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New Diphosphine Ligands Based on Heterocyclic Aromatics Inducing Very High Regioselectivity in Rhodium-Catalyzed Hydroformylation: Effect of the Bite Angle

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The effect of the bite angle on regioselectivity in the rhodium-catalyzed hydroformylation reaction was studied with a series of bidentate diphosphines based on xanthene-like backbones as ligands. The bite angles of these ligands are fine-tuned by subtle alterations of the backbone of the ligands. When the bridge (X) in the 10-position of xanthene is varied, the bite angle as calculated from molecular mechanics increases stepwise from 102 to 131°, whereas the changes in steric bulk and electronic effects are virtually absent for the following ligands: bis(2-(diphenylphosphino)phenyl) ether (DPEphos, 1), X = H, H; 4,6-bis(diphenylphosphino)-10,10-dimethylphenoasaxilin (Sixanphos, 2), X = Si(CH₃)₃; 2,8-dimethyl-4,6-bis(diarylphosphino)phenoaxathiin (Thixanphos, 3), X = S; 9,9-dimethyl-4,6-bis(diphenylphosphino)xanthene (Xanthos, 4), X = C(CH₃)₂; 4,6-bis(diphenylphosphino)hexafluorobenzofuran (DBFphos, 5), X = bond. In the hydroformylation of 1-octene the regioselectivity increased regularly with increasing bite angle: at 40 °C up to 98.3% n-aldehyde was obtained with Xanthos, without isomerization or hydrogenation of 1-octene. DBFphos does not form chelates, and consequently no increased selectivity was observed. The selectivity of the catalyst was almost unaffected by raising of the temperature to 90 °C, resulting in a higher turnover frequency (tof) with a constant selectivity: 97.7% n-aldehyde, 0.5% isomerization, and a tof value of 800 mol (mol of Rh)⁻¹ h⁻¹. Xanthos induces the highest selectivity for the formation of the linear aldehyde reported for diphosphines in the hydroformylation of 1-alkenes until now. The complexes (diphosphine)Rh(H)(CO)₂(PPh₃) and (diphosphine)Rh(H)(CO)₂ were prepared and identified with H, 31P, and 13C NMR. The enhanced selectivity to the linear aldehyde was also observed for styrene (70% n-aldehyde with xanthos compared to 11% with triphenylphosphine). An X-ray crystal structure of the Xanthos ligand is presented (orthorhombic, space group Pbnm, with a = 8.7678(8) Å, b = 18.967(1) Å, c = 19.181(1) Å, V = 3189.8(4) Å³, and Z = 4).

Introduction

Hydroformylation of alkenes is one of the most important homogeneously catalyzed reactions in industry.¹⁻⁵ Much effort has been made to enhance the regioselectivity of the reaction toward the formation of the more desirable normal aldehyde and to minimize the undesired side reaction of isomerization of the substrate alkene. The rhodium phosphine catalysts, introduced by Wilkinson,⁶,⁷ have been shown to be more selective, and they give higher rates under milder conditions than the older cobalt carbonyl catalysts. The generally accepted mechanism for the dissociative pathway as proposed by Wilkinson, a modification of the reaction mechanism as proposed by Heck and Breslow for the cobalt-catalyzed hydroformylation,⁶ is shown in Scheme 1.

The steric and electronic properties of the ligands have a dramatic influence on the reactivity of organometallic complexes. The concept of the cone angle as a measure for the steric bulk of monodentate phosphine
and phosphite ligands, introduced by Tolman,\(^9\) has been widely accepted and applied in the development of new ligands.

Increasing the steric bulk of monodentate phosphines, i.e., increasing the cone angle, leads to higher regioselectivity in the hydroformylation.\(^10\) Bulky phosphine and diphosphite ligands have been proven to be very successful for obtaining high normal to iso ratios,\(^11,21\) although the monodentates also cause significant isomerization.\(^11\) Work in our group has shown that bulky monophosphites can induce extremely high reaction rates,\(^13,14\) whereas bulky diphosphites can give rise to good enantioselectivity.\(^15-17\)

The effect of diphosphines on selectivity in rhodium-catalyzed hydroformylation has been studied by Hughes and Unruh.\(^18\) They found that rhodium complexes formed from the reaction of (PPh\(_3\))\(_2\)Rh(H)(CO) with various rigid chelating diphosphines led to increased linear to branched ratios when the ligand to rhodium ratio was 1.5 or higher. They proposed a mechanism in which three phosphines are coordinated to rhodium at the point where the aldehyde regiochemistry is determined. The complex proposed to account for this increase in linear to branched ratio is a dimeric rhodium complex, in which two ligands are chelating to one rhodium center, while one ligand is bridging between two rhodium centers (see Figure 1). This complex was later actually observed by \(^{31P}\) NMR.\(^19\)

An increase of rate due to possible intramolecular binuclear elimination, as observed by Stanley and co-workers,\(^20,21\) was not found for these systems.

