η^5-Rhodium(I) Complexes of a λ^4-Phosphinine Anion: Syntheses, X-ray Crystal Structures, and Application in the Catalyzed Hydroformylation of Olefins

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2,6-Bis(trimethylsilyl)-4,5-diphenylphosphinine **1** and 2,3,5,6-tetraphenylphosphinine **2** react with *tert*-butyllithium to afford the expected λ^4-phosphinine anions **3** and **4**. These anions react with $[Rh(COD)Cl]_2$ to yield the corresponding η^5-complexes **5** and **6**, in which coordination occurs through the anionic carbocyclic π-system of the ring. Both complexes were fully characterized by conventional spectroscopic techniques, and their X-ray crystals structures were recorded. The catalytic activity of **5** and **6** was tested in the hydroformylation of olefins. Good conversion yields and turnover frequencies were obtained in the hydroformylation of styrene and cyclohexene under mild conditions with low catalyst loading. The hydroformylation of styrene occurs with a high regioselectivity (93/7) in favor of the branched isomer. Interestingly, catalyst **6** catalyzes the transformation of 2,3-dimethyl-2-butene into 3,4-dimethylpentanal through a tandem isomerization/hydroformylation process.

Introduction

Low-coordinated phosphorus ligands possess very specific electronic properties that markedly differ from that of their nitrogen counterparts and classical tertiary phosphines.[1] Obviously, the intrinsic high reactivity of the P=C double bonded systems implies that, in practice, only kinetically (sterically crowded) or thermodynamically stabilized (conjugation, aromaticity) ligands can be employed in catalysis. Recent works by many groups, including ours, have definitively demonstrated that such compounds should find important applications. Thus, phospha- and diphosphaferrocenes already proved to be valuable systems in different catalytic processes such as ring opening of epoxides,[2] enantioselective hydrogenation,[3] Suzuki cross-coupling,[4] Miyaura synthesis of boronic esters,[5] enantionselective isomerization of allyl alcohols,[6] asymmetric allylic alkylation,[7] and cycloaddition.[8] Importantly, the groups of Yoshifuji, Ozawa, and Ito[9] and Brookhardt[10] also showed that cationic palladium complexes of sterically hindered phosphaalkene could be successfully employed in a series of catalytic transformations of significant synthetic value. Another important molecule in this series is the phosphinine, the phosphorus equivalent of pyridine.[11] Although many synthetic routes, which allow the preparation of numerous functional derivatives, have been devised, these ligands were essentially employed in coordination chemistry and more especially for the stabilization of highly reduced species.[12] Only a few articles are relative to their use in homogeneous catalysis. Undoubtedly the most significant report was made by the group of Breit in collaboration with the BASF firm. Rhodium(I) complexes of 2,4,6-trisubstituted phosphinines were found to be active catalysts in the hydroformylation of olefins under relatively mild conditions.[13,14] Importantly, some of these complexes were

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able to achieve an isomerization prior to hydroformylation of tetrasubstituted olefins such as 2,3-dimethyl-2-butene to form 3,4-dimethylpentanal.[14] Finally, an η^6-phosphinine Fe(0) complex was used for the catalyzed synthesis of functional pyridines from alkynes and nitriles.[15]

Why are phosphinines so rarely employed in catalysis? Many experiments and attempts performed in our laboratories have shown that, in some cases, phosphinine complexes are highly sensitive toward nucleophilic attack on the phosphorus atom. Although this reactivity has not been fully rationalized, one may propose that coordination on a relatively electron-poor metal fragment induces a significant decrease of the aromatic character and the concomitant increase of the positive charge at phosphorus. Therefore non-kinetically protected phosphinines are not good candidates for catalytic purposes. An illustration was given by the reaction of a neutral platinum(II) 2,2′-biphosphinine complex with traces of alcohol.[16]

