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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-dimethylphenoxasilin (Sixantphos, **2**), X = $Si(CH_3)_2$; 2,8-dimethyl-4,6-bis(diphenylphosphino)phenoxathiin (Thixantphos, **3**), X = S; 9,9-dimethyl-4,6-bis(diphenylphosphino)xanthene (Xantphos, **4**), X = $C(CH_3)_2$; 4,6-bis(diphenylphosphino)dibenzofuran (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 80 °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 (diphosphine)Rh(H)(CO)(PPh_3) and (diphosphine)-Rh(H)$(CO)_2$ were prepared and identified with ^{1}H, ^{31}P, and ^{13}C 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) Å^3, 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 phosphine

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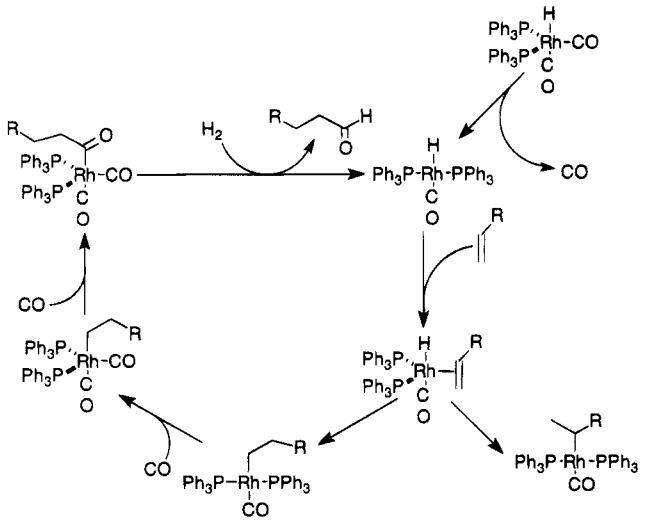
Scheme 1



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,[13,14] 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 $(PPh_3)_3Rh(H)(CO)$ 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 ^{31}P NMR.[19]

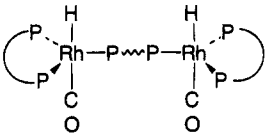
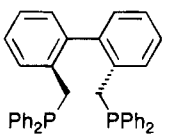


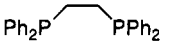
Figure 1. Bridged dimeric species as proposed by Hughes and Unruh.

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. $\angle P-Rh-P = 90°$) 1,2-bis(diphenylphosphino)ethane (dppe) gave a linear to branched ratio of only 2.1.[22,23]



BISBI (6)



dppe

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 (β_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

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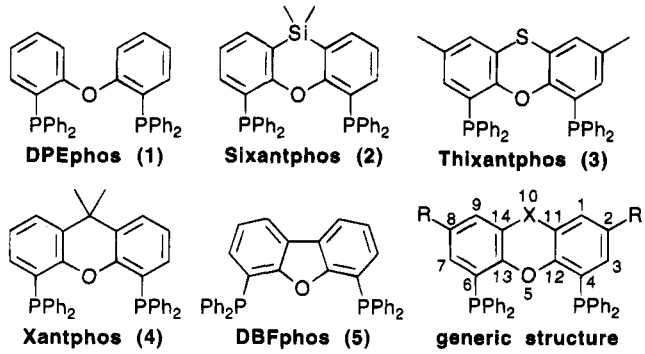

Figure 2. Ligands studied in this work and generic structure showing numbering scheme.

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

ligand name	X	R	β_n,[a] deg	flexibility range,[a] deg
DPEphos (**1**)	H, H	H	102.2	86–120
Sixantphos (**2**)	$Si(CH_3)_2$	H	108.7	93–132
Thixantphos (**3**)	S	CH_3	109.4	94–130
Xantphos (**4**)	$C(CH_3)_2$	H	111.7	97–135
DBFphos (**5**)	bond	H	131.1	117–147

[a] See text.

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 synthesis of DBFphos, for which Haenel and co-workers[28] reported a yield of 50% after repeated recrystallizations to remove the monophosphine. The ligands are very stable and insensitive toward oxidation by air, both in solution and in the solid phase.