An important recent study by Casey and co-workers has indicated that the bite angle of bidentate diphosphines can have a dramatic influence on the regioselectivity of the rhodium-catalyzed hydroformylation of 1-alkenes. For the bis-equatorially coordinated 2,2'-bis-[(diphenylphosphino)methyl]-1,1'-biphenyl (BISBI, 6), a linear to branched aldehyde ratio as high as 66:1 was reported, while the equatorially–axially coordinating (i.e., \(\angle P-Rh-P = 90^\circ\)) 1,2-bis(diphenylphosphino)ethane (dppe) gave a linear to branched ratio of only 2.1.\(^22,23\)

The observed selectivity is likely to be due to the bite angles of the ligands, but so far no detailed study has been done on the effect of subtle changes of the bite angle in a series of ligands with similar electronic properties and steric size, thus solely examining the influence of the bite angle.

Here we present a study of the effect of the bite angle alone in a series of new bidentate diphosphines, based on xanthene-like backbones, on the regioselectivity in the rhodium-catalyzed hydroformylation reaction. The bite angles of these ligands are fine-tuned by subtle alterations in the backbone of the ligands.

**Results and Discussion**

**Molecular Mechanics.** We used molecular mechanics in our development of new bidentate diphosphines. The natural bite angle (\(\beta_{n}\)) and flexibility range of new candidates were calculated using the Sybyl program\(^24\) with an augmented TRIPOS force field, analogously to the method used by Casey and Whiteker.\(^25\) The natural bite angle is defined as the preferred chelation angle determined only by ligand backbone constraints and not by metal valence angles. The flexibility range is defined as the accessible range of bite angles within less than 3 kcal mol\(^{-1}\) excess strain energy from the calculated natural bite angle.

To examine the effect of the bite angle on the selectivity in rhodium-catalyzed hydroformylation, we...
developed a series of new bidentate ligands based on rigid heterocyclic xanthene-like aromatics. By varying the bridge in the 10-position (Figure 2 and Table 1), we were able to induce small variations in the bite angle.

According to our molecular mechanics calculations, these ligands have natural bite angles ranging from 102 to 131° and a flexibility range of ca. 35°.

Ligand Synthesis. The ligands were easily obtained in good yields (typically 70–80%) by deprotonation of the backbones with 3 equiv of sec-butyllithium/TMEDA in ether. Due to the presence of the ether oxygen, selective dilithiation at the positions ortho to the ether bridge takes place.26,27 The dilithiated species is then reacted with chlorodiphenylphosphine. Washing with water to remove lithium salts, followed by washing with hexanes to remove sec-butyldiphenylphosphine, yielded the pure product as a powder. No purification by column chromatography is necessary, but all ligands were recrystallized before utilization in catalysis. These reaction conditions lead to a considerably more efficient ligand synthesis.

The X-ray crystal structure of the free Xantphos ligand is shown in Figure 3. The symmetric unit orientation of the diphenylphosphine moieties is nearly ideal. The observed P-**P distance in the free ligand is 3.84 Å, which MM studies indicate that a decrease of the P-**P distance to 3.84 Å is necessary for chelation. The P-Rh-P angle of 111.7°, a decrease of only 0.24 Å. The P atoms are brought together by means of a slight decrease of the angle between the two phenyl planes in the backbone of the ligand from ca. 166 to 158°.

The ¹³C NMR spectra of free Xantphos, Thixantphos, and Sixantphos all show a virtual triplet signal for C-ipsos on the backbone. This resonance is the result of a through-space coupling of the two phosphorus atoms. The orientation of the lone pairs of the two phosphorus atoms is such that it causes degeneracy of the magnetic resonances of the P nuclei. In the ¹³C NMR the degenerate magnetic resonance of the phosphorus causes the ipsos carbon atom to couple with the two phosphorus atoms, with observed Jipso-P coupling constants of 40–60 Hz. This type of coupling has been reported for bulky diphosphites as an eight-bond coupling by Pastor and co-workers.28 By simulation of the NMR spectra (using genMR software30) it was possible to define a minimal P–P coupling for these ligands; a smaller coupling would lead to second-order signals above the noise level. The appearance of this P–P coupling is a strong indication that the structure in solution of the free ligands is similar to the crystal structure of Xantphos. This through-space coupling is not observed for DPEphos (due to the absence of such a rigid backbone) and DBFphos (in which the P-Rh-P angle of 111.7°, a decrease of only 0.24 Å. The P atoms are brought together by means of a slight decrease of the angle between the two phenyl planes in the backbone of the ligand from ca. 166 to 158°.

