is above 97% for 1-octene and 1-hexene) at high temperature (140°C) shown by these tetraphosphane ligands is remarkable considering the low regioselectivity commonly observed under similar reaction conditions when other bisphosphane analogues are used. The steric and electronic effects of substituents on the diarylphosphane moiety have also been examined.

Keywords: biaryls · hydroformylation · phosphane ligands · regioselectivity · rhodium

Introduction

Hydroformylation of olefins represents one of the most important reactions in industry. The reaction is catalyzed by homogeneous catalysts and leads to products containing an aldehyde group that are versatile intermediates and building blocks for various pharmaceuticals, agrochemicals, commodity and fine chemicals.[1] Production volumes obtained by using this process are estimated to be over nine million tons annually. Most commercial hydroformylation processes use highly reactive rhodium catalysts that are modified with either mono- or bisphosphorus ligands to address the issue of regio- and stereoselectivity. Phosphane- and phosphite-based systems giving highly regioselective linear aldehydes have been reported. Some elegant examples include Bisbi,[2] Xantphos,[3] Biphephos,[4] Naphos,[5] calix[4]arene bisphosphite,[6] pyrrole-based bisphosphoramidite,[7] and self-assembled bisphosphane.[8] Hydroformylation with these catalytic systems are generally carried out at a relatively low temperature (below 125°C) to ensure high regioselectivity. Since hydroformylation reactions at high temperatures afford higher reaction rates, from the view of industrial applications, it is desirable to develop regioselective ligands for high-temperature hydroformylation. Another challenge that is important to industry is the hydroformylation of long-chained olefins; in these cases, the produced aldehydes have high boiling points and thus require high-temperature distillation during the production process, which means that the ligands used in the reaction must be tolerant towards high temperatures. Herein, we would like to report the design and synthesis of a new class of tetraphosphane ligands **1** that are based on a biphenyl backbone, and describe their application in the highly regioselective hydroformylation of terminal olefins.[9]



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One of the reasons for the reduced regioselectivity of Rh-catalyzed hydroformylation reactions at high temperature is the formation of unselective catalytic species due to the dissociation of phosphorus ligands from the metal center. Carbonyl monoxide is a strong π acid that competes to bind to the rhodium center with the phosphorus ligand; at high tem-

[a] Dr. S. Yu, X. Zhang, Dr. Y. Yan, C. Cai, Prof. L. Dai, Prof. X. Zhang
Department of Chemistry and Chemical Biology
& Pharmaceutical Chemistry, Rutgers
The State University of New Jersey
Piscataway, New Jersey 08854 (USA)
Fax: (+1) 732-445-6312
E-mail: xumu@rci.rutgers.edu

[b] Prof. L. Dai
College of Materials Science and Chemical Engineering
Zhejiang University, Hangzhou 310027
Zhejiang (P.R. China)
Fax: (+86) 571-8795-2693
E-mail: dailiyan@zju.edu.cn

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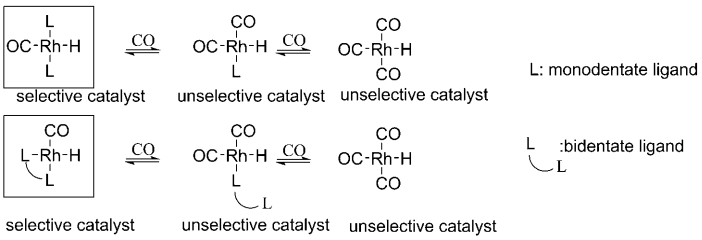
perature the exchange between the ligands is also accelerated. To ensure the formation of the selective catalytic species, usually a large excess of monophosphorus ligands are used. The development of bisphosphorus ligands affords higher regioselectivity and requires lower amounts of ligand, which may partly arise from the formation of more selective, bulky, and robust catalytic species (Scheme 1). Thus, we envisaged that tetraphosphane ligand **1** should afford better regioselectivity at high temperatures than its bisphosphane analogue Bisbi for the following reasons: 1) Ligand **1** has a higher concentration of the selective catalytic species due to the presence of multiple chelating modes: a rhodium metal center can form four possible equivalent bidentate complexes. 2) When ligand **1** coordinates to the metal to form a bidentate system, the nearby intramolecular free phosphorus atoms can effectively increase the local phosphorus concentration around the metal center and enhance the chelating ability. When a phosphane moiety in the bidentate ligand dissociates from the metal, two intermediates are formed by recoordination of another two phosphane moieties to the Rh center to reform the bidentate system (Scheme 2). Such "enhanced multidentarity" has been demonstrated to enhanced the ligands' ability to stabilize catalytic systems and promote their longevity in transition-metal-catalyzed coupling reactions.[10]

