A New Bidentate Aminophosphole−Olefin Ligand for the Rhodium-Catalyzed Hydroformylation of Mono- and Disubstituted Olefins

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Reaction of 1-bromo-2,5-diphenylphosphole with 10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine resulted in the formation of the corresponding aminophosphole **3**, which was structurally characterized. Reaction of **3** with $[Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4]$ and $[Rh(COD)_2][BF_4]$ afforded the complexes $[Rh_2(\mu\text{-}Cl)_2(\mathbf{3})_2]$ (**4**) and $[Rh(COD)(\mathbf{3})][BF_4]$ (**5**), respectively. In both complexes, characterized by NMR as well as by X-ray crystallography, ligand **3** behaves as a chelate through coordination of the phosphorus atom and the olefinic part of the ligand to the rhodium center. The activity of both complexes was tested in the hydroformylation of mono- and disubstituted olefins at 20 bar of CO/H_2 pressure. Complex **5** proves to be the most efficient catalyst.

Introduction

The electronic environment of the metal center in a transition-metal catalyst is a determining factor for both the catalytic performance and the selectivity of the catalyst. Careful ligand design can be used to make subtle changes to this electronic environment. Since the electronic properties of phosphine derivatives, stable carbenes, and nitrogen-containing compounds can be readily modified through changes to their substitution patterns, they are commonly found in many ligands of transition-metal catalysts. Recently it was shown that olefins, more commonly considered as substrates, can be functionalized and used as ligands in efficient catalytic systems.[1] Inspired by these results, we have been involved in the largely unexploited synthesis and study of mixed bidentate ligands featuring a phosphorus and an olefinic moiety,[2,3] as TROPP ligands discovered by Grutzmacher et al.[4] We reported on the synthesis of a dibenzo[*a*,*d*]cycloheptenyl dibenzophosphole ligand and the catalytic activity of its palladium(II) complex. This complex was found to be of particular interest for Suzuki−Miyaura cross-coupling in the synthesis of diaryl rings from halogenoaryls and phenylboronic acids.[5] The most significant features of this ligand are the rigid concave bidentate binding site and its strong π-accepting capacity, as it has been shown that TROPP ligands are able to stabilize anionic rhodium complexes, a specific ability of strongly electron withdrawing ligands.[6]

In the present paper we report the synthesis of a diphenylphosphole tethered to a dibenzoazepine moiety. This ligand also features a coordination site composed of a phosphole in close proximity to an olefin. The nitrogen atom of the dibenzoazepine is too close to the phosphole to coordinate a metal, but it does allow a mild and straightforward ligand synthesis. Interestingly, it was found that Rh(I) complexes of this new ligand exhibit promising activity in the hydroformylation of both mono- and disubstituted olefins.

Results and Discussion

Ligand **3** was synthesized in a one-pot synthetic approach from 1,1′-bis(2,5-diphenylphosphole) (**1**).[7] The first step involves the cleavage of the P−P bond with bromine in dichloromethane at low temperature to afford the 1-bromophosphole **2**.[7] This intermediate does not need to be isolated: addition of 1 equiv of 10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine to the crude reaction mixture in the presence of 2 equiv of triethylamine at low temperature univocally yielded **3**, which was recovered as a yellow solid in 80% yield (Scheme 1). The solid phosphole **3** proved to be very stable to both air and moisture.

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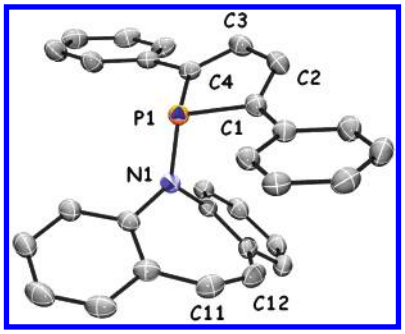
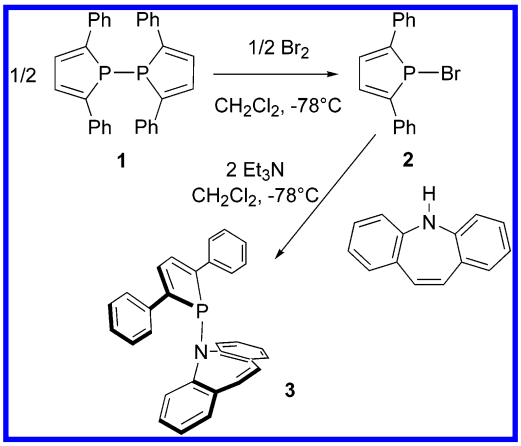


