Selective hydroformylation of internal alkenes to linear aldehydes - Novel phosphacyclic diphosphines and their applications
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The Influence of the Bite Angle on the Hydroformylation of Internal Olefins to Linear Aldehydes

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Abstract.

A novel series of ligands (1-10) that induce wide bite angles (106 ° < βn < 131 °) has been synthesised. Compared to the Xantphos series (e.g. 13 versus 5) the introduction of the phosphacyclic-moiety results in ligands with a slightly larger bite angle. High pressure IR and high pressure NMR studies of the (diphosphine)RhH(CO)2 complexes show that most ligands (3 - 7) adopt a bis-equatorial binding mode exclusively in the trigonal bipyramidal rhodium complex. Subtle changes in ligand structure have a large impact on activity and selectivity in the hydroformylation of 1-octene and trans-2-octene. Rates up to 3275 (mol aldehyde). (mol Rh)⁻¹h⁻¹ (p(CO/H2) = 20 bar, T = 353 K, [Rh] = 1 mM, [1-octene] = 637 mM) and regio-selectivities > 99% towards the linear product were obtained when 1-octene was used as substrate. For trans-2-octene rates up to 250 (mol aldehyde). (mol Rh)⁻¹h⁻¹ (p(CO/H2) = 3.6 bar, T = 393 K, [Rh] = 1 mM, [trans-2-octene] = 640 mM) and high regio-selectivities up to 96% towards the linear product, that are unprecedented, were obtained. A correlation between the selectivity for the hydroformylation of 1-octene and trans-2-octene has been observed suggesting that the selectivity determining step remains unchanged between terminal and internal olefins. Ligands with a larger bite angle lead to more selective systems, but above 125 ° the regio-selectivity drops. Furthermore it is no longer the selective formation of linear alkyl species that determines the high regio-selectivities. Instead the differences in rate of β-hydrogen elimination from the branched alkyl intermediate and the linear alkyl intermediate versus CO-insertion determine the regio-selectivity. For both substrates a decrease in activity with an increase in bite angle is observed. It is suggested that the aforementioned rates of β-hydrogen elimination versus CO-insertion must play a crucial role in this bite angle effect on activity, because previous studies have shown that an increase in bite angle leads to an increase in activity.
Introduction.

To date the hydroformylation reaction is one of the most important homogeneously catalysed reactions in the world, covering an annual production of almost eight million tons of aldehydes and alcohols from which butanal and 2-ethylhexanol are the most important products.\textsuperscript{1,2} Nowadays, the design of new ligands and systematic tuning of their electronic and steric properties are common research topics in this area as it provides insight in regio-, and chemoselectivity and the overall catalytic activity.\textsuperscript{3-11} Tolman introduced the cone angle $\theta$ and the electronic parameter $\chi$ to classify phosphorus ligands with respect to their steric bulk and phosphine basicity.\textsuperscript{12} Both parameters have been used extensively as a measure of ligand properties in hydroformylation studies.\textsuperscript{13,14} Casey and Whiteker developed the concept of natural bite angle (the P-M-P angle) as an additional characteristic of diphosphine ligands to rationalize the correlation found between the regioselectivity and the co-ordination mode of bidentate ligands possessing wide bite angles.\textsuperscript{5} Many articles and reviews have appeared that discusses the effect of the bite angle on activity and selectivity for a number of catalytic reactions.\textsuperscript{15-29} The bite angle not only induces steric effects, but also electronic effects, as the P-M-P angles clearly affect the nature of the complex ground state or intermediate states. In a review by Freixa and van Leeuwen an attempt is made to separate the contributions of the steric bite angle effect and the electronic bite angle effect to the selectivities and rates for several catalytic reactions, including hydroformylation.\textsuperscript{16} For hydroformylation it was first believed that the co-ordination mode of the diphosphine in the (diphosphine)RhH(CO)$_2$ complex, either equatorial-equatorial (ee) or apical-equantorial (ae) (Figure 1), was a key factor in controlling the regioselectivity of the hydroformylation reaction. Later studies by van Leeuwen \textit{et al.}\textsuperscript{3} showed that the co-ordination mode is not the sole factor determining the outcome of the reaction.

It has been reported that phosphacyclic derivatives of different ligands with the right backbone, e.g. ligands based on 2,2$'$-dimethylbisphenyl, and xanthene backbones, like cyclic phosphines,\textsuperscript{10,21} cyclic phosphites,\textsuperscript{9,22-24} cyclic phosphonites\textsuperscript{25} and cyclic phosphorus diamides,\textsuperscript{26} result in catalysts that show a high activity and selectivity for the hydroformylation of terminal olefins. Especially the catalytic

\[
\begin{align*}
\text{P}^\text{P} \text{Rh-H} & \quad \text{P}^\text{P} \text{Rh-CO} \\
\text{ee} & \quad \text{ae}
\end{align*}
\]

\textbf{Figure 1} ee-ae equilibrium in rhodium trigonal bipyramidal complex.
activity is enhanced considerably compared to non-cyclic analogues. Decreased phosphorus basicity and increased electron ‘elasticity’, that is attributed to the extended conjugation of the ligand π-system, are considered to be the main reasons for this observed effect.4,10,13,27

Generally terminal olefins are used as substrates, while from an economical point of view internal olefins or a mixture of internal olefins and terminal olefins are substrates of choice, yet linear aldehydes and alcohols are the preferred products. In order to obtain linear aldehydes from internal olefins the system has to catalyse isomerisation between the internal and terminal olefin as the thermodynamic mixture contains in general less than 5% of the terminal olefin. In addition the hydroformylation of the terminal olefin must be many times faster than the hydroformylation of the internal olefin. Also, a high selectivity towards the linear aldehyde is required. Nevertheless, catalysts that fulfil all these requirements are not per se good catalysts for the hydroformylation of internal olefins to linear aldehydes.28 Although considerable progress in this field has been made by the use of bulky phosphites,22,24,29 and phosphonites25 these systems suffer from a low long term stability due to alcoholysis, hydrolysis and thermal instability.30,31 Phosphines are more resistant to these degradation reactions, but afford in general less active catalysts. To date only few rhodium-diphosphine systems are known which show a respectable activity and selectivity for the hydroformylation of internal olefins. Van Leeuwen et al. introduced phenoxaphosphino-, and dibenzophosphole-modified xanthene ligands (11–12, Figure 2),10,21 while Beller et al. introduced Naphos-type ligands with various electron-withdrawing substituents (Figure 3).8

Recently, the effect of natural bite angle on the catalytic activity and selectivity on the hydroformylation of terminal olefins was investigated for which a series of diphosphine ligands with different xanthene-type backbones was prepared.4,11 These ligands, however, are not suitable for a study of the bite angle effect on the hydroformylation of internal alkenes to linear aldehydes as the rate of isomerisation from the internal olefin to the terminal olefin is too low to ensure fast and selective catalysis. Xanthene-type ligands bearing phosphacyclic-moieties do give systems that are suitable for the hydroformylation of internal alkenes.10,21 To obtain a better understanding of how the bite angle affects the hydroformylation activity and selectivity of internal olefins, we synthesised a range of phenoxaphosphino-modified xanthene-type ligands that show a regular increase in natural bite angle (Figure 2, ligands 1–8). In addition, two new dibenzophosphole xanthene-type ligands have been synthesised (9–10) to obtain a better insight in the effect of ligand backbone and other phosphacyclic moieties. The co-ordination chemistry, and the performance in the rhodium catalysed hydroformylation of 1-octene and trans-2-octene for this novel series of ligands will be described. Furthermore, deuterioformylation reactions of 1-hexene with ligands 1, 5 and 7 were performed. The number and position of the deuterium atoms that are incorporated in the aldehyde and isomerised hexenes give
Figure 2 The phosphacyclic xanthene type ligands. 11 and 12 were reported previously.\textsuperscript{10,21}

Figure 3 Naphos-type ligands suitable for hydroformylation of internal alkenes.
detailed information about the reversibility of the different reaction steps during hydroformylation.\textsuperscript{28,32-35}

Results.

Synthesis.

A total of ten novel ligands that are closely related in either backbone structures or phosphine-moieties were synthesised (1 – 10). The ligand backbones were prepared according to literature procedures or were commercially available. Selective dilithiation of the backbones followed by the reaction with the chlorophosphine yields the corresponding ligands in moderate to high yields (30-80\%) (Scheme 1). Accidentally, in $^{31}$P{$^1$H} NMR no distinction between the two different phosphorus-signals of 6 could be made, but they lose their degeneracy in the (6)Rh(CO)$_2$H complex.

Ligands with the phenoxazine backbone (7 and 10) were obtained via a slightly modified procedure. The secondary amine functionality of phenoxazine was protected using chloro-\textit{t}-butyl-dimethylsilane. Lithiation of the protected backbone followed by the reaction with the chlorophosphine and subsequent deprotection gave the ligands in moderate yields after crystallization (30\%-43\%). For the synthesis of 8 phenyllithium instead of \textit{n}-butyllithium was used as metallating agent in order to prevent side product formation by nucleophilic substitution of the phenyl of the phosphine by \textit{n}-butyllithium.