The ¹³C NMR spectra of free Xantphos, Thixantphos, and Sixantphos all show a virtual triplet signal for C-ipsos on the backbone. This resonance is the result of a through-space coupling of the two phosphorus atoms. The orientation of the lone pairs of the two phosphorus atoms is such that it causes degeneracy of the magnetic resonances of the P nuclei. In the ¹³C NMR the degenerate magnetic resonance of the phosphorus causes the ipsos carbon atom to couple with the two phosphorus atoms, with observed Jipso-P coupling constants of 40–60 Hz. This type of coupling has been reported for bulky diphosphites as an eight-bond coupling by Pastor and co-workers.28 By simulation of the NMR spectra (using genMR software30) it was possible to define a minimal P–P coupling for these ligands; a smaller coupling would lead to second-order signals above the noise level. The appearance of this P–P coupling is a strong indication that the structure in solution of the free ligands is similar to the crystal structure of Xantphos. This through-space coupling is not observed for DPEphos (due to the absence of such a rigid backbone) and DBFphos (in which the P–P distance is apparently too large: MM calculations gave P–P = 5.760 Å; PM3 calculations gave P–P = 5.956 Å).

Since electronic effects of the variations in the backbone are expected to be small9 and the steric sizes of the substituents on phosphorus are identical in all ligands, the effect of solely the P–Rh–P chelation angle can be studied in detail.

Hydroformylation of 1-Octene. We tested the selectivity of our ligands in the rhodium-catalyzed hydroformylation of 1-octene. Work by Hughes and Unruh29 on the effect of different ligand to rhodium ratios for bidentate diphosphines on the observed selectivity led us to investigate the optimal ligand to rhodium ratio for our ligands. Table 2 represents the data for Thixantphos as an example.

---

**Table 1. Calculated Natural Bite Angle and Flexibility Range for the Ligands 1–5**

<table>
<thead>
<tr>
<th>ligand name</th>
<th>X</th>
<th>R</th>
<th>( \beta_{\text{av}} ) deg</th>
<th>flexibility range, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPEphos (1)</td>
<td>H</td>
<td>H</td>
<td>102.2</td>
<td>86–120</td>
</tr>
<tr>
<td>Sixantphos (2)</td>
<td>Si(CH₃)₂</td>
<td>H</td>
<td>108.7</td>
<td>93–132</td>
</tr>
<tr>
<td>Thixantphos (3)</td>
<td>S</td>
<td>CH₃</td>
<td>109.4</td>
<td>94–130</td>
</tr>
<tr>
<td>Xantphos (4)</td>
<td>C(CH₃)₂</td>
<td>H</td>
<td>111.7</td>
<td>97–135</td>
</tr>
<tr>
<td>DBFphos (5)</td>
<td>bond</td>
<td>H</td>
<td>131.1</td>
<td>117–147</td>
</tr>
</tbody>
</table>

* See text.

---

![Figure 2. Ligands studied in this work and generic structure showing numbering scheme.](image)

![Figure 3. ORTEP representation of the Xantphos ligand. Thermal ellipsoids are drawn at the 50% probability level.](image)
L/Rh ratios from 1.1 to 10 were examined, and an optimum was found at 2.2. A higher ratio did not lead to improved regio- or chemoselectivity.

Molecular modeling studies, as well as CPK or Drediding molecular models, show that due to the rigid structure of the ligands the presence of a binuclear species as proposed by Hughes and Unruh (see Figure 1) is very unlikely. Furthermore, a third phosphine ligand is readily replaced with carbon monoxide under an atmosphere of CO (see below). The observed optimal L/Rh ratio is probably the result of a dissociation equilibrium and is dependent on the absolute concentration.

We chose the following standard conditions to compare the selectivity and activity of the ligands: \( T = 40 \, ^\circ\text{C} \), \( \text{CO/H}_2 = 1 \), \( p(\text{CO/H}_2) = 10 \, \text{bar} \), substrate/Rh = 674, [Rh] = 1.78 mM. In all cases the percent isomerization was \(< 1\%\) and the percent hydrogenation was zero.

<table>
<thead>
<tr>
<th>L/Rh ratio</th>
<th>normal/branched</th>
<th>% n-aldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>5.7</td>
<td>85.1</td>
</tr>
<tr>
<td>2.0</td>
<td>40.5</td>
<td>97.6</td>
</tr>
<tr>
<td>2.2</td>
<td>47.6</td>
<td>97.9</td>
</tr>
<tr>
<td>5.0</td>
<td>45.1</td>
<td>97.8</td>
</tr>
<tr>
<td>10.0</td>
<td>46.4</td>
<td>97.8</td>
</tr>
</tbody>
</table>

*Conditions: \( T = 40 \, ^\circ\text{C} \), CO/H\(_2\) = 1, \( p(\text{CO/H}_2) = 10 \, \text{bar} \), substrate/Rh = 674, [Rh] = 1.78 mM. In all cases the percent isomerization was \(< 1\%\) and the percent hydrogenation was zero.*

The flexibility of BISBI allows the formation of a rhodium complex with a slightly less rigidly defined geometry, thus giving somewhat lower selectivity to \( n \)-alkyl intermediates. This effect of the flexibility on the observed selectivity becomes much more pronounced at higher temperatures.