Figure 1. View of one molecule of **3**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P1−N1, 1.697(1); P1−C1, 1.825(1); P1−C4, 1.817(1); C1−C2, 1.354(2); C2−C3, 1.447(2); C3−C4, 1.350(2); N1−P1−C1, 108.60(5); N1−P1−C4, 107.56(5); C1−P1−C4, 91.07(6); P1−C1−C2, 108.5(1); C1−C2−C3, 115.1(1); C2−C3−C4, 115.3(1); C3−C4−P1, 108.8(1).

Scheme 1



Ligand **3** was fully characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. A view of one molecule of **3** is presented in Figure 1, with the most significant metric parameters listed in the corresponding legend. Crystal data and structure refinement details are presented in Table 1. The solid-state structure of **3** does not deserve special comment, and all data compare with those obtained for similar 2,5-diphenylphosphole derivatives.[5,8]

Three different rhodium precursors were used in an attempt to synthesize the corresponding Rh(I) complexes of **3**: $[Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4]$, $[Rh(COD)_2][BF_4]$, and the dimeric $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ complex. Unfortunately, reaction of **3** with $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ did not proceed cleanly and afforded a mixture of products. A detailed examination of the different coupling patterns observed in the ^{31}P NMR spectrum was used to elucidate the structure of the major product. The ^{31}P NMR signals of this species consist of a classical ABX spin system, with $^1J_{PRh} = 158.0, 110$ Hz and the large value $^2J_{PP} = 401.0$ Hz, which strongly suggest that two phosphorus atoms are coordinated to the metal in a trans fashion. We believe this to be due to the coordination of two ligand molecules, one probably behaving as a bidentate chelate and the second one as a monodentate ligand through coordination of the phosphorus atom only. We were not able to isolate this product from the reaction mixture.

A similar ABX spin system was observed in the product of the reaction of **3** with $^1/_2$ equiv of $[Rh(\eta^2\text{-}C_2H_4)_2Cl]_2$ in dichloromethane under reflux. In this case, the major product, however, gave rise to a doublet at 157.9 ppm. This major product could be crystallized from the crude reaction mixture using hexanes and isolated in 65% yield as an air- and moisture-stable solid (**4**; Scheme 2). Using NMR spectroscopy, **4** was fully characterized. It compromises a dimeric structure, resulting from the displacement of the two ethylene ligands by **3**. Complex **4** proved to be sensitive to neither air nor moisture. The proposed structure of **4**, on the basis of the NMR data, was confirmed by an X-ray crystal structure analysis. Its structure contains two square-planar rhodium centers bridged by two chloride atoms. A plot of the structure and the corresponding tables are presented in the Supporting Information.

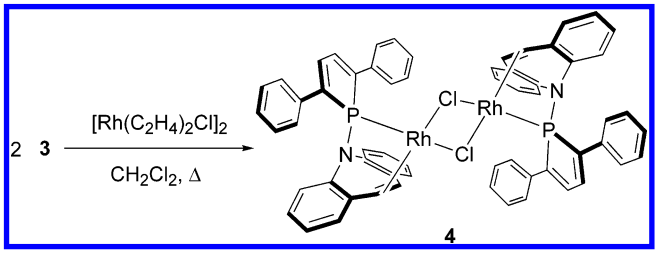
Finally, reaction of **3** with $[Rh(COD)_2][BF_4]$ in dichloromethane at room temperature cleanly yielded complex **5**, which was isolated as an air- and moisture-stable orange solid (Scheme 3). Coordination of the phosphorus atom was observed in the ^{31}P NMR spectrum and that of the olefin moiety in both the ^1H and the ^{13}C NMR spectrum. In the ^1H NMR spectrum a high-frequency shift is observed for the vinylic protons: from δ 6.04 ppm in **3** to δ 6.94 ppm in **5**. In the ^{13}C NMR spectrum, a low-frequency shift is observed for these two vinylic carbon atoms: from δ 131.1 ppm in **3** to δ 100.0 ppm in **5**. Similar