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 orientation of the diphenylphosphine moieties is nearly 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

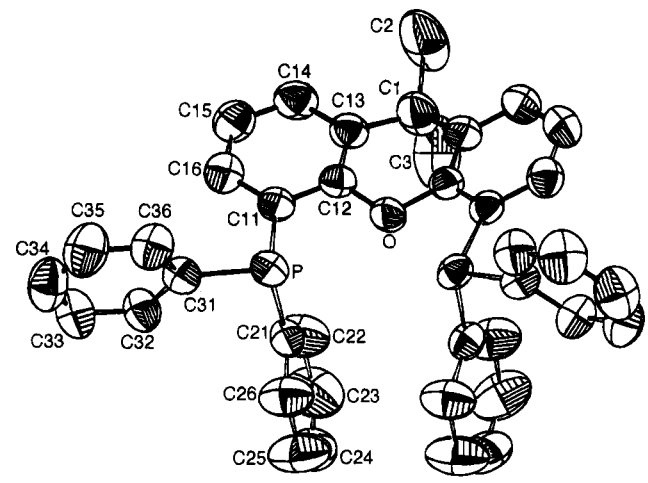

Figure 3. ORTEP representation of the Xantphos ligand. Thermal ellipsoids are drawn at the 50% probability level.

with 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 ^{13}C NMR spectra of free Xantphos, Thixantphos, and Sixantphos all show a virtual triplet signal for C-*ipso* 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 ^{13}C NMR the degenerate magnetic resonance of the phosphorus causes the *ipso* carbon atom to couple with the two phosphorus atoms, with observed $^1J_{^{13}C-P}$ 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.[29] By simulation of the NMR spectra (using geNMR software[30]) 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 small[9] 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 Unruh[18] 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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Table 2. Results of the Rhodium-Catalyzed Hydroformylation of 1-Octene with the Thixantphos Ligand at Different Ligand to Rhodium Ratios[a]

L/Rh ratio	normal/ branched	% *n*-aldehyde
1.1	5.7	85.1
2.0	40.5	97.6
2.2	47.6	97.9
5.0	45.1	97.8
10.0	45.4	97.8

[a] Conditions: T = 40 °C, CO/H_2 = 1, $p(CO/H_2)$ = 10 bar, substrate/Rh = 674, [Rh] = 1.78 mM. In all cases the percent isomerization was <1 and the percent hydrogenation was zero.

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 Dreiding 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 °C, CO/H_2 = 1; $p(CO/H_2)$ = 10 bar, ligand/Rh = 2.2, substrate/Rh = 674, [Rh] = 1.78 mM (see Table 3).

DPEphos, with a calculated natural bite angle of 102.2°, induced an enhanced selectivity (compared to most diphosphines), but this selectivity was not very pronounced. The ligands with a one-atom bridge between C(11) and C(14) (Sixantphos, X = $Si(CH_3)_2$; Thixantphos, X = S; Xantphos, X = $C(CH_3)_2$) having a calculated natural bite angle near 110° showed a very high regioselectivity and a very low rate of isomerization to internal alkenes. DBFphos, with a calculated natural bite angle of 131.1°, proved not to be very selective.

Under these mild reaction conditions, the selectivities toward the linear aldehyde observed for Sixantphos, Thixantphos, and especially Xantphos are somewhat higher than that observed for BISBI. This is mainly due to the very low selectivity to isomerization of 1-octene. The normal to branched ratios of our ligands are very close to that of BISBI. Furthermore, no hydrogenation was observed.

Upon raising the temperature to 80 °C, we observed a large increase in the rate of the reaction (Table 4); the turnover frequency increases by a factor of 38 (for Sixantphos) to 80 (for Xantphos). The selectivity of the reaction, however, has hardly changed at this higher temperature. Hydrogenation is still not detected, the normal to branched ratios decrease slightly, and a slight increase of isomerization is observed. Especially for Xantphos, these effects are very small. The normal to branched ratio decreases from 57.1 to 53.5, with an increase of isomerization from 0% to 0.5%, resulting in a net decrease of selectivity for the formation of the linear aldehyde of only 0.5%.

At this temperature the difference between BISBI and our more rigid ligands becomes more pronounced. Even though the normal to branched ratio increases from 58.2 to 80.5 for BISBI, the selectivity toward the linear aldehyde decreases form 95.5% to 89.6%. This is a 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.[18]

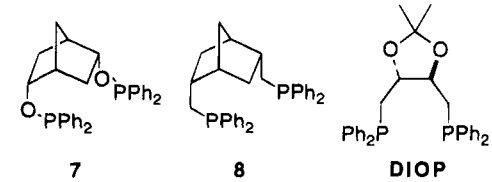
According to MM calculations, BISBI is very flexible; we calculated a natural bite angle of 122.6° and a flexibility range of 101−148° for a rhodium complex, while Casey and co-workers calculated a natural bite angle of 113° and a flexibility range of 92−155°.[23] These results are supported by studies of the fluxional behavior of BISBI in solution, in which a rapid exchange of the two phosphine moieties was observed.[23] Furthermore, X-ray structural analyses of transition-metal complexes of BISBI show a wide variety of P−M−P chelation angles: ∠P−Mo−P = 103.5° in (BISBI)Mo$(CO)_4$,[31] ∠P−Ir−P = 117.9° in (BISBI)Ir(H)$(CO)_2$, ∠P−Rh−P = 124.8° in (BISBI)Rh(H)(CO)(PPh_3),[23] and ∠P−Fe−P = 152.0° in (BISBI)Fe$(CO)_3$.[32]