**Hydroformylation of Styrene.** Hydroformylation of styrene with a (Xanthphos)Rh catalyst resulted in relatively high selectivity for the linear aldehyde (a linear to branched ratio of up to 2.35 was obtained; see Table 5).

This is remarkable, since styrene is a substrate with a distinct preference for the formation of the branched aldehyde due to the stability of the 2-alkyl-rhodium species, induced by the formation of a \( 2 \)-allyl complex (ref 13 and references cited therein). Wilkinson reported hydroformylation with \( \text{PPh}_3 \)Rh(H)(CO) as a catalyst at 25 \( ^\circ\text{C} \) and 1 bar of CO/H\(_2\), yielding a linear to branched ratio of 0.13 (up to 0.27 using excess PPh\(_3\)). Higher temperature and pressure (62 bar of CO/H\(_2\) at 70 \( ^\circ\text{C} \)) lead to higher selectivity for the branched aldehyde, yielding a linear to branched ratio of 0.08.33

The effect of ligands with a large bite angle on the rhodium-catalyzed hydroformylation of styrene was investigated by Yamamoto, who observed a very high selectivity for the branched aldehyde with \( \text{PPh}_3 \)Rh(H)(CO) as a catalyst at 25 \( ^\circ\text{C} \) and 1 bar of CO/H\(_2\), yielding a linear to branched ratio of 0.13 (up to 0.27 using excess PPh\(_3\)). Higher temperature and pressure (62 bar of CO/H\(_2\) at 70 \( ^\circ\text{C} \)) lead to higher selectivity for the branched aldehyde, yielding a linear to branched ratio of 0.08.33

However, another ligand with a large natural bite angle, DIOP, showed much lower selectivity to the branched aldehyde and a resulting increased selectivity toward the linear aldehyde. For this ligand we (and

![Diagram](image-url)
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Table 3. Results of the Hydroformylation of 1-Octene at 40 °C

<table>
<thead>
<tr>
<th>ligand</th>
<th>calcd bite angle, deg</th>
<th>flexibility range, deg</th>
<th>normal/branched %</th>
<th>% n-aldehyde</th>
<th>% isomerization</th>
<th>tof b</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPEphos</td>
<td>102.2</td>
<td>86–120</td>
<td>10.5</td>
<td>91.3</td>
<td>&lt;1</td>
<td>0.5</td>
</tr>
<tr>
<td>Sixanphos</td>
<td>108.7</td>
<td>93–135</td>
<td>35.0</td>
<td>96.3</td>
<td>1</td>
<td>4.4</td>
</tr>
<tr>
<td>Thixanphos</td>
<td>109.4</td>
<td>94–130</td>
<td>47.6</td>
<td>97.0</td>
<td>3</td>
<td>13.2</td>
</tr>
<tr>
<td>Xantphos</td>
<td>111.7</td>
<td>97–135</td>
<td>57.1</td>
<td>98.3</td>
<td></td>
<td>10.0</td>
</tr>
<tr>
<td>DBFphos</td>
<td>131.1</td>
<td>117–147</td>
<td>3.4</td>
<td>76.1</td>
<td>1.6</td>
<td>1.9</td>
</tr>
<tr>
<td>BISBI</td>
<td>122.6</td>
<td>101–148</td>
<td>58.2</td>
<td>95.5</td>
<td>2.9</td>
<td>30.0</td>
</tr>
</tbody>
</table>

a Conditions: CO/H₂ = 1, p(CO/H₂) = 10 bar, substrate/Rh = 674, ligand/Rh = 2.2, [Rh] = 1.78 mM. In all cases the percent hydrogenation was zero. b Turnover frequency (mol of alkene (mol of Rh)⁻¹ h⁻¹).

Table 4. Results of the Hydroformylation of 1-Octene at 80 °C

<table>
<thead>
<tr>
<th>ligand</th>
<th>calcd bite angle, deg</th>
<th>flexibility range, deg</th>
<th>normal/branched %</th>
<th>% n-aldehyde</th>
<th>% isomerization</th>
<th>tof b</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPEphos</td>
<td>102.2</td>
<td>86–120</td>
<td>6.7</td>
<td>87.0</td>
<td>0</td>
<td>250</td>
</tr>
<tr>
<td>Sixanphos</td>
<td>108.7</td>
<td>93–132</td>
<td>34</td>
<td>94.2</td>
<td>3</td>
<td>168</td>
</tr>
<tr>
<td>Thixanphos</td>
<td>109.4</td>
<td>94–130</td>
<td>41</td>
<td>93.0</td>
<td>4.7</td>
<td>445</td>
</tr>
<tr>
<td>Xantphos</td>
<td>111.7</td>
<td>97–135</td>
<td>53.8</td>
<td>97.7</td>
<td>0.5</td>
<td>800</td>
</tr>
<tr>
<td>DBFphos</td>
<td>131.1</td>
<td>117–147</td>
<td>3</td>
<td>71</td>
<td>5.5</td>
<td>125</td>
</tr>
<tr>
<td>BISBI</td>
<td>122.6</td>
<td>101–148</td>
<td>80.5</td>
<td>89.6</td>
<td>9.3</td>
<td>850</td>
</tr>
</tbody>
</table>

a Conditions: CO/H₂ = 1, p(CO/H₂) = 10 bar, substrate/Rh = 674, ligand/Rh = 2.2, [Rh] = 1.78 mM. In all cases the percent hydrogenation was zero.