Table 1. Summary and of Data Collection and Structure Refinement Details for 3 and 5

	3	**5**
cryst size (mm)	0.20 × 0.20 × 0.20	0.22 × 0.11 × 0.09
empirical formula	$C_{30}H_{22}NP$	$C_{38}H_{34}NPRhBF_4 \cdot CH_2Cl_2$
mol mass	427.46	774.83
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	9.1980(10)	13.0450(10)
b (Å)	12.9790(10)	18.6660(10)
c (Å)	18.7910(10)	15.6270(10)
α (deg)	90.00	90.00
β (deg)	103.1260(10)	109.7510(10)
γ (deg)	90.00	90.00
V (Å^3)	2184.7(3)	3581.3(4)
Z	4	4
calcd density (g cm^{-3})	1.300	1.437
abs coeff (cm^{-1})	0.144	0.646
θ_{max} (deg)	30.03	30.03
F(000)	896	1580
index ranges	−12 to +12; −18 to +16; −26 to +26	−18 to +18; −23 to +26; −22 to +21
no. of rflns collected/indep	11 759/6367	18 499/10 414
no. of rflns used	4830	7941
R_{int}	0.0261	0.0213
abs cor: min, max	0.9717, 0.9717	0.8710, 0.9442
no. of params refined	289	435
no. of rflns/params	16	18
final R1[a]/wR2 ($I > 2\sigma(I)$)[b]	0.0422/0.1241	0.0463/0.1503
goodness of fit on F^2	1.076	1.054
diff peak/hole (e Å^{-3})	0.294(0.047)/ −0.404(0.047)	0.609(0.090)/ −0.740(0.090)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

Scheme 2



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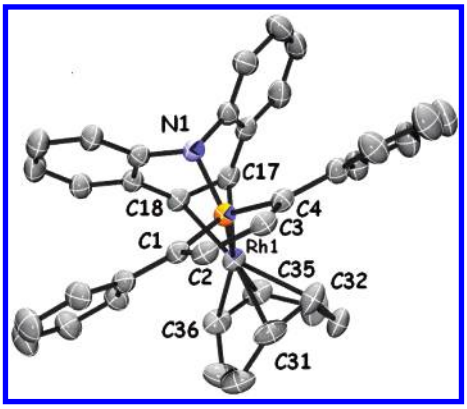
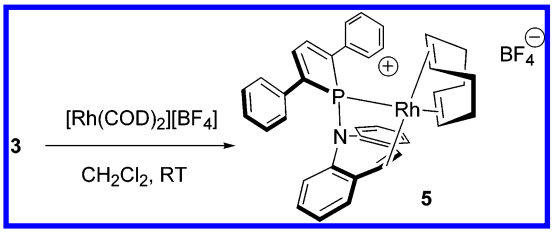


Figure 2. View of one molecule of **5**. The numbering is arbitrary and different from that used in NMR spectra. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh1−C17, 2.341(3); Rh1−C18, 2.286(3); Rh1−C31, 2.191(3); Rh1−C32, 2.185(3); Rh1−C35, 2.322(3); Rh1−C36, 2.308(3); Rh1−P1, 2.2116(7); C31−C32, 1.375(5); C35−C36, 1.353(5); C17−C18, 1.389(4); P1−N1, 1.717(2); P1−C1, 1.821(3); P1−C4, 1.833(3); C1−C2, 1.351(4); C2−C3, 1.455(4); C3−C4, 1.356(4); N1−P1−C1, 104.7(1); N1−P1−C4, 103.2(1); C1−P1−C4, 94.0(1); P1−C1−C2, 107.0(2); C1−C2−C3, 115.9(2); C2−C3−C4, 117.5(2); C3−C4−P1, 105.6(2).