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 (Xantphos)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 π-allyl complex (ref 13 and references cited therein). Wilkinson[7] reported hydroformylation with $(PPh_3)_3Rh(H)(CO)$ as a catalyst at 25 °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 °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°.[25,35]



7 **8** **DIOP**

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

Table 3. Results of the Hydroformylation of 1-Octene at 40 °C[a]

ligand	calcd bite angle, deg	flexibility range, deg	normal/branched	% *n*-aldehyde	% isomerization	tof[b]
DPEphos	102.2	86–120	10.5	91.3	0	5
Sixantphos	108.7	93–132	35.0	96.3	<1	4.4
Thixantphos	109.4	94–130	47.6	97.0	1	13.2
Xantphos	111.7	97–135	57.1	98.3	0	10
DBFphos	131.1	117–147	3.4	76.1	1.6	1.9
BISBI	122.6	101–148	58.2	95.5	2.9	30

[a] Conditions: $CO/H_2 = 1$, $p(CO/H_2) = 10$ 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[a]

ligand	calcd bite angle, deg	flexibility range, deg	normal/ branched	% *n*-aldehyde	% isomerization	tof
DPEphos	102.2	86–120	6.7	87.0	0	250
Sixantphos	108.7	93–132	34	94.2	3	168
Thixantphos	109.4	94–130	41	93.0	4.7	445
Xantphos	111.7	97–135	53.5	97.7	0.5	800
DBFphos	131.1	117–147	3	71	5.5	125
BISBI	122.6	101–148	80.5	89.6	9.3	850

[a] Conditions: $CO/H_2 = 1$, $p(CO/H_2) = 10$ bar, substrate/Rh = 674, ligand/Rh = 2.2, [Rh] = 1.78 mM. In all cases the percent hydrogenation was zero.

Scheme 2

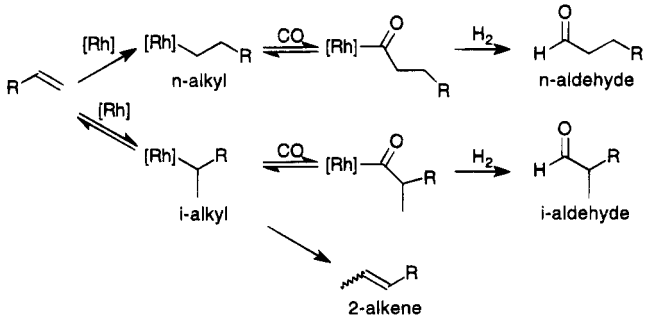


Table 5. Results of the Hydroformylation of Styrene[a]

ligand	*T*, °C	*p*, bar	normal/ branched	% *n*-aldehyde	tof
Xantphos	60	10	0.77	43.5	128
	80		0.88	46.8	724
	120		2.35	70.1	4285
PPh_3[7]	25	1	0.13	11.5	10
PPh_3[33]	70	62	0.08	7.4	*b*
7[34]	30	40	0.03–0.05	3–5	9.7
8[35]	50	8	0.77	43.5	0.32
	50	40	0.12	11	(a)
	20	25	0.04	4	2.1
DIOP[36]	25	1	0.25–0.49[c]	20–32.5[c]	*b*

[a] Conditions: $CO/H_2 = 1$, substrate/Rh = 674, [Rh] = 1.78 mM. [b] Not reported. [c] Depending on the rhodium precursor used.

Casey[23]) 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.[36]

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 hydroformylation of 1-hexene[23] or 1-octene.[35] Therefore, the effect of **8** on the selectivity (toward the branched aldehyde) in the hydroformylation of styrene remains unexplained.

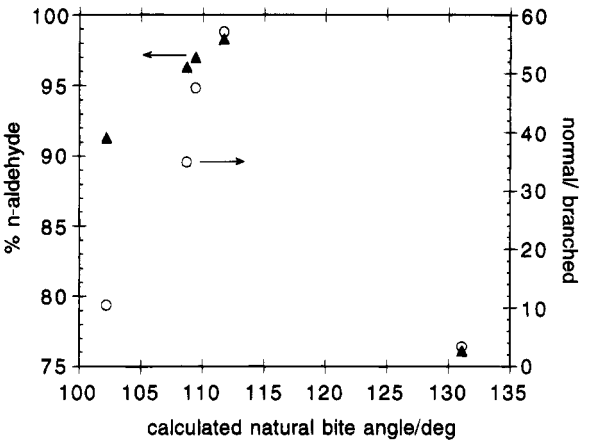


Figure 4. Selectivity versus calculated natural bite angle (β_n) in the hydroformylation of 1-octene. Normal to branched ratio versus β_n is indicated by open circles and the percentage of linear aldehyde versus β_n with full triangles (data from Table 2).

