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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-dimethylphenoasilin (Sixantphos, 2), X = Si(CH3)3; 2,8-dimethyl-4,6-bis(diphenylphosphino)phenoxyathiin (Thixantphos, 3), X = S; 9,9-dimethyl-4,6-bis(diphenylphosphino)xanthene (Xantphos, 4), X = C(CH3)3; 4,6-bis(diphenylphosphino)dibenzo furan (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 Xantphos, 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. Xantphos induces the highest selectivity for the formation of the linear aldehyde reported for diphosphines in the hydroformylation of 1-alkenes until now. The complexes (diphenylphosphino)Rh(H)(CO)(PPh3) and (diphenylphosphino) RhH(CO)2 were prepared and identified with ¹H, ³¹P, and ¹³C NMR. The enhanced selectivity to the linear aldehyde was also observed for styrene (70% n-aldehyde with xantphos compared to 11% with triphenylphosphine). An X-ray crystal structure of the Xantphos 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,⁸ 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 phosphate

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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 phosphite and diphosphite ligands have been proven to be very successful for obtaining high normal to iso ratios,11,12 although the monodentates also cause significant isomerization.11 Work in our group has shown that bulky monophosphites can induce extremely high reaction rates,13-20 whereas bulky diphosphites can give rise to good enantioselectivity.16-17

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$_3$)$_3$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

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 ($\beta_{\text{nat}}$) 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 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 name X R P° deg range,° deg

<table>
<thead>
<tr>
<th>ligand name</th>
<th>X</th>
<th>R</th>
<th>β°,a 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>Sixanthphos (2)</td>
<td>Si(CH₃)₂</td>
<td>H</td>
<td>108.7</td>
<td>93–132</td>
</tr>
<tr>
<td>Thixanthphos (3)</td>
<td>Si</td>
<td>CH₃</td>
<td>138.4</td>
<td>94–130</td>
</tr>
<tr>
<td>Xantphos (4)</td>
<td>O(CH₂)₂</td>
<td>C₂</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>

*a* See text.

The X-ray crystal structure of the free Xantphos ligand is shown in Figure 3. The symmetric unit contains a half-molecule, with four atoms (O, C1, C2, and C3) at special positions on a mirror plane. The structure clearly shows that only very little adjustment of the structure is necessary to form a chelate; the ideal. The observed P–P distance in the free ligand is 4.080 Å, while MM studies indicate that a decrease of the P–P distance to 3.84 Å is necessary for chelation of a 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, Thixanthphos, and Sixanthphos 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 ipso carbon atom to couple with the two phosphorus atoms, with observed ¹³C-ipso coupling constants of 40–60 Hz. This type of coupling has been reported for bulky diphenylphosphines as an eight-bond coupling by Pastor and co-workers.28 By simulation of the NMR spectra (using geNMR software) 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 DPFphos (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 small 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.

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result of the large increase of the selectivity to isomerization of 1-octene to 2-octene from 2.9% to 9.3%.

The increase of the linear to branched ratio in aldehyde with an increasing amount of isomerization is due to an increased tendency of the branched alkyl species to form the 2-alkene instead of the branched aldehyde (Scheme 2). In spite of the fact that the proportion of branched alkyl is higher at 80 °C, the net result is a higher normal to branched ratio. A similar effect was observed by Hughes and Unruh for other rigid ligands, based on cycloalkane backbones.19

According to MM calculations, BISBI is very flexible; we calculated a natural bite angle of 122.6° and a flexibility range of 101–148° for a rhodium complex, while Casey and co-workers calculated a natural bite angle of 113° and a flexibility range of 92–155°.20 These results are supported by studies of the fluxional behavior of BISBI in solution, in which a rapid exchange of the two phosphine moieties was observed.21 Furthermore, X-ray structural analyses of transition-metal complexes of BISBI show a wide variety of P-M-P chelation angles: ∠P-Mo-P = 108.5° in (BISBI)Mo(CO)5,22 ∠P-Ir-P = 117.9° in (BISBI)Ir(H)(CO)5,23 ∠P-Rh-P = 124.8° in (BISBI)Rh(H)(CO)(PPh3)2,24 and ∠P-Fe-P = 152.0° in (BISBI)Fe(CO)5.25