Scheme 3

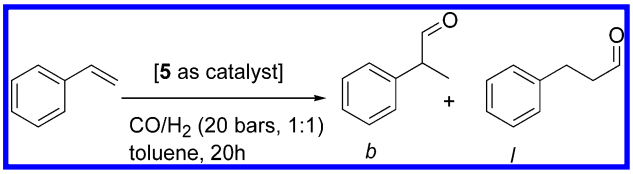


displacements were observed in Rh(I) complexes of the TROPP ligands and their functional derivatives.[3,6a]

Crystals of **5**, suitable for X-ray crystal structure analysis, were obtained by slow diffusion of hexanes into a dichloromethane solution of the complex at 4 °C. A view of one molecule of **5** is presented in Figure 2, and the most significant bond lengths and bond angles are listed in the corresponding legend. Crystal data and structural refinement details are presented in Table 1. As can be seen, the overall geometry around the central rhodium is planar, and both the phosphorus and the olefinic part of the ligand are coordinated in a cis fashion. Metric parameters in **5** compare with those recorded for other TROPP Rh(I) complexes. At 2.2116(7) Å the Rh(1)−P(1) bond compares with similar Rh−P bonds in other reported TROPP derivatives such as the complexes $[Rh(^{Me}TROPP)_2]^+$ (2.226(1) and 2.260(1) Å) and [Rh(bis{TROPphenylphosphano}-ethane)$_2$]$^+$ (2.208(2) and 2.227(2) Å).[3,6a] Similar conclusions can be drawn for the coordinated C═C bond, which is lengthened (1.389(4) Å in **5** vs 1.339(2) in **3**).

The catalytic activity of complexes **4** and **5** was investigated in the hydroformylation of several olefins. No reaction was observed when the olefin ligand was used as a substrate using 0.5% amount of catalyst at 80 °C for 24 h. In experiments using 1-octene as a substrate, the catalysts showed encouraging turnover rates but little or no selectivity toward the branched or the linear product. Preliminary tests on styrene revealed that complex **5** is a moderately active yet highly selective catalyst (Scheme 4). When the reaction was carried out at room temperature with low CO/H_2 pressure (20 bar) and a catalyst charge of 0.5%, a conversion of 75% was reached after 20 h

Scheme 4



Scheme 5

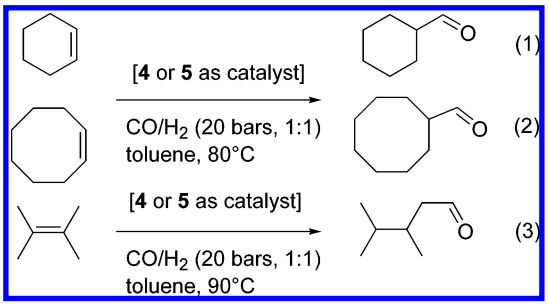


Table 2. Catalysis Results from Hydroformylation of Styrene with 20 bar of CO/H_2 (1/1) in Toluene ([styrene] = 0.28 M), with Complex 5 as Catalyst

temp (°C)	cat. (%)	yield (%)	TOF (h^{-1})	*b*/*l*
room temp	1	75	3.75	96/4
room temp	0.5	75	7.5	94/6
40	0.5	80	8	90/10

with a 94/6 branched/linear ratio (*b*/*l*). Increasing the catalyst charge to 1% led to a similar conversion in 20 h with a *b*/*l* ratio of 96/4. The results of these experiments are reported in Table 2. Complex **4** did not promote this particular reaction. We also found that using Rh(acac)$(CO)_2$ precursor in the presence of an excess amount of ligand (20 equiv) yielded significant amounts of aldehyde, albeit at a lower conversion. We therefore did not further pursue this method.