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.[23] 113°, X-ray (BISBI)Rh(H)(CO)(PPh_3) 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

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(36) Brown, J. M.; Cook, S. J.; Khan, R. *Tetrahedron* **1986**, *42*, 5105–5109.

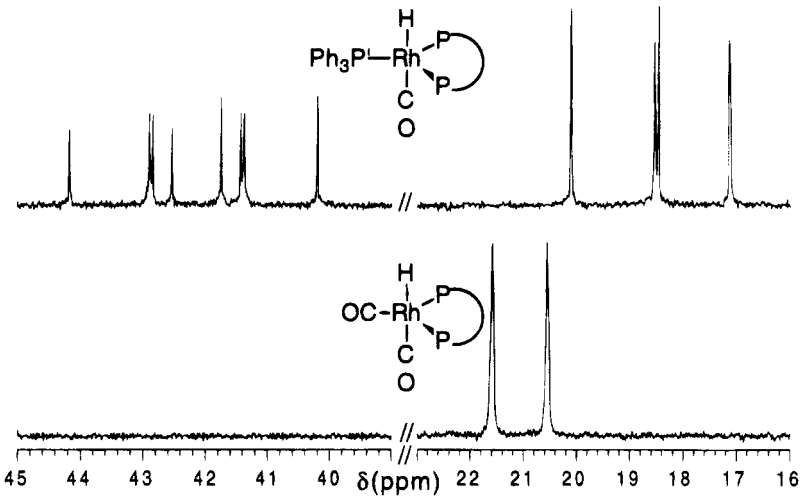

Figure 5. ^{31}P NMR spectra for (Xantphos)Rh(H)(CO)(PPh_3) (**9**; top) and (Xantphos)Rh(H)$(CO)_2$ (**10**; bottom) in C_6D_6 at 25 °C.

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)(PPh_3) complexes were synthesized for all ligands. Facile exchange of PPh_3 in $(PPh_3)_3$Rh(H)(CO) with the diphosphines gave quantitative yield (although some loss was observed during the workup procedure).

Detailed studies of the $^{31}P\{^1H\}$ 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 PPh_3 ($^2J = 114-129$ Hz) show that these ligands are indeed coordinated bis-equatorially. The attempts to synthesize (DBFphos)Rh(H)(CO)(PPh_3) (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)(PPh_3) led to facile displacement of the remaining PPh_3. The complex (diphosphine)Rh(H)$(CO)_2$ formed by this exchange (presumably the catalytically active species in the hydroformylation reaction) is stable under an atmosphere of CO. The $^{31}P\{^1H\}$ NMR spectra of these compounds (see Figure 5 for the spectra of the Xantphos complexes) exhibit a clean doublet for the diphosphine, 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)(PPh_3) (**9**), (Xantphos)Rh(H)$(CO)_2$ (**10**), (Sixantphos)Rh(H)(CO)(PPh_3) (**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)(PPh_3) complexes. This is especially clear in the ^1H NMR spectra of **9** and (Thixantphos)Rh(H)(CO)(PPh_3) (**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,[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,[25] 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[37] (CAChe MOPAC version 94.10, derived from MOPAC version 6.00[38]) were performed using the CAChe WorkSystem version 3.7,[39] 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 CaH_2. Dibenzofuran, *sec*-butyllithium, and dimethyldichlorosilane were purchased from Janssen; dibenzofuran was recrystallized from ethanol before use. Chlorodiphenylphosphine and TMEDA were purchased from Aldrich and distilled prior to use. 9,9-Dimethylxanthene, diphenyl ether, and *n*-butyllithium were purchased from Aldrich and used as received. ^{13}CO was purchased from Isotec Inc.

$(PPh_3)_3Rh(H)(CO)$[40] and dimethylphenoxathiin[41] were prepared according to literature procedures.

^1H NMR (300 MHz) and ^{31}P NMR spectra (121.5 MHz, referenced to external 85% H_3PO_4) were recorded on a Bruker AMX-300 spectrometer; ^{13}C 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 geNMR 3.5M software.[30] P′ represents the PPh_3 phosphorus atom in characterizations of couplings in NMR spectra. IR spectra were obtained on a Nicolet 510 FT-IR. Mass spectroscopy was measured on a JEOL JMS-SX/SX102A. Melting points were measured on a Gallenkamp MFB-595 melting point apparatus and are uncorrected.

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 (23.5 mmol) in 15 mL of THF was added dropwise to a stirred mixture of 20.6 mL of *n*-butyllithium (2.5 M in hexane, 51.7 mmol) and 8.3 mL of TMEDA (51.7 mmol). The reaction mixture was stirred for 16 h. Then a solution of 9.3 mL of chlorodiphenylphosphine (51.7 mmol) in 15 mL of hexanes was added dropwise to the reaction mixture at room temperature. During the addition, the temperature was kept constant with a water bath. A white precipitate was formed. The mixture was stirred for another 16 h; then 30 mL of CH_2Cl_2 and 30 mL of water were added and the mixture was stirred vigorously. The water layer was then removed, the organic phase was dried with $MgSO_4$, 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 (83%).