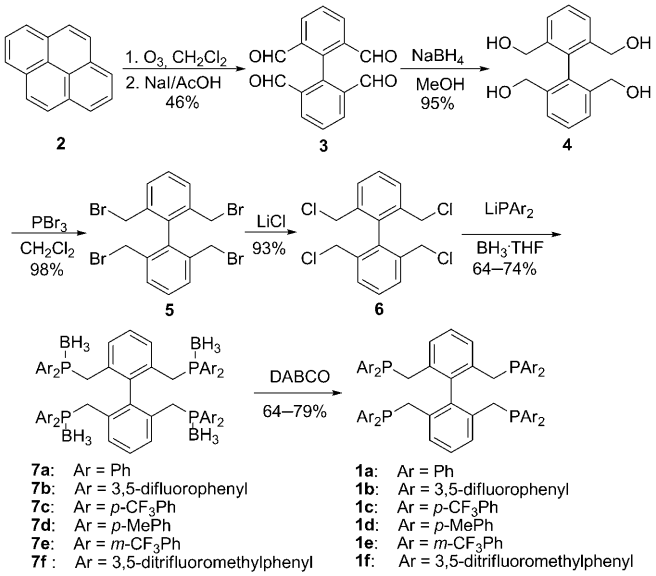


Scheme 1. Ligand dissociation in hydroformylation.

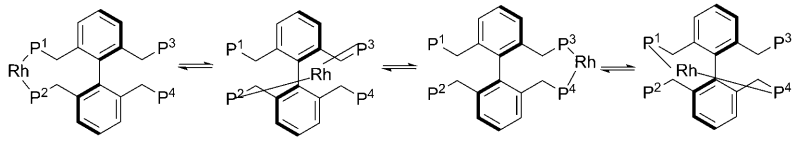
This multidentarity effect has also been observed in our previously developed pyrrole-based tetraphosphoramidite ligands for the regioselective hydroformylation of internal olefins, styrene and its derivatives, vinyl acetates, and dienes, which all show exceptionally high regioselectivity towards the formation of linear aldehydes.[11] The peculiar behavior of those ligands was ascribed to the large bite angle formed by coordination with the metal (nine-membered ring), the multiple coordination modes increase the concentration of the selective catalytic species, and the electron-withdrawing property of the *N*-pyrrolylphosphorus moiety.[7] Ligand **1** has similar coordination modes to those of the tetraphosphoramidite, but with more electron-rich phosphorus moieties. The latter character may reduce the extent of double-bond isomerization during the hydroformylation process as observed for electron-donating bisphosphanes such as Bisbi.[2] Thus, we envisioned that ligand **1** could be a good candidate for the regioselective hydroformylation of terminal olefins with low isomerization.

Results and Discussion

The synthesis of ligand **1** was realized as shown in Scheme 3. Starting from the ozonolysis of pyrene (**2**), reduction of biphenyl-2,2′,6,6′-tetracarbaldehyde (**3**) by sodium borohydride, and bromination of 2,2′,6,6′-tetrakis(hydroxymethyl)-biphenyl (**4**), tetrabromide **5** was prepared in high yields.[12] Whereas the synthesis of Bisbi by reaction of lithium diphenylphosphane with 2,2′-bisbromomethyl-1,1′-biphenyl was reported to occur in high yield,[2a] the reaction of tetrabromide **5** with lithium diphenylphosphane gave a complex mixture of unidentified products as monitored by ^{31}P NMR spectroscopy in situ. The reactivity of tetrabromide **5** was thus very different from its corresponding dibromide, 2,2′-bisbromomethyl-1,1′-biphenyl. To overcome this problem, we converted tetrabromide **5** into the less reactive tetrachloride **6** by the reaction of the tetrabromide with lithium chloride in DMF at room temperature; the



Scheme 3. The synthesis of tetraphosphane ligand **1**.



Scheme 2. Enhanced chelating ability of **1** through multiple chelating modes and increased local phosphorus concentration.

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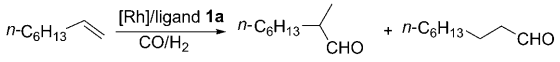
tetrachloride **6** was obtained in high yield (93%). We were pleased to find that the reaction of tetrachloride **6** with lithium diarylphosphane[13] cleanly afforded the desired tetraphosphane as indicated by a single peak in ^{31}P NMR spectra, which was recorded in situ. Since tetraphosphane **1** is an air-sensitive compound, tetraphosphane **1** was protected in situ with borane for purification. A simple deprotection of the borane with 1,4-diazabicyclo[2.2.2]octane (DABCO) afforded the desired tetraphosphane ligand **1** in 64–79% yield.

Hydroformylation of terminal olefins with the new ligand **1a** was then investigated. The hydroformylation reaction was conducted in toluene with 1-octene as the standard substrate and decane as internal standard. The rhodium catalyst was prepared in situ by mixing the ligand **1a** with [Rh(acac)(CO)$_2$] (acac = acetylacetonate) in toluene. The substrate/catalyst ratio was 2000 and the catalyst concentration was 1.0 mM. The reaction was terminated after one hour.

