Synthesis of Pyrrolyl-, Indolyl-, and Carbazolylphosphanes and Their Catalytic Application as Ligands in the Hydroformylation of 2-Pentene

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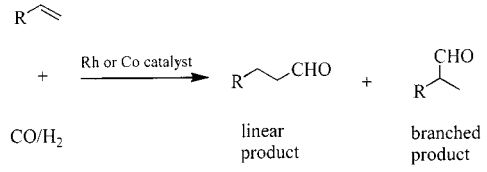
The synthesis of π-acceptor ligands of the type PAr_xR_{3-x} (x = 0–2; R = pyrrolyl, indolyl, carbazolyl; Ar = aryl) (**1**–**8**, **10**, **12**, **13**) and P(pyrrolyl)$_2$(carbazolyl) (**11**) is described. These ligands can be prepared in good to excellent yields by treatment of the corresponding free heterocyclic amines with phosphorus chlorides in the presence of base. The utilization of pyrrolyl-, indolyl-, and carbazolylphosphanes in the rhodium-catalyzed hydroformylation of 2-pentene demonstrates the influence of the ligand π-acidity on regioselectivity and activity in the hydroformylation of internal olefins. In general, increasing π-acidity of the ligand results in an increased yield of the linear oxo product. The best *n*/*iso* ratios of about 60:40 are obtained at low synthesis gas pressure (10 bar) in the presence of the P(pyrrolyl)$_3$ (**1**) ligand.

Introduction

The hydroformylation of olefins (Scheme 1) was discovered in 1938 by Otto Roelen and is one of the most important homogenous catalytic processes in industry.[1] Nowadays more than 6.6 million tons of aldehydes and alcohols are produced annually from olefins by this method. The primary commercial application of the oxo products is as plasticizer alcohols, especially for manufacturing poly(vinyl chloride). For the last 50 years the major product made by hydroformylation has been 2-ethylhexanol, produced by hydroformylation of propene, followed by an aldol condensation of the resulting *n*-butyraldehyde and subsequent reduction.



Scheme 1. Hydroformylation of terminal olefins

As a consequence of the debate concerning the environmental impact of current plasticizer products, there is growing interest in new plasticizer alcohols.[2] In order to be viable, the respective olefin feedstock has to be economically competitive compared to propene. This requirement is only fulfilled by mixtures of internal and terminal olefins, such as raffinate II, which consists of 1-butene, (*E*/*Z*)-2-butene, and butane. Thus, the selective hydroformylation of internal olefins to give linear aldehydes is an important goal in carbonylation chemistry.

In order to obtain the linear aldehyde as the major product, isomerization of the internal olefin must be faster than the hydroformylation reaction. In addition, there should be a reasonable difference in the rates of hydroformylation of the internal and terminal olefins and the catalyst should be highly *n*-selective for the terminal olefin.[3] It is well known that carbonylcobalt-based homogeneous catalysts display similar activities both for terminal and for internal olefins. Unfortunately, cobalt catalysts show low turnover frequencies and need relatively high reaction temperatures and pressures (up to 190 °C and 250 bar).[4] While water-soluble cobalt catalysts work under milder conditions, the *n*/*iso* ratios of cobalt-catalyzed hydroformylation reactions are comparatively low.[5]

In general, phosphanerhodium catalysts display much higher activities for terminal olefins than for internal olefins, which are converted very slowly with little isomerization.[6] Coordinatively unsaturated rhodium species, however, exhibit activity towards isomerization of the substrate. Such unsaturated species are formed in the presence of sterically demanding phosphites or phosphanes. To date, the most selective catalysts for the hydroformylation of internal olefins to give linear aldehydes are based on rhodium modified by sterically hindered chelating phosphites.[7] Because of the limited stability of these ligands, there is considerable interest in new hydroformylation catalysts for the conversion of internal olefins. Clearly, phosphanes would offer advantages over phosphites in terms of stability. Van Leeuwen and co-workers have recently described an important advance, demonstrating that dibenzophospholyl- and phenoxaphosphanyl-substituted xanthene ligands preferentially give linear aldehydes in the hydroformylation of 2- and 4-octene, albeit at rates too low for industrial application.[8]

Building on our interest in using carbon monoxide for the synthesis of bulk and fine chemicals,[9] we were curious

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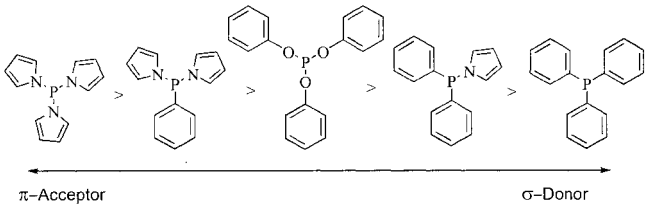
about how the electronic properties of the phosphane ligands would influence the *n*/*iso* ratios in the hydroformylation of internal olefins. In general, a higher regioselectivity is obtained with ligands that possess strong π-acceptor and weak σ-donor properties.[10] Investigations based on the ν_{co} band positions and ^{31}P NMR parameters in Rh(acac)(CO)L complexes[11] show the high π-acceptor character of 1-pyrrolylphosphanes compared to phosphanes and even phosphites (Scheme 2). Despite their interesting electronic properties, 1-pyrrolylphosphanes have only rarely been applied as ligands in homogeneous catalysis. While Breit used tris(1-pyrrolyl)phosphane for the regioselective hydroformylation of styrene with limited success,[12] Ziolkowski and co-workers demonstrated that the hydroformylation of hex-1-ene proceeds in good yield in the presence of tris(1-pyrrolyl)phosphane and 1-(diphenylphosphanyl)pyrrole.[13] In this manuscript we describe the synthesis of a number of novel substituted pyrrolyl-type phosphanes, as well as their first application in the hydroformylation of an internal olefin.