^1H NMR ($CDCl_3$): δ 7.40–7.18 (ar, 11 H), 6.98 (dt, J = 0.7, 7.3 Hz), 6.84 (ddd, J = 4.5, 7.5, 14 Hz), 6.71 (ddd, J = 0.7, 4.3, 7.5 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.4. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.8 (d, J = 22.65 Hz), 137.2 (d, J = 11.3 Hz), 14.6, 134.3, 130.7, 129.6 (d, J = 16.6 Hz), 129.0, 128.9, 128.7, 124.1, 118.6. IR ($CHCl_3$, cm^{-1}): 3073 (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 $C_{36}H_{28}OP_2$ 538.1615), Mp: 175–176 °C.

10,10-Dimethylphenoxasilin (14).[42,43] At room temperature a solution of 8.00 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*-butyllithium 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 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 $MgSO_4$. 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 ($CDCl_3$): δ 7.56 (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, $(CH_3)_2Si$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.2, 134.5, 131.7, 123.1, 119.7 (C–Si), 118.5, 0.2 ($(CH_3)_2$-Si). IR ($CHCl_3$, cm^{-1}): 3070, 3008, 2957, 2901, 1604, 1593, 1574, 1426, 1370, 1301, 1270, 885, 845, 807. Exact mass (MS): 226.0808 (calcd for $C_{14}H_{14}OSi$ 226.0814).

4,6-Bis(diphenylphosphino)-10,10-dimethylphenoxasilin (Sixantphos; 2). At room temperature 12.6 mL of *sec*-butyllithium (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 CH_2Cl_2; this solution was washed with water and dried with $MgSO_4$ 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 ($CDCl_3$): δ 7.50 (dd, 2H, J = 7.2, 1.7 Hz, CHC*H*CSi), 7.16–7.31 (ar, 20 H, $P(C_6H_5)_2$), 7.00 (t, 2H, J = 7.3 Hz, PCCHC*H*CH), 6.79 (dq, 2 H, J = 7.5, 1.7 Hz, OCPCC*H*), 0.50 (s, 6 H, $(CH_3)_2Si$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −17.6. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.9 (t, J = 6.8 Hz), through-space P–P coupling ≥60 Hz, 136.4, 134.5, 133.9 (t, J = 10.6 Hz, P–*C*(Ph), 127.9, 127.3 (t, J = 10.9 Hz, *C*O), 122.8, 118.5, -0.4 ($(CH_3)_2Si$). IR ($CHCl_3$, cm^{-1}): 3059, 3007, 2960, 1580, 1572, 1434, 1399, 1370, 1120, 885, 857. Exact mass (MS): 595.1741 (M + H) (calcd for $C_{38}H_{32}OP_2Si$ 594.1698). Mp: 245–245.5 °C. Anal. Calcd for $C_{38}H_{32}OP_2Si$: C, 76.75; H, 5.43. Found: C, 76.04; H, 5.61.

2,8-Dimethyl-4,6-bis(diphenylphosphino)phenoxathiin (Thixantphos: 3). This compound was prepared

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(38) Stewart, J. J. P. QCPE No. 455.
(39) CAChe WorkSystem 3.7; CAChe Scientific Inc., 18700 N. W. Walker Road, Building 92-01, Beaverton, OR 97006.
(40) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 59–60.
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similarly to Sixantphos from 3.00 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.

^{1}H NMR ($CDCl_3$): δ 7.16–7.35 (ar, 20 H, P(C_6H_5), 6.87 ("d", J =1.6 Hz, C(P(Ph)$_2$)C*H*C(CH_3)), 6.23 (bs, 2H, C(S)C*H*C(CH_3)), 2.07 (s, 6H, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −17.3. ^{13}C{^{1}H} NMR ($CDCl_3$): 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 (CH_3). IR ($CHCl_3$, cm^{-1}): 3004 (m), 2961 (m), 2926 (m), 1435 (s), 1407 (vs), 1244 (m), 695 (m). Exact mass (MS): 596.1483 (calcd for $C_{38}H_{30}OP_2S$ 596.1492). Mp: 179.5–180 °C. Anal. Calcd for $C_{38}H_{30}OP_2S$: C, 76.49; H, 5.07. Found: C, 75.64; H, 5.53.