Molecular mechanics calculations of ligands 1 – 10 show the effect of the heterocycle on the calculated natural bite angle and the flexibility range (Table 1).\textsuperscript{5} The calculations show that the rigid 2,8-dimethylphenoxaphosphino-moietty causes an increase of the bite angle compared to the corresponding diphenylphosphino analogues, while the introduction of the methyl substituents on the phenoxaphosphino-moietty causes a decrease in bite angle compared to the unsubstituted phenoxaphosphine (Figure 4). Ligand 8 has a calculated natural bite angle that is much wider than expected from the ligand backbone structure, as calculations performed on the diphenylphosphino-analogue show a much smaller bite angle. In the case of 8 the phenyl-substituent in the backbone structure is in close proximity of one of the methyl-substituents on each phenoxaphosphino-moietty,

![Scheme 1 Synthesis of ligands 1 – 10. i) \textit{n}-BuLi, TMEDA, 0 °C, ii) chlorophosphine, -78 ºC.](image-url)
Table 1 Calculated natural bite angles and flexibility ranges for the phenoxaphosphino-modified xanthos-type ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>backbone</th>
<th>$\beta_n$ (°)</th>
<th>Flexibility range (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10,11-Dihydrodibenzo[bf]oxepine</td>
<td>105.7</td>
<td>91 – 128</td>
</tr>
<tr>
<td>2</td>
<td>2,7-di-t-butyl-10,10-dimethylphenoxasilin</td>
<td>108.0</td>
<td>106 – 137</td>
</tr>
<tr>
<td>3</td>
<td>2,7-dimethylphenoxathiin</td>
<td>112.5</td>
<td>107 – 140</td>
</tr>
<tr>
<td>4</td>
<td>10-isopropylidenexanthene</td>
<td>114.2</td>
<td>110 – 144</td>
</tr>
<tr>
<td>5</td>
<td>9,9-dimethylxanthene</td>
<td>116.0</td>
<td>100 – 134</td>
</tr>
<tr>
<td>6</td>
<td>benzo[k,l]xanthene</td>
<td>124.3</td>
<td>117 – 156</td>
</tr>
<tr>
<td>7</td>
<td>phenoxazine</td>
<td>124.5</td>
<td>113 – 151</td>
</tr>
<tr>
<td>8</td>
<td>10-phenylphenoxaphosphine</td>
<td>131.2</td>
<td>126 – 153</td>
</tr>
<tr>
<td>9</td>
<td>2,7-dimethylphenoxathiin</td>
<td>111.8</td>
<td>98 – 133</td>
</tr>
<tr>
<td>10</td>
<td>phenoxazine</td>
<td>128.9</td>
<td>117 – 145</td>
</tr>
<tr>
<td>11</td>
<td>2,7-di-t-butyl-9,9-dimethylxanthene</td>
<td>123.1</td>
<td>107 – 142</td>
</tr>
<tr>
<td>12</td>
<td>2,7-di-t-butyl-9,9-dimethylxanthene</td>
<td>121.4</td>
<td>107 – 138</td>
</tr>
</tbody>
</table>

$^a$ The natural bite angle ($\beta_n$) and the flexibility range were calculated as by Casey and Whiteker. $\beta_n$ is defined as the preferred chelation angle determined only by backbone constraints and not by metal valence angles. The flexibility range is defined as the accessible range of bite angles within 3 kcal mol$^{-1}$ excess strain energy from the calculated natural bite angle. $^b$ See also [10][21].

Figure 4 Effect of phosphine-moietry on bite angle and flexibility range ($\beta_n$, flexibility range).

thereby forcing the phenoxaphosphino-moieties to adopt a different orientation from that initially expected, which results in an increased bite angle.
(Diphosphine)Rh(CO)$_2$H Complexes.

To determine whether the variation in ligand backbone has an influence on the chelation behaviour of the ligands we studied the solution structures of the (diphosphine)Rh(CO)$_2$ complexes, the resting state of the catalyst under hydroformylation conditions, by high pressure IR and high pressure NMR spectroscopy. The complexes were prepared in situ from Rh(CO)$_2$(acac) and diphosphine (1.1 equivalents) under 16 bar of CO/H$_2$ (1:1). For ligands 1 - 8 the formation of (diphosphine)Rh(CO)$_2$H was observed to occur within 1 h at 40 °C. The $^{31}$P{H} NMR spectrum at 273K of the complexes with 2 - 5, 7 and 8 showed a characteristic doublet in the range from -33 ppm up to -20 ppm. For ligands 1, 9 and 10 [(diphosphine)Rh(CO)$_2$]$_2$ were observed as the major complexes. These dimers exhibit a splitting pattern in $^{31}$P{H} NMR consistent with an AA'AA'XX' spin system at -27.4 ppm for 1, 4.8 ppm for 9, and -0.4 ppm for 10.$^{36}$ The complex (1)Rh(CO)$_2$H was observed in lower quantities showing two broad doublets, indicating mainly a co-ordination. (9 - 10)Rh(CO)$_2$H were not observed at all. For (6)Rh(CO)$_2$H a doublet doublet per phosphorus atom was observed due to the inequivalence of the two phosphorus atoms. In the $^1$H NMR at 273K the hydride appeared in the range from -9.2 ppm up to -8.7 ppm as triplet of doublets for ligands 1, 3-4, triplet for 2, 5 - 7 or broad (distorted) singlet for 8. The characteristic hetero-nuclear coupling constants and chemical shifts are shown in Table 2.

Probably due to the high concentration that is required for high pressure NMR often small amounts of additional rhodium-phosphine species were observed. Both $^1$H NMR and $^{31}$P{H} NMR using $^{13}$CO exclude these species as either hydride or carbonyl containing complexes. For ligand 8 many other phosphorus-rhodium species, besides formation of (8)Rh(CO)$_2$H, are observed in considerable amounts in $^{31}$P{H} NMR. The relatively high concentration of ligand and rhodium that is necessary for high

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$^1$J(Rh,H), Hz</th>
<th>$^1$J(Rh,P), Hz</th>
<th>$^3$J$_{pp}$ (P,H), Hz</th>
<th>$^3$J(P,P), Hz</th>
<th>$^3$P{H} (ppm)</th>
<th>$^3$H (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.9</td>
<td>124 / 129</td>
<td>42</td>
<td>--</td>
<td>-20.4</td>
<td>-8.9</td>
</tr>
<tr>
<td>2</td>
<td>n.o.$^b$</td>
<td>150</td>
<td>6.6</td>
<td>--</td>
<td>-23.7</td>
<td>-8.7</td>
</tr>
<tr>
<td>3</td>
<td>2.9</td>
<td>153</td>
<td>12.4</td>
<td>--</td>
<td>-25.3</td>
<td>-8.9</td>
</tr>
<tr>
<td>4</td>
<td>2.8</td>
<td>154</td>
<td>12.5</td>
<td>--</td>
<td>-27.2</td>
<td>-9.0</td>
</tr>
<tr>
<td>5</td>
<td>n.o.</td>
<td>151</td>
<td>7.7</td>
<td>--</td>
<td>-29.0</td>
<td>-9.0</td>
</tr>
<tr>
<td>6$^c$</td>
<td>n.o.</td>
<td>153 / 149</td>
<td>6.6</td>
<td>63</td>
<td>-33.0</td>
<td>-9.2</td>
</tr>
<tr>
<td>7$^d$</td>
<td>n.o.</td>
<td>153</td>
<td>13.5</td>
<td>--</td>
<td>-30.8</td>
<td>-9.2</td>
</tr>
<tr>
<td>8</td>
<td>n.o.</td>
<td>153</td>
<td>bs</td>
<td>--</td>
<td>-25.7</td>
<td>-8.9</td>
</tr>
</tbody>
</table>

$^a$Conditions: p(CO/H$_2$)(1:1) = 20 bar, solvent = toluene-d$_8$, T = 273K. $^b$n.o.: not observed. $^c$solvent = toluene-d$_8$/THF. $^d$solvent = THF-d$_8$. 

Table 2 Selected high pressure NMR data (Diphosphine)RhH(CO)$_2$ complexes'
pressure NMR when compared to the conditions of a catalytic reaction is a plausible cause for the observation of so many species in which co-ordination of the additional phosphine of the ligand backbone can be involved. The disappearance of the signal of the free phosphorus of the ligand backbone at -53 ppm indicates that this phosphorus atom is indeed co-coordinating, reinforcing this hypothesis. The distorted broad signal at -8.9 ppm in \textsuperscript{1}H NMR might be the result of two overlapping signals, which would indicate the presence of more than one rhodium-hydride species. Even at 183K the signals could not be separated. Formation of telomeric, oligomeric or polymeric structures is not excluded. Characterisation of the different species has not been attempted.

The IR frequencies of the absorption bands of the (1–8)Rh(CO)\textsubscript{2}H complexes in the carbonyl region are summarised in Table 3. For the rhodium complexes with ligands 3 – 7 only two absorption bands were observed. By performing a hydride-deuterium exchange the two bands shifted to a lower frequency. This indicates that the ligands are co-ordinated in an ee-fashion, as in this isomer a trans relationship between the hydride and carbonyl ligand exists, which results in coupling of the vibrations. By exchange of H for D this resonance interaction becomes much smaller which leads to a shift of the carbonyl bands of the ee-isomer.\textsuperscript{3} Only when ligands 1, 2 and 8 were used the existence of an equilibrium between ee and ae co-coordinating rhodium complexes was observed as complexes with these ligands showed all four absorption bands in the carbonyl frequency region. Unlike the high pressure NMR experiments, no formation of the dimeric [(1)Rh(CO)\textsubscript{2}] was observed. This is ascribed to the low concentrations that are used for high pressure IR and which are similar to those of catalytic runs, while high pressure NMR needs much higher concentrations, which favours the formation of dimeric rhodium species.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>(v_1) (\text{cm}^{-1})</th>
<th>(v_2) (\text{cm}^{-1})</th>
<th>(v_3) (\text{cm}^{-1})</th>
<th>(v_4) (\text{cm}^{-1})</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>2040</td>
<td>1999</td>
<td>1978</td>
<td>1956</td>
</tr>
<tr>
<td>2</td>
<td>2041</td>
<td>2000(vw)</td>
<td>1981</td>
<td>1953(vw)</td>
</tr>
<tr>
<td>3</td>
<td>2042</td>
<td>---</td>
<td>1985</td>
<td>---</td>
</tr>
<tr>
<td>4\textsuperscript{c}</td>
<td>2037</td>
<td>---</td>
<td>1979</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>2040</td>
<td>---</td>
<td>1983</td>
<td>---</td>
</tr>
<tr>
<td>6\textsuperscript{c}</td>
<td>2036</td>
<td>---</td>
<td>1979</td>
<td>---</td>
</tr>
<tr>
<td>7</td>
<td>2040</td>
<td>---</td>
<td>1984</td>
<td>---</td>
</tr>
<tr>
<td>8\textsuperscript{c}</td>
<td>2038</td>
<td>2004</td>
<td>1980</td>
<td>1954</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Conditions: \(p(\text{CO}/\text{H}_2)(1:1) = 20\text{bar}, \text{solvent} = \text{cyclohexane, } T = 313\text{K}.
\textsuperscript{b} Vibrational bands belonging to either the ee or ae configuration were assigned by performing a H-D exchange. \textsuperscript{c} Solvent = 2-methyltetrahydrofuran.
For 10 only the dimeric complex \([(10)\text{Rh(CO)}_2]_2\) was observed in the IR spectrum. This complex exhibits absorption bands for the terminal carbonyl ligands (2004 cm\(^{-1}\)/1980 cm\(^{-1}\)) and two absorption bands in the bridging carbonyl ligands (1792 cm\(^{-1}\)/1762 cm\(^{-1}\)). Similar dimeric complexes were also observed for 12.\(^{13,14}\) \([(12)\text{Rh(CO)}_2]_2\) was reported to be the resting state of the catalyst. For 9 clearly other species were also formed. Besides two absorption bands for the terminal carbonyl ligands (2010 cm\(^{-1}\)/1985 cm\(^{-1}\)) and two absorption bands for the bridging carbonyl ligands (1801 cm\(^{-1}\)/1733 cm\(^{-1}\)), also absorptions at 2066 cm\(^{-1}\)(m) and 1994 cm\(^{-1}\)(s) were observed. In addition none of the CO bands shifted upon using D\(_2\) instead of H\(_2\). Clearly some other complexes are present when this ligand is used. This complex was not stable since the carbonyl absorptions diminished and many other absorptions with a low intensity appeared after overnight measurement at 80 °C.