Scheme 2

Figure 4. Selectivity versus calculated natural bite angle (φₙ) in the hydroformylation of 1-octene. Normal to branched ratio versus βₙ is indicated by open circles and the percentage of linear aldehyde versus θₙ with full triangles (data from Table 2). The effect of the bite angle is very subtle. For the chelating ligands in this series, we found a regular increase of both the normal/branched ratios and the percentage of linear aldehyde formed with increasing calculated natural bite angle in the hydroformylation of 1-octene (Figure 4). This correlation is observed at both 40 and 80 °C. For the ligand DBFphos no chelates were observed, and its selectivity is consequently out of the range. The very high selectivity of Xantphos (calculated natural bite angle 111.7°) and BISBI (our calculated natural bite angle 122.6° (lit. 113°, X-ray (BISBI)/Rh(H)(CO)(PPh₃) 121.8°) indicates that the optimum is near 112–120°. Selectivity in the hydroformylation reaction increases when the bite angle of the ligand becomes larger. However, the rigidity of the ligand is also an important factor. This is strongly supported by the results obtained for the more flexible BISBI ligand, which shows a lower selectivity. The importance of this

Casey calculated a normal bite angle of 102.3°. A normal to branched ratio of 0.25–0.47 was obtained, depending on the rhodium precursor used.

Casey and co-workers reported that they were unable to isolate any monomeric metal complexes of 8. Furthermore, no enhanced selectivity for the linear aldehyde was found using the (8)Rh catalyst system in the

Table 5. Results of the Hydroformylation of Styrene

<table>
<thead>
<tr>
<th>ligand</th>
<th>T, °C</th>
<th>p, bar</th>
<th>normal/branched %</th>
<th>% n-aldehyde</th>
<th>% isomerization</th>
<th>tof b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xantphos</td>
<td>60</td>
<td>10</td>
<td>0.77</td>
<td>43.5</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td></td>
<td>0.88</td>
<td>46.8</td>
<td>724</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td></td>
<td>2.35</td>
<td>70.1</td>
<td>4285</td>
<td></td>
</tr>
<tr>
<td>PPh₃</td>
<td>25</td>
<td>1</td>
<td>0.13</td>
<td>11.5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>PPh₃</td>
<td>70</td>
<td>0.08</td>
<td>7.4</td>
<td></td>
<td></td>
<td>b</td>
</tr>
<tr>
<td>PPh₃</td>
<td>50</td>
<td>0.03–0.05</td>
<td>3–5</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPh₃</td>
<td>50</td>
<td>0.77</td>
<td>43.5</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DIOP</td>
<td>25</td>
<td>0.12</td>
<td>11</td>
<td></td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.04</td>
<td>4</td>
<td></td>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.25–0.49</td>
<td>20–32.5</td>
<td></td>
<td></td>
<td>b</td>
</tr>
</tbody>
</table>

a Conditions: CO/H₂ = 1, substrate/Rh = 674, [Rh] = 1.78 mM. b Not reported. c Depending on the rhodium precursor used.

ligand rigidity becomes even more pronounced at higher temperatures. Rigid ligands with a larger calculated bite angle are unable to form stable chelates, as was demonstrated with DBFphos and 8.

**Rhodium Complexes.** In order to investigate the coordination behavior of our series of ligands, (diphosphine)Rh(H)(CO)(PPh₃) complexes were synthesized for all ligands. Facile exchange of PPh₃ in (PPh₃)Rh(H)(CO) with the diphosphines gave quantitative yield (although some loss was observed during the workup procedure).

Detailed studies of the ³¹P{¹H} NMR spectra led to the conclusion that the two phosphine moieties of the diphosphine in the complex were equivalent for all ligands (except DBFphos). The coupling constants between the diphosphine P and PPh₃ (J = 114–129 Hz) show that these ligands are indeed coordinated bis-equatorially. The attempts to synthesize (DBFphos)Rh(H)(CO)(PPh₃) (DBFphos has a calculated natural bite angle of 131°) did not yield any characterizable complex.

Bubbling CO through a solution of (diphosphine)Rh(H)(CO)PPh₃ led to facile displacement of the remaining PPh₃. The complex (diphosphine)Rh(H)(CO) formed by this exchange (presumably the catalytically active species in the hydroformylation reaction) is stable under an atmosphere of CO. The ³¹P{¹H} NMR spectra of these compounds (see Figure 5 for the spectra of the Xantphos complexes) exhibit a clean doublet for the phosphine atoms of the ligands, indicating that these ligands are also coordinated in a bis-equatorial fashion in these complexes.

