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Tetraphenol-based diphosphite ligands: synthesis, characterization, and application in the rhodium-catalyzed hydroformylation of octenes

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ABSTRACT

A new class of diphosphites is described, based on a tetraphenol backbone. Ligands **TP1**–**TP5** were synthesized and fully characterized and their application in the hydroformylation of octenes was investigated. Ligand **TP3**, bearing a 1-naphthoxy substituent on the phosphorus, shows the highest regioselectivity toward the linear aldehyde.

1. Introduction

The rhodium-catalyzed hydroformylation of alkenes is one of the largest applications of homogeneous catalysis in industry today.[1,2] In particular, the selective production of higher linear aldehydes, which are intermediates in the production of detergent alcohols, has been of interest for both academia and industry for the last three decades.[1,3] In this respect, much attention has been paid to phosphorus-based ligands, mostly phosphines[4] and phosphites,[5] but phosphinites[6] and phosphonites[7] have also been reported.

Van Leeuwen and Roobeek discovered that Rh-catalysts based on bulky monophosphites give very high rates in the hydroformylation of alkenes.[8] Bryant and co-workers at Union Carbide greatly extended Van Leeuwen's work toward more stable monophosphites, and later to diphosphites that show higher regioselectivity (Fig. 1).[2,9]

Phosphites, being better π-acceptors than phosphines, generally weaken the M–CO bond leading to faster CO dissociation and thus higher reaction rates.[5] Moreover, they are most often straightforward to prepare and stable toward oxidation.

The combination of these aspects makes bulky diphosphites an interesting class of ligands, particularly if they can be prepared in a modular way. This often enables 'fine-tuning' toward desired properties, such as high selectivity and rate in homogeneous catalytic reactions.[10]

Herein, we report on the synthesis and characterization of a new class of diphosphite ligands based on a tetraphenol backbone, and their application in the rhodium-catalyzed hydroformylation of *n*-octenes.

The tetraphenol backbone **TP0**, was synthesized according to a modified literature procedure.[11] An acid-catalyzed condensation reaction between 4-*tert*-butylphenol and isophthalaldehyde yielded the crude tetraphenol **TP0**, which was purified by means of steam distillation to remove excess 4-*tert*-butylphenol. Recrystallization from acetone gave **TP0** in 72% yield (Scheme 1).

The tetraphenol backbone allows further modular modification, which makes automated synthesis viable: after the treatment of **TP0** with PCl_3 in the presence of Et_3N, the corresponding bis(phosphochloridite) is formed quantitatively. Subsequent reaction with the appropriate substituted phenol gave ligands **TP1**–**TP5** as white powders, after recrystallization from acetone/isopropanol, in good yields (Fig. 2). These ligands proved to be air-stable, but prone to hydrolysis when kept in solution.

Ligands **TP1**–**TP5** were fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy as well as by elemental analysis. **TP1**, **TP2**, and **TP4** all show a singlet in the ^{31}P NMR spectrum at around $\delta_P = 122$ ppm, a common value for constrained phosphites.[12] In contrast, **TP5** shows a singlet at $\delta_P = 136.6$ ppm, which occurs at relatively low field compared to other phosphites. We propose that this downfield shift might be due to the rather bulky substituents

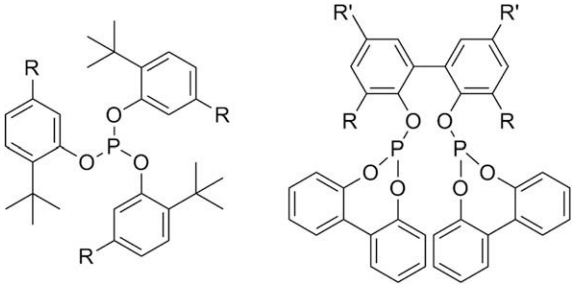

Figure 1. Van Leeuwen's bulky monophosphite and a typical Union Carbide bulky diphosphite.