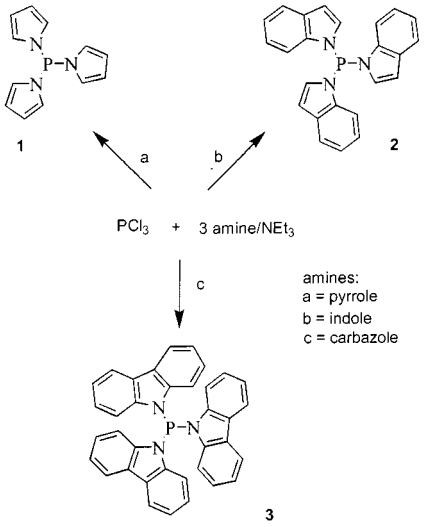


Scheme 2. π-Acceptor and σ-donor properties of different P ligands

Results and Discussion

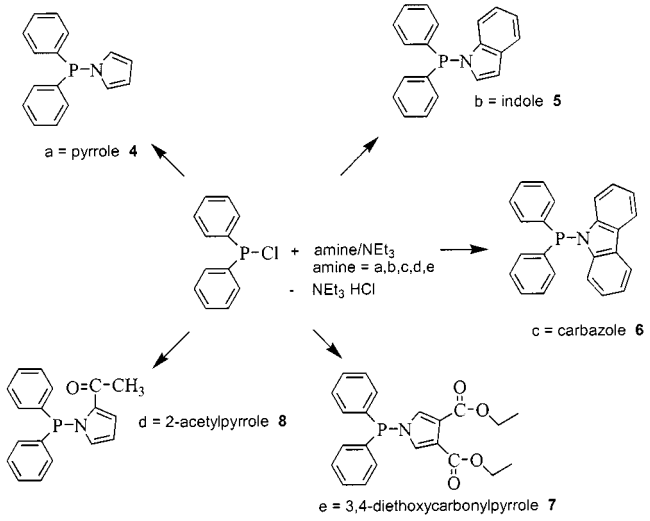
Ligand Synthesis

There are two known routes for the preparation of 1-pyrrolylphosphanes. Treatment of alkali metal pyrrolides with the appropriate phosphorus chloride produces 1-pyrrolylphosphanes in only moderate yields.[14] More recently



Scheme 3. Synthesis of ligands **1**–**3**

Moloy[11] et al. have shown that 1-pyrrolylphosphanes can be obtained in good yields by direct treatment of chlorophosphanes with pyrrole in the presence of NEt_3. As shown in Scheme 3, this procedure was also successful, giving tris(1-indolyl)- and tris(9-carbazolyl)phosphane in 90 and 92% yield, respectively. Hence, addition of 3 equiv. variously of pyrrole, indole, or carbazole to PCl_3 in THF at 0 °C and subsequent heating to reflux gave ligands **1**–**3** as colorless solids after crystallization from *n*-hexane. Similarly, ligands **4**–**8** were synthesized by treatment of chlorodiphenylphosphane with indole, carbazole, and substituted pyrroles, with yields higher than 60% (Scheme 4).

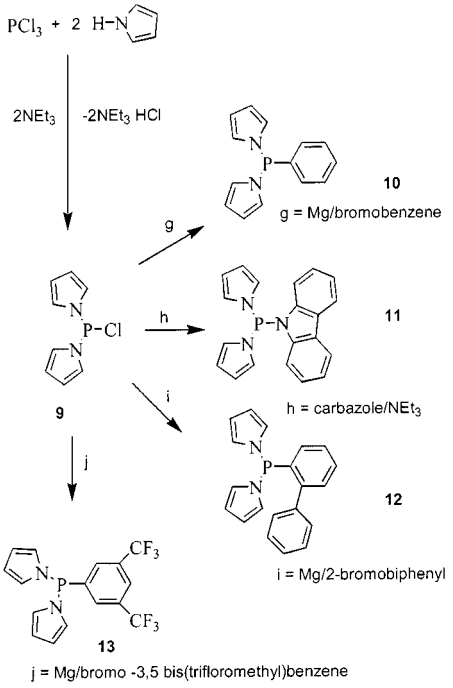


Scheme 4. Synthesis of ligands **4**–**8**

Monitoring of the ligand synthesis by ^{31}P NMR spectroscopy showed that the substitution steps at the P–Cl bonds occur sequentially, with all intermediates – $RPCl_2$, R_2PCl, and R_3P – being observed during the course of the reaction. This observation enabled a simple synthesis of bis(1-pyrrolyl)phosphanes containing a third, different substituent at the phosphorus atom to be accomplished. Treatment of 2 equiv. of pyrrole with PCl_3 in THF gave chlorobis(1-pyrrolyl)phosphane (**9**) in excellent yield (96%). Subsequent treatment of **9** either with Grignard reagents or with carbazole afforded ligands **10**–**13** in good yield (76–84%) (Scheme 5). The structure of all new ligands was unambiguously proven by means of ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, together with mass spectrometry and elemental analysis.