The effects of the ligand/metal ratio on hydroformylation of terminal olefins with the tetraphosphane ligand **1a** were examined. As shown in Table 1 (entries 1–4), a slight decrease in both the linear/branched (*n*/*i*) ratio and isomerization were observed when the ligand/metal ratio was increased from 1:1 to 6:1. The effects of reaction temperature on the hydroformylation reaction were also investigated (Table 1, entries 3, and 5–7). To our delight, only a slight decrease in the *n*/*i* ratio was observed when the reaction temperature was increased from 100 to 140 °C. As expected, hydroformylation at lower temperatures led to less olefin isomerization. Finally, the effects of CO/H$_2$ pressure were tested (Table 1, entries 3, 8–10). At high CO/H$_2$ pressure, the regioselectivities were low, however, the regioselectivities could be increased by lowering the CO/H$_2$ pressure. The highest regioselectivity (*n*/*i* ratio 66.7) was obtained under a CO/H$_2$ pressure of 5/5 atm. However, a significant amount of isomerization was observed under this pressure, indicating that low CO/H$_2$ pressures facilitate the olefin isomerization.

Table 1. Optimization of reaction conditions for the hydroformylation of 1-octene with Rh/ligand (L) **1a**.[a]

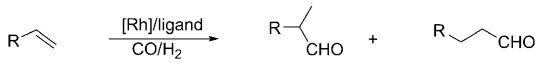


	L/Rh	*T* [°C]	CO/H$_2$ [atm]	*n*/*i*[b]	Linear [%][c]	Isomerization [%][d]	TON[e]
1	1:1	100	10/10	53.7	98.2	7.9	1.8×10^3
2	2:1	100	10/10	53.4	98.2	7.3	1.8×10^3
3	4:1	100	10/10	50.5	98.1	5.6	1.8×10^3
4	6:1	100	10/10	48.9	98.0	5.6	1.8×10^3
5	4:1	140	10/10	45.2	97.8	6.5	1.8×10^3
6	4:1	120	10/10	49.8	98.0	5.8	1.8×10^3
7	4:1	80	10/10	34.2	97.2	3.4	1.4×10^3
8	4:1	100	30/30	16.5	94.3	2.9	1.2×10^3
9	4:1	100	20/20	22.3	95.7	3.0	1.2×10^3
10	4:1	100	5/5	66.7	98.5	17.3	1.6×10^3

[a] Reagents and conditions: substrate/catalyst ratio = 2000, [Rh] (1.0 mM), toluene, 1 h, decane as internal standard. [b] Linear/branched ratio determined by GC analysis. [c] Percentage of linear aldehyde in all aldehydes. [d] Isomerization of internal olefin. [e] Turnover number, determined by GC analysis.

For comparison, bisphosphane ligand Bisbi was prepared and employed in the hydroformylation of terminal olefins under the same reaction conditions. The results, summarized in Table 2, clearly show that, in all cases, the use of tetraphosphane ligand **1a** afforded higher regioselectivity than Bisbi under the same reaction conditions. It should be noted that, at high temperature, a dramatic decrease in the regioselectivity and a high percentage of isomerization was observed with bisphosphane ligand Bisbi (Table 2, entries 1, 2, and 8). For example, in the hydroformylation of 1-octene, the regioselectivity was much lower (*n*/*i* = 2.4) and the extent of isomerization was significant (24%) at 140 °C with Bisbi as ligand (Table 2, entry 2); whereas, the regioselectivity remained high (*n*/*i* = 45.2) and the isomerization remained low (6.5%) using tetraphosphane ligand **1a** at the same temperature (Table 2, entry 1). At lower temperature (100 °C), both tetraphosphane **1a** and bisphosphane Bisbi afforded high regioselectivity and low isomerization, with *n*/*i* ratios greater than 40 and isomerization less than 10% (Table 2, entries 5, 6, 11, and 12). The similar performances with both ligands at low temperature and dramatic differences observed at high temperature suggest that the superior performance of ligand **1a** at high temperature is indeed due to the enhanced chelating ability of ligands **1**. This result is also important from the practical point of view because highly regioselective hydroformylation can, under these conditions, now be carried out at higher temperature, with subsequently higher reaction rates.

Table 2. Comparison of tetraphosphane and bisphosphane ligands.[a]



	Substrate	*T* [°C]	Ligand	*n*/*i*[b]	Linear [%][c]	Isomerization [%][d]	TON[e]	TOF[f] [h^{-1}]
1	1-octene	140	**1a**	45.2	97.8	6.5	1.8×10^3	9.3×10^3
2	1-octene	140	Bisbi	2.4	70.6	24	1.5×10^3	6.2×10^3
3	1-octene	120	**1a**	49.8	98.0	5.8	1.8×10^3	7.3×10^3
4	1-octene	120	Bisbi	29.5	96.7	8.7	1.8×10^3	5.7×10^3
5	1-octene	100	**1a**	50.5	98.1	5.6	1.8×10^3	2.5×10^3
6	1-octene	100	Bisbi	45.2	97.8	6.7	1.6×10^3	3.4×10^3
7	1-hexene	140	**1a**	43.8	97.8	7.7	1.8×10^3	9.5×10^3
8	1-hexene	140	Bisbi	4.9	83.1	20	1.6×10^3	8.7×10^3
9	1-hexene	120	**1a**	48.5	98.0	7.1	1.8×10^3	6.6×10^3
10	1-hexene	120	Bisbi	35.8	97.3	9.1	1.8×10^3	6.0×10^3
11	1-hexene	100	**1a**	48.6	98.0	6.6	1.8×10^3	3.3×10^3
12	1-hexene	100	Bisbi	43.2	97.7	9.4	1.7×10^3	2.6×10^3