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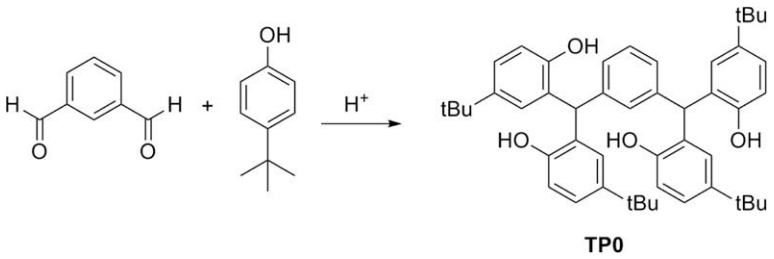
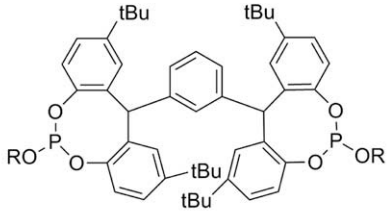


TP0

Scheme 1. Synthesis of the tetraphenol backbone.



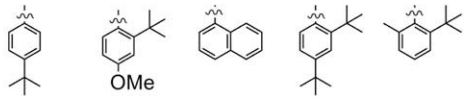
Ligand	TP1	TP2	TP3	TP4	TP5
R					
^{31}P NMR δ	122.1	122.6	119, 129	122.1	136.6

Figure 2. Tetraphenol ligands **TP1**–**TP5** and their ^{31}P NMR shifts.

at both the *ortho* positions of the phenol. Interestingly, ligand **TP3** exhibits two signals in the ^{31}P NMR spectrum, at δ_P = 119 ppm (minor) and at δ_P = 129 ppm (major), respectively (25 °C, toluene-d_8). We argue that this might be caused by two different conformers of the ligand.[13]

In order to obtain insight on the electronic properties of **TP1**–**TP5**, we investigated the Tolman electronic parameter *v*.[14] This parameter is based on the infrared frequencies of the A_1 and B_1 vibrations of CO in **L**Ni(CO)$_2$ complexes, where L is a bidentate ligand.[15] The corresponding (**TP**)Ni(CO)$_2$ complexes were synthesized[10] and their CO stretching frequencies determined. The ATR-IR frequencies of the A_1 and B_1 vibrations of CO are summarized in Table 1, along with the corresponding data for the triphenylphosphine complex $(PPh_3)_2Ni(CO)_2$ and the triphenyl phosphite complex $[P(OPh)_3]_2Ni(CO)_2$.[15]

It is clear that the tetraphenol ligands are typical phosphites, because the A_1 and B_1 frequencies are very similar to those for triphenyl phosphite. Importantly, ligands **TP1**–**TP5** show only small differences in their Tolman electronic parameter *v*, which provides evidence that the differences in catalytic performance are based on the different steric properties of the R group of the ligands. Ligands **TP1**–**TP4** show a well-behaved bidentate coordination to nickel, whereas in the case of ligand **TP5** multiple species, identified as the mono-coordinated complex ($LNi(CO)_3$, $\nu = 2083\ cm^{-1}$) and the tris-coordinated complex ($L_3Ni(CO)$, $\nu = 2011\ cm^{-1}$), were present.[15] **TP5** also shows multiple species in combination with Rh(acac)(CO)$_2$ under relatively dilute conditions, multiple species as was evident in the ^{31}P NMR spectrum.

Table 1
IR frequencies of the A_1 and B_1 vibrations of CO in (**L**)Ni(CO)$_2$

Ligand	A_1 (cm^{-1})	B_1 (cm^{-1})
PPh_3[a]	2008	1952
$P(OPh)_3$[a]	2045	1996
TP1	2043	1995
TP2	2040	1987
TP3	2043	1991
TP4	2041	1990
TP5[b]	2043	2002

[a] Literature values.[15]
[b] Multiple species present.

We argue that this phenomenon might be due to a steric effect, caused by the two *ortho* substituents on the R group of ligand **TP5**, whereas ligands **TP1**–**TP4** possess only one *ortho* substituent in that position.

Ligands **TP1**–**TP5** were first applied in the rhodium-catalyzed hydroformylation of 1-octene (Scheme 2).

The reaction was performed using Rh(acac)(CO)$_2$ as the metal precursor and 4 equiv of ligand. After catalyst preformation for 2 h at 80 °C and 20 bar of CO/H_2 (1:1), 1250 equiv of 1-octene was added. The gas uptake curves were recorded automatically for all catalytic systems and the turnover frequencies (TOF) were determined at 20% conversion (Fig. 3 and Table 2).