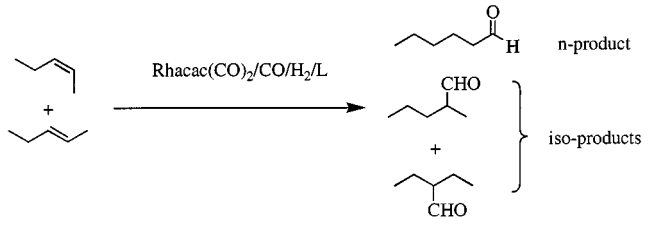
Hydroformylation Experiments

All of the synthesized ligands (**1**–**8** and **10**–**13**) were tested in the rhodium-catalyzed hydroformylation of 2-pentene (Scheme 6, Tables 1–4), which was used as a model for the oxo reaction of 2-butene (a major component in raffinate II). The active catalysts were prepared in situ by mixing $Rh(acac)(CO)_2$ with the appropriate quantity of phosphane in anisole as the solvent, in the presence of isooctane (internal standard for gas chromatography). As in industrial hydroformylation processes, a comparatively small amount



Scheme 5. Synthesis of ligands **10**−**13**

of metal (0.01 mol %) with a large excess of ligand (P/Rh = 50:1−100:1) was used in the test reactions. In general, the hydroformylation experiments were performed at 120 °C and 25 or 50 bar of synthesis gas (H_2/CO = 1:1). It should be noted that the *n*/*iso* ratio is defined throughout this study as the ratio of 1-hexanal to 2-methylpentanal and 2-ethylbutanal (Scheme 6).



Scheme 6. Hydroformylation of 2-pentene

At the start of our investigations, $RPPh_2$ (R = pyrrolyl, indolyl, carbazolyl) ligands **4**−**8** were compared with the well-known Rh/PPh_3 catalyst system and a phosphane-free Rh catalyst (so-called "unmodified Rh") (see Table 1). The phosphane-free catalyst afforded 96% conversion and an *n*/*iso* ratio of 39:61 at 50 bar, while at 25 bar the conversion was only 56% after 6 h (*n*/*iso* = 41:59). The Rh/PPh_3 catalyst gave complete conversion at 50 bar synthesis gas and 79% conversion at 25 bar. High selectivities (*n*/*iso* > 7:93) for the branched products were observed in both cases (Table 1, Entries 1−5).

Compared to the reference systems, the 1-(diphenylphosphanyl)pyrrole ligands **4**, **7**, and **8**, and also the 1-(diphenylphosphanyl)indole ligands **5** and the (9-carbazole)diphenylphosphanyl ligands **6**, gave lower degrees of conversion. On the other hand, the *n*/*iso* ratio was significantly improved compared to that of the Rh/PPh_3 system. This demonstrates the influence of electronic parameters in controlling the regioselectivity, since the phenyl and pyrrolyl groups have similar steric bulks. In the presence of all these ligands a decrease in the synthesis gas pressure resulted not only in a decrease in the degree of conversion but also in an increase in the quantity of linear aldehyde. The higher *n*/*iso* selectivity is explained by the fact that at lower pressures $HRh(CO)(PR_3)_3$ is the main active catalyst species, while $HRh(CO)_2(PR_3)_2$ becomes the more important active catalyst at higher pressures. The latter catalyst is sterically clearly less crowded and thus enables the hydroformylation giving the branched product to proceed more easily. Regardless of the synthesis gas pressure used, a small amount of 1-pentene was detected in all reaction mixtures.

The most significant *n*/*iso* ratio difference between 50 and 25 bar synthesis gas pressure was found in the case of 1-(diphenylphosphanyl)pyrrole (**4**) as the ligand (Table 1, Entries 6−8). With this ligand, both a higher total yield of aldehyde and a higher yield of the desired linear *n*-hexanal (compared to the reference systems) were obtained at 25 bar. Electron-withdrawing groups such as 3,4-diethoxycarbonyl or 2-acetyl at the pyrrolyl ring afford better *n*/*iso* ratios, but also lower total yields of aldehyde than obtained with ligand **4** (Table 1, Entries 13−15). In the case of 2-acetyl-1-(diphenylphosphanyl)pyrrole (**8**), there was virtually no conversion under the standard reaction conditions, which might be explained by the lower stability of the ligand.

We next attempted to improve the quantity of linear aldehyde obtained, by using ligands with two pyrrolyl groups. Phenyl (**10**), 2-biphenylyl (**12**), and bis(3,5-trifluoromethyl)-phenyl (**13**) groups were used as additional aromatic substituents on the phosphorus atom. In addition, a ligand with two pyrrolyl substituents and one carbazole moiety (**11**) was tested. As with ligands **4**−**8**, a decrease in the pressure from 50 to 25 or 10 bar resulted both in a smaller degree of conversion and in an increase in *n*-hexanal, the desired product. In agreement with this concept, ligands **10**, **12**, and **13** (Table 2) gave better results than (1-diphenylphosphanyl)pyrrole (**4**).