[a] Reagents and conditions: substrate/catalyst ratio = 2000, [Rh] (1.0 mM), ligand/Rh ratio = 4:1, CO/H$_2$ (10/10 atm), 1 h, toluene, decane as internal standard. [b] Linear/branched ratio determined by GC analysis. [c] Percentage of linear aldehyde in all aldehydes. [d] Isomerization of internal olefin. [e] Turnover number, determined by GC analysis. [f] Turnover frequency, determined by GC analysis, reaction time = 10 min.

Ligands **1b–f** were then applied to rhodium-catalyzed hydroformylation of terminal olefins 1-hexene and 1-octene

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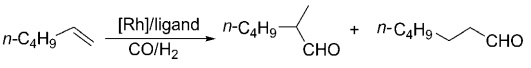
under a range of reaction temperatures (Tables 3 and 4). It was found that the introduction of substituents at the diphenylphosphane moiety of **1a** affected both the regioselectivity of the aldehydes and the activity of the catalytic system. In both cases, the catalytic system with ligands **1b**, **1c**, **1e**, and **1f**, which contain electron-withdrawing substituents, showed higher activity than with ligand **1d**, which contains an electron-donating group. The trend for those ligands on the regioselectivity, however, was not as clear. Whereas ligand **1b** afforded the best linear to branch ratio at 140 °C for 1-hexene (87.9), ligand **1f** was found to be somewhat better than **1b** for 1-octene under similar reaction conditions (52.4 versus 47.4) (see Table 3, entry 1, and Table 4, entries 1 and 11). The position of the substituents may also exert some influence on the regioselectivity. Ligand **1c**, containing a trifluoromethyl substituent at the *para*-position of the diphenylphosphane moiety, gave a higher linear to branch ratio for the hydroformylation of the 1-hexene than the corresponding ligand **1e** with the same substituent at the *meta*-position (see Table 3, entries 4 and 9). Apparently, ligand **1e** has a larger steric effect than ligand **1c**. This effect was reversed when 1-octene was examined (see Table 4, entries 4 and 9). With one more trifluoromethyl substituent at the *meta*-position of the diphenylphosphane moiety, the increase in the regioselectivity observed for the reaction with 1-octene was continued, whereas that with 1-hexene decreased (see Table 3, entry 11 and Table 4, entry 11). From these results, it can clearly be seen that subtle changes in the substrate chain length can require a change in the choice of suitable ligand.

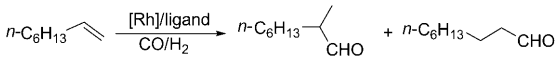
Table 3. Hydroformylation of 1-hexene by using tetraphosphane ligands **1b–f** at a range of temperatures.[a]



	L	T [°C]	n/i[b]	Linear [%][c]	Isomerization [%][d]	TON[e]	TOF[f] [h^{-1}]
1	**1b**	140	87.9	98.9	4.8	1.8×10^3	1.1×10^4
2	**1b**	120	92.1	98.9	4.6	1.8×10^3	7.6×10^3
3	**1b**	100	125.9	99.2	4.2	1.8×10^3	5.7×10^3
4	**1c**	140	64.1	98.5	5.1	1.8×10^3	9.9×10^3
5	**1c**	120	87.3	98.9	4.8	1.8×10^3	7.3×10^3
6	**1c**	100	95.7	98.9	4.5	1.8×10^3	5.1×10^3
7	**1d**	140	41.3	97.6	7.4	1.4×10^3	6.1×10^3
8	**1d**	120	44.8	97.8	7.2	1.1×10^3	5.3×10^3
9	**1e**	140	32.4	97.0	8.7	1.8×10^3	1.1×10^4
10	**1e**	120	55.2	98.2	6.5	1.8×10^3	9.9×10^3
11	**1f**	140	28.8	96.6	8.8	1.8×10^3	1.6×10^4
12	**1f**	120	49.3	98.0	6.6	1.8×10^3	1.3×10^4

[a] Reagents and conditions: substrate/catalyst ratio = 2000, [Rh] (1.0 mM), toluene, 1 h, decane as internal standard. [b] Linear/branched ratio determined by GC analysis. [c] Percentage of linear aldehyde in all aldehydes. [d] Isomerization of internal olefin. [e] Turnover number, determined by GC analysis.