The substrates cyclohexene and cyclooctene were used to investigate the conversion of disubstituted olefins by catalysts **4** and **5** (Scheme 5, eqs 1 and 2). As expected, complex **5** turned out to be the most efficient catalyst. With a low CO/H_2 pressure of 20 bar at 80 °C, the conversion of cyclohexene proceeded with a 40% yield using only 0.025 mol % of catalyst at TOF = 400 h^{-1}. This performance compares with those of known catalytic systems.[9,10] Less satisfying results were obtained with dimer **4**, which only yielded a TOF of 137.5. A TON of 290 was obtained in the conversion of cyclooctene into cyclooctanecarbaldehyde (29% of conversion in 24 h at 80 °C using 0.1% of catalyst). Results obtained in the conversion of cylohexene and cyclooctene are presented in Table 3. Finally, we tested the activity of complex **4** and **5** in the isomerization/hydroformylation process of the tetrasubstituted tetramethylethylene into 3,4-dimethylpentanal (Table 3; Scheme 5, eq 3). Very few catalysts are able to promote this reaction. To the best of our knowledge, the most efficient system was reported by Breit in 2004 using 2,6-disusbtituted phosphinines (TOF = 118 h^{-1} under 60 bar of syngas at 100 °C in toluene).[10] More recently we reported on the use of a (η^5-cyclophosphahexadienyl)rhodium complex to catalyze this transformation, albeit with a lower TOF.[11] Complex **5** catalyzes the transformation

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Table 3. Catalysis Results from Hydroformylation of Cyclohexene, Cyclooctene, and 2,3-Dimethylbut-2-ene with 20 bar of CO/H_2 (1/1) in Toluene ([cyclohexene] = [cyclooctene] = 1.66 M and [2,3-dimethylbut-2-ene] = 1.38 M) with Catalysts 4 and 5

cat.	temp (°C)	substrate	time (h)	cat. (%)	yield (%)	TOF (h^{-1})
5	80	cyclohexene	4	0.025	40	400
4	80	cyclohexene	4	0.1	55	137.5
5	80	cyclooctene	24	0.1	29	290
5	90	C_2Me_4	48	0.1	24	5
5	90	C_2Me_4	24	0.1	14.5	6
4	90	C_2Me_4	24	0.1	12	5

using a CO/H_2 pressure of 20 bar at 90 °C. The TOF observed is modest but encouraging, considering the milder experimental conditions in comparison to those reported earlier.

In conclusion, we succeeded in the synthesis of a mixed bidentate aminophosphole−alkene ligand. Importantly, this new ligand, when coordinated to the cationic $[Rh(COD)]^+$ fragment, proves to be an efficient hydroformylation catalyst, especially in the case of 1,2- and 1,1-disubstituted olefin derivatives. To the best of our knowledge, similar ligands were never employed in homogeneous catalyzed hydroformylations. Theoretical studies are currently ongoing, but one may propose that the good activity of ligand **3** results from the strong π-accepting capacities of both the phosphorus and the olefin moiety of the ligand. Further studies exploring the use of our ligand in other synthetic transformations are also underway, and the results will be reported in due course.

Experimental Section

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glovebox techniques and dry deoxygenated solvents. Dry hexanes were obtained by distillation from Na/benzophenone. Dry dichloromethane was distilled on P_2O_5, dry triethylamine on KOH, and dry toluene on metallic Na. Nuclear magnetic resonance spectra were recorded on a Bruker AC-300 SY spectrometer operating at 300.0 MHz for ^1H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P. Solvent peaks are used as internal reference relative to Me_4Si for ^1H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to an 85% H_3PO_4 external reference. Coupling constants are given in hertz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. 1,1′-Bis(2,5-diphenylphosphole) (**1**) was prepared by following a published procedure,[7] and its precursor, the 1,2,5-triphenylphosphole, is easily available on a multigram scale from the simple reaction of dichlorophenylphosphine with 1,4-diphenyl-1,3-butadiene.[12] All other reagents and chemicals were obtained commercially and used as received. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. Hydroformylation reactions were performed in a stainless steel autoclave, equipped with a magnetic stirrer, and heated by an oil bath. Hydrogen and carbon monoxide were purchased from Air Liquide. The GC yields were determined on a PERICHROM 2100 gas chromatograph equipped with a 30 m × 0.22 mm PERICHROM column (SILICONE OV1, CP-SIL 5 CB).