Thus their use in catalysis would probably be restricted to very specific transformations that avoid the presence of nucleophilic and/or strongly basic reagents. An interesting way to circumvent the limitations discussed above is to exploit the reactivity of the ring in the synthesis of highly functionalized phosphinine-based derivatives. In fact, it is well known that phosphinines react with various reagents to give a variety of monocyclic and bicyclic structures.[11] Recently, Breit and colleagues have shown that a barrelene ligand, which is available through a [4+2] cycloaddition of benzyne with a 2,4,6-triaryl-substituted phosphinine, could be employed as ligand in the rhodium-catalyzed hydroformylation of olefins.[17,18] Three years ago, we launched a large program aiming at exploring the potential of λ^4-phosphinine anions[19] as ligands. We found that these molecules could yield interesting complexes depending on both the nature of the substitution scheme of the ring and the nature of the metal fragment. Thus, when two ancillary groups are present at the periphery of the ring, η^1-P-complexes can be formed.[20,21] Some of these complexes have found interesting applications in catalysis. In the absence of chelating ligands, η^2- or η^5-complexes are favored. Thus η^2-(P−C) Pt(II) and Pd(II) complexes have recently been synthesized and structurally characterized.[22] Some π-complexes with Fe(II) had been previously evidenced by Märkl, Dimroth, and Massa,[23] and more recently we showed that lithium salts of the anions also adopt the η^5-bonding mode.[24] Other complexes of these anions featuring slightly different coordination mode were also isolated.[25]

Herein we report on the successful synthesis of η^5-Rh(I) complexes of λ^4-phosphinine anions and on their use in the catalyzed hydroformylation of olefins.

Results and Discussion

For this study, the 2,6-bis(trimethylsilyl)-3,5-bis(diphenylphosphinine) **1** and 2,3,5,6-tetraphenylphosphinine **2** were chosen for their availability and their resistance toward air and moisture. Additionally, these two ligands present very different substitution schemes especially regarding the steric bulk around phosphorus. Reactivity of phosphinines toward nucleophiles is now well established,[19,24] and we found that *t*-BuLi reacts readily at the phosphorus atom of **1** and **2** in THF at −78 °C. The complete formation of λ^4-phosphinine anions **3** and **4**, respectively, was confirmed by ^{31}P NMR spectroscopy. As previously shown, the formation of the λ^4-phosphinine anion results in a very important upfield shift (from 269.4 ppm in **1** to −25.9 ppm in **3** and from 206.0 ppm in **2** to −9.0 in **4**). Anion **3** was also structurally characterized as its $[Li(Et_2O)_2]$ salt (see Supporting Information). Anions **3** and **4** were reacted with half an equivalent of $[Rh(COD)Cl]_2$ at room temperature in THF to provide complexes **5** and **6** respectively. After one night of stirring at room temperature in the case of **5**, and a few minutes for **6**, the reaction was complete as attested by the change in color (from intense pink to orange in the case of **5**, from dark blue to orange for **6**). In ^{31}P NMR spectroscopy, the formation of both complexes was evidenced by the appearance of a doublet at 17.41 ppm for **5** ($^1J_{RhP} = 7.3$ Hz) and −4.67 ppm for **6** ($^1J_{RhP} = 9.1$ Hz). The low magnitude of these $^1J_{RhP}$ coupling constants strongly suggested that η^5-coordination had occurred, a large $^1J_{RhP}$ coupling constant being expected for η^1-complexes (for example, a value of 103.4 Hz was measured for an η^1-phosphinine complex of rhodium[21]). Both species were isolated pure as yellow and bright orange powders, respectively, and fully characterized by ^{1}H and ^{13}C NMR and elemental analysis (Scheme 2). Importantly, complexes **5** and **6** were found to be air-stable, and no apparent decomposition was observed after exposure for several weeks.

Suitable crystals of **5** and **6** were obtained, and their X-ray structures were determined. Views of one molecule of **5** and **6** are presented in Figures 1 and 2, respectively, and significant metric parameters (bond distances and angles) are listed below. As expected from ^{31}P NMR spectroscopy, **5** and **6** feature an η^5-coordination of the ligand to the metal, coordination occurring