Table 4. Hydroformylation of 1-octene by using tetraphosphane ligands **1b–f** at a range of temperatures.[a]



	L	T [°C]	n/i[b]	Linear [%][c]	Isomerization [%][d]	TON[e]	TOF [h^{-1}][f]
1	**1b**	140	47.4	97.9	5.7	1.9×10^3	1.0×10^4
2	**1b**	120	53.7	98.2	5.4	1.9×10^3	9.1×10^3
3	**1b**	100	77.9	98.7	4.9	1.8×10^3	7.4×10^3
4	**1c**	140	17.9	94.7	7.1	1.9×10^3	9.7×10^3
5	**1c**	120	33.5	97.1	6.8	1.9×10^3	7.9×10^3
6	**1c**	100	63.2	98.4	5.2	1.9×10^3	5.3×10^3
7	**1d**	140	24.4	96.0	7.7	1.6×10^3	6.3×10^3
8	**1d**	120	38.9	97.5	7.4	1.2×10^3	5.5×10^3
9	**1e**	140	42.8	97.7	5.4	1.9×10^3	1.2×10^4
10	**1e**	120	67.3	98.5	4.5	1.9×10^3	9.1×10^3
11	**1f**	140	52.4	98.1	5.6	1.9×10^3	1.4×10^4
12	**1f**	120	64.1	98.4	5.1	1.8×10^3	1.1×10^4

[a] Reagents and conditions: substrate/catalyst ratio = 2000, [Rh] (1.0 mM), toluene, 1 h, decane as internal standard. [b] Linear/branched ratio determined by GC analysis. [c] Percentage of linear aldehyde in all aldehydes. [d] Isomerization of internal olefin. [e] Turnover number, determined by GC analysis.

Conclusion

A series of substituted tetraphosphane ligands **1**, have been designed, synthesized, and applied in the rhodium-catalyzed hydroformylation of terminal olefins. Compared with the low regioselectivity at high temperature commonly observed when other bisphosphane analogues are used, the high performance achieved by the tetraphosphane ligands **1** is remarkable. The steric and electronic effects of substituents on the diarylphosphane moiety were also examined. Further applications of the ligands and studies on the mechanism are under investigation and will be reported in due course.

Experimental Section

General: All reactions and manipulations were performed either in a nitrogen-filled glove box or by using standard Schlenk techniques, unless otherwise noted. Solvents were dried according to standard procedures and degassed with N_2. Column chromatography was performed with 200–400 mesh silica gel supplied by Natland International Corporation. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded with either a Bruker advance 400 MHz NMR spectrometer or a Varian VNMRS 300 MHz spectrometer. GC analyses were conducted with a Helwett–Packard 6890 gas chromatograph fitted with capillary columns.

Synthesis of 4: LiCl (2.82 g, 67.2 mmol) was added to a solution of **3** (2.2 g, 4.2 mmol) in DMF (80 mL). The reaction mixture was stirred at RT for 6 h then cooled to 0 °C and an aqueous solution of HCl (5%, 30 mL) was added carefully. After stirring for 5 min, the mixture was extracted with diethyl ether (4 × 40 mL) and washed with a saturated aqueous solution of NaCl (80 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated to dryness. Pure product was obtained as a white solid by recrystallization from CH_2Cl_2/hexanes (1.35 g, 93% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.74–7.62 (m, 4H), 7.59–7.56 (m, 2H), 4.28 ppm (s, 8H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 137.0, 135.8, 131.2, 130.2, 45.0 ppm; HRMS (EI$^+$): *m/z*: calcd for $C_{16}H_{14}Cl_4$: 345.9853 $[M]^+$; found: 345.9850.

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Synthesis of 5a: Typical procedure: *n*BuLi (5.28 mL, 2.5 M in hexane, 13.2 mmol) was added dropwise to a cooled (−78 °C) solution of diphenylphosphane (2.32 mL, 13.2 mmol) in THF (10 mL). After stirring for 10 min, the reaction mixture was allowed to warm to RT and stirred for 30 min. The reaction mixture was cooled to −78 °C and **4** (1.05 g, 3 mmol) in THF (10 mL) was added dropwise. After addition, the reaction mixture was allowed to warm to RT slowly and stirred overnight. The reaction mixture was cooled to 0 °C and a cold solution of BH_3 (1.0 M in THF, 132 mL, 132 mmol) was added dropwise. The mixture was allowed to warm to RT and stirring was continued for 4 h. The reaction mixture was cooled to 0 °C and water (20 mL) was added carefully to quench the excess BH_3. Volatile material was removed under vacuum and CH_2Cl_2 (50 mL) and water (50 mL) were added to the residue. The mixture was stirred for 10 min until all of the residue dissolved. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (2×25 mL). The combined organic phase was washed with a saturated aqueous solution of NaCl (50 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure to obtain an off-white solid. EtOAc (10 mL) was added to the crude solid and the resulting suspension was stirred for 30 min and filtered. The residue was washed with cold EtOAc (2×5 mL) to give the pure borane-protected title compound **5a** as a colorless solid (2.5 g, 73.8 %). ^{1}H NMR (300 MHz, $CDCl_2$): δ = 7.58–7.52 (m, 16H), 7.45–7.39 (m, 8H), 7.36–7.31 (m, 16H), 7.03–6.97 (m, 2H), 6.87–6.84 (m, 4H), 3.16 (d, J = 13.4 Hz, 8H), 1.53–0.75 ppm (br s, 12H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 133.1, 132.5 (d, J = 9.1 Hz), 131.5, 131.3, 130.6, 130.4, 129.2 (d, J = 9.9 Hz), 127.5, 30.2 ppm (d, J = 30 Hz); ^{31}P NMR (146 Hz, CD_2Cl_2): δ = 15.2 ppm; HRMS (ES$^+$): *m*/z: calcd for $C_{64}H_{66}NaP_4B_4$: 1025.4385 [M+Na$^+$]; found: 1025.4431.