While the Rh-catalysts based on ligands **TP1**–**TP4** show similar activities in the hydroformylation of 1-octene, it is obvious that the system Rh/**TP5** has a lower reaction rate. Since there is no significant difference in the Tolman electronic parameter (vide supra), this effect seems to be purely steric in nature.

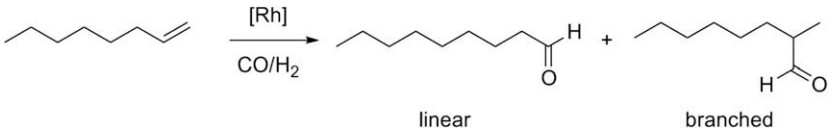
The product distributions of the hydroformylation reactions were determined by GC analysis (Table 2). No hydrogenation was observed in any of these reactions and the formation of aldol products was typically below 0.5%. Up to 10% internal octenes were formed by isomerization during the course of the hydroformylation. However, only nonanal and 2-methyloctanal were observed as the products.

Although the catalyst based on ligand **TP2** shows the highest activity among the systems investigated, the regioselectivity toward nonanal, expressed as the ratio between the amount of linear aldehydes divided by the sum of all the branched aldehydes, is low (l/b = 2.7) and comparable with catalysts based on monodentate phosphite ligands. The system based on Rh/**TP3**, however, gives a much higher regioselectivity (l/b = 12.3). We argue that this might be caused by a more constrained environment around the metal center, leading to the observed higher selectivity.

In order to follow the l/b ratio in time, samples were taken during the reaction. The selectivity toward the linear aldehyde decreases slowly as the reaction proceeds (Fig. 4).

Due to the double bond isomerization activity of these systems, the regioselectivity drops with time. As less reactive internal octenes accumulate, their slow conversion leads to a decreased linearity of the product. Remarkably, only 2-methyloctanal and none of the other possible branched aldehydes was formed.

Given the high reaction rate of ligand **TP2** and the high selectivity toward the linear aldehyde of **TP3** and the substantial amounts



Scheme 2. The rhodium-catalyzed hydroformylation of 1-octene.

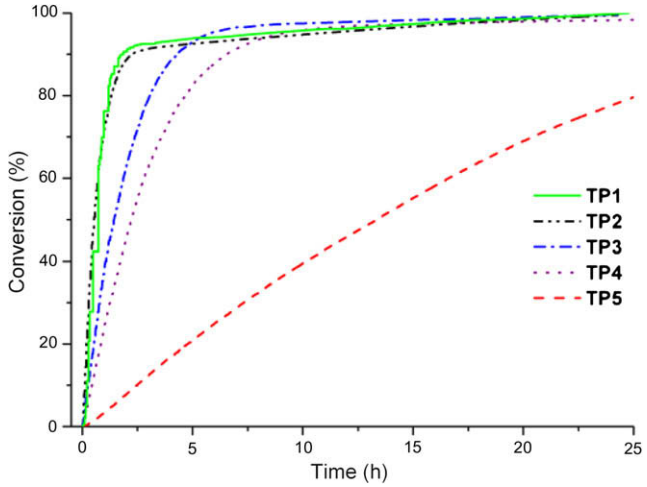


Figure 3. Gas uptake curves for the hydroformylation of 1-octene with diphosphite ligands **TP1**–**TP5**.

Table 2
Hydroformylation of 1-octene

Ligand	Conversion (%)	*l*/*b*[a]	Aldol product (%)	TOF[b] (h^{-1})
TP1	98	4.6	0.1	800
TP2	99	2.7	0.1	1400
TP3	99	12.3	0.3	460
TP4	99	7.4	0.5	300
TP5	99	2.7	0.1	55

Conditions: Rh/L/substrate = 1:4:1250, 80 °C, 20 bar CO/H_2 (1:1), toluene, [Rh] = 1.92 mM, Rh precursor = $Rh(acac)(CO)_2$, V_{tot} = 8 mL, *t* = 24 h.
[a] Amount of linear aldehyde/amount of sum of all branched aldehydes.
[b] TOF determined at 20% conversion.