9,9-Dimethyl-4,6-bis(diphenylphosphino)xanthene (Xantphos; 4). This compound was prepared similarly to Sixantphos from 1.00 g of 9,9-dimethylxanthene (4.76 mmol). Yield: 2.05 g of yellow-white powder (74.6%). ^{1}H NMR ($CDCl_3$): δ 7.40 (dd, 2H, J = 7.8, 1.0 Hz, CPC*H*CH), 7.15–7.26 (ar, 20 H), P(C_6H_5)), 6.96 (t, 2H, J = 7.7 Hz, CHC*H*CH), 6.54 (dd, 2H, J = 7.4, 1.4 Hz, CHC*H*CC), 1.65 (s, 6H, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −17.5. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.2 (t, J = 5.3 Hz), through-space P–P coupling ≥60 Hz, 133.7 (t, J = 10.1 Hz), 131.9, 129.7, 128.0 (ar), 126.1, 125.7 (t, J = 9.8 Hz), 123.1, 67.8 (CMe_2), 31.6 (CH_3). IR ($CHCl_3$, cm^{-1}): 3073 (w), 2974 (w), 1435 (s), 1405 (vs), 1243 (m), 695 (m). Exact mass (MS): 578.1916 (calcd for $C_{39}H_{32}OP_2$ 578.1928). Mp: 221–222 °C. Anal. Calcd for $C_{39}H_{32}OP_2$: C, 80.94; H, 5.58. Found: C, 80.69; H, 5.87.

X-ray Crystal Structure Determination of Xantphos. Crystals of Xantphos suitable for X-ray diffraction were grown from hot 1-propanol. Xantphos crystallizes in the orthorhombic space group *Pbnm*, with a = 8.7678(8) Å, b = 18.967(1) Å, c = 19.181(1) Å, V = 3189.8(4) Å^3 and Z = 4. The data collection was carried out at room temperature. The structure was solved by direct methods.[44] The hydrogen atoms were calculated. The structure was refined to R = 0.063 and R_w = 0.085, for 1825 observed reflections. The symmetric unit contains a half-molecule with four atoms (O, C1, C2, and C3) at special positions on a mirror plane. Crystal data and collection parameters, atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates are included in the supplementary material.

1,8-Bis(diphenylphosphino)dibenzofuran (DBFphos; 5). At −65 °C 66.2 mL of *sec*-butyllithium (1.3 M in 98/2 cyclohexane/hexane, 84.0 mmol) was added dropwise to a stirred solution of 4.82 g of dibenzofuran (28.7 mmol) and 12.8 mL of TMEDA (84.0 mmol) in 280 mL of dry ether. After all the *sec*-butyllithium was added, the cooling bath was removed, and the reaction mixture was warmed to room temperature. After 16 h, the mixture was cooled to −65 °C, and a solution of 18.53 mL of chlorodiphenylphosphine (84.0 mmol) in 50 mL of hexanes was added dropwise. The cooling bath was removed, and the reaction mixture was stirred for another 16 h. The ether was removed *in vacuo*; the resulting solid oil was dissolved in 100 mL of CH_2Cl_2 and the solution washed with 60 mL of deoxygenated water, dried with $MgSO_4$, and evaporated to dryness. The resulting oil was washed twice with 30 mL of hexanes and dried *in vacuo*. The resulting white crystals are air-stable. Yield: 12.2 g of white powder (81%).

^{1}H NMR ($CDCl_3$): δ 7.95 (dd, 2H, J = 7.7, 0.9 Hz, CHC*H*CC), 7.2–7.35 (ar, 22H, P(C_6H_5)$_2$ + CHC*H*CH), 7.08 (dt, 2 H, J = 6.9, 0.84 Hz, PCCHC*H*CH). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −16.5. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 136.3 (d, J = 10.5 Hz, C-*ipso*), 134.5, 134.2, 132.6 (d, J = 9.8 Hz, OCCP*C*H), 129.2, 128.9, 128.9, 124.1 (CO), 123.7, 122.2, 122.0, 121.9. IR ($CHCl_3$, cm^{-1}): 3059 (w), 3004 (w), 1435 (vs), 1411 (vs), 1390 (vs), 1180 (vs), 395 (m). Exact mass (MS): 536.1469 (calcd for $C_{36}H_{26}OP_2$ 536.1459). Mp: 211–214 °C (lit.[28] mp 212–216 °C).

(44) *XTAL3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland, 1992.

(Xantphos)Rh(H)(CO)(PPh$_3$) (9). A solution of (PPh$_3$)$_3$Rh(H)(CO) (100 mg, 0.11 mmol) and Xantphos (63.6 mg, 0.11 mmol) in 10 mL of benzene was stirred for 4 h at 30 °C. The solvent was evaporated *in vacuo*. The resulting yellow solid was washed with 1 mL of methanol and dried *in vacuo*. The ^{13}C resonances of the carbonyl were measured on a ^{13}CO-enriched complex.