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 (Xanthos)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 σ-allyl complex (ref 13 and references cited therein). Wilkinson reported hydroformylation with (PPh3)2RhH(CO) as a catalyst at 25 °C and 1 bar of CO/H2, yielding a linear to branched ratio of 0.13 (up to 0.27 using excess PPh3). Higher temperature and pressure (62 bar of CO/H2 at 70 °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 7, a diphosphinite ligand with a calculated natural bite angle of 118°,34 and 8, a diphosphine with a calculated natural bite angle of 123°.24,25

![Image](https://example.com/image.png)

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

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**Table 2. Results of the Rhodium-Catalyzed Hydroformylation of 1-Octene with the Thioxanthophos Ligand at Different Ligand to Rhodium Ratios**

<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>45.4</td>
<td>97.8</td>
</tr>
</tbody>
</table>

*Conditions: T = 40 °C, CO/H2 = 1, p(CO/H2) = 10 bar, substrate/Rh = 674, [Rh] = 1.78 mM. In all cases the percent isomerization was <1 and the percent hydrogenation was zero.*
Rhodium-Catalyzed Hydroformylation


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</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>0</td>
<td>5</td>
</tr>
<tr>
<td>Sixanthos</td>
<td>108.7</td>
<td>93–132</td>
<td>35.0</td>
<td>96.3</td>
<td>&lt;1</td>
<td>4.4</td>
</tr>
<tr>
<td>Thixantphos</td>
<td>109.4</td>
<td>94–130</td>
<td>47.6</td>
<td>97.0</td>
<td>1</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>0</td>
<td>10</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</td>
</tr>
</tbody>
</table>

* 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.  

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</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>Sixanthos</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>Thixantphos</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>53.5</td>
<td>97.7</td>
<td>0.5</td>
<td>860</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>

* 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.

Figure 4. Selectivity versus calculated natural bite angle (φn) in the hydroformylation of 1-ocntene. Normal to branched ratio versus ϕn is indicated by open circles and the percentage of linear aldehyde versus ϕn with full triangles (data from Table 2). The hydroformylation of 1-hexene or 1-octene. Therefore, the effect of ø on the selectivity (toward the branched aldehyde) in the hydroformylation of styrene remains unexplained.

In summary, the distinct effect of minor changes in the ligand backbone by alterations of the bridge between C11 and C14 on the observed selectivity shows that 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) 124.8°)) 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

Table 5. Results of the Hydroformylation of Styrene

<table>
<thead>
<tr>
<th>ligand</th>
<th>T, °C, p, bar</th>
<th>normal/branched</th>
<th>% n-aldehyde</th>
<th>tof</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xantphos</td>
<td>60, 10</td>
<td>0.77</td>
<td>43.5</td>
<td>128</td>
</tr>
<tr>
<td></td>
<td>80, 0.88</td>
<td>46.8</td>
<td>724</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120, 2.35</td>
<td>70.1</td>
<td>4285</td>
<td></td>
</tr>
<tr>
<td>PPh3</td>
<td>25, 1</td>
<td>0.13</td>
<td>11.5</td>
<td>10</td>
</tr>
<tr>
<td>PPh3</td>
<td>70, 0.08</td>
<td>7.4</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>PPh3</td>
<td>30, 0.03–0.05</td>
<td>3–5</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>50, 0.77</td>
<td>43.5</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>50, 0.12</td>
<td>11</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>20, 0.04</td>
<td>4</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DIOP</td>
<td>25, 0.25–0.49</td>
<td>20–32.5°</td>
<td>b</td>
<td></td>
</tr>
</tbody>
</table>

* Conditions: CO/H2 = 1, substrate/Rh = 674, [Rh] = 1.78 mM.  

(a) Not reported.