Synthesis of Phosphole 3. To a solution of the bis(phosphole) **1** (600 mg, 1.275 mmol) in dichloromethane (5 mL) was added bromine (66 μL, 1.275 mmol) at −78 °C. The solution turned from orange to red and was stirred at room temperature for 30 min. Completion of the reaction was confirmed by ^{31}P NMR. A solution of 10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine (495 mg, 2.551 mmol) and triethylamine (711 μL, 5.102 mmol) in dichloromethane (5 mL) was slowly added to the bromophosphole solution at −78 °C. The reaction was complete after 30 min, as observed by ^{31}P NMR. The reaction mixture was concentrated in vacuo, washed with hydrochloric acid, extracted with DCM (2 × 15 mL), and dried ($MgSO_4$), and the solvent was removed under reduced pressure to yield crude **3** as a yellow solid. Washing with methanol afforded the purified ligand **3** in 80% yield. Anal. Calcd for $C_{30}H_{22}NP$: C, 84.29; H, 5.19. Found: C, 84.15; H, 5.21. ^1H NMR (C_6D_6): δ 6.04 (s, 2 H, C*H*═C*H*), 6.44 (d, $^3J_{HP}$ = 10.2 Hz, 2 H, $H_{\beta-phosphole}$), 6.75−6.89 (m, 4 H, H_{phenyl}), 6.97−7.06 (m, 2 H, H_{phenyl}), 7.14 (m, 2 H, H_{phenyl}), 7.23 (m, 4 H, H_{phenyl}), 7.33 (m, 2 H, H_{phenyl}), 7.60 (d, $^3J_{HH}$ = 7.2 Hz, 4 H, H_{phenyl}). ^{13}C NMR (C_6D_6): δ 126.0 (C_{phenyl}), 127.2 (C_{phenyl}), 127.8 (d, J_{CP} = 2.7 Hz, C_{phenyl}), 128.4 (C_{phenyl}), 128.9 (C_{phenyl}), 129.0 (C_{phenyl}), 129.1 (C_{phenyl}), 131.1 (*C*H═*C*H), 131.6 (d, $^2J_{CP}$ = 13.4 Hz, $C_{\beta-phosphole}$), 135.8 (d, $^2J_{CP}$ = 1.6 Hz, C_{ipso}), 137.9 (d, $^1J_{CP}$ = 17.6 Hz, $C_{\alpha-phosphole}$), 147.3 (d, J_{CP} = 8.8 Hz, C_{phenyl}), 150.0 (d, J_{CP} = 3.8 Hz, C_{phenyl}). ^{31}P NMR (C_6D_6): 62.9 (d, $^3J_{PH}$ = 10.2 Hz).