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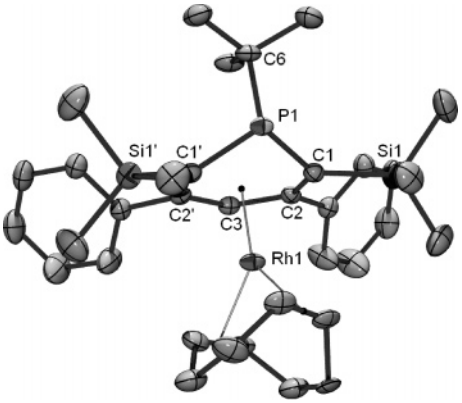
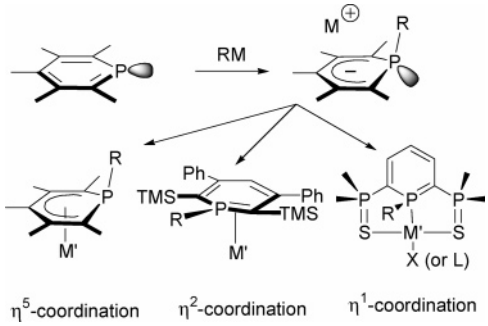
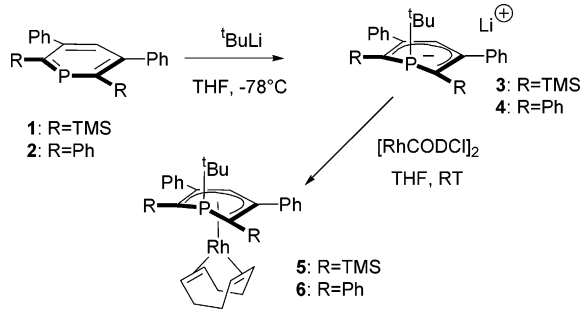


Figure 1. ORTEP view of one molecule of complexe **5**. Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the assignment of NMR spectra. The complex co-crystallized with one molecule of hexane, which as been omitted for clarity. Note that the molecule contains a crystallographic mirror plane. Relevant distances (Å) and bond angles (deg): Rh1−C1, 2.387(2); Rh1−C2, 2.298(2); Rh1−C3, 2.217(3); P1−C1, 1.831(2); P1−C6, 1.912(3); Si1−C1, 1.902(2); C1−C2, 1.416(3); C2−C3, 1.431(3); C1−P1−C1′, 98.3(2); C1−P1−C6, 105.4(1); C2−C1−P1, 118.4(2); C1−C2−C3, 121.4(2); C2−C3−C2′, 126.1(3); P1−C1−Si1, 116.3(1); P1−C1−Rh1, 90.6(1); C1−Rh−C1′, 70.9(1); C2−Rh1−C2′, 67.4(1); Si1−C1−Rh1, 118.2(1).

Scheme 1



Scheme 2



through the pentadienyl fragment of the phosphinine backbone. In both structures, relatively long C−C bond distances (from 1.416(3) to 1.431(3) Å in **5** and from 1.408(3) to 1.439(3) Å in **6**) account for the delocalization of the negative charge in the carbocyclic system. These data are similar to those recorded in η^5-lithium complexes and free anions (cryptated species).[24] As expected, the phosphorus atom in **5** and **6** is sp^3-hybridized ($\sum$ angles = 309.1° in **5** and 308.3° in **6**) and the lone pair is still available though sterically protected by the presence of the *t*-Bu group at phosphorus and the two

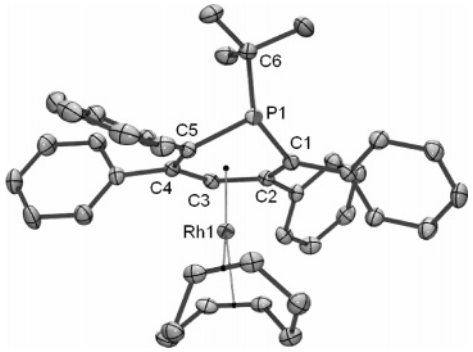
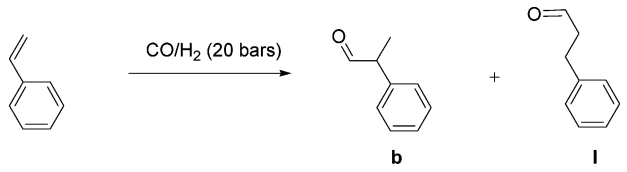


Figure 2. ORTEP view of one molecule of complex **6**. Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the assignment of NMR spectra. Relevant distances (Å) and bond angles (deg): Rh1−C1, 2.420(2); Rh1−C2, 2.336(2); Rh1−C3, 2.208(2); Rh1−C4, 2.226(2); Rh1−C5, 2.282(2); P1−C1, 1.834(2); P1−C5, 1.830(2); P1−C6, 1.896(2); C1−C2, 1.408(3); C2−C3, 1.439(3); C3−C4, 1.426(3); C4−C5, 1.422(3); C5−P1−C1, 96.5(1); C5−P1−C6, 105.5(1); C1−P1−C6, 106.3(1); C2−C1−P1, 118.9(2); C1−C2−C3, 121.8(2); C4−C3−C2, 126.5(2); C5−C4−C3, 118.8(2); C4−C5−P1, 121.6(2); C5−Rh1−C1, 71.05(7); P1−C1−Rh1, 88.91(8).