Casey (32) calculated a natural bite angle of 102.3°. A normal to branched ratio of 0.25–0.47 was obtained, depending on the rhodium precursor used. (32) Casey, C. P.; Whiteker, G. T.; Campana, C. F.; Powell, D. R. Inorg. Chem. 1990, 29, 3376–3381.

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

Scheme 2

[Scheme 2 image]

Figure 4. Selectivity versus calculated natural bite angle (ϕn) in the hydroformylation of 1-ocntene. Normal to branched ratio versus ϕn is indicated by open circles and the percentage of linear aldehyde versus ϕn with full triangles (data from Table 2). The hydroformylation of 1-hexene or 1-octene. Therefore, the effect of ø on the selectivity (toward the branched aldehyde) in the hydroformylation of styrene remains unexplained.

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Table 6. Results of the Hydroformylation of Styrene

<table>
<thead>
<tr>
<th>ligand</th>
<th>T, °C, p, bar</th>
<th>normal/branched</th>
<th>% n-aldehyde</th>
<th>tof</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xantphos</td>
<td>60, 10</td>
<td>0.77</td>
<td>43.5</td>
<td>128</td>
</tr>
<tr>
<td></td>
<td>80, 0.88</td>
<td>46.8</td>
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<td>120, 2.35</td>
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<td>4285</td>
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<tr>
<td>PPh3</td>
<td>25, 1</td>
<td>0.13</td>
<td>11.5</td>
<td>10</td>
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<td>PPh3</td>
<td>70, 0.08</td>
<td>7.4</td>
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<td>PPh3</td>
<td>30, 0.03–0.05</td>
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</tr>
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<td>8</td>
<td>50, 0.77</td>
<td>43.5</td>
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<td>8</td>
<td>50, 0.12</td>
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<td>(a)</td>
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<tr>
<td>20, 0.04</td>
<td>4</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>DIOP</td>
<td>25, 0.25–0.49</td>
<td>20–32.5°</td>
<td>b</td>
<td></td>
</tr>
</tbody>
</table>

* Conditions: CO/H2 = 1, substrate/Rh = 674, [Rh] = 1.78 mM.  

(a) Not reported.

Casey (32) calculated a natural bite angle of 102.3°. A normal to branched ratio of 0.25–0.47 was obtained, depending on the rhodium precursor used. (32) Casey, C. P.; Whiteker, G. T.; Campana, C. F.; Powell, D. R. Inorg. Chem. 1990, 29, 3376–3381.

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

Scheme 2

[Scheme 2 image]
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) (9), (Xantphos)Rh(H)(CO)₂ (10), (Sixantphos)Rh(H)(CO)(PPh₃) (11), and (Sixantphos)Rh(H)(CO)₂ (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 (diphosphine)Rh(H)(CO)(PPh₃) complexes. This is especially clear in the ¹H NMR spectra of 9 and (Thixanthphos)Rh(H)(CO)(PPh₃) (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 6.0.24 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,29 using a Rh-P bond length of 2.315 Å.

Minimizations were performed using the standard Sybyl minimizer MAXIMIN2.

The structures were allowed to converge fully, with a termination criterion of a rms gradient of less than 0.001 kcal mol⁻¹ Å⁻¹.

MOPAC-PM3 calculations (CACheMOPAC version 94.10, Beaverton, OR CAChe Scientific Inc., Beaverton, OR) were performed using the CAChe WorkSystem version 3.7.29 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, sec-butyllithium, and dimethyldichlorosilane were purchased from Janssen; dibenzofuran was recrystallized from ethanol before use. Chlorodiphenylphosphine was purchased from Aldrich and used as received. 13C0 was purchased from Isotec Inc.

(PPh₃)₂Rh(H)(CO)₄0 and dimethylphenoxathiin (Thixantphos: 3) were prepared according to literature procedures.