Crystals suitable for crystal structure determination were obtained for (3)Rh(CO)H(PPh\(_3\)) and (5)Rh(CO)H(PPh\(_3\)) and the molecular structures are depicted in Figure 5. These crystals were obtained by the addition of either 3 or 5 to Rh(CO)H(PPh\(_3\)) dissolved in dichloromethane, which resulted in displacement of two PPh\(_3\) ligands. Subsequently, ethanol is added to form a two-layer system. Slow diffusion of ethanol into the dichloromethane layer resulted in crystals of (3)Rh(CO)H(PPh\(_3\)) and (5)Rh(CO)H(PPh\(_3\)). Selected bond lengths and angles are shown in Table 4. The crystal structures reveal that the phosphorus atoms define the equatorial plane with the rhodium atom located slightly above this plane directed toward the carbonyl ligand. The positions of the hydride ligands were determined from difference Fourier maps. Their positions are not accurate, but are in line with \(^1\)H NMR spectroscopy results of the (diphosphine)Rh(CO)\(_2\)H complexes (vide supra). The P-M-P angles in the complexes differ much from the calculated natural bite angle and are possibly influenced by

![Table 4: Selected bond lengths and angles for (3)Rh(CO)\(_2\)H and (5)Rh(CO)\(_2\)H](attachment:image)

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Rh-P(1)</th>
<th>Rh-P(2)</th>
<th>Rh-P(3)</th>
<th>Rh-C(1)</th>
<th>Rh-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3)Rh(CO)(_2)H</td>
<td>2.2913(6)</td>
<td>2.2839(7)</td>
<td>2.3161(70)</td>
<td>1.910(2)</td>
<td>1.7591</td>
</tr>
<tr>
<td>(5)Rh(CO)(_2)H</td>
<td>2.3107(4)</td>
<td>2.3046(4)</td>
<td>2.3193(5)</td>
<td>1.8927(17)</td>
<td>1.5813</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles (°)</th>
<th>P(1)-Rh-P(2)</th>
<th>P(1)-Rh-P(3)</th>
<th>P(2)-Rh-P(3)</th>
<th>P(1)-Rh-C(1)</th>
<th>P(2)-Rh-C(1)</th>
<th>P(3)-Rh-C(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3)Rh(CO)(_2)H</td>
<td>123.02(2)</td>
<td>117.59(2)</td>
<td>114.71(2)</td>
<td>97.28(8)</td>
<td>97.38(8)</td>
<td>96.98(8)</td>
</tr>
<tr>
<td>(5)Rh(CO)(_2)H</td>
<td>120.38(2)</td>
<td>119.55(2)</td>
<td>118.03(2)</td>
<td>94.70(5)</td>
<td>97.95(5)</td>
<td>91.58(6)</td>
</tr>
</tbody>
</table>

67
Figure 5 Crystal structures and numbering schemes for (3)Rh(CO)$_2$H (top) and (5)Rh(CO)$_2$H (+CH$_2$Cl$_2$)(bottom) (H-atoms have been omitted for clarity). Displacement ellipsoids are shown at 50 % probability.
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stereoelectronic interactions of the phenoxaphosphino-moieties of 3 and 5 and the phenyl-groups of PPh₃; the crystal structures show several π-π-stacking interactions. The P-M-P angles are, however, well within the calculated flexibility range.

Hydroformylation of 1-octene.

Hydroformylation of 1-octene was carried out at 80 °C under 20 bar of 1:1 CO/H₂ using a 1.0 mM solution of rhodium diphosphine catalyst prepared from Rh(CO)₂(acac) and 5 equivalents of ligand. The production of octene isomers, nonanal, and 2-methyloctanal was monitored by gas chromatography. Turn-over frequencies were determined and averaged after ~ 20 % conversion. The results of the experiments are presented in Table 5.

In contrast to previous studies on the effect of bite angle on selectivity for the hydroformylation of 1-octene, hardly any effect of the bite angle on the selectivity for the linear aldehyde is observed for

<table>
<thead>
<tr>
<th>Ligand</th>
<th>X</th>
<th>βₚ (°)</th>
<th>TOF</th>
<th>l/b</th>
<th>% Isom (%)</th>
<th>Sel (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>C₂H₄</td>
<td>105.7</td>
<td>1900</td>
<td>5.5</td>
<td>2.8</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>Si(CH₃)₂</td>
<td>108.0</td>
<td>2250</td>
<td>14</td>
<td>6.8</td>
<td>87</td>
</tr>
<tr>
<td>3</td>
<td>S</td>
<td>112.5</td>
<td>3275</td>
<td>22</td>
<td>10.5</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>Isoprop</td>
<td>114.2</td>
<td>1800</td>
<td>23</td>
<td>9.7</td>
<td>86</td>
</tr>
<tr>
<td>5</td>
<td>C(CH₃)₂</td>
<td>116.0</td>
<td>1800</td>
<td>23</td>
<td>10.0</td>
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<td>fused ring</td>
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<td>1600</td>
<td>30</td>
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<td>84</td>
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<tr>
<td>7</td>
<td>NH</td>
<td>124.5</td>
<td>1550</td>
<td>33</td>
<td>11.6</td>
<td>85</td>
</tr>
<tr>
<td>8</td>
<td>PPh</td>
<td>131.2</td>
<td>1100</td>
<td>18</td>
<td>7.5</td>
<td>87</td>
</tr>
<tr>
<td>9</td>
<td>S</td>
<td>111.8</td>
<td>343</td>
<td>&gt; 99</td>
<td>14.2</td>
<td>85</td>
</tr>
<tr>
<td>10</td>
<td>NH</td>
<td>128.9</td>
<td>144</td>
<td>&gt; 99</td>
<td>11.5</td>
<td>87</td>
</tr>
<tr>
<td>11</td>
<td>C(CH₃)₂</td>
<td>123.1</td>
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<td>67</td>
<td>10.0</td>
<td>89</td>
</tr>
<tr>
<td>12</td>
<td>C(CH₃)₂</td>
<td>121.4</td>
<td>453</td>
<td>62</td>
<td>10.8</td>
<td>88</td>
</tr>
</tbody>
</table>

*Conditions: p(CO/H₂)(1:1) = 20 bar, ligand/Rh = 5, substrate/Rh = 637, [Rh] = 1.00 mM in toluene, number of experiments is 3. In none of the experiments was hydrogenation observed. 'X = refers to the top bridging group in the ligand (see Figure 2). βₚ = the natural bite angle (see Table 1). ' Linear to branched ratio, percent linear aldehyde, percent isomerisation to 2-octene and turnover frequency were determined at ~ 20% alkene conversion. 'Turnover frequency = (mol aldehyde)(mol Rh)⁻¹.h⁻¹. 'Percentage of linear aldehyde of all products (including isomerisation towards internal alkenes).
ligands 1 – 8. The l/b ratio and the percentage of isomerisation to internal octenes increases, but both increase with increasing bite angle up to a bite angle of 125° only. The observed increase in l/b ratio is attributed to an increased tendency of the branched alkyl rhodium species to undergo β-hydrogen elimination instead of alkyl migration. After an initial increase in catalytic activity with increasing bite angle from 105.7° up to 112.5° a drop in activity with further increasing bite angle is observed.

Ligand 3, that according to the reported Hammet constant has the strongest electron withdrawing capacities with the sulfur moiety ($\sigma_m(SPh) = 0.23$) in the ligand backbone, gives a catalytic system that shows almost twice the activity compared to the results obtained when the other phenoxaphosphino-modified ligands are employed. These results show that small structural and electronic differences can have a huge impact on catalysis results.

Very high regio-selectivities and high percentages of isomerisation are observed for the dibenzophosphole ligands 9 and 10. For both ligands the hydroformylation activity is very low, but this can be a result of preferred formation of the rhodium-dimer resting state.