The ¹H NMR spectra of the (Xantphos)Rh(H)(CO)PPh₃, (Xantphos)Rh(H)(CO)(PPh₃)(9), (Xantphos)Rh(H)(CO)(PPh₃) (Xantphos)Rh(H)(CO)(PPh₃) (10), (Sixantphos)Rh(H)(CO)(PPh₃) (11), and (Sixantphos)Rh(H)(CO)(PPh₃) (12) complexes show an inequivalence of the two methyl groups, indicating a rigid conformation of the ligand (formally, the absence of a mirror plane through the equatorial plane dictates the inequivalence of the methyl and phenyl groups). Furthermore, the ortho hydrogens of the phenyl groups on the diphenylphosphine moieties positioned in the equatorial plane and the axial plane are inequivalent in the (diphenylphosphine)Rh(H)(CO)(PPh₃) complexes. This is especially clear in the ¹H NMR spectra of the Xantphos ligand (13). This strongly indicates that in solution the two diphenylphosphine moieties are rigidly placed in space around the rhodium center.

Unfortunately, the crystals we have obtained for 9 are not suitable for a conclusive structure determination. The inequivalence of the phenyl groups at the phosphorus atoms of the ligands indicates, however, that the structure of the coordinated ligand (in solution) is probably very similar to the crystal structure of free Xantphos (Figure 3). The structure of the ligand determines therefore the geometry of the complex.

Therefore, we think that the enhanced selectivity for the linear aldehyde in the hydroformylation of styrene and the low isomerization of 1-octene (even at higher temperatures) is induced by a well-defined “docking area” on the rhodium center. The size of the bite angle dictates directly the shape of this docking area. The fact that isomerization is almost absent in these catalyst systems indicates that the strict geometry is inducing the formation of the 1-alkyl species (leading to the linear aldehyde) and actually inhibits the formation of 2-alkyls.

**Conclusion**

A homologous series of diphosphines, based on rigid heterocyclic aromatics, allowed an investigation of the effect of slight alterations of the P–Rh–P bite angle only, without modifying other steric or electronic properties. The distinct effect of these alterations on the selectivity in the rhodium-catalyzed hydroformylation showed that the P–Rh–P bite angle has a pronounced effect on the selectivity. Comparison with BISBI shows that the rigidity of the ligand backbone is essential for obtaining high selectivity in the hydroformylation reaction. The rigidity of the ligands causes the chelated complexes to be stable, even at elevated temperatures. Therefore, selectivity was not lost at higher temperatures and the turnover frequency can be increased to a synthetically useful level. Comparison of the results obtained with these ligands revealed a regular increase of selectivity with an increasing bite angle, up to the point where the calculated bite angle has increased to such an extent that chelation is no longer possible. The Xantphos ligand has been shown to induce the highest selectivity reported so far for the formation of linear aldehydes with diphosphines in rhodium-catalyzed hydroformylation.
Experimental Section

Computational Details. The molecular mechanics calculations were performed on a Silicon Graphics Indigo workstation using the program Sybyl, version 6.03, with an augmented TRIPOS force field. We developed our own parameters for the phosphine-type phosphorus atom and the silane-type silicon atom, which are not defined in the standard TRIPOS force field. These parameters are included in the supplementary material.

Calculations were performed similarly to the method described by Casey and Whiteker, using a Rh-P bond length termination criterion of a rms gradient of less than 0.001 kcal mol⁻¹ Å⁻¹.

MOPAC-PM3 calculations were performed using the CAChe Worksystem version 3.7, on an Apple Power Macintosh 950, equipped with two CAChe CXP coprocessors. Geometry optimization was performed using eigenvector following (EF).

Synthesis. All preparations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Solvents were carefully dried and freshly distilled prior to use. Hexanes, THF, benzene, toluene, and ether were distilled from sodium, dichloromethane, and methanol from CaH₂. Dibenzofuran was purchased from Janssen; dibenzofuran was recrystallized from ethanol before use. Chlorodiphenylphosphine and TMEDA were purchased from Aldrich and used as received. CO was purchased from Isotec Inc.

(PPh₃)₃Rh(H)(CO)₄0 and dimethylphenoxasilane were purchased from Janssen; dibenzofuran was recrystallized from ethanol before use. Chlorodiphenylphosphine and TMEDA were purchased from Aldrich and used as received. CO was purchased from Isotec Inc.

1H NMR (300 MHz) and 31P NMR spectra (121.5 MHz, CDCl₃) of 4.00 g of diphenyl ether was added dropwise to a solution of 1.00 g of (41) bis(2-(diphenylphosphino)phenyl) Ether (DPEphos; 41) and 2.1 mL of TMEDA (13.3 mmol) in 50 mL of dry THF. The reaction mixture was stirred for 1 h. After that, the resulting solid oil was dissolved in CH₂Cl₂; this solution was filtered and crystallized from 1-propanol. The resulting white crystals were washed with acetone and then CH₂Cl₂. The resulting solid was washed with hexanes and crystallized from 1-propanol. The resulting white crystals are air-stable. Yield: 1.78 g white crystals (68%).