At 50 bar, all ligands except **11** gave very good yields of C_6 aldehydes (95−99%), with greater steric demand in the aryl group resulting in an increased quantity of linear aldehyde. Hence, ligand **10** gave an *n*/*iso* ratio of 20:80, while ligands **12** and **13** gave 34:66 and 30:70, respectively. Such behavior has also been observed with phosphite ligands.[15] Nevertheless, at high pressure (50 bar) none of the ligand-modified catalyst systems gave an *n*/*iso* ratio higher than that afforded by the ligand-free catalyst. Advantageously, however, this was not true for hydroformylations performed at lower pressures (25 and 10 bar). Here, ligands **10** and **13** not only gave rise to higher selectivities for *n*-hexanal, but also produced total yields of aldehyde significantly higher than those afforded by the unmodified carbonylrhodium catalyst (Table 2, Entries 3−4, 11−12).

In order to evaluate the influence of π-acceptor pyrrole-like phosphanes systematically, a series of experiments was

Table 1. Hydroformylation of 2-pentene with $PRPh_2$ ligands [general conditions: 23.7 mmol (1.67 g) of 2-pentene, 0.00237 mmol (0.61 mg) of $Rh(acac)(CO)_2$, 25 mL of anisole, 2 mL of isooctane, 120 °C, 6 h]

Entry	L	Rh [mol %]	Rh/L	*p* [bar]	Total yield of aldehydes [%]	*n*/*iso*
1	–	0.01	–	50	96	39:61
2	–	0.01	–	25	56	41:59
3[a]	–	0.01	–	10	10.5	33:67
4	PPh_3	0.01	1:100	50	99	7:93
5	PPh_3	0.01	1:100	25	79	8:92
6	**4**	0.01	1:100	50	78	9:91
7	**4**	0.01	1:100	25	66	33:67
8	**4**	0.01	1:100	17	48	36:64
9	**5**	0.01	1:100	50	83	20:80
10	**5**	0.01	1:100	25	34	27:73
11	**6**	0.01	1:100	50	74	27:73
12	**6**	0.01	1:100	25	43	37:63
13	**7**	0.01	1:100	50	59	24:76
14	**7**	0.01	1:100	25	33	37:63
15	**8**	0.01	1:100	50	3	19:81
16	**8**	0.01	1:50	50	34	29:71
17	**8**	0.01	1:50	25	14	38:62

[a] 16 h.

Table 2. Hydroformylation of 2-pentene with $PR(pyrrolyl)_2$ as ligands [general conditions: 23.7 mmol (1.67 g) of 2-pentene, 0.00237 mmol (0.61 mg) of $Rh(acac)(CO)_2$, 25 mL of anisole, 2 mL of isooctane, 120 °C, 6 h]

Entry	L	Rh [mol %]	Rh/L	*p* [bar]	Total yield of aldehydes [%]	*n*/*iso*
1	**10**	0.01	1:100	50	95	20:80
2	**10**	0.01	1:100	25	81	39:61
3	**10**	0.01	1:100	17	53	45:55
4	**10**	0.01	1:100	10	25	54:46
5	**11**	0.01	1:100	50	60	27:73
6	**11**	0.01	1:100	25	28	37:63
7	**12**	0.01	1:100	50	96	34:66
8	**12**	0.01	1:100	25	43	38:62
9	**12**	0.01	1:100	17	26	39:61
10	**13**	0.01	1:100	50	99	30:70
11	**13**	0.01	1:100	25	73	43:57
12	**13**	0.01	1:100	10	23	52:48

Table 3. Hydroformylation of 2-pentene with PR_3 (R = pyrrolyl, indolyl, carbazolyl) ligands [general conditions: 23.7 mmol (1.67 g) of 2-pentene, 0.00237 mmol (0.61 mg) of $Rh(acac)(CO)_2$, 25 mL of anisole, 2 mL of isooctane, 120 °C, 6 h]

Entry	L	Rh [mol %]	Rh/L	*p* [bar]	Total yield of aldehydes [%]	*n*/*iso*
1	**1**	0.01	1:100	50	89	23:77
2	**1**	0.01	1:100	25	89	47:53
3	**2**	0.01	1:100	50	90	38:62
4	**2**	0.01	1:100	25	34	40:60
5	**3**	0.01	1:100	50	86	37:63
6	**3**	0.01	1:100	25	46	40:60

performed with tris(1-pyrrolyl)phosphane (**1**), tris(1-indolyl)phosphane (**2**), and tris(9-carbazolyl)phosphane (**3**) (see Table 3). Again, excellent yields of C_6 aldehydes were obtained at 50 bar synthesis gas pressure in the presence of all three ligands, with regioselectivities somewhat lower than those obtained with the ligand-free catalyst system. When 2-pentene was treated in the presence of tris(1-pyrrolyl)phosphane (**1**) at 25 bar, an 89% yield of C_6 aldehydes was obtained and *n*-hexanal was formed in 43% yield (Table 3, Entry 2). Here, both the conversion and the product selectivity towards the linear aldehyde were significantly higher than those obtained from reactions in the presence of the reference catalyst systems.