**Hydroformylation of trans-2-octene.**

Hydroformylation of trans-2-octene was carried out at 120 °C under 3.6 bar of 1:1 CO/H$_2$ using a 1.0 mM solution of rhodium diphosphine catalyst prepared from Rh(PPh$_3$)$_3$H(CO) and 10 equivalents of ligand. The relatively high temperature and low pressure are necessary to enhance the rate of isomerisation, thereby continuously maintaining the formation of terminal alkenes. The production of alkene isomers, linear and branched aldehydes were monitored by gas chromatography. Turn-over frequencies were determined after 2 h reaction time. The results of the hydroformylation experiments are summarised in Table 6.

By comparing ligands 1 – 8 a clear bite angle effect on catalytic activity and regio-selectivity is observed in the hydroformylation of trans-2-octene, see Figure 6. Contrary to the results obtained with the non-cyclic analogues for the hydroformylation of 1-octene, an increased bite angle leads to a strong decrease in hydroformylation activity. While the activity decreases an increase in regio-selectivity is observed that correlates with the regio-selectivity for the hydroformylation of 1-octene, see Figure 7 for a parity plot. As it is expected that the rate of isomerisation is crucial for obtaining good catalysts for the selective hydroformylation of internal alkenes to linear aldehydes it is not surprising that the ligands showing the highest rate of isomerisation in the hydroformylation of 1-octene, show the highest regio-selectivity in the hydroformylation of trans-2-octene. In addition, ligands with a higher rate of isomerisation show a lower hydroformylation activity, as β-hydrogen elimination is non-productive.
The Influence of the Bite Angle on the Hydroformylation of Internal Olefins to Linear Aldehydes

Figure 6 Turn over frequency (triangles) and regio-selectivity (squares) vs the calculated natural bite angle in the hydroformylation of \textit{trans}-2-octene (Ligands 1 - 8).

<table>
<thead>
<tr>
<th>Ligand</th>
<th>X</th>
<th>$\beta_n$ (°)</th>
<th>TOF$^{c,d}$</th>
<th>l/b$^{e}$</th>
<th>Sel$^{c,e}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C$_2$H$_4$</td>
<td>105.7</td>
<td>250</td>
<td>0.4</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>Si(CH$_3$)$_2$</td>
<td>108.0</td>
<td>193</td>
<td>2.6</td>
<td>72</td>
</tr>
<tr>
<td>3</td>
<td>S</td>
<td>112.5</td>
<td>151</td>
<td>4.4</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>Isoprop</td>
<td>114.2</td>
<td>143</td>
<td>5.8</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>C(CH$_3$)$_2$</td>
<td>116.0</td>
<td>143</td>
<td>4.3</td>
<td>81</td>
</tr>
<tr>
<td>6</td>
<td>Fused ring</td>
<td>124.3</td>
<td>63</td>
<td>8.0</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>NH</td>
<td>124.5</td>
<td>38</td>
<td>8.3</td>
<td>89</td>
</tr>
<tr>
<td>8</td>
<td>PPh</td>
<td>131.2</td>
<td>8</td>
<td>3.7</td>
<td>79</td>
</tr>
<tr>
<td>9</td>
<td>S</td>
<td>111.8</td>
<td>78 (64$^f$)</td>
<td>18.3 (22.7$^f$)</td>
<td>95 (96$^f$)</td>
</tr>
<tr>
<td>10</td>
<td>NH</td>
<td>128.9</td>
<td>60$^f$</td>
<td>24.7$^f$</td>
<td>96$^f$</td>
</tr>
<tr>
<td>11</td>
<td>C(CH$_3$)$_2$</td>
<td>123.1</td>
<td>140 (112$^f$)</td>
<td>6.6 (9.2$^f$)</td>
<td>87 (90$^f$)</td>
</tr>
<tr>
<td>12</td>
<td>C(CH$_3$)$_2$</td>
<td>121.4</td>
<td>65$^f$</td>
<td>9.5$^f$</td>
<td>90$^f$</td>
</tr>
</tbody>
</table>

$^a$ Conditions: $p$(CO/H$_2$)(1:1) = 3.6 bar, ligand/Rh = 10, substrate/Rh = 640, [Rh] = 1.00 mM in toluene, number of experiments is 2. In none of the experiments was hydrogenation observed. $^b$ X refers to the top bridging group in the ligand (see Figure 2). $^c$ $\beta_n$ is the natural bite angle (see Table 1). $^d$ Linear to branched ratio, percent linear aldehyde and turnover frequency were determined after 2h. $^e$ Turnover frequency = (mol aldehyde)/(mol Rh)$^3$. $^f$ Percentage of linear aldehyde of all products other than octenes. $^g$ p(CO/H$_2$)(1:1) = 2.0 bar.
Unprecedented high regio-selectivities at moderate activities for the hydroformylation of trans-2-octene are obtained when the dibenzophosphole type ligands 9 and 10 are used. These results can be attributed to the combination of the high isomerisation activity and the very high regio-selectivity of these ligands. Compared to ligands 1 – 8 only a small difference in hydroformylation activity between the 1-octene and trans-2-octene is observed, especially for 10.

In an attempt to improve the regio-selectivity even further, the effect of ligand concentration on activity and selectivity was investigated for 9. Upon increasing the ligand:rhodium ratio from 5 to 40 equivalents a gradual decrease in TOF from 75 mol.mol\(^{-1}.h\)\(^{-1}\) to 34 mol.mol\(^{-1}.h\)\(^{-1}\) was observed. Within this range the regio-selectivity did not change. This indicates a very strong co-ordination of the diphosphine to the rhodium metal; the formation of an inactive (diphosphine)\(_2\)Rh-species is favored at increased ligand:rhodium ratios.

**Deuterioformylation of 1-hexene.**

Deuterioformylation of 1-hexene was carried out under similar conditions as the hydroformylation experiments. 1-Hexene was used for the deuterioformylation instead of 1-octene to facilitate comparison with literature data of the \(^1\)H and \(^2\)H spectra.\(^{32}\) The percentages of deuterated species formed in the deuterioformylation were calculated using GC and \(^2\)H\(_{\{\text{H}\}}\) NMR data on the ratio of heptanal to branched aldehydes, percent conversion, percent isomerisation towards internal hexenes and deuterium contents of aldehydes and recovered hexenes. Activities were comparable to the 1-octene
hydroformylation experiments, while the regio-selectivities are somewhat lower than those obtained with 1-octene. Table 7 summarizes the deuterioformylation results.

Previous studies by Casey, Lazzaroni, Pino, and van Leeuwen have shown that the formation of the alkyl rhodium intermediate is reversible at elevated temperatures. By a similar experimental method, the amount of initial linear alkyl rhodium formation and branched alkyl rhodium formation can be easily deduced. Detailed dissection of the labeling results of catalysis with 1, 5 and 7 shows that the initial ratio of linear-alkyl to branched-alkyl intermediates is ~ 4.2 - 4.4 (Table 8). These results prove that when these ligands are used the differences in observed l/b ratio are not only the result of preferential formation of the linear aldehyde, but are mainly the result of different rates of β-hydrogen elimination. In all three cases > 92% of the linear alkyl intermediate reverts to the aldehyde directly. On the other hand, the branched alkyl intermediate partitions between conversion towards the branched aldehyde, 1-hexene, and cis- and trans-2-hexene.

Table 7 Deuterioformylation of 1-hexene

<table>
<thead>
<tr>
<th>Ligand</th>
<th>conversion to aldehydes (%)</th>
<th>1-hexene (%)</th>
<th>2-hexene-d₁ (%)</th>
<th>heptanal-d₁ (%)</th>
<th>2-methyl hexanal-d₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.7</td>
<td>77.1</td>
<td>1.34</td>
<td>0.29</td>
<td>0.6</td>
</tr>
<tr>
<td>5</td>
<td>23.8</td>
<td>71.5</td>
<td>0.56</td>
<td>1.76</td>
<td>2.4</td>
</tr>
<tr>
<td>7</td>
<td>13.9</td>
<td>83.2</td>
<td>0.68</td>
<td>1.13</td>
<td>1.6</td>
</tr>
</tbody>
</table>

*Conditions: p(CO/D₂) = 20 bar (~1:1, see experimental section for more details), ligand/Rh = 5, substrate/Rh = 806, [Rh] = 1.000 mM in toluene. In none of the experiments was hydrogenation observed. It is important to note that the amounts of deuterated hexenes do not reflect the actual percentages of formed (1- and 2-alkyl)rhodium intermediates as also non-productive β-D elimination occurs. Deuterium labels were almost exclusively found in the formyl group and the position β to the formyl group. Only traces of deuterium label was found at the α position to the formyl group.

Table 8 Partitioning of (alkyl)rhodium intermediates

<table>
<thead>
<tr>
<th>Ligand</th>
<th>(1-alkyl) intermediate</th>
<th>(2-alkyl) intermediate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/1</td>
<td>2/1</td>
</tr>
<tr>
<td></td>
<td>heptanal (%)</td>
<td>CH₂=CD₃H₅ (%)</td>
</tr>
<tr>
<td>1</td>
<td>4.22</td>
<td>4.9</td>
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<td>4.42</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>4.37</td>
<td>25</td>
</tr>
</tbody>
</table>

CH₂=CD₃H₅ + heptanal = 100 % (data converted from Table 6). CDH=CH₂C₃H₇ + 2-methylhexanal = 100 % (data converted from Table 6).
From these results it can be concluded that increasing the bite angle in a branched alkyl rhodium intermediate causes a decrease in branched aldehyde formation, while the percentage of isomerisation towards both 1-hexene and 2-hexene increases.

Discussion.