Synthesis of Complex 4. To a solution of $[Rh(C_2H_4)_2Cl]_2$ (22.7 mg, 0.058 mmol) in dichloromethane (2 mL) was added a solution of **3** (50 mg, 0.117 mmol) in dichloromethane (3 mL) dropwise at room temperature. The mixture was refluxed for 2 h and then cooled to 4 °C. Complex **4** was then isolated by slow diffusion of hexanes into the crude reaction mixture. After filtration, the red-orange powder was dried under vacuum (43 mg, 65%). Anal. Calcd for $C_{60}H_{44}Cl_2N_2P_2Rh_2$: C, 63.68; H, 3.92. Found: C, 63.31; H, 3.91. ^1H NMR (CD_2Cl_2): δ 4.89 (s, 4 H, *H*C═C*H*), 6.62−6.74 (m, 8 H, H_{phenyl}), 6.79−6.85 (m, 4 H, H_{phenyl}), 6.90 (d, 4 H, $^3J_{PH}$ = 26.7 Hz, $H_{\beta-phosphole}$), 7.13−7.32 (m, 16 H, H_{phenyl}), 8.13 (d, 8 H, $^3J_{HH}$ = 7.1 Hz, H_{phenyl}). ^{13}C NMR (CD_2Cl_2): 62.5 (d, $^1J_{CRh}$ = 15.1 Hz, H*C*═*C*H), 127.6 (d, J_{CRh} = 2.1 Hz, C_{phenyl}), 128.1 (C_{phenyl}), 128.4 (d, J_{CP} = 4.6 Hz, C_{phenyl}), 128.7 (d, J_{CRh} = 3.4 Hz, C_{phenyl}), 129.1 (C_{phenyl}), 129.5 (C_{phenyl}), 129.7 (d, J_{CP} = 3.5 Hz, C_{phenyl}), 134.1 (d, $^2J_{CP}$ = 16.8 Hz, $C_{\beta-phosphole}$), 135.8 (d, $^2J_{CP}$ = 13.3 Hz, C_{ipso}), 141.4 (d, $^1J_{CP}$ = 52.7 Hz, $C_{\alpha-phosphole}$), 141.9 (d, J_{CP} = 8.9 Hz, C_{phenyl}), 143.6 (C_{phenyl}). ^{31}P NMR (CD_2Cl_2): 157.95 (dt, $^3J_{PH}$ = 26.7 Hz, $^1J_{PRh}$ = 196.8 Hz).

Synthesis of Complex 5. A solution of **3** (50 mg, 0.117 mmol) in dichloromethane (3 mL) was added dropwise at room temperature to a solution of $[Rh(COD)_2][BF_4]$ (47.5 mg, 0.117 mmol) in dichloromethane (3 mL). After 20 min, the reaction mixture was concentrated in vacuo. Hexane (20 mL) was added, and the mixture was stirred for 1 h. The resultant orange-brown solid was filtered off, washed with hexane, and dried (82 mg, 97%). Anal. Calcd for $C_{38}H_{34}BF_4NPRh$: C, 62.92; H, 4.72. Found: C, 63.02; H, 4.78. ^1H NMR (CD_2Cl_2): δ 2.26−2.74 (m, 8 H, CH_2 of COD), 4.74−4.77 (m, 2 H, C*H* of COD), 5.92−5.96 (m, 2 H, C*H* of COD), 6.94 (d, $^2J_{HRh}$ = 1.1 Hz, 2 H, C*H*═C*H*), 7.0 (d, $^3J_{PH}$ = 26.7 Hz, 2 H, $H_{\beta-phosphole}$), 7.06−7.16 (m, 8 H, H_{phenyl}), 7.37−7.40 (m, 4 H, H_{phenyl}), 7.57 (d, J = 7.3 Hz, 2 H, H_{phenyl}), 7.76−7.83 (m, 4 H, H_{phenyl}). ^{13}C NMR (CD_2Cl_2): δ 28.0 (*C*H_2 of COD), 29.3 (*C*H_2 of COD), 29.7 (*C*H_2 of COD), 31.4 (*C*H_2 of COD), 96.5 (d, $^1J_{CRh}$ = 9.7 Hz, *C*H_{cis-P} of COD), 100.1 (d, $^1J_{CRh}$ = 6 Hz, *C*H═*C*H), 116.1 (dd, $^1J_{CRh}$ = 9.7 Hz, $^1J_{CP}$ = 4.5 Hz, *C*$H_{trans-P}$ of COD), 127.6 (d, J_{CP} = 5.2 Hz, C_{phenyl}), 128.5 (C_{phenyl}), 129.2 (C_{phenyl}), 129.3 (d, J_{CP} = 1.4 Hz, C_{phenyl}), 129.7 (C_{phenyl}), 130.6 (d, J_{CP} = 3.8 Hz, C_{phenyl}), 131.4 (C_{phenyl}), 133.4 (d, J_{CP} = 13 Hz, C_{phenyl}), 135.5 (d, $^2J_{CP}$ = 16.2 Hz, $C_{\beta-phosphole}$), 138.7 (dd, $^2J_{CP}$ = 7.2 Hz, $^3J_{CRh}$ = 1.2 Hz, C_{ipso}), 141.5 (dd, $^1J_{CP}$ = 49.3 Hz, $^2J_{CRh}$ = 1.8 Hz, $C_{\alpha-phosphole}$), 142.3 (dd, J_{CP} = 3.2 Hz, J_{CRh} = 1.4 Hz, C_{phenyl}). ^{31}P NMR (CD_2Cl_2): δ 141.35 (dt, $^3J_{PH}$ = 26.7 Hz, $^1J_{PRh}$ = 149.4 Hz).