1H NMR (300 MHz) and 31P NMR spectra (121.5 MHz, referenced to external 85% H3PO4) were recorded on a Bruker AMX-300 spectrometer; 13C NMR spectra were recorded on a Bruker AC-200 (at 50 MHz), AMX-300 (at 75.5 MHz), or ARX-400 spectrometer (at 100 MHz). Assignments in complex NMR spectra were aided by simulation with gNMR 3.5M software. 29P represents the PPh₃ phosphorus atom in characterizations of couplings in NMR spectra. IR spectra were obtained on a Nicotol 510 FT-IR. Mass spectroscopy was measured on a JEOL JMS-SWSXlO2A.

Gas chromatography was performed on a Carlo Erba GC 6000 Vega series or an Interscience Mega 2 series apparatus (split/splitless injector, J&W Scientific, DB1 30 m column, film thickness 3.0 µm, carrier gas 70 kPa of He, FID detector).

Bis(2-diphenylphosphino)phenyl) Ether (DPEphos; 1). At room temperature a solution of 4.00 g of diphenyl ether (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. The ethereal solution of bis(2-lithiophenyl) ether and a solution of 5.7 mL of dimethylchlorosilane (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 semi-solid oil was crystallized from methanol, resulting in white crystals with a grassy odor. Yield: 4.82 g (45%).

1H NMR (CDC1₃): δ 7.56 (dd, 2H, J = 7.2, 1.7 Hz), 7.45 (dt, 2H, J = 7.7, 1.7 Hz), 7.22 (dd, 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, 123.1, 119.7 (C-Si), 118.5, 0.2 (CH₂)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 C14H14O).

4,6-Bis(diphenylphosphino)-10,10-dimethylphenoxasilin (Sixanthphos; 2). At room temperature 12.6 mL of sec-butylithium (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 2.6 mL of chlorodiphenylphosphine (13.3 mmol) in 15 mL of hexanes was added dropwise, and the reaction mixture was stirred for another 16 h. The solvent was removed in vacuo. The resulting solid oil was dissolved in CH2Cl2; this solution was washed with water and dried with MgSO₄ and the solvent removed in vacuo. The resulting oil 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 (CDC1₃): δ 7.50 (dd, 2H, J = 7.2, 1.7 Hz, CHCHCSi), 7.16-7.31 (ar, 20 H, P(C₆H₅)₂), 7.00 (t, 2H, J = 7.2, 0.9 Hz), 0.51 (s, 6H, (CH3)2Si). 13C{1H} NMR (CDCl₃): δ 160.2, 134.5, 131.7, 123.1, 119.7 (C-Si), 118.5, 0.2 (CH₂)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 C14H14O).

14,14-Dimethyl-4,6-bis(diphenylphosphino)phenoxathin (Thixanthphos: 3). This compound was prepared


(24) Stewart, J. J. P. QCPE No. 455.

(29) CAChe WorkSystem 3.7; CAChe Scientific Inc., 18700 N. W. Walker Road, Building 92-01, Beaverton, OR 97006.


mL of water were added and the mixture was stirred vigorously. The water layer was then removed, the organic phase was dried with MgSO₄, and the solvent was removed in vacuo. The resulting sticky solid was washed with acetone and then dried in vacuo. Yield: 10.5 g of white powder (85%).

13C NMR (CDCl₃): δ 159.8 (d, J = 22.65 Hz), 157.2 (d, J = 11.8 Hz), 146.1, 130.7, 128.6 (d, J = 16.6 Hz), 129.0, 128.9, 128.7, 124.1, 118.6. IR (CHCl₃, cm⁻¹): 3072 (m), 3005 (m), 1585 (s), 1566 (s), 1479 (s), 1461 (s), 1434 (s), 1183 (s), 1070 (m), 877 (m), 697 (m).

Exact mass (MS, FAB): 539.1656 (M + H) (calcd for C38H32O3P2Si 538.1615). Mp: 175-176 °C.