Scheme 3



substituents at the α-position of phosphorus. This probably accounts for the good resistance of the two complexes toward air oxidation.

These two complexes were then evaluated as catalysts in the hydroformalytion of alkenes. The experimental conditions employed are close to those reported by Breit et al. with λ^3-phosphinines as ligands.[13,14] One major difference, however, is found in the metal-to-ligand ratio: indeed, 5−20 equiv of ligand per equivalent of [Rh(CO)$_2$acac] was used by Breit et al. In our experiments, as the catalyst is preformed, metal/ligand ratio has to be 1:1. To draw a precise comparison between the two catalytic systems, the substrate/metal ratios were chosen as close as possible to those used by Breit. First, the classical hydroformylation of styrene was tested in toluene with complexes **5** and **6** as catalyst (Scheme 3, Table 2). In this reaction, two products can be obtained, the linear 3-phenylpropanal and the branched 2-phenylpropanal, the latter being the most valuable one. Complexes **5** and **6** showed an interesting activity, and a good regioselectivity was obtained in both cases using the ratio Rh:ligand:styrene = 1:1:200, at temperatures from 25 to 40 °C and under a pressure of 20 bar. Complex **6** proved to be more active than **5**. A conversion of 20.3% was reached after 4 h at 40 °C for complex **5**, whereas with **6**, 24.2% of the substrate was converted at room temperature. Turnover frequencies for **5** and **6** were 10.2 h^{-1} at 40 °C and 16.1 h^{-1} at 25 °C, respectively. One may reasonably propose that this difference results from the steric crowding induced by the silyl groups in **5**. Regioselectivity was also enhanced on going from **5** to **6**. A selectivity of 93% in favor of the branched derivative was recorded for **6**, whereas 89%

Table 1. Crystal Data and Structural Refinement Details for Structures of Compounds 5 and 6

	5	6
cryst size [mm]	0.20 × 0.18 × 0.18	0.20 × 0.14 × 0.12
empirical formula	$C_{41}H_{64}PRhSi_2$	$C_{41}H_{42}PRh$
molecular mass	746.98	668.63
cryst syst	monoclinic	monoclinic
space group	$P2_1/m$	$P2_1/n$
a [Å]	8.447(5)	8.6680(10)
b [Å]	24.218(5)	19.3790(10)
c [Å]	9.788(5)	18.8010(10)
α [deg]	90.00	90.00
β [deg]	100.410(5)	91.8700(10)
γ [deg]	90.00	90.00
V [Å]^3	1969.4(16)	3156.5(4)
Z	2	4
calcd density [g·cm^{-3}]	1.260	1.407
abs coefficient [cm^{-1}]	0.562	0.621
$2\theta_{max}$ [deg]	30.02	29.95
F(000)	796	1392
index ranges	−11 11; −34 15; −10 10	−12 12; −24 27; −26 26
no. of reflns collected/indep	6822/5022	14 887/9120
no. of reflns used	4182	6967
R_{int}	0.0184	0.0296
abs corr	0.8959 min., 0.9056 max.	0.8859 min., 0.9292 max.
no. of params refined	235	403
no. of reflns/params	17	17
final R1[a]/wR2 [$I > 2\sigma(I)$][b]	0.0409/0.1111	0.0400 /0.1033
goodness-of-fit on F^2	1.092	1.021
diff peak/hole [e·Å^{-3}]	0.894(0.084)/−0.688(0.084)	1.273(0.094)/−1.193(0.094)

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

Table 2. Catalysis Results from Hydroformylation of Styrene with 20 bar CO/H_2 (1:1) in Toluene (c_o = 0.42 M), with 0.5% of Catalyst

catalyst	temp (°C)	time (h)	conversion (%)	TOF (h^{-1})	b/l
5	40	4	20.3	10.2	89/11
5	40	24	94.0	7.8	89/11
6	25	3	24.2	16.1	93/7
6	40	20	100.0		93/7

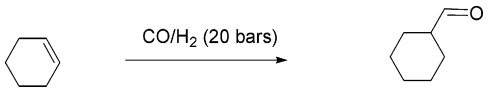
Table 3. Catalysis Results from Hydroformylation of Cyclohexene and 2,3-Dimethylbut-2-ene with Catalyst 6, 20 bar CO/H_2 (1:1) in Toluene (c_o = 2.36 M), at 90 °C

substrate	catalyst charge (%)	time (h)	conversion (%)	TOF (h^{-1})
cyclohexene	0.024	4	62.2	647.9
2,3-dimethylbut-2-ene	0.1	47	18.5	4