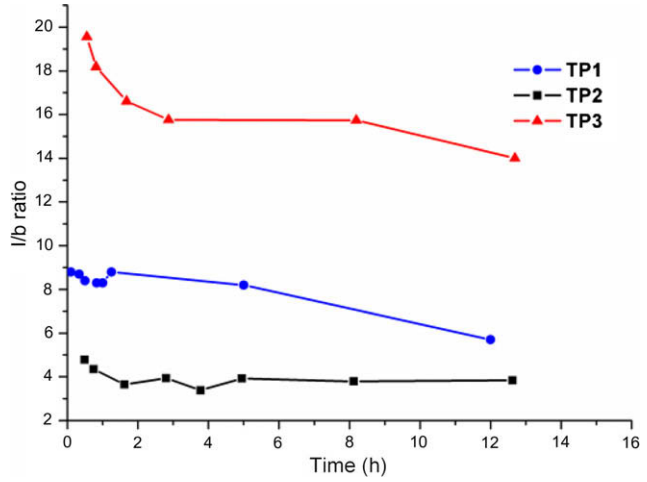


Figure 4. Regioselectivity during the hydroformylation of 1-octene.

(~10%) of octene isomers that are formed in the hydroformylation of 1-octene, we were interested in the performance of these ligands in the hydroformylation of internal octenes, such as *trans*-2-octene.

First, we applied our standard conditions for the hydroformylation of terminal olefins, that is, 20 bar of CO/H_2 (1:1) and 80 °C, also for the hydroformylation of *trans*-2-octene. However, under these conditions the reaction proceeded very slowly and the regioselectivity was poor (Fig. 5, Table 3). Therefore, we applied typical isomerization conditions: low pressure (10 bar) and high temperature (140 °C). Both the reaction rate and regioselectivity improved significantly. In contrast to the observations made for 1-octene, where 1-nonanal and 2-methyloctanal were observed as the major products, 3-ethylheptanal was also formed in substantial amounts.

Moreover, from the gas uptake curves of the systems Rh/**TP2** and Rh/**TP3** under isomerization conditions (10 bar, 140 °C), it becomes obvious that catalyst deactivation occurred before all the substrate was consumed (respectively, 67% and 39% conversion, Fig. 5). The red/brown color of the mixture at the end of the reaction indicated the formation of inactive rhodium clusters. To avoid this problem, 20 instead of 4 equiv of ligand with respect to Rh was added in order to stabilize the Rh species. However, the formation of inactive rhodium clusters could not be circumvented, which might be due to ligand decomposition at elevated temperatures.[16]

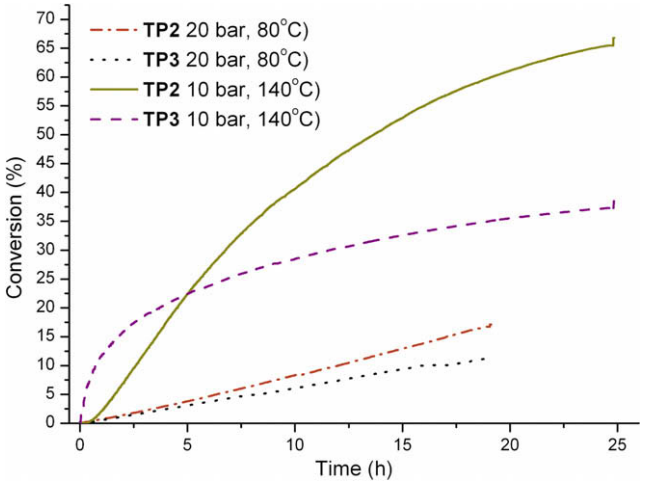


Figure 5. Gas uptake curves for the hydroformylation of *trans*-2-octene under different conditions.

Table 3
Hydroformylation of *trans*-2-octene

Ligand	Time (h)	*P* (bar)	*T* (°C)	Conversion (%)	*l*/*b*[a]	TOF[b]
TP2	18	20	80	17	0.18	11
TP3	18	20	80	11	0.67	8
TP2	25	10	140	67	1.27	56
TP3	25	10	140	39	1.92	68
TP3[c]	35	10	140	45	1.55	10

Conditions: Rh/L/substrate = 1:4:1250, solvent = toluene, [Rh] = 1.92 mM, Rh precursor = $Rh(acac)(CO)_2$.
[a] Branched = sum of all non-linear aldehydes.
[b] At 20% conversion.
[c] Rh/L = 1:20.