^{1}H NMR (C_6D_6): δ 7.82 (apparent q, 4H, J = 4.8 Hz, ar), 7.66 (m, 6H, ar), 7.53 (apparent q, 4H, J = 4.9 Hz, ar), 7.11 (dd, 2H, J = 7.3, 1.3 Hz, CHC*H*CC), 7.0–6.9 (ar), 6.79 ("d", 4 H), 1.48 (s, 3H, CCH_3), 1.38 (s, 3H, CCH_3), −9.14 (J_{H-P} = 12.2 Hz, $J_{H-P'}$ = 18.2 Hz, J_{H-Rh} = 1.7 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 42.67 (J_{P-Rh} = 151.1 Hz, $J_{P'-P}$ = 119.1 Hz, PPh$_3$), 25.65 (J_{P-Rh} = 127.9 Hz, $J_{P-P'}$ = 119.1 Hz, Xantphos-P). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 156.9 (t, J =5.6 Hz), 141.9 (dt, J = 4.4, 31.1 Hz), 140.1 (t, J = 18.9 Hz), 137.6 (t, J = 18 Hz), 135.6 (s), 134.9 (ar), 134.8 (ar), 134.6 (ar), 134.6 (ar), 134.5 (ar), 134.4 (ar), 134.2 (ar), 36.9 (s, *C*(CH_3)$_2$), 31.0, (s, CH_3), 24.7 (s, CH_3). IR (ν_{CO}, $CHCl_3$, cm^{-1}): 1996.9 (vs), 1909.66 (m). MS (*m/z*): 961 (M − CO), 726 (M − PPh$_3$ − 2H), 698 (M − PPh$_3$ − CO − 2H). Anal. Calcd for $C_{58}H_{48}O_2P_3Rh$: C, 71.61; H, 4.98. Found: C, 71.02; H, 4.95.

(Xantphos)Rh(H)(^{13}CO)(PPh$_3$) (9-^{13}CO). The ^{13}C resonances of the carbonyl were measured on ^{13}CO-enriched **9**. The complex was synthesized as for **9**, but a gentle stream of ^{13}CO was led through the reaction mixture for ca. 2 min, after which the workup procedure described for **9** was performed.

^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 205.5 ("dq", J_{C-Rh} = 53.8 Hz, J_{C-P} = 10.3 Hz, Rh−*C*O).

(Xantphos)Rh(H)(CO)$_2$ (10) and (Xantphos)Rh(H)(^{13}CO)$_2$ (10-^{13}CO). A gentle stream of CO was led through a C_6D_6 solution of **9** in an NMR tube for 45 min. The tube was sealed under 1 atm of CO.

10-^{13}CO was prepared similarly to **10**, using ^{13}CO for ca. 10 min.

^{1}H NMR (C_6D_6): δ 7.1–7.02 (ar, 10H), 6.91–6.85 (ar, 12H), 6.70 (t, J = 7.7 Hz, 2H), 6.60 (ar, 2H), 1.38 (s, 6H, CH_3), −8.53 (m, 1H, J_{Rh-H} = 6.4 Hz, J_{P-H} = 10.0 Hz, J_{C-H} = 16.5, Rh−H). ^{31}P{^{1}H} NMR (C_6D_6): δ 21.08 (dt, J_{P-Rh} = 126.5 Hz, J_{P-C} = 10.8 Hz). ^{13}C NMR (C_6D_6): δ 201.1 (dt, J_{C-Rh} = 65.7 Hz, J_{C-P} = 10.6 Hz). IR (ν_{CO}, C_6H_6, cm^{-1}): 1989.9 (s), 1969.2 (vs), 1940.1 (vs).

(Sixantphos)Rh(H)(CO)(PPh$_3$) (11). This compound was prepared similarly to **9**.

^{1}H NMR (C_6D_6): δ 7.64–7.58 (9H, ar), 7.46–7.35 (6H, ar), 7.23 (dd, 2H, CHC*H*CSi), 6.9–6.80 (ar, 22 H), 6.76 (t, J = 7.3 Hz, 2H), 0.28 (s, 3H, SiCH_3), 0.20 (s, 3H, SiCH_3), −9.11 (J_{H-P} = 11.8 Hz, $J_{H-P'}$ = 18.2 Hz, J_{H-Rh} = 2.3 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.34 (J_{P-Rh} = 167.8 Hz, $J_{P'-P}$ = 125.0 Hz, PPh$_3$), 27.82 (J_{P-Rh} = 146.5 Hz, $J_{P-P'}$ = 125.0 Hz, Sixantphos-P). ^{13}C{^{1}H} NMR (50 MHz, C_6D_6): δ 162.4 (t), 140.4 (dt), 139.1 (t), 136.3 (dd), 134.4–122 (ar), −1.0 (*C*H_3), −3.0 (*C*H_3). IR (ν_{CO}, C_6H_6, cm^{-1}): 1996.9 (vs), 1911.0 (w).

(Sixantphos)Rh(H)(CO)$_2$ (12). This compound was prepared similarly to **10**.