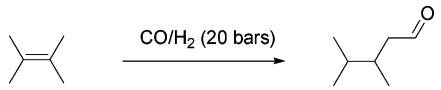
was obtained for **5**. These results can be compared to those collected by Breit for the same reaction. At the same temperature, better turnover frequency and regioselectivity were measured (TOF = 28.7 h^{-1}, selectivity = 95%).[13] However a high ligand loading with respect to the metal (Rh:ligand = 1:5) had to be used with phosphinines. A comparison can also be drawn with the dirhodium(I) bisimidazolium carbene complex of Peris and Fernandez. A turnover frequency of 16.7 h^{-1} was recorded under more drastic conditions (40 °C, 80 bar), with a Rh:ligand ratio of 400. This catalyst showed a higher selectivity (99%) than our system.[26]

Catalyst **6** was thus tested in the hydroformylation of more substituted substrates, namely, cyclohexene and 2,3-dimethylbut-2-ene. In the first case, very good results were obtained. Indeed, in 4 h, 62.2% of the substrate was converted to cyclohexanecarbaldehyde under mild conditions (20 bar of pressure, 90 °C) and

Scheme 4



Scheme 5



only a low loading of catalyst was needed (ratio **6**:cyclohexene = 1:4160). Furthermore the TOF was found to be rather good (648 h^{-1}). This performance can be compared to the 1959 h^{-1} obtained by Breit's using 40 bar of pressure and a Rh:ligand ratio of 1:20.[14] Note that, recently, a Rh(I) complex featuring a 1-phosphabarrelene as ligand was also successfully employed in this transformation.[17] A high TOF of 11 429 h^{-1} was measured, with a pressure of 10 bar at 120 °C using the same Rh:ligand ratio of 1:20 and a higher initial concentration (c_o = 3.56 M vs 2.36 M in the present case and with Breit's phosphinine ligand[14]). In the case of the 2,3-dimethylbut-2-ene, isomerization takes place prior to hydroformylation, which then, in turn, yields 3,4-dimethylpentanal as final product. This reaction is difficult to perform and requires, at the industrial scale, very high pressures and temperatures.[27] A quite promising result was obtained using 20 bar CO/H_2 (1:1) in toluene at 90 °C with the ratio **6**:substrate = 1:1000. A TOF of 4 h^{-1} was obtained with a conversion of 18.5% after 47 h. Under much more drastic conditions (60 bar, 100 °C) phosphinine-based catalysts reached a TOF of 118 h^{-1}.[14] Complex **6** exhibits an interesting catalytic activity in the hydroformylation of styrene, cyclohexene, and 2,3-dimethylbut-2-ene under very mild conditions. Its performances compare with those of phosphinine-

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based systems. To further understand what type of intermediate was involved in the catalysis and to be sure that our system was not a λ^3-phosphinine-complex precursor, a THF solution of **6** was placed for half an hour in the hydroformylation conditions (CO/H_2, 1:1, 20 bar). The yellow solution turned red. The ^{31}P NMR spectrum consisted of a broad peak at 45 ppm, accounting for the formation of fluxional compounds. The same experiment was performed with only CO (20 bar) and only H_2 (20 bar), giving the same result in the first case, the complex being unaltered by H_2 even after 3 h under pressure. In all circumstances, no formation of λ^3-phosphinine was observed. At this point, the question of the stability of our system toward ligand elimination can be discussed, as the ratio ligand/metal is very low compared to literature. Interestingly, the regioselectivity of catalyst **6** in the case of the styrene hydroformylation is not as good as the one obtained with a unmodified rhodium catalyst ($Rh_4(CO)_{12}$), which reaches 98% for the branched product at 20 °C.[28] The 93% obtained in the case of **6** is an undubious proof that the ligand is still present on the metal center during the catalysis. In general, hydroformylation catalysts feature two-electron-donor ligands such as phosphine or carbene. Complex **6** is a rare example of π-complex-based catalysts. Indeed, during the past decade, Alper et al. developed an original zwitterionic Rh(I) catalyst featuring the tetraphenylborate anion coordinated in an η^6-fashion to the metal center. These catalysts also proved to be very active in the hydroformylation of olefins, such as styrene, and alkynes.[29]