1H NMR (CDCl₃): δ 7.50 (dd, 2H, J = 7.2, 1.7 Hz), 7.45 (dt, 2H, J = 7.7, 1.7 Hz), 7.22 (d, 2H, J = 8.4 Hz), 7.17 (dt, 2H, J = 7.2, 0.9 Hz), 0.51 (s, 6H, (CH₃)₂Si). 13C(¹H) NMR (CDCl₃): δ 160.2, 134.5, 131.7, 119.7 (C-Si), 118.5, 0.2 ((CH₃)₂Si). IR (CHCl₃ cm⁻¹): 3070, 3008, 2957, 2901, 1604, 1593, 1574, 1426, 1370, 1301, 1270, 885, 845, 807. Exact mass (MS): 226.0808 (calcd for C₁₃H₁₂O₅Si). 4.6-Bis(diphenyolphosphino)-10,10-dimethylphenoxasilin (Sixanthos; 2). At room temperature 12.6 mL of sec-butylithium in hexanes (1.3 M in 98/2 cyclohexane/hexane, 13.3 mmol) was added dropwise to a stirred solution of 1.00 g of 14 (4.42 mmol) and 2.1 mL of TMEDA (13.3 mmol) in 50 mL of dry ether. When all sec-butyllithium was added, the reaction mixture was stirred for 16 h. Then a solution of bis(2-liothiophenyl) ether and a solution of 5.7 mL of dimethyldichlorosilane (47.0 mmol) in 75 mL of ether were added simultaneously to 40 mL of ether over 1 h. The reaction mixture was stirred for 16 h and then hydrolyzed by addition of 30 mL of water. The hydrolyzed mixture was stirred for 2 h. The organic layer was separated and the aqueous layer was extracted with 30 mL of ether. The combined organic layers were treated with Norit and dried with MgSO₄. The solvent was removed in vacuo. Small crystals formed during the concentration. The semisolid oil was crystallized form methanol, resulting in white crystals with a grassy odor. Yield: 4.82 g (45%).

1H NMR (CDCl₃): δ 7.08-7.10 (m, 11 H), 6.98 (s, 2H, J = 7.4 Hz), 5.47 (s, 2H, J = 6.8 Hz). 13C(¹H) NMR (CDCl₃): δ 158.0, 140.8, 130.7, 129.8, 129.9, 129.0, 128.9, 127.8, 124.1, 118.6. IR (CHCl₃ cm⁻¹): 3073 (m), 3005 (m), 1585, 1540, 1520, 1461, 1426, 1370, 1301, 1271, 885, 845, 807. Exact mass (MS): 226.0808 (calcd for C₁₃H₁₂O₅Si).
similarly to Sixantphos from 3.00 g of dimethylxanthene (4.76 mmol). A solution of (PPh3)3Rh(0)CO in 50 mL of dry THF was stirred for 2 h. A solution of (EtO)3Al in 10 mL of THF was then added, and the mixture was stirred for 2 h. The resulting yellow solid was washed with 1 mL of methanol and dried in vacuo. The resulting yellow solid was used for further characterization.

(Xanaphos)Rh(H)(CO)(PPh3) (9). A solution of (PPh3)3Rh(H)(CO) in 100 mL of benzene was stirred for 1 h at 30 °C. The resulting yellow solid was washed with 1 mL of methanol and dried in vacuo. The resulting yellow solid was used for further characterization.

(Xanaphos)Rh(H)(CO)(PPh3) (10). A gentle stream of CO was led through the reaction mixture for ca. 2 min, after which the workup procedure described for 9 was performed.

(Xanaphos)Rh(H)(CO)2 (11). This compound was prepared similarly to 9, using 10,13CO for ca. 10 min.

(Xanaphos)Rh(H)(CO)(PPh3) (12). This compound was prepared similarly to 10.

(Yco, C6H5, cm⁻³): 1996.9 (vs), 1909.6 (m). MS (m/z): 961 (M - CO), 726 (M - PPh3 - 2H), 698 (M - PPh3 - CO - 2H). Anal. Calcd for C36H26Cl2P3Rh: C, 76.49; H, 5.07. Found: C, 75.64; H, 5.53.

(Xanaphos)Rh(H)(CO)(PPh3) (13). This compound was prepared similarly to 9.

(Yco, C6H5, cm⁻³): 1989.9 (s), 1969.2 (vs), 1940.1 (w).

(Xanaphos)Rh(H)(CO)2 (14). A gentle stream of CO was led through the reaction mixture for ca. 9 min, after which the workup procedure described for 9 was performed.

(Xanaphos)Rh(H)(CO)(PPh3) (15). The 13C resonances of the carbonyl were measured on 13C-enriched samples.