^{1}H NMR (C_6D_6): δ 7.51 (b, ar, ortho PPh$_2$), 7.38 (m, ar, meta, para PPh$_2$), 7.22 (dd, J = 7.0, 1.8 Hz, 2 H), 7.1–7.0 (m, ar, PPh$_3$), 6.9–6.8 (m, ar), 6.77 (dd, J = 7.9, 2.0 Hz, 2 H), 6.71 (t, J = 10 Hz, 2 H), 0.26 (s, 6H, Si(CH_3)$_2$), −8.45 (dt, 1H, J_{P-H} = 22.7 Hz, J_{Rh-H} = 7.7 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 22.26 (d, J_{P-Rh} = 123.9). IR (ν_{CO}, C_6H_6, cm^{-1}): 1989.9 (m), 1966.4 (m), 1940.1 (vs).

(Thixantphos)Rh(H)(CO)(PPh$_3$) (13). This compound was prepared similarly to **9**.

^{1}H NMR (C_6D_6): δ 7.71 (apparent q, 5 H, ar), 7.58 (m, 7H, ar), 7.41 (apparent q, 5 H, ar), 6.83–7.0 (ar, 28 H, ar), 6.75 ("d", J = 1.6 Hz, C(P(Ph)$_2$)C*H*C(CH_3)), 6.44 (bs, 2H, C(S)C*H*C(CH_3)), 1.69 (s, 6H, CH_3), −9.19 (ddt, J_{H-Rh} = 0.6 Hz, J_{H-P} = 11.1 Hz, $J_{H-P'}$ =18.6 Hz). ^{31}P NMR (C_6D_6): δ 42.84 ($J_{P'-Rh}$ = 143.8 Hz, $J_{P'-P}$ = 113.9 Hz, PPh$_3$), 28.3 (J_{P-Rh} = 127.2 Hz, J_{PP-P} = 113.9 Hz, Thixantphos-P). IR (ν_{CO}, C_6H_6, cm^{-1}): 2000 (vs),

1918 (m). MS (*m/z*): 961 (M − CO), 726 (M − PPh_3 − 2H), 698 (M − PPh_3 − CO − 2H).

(Thixantphos)Rh(H)(CO)$_2$ (15). This compound was prepared similarly to **10**.

^{1}H NMR (C_6D_6): 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)$_2$)C*H*C(CH$_3$)), 6.33 (m, 2H, C(S)C*H*C(CH$_3$)), 1.69 (s, 6H, C*H*$_3$), −8.55 (dt, J_{H-Rh} = 6.3 Hz, J_{H-P} = 14.7). ^{31}P{^{1}H} NMR (C_6D_6): δ 23.39 (d, J_{P-Rh} = 127.9 Hz). IR (ν_{CO}, C_6H_6, cm^{-1}): 1993 (s), 1975 (s), 1940 (s).

(DPEphos)Rh(H)(CO)(PPh$_3$) (16). This compound was prepared similarly to **9**.

^{1}H NMR (C_6D_6): δ 7.66−7.48 (ar), 7.0−6.8 (ar), 7.06−6.95 (m, ar, PPh_3), 6.63 (apparent t, ar), 6.51 (apparent t, ar), −8.87 (apparent dq, J_{P-H} = $J_{P'-H}$ = 26.9 Hz, J_{Rh-H} = 3.6 Hz, 1H, Rh−*H*). ^{31}P NMR (C_6D_6): δ 44.192 ($J_{P'-Rh}$ = 168.0 Hz, $J_{P'-P}$ = 129.0 Hz, PPh_3), 27.8 (J_{P-Rh}= 148.2 Hz, $J_{P-P'}$ = 129.0 Hz, DPEphos-P). ^{13}C{^{1}H} NMR (C_6D_6): 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, 128.4−126.9 (ar), 122.7, 120.8. IR (ν_{CO}, C_6H_6, cm^{-1}): 2009.3 (vs), 1924.9 (m).

(DPEphos)Rh(H)(CO)$_2$ (17). This compound was prepared similarly to **10**.

^{1}H NMR (C_6D_6): δ 7.66−7.48 (ar), 7.0−6.8 (ar), 7.06−6.95 (m, ar, PPh_3), 6.66 (apparent t, ar), 6.41 (apparent t, ar), −8.59 (dt, 1H, J_{P-H} = 45.1 Hz, J_{Rh-H} = 10.6 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 25.54 (d, J_{P-Rh} = 123.9). IR (ν_{CO}, C_6H_6, cm^{-1}): 1992.7 (s), 1978.9 (m), 1940.1 (vs).

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 diphosphine was placed in the autoclave and the system was flushed three times with 10 bar of CO/H_2 (1/1). Then, 3.0 mL of a 5 mM solution of Rh(acac)(CO)$_2$ 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/H_2.

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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