Spectroscopy. The high pressure NMR data of the \((1 - 8)\text{RhH(CO)}_2\) and \([(9 - 10)\text{Rh(CO)}_2\] complexes are in line with the results obtained with high pressure IR. For \((1 - 8)\text{RhH(CO)}_2\) the small rhodium-proton coupling constant and phosphorus-proton coupling constant and the large rhodium-phosphorus coupling constant indicate that the dynamic equilibrium between ee and ae isomers is shifted towards the ee isomer. Quantitative estimations of the ee:ae ratios for \((1 - 2, 8)\text{RhH(CO)}_2\) cannot be made using the averaged phosphorus-proton coupling constants, as the ae and ee phosphorus-proton coupling constants are not known for these phosphacyclic diphosphines. As is indicated in Table 2 they can differ substantially between the different ligands; e.g. a relatively large phosphorus-proton coupling is observed for complexes with ligands 3 and 7 and a low phosphorus-proton coupling is observed for the complex with ligand 2. High pressure IR indicates exclusive formation of ee isomers for the former two complexes and an ee-ae mixture for the latter complex. In non-disturbed trigonal bipyramidal complexes the phosphorus-hydride coupling should be very small,

therefore the results imply that in most cases the trigonal bipyramidal rhodium complexes are highly distorted with the phosphines bent out of the equatorial plane. The rhodium-proton coupling constants are also indicative of the ee:ae ratio. The ae co-ordinated isomers have often large rhodium-proton coupling constants, while for purely ee co-ordinating ligands, like BISBI, small coupling constants are observed. Moreover, in previous studies increasing ee:ae ratios were accompanied by decreasing rhodium-proton coupling constants. It is surprising that for \((2)\text{RhH(CO)}_2\) the rhodium-proton coupling could not be resolved \((\text{J(Rh,H)} < 2 \text{ Hz})\) even at low temperatures (183K), while high pressure IR clearly shows absorption bands belonging to the ae isomer, albeit in a small amount.

The results obtained by high pressure IR suggest that the electron-density around rhodium is similar for all \((1 - 8)\text{RhH(CO)}_2\) complexes as all bands are within close range. Comparison of the CO-stretch frequencies with the \((\text{diphosphine)}\text{RhH(CO)}_2\) complexes of the diphenylphosphine-analogues of ligands \(1 - 8\) shows that all ligands have similar electronic properties. The large differences in catalytic activity between these two systems are therefore attributed to extended \(\pi\)-conjugation and increased effective steric bulk upon introduction of the phenoxyphosphino-moiety and are to a lesser extent the result of decreased phosphorus basicity.

Catalysis: Activity. Widening the bite angle in the square planar \((\text{diphosphine)}\text{Rh(CO)}H\) complex, one of the supposed intermediates in the hydroformylation reaction, would certainly accelerate the
overall reaction by increasing the concentration this intermediate complex as a trans co-ordination of the diphosphine is energetically more favorable than a cis co-ordination. If other effects are absent or counterbalance one another (i.e. alkene and CO association/dissociation, hydride and alkyl migration, and hydrogenolysis) then this leads to an increase in hydroformylation activity as was postulated previously. In the same study an increased rate of alkene co-ordination for ligands with a wider bite angle was also proposed in order to explain the effect on reaction rate in accord with other studies. While these positive effects of widening the bite angle on activity are certainly not ruled out for 1 – 8, the results indicate that another step in the catalytic cycle becomes rate-limiting. This effect is especially pronounced in the hydroformylation of trans-2-octene. The decrease of hydroformylation activity with increased bite angle might be explained by a step later in the catalytic cycle becoming rate limiting. In the trigonal bipyramidal rhodium complex, increasing the bite angle results in increased steric congestion around rhodium especially in the apical position. In addition, with the exception of 2 and 7 an increased bite angle leads to a decreased phosphorus-hydride coupling, which is indicative of approaching a more perfect trigonal bipyramidal structure. This might be an indication that ligands with a larger bite angle lead to less distorted trigonal bipyramidal complexes and thereby to an increased effective steric bulk (Figure 8).

According to this postulation it is more favorable for complexes of B (Scheme 2) with wide bite angle ligands to undergo β-hydrogen elimination (B → A) than CO-association (B → C) as required for hydroformylation. From the deuterioformylation experiments it can be concluded that isomerisation towards internal olefins is faster than isomerisation towards the terminal olefin. Also, the rate of

\[
\begin{align*}
\text{Figure 8 Effect of bite angle on space around rhodium.}
\end{align*}
\]

\[
\begin{align*}
\text{Scheme 2 } \beta\text{-Hydrogen elimination vs CO-association.}
\end{align*}
\]
isomerisation is faster than the rate of CO-insertion. Additionally, CO-insertion in to the branched alkyl rhodium intermediate is slower than CO-insertion in to the linear alkyl rhodium intermediate, especially when bulky ligands are used this CO-insertion is hampered. Thus, it is reasoned that systems that show a higher rate of isomerisation (thus ligands with wide bite angles) show a lower hydroformylation activity. For 1-octene hydroformylation these effects are less pronounced as differences between the rate of β-hydrogen elimination from the linear alkyl rhodium species are smaller and since CO-association to a linear alkyl rhodium intermediate is sterically less demanding.

Another explanation for the bite angle effect on the activity in hydroformylation is found in a decreased rate of alkene insertion. The increased steric congestion around rhodium hampers the olefin from entering the coordination sphere. For internal olefins this effect is stronger than for terminal olefins.

**Catalysis: Regio-selectivity.** Concerning regio-selectivity the series does follow the trend that was observed before; \(^4\) i.e. ligands possessing larger bite angles lead to more regio-selective systems. It must be noted that the origin of the regio-selectivity is different from that reported previously in which the increase in selectivity is attributed to more selective formation of the linear alkyl-rhodium species. In the present study using 1 – 8 the differences in regio-selectivity are caused by the differences in rate of β-hydrogen elimination of the branched alkyl intermediate compared to the linear alkyl intermediate as supported by the deuterioformylation experiments. The branched alkyl intermediate reverts to an olefin complex but the linear alkyl intermediate is converted directly to the aldehyde. \(^{32}\) As more linear than branched products are formed for hydroformylation of trans-2-octene using 2 – 8 it can be concluded that most products are formed via *in situ* generated terminal olefins. The order in the regio-selectivities of the different systems is therefore unchanged. It can be concluded that the formation of terminal olefins from internal olefins is faster than the formation of branched aldehydes.

Upon increasing the natural bite angle to 131 ° with ligand 8 a decrease in regio-selectivity is observed. Although this might be due to possible co-ordination of the phosphine in the ligand backbone, thereby acting partially as a monophosphine, it is unlikely that this is happening, since at low phosphorus concentrations and under CO pressure the mono-phosphine would dissociate. A more plausible reason is that systems possessing too large bite angles again lead to less regio-selective systems by relatively increasing the rate of β-hydrogen elimination from the linear alkyl intermediate. An optimum bite angle is found around 120 ° to 125 °. Previous studies on a dibenzofuran based diphenylphosphine (4,6-bis(diphenylphosphinodibenzofuran, \(\beta_p = 131.1 °\)) also showed a decrease in selectivity compared to similar ligands with a smaller bite angle.\(^{11}\)

The results with the dibenzophosphole type ligands 9, 10 and 12 show that very subtle changes in either backbone structure or cyclic phosphino-moiety can have a tremendous influence on the catalysis
results. How these subtle changes influence catalysis is not yet understood. Unfortunately, the preferential formation of the rhodium dimer complex hampers a detailed in situ study.

Conclusions.

Within the series of Xantphenoxaphos-type ligands no distinct effect of the natural bite angle on the co-ordination mode of the (1 - 8)Rh(CO)2H complexes has been found. Most ligands show ee co-ordination preferentially and only for ligands 1, 2 and 8 also ee co-ordination was observed. The decrease of catalytic activity with an increase in natural bite angle is attributed to differences in the rate of β-hydrogen elimination and CO-association in the intermediate (1 - 8)Rh(CO)(alkyl) complex, and these are mainly determined by steric factors. The differences in selectivity are also attributed to the differences in rate of β-hydrogen elimination as deuterioformylation experiments have shown that the initial ratio of (linear alkyl)rhodium intermediate:(branched alkyl)rhodium intermediate is equal when 1, 5 and 7 are used. To the best of our knowledge, thixantphenoxaphos (3) gives an unprecedented high activity with a respectable selectivity in the rhodium-diphosphine catalysed hydroformylation of terminal olefins. Noteworthy, though, are the recent results obtained by Stanley et al., who improved existing systems by the addition of water to the reaction medium.42

High regio-selectivities are observed when the dibenzophosphole-type ligands 9 and 10 are used for the hydroformylation of trans-2-octene, which are unprecedented. These regio-selectivities even supersede the regio-selectivities often reported for the hydroformylation of terminal olefins. Despite their moderate 1-octene hydroformylation activity, 9 and 10 still show an acceptable activity in hydroformylation of trans-2-octene.

Acknowledgement. Financial support from Celanese Chemicals Europe, G.m.b.h., Germany is gratefully acknowledged. We thank Martin Lutz for solving the crystal structures.

Experimental.