The complex was synthesized as for 9, but a gentle stream of 13CO was led through the reaction mixture for ca. 2 min, after which the workup procedure described for 9 was performed.

(Xanaphos)Rh(H)(CO)2 (16). A gentle stream of CO was led through the reaction mixture for ca. 9 min, after which the workup procedure described for 9 was performed.

(Xanaphos)Rh(H)(CO)(PPh3) (17). A gentle stream of CO was led through the reaction mixture for ca. 9 min, after which the workup procedure described for 9 was performed.

(Xanaphos)Rh(H)(CO)(PPh3) (18). A gentle stream of CO was led through the reaction mixture for ca. 9 min, after which the workup procedure described for 9 was performed.

(Xanaphos)Rh(H)(CO)(PPh3) (19). A gentle stream of CO was led through the reaction mixture for ca. 9 min, after which the workup procedure described for 9 was performed.

(Xanaphos)Rh(H)(CO)(PPh3) (20). A gentle stream of CO was led through the reaction mixture for ca. 9 min, after which the workup procedure described for 9 was performed.

(Xanaphos)Rh(H)(CO)(PPh3) (21). A gentle stream of CO was led through the reaction mixture for ca. 9 min, after which the workup procedure described for 9 was performed.

(Xanaphos)Rh(H)(CO)(PPh3) (22). A gentle stream of CO was led through the reaction mixture for ca. 9 min, after which the workup procedure described for 9 was performed.

(Xanaphos)Rh(H)(CO)(PPh3) (23). A gentle stream of CO was led through the reaction mixture for ca. 9 min, after which the workup procedure described for 9 was performed.

(Xanaphos)Rh(H)(CO)(PPh3) (24). A gentle stream of CO was led through the reaction mixture for ca. 9 min, after which the workup procedure described for 9 was performed.
Rhodium-Catalyzed Hydroformylation


(Thixantphos)Rh(H)(CO)3 (15). This compound was prepared similarly to 10.
1H NMR (C6D6): δ 7.51 (ar, 8 H), 7.03 (ar, 10 H), 7.38 (ar, 6 H), 6.90 (ar, 14 H), 6.73 (‘d”, 2 H, C(Ph)2CHC(CH3)2), 6.33 (m, 2H, C(Ph)2CHC(CH3)2), 1.89 (s, 6H, CH3), –8.55 (dt, JH-Rh = 6.3 Hz, JH-P = 14.7). 31P{1H} NMR (C6D6): δ 23.39 (Jp-Rh = 127.9 Hz). IR (υCO, C6H6, cm⁻¹): 1975 (s), 1940 (s).

(DPEphos)Rh(H)(CO)(PPh3) (16). This compound was prepared similarly to 9.
1H NMR (C6D6): δ 7.66-7.48 (ar), 7.0-6.8 (ar), 7.06-6.95 (m, ar, PPh3), 6.63 (apparent t, ar), 6.51 (apparent t, ar), –8.87 (apparent dq, Jp-H = Jp-H = 26.9 Hz, JRh-H = 3.6 Hz, 1H, Rh–H). 31P NMR (C6D6): δ 44.192 (Jp-Rh = 168.0 Hz, Jp-P = 129.0 Hz, PPh3), 27.8 (Jp-P = 148.2 Hz, Jp-P = 129.0 Hz, DPEphos-P). 13C{1H} NMR (C6D6): δ 158.2 (t, J = 5.7 Hz), 135.4 (t, J = 8 Hz), 133.9 (t, J = 8.0 Hz), 133.1, 132.8, 132.5, 132.0, 129.3, 128.4-128.9 (ar), 122.7, 120.8. IR (υCO, C6H6, cm⁻¹): 2009.3 (s), 1978.9 (m), 1940.1 (s).

Hydroformylation Experiments. Hydroformylation reactions were performed in a 180 mL stainless steel autoclave, equipped with a glass inner beaker, a substrate inlet vessel, a liquid sampling valve, and a magnetic stirring rod. The temperature was controlled by an electronic heating mantle. The desired amount of diphosamine was placed in the autoclave and the system was flushed three times with 10 bar of CO/H2 (1/1). Then, 3.0 mL of a 5 mM solution of Rh(acaac)-(CO)3 in toluene was added, and the autoclave was pressurized to 6 bar. The autoclave was heated to the desired temperature and was stirred for 16 h. The desired amount of substrate and n-decane (internal standard) were placed in the substrate vessel and then pressed into the autoclave with 10 bar of CO/H2.

Samples were removed via the liquid sampling valve and quenched immediately with excess triphenyl phosphate to avoid isomerization. The samples were analyzed by temperature-controlled gas chromatography.

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Supplementary Material Available: Tables giving additional parameters for phosphine-type phosphorus and phenoxasilene-type silicon for the TRIPOS force field in Sybyl6.03 and text giving additional details of the X-ray structure determination and tables of crystal data and collection parameters, atomic coordinates, bond lengths, bond angles, and thermal parameters (11 pages). Ordering information is given on any current masthead page.

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