10,10-Dimethylphenoxasilin (14). At room temperature a solution of 8.0 g of diphenyl ether (47.0 mmol) in 35 mL of THF was added dropwise to a mixture of 41.4 mL of 2.5 M n-butylithium in hexanes (103.4 mmol) and 16.7 mL of TMEDA (103.4 mmol). When all the phenyl ether was added, the reaction mixture was stirred for 16 h. The ethereal solution of bis(2-lithiophenyl) ether and a solution of 5.7 mL of dimethylchlorosilane (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 semi-solid oil was crystallized from methanol, resulting in white crystals with a grassy odor. Yield: 8.42 g (46%).
similarly to Sixantphos from 3.0 g of dimethylphenoxathiin (13.14 mmol). Yield: 5.56 g of white crystals (71%). Analytically pure material was obtained by crystallization from hot 1-propanol.

1H NMR (CDCl3): δ 7.16–7.35 (ar, 20 H, C(P(Ph)z)CH), 6.87 (‘d’, J = 8 Hz, C(P(Ph)z)CH2), 6.23 (‘s’, 2H, C(Si(Ph)z)CH), 2.07 (‘d’, J = 6.5 Hz, C(Si(Ph)z)CH3) δ = −17.3 (Si(Ph)z)NMR (CDCl3): δ 137.0 (t, J = 6.8 Hz), through-space P–P coupling ≥ 40 Hz, 133.7 (t, J = 10.6 Hz), 133.7, 132.5, 128.0–128.1 (ar), 127.1 (t, J = 12.1 Hz), 119.3, 20.4 (CH3). IR (CHCl3, cm−1): 3059 (w), 3004 (w), 1435 (vs), 1411 (vs), 1390 (vs), 1180 (w), 1059 (s), 963 (w), 766 (m), 695 (m). Exact mass (MS): 596.1498 (calcd for C53H56OP5S 596.1492). Mp: 179.5–180 °C. Anal. Calcd for C53H56OP5S: C, 76.49; H, 5.07. Found: C, 75.64; H, 5.53.

This compound was prepared similarly to Sixantphos from 3.00 g of dimethylphenoxathiin (4.76 mmol). This compound was prepared similarly to Sixantphos from 1.00 g of 9,9-dimethylxanthene (4.76 mmol). This compound was prepared similarly to Sixantphos from 3.00 g of dimethylphenoxathiin (4.76 mmol). This compound was prepared similarly to Sixantphos from 3.00 g of dimethylphenoxathiin (4.76 mmol). This compound was prepared similarly to Sixantphos from 3.00 g of dimethylphenoxathiin (4.76 mmol). This compound was prepared similarly to Sixantphos from 3.00 g of dimethylphenoxathiin (4.76 mmol). This compound was prepared similarly to Sixantphos from 3.00 g of dimethylphenoxathiin (4.76 mmol).
Rhodium-Catalyzed Hydroformylation

1918 (m). MS (m/z): 961 (M−CO), 726 (M−PPh3−2H), 698 (M−PPh3−CO−2H).

(Thixanthphos)Rh(H)(CO)2 (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(P(Ph)2CHC(CH2)), 6.33 (m, 2H, C(S)/CH(CH2)), 1.69 (s, 6H, CH2), −8.55 (dt, JRh−PPh3 = 6.3 Hz, JRh−PPh3 = 14.7). 31P{1H} NMR (C6D6): δ 23.39 (d, JP−Rh = 127.9 Hz). IR (νCO, C6H6, cm⁻¹): 1993 (s), 1975 (s), 1940 (vs).

(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), 7.05−6.95 (m, PPh3), 6.63 (apparent t, ar), 6.51 (apparent t, ar), −8.87 (apparent dq, JP−H = JF−H = 26.9 Hz, JRh−H = 3.6 Hz, 1H, Rh−H). 31P{1H} NMR (C6D6): δ 44.192 (JF−Rh = 168.0 Hz, JF−P = 129.0 Hz, PPh3), 27.8 (JF−Rh = 148.2 Hz, JF−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 (νCO, C6H6, cm⁻¹): 2009.3 (vs), 1924.9 (m).

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.

Samples were removed via the liquid sampling valve and quenched immediately with excess triphenyl phosphite 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 phenoxasilin-type silicon for the TRIPOS force field in Sybyl 6.03 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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