Computational details. The molecular mechanics calculations were performed using CAChe WorkSystem version 4.0, on an Apple Power MacIntosh 950, equipped with two CAChe CXP co-processors. Calculations were carried out similarly to the method described by Casey and Whiteker,5 using a Rh-P bond length of 2.315 Å. Minimisation's were done using the block-diagonal Newton-Raphson method, allowing the structures to converge with a termination criterion of a rms factor of 0.0001 kcal mol⁻¹ Å⁻¹ or less.
General procedure. All air- or water-sensitive reactions were performed using standard Schlenk techniques under an atmosphere of purified argon. Toluene was distilled from sodium, THF from sodium/benzophenone, and hexanes from sodium/benzophenone/triglyme. Isopropanol and dichloromethane from CaH₂. Chemicals were purchased from Acros Chimica, and Aldrich Chemical Co. Benzo[k,l]xanthene,⁴³,⁴⁴ 10,11-dihydrodebenzo[b,f]oxepine,⁴⁵ 9-isopropylidenexanthene,⁴⁶ 10-phenylphenoxyphosphine,⁴⁷ 2,8-dimethyl-10-chlorophenoxyphosphine,⁴⁸ 2,7-di-tert-butyl-10,10-dimethylphenoxyasilin,⁴⁹,⁵⁰ 2,7-dimethylphenoxythiin,⁵¹ 9-(tert-butylidimethylsilyl)phenoxyazine,⁵² 2,7-di-tert-butyl-9,9-dimethyl-4,5-bis(10-phenoxyphosphino)xanthene (11),¹⁰,²¹ and 4,5-bis(9-dibenzo[b,d]phospholyl)-2,7-di-tert-butyl-9,9-dimethylxanthene (12)¹⁰,²¹ were prepared according to literature procedures. Silica gel 60 (230-400 mesh) purchased from Merck was used for column chromatography. Melting points were determined on a Gallenkamp MFB-595 melting point apparatus in open capillaries and are reported uncorrected. NMR spectra were recorded on a Varian Mercury 300 or Inova 500 spectrometer. ³¹P and ¹³C spectra were measured ¹H decoupled. TMS was used as a standard for ¹H and ¹³C NMR and 85% of H₃PO₄ in H₂O for ³¹P NMR. Infrared spectra were recorded on a Nicolet 510 FT-IR spectrophotometer. High pressure IR spectra were measured using a 50 mL homemade stainless steel autoclave equipped with mechanical stirrer and ZnS windows. Hydroformylation reactions were carried out in a 200 mL homemade stainless steel autoclave. Both high pressure IR and hydroformylation experiments were conducted at a stirring rate of 800 rpm. The alkene was filtered over neutral activated alumina to remove peroxide impurities. The reactions were stopped by quenching the reaction mixture with tri-n-butylphosphite, cooling on ice and venting the gases. Synthesis gas (CO/H₂, 1:1, 99.9%) was purchased from Air Liquide. D₂ was purchased from Hoekloos. ¹³CO (99%) was purchased from Cambridge Isotope Laboratories. Gas chromatographic analysis were run on an Interscience HR GC Mega 2 apparatus (split/splitless injector, J&W Scientific, DB-1 30m column, film thickness 3.0 mm, carrier gas 70 kPa He, FID detector) equipped with a Hewlett Packard Data system (Chrom-Card) using decane as an internal standard.

4,5-bis(2,8-dimethyl-10-phenoxyphosphino)-10,11-dihydrodibenzo[b,f]oxepine
(Homoxanthophenoxaphos, 1)

At 0 °C 1.9 mL of n-butyllithium (2.5 M in hexanes, 4.8 mmol) was added to a stirred solution of 380 mg of 10,11-dihydrodibenzo[b,f]oxepine (1.9 mmol) and 0.73 mL of TMEDA (4.8 mmol) in 10 mL diethylether. The resulting solution was warmed to room temperature overnight. The reaction mixture was cooled to −78 °C and a solution of 1.25 g of 10-chloro-2,8-dimethylphenoxyphosphine (4.8 mmol) in 10 mL toluene was added. The reaction mixture was slowly warmed to room temperature overnight. Next the diethylether was removed in vacuo and the mixture was diluted with 30 mL of
dichloromethane and hydrolyzed with 10 mL of a 10% aqueous HCl solution. The water layer was removed and the organic layer was dried over MgSO₄. The solvents were removed *in vacuo* and the resulting white solid was crystallized from 2-propanol/toluene. Yield: 860 mg of white crystals (68%). M.p. 247 - 249 °C. ³¹P{¹H} NMR (CDCl₃): δ = -69.12. ¹H NMR (CDCl₃): δ = 7.67 (d, ³J(P,H) = 1.5 Hz, 4H), 7.12 (dd, ³J(H,H) = 8.0 Hz, ⁴J(H,H) = 2.0 Hz, 4H), 7.07 (d, ³J(H,H) = 8.5 Hz, 4H), 7.01 (dd, ³J(H,H) = 7.0 Hz, ⁴J(H,H) = 2.5 Hz, 2H), 6.89 (dd, ³J(H,H) = 7.0 Hz, ⁴J(H,H) = 1.5 Hz, 2H), 6.86 (t, ³J(H,H) = 7.0 Hz), 3.07 (s, 4H), 2.24 (s, 12H). ¹³C{¹H} NMR (CDCl₃): δ = 158.01 (t, 10.9 Hz), 153.23 (s), 135.10 (t, 18.7 Hz), 132.86 (t, 16.6 Hz), 132.68 (s), 132.449 (t, 4.9 Hz), 131.34 (s), 131.02 (s), 123.91 (s), 118.83 (s), 117.24 (s), 32.58 (s), 20.51 (s). Anal. Calcd. for C₆₂H₄₃O₃P₂: C, 77.77; H, 5.28. Found: C, 77.95; H, 5.40.

4,5-bis(2,8-dimethyl-10-phenoxaphosphino)-2,7-di-t-butyl-10,10-dimethylphenoxasilin (Sixantphenoxaphos, 2)

At 0 °C 3.6 mL of n-butyllithium (2.5 M in hexanes, 9.0 mmol) was added to a stirred solution of 1.23 g of 2,7-di-t-butyl-10,10-dimethylphenoxasilin (3.6 mmol) and 1.4 mL of TMEDA (9.3 mmol) in 20 mL diethylether. The resulting solution was warmed to room temperature overnight. The reaction mixture was cooled to -78 °C and a solution of 2.4 g of 10-chloro-2,8-dimethylphenoxaphosphine (9.1 mmol) in 10 mL toluene was added. The reaction mixture was slowly warmed to room temperature overnight. Next the diethylether is removed *in vacuo* and the mixture is diluted with 60 mL of dichloromethane and hydrolyzed with 20 mL of a 10% aqueous HCl solution. The water layer was removed and the organic layer was dried over MgSO₄. The solvents were removed *in vacuo* and the resulting yellow/white foam was crystallized from 2-propanol/toluene. Yield: 1.3 g of white crystals (44.4%). M.p. 300 - 302 °C. ³¹P{¹H} NMR (CDCl₃): δ = -72.09. ¹H NMR (CDCl₃): δ = 8.06 (s, 4H), 7.42 (d, ³J(H,H) = 2.5 Hz, 2H), 7.22 (dd, ³J(H,H) = 8.5 Hz, ⁴J(H,H) = 2.0 Hz, 4H), 7.17 (d, ³J(H,H) = 8.0 Hz, 4H), 7.17 (d, ³J(H,H) = 2.0 Hz, 2H), 2.39 (s, 12H), 1.20 (s, 18H), 0.49 (s, 6H). ¹³C{¹H} NMR (CDCl₃): δ = 156.41 (t, 11.0 Hz), 151.13 (s), 142.05 (s), 132.57 (m), 131.35 (s), 129.54 (s), 128.41 (s), 128.28 (s), 126.12 (s), 125.42 (vt), 115.70 (s), 114.37 (s), 31.28 (s), 28.24 (s), 17.72 (s), -3.0 (s). Anal. Calcd. for C₅₀H₅₂O₃P₂Si: C, 75.92; H, 6.63. Found: C, 75.75; H, 6.65.

4,5-bis(2,8-dimethyl-10-phenoxaphosphino)-2,7-dimethylphenoxathiin (Thixantphenoxaphos, 3)

At 0 °C 11.0 mL of n-butyllithium (2.5 M in hexanes, 27.6 mmol) was added to a stirred solution of 2.5 g of 2,7-dimethylphenoxathiin (11.0 mmol) and 4.2 mL of TMEDA (27.4 mmol) in 50 mL diethylether. The resulting solution was warmed to room temperature overnight. The reaction mixture was cooled to -78 °C and a solution of 7.2 g of 10-chloro-2,8-dimethylphenoxaphosphine (27.4 mmol)
in 30 mL toluene was added. The reaction mixture was slowly warmed to room temperature overnight. Next the diethylether was removed \textit{in vacuo} and the mixture was diluted with 120 mL of dichloromethane and hydrolyzed with 40 mL of a 10% aqueous HCl solution. The water layer was removed and the organic layer was dried over MgSO$_4$. The solvents were removed \textit{in vacuo} and the resulting yellow solid was crystallized from 2-propanol/toluene. Yield: 3.3 g of white crystals (43.5%). M.p. 333 - 338 °C (dec.). $^3$P{\textsuperscript{1}H} NMR (CDCl$_3$): $\delta$ = -71.28. $^1$H NMR (CDCl$_3$): $\delta$ = 7.77 (bs, 4 H), 7.17 (dd, $^3$J(H,H) = 8.4 Hz, $^4$J(H,H) = 2.1 Hz, 4H), 7.08 (dd, $^3$J(H,H) = 8.4 Hz, 4H), 6.78 (bs, 2H), 6.46 (bs, 2H), 2.32 (s, 12H), 2.03 (s, 6H). $^{13}$C{\textsuperscript{1}H} NMR (CDCl$_3$): $\delta$ = 153.89 (s), 152.61 (t, 12.2 Hz), 149.86 (s), 135.53 (t, 20.8 Hz), 134.61 (s), 132.93 (t, 4.8 Hz), 131.76 (s), 129.74 (t, 15.8 Hz), 128.37 (s), 120.42 (s), 117.97 (t, 3.6 Hz), 117.67 (s), 20.93 (s). Anal. Calcd. for C$_{42}$H$_{34}$O$_3$P$_2$S: C , 74.10 ; H , 5.03 . Found : C , 73.48 ; H , 4.98.