Synthesis of ligand 1a: Typical procedure: Compound **5a** (501 mg, 0.5 mmol) was added in portions to a solution of DABCO (448 mg, 4 mmol) in toluene (10 mL). The resulting suspension was stirred for 30 min at RT then slowly heated to 60 °C. Stirring was continued for 6 h at 60 °C then the reaction mixture was cooled to RT and additional toluene (10 mL) was added. The diluted solution was charged on a short silica gel column by cannula and eluted with toluene (40 mL). The solvent was removed under vacuum to give the desired ligand **1a** as a white solid (376 mg, 79.4 %). ^{1}H NMR (300 MHz, $CDCl_2$): δ = 7.32–7.22 (m, 40H), 6.91–6.86 (m, 2H), 6.76–6.74 (m, 4H), 3.24 ppm (s, 8H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 139.6, 139.3, 137.1, 137.0, 133.5, 133.3, 128.9, 128.7, 127.4, 35.0 ppm (d, J = 25.8 Hz); ^{31} P NMR (146 Hz, CD_2Cl_2): δ = −15.3; HRMS (ES$^+$): *m*/*z*: calcd for $C_{64}H_{55}P_4$: 947.3254 [M+H]$^+$; found: 947.3237.

Complex 5b: Prepared according to the typical procedure by using di(3,5-difluorophenyl)phosphane (7.9 g, 30.6 mmol), *n*BuLi (2.5 M in hexane, 12.3 mL, 30.6 mmol), 2,2′,6,6′-tetrakis(chloromethyl)biphenyl (2.4 g, 6.9 mmol), and BH_3 (1.0 M in THF, 300 mL, 300 mmol). Yield: 5.1 g (64.1 %); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.14 (m, 16H), 7.12 (t, J = 8.0 Hz, 2H), 6.99–6.92 (m, 16H), 6.74 (d, J = 8.0 Hz, 4H), 3.34 (d, J = 13.6 Hz, 8H), 1.45–0.52 ppm (br s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1 (ddd, ^1J = 254.2, ^2J = 16.1 Hz, ^3J = 11.8 Hz), 138.1, 133.5 (dt, ^1J = 52.3, ^2J = 8.0 Hz), 132.1, 129.9 (dd, ^1J = 4.6, ^2J = 1.5 Hz), 128.8, 115.1 (ddd, ^1J = 18.5, ^2J = 10.5, ^3J = 8.6 Hz), 107.8 (t, J = 24.9 Hz), 29.8 ppm (d, J = 33.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −105.2 ppm; ^{31}P NMR (161 MHz, $CDCl_3$): δ = 19.0 ppm; HRMS (ESI): *m*/z: calcd for $C_{64}H_{50}B_4F_{16}P_4$: 1290.298 [M]$^+$; found: 1290.296.

Compound 1b: Prepared according to the typical procedure by using complex **5b** (1.3 g, 1.0 mmol) and DABCO (0.896 g, 8.0 mmol). Yield: 901 mg (73.0 %); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (t, J = 7.6 Hz, 2H), 6.85–6.72 (m, 28H), 3.21 ppm (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8, 138.3 (d, J = 24 Hz), 135.6 (dd, ^1J = 5.5, ^2J = 3.2 Hz), 130.9, 129.1, 128.9 (q, J = 2.8 Hz), 128.5, 128.2, 125.3, 115.4 (td, ^1J = 14, ^2J = 7.3 Hz), 105.0 (t, J = 24.8), 35.0 ppm (q, J = 5.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −108.1 ppm; ^{31}P NMR (146 MHz, $CDCl_3$): δ = −11.1 ppm; HRMS (ESI): *m*/z: calcd for $C_{64}H_{39}F_{16}P_4$: 1235.8634 [M+H]$^+$; found: 1235.8623.