X-ray Crystallography for Complexes 3 and 5. Yellow blocks of **3** crystallized by slow diffusion of hexanes into a saturated dichloromethane solution of **3**. Orange needles of complex **5** were obtained by diffusing hexanes at 4 °C into a dichloromethane solution of complex **5**. Data were collected on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.710 73 Å) X-ray source

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and a graphite monochromator at 150 K. Experimental details are described in Table 1. The crystal structures were solved using SIR 97[13] and SHELXL97.[14] ORTEP drawings were made using ORTEP III for Windows.[15] These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax, (internat.) +44-1223/336-033; e-mail, deposit@ccdc.cam.ac.uk).

General Procedure for Styrene Hydroformylation. To a solution of styrene (95 μL, 0.826 mmol) in toluene (3 mL) was added the catalyst **5** (3 mg, 0.004 mmol for 0.5%; 6 mg, 0.008 mmol for 1%) under nitrogen. After complete dissolution of the complex, the solution was placed in the high-pressure apparatus, which was then charged with CO (10 bar) and then H_2 (10 bar). After the reaction time at the temperature indicated in Table 2, the autoclave was cooled to room temperature and depressurized and the reaction mixture was analyzed by GC with internal standard and correction factors.

General Procedure for Cyclohexene and Cyclooctene Hydroformylation. To a solution of cyclohexene (840 μL, 8.29 mmol) or cyclooctene (1080 μL, 8.29 mmol) in toluene (5 mL) was added catalyst **5** (1.5 mg, 2.1 μmol for 0.025%; 6 mg, 8.3 μmol for 0.1%) or catalyst **4** (4.7 mg, 4.2 μmol for 0.1% in rhodium) under nitrogen. After complete dissolution of the complex, the solution was placed in the high-pressure apparatus, which was then charged with CO (10 bar) and then H_2 (10 bar). After the reaction time at the temperature indicated in Table 3, the autoclave was cooled to room temperature and depressurized and the reaction mixture was analyzed by GC with internal standard and correction factors.

General Procedure for 2,3-Dimethylbut-2-ene Hydroformylation. To a solution of 2,3-dimethylbut-2-ene (490 μL, 4.13 mmol) in toluene (3 mL) was added the catalyst **5** (3 mg, 4.1 μmol for 0.1%) or the catalyst **4** (2.3 mg, 2.1 μmol for 0.1% in rhodium) under nitrogen. After complete dissolution of the complex, the solution was placed in the high-pressure apparatus, which was then charged with CO (10 bar) and then H_2 (10 bar). After the reaction time at the temperature indicated in Table 3, the autoclave was cooled to room temperature and depressurized and the reaction mixture was analyzed by GC with internal standard and correction factors.

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Supporting Information Available: CIF files and tables giving crystallographic data for **4** (including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters). This material is available free of charge via the Internet at http://pubs.acs.org.

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