4,5-bis(2,8-dimethyl-10-phenoxaphosphino)-9-isopropylidenexanthen e (Isopropxanthphenoxaphos, 4)

At 0 °C 5.8 mL of n-butyllithium (2.5 M in hexanes, 14.5 mmol) was added to a stirred solution of 1.3 g of 10-isopropylidenexanthen e (6.8 mmol) and 2.25 mL of TMEDA (14.6 mmol) in 30 mL diethylether. The resulting solution was warmed to room temperature overnight. The reaction mixture was cooled to -78 °C and a solution of 3.8 g of 10-chloro-2,8-dimethylphenoxaphosphine (14.5 mmol) in 10 mL toluene was added. The reaction mixture was slowly warmed to room temperature overnight. Next the diethylether was removed \textit{in vacuo} and the mixture was diluted with 60 mL of dichloromethane and hydrolyzed with 20 mL of a 10% aqueous HCl solution. The water layer was removed and the organic layer was dried over MgSO$_4$. The solvents were removed \textit{in vacuo} and the resulting yellow solid was precipitated from 2-propanol/toluene. Yield: 1.5 g of a slightly tanned powder (38.8%). M.p. 333 - 335 °C (dec.). $^3$P{\textsuperscript{1}H} NMR (CDCl$_3$): $\delta$ = -71.10. $^1$H NMR (CDCl$_3$): $\delta$ = 7.86 (bd, $^3$J(P,H) = 8.7 Hz, 4H), 7.22 (dd, $^3$J(H,H) = 7.2 Hz, $^4$J(H,H) = 2.7 Hz, 2H), 7.17 (dd, $^3$J(H,H) = 8.4 Hz, $^4$J(H,H) = 2.1 Hz , 4H), 7.11 (d, $^3$J(H,H) = 8.1 Hz, 4H), 6.92 (t, $^3$J(H,H) = 7.5 Hz , 2H), 6.75 (bddd, $^3$J(H,H) = 7.8 Hz, $^4$J(H,H) = 1.8 Hz, 2H), 2.33 (s, 12H), 2.00 (s, 6H). Anal. Calcd. for C$_{44}$H$_{36}$O$_3$P$_2$: C , 78.33 ; H , 5.38. Found: C, 78.45; H, 5.53.

4,5-bis(2,8-dimethyl-10-phenoxaphosphino)-9,9-dimethylxanthene (Xantphenoxaphos, 5)

At 0 °C 6 mL of n-butyllithium (2.5 M in hexanes, 15 mmol) was added to a stirred solution of 1 g of 9,9-dimethylxanthene (4.8 mmol) and 2.2 mL of TMEDA (15 mmol) in 20 mL of diethylether. The resulting solution was warmed to room temperature and stirred overnight. The reaction mixture was cooled to -78 °C and a solution of 3.9 g of 10-chloro-2,8-dimethylphenoxaphosphine (15 mmol) in 20
mL of toluene was added. The reaction mixture was slowly warmed to room temperature and stirred overnight. Next the diethylether was removed in vacuo and the mixture was diluted with 40 mL of dichloromethane and hydrolyzed with 10 mL of a 10% aqueous HCl solution. The water layer was removed and the organic layer was dried over MgSO₄. The solvents were removed in vacuo and the resulting yellow/white solid was crystallized from 2-propanol/toluene. Yield: 1.9 g of white crystals (59%). M.p. 328 - 329 °C. ³¹P{¹H} NMR (CDCl₃): δ= -70.96. ¹H NMR (CDCl₃): δ = 7.98 (d, J(P,H) = 6.0 Hz, 4 H), 7.29 (dd, J(H,H) = 5.0 Hz, 4J(H,H) = 1.5 Hz, 4H), 7.18 (dd, J(H,H) = 8.5 Hz, 4J(H,H) = 2.5 Hz, 4H), 7.11 (d, J(H,H) = 8 Hz, 2H), 6.90 (t, J(H,H) = 8.0 Hz, 2H), 6.75 (bd, J(H,H) = 7.5 Hz, 2H), 2.35 (s, 12H), 1.55 (s, 6H). ¹³C{¹H} NMR (CDCl₃): δ = -154.35 (s), 152.41 (t, J(C,P) = 10.56 Hz), 135.76 (t, J(C,P) = 21.55 Hz), 132.96 (t, J(C,P) = 5.4 Hz), 132.09 (s), 130.26 (s), 127.79 (vt, J(C,P) = 11.44 Hz), 127.18 (s), 123.76 (s), 118.16 (s), 117.66 (s), 34.58 (s), 32.59 (s), 20.85 (s). Anal. Calcd. for C₄₃H₃₆O₃P₂: C, 77.93; H, 5.48. Found: C, 77.91; H, 5.54.

6,7-bis(2,8-dimethyl-10-phenoxaphosphino)benzo[k,l]xanthene (Benzoxanthphenoxyphosphos, 6)

At 0 °C 0.8 mL of n-butyllithium (2.5 M in hexanes, 2.0 mmol) was added to a stirred solution of 180 mg of benzo[k,l]xanthene (0.82 mmol) and 0.31 mL of TMEDA (2 mmol) in 10 mL diethylether. The resulting solution was warmed to room temperature overnight. The reaction mixture was cooled to -78 °C and a solution of 525 mg of 10-chloro-2,8-dimethylphenoxaphosphine (2.0 mmol) in 5 mL toluene was added. The reaction mixture was slowly warmed to room temperature overnight. Next the diethylether was removed in vacuo and the mixture was diluted with 40 mL of dichloromethane and hydrolyzed with 10 mL of a 10% aqueous HCl solution. The water layer was removed and the organic layer was dried over MgSO₄. The solvents were removed in vacuo and the resulting yellow solid was crystallized from 2-propanol/toluene. Yield: 280 mg of yellow crystals (51%). M.p. 308 - 310 °C. ³¹P{¹H} NMR (CDCl₃): δ= -70.86. ¹H NMR (CDCl₃): δ = 8.14 (bd, J(H,H) = 6.5 Hz, 2H), 7.94 (bd, J(H,H) = 6.5 Hz, 2H), 7.86 (dd, J(H,H) = 8.0 Hz, 4J(H,H) = 1.5 Hz, 1H), 7.70 (d, J(H,H) = 7.0 Hz, 1H), 7.50 (d, J(H,H) = 7.5 Hz, 1H), 7.40 (t, J(H,H) = 7.5 Hz, 1H), 7.26 - 7.2 (m, 5H), 7.17 - 7.13 (m, 8.0 Hz, 4H), 6.95 (t, 8.0 Hz, 1H), 6.88 (dd, J(H,H) = 8.5 Hz, 4J(H,H) = 1.5 Hz, 1H), 6.73 (bd, J(H,H) = 7.5 Hz, 1H), 2.39 (s, 6H), 2.37 (s, 6H). ¹³C{¹H} NMR (CDCl₃): δ = 155.59 (s), 154.98 (s), 154.41 (t, 10.9 Hz), 136.58 (vt), 136.56 (s), 136.05 (vt), 134.81 (s), 134.06 (m), 132.87 (s), 132.55 (s), 131.76 (s), 129.56 (s), 129.18 (s), 128.25 (s), 126.65 (s), 125.03 (s), 124.81 (s), 122.17 (s), 121.72 (s), 121.63 (s), 119.40 (s), 119.15 (s), 118.96 (t, 2.7 Hz), 118.43 (s), 118.43 (s), 118.34 (s), 116.28 (s), 20.83 (s), 20.80 (s). Anal. Calcd. for C₄₄H₃₂O₃P₂: C, 78.80; H, 4.81. Found: C, 79.52; H, 5.01.
4,5-bis(2,8-dimethyl-10-phenoxaphosphino)phenoxazine (Nixantphenoxaphos, 7)

At 0 °C 13.8 mL of n-butyllithium (2.5 M in hexanes, 34.5 mmol) was added to a stirred solution of 4.0 g of 9-(t-butyldimethylsilyl)phenoxazine (13.5 mmol) and 5.2 mL of TMEDA (34.5 mmol) in 200 mL diethylether. The resulting solution was warmed to room temperature overnight. The reaction mixture was cooled to −78 °C and a solution of 9.1 g of 10-chloro-2,8-dimethylphenoxaphosphine (34.5 mmol) in 60 mL toluene was added. The reaction mixture was slowly warmed to room temperature overnight. Next the diethylether was removed in vacuo and the mixture was diluted with 120 mL of dichloromethane and hydrolyzed with 40 mL of a 10% aqueous HCl solution. The water layer was removed and the organic layer was dried over MgSO₄. The solvents were removed in vacuo and the resulting brown paste was dissolved in 100 mL of THF. 8.62 g of n-(Bu)₄NF.3H₂O (33 mmol) was added and the reaction mixture was stirred for two days at room temperature. Then 50 mL of brine and 200 mL of dichloromethane were added. The water layer was removed and the organic layer was dried on MgSO₄. The solvents were removed in vacuo and the resulting yellow solid was crystallized from dichloromethane/ethanol. Yield: 2.6 g of brown/yellow microcrystals (30%). M.p. 276 °C (dec.).

1H NMR (CDCl₃): δ = -70.71. 1H NMR (CDCl₃): δ = 7.98 (d, 3J(P,H) = 9.5 Hz, 4H), 7.20 (dd, 3J(H,H) = 8.5 Hz, 4J(H,H) = 1.9 Hz, 4H), 7.06 (d, 3J(H,H) = 8.5 Hz, 4H), 6.41 (t, 3J(H,H) = 7.5 Hz, 2H), 6.18 (d, 3J(H,H) = 7.5 Hz, 2H), 5.93 (dd, 3J(H,H) = 7.5 Hz, 4J(H,H) = 1.8 Hz, 2H), 4.76 (bs, 1H), 2.37 (s, 12H). 13C NMR (CDCl₃): δ = 155.38 (s), 136.63 (vt, 21.9 Hz), 135.01 (s), 133.87 (t, 5.5 Hz), 133.67(t, 2.4 Hz), 132.56 (s), 131.91 (s), 125.01 (s), 124.82 (s), 118.67 (s), 118.25 (s), 114.57 (s), 20.83 (s), 20.82 (s). Anal. Calcd. for C₄₀H₃₁NO₃P₂: C, 75.58; H, 4.92; N, 2.20. Found: C, 75.14; H, 4.89; N, 2.31.