Table 4. Hydroformylation of 2-pentene with $P(pyrrolyl)_3$ ligand [general conditions: 23.7 mmol (1.67 g) of 2-pentene, 0.00237 mmol (0.61 mg) or 0.00711 mmol (1.83 mg) of $Rh(acac)(CO)_2$, 25 mL of anisole, 2 mL of isooctane, 120 °C, 6 h]

Entry	L	Rh [mol %]	Rh/L	*p* [bar]	Total yield of aldehydes [%]	*n*/*iso*
1	**1**	0.01	1:100	50	89	23:77
2	**1**	0.01	1:100	25	88	47:53
	1	0.01	1:50	25	73	46:54
3	**1**	0.01	1:100	17	67	52:48
4	**1**	0.01	1:100	10	40	56:44
5	**1**	0.03	1:50	10	56	60:40
6	**1**	0.03	1:50	5	11	61:39

Catalysts based on ligands **2** and **3**, which possess less π-acceptor and more basic character than **1**, produced significantly lower degrees of conversion/total yield of aldehydes at lower pressure (Table 3, Entries 4, 6). The catalysis results obtained clearly show that the consecutive substitution of phenyl groups by π-acceptor pyrrole units in triphenylphosphane results in ligands that can provide an increased amount of linear aldehyde in the hydroformylation of 2-pentene. Comparing the results obtained from the model reaction in the presence of the different ligands, it is obvious that ligands **4**–**7** give the lowest *n*/*iso* ratios, both at 50 and

at 25 bar. The total yield of C_6 aldehydes is also comparatively low with these ligands. At 50 bar, phosphanes with more than one pyrrolyl, indolyl, or carbazolyl group give results similar to those obtained using the unmodified Rh catalyst. At 25 bar synthesis gas pressure, however, good yields of C_6 aldehydes are observed with ligands **1**, **10**, and **13**.

Electronic effects aside, the *n*/*iso* ratio can be further improved by the introduction of steric hindrance, as shown for the series of arylbis(1-pyrrolyl)phosphanes. Interestingly, of all the ligands tested, tris(1-pyrrolyl)phosphane (**1**) gave the highest *n*/*iso* ratio at 25 bar. On account of this we conducted an additional optimization study of the hydroformylation of the model system with this ligand (see Table 4).

A further decrease in the synthesis gas pressure to 10 bar produced an increase in the *n*/*iso* ratio, to 56% *n*-hexanal and 44% of isopentanals, although at lower pressure the total yields of aldehyde was reduced to 40%. We thus performed two experiments, at 10 and 5 bar with higher catalyst loadings (300 ppm of rhodium) (Table 4, Entries 5−6). Thanks to the higher ligand concentration in solution (compare Entries 4 and 5), the *n*/*iso* ratio was increased to 60:40 at 10 bar, while the total yield of C_6 aldehydes increased to 56%.

Conclusion

In conclusion, we have shown that a number of 1-pyrrolyl-like phosphanes can easily be synthesized by treatment of phosphorus chlorides and *N*-heteroaromatics or by treatment of chlorobis(1-pyrrolyl)phosphane with Grignard reagents.

The application of these ligands to the rhodium-catalyzed hydroformylation of internal olefins has been demonstrated for the first time. At higher pressures, the Rh/PR_3 systems behave similarly to unmodified carbonylrhodium catalysts. At lower synthesis gas pressures (< 25 bar), however, improved results are obtained with ligands **1**, **10** and **13**. Although the observed regioselectivities are far from satisfactory, the results demonstrate that the hydroformylation of internal olefins proceeds in the presence of certain pyrrolylphosphanes in good to very good yields (total yield of all aldehydes). Even with simple monophosphanes the *n*/*iso* ratio can be modified to some extent, to afford the linear aldehyde as the major product. Improvements in the regioselectivity might be anticipated from use of chelating and sterically more demanding ligands. We are at present conducting further work in this area.

Experimental Section

General Information: All reactions were carried out under an inert gas, using standard high-vacuum Schlenk line techniques. Diethyl ether, tetrahydrofuran, toluene, and hexane were distilled under argon from NaK/benzophenone prior to use. − ^1H, ^{13}C, and ^{31}P NMR spectra were recorded with a Bruker ARX 400 NMR instrument, using the solvent as an internal standard (δ in ppm, *J* in Hz). − Mass spectra were recorded with an AMD 402−3 (Intectra GmbH) spectrometer. − Gas chromatograms were recorded with a Hewlett−Packard HP 6890 series gas chromatograph (column: HP1; 25 m).

Hydroformylation Experiments: 2-Pentene (2.6 mL, 1.7 g, 23.7 mmol), the corresponding amount of ligand, and isooctane (2 mL) as internal standard were added under argon to a solution of $Rh(acac)(CO)_2$ (0.61 mg, 2.37×10^{-6} mol, 0.01 mol % for pentene) in anisole (22 mL). This mixture was transferred to a cooled (0 °C) 100-mL stainless steel autoclave equipped with a magnetic stirrer, and pressurized to 5 bar synthesis gas (CO/H_2 = 1:1). The autoclave was heated to 120 °C (ca. 15 min). The pressure at this temperature was adjusted to the desired value, and this value was maintained throughout the reaction (6 h). The autoclave was then cooled to 0 °C and the pressure was released. The resulting reaction mixture was analyzed by gas chromatography.

Ligand Synthesis. − General Procedure for the Preparation of Ligands 1−8 and 10 (Method 1): PCl_3, PPh_2Cl, or $PPhCl_2$ (20 mmol) was added to a cooled (0 °C) solution of NEt_3 (60, 40, or 20 mmol) in THF (100 mL) in a 250-mL three-necked, round-bottomed flask. A solution of the corresponding stoichiometric amount of pyrrole, indole or carbazole in THF (20 mL) was then added while the temperature was kept at 0 °C. The reaction mixture was stirred for 1 h at room temperature and then heated to reflux for a further 6 h. After this had cooled to room temperature, the solvent was removed in vacuo and the residue was dissolved in 100 mL of toluene. The mixture was filtered and the solvent removed in vacuo. The title compounds were crystallized from hot *n*-hexane. The products were all colorless solids, except for $(pyrrole)PPh_2$, which was a colorless oil.