Complex 5c: Prepared according to the typical procedure by using di(*p*-trifluoromethylphenyl)phosphane (6.5 g, 20.3 mmol), *n*BuLi (2.5 M in hexane, 8.1 mL, 20.3 mmol), 2,2′,6,6′-tetrakis(chloromethyl)biphenyl (**5c**; 1.6 g, 4.6 mmol), and BH_3 (1.0 M in THF, 200 mL, 200 mmol). Yield: 4.9 g (68.9 %); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (t, J = 6.4 Hz, 16H), 7.66 (d, J = 6.4 Hz, 16H), 6.99 (t, J = 7.6 Hz, 2H), 6.63 (d, J = 7.6 Hz, 4H), 3.52 (d, J = 13.6 Hz, 8H), 1.40–0.60 ppm (br s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.6 (t, J = 7.7 Hz), 134.3 (d, J = 52.3 Hz), 133.3 (qd, ^1J = 33.6, ^2J = 2.3 Hz), 132.5 (d, J = 9.5 Hz), 129.7 (d, J = 1.5 Hz), 128.5, 126.0 (dd, ^1J = 9.8, ^2J = 3.8 Hz), 123.3 (q, J = 270.1 Hz), 29.6 ppm (d, J = 33.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −63.4 ppm; ^{31}P NMR (161 MHz, $CDCl_3$): δ = 16.2 ppm; HRMS (ESI): *m*/z: calcd for $C_{72}H_{58}B_4F_{24}P_4$: 1546.3478 [M]$^+$; found: 1546.3466.

Compound 1c: Prepared according to the typical procedure by using complex **5c** (773 mg, 0.5 mmol) and DABCO (0.448 g, 4.0 mmol). Yield: 559 mg (75.0 %); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.6 Hz, 16H), 7.21 (t, J = 18.2 Hz, 16H), 6.97 (t, J = 7.6 Hz, 2H), 6.70 (d, J = 7.6 Hz, 4H), 3.20 ppm (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7 (t, J = 26.4 Hz), 138.6, 136.2 (d, J = 10.8 Hz), 133.2 (d, J = 30.0 Hz), 131.4 (q, J = 33.5 Hz), 128.7 (d, J = 4.5 Hz), 128.2, 125.4 (t, J = 3.1 Hz), 123.8 (q, J = 270.2 Hz), 34.9 ppm (dd, ^1J = 10.2, ^2J = 5.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.9 ppm; ^{31}P NMR (146 MHz, $CDCl_3$): δ = −14.1 ppm; HRMS (ESI): *m*/z: calcd for $C_{72}H_{47}F_{24}P_4$: 1491.2245 [M+H$^+$]; found: 1491.2237.

Complex 5d: Prepared according to the typical procedure by using di(4-methylphenyl)phosphane (9.1 g, 42.8 mmol), *n*BuLi (2.5 M in hexane, 17.2 mL, 42.8 mmol), 2,2′,6,6′-tetrakis(chloromethyl)biphenyl (3.4 g, 9.7 mmol), and BH_3 (1.0 M in THF, 200 mL, 200 mmol) in THF (250 mL). Yield: 7.6 g (71.2 %); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (t, J = 9.2 Hz, 16H), 7.13–7.08 (m, 16H), 6.97 (t, J = 7.8 Hz, 2H), 6.85 (d, J = 7.8 Hz, 4H), 3.17 (d, J = 13.6 Hz, 8H), 2.35 (s, 24H), 1.15–0.85 ppm (br s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.1 (d, J = 2.2 Hz), 138.8 (d, J = 7.7 Hz), 132.9, 132.0 (d, J = 9.4 Hz), 129.7 (d, J = 5.0 Hz), 127.9, 127.4, 127.1, 29.9 (d, J = 35 Hz), 21.3 ppm; ^{31}P NMR (161 MHz, $CDCl_3$): δ = 13.3 ppm; HRMS (ESI): *m*/z: calcd for $C_{72}H_{82}B_4P_4$: 1114.5722 [M]$^+$; found: 1114.5739.

Compound 1d: Prepared according to the typical procedure by using complex **5d** (1.10 g, 1.0 mmol) and DABCO (0.896 g, 8.0 mmol). Yield: 825 mg (78.0 %); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (t, J = 7.2 Hz, 16H), 7.04 (d, J = 7.2 Hz, 16H), 6.90 (t, J = 7.6 Hz, 2H), 6.78 (d, J = 7.6 Hz, 4H), 3.16 (s, 8H), 2.33 ppm (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 136.8 (d, J = 11.4 Hz), 135.9 (d, J = 14.5 Hz), 133.0 (d, J = 20.1 Hz), 129.4 (d, J = 10.1 Hz), 129.0 (d, J = 6.8 Hz), 128.0 (d, J = 5.1 Hz), 126.9, 34.7 (d, J = 14.1 Hz), 21.3 ppm; ^{31}P NMR (146 MHz, $CDCl_3$): δ = −16.4 ppm; HRMS (ESI): *m*/z: calcd for $C_{72}H_{71}P_4$: 1059.4501 [M+H$^+$]; found: 1059.4522.