In conclusion, we have reported on the synthesis of a new class of tetraphenol-based diphosphite ligands. The ligands were tested in the rhodium-catalyzed hydroformylation of 1-octene and *trans*-2-octene. In the hydroformylation of 1-octene, Rh/**TP3** showed good regioselectivity toward the desired nonanal (*l*/*b* = 19.6 in the beginning of the reaction). In order to explain the differences in catalytic performance among the ligands, the electronic properties of the ligands were compared via the Tolman electronic parameter *v*. As this parameter shows no significant differences for the ligands, the different performance in catalysis is attributed to steric and conformational changes.

2. Synthesis of 4,4′,4,4‴-tetra-*tert* -butyl-2,2′,2,2‴-(phenylenemethanediyl)tetraphenol (TP0)

A mixture of *p*-*tert*-butylphenol (72 g, 0.48 mol) and isophthalic dicarboxaldehyde (8.1 g, 0.06 mol) was heated with stirring until a homogeneous melt had formed (100–110 °C). Concentrated HCl (8 ml) was added and the reaction continued for a further 6 h. The excess phenol was then removed by steam distillation and the residue was recrystallized from acetone. Yield: [0.0429 mol, 29.94 g, 71.5%]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.24 (m, 1H), 7.11–7.05 (m, 7H), 6.93 (d, J = 2.4 Hz, 4H), 6.71 (d, J = 8.4 Hz, 4H), 5.83 (s, 2H), 5.24 (br s, 4H, –OH), 1.13 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.93, 143.65, 141.99, 128.11, 127.28, 124.64, 115.74, 77.66, 77.02, 76.39, 45.14, 34.04, 31.40. Elemental Anal. Calcd for $C_{48}H_{58}O_4{\cdot}2(CH_3)CO$: C, 79.57; H, 8.66. Found: C, 79.74; H, 8.43.

3. General synthesis of tetraphenol ligands

The tetraphenol backbone (**TP0**) (2.1 g, 3 mmol) and Et_3N (5.4 ml, 36 mmol) were added dropwise to a solution of PCl_3 (0.6 mg, 6.5 mmol) in 35 ml of THF at −10 °C and the mixture was stirred for 30 min. The appropriate phenol (6.05 mmol) dissolved in 10 ml of THF was added dropwise at −10 °C. The mixture was stirred for 1 h at room temperature. Salts were filtered off over a short pad of basic alumina (4 cm) and all the volatiles were evaporated. The residue was recrystallized from acetone/isopropanol to yield the desired product as a white powder.

3.1. TP1

4-*tert*-Butylphenol was used as the phenol. Yield: [0.96 mmol, 1.01 g, 32%]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.35 (m, 2H), 7.33–7.30 (m, 2H), 7.24 (d, J = 2.9 Hz, 4H), 7.20–7.06 (m, 8H), 6.99 (dd, J = 8.5, 0.9, 4H), 6.85–6.77 (m, 4H), 5.77 (s, 2H), 1.08 (s, 54H). ^{13}C NMR (125 MHz, CD_2Cl_2): 150.08, 149.96, 147.34, 146.99, 143.45, 134.50, 128.58, 128.14, 127.94, 126.48, 126.37, 126.24, 126.14, 125.47, 125.31, 123.40, 120.31, 120.22, 120.16, 53.24, 34.32, 34.25, 31.83, 31.14. ^{31}P NMR (CD_2Cl_2): δ 122.08. Elemental Anal. Calcd for $C_{68}H_{80}O_6P_2$: C, 77.39; H, 7.64. Found: C, 77.33; H, 7.45.

3.2. TP2

2-*tert*-Butyl-4-methoxyphenol was used as the phenol. Yield: [0.84 mmol, 937 mg, 28%]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.43 (m, 2H), 7.33 (s, 4H), 7.11–6.96 (m, 12H), 6.48–6.43 (m, 4H), 5.72 (s, 2H), 3.29 (s, 6H), 1.36 (s, 18H), 1.09 (s, 36H). ^{13}C NMR (125 MHz, CD_2Cl_2): 155.57, 147.77, 146.54, 146.43, 144.89, 144.60, 141.82, 141.78, 133.76, 128.87, 128.74, 128.06, 127.80, 127.02, 126.48, 125.29, 125.14, 122.93, 120.41, 120.11, 114.32, 109.99, 55.57, 45.57, 34.67, 34.16, 31.11, 29.15. ^{31}P NMR (81 MHz, $CDCl_3$): δ 122.61.