Tris(1-pyrrolyl)phosphane (1): Method 1, *M* = 229.08 g/mol, yield 65%. − ^{31}P NMR(166 MHz, $CDCl_3$): δ = 79.6. − ^{13}C NMR (166 MHz, $CDCl_3$): δ = 122.8 (d, J_{PC} = 14.3 Hz), 113 (d, J_{PC} = 4.8 Hz). − ^1H NMR (400 MHz, $CDCl_3$): δ = 6.77 (pquint, *J* = 2.0 Hz, 6 H), 6.34 (pt, *J* = 2.0 Hz, 6 H). - MS (70 eV): *m*/*z* (%) = 230 (11) [M^+ + 1], 229 (86) [M^+], 164 (11), 163 (100), 136 (65), 135 (26), 118 (13), 97 (12), 96 (21), 70 (27), 69 (25). − HRMS: calcd. for $C_{12}H_{12}N_3P$ [M^+] 229.07689; found 229.07599.

Tris(1-indolyl)phosphane (2): Method 1, *M* = 379.12 g/mol, yield 90%. − ^{31}P NMR (166 MHz, $CDCl_3$): δ = 67.2. − ^{13}C NMR (166 MHz, $CDCl_3$): δ = 139.0 (d, J_{PC} = 19.1 Hz), 131.0 (d, J_{PC} = 2.9 Hz), 127.0, 123.5, 122.0, 121.3, 111.5 (d, J_{PC} = 14.3 Hz), 108.5. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45−7.6 (m, 6 H), 7.05−7.2 (m, 6 H), 6.85−6.92 (m, 3 H), 6.55−6.65 (m, 3 H). − MS (70 eV): *m*/*z* (%) = 379 (36.8) [M^+], 263 (100), 147 (10), 116 (11). − HRMS: calcd. for $C_{24}H_{18}N_3P$ [M^+] 379.12384; found 379.12387.

Tris(9-carbazolyl)phosphane (3): Method 1, *M* = 529.17 g/mol, yield 92%. - ^{31}P NMR (166 MHz, $CDCl_3$): δ = 77.2. − ^{13}C NMR (166 MHz, $CDCl_3$): δ = 142.48 (d, J_{PC} = 9.1 Hz), 140.1, 139.8, 124.3, 120.9, 113.7 (d, J_{PC} = 13.1 Hz). − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.8−8.0 (m, 6 H), 7.3−7.4 (m, 2 H), 6.80−7.20 (m, 16 H). − MS (70 eV): *m*/*z* (%) = 529 (35) [M^+], 363 (100), 197 (20), 166 (30). − $C_{36}H_{24}N_3P$: calcd. C 81.6, H 4.6, N 7.9; found C 81.6, H 4.55, N 8.3.

1-(Diphenylphosphanyl)pyrrole (4): Method 1, *M* = 251.09 g/mol, yield 85%. - ^{31}P NMR (166 MHz, $CDCl_3$): δ = 48.2. − ^{13}C NMR (166 MHz, $CDCl_3$): δ = 136.9 (d, J_{PC} = 12.4 Hz), 131.9 (d, J_{PC} = 21 Hz), 129.6, 128.5 (d, J_{PC} = 6.7 Hz), 125.4 (d, J_{PC} = 12.4), 111.5 (d, J_{PC} = 3.8 Hz). − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.15−7.35 (m, 10 H), 6.75 (pquint, *J* = 2.0 Hz, 2 H), 6.24 (t, *J* = 2.18 Hz, 4

H). − MS (70 eV): *m*/*z* (%) = 251 (98) [M$^+$], 183 (100), 174 (14), 152 (13), 107 (16), 67 (27). − HRMS: calcd. for $C_{16}H_{14}NP$ [M$^+$] 251.08640; found 251.08713.

1-(Diphenylphosphanyl)indole (5): Method 1, *M* = 301.16 g/mol, yield 67%. - ^{31}P NMR (161 MHz, $CDCl_3$): δ = 35.8. − ^{13}C NMR (166 MHz, $CDCl_3$): δ = 141.1 (d, $^2J_{PC}$ = 18.1 Hz), 136.2 (d, $^2J_{PC}$ = 12.4 Hz), 131.9 (d, $^1J_{PC}$ = 21.0 Hz), 130.4 (d, J_{PC} = 2.8 Hz), 130.1 (d, J_{PC} = 2.8 Hz), 129.6, 128.6 (d, J_{PC} = 6.7 Hz), 122.1, 112.2 (d, J_{PC} = 15.3 Hz), 106.5. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75−7.70 (m, 1 H), 7.40−7.20 (m, 11 H), 7.20−7.05 (m, 2 H), 6.93−6.86 (m, 1 H), 6.60−6.55 (m, 1 H). − MS (70 eV): *m*/*z* (%) = 301 (100) [M$^+$], 222 (10), 183 (65), 152 (10), 107 (10), 77 (8). − $C_{20}H_{16}NP$: calcd. C 79.7, H 5.4, N 4.65; found C 79.5, H 5.1, N 5.1.