4,5-bis(2,8-dimethyl-10-phenoxaphosphino)-10-phenylphenoxaphosphine (Phosxantphenoxaphos, 8)

At room temperature 23 mL of phenyllithium (1.8 M in hexanes, 41.4 mmol) was added to a stirred solution of 1.5 g of 10-phenylphenoxaphosphine (5.4 mmol) and 6.24 mL of TMEDA (40.7 mmol) in 30 mL diethylether. The dark brown reaction mixture was heated at reflux temperature for two days. Then the reaction mixture was cooled to −78 °C and a solution of 10.7 g of 10-chloro-2,8-dimethylphenoxaphosphine (40.7 mmol) in 80 mL toluene. The reaction mixture was slowly warmed to room temperature overnight. Next the diethylether was removed in vacuo and the mixture was diluted with 120 mL of dichloromethane and hydrolyzed with 40 mL of a 10% aqueous HCl solution. The water layer was removed and the organic layer was dried over MgSO₄. The resulting solid was filtered through silicagel (eluent: toluene). The solvent was removed in vacuo and the resulting white solid was purified by several washings with boiling hexanes. Yield: 1.5 g of a white powder (37.9%).
Alternatively, crystals can be obtained from dichloromethane/ethanol. M.p. 256 - 258 °C. $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta$ = -53.08, -70.38 (ratio 1:2). $^1$H NMR (CD$_2$Cl$_2$): $\delta$ = 7.93 (m, 2H), 7.84 (m, 2H), 7.40 (ddd, $^3$J(P,$H$) = 10.5 Hz, $^3$J(H,H) = 6.3 Hz, $^4$J(H,H) = 2.4 Hz, 2H), 7.23 (m, 5H), 7.14 (d, $^3$J(H,H) = 7.2 Hz, 4H), 7.09 (m, 4H), 6.96 (m, 4H), 2.34 (s, 6H), 2.32 (s, 6H). $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ = 157.05 (t, 10.3 Hz), 154.18 (d, 6.8 Hz), 140.17 (d, 21.2 Hz), 136.24 (d, 35.7 Hz), 136.02 (s), 135.74 (t, 20.61 Hz), 135.59 (t, 19.9 Hz), 133.52 (dt, 12.5 Hz, 5.6 Hz), 132.63 (s), 132.46 (s), 132.36 (s), 130.54 (vt, 17.1 Hz), 129.46 (s), 129.03 (d, 6.9 Hz), 124.94 (d, 11.7 Hz), 119.97 (d, 4.8 Hz), 118.29 (t, 2.8 Hz), 118.01 (d, 11.1 Hz), 20.95 (s), 20.90 (s). Anal. Calcd. for C$_{46}$H$_{35}$O$_3$P$_3$: C, 75.82; H, 4.84. Found: C, 75.89; H, 4.74.

4,5-bis(9-dibenzo[b,d]phospholyl)-2,7-dimethylphenoixathiin (DBP-Thixantphos, 9)

At 0 °C 4.4 mL of n-butyllithium (2.5 M in hexanes, 11.0 mmol) was added to a stirred solution of 1.1 g of 2,7-dimethylphenoixathiin (4.7 mmol) and 1.7 mL of TMEDA (27.4 mmol) in 25 mL diethylether. The resulting solution was warmed to room temperature overnight. The reaction mixture was cooled to −78 °C and a solution of and 2.4 g 9-chlorodibenzo[b,d]phosphole (11.0 mmol) in 10 mL toluene was added. The reaction mixture was slowly warmed to room temperature overnight. Next the diethylether was removed in vacuo and the mixture was diluted with 100 mL of dichloromethane and hydrolyzed with 30 mL of a 10% aqueous HCl solution. The water layer was removed and the organic layer was dried over MgSO$_4$. The solvents were removed in vacuo and the resulting yellow solid was crystallized from 2-propanol/toluene. Yield: 1.3 g of colorless crystals (47%). M.p. 345 °C (dec.). $^{31}$P{$^1$H} NMR (THF-d$_8$): $\delta$ = -19.78. $^1$H NMR (THF-d$_8$): $\delta$ = 8.1 (dd, $^3$J(H,H) = 7.5 Hz, $^3$J(H,H) = 1.6 Hz, 4H), 8.09 (d, $^3$J(H,H) = 7.5 Hz, 4H), 7.45 (t, $^3$J(H,H) = 7.5 Hz, 4H), 7.36 (t, $^3$J(H,H) = 7.2 Hz, 4H), 6.95 (bs, 2H), 6.32 (bs, 2H), 1.99 (s, 6H). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ = 153.38 (t, 11.6 Hz), 143.91 (s), 142.31 (t, 2.3 Hz), 134.53 (s), 131.36 (t, 6.2 Hz), 129.99 (s), 129.03 (s), 128.54 (s), 128.25 (s), 127.38 (t, 3.1 Hz), 126.24 (vt, 13.1 Hz), 121.38 (s), 20.41 (s). Anal. Calcd. for C$_{38}$H$_{26}$O$_3$P$_2$: C, 75.82; H, 4.84. Found: C, 75.89; H, 4.74.

4,5-bis(9-dibenzo[b,d]phospholyl)-phenoxazine (DBP-Nixantphos, 10)

At 0 °C 6.8 mL of n-butyllithium (2.5 M in hexanes, 16.9 mmol) was added to a stirred solution of 2.2 g of 9-(t-butyldimethylsilyl)phenoxazine (7.4 mmol) and 2.6 mL of TMEDA (16.9 mmol) in 100 mL diethylether. The resulting solution was warmed to room temperature overnight. The reaction mixture was cooled to −78 °C and a solution 3.7 g of 9-chlorodibenzo[b,d]phosphole (16.9 mmol) in 30 mL toluene was added. The reaction mixture was slowly warmed to room temperature overnight. Next the diethylether was removed in vacuo and the mixture was diluted with 100 mL of dichloromethane and
hydrolyzed with 30 mL of a 10% aqueous HCl solution. The water layer was removed and the organic layer was dried over MgSO₄. The solvents were removed in vacuo and the resulting brown paste was dissolved in 100 mL of THF. 4.22 g of n-(Bu)₄NF·3H₂O (16.2 mmol) was added and the reaction mixture was stirred for two days at room temperature. Then 30 mL of brine and 100 mL of dichloromethane were added. The water layer was removed and the organic layer was dried on MgSO₄. The solvents were removed in vacuo and the resulting yellow solid was crystallized from dichloromethane/ethanol. Yield: 1.6 g of yellow crystals (43%). M.p. 268 °C (dec.). $^{31}$P{¹H} NMR (THF-d₈): δ = -20.52. $^1$H NMR (THF-d₈): δ =8.22 (dd, $^3$J(H,H) = 7.2 Hz, $^4$J(H,H) = 1.2 Hz, 4H), 7.99 (d, $^3$J(H,H) = 7.5 Hz, 4H), 7.44 (t, $^3$J(H,H) = 7.2 Hz, 4H), 7.37 (t, $^3$J(H,H) = 7.2 Hz, 4H), 6.41 (td, $^3$J(H,H) = 7.5 Hz, $^3$J(P,H) = 1.2 Hz, 2H), 6.30 (d, $^3$J(H,H) = 7.8 Hz, 2H), 5.93 (dd, $^3$J(H,H) = 7.5 Hz, $^4$J(H,H) = 1.2 Hz, 2H), 5.5 (s, 1H). $^{13}$C{¹H} NMR (THF-d₈): δ = 147.58 (t, 10.8 Hz), 144.98 (s), 143.11 (s), 133.92 (s), 132.45 (t, 13.1 Hz), 129.45 (s), 128.24 (s), 125.04 (s), 124.63 (vt, 12.6 Hz), 122.78 (s), 122.34 (s), 115.03 (s). Anal. Calcd. for C₄₆H₃₅O₃P₃: C, 78.97; H, 4.23; N, 2.56. Found: C, 79.11; H, 4.33; N, 2.41.

**Hydroformylation.** In a typical experiment the autoclave was charged with a 8.5 mL solution of Rh(CO)₅(acac) and 5 equivalents of ligand in toluene. After purging the solution three times with CO/H₂ (1:1), the reactor was brought to 16 bar of CO/H₂. Next the autoclave was heated to 80 °C. After 1 hour at 80 °C the substrate and internal standard are charged to the reaction mixture by overpressure of CO/H₂ (1:1).

**Deuterioformylation.** In a typical experiment the autoclave was charged with a 8.5 mL solution of Rh(CO)₅(acac) and 5 equivalents of ligand in toluene. After purging the solution three times with D₂, the reactor was brought to 8 bar of D₂ and further pressurised to 16 bar with CO. Next the autoclave was heated to 80 °C. After 1 hour at 80 °C the substrate was charged to the reaction mixture by overpressure of CO. Samples of the crude reaction mixture were analysed by GC. Thereafter the reaction mixture was distilled to separate the hexenes from the aldehydes. Deuterium contents were determined by $^2$H NMR, data identical to the data reported by Casey et al. was obtained.³²

**High pressure NMR experiments.** In a typical experiment a solution of 5.2 mg of Rh(CO)₅(acac) (20 µmol) and 1.1 equivalent of ligand in 1.5 mL of toluene-d₈ were pressurised to 16 bar of CO/H₂. In the NMR-spectrometer the tube was heated to 40 °C till complete formation of the rhodium-hydride was observed. NMR-spectra at different temperatures were recorded.
**High pressure FT-IR experiments.** In a typical experiment the high pressure IR autoclave was charged with a solution of 4 mg of Rh(CO)$_2$(acac) and 1.1 equivalents of ligand in 15 mL of cyclohexane. The autoclave was purged three times with 10 bar CO/H$_2$ (1:1), pressurised to 16 bar and heated to 40 °C. Catalyst formation was monitored in time. Hydride-deuterium exchange was carried out by cooling the autoclave to room temperature, venting the gases, and purging the solution three times with 5 bar of D$_2$. Next the autoclave was pressurised to 5 bar D$_2$, finally the autoclave is brought to 10 bar by further pressurisation with CO.
References.


The Influence of the Bite Angle on the Hydroformylation of Internal Olefins to Linear Aldehydes