3.3. TP3

1-Naphthol was used as the phenol. Yield: [2.1 mmol, 2.2 g, 70%]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8 Hz, 2H), 7.82 (d, J = 8 Hz, 2H), 7.68–7.60 (m, 2H), 7.46–7.42 (m, 3H), 7.42–7.47 (m, 8H), 7.28 (s, 4H), 7.09–7.05 (m, 3H), 6.95–6.85 (m, 6H), 5.60 (s, 2H), 1.13 (s, 36H). ^{13}C NMR (125 MHz, CD_2Cl_2): 147.71, 147.63, 146.44, 146.32, 134.87, 134.59, 128.72, 127.64, 127.52, 127.44, 127.35, 126.62, 126.51, 126.25, 126.08, 125.84, 125.73, 125.58, 125.26, 124.24, 123.82, 123.12, 122.54, 122.28, 115.10, 114.87, 95.04, 34.32, 31.43. ^{31}P NMR (162 MHz, $CDCl_3$): δ 131.38. Elemental Anal. Calcd for $C_{68}H_{68}O_6P_2$: C, 78.29; H, 6.57. Found: C, 77.93; H, 6.23.

3.4. TP4

2,4-Di-*tert*-butylphenol was used as the phenol. Yield: [2.4 mmol, 2.8 g, 81%]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 2.5 Hz, 2H), 7.28–7.20 (m, 8H), 7.08–7.01 (m, 6H), 6.78–6.74 (m, 2H), 6.61 (dt, J = 4.9 Hz, 0.8 Hz, 4H), 5.83 (s, 2H), 1.42 (s, 18H), 1.29 (s, 54H). ^{13}C NMR (125 MHz, CD_2Cl_2): 151.58, 149.08, 147.85, 147.49, 146.54, 146.08, 145.75, 138.95, 133.85, 128.79, 126.45, 125.34, 124.92, 124.53, 124.03, 123.50, 123.02, 119.89, 119.07, 118.84, 118.70, 110.41, 45.76, 34.90, 34.82, 34.33, 34.22, 31.18, 29.95. ^{31}P NMR (81 MHz, CD_2Cl_2): δ 122.12. Elemental Anal. Calcd for $C_{76}H_{96}O_2P_2{\cdot}CH_2Cl_2$: C, 73.84; H, 7.89. Found: C, 74.32; H, 8.19.

3.5. TP5

2-Methyl-6-*tert*-butylphenol was used as the phenol. Yield: [2.3 mmol, 2.5 g, 78%]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 2.5 Hz, 2H), 7.26–7.20 (m, 6H), 7.13–7.03 (m, 8H), 7.01–6.90 (m, 4H), 6.77–6.65 (m, 2H), 6.22 (s, 2H), 2.52 (s, 6H), 1.49 (s, 54H). ^{13}C NMR (125 MHz, CD_2Cl_2): 149.44, 149.35, 147.82, 147.53, 146.92, 146.88, 145.97, 145.80, 139.54, 139.30, 139.21, 138.97, 128.70, 127.58, 124.68, 124.57, 124.40, 123.94, 123.16, 120.48, 115.12, 114.88, 35.08, 32.53, 31.27, 30.00, 25.78. ^{31}P NMR (81 MHz, CD_2Cl_2): δ 172.59. Elemental Anal. Calcd for $C_{70}H_{84}O_6P_2{\cdot}CH_2Cl_2$: C, 72.99; H, 7.42. Found: C, 72.32; H, 7.57.

4. Synthesis of (L)Ni(CO)$_2$

10 mg (0.036 mmol) Ni(cod)$_2$,[17] and 1 equiv of TP ligand (0.036 mmol) were dissolved in 2 mL of toluene. CO was bubbled through the slightly yellow solution for 30 s, during which the solution turned colorless. All the volatiles were removed in vacuo and the remaining solid was used in the ATR-IR measurement.

5. General procedure for the hydroformylation experiments

Reactions were carried out in an AMTEC SPR16 parallel setup. Rh(acac)(CO)$_2$ (3.7 mg, 14.4 μmol) and 4 equiv of the ligand (57.6 μmol) were dissolved in 5 mL of toluene and transferred into an argon-filled reaction vessel. The reaction vessel was heated and pressured to the desired temperature and pressure. After 2 h of preformation, the substrate mixture consisting of 18 mmol of 1-octene and 6 mmol of decane (internal standard) was added. The reaction vessel was pressured and heated to the desired reaction pressure and temperature.

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