9-(Diphenylphosphanyl)carbazole (6): Method 1, *M* = 351.28 g/mol, yield 71%. − ^{31}P NMR (166 MHz, $CDCl_3$): δ = 32.2. − ^{13}C NMR (166 MHz, $CDCl_3$): δ = 144.1 (d, $^2J_{PC}$ = 7.6 Hz), 134.8 (d, $^2J_{PC}$ = 13.4 Hz), 131.8 (d, J_{PC} = 20.0 Hz), 129.7, 129.0 (d, J_{PC} = 5.7 Hz), 126.3, 126.0, 121.2, 120.4, 114.1 (d, J_{PC} = 12.4 Hz). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07−8.04 (m, 2 H), 7.52−7.50 (m, 2 H), 7.46−7.41 (m, 4 H), 7.34−7.30 (m, 6 H), 7.28−7.22 (m, 4 H). − MS (70 eV): *m*/*z* (%) = 351 (100) [M$^+$], 274 (6), 185 (70), 166 (10), 107 (10), 77 (3). − $C_{24}H_{18}NP$: calcd. C 82.02, H 5.17, N 3.99; found C 82.08, H 5.25, N 4.12.

Diethyl 1-(Diphenylphosphanyl)pyrrole-3,4-dicarboxylate (7): Method 1, *M* = 395.13 g/mol, yield 80%. − ^{31}P NMR (166 MHz, $CDCl_3$): δ = 56.4. − ^{13}C NMR (166 MHz, $CDCl_3$): δ = 163.8, 134.3 (d, $^2J_{PC}$ = 13.3 Hz), 132.0, 131.8 (d, J_{PC} = 12.4 Hz), 130.5, 128.4 (d, J_{PC} = 7 Hz), 118.5, 60.0, 14.2. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.3−7.4 (m, 2 H), 7.15−7.25 (m, 2 H), 4.20 (q, *J* = 7.0 Hz, 4 H), 1.20 (t, *J* = 7.0 Hz, 6 H). − MS (70 eV): *m*/*z* (%) = 396 (18) [M$^+$ + 1], 395 (83) [M$^+$], 350 (19), 323 (8), 185 (100). − HRMS: calcd. for $C_{22}H_{22}NPO_4$ [M$^+$] 395.12863; found 395.12749.

2-Acetyl-1-(diphenylphosphanyl)pyrrole (8): Method 1, *M* = 293.1 g/mol, yield 77%. − ^{31}P NMR (166 MHz, $CDCl_3$): δ = 55.4. − ^{13}C NMR (166 MHz, $CDCl_3$): δ = 188.4, 138, 137.8, 136.7 (d, J_{PC} = 6.7 Hz), 133.1 (d, J_{PC} = 7.6 Hz), 133.0 (d, J_{PC} = 22.9 Hz), 129.0 (d, J_{PC} = 6.7 Hz), 122.0 (d, J_{PC} = 3.8 Hz), 111.7, 26.6. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26−7.32 (m, 6 H), 7.14−7.20 (m, 4 H), 7.03 (dt, *J* = 1.4, *J* = 3.8 Hz, 1 H), 6.31−6.33 (m, 1 H), 6.12 (pt, *J* = 3.0 Hz, 1 H), 2.3 (s, 3 H).

Phenylbis(1-pyrrolyl)phosphane (10): Method 1, *M* = 229.22 g/mol, yield 76%. - ^{31}P NMR (166 MHz, $CDCl_3$): δ = 70.5. − ^{13}C NMR (166 MHz, $CDCl_3$): δ = 136.9 (d, J_{PC} = 4.8 Hz), 130.9, 130.5 (d, J_{PC} = 10.5 Hz), 129.0, 125.2 (d, J_{PC} = 16.6 Hz), 112.8 (d, J_{PC} = 4.0 Hz). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25−7.33 (m, 3 H), 6.98−7.00 (m, 2 H), 6.84 (pquint, *J* = 2.0 Hz, 4 H), 6.2 (br. s, 4 H). − MS (70 eV): *m*/*z* (%) = 240 (7) [M$^+$], 174 (100), 147 (19), 152 (13), 96 (12), 107 (16), 77 (11). − HRMS: calcd. for $C_{14}H_{13}N_2P$ [M$^+$] 240.08279; found 240.08163.

Preparation of Chlorobis(1-pyrrolyl)phosphane (9): PCl_3 (7.0 mL, 80 mmol) was added to a cooled (0 °C) solution of NEt_3 (25 mL, 18 mmol) in THF (200 mL) in a 500-mL three-necked, round-bottomed flask. A solution of pyrrole (11.2 mL, 160 mmol) in THF (20 mL) was then added, while the temperature was maintained at 0 °C. The reaction mixture was stirred for 6 h at room temperature. The mixture was then filtered and the solvent removed in vacuo. The residue was distilled in vacuo at 10^{-3} Torr to afford **9** (15.3 g, 96% yield) as a colorless liquid. − B.p. 60 °C (10^{-3} Torr); *M* = 198.59 g/mol. − ^{31}P NMR (166 MHz, C_6D_6): δ = 104.7. − ^{13}C NMR (166 MHz, C_6D_6): δ = 122.6 (d, $^2J_{PC}$ = 17.2 Hz), 113.9 (d, $^3J_{PC}$ = 4.7 Hz). − ^{1}H NMR (400 MHz, C_6D_6): δ = 6.7 (pquint, *J* = 2.2 Hz, 2 H), 6.18 (pt, *J* = 2.2 Hz, 2 H).