Complex 5e: Prepared according to the typical procedure by using di(*m*-trifluoromethylphenyl)phosphane (8.3 g, 25.7 mmol), *n*BuLi (2.5 M in hexane, 10.3 mL, 25.7 mmol), 2,2′,6,6′-tetrakis(chloromethyl)biphenyl (2.0 g, 5.8 mmol), and BH_3 (250 mL, 1.0 M in THF, 250 mmol). Yield: 6.0 g (67.1 %); white solid; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.98 (d, J = 10.8 Hz, 8H), 7.88 (t, J = 8.8 Hz, 8H), 7.75 (t, J = 8.8 Hz, 8H), 7.57 (td, ^1J = 7.6 Hz, ^2J = 2.0 Hz, 8H), 6.96 (t, J = 8.0 Hz, 2H), 6.62 (d, J = 8.0 Hz, 4H), 3.47 (d, J = 13.2 Hz, 8H), 1.51–0.60 ppm (br s, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 139.3 (t, J = 7.8 Hz), 135.9 (d, J = 7.8 Hz), 132.5 (d, J = 66.2 Hz), 132.2 (qd, ^1J = 32.7, ^2J = 10.9 Hz), 130.6, 130.4 (d, J = 9.3 Hz), 130.3 (dd, ^1J = 6.0, ^2J = 1.0 Hz), 129.4 (dt, ^1J = 11.9, ^2J = 3.6 Hz), 129.2 (t, J = 4.3 Hz), 128.8, 121.4 (qd, ^1J = 270.2, ^2J = 1.7 Hz), 30.6 ppm (d, J = 33.8 Hz); ^{19}F NMR (376 MHz, CD_2Cl_2): δ = −63.2 ppm; ^{31}P NMR (161 MHz, CD_2Cl_2): δ = 17.0 ppm; HRMS (ESI): *m*/z: calcd for $C_{72}H_{58}B_4F_{24}P_4$: 1546.3478 [M]$^+$; found: 1546.3463.

Compound 1e: Prepared according to the typical procedure by using complex **5e** (1.5 g, 1.0 mmol) and DABCO (0.896 g, 8.0 mmol). Yield: 954 mg (64.0 %); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (t, J = 6.4 Hz, 8H), 7.48 (d, J = 3.2 Hz, 8H), 7.42–7.33 (m, 16H), 6.98 (t, J = 7.6 Hz, 2H), 6.64 (d, J = 7.6 Hz, 4H), 3.28 ppm (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6, 139.4 (d, J = 8.0 Hz), 138.4, 136.0 (d, J = 74.4 Hz), 134.1, 131.0 (q, J = 32.7 Hz), 129.5 (d, J = 20.8 Hz), 129.0, 128.6, 128.1, 127.9, 125.8 (d, J = 3.7 Hz), 121.4 (q, J = 397.7 Hz), 35.4 ppm (dd, ^1J = 33.8, ^2J = 5.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.8 ppm;

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^{31}P NMR (146 MHz, $CDCl_3$): $\delta = -13.1$ ppm; HRMS (ESI): *m*/z: calcd for $C_{72}H_{47}F_{24}P_4$: 1491.2245 [$M+H^+$]; found: 1491.2233.

Compound 1 f: The corresponding borane complex has poor solubility in toluene and other commonly used solvents. Thus, this ligand was synthesized directly without protection of the borane. Compound **1 f** was prepared according to the typical procedure by using di(3,5-ditrifluoromethylphenyl)phosphane (3.7 g, 8.0 mmol), *n*BuLi (2.5 M in hexane, 3.2 mL, 8.0 mmol), and 2,2′,6,6′-tetrakis(chloromethyl)biphenyl (635.0 mg, 1.8 mmol). Yield: 3.0 g (81.7%); white solid; ^{1}H NMR (400 MHz, [D_8]THF): $\delta = 8.10$ (s, 8H), 7.77 (s, 16H), 7.21 (t, $J = 7.2$ Hz, 2H), 6.88 (d, $J = 7.2$ Hz, 4H), 3.61 ppm (s, 8H); ^{13}C NMR (100 MHz, [D_8]THF): $\delta =$ 141.8 (d, $J = 12.4$ Hz), 139.4, 137.4, 134.0, 133.3 (q, $J = 35.1$ Hz), 130.2 (d, $J = 19.1$ Hz), 124.8, 124.3 (q, $J = 271$ Hz), 36.3 ppm (d, $J = 24.1$ Hz); ^{19}F NMR (376 MHz, [D_8]THF): $\delta = -64.3$ ppm; ^{31}P NMR (146 MHz, C_4D_8O): $\delta = -10.0$ ppm; HRMS (ESI): *m*/z: calcd for $C_{80}H_{39}F_{48}P_4$: 2035.1236 [$M+H^+$]; found: 2035.1231.

General procedure for the regioselective hydroformylation of terminal olefins with 1: A 2 mL vial containing a magnetic stirring bar was charged with ligand **1** (4 μmol) and [Rh(acac)$(CO)_2$] (1 μmol in 0.1 mL toluene). The mixture was stirred for 5 min then 1-octene (2 mmol) was added followed by decane (0.1 mL) as the internal standard. Additional toluene was added to bring the total reaction volume to 1 mL. The reaction mixture was transferred to an autoclave, which was sealed and purged with nitrogen three times and subsequently charged with CO (10 atm) and H_2 (10 atm). The autoclave was then heated to 140 °C (oil bath) and the pressure was adjusted to 20 atm. After 1 h, the autoclave was taken out of the oil bath and cooled in ice-cold water. The pressure was carefully released in a well-ventilated hood and the reaction mixture was immediately analyzed by GC.

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