Preparation of (9-Carbazolyl)bis(1-pyrrolyl)phosphane (11): P(pyrrolyl)$_2$Cl (**9**) (3.98 g, 20 mmol) was added to a cooled (0 °C) solution of NEt_3 (2.5 g, 25 mmol) in THF (50 mL) in a 100-mL three-necked, round-bottomed flask. A stoichiometric amount of carbazole in THF (20 mL) was then added, while the temperature was maintained at 0 °C. The reaction mixture was stirred for 1 h at room temperature and then heated to reflux for a further 6 h. After this had cooled to room temperature, the solvent was removed in vacuo and the residue was dissolved in 50 mL of toluene. The mixture was filtered and the remaining solvent was removed in vacuo. After crystallization from hot *n*-hexane, **11** was obtained (5.2 g, 79% yield). − *M* = 329.11 g/mol. − ^{31}P NMR (166 MHz, $CDCl_3$): δ = 80.4. − ^{13}C NMR (166 MHz, $CDCl_3$): δ = 141.8 (d, $^2J_{PC}$ = 8.6 Hz), 126.5, 126.3 (d, J_{PC} = 1.9 Hz), 122.9 (d, $^2J_{PC}$ = 13.4 Hz), 122.0, 120.1, 113.2 (d, $^3J_{PC}$ = 3.8 Hz), 112.8 (d, J_{PC} = 13.4 Hz). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00−7.90 (m, 2 H), 7.28−7.16 (m, 4 H), 7.12−7.04 (m, 2 H), 6.79 (pquint, *J* = 2.0 Hz, 4 H), 6.25−6.3 (m, 4 H). − MS (70 eV): *m*/*z* (%) = 329 (37) [M$^+$], 263 (60), 167 (100), 140 (13). − HRMS: calcd. for $C_{20}H_{16}N_3P$ 329.10818; found 329.10895.

General Procedure for the Preparation of Ligands 12−13 (Method 2): A Grignard reagent was prepared from the appropriate aryl bromide and magnesium in Et_2O in a 50-mL three-necked, round-bottomed flask. The Grignard solution was then added to a solution of (pyrrolyl)$_2$PCl (3.98 g, 20 mmol) in THF (50 mL) in a 100-mL three-necked, round-bottomed flask. The reaction mixture was stirred for 1 h at room temperature and heated to reflux for a further 6 h. After the reaction mixture had cooled to room temperature, the solvent was removed in vacuo and the residue was dissolved in 50 mL of toluene. The mixture was filtered and the solvent was removed in vacuo. The title compounds were crystallized from hot *n*-hexane.

(1,1′-Biphenyl-2-yl)bis(1-pyrrolyl)phosphane (12): Method 2, *M* = 316.11 g/mol, yield 84%. − ^{31}P NMR (166 MHz, $CDCl_3$): δ = 68.4. − ^{13}C NMR (166 MHz, $CDCl_3$): δ = 146.4 (d, J_{PC} = 27.7 Hz), 139.7 (d, J_{PC} = 5.7 Hz), 135.1 (d, J_{PC} = 13.4 Hz), 130.5 (d, J_{PC} = 11.5 Hz), 130.4, 129.8 (d, J_{PC} = 4.8 Hz), 128.7 (d, J_{PC} = 3.8 Hz), 127.9, 127.6, 127.5, 124.3 (d, J_{PC} = 14.3 Hz), 112.0 (d, J_{PC} = 3.8 Hz). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.25 (pt, 4 H), 6.7 (pquint, 4 H), 6.74−6.77 (m, 1 H), 6.96−6.98 (m, 2 H), 7.20−7.27 (m, 4 H), 7.33 (tt, *J* = 7.0 , *J* = 0.8 Hz, 1 H), 7.45 (td, *J* = 7.0, *J* = 0.8 Hz, 1 H). − MS (70 eV): *m*/*z* (%) = 316 (30) [M$^+$], 250 (15), 183 (100), 154 (30), 67 (15), 77 (5). − $C_{20}H_{17}N_2P$: calcd. C 75.9, H 5.4, N 8.9; found C 75.75, H 5.67, N 8.83.

[3,5-Bis(trifluoromethyl)phenyl]bis(1-pyrrolyl)phosphane (13): Method 2, *M* = 376.06 g/mol, yield 80%. − ^{31}P NMR (166 MHz, $CDCl_3$): δ = 64.1. − ^{13}C NMR (166 MHz, $CDCl_3$): δ = 113.5 (d, J_{PC} = 4.8 Hz), 123.9, 124.5 (d, J_{PC} = 15.2 Hz), 130, 130.3 m, 132 (d, J_{PC} = 3.8 Hz), 141 (d, J_{PC} = 11.44). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.30 (pt, *J* = 2.18 Hz, 4 H), 6.85 (pquint, *J* = 2.2, 4 H), 7.34 (s, 1 H), 7.35 (s, 1 H), 7.85 (s, 1 H). − MS (70 eV): *m*/*z* (%) = 376 (100) [M$^+$], 310 (87), 241 (17), 213 (4), 172 (4), 163 (38), 69 (5). − HRMS: calcd. for $C_{16}H_{11}N_2PF_6$ [M$^+$] 376.05640; found 376.05590.

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