Conclusion

In conclusion, we have synthesized and fully characterized the first η^5-coordinated Rh(I) complexes of λ^4-phosphinine anions. These new complexes behave as active and regioselective catalysts in the hydroformylation of olefins. Importantly, the difficult hydroformylation of a tetrasubstituted alkene into the corresponding aldehyde was performed under very mild conditions. Further studies will focus on the possible mechanism of this transformation as well as on the evaluation of these new type of catalysts in other processes. These studies are currently in progress in our laboratories, and 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 THF and hexanes were obtained by distillation from Na/benzophenone. Dry dichloromethane was distilled on P_2O_5 and dry toluene on metallic Na. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 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 a 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; bs, broad singlet. *tert*-Buthyllithium in ether solution was purchased from Aldrich. Phosphinines **1** and **2** were prepared following procedures described in refs 30 and 31. Elemental analyses were performed by the "Service d'analyses du CNRS" at Gif sur Yvette. Hydroformylation reactions were performed in a stainless steel autoclave fitted with a glass container, equipped with a magnetic stirrer, and heated by an oil bath. Hydrogen and carbon monoxide were purchased from Air Liquide.

Synthesis of 5. To a solution of phosphinine **1** (200 mg, 0.509 mmol) in THF (5 mL) was added a solution of *t*-BuLi in ether (300 μL, 0.509 mmol, 1.7 M) at −78 °C. The solution turned from colorless to bright pink. The solution was warmed to room temperature, and completion of the reaction was checked by ^{31}P NMR. $[RhCODCl]_2$ (0.26 mmol, 126 mg) was added to the mixture at room temperature. The solution was left stirring for one night. The solution obtained was then orange. Solvent was removed in vacuo. Salts were removed by extraction and filtration in hexane (3 × 5 mL) over Celite. Solvent was removed in vacuo, and the compound was isolated as a yellow powder (285 mg, 85%). Anal. Calcd for $C_{35}H_{50}PRhSi_2$: C, 63.61; H, 7.63. Found: C, 63.79; H, 7.84. ^1H NMR (C_6D_6): 0.24 (s, 18 H, Si−(CH_3)$_3$), 1.03 (d, $^3J_{HP}$ = 12.0 Hz, 9 H, P-C-(CH_3)), 1.85, 2.18 (2 m, 8 H, CH_2 of COD), 4.32 (m, 4 H, *C*H of COD), 5.49 (s, 1 H, H_4), 7.16−7.23, 7.45−7.49 (2 m, 10 H, C*H* of phenyls). ^{13}C NMR (C_6D_6): 3.41 (d, $^3J_{CP}$ = 8 Hz, Si-(CH_3)$_3$), 27.83 (d, $^2J_{CP}$ = 17 Hz, P-C-(CH_3)$_3$), 31.57 (s, CH_2 of COD), 39.03 (d, $^2J_{CP}$ = 36 Hz, P-*C*-(CH_3)$_3$), 59.4 (d, $^1J_{CP}$ = 54 Hz, C_2-TMS), 73.63 (s, *C*H of COD), 95.13 (d, $^3J_{CP}$ = 6 Hz, C_4H), 128.01, 128.14, 130.03 (3 s, *C*H of phenyls), 128.73 (s, C_{ipso} of phenyls), 143.54 (s, C_3-Ph). ^{31}P NMR (C_6D_6): −17.21 (d, $^2J_{PRh}$ = 7.3 Hz).

Synthesis of 6. To a solution of phosphinine **2** (200 mg, 0.5 mmol) in THF (5 mL) was added a solution of *t*-BuLi in ether (300 μL, 0.5 mmol, 1.7 M) at −78 °C. The solution turned from colorless to dark blue. The solution was warmed to room temperature, and completion of the reaction was checked by ^{31}P NMR. $[RhCODCl]_2$ (0.25 mmol, 124 mg) was added to the mixture at room temperature. The solution became green and then orange within a few minutes. Solvent was removed in vacuo. Salts were removed by extraction and filtration in dichloromethane (3 × 5 mL) over Celite. Solvent was removed in vacuo, and the compound was isolated as an orange powder (264 mg, 88%). Anal. Calcd for $C_{41}H_{42}PRh$: C, 73.65; H, 6.33. Found: C, 73.72; H, 6.60. ^1H NMR ($CDCl_3$): 0.67 (d, $^3J_{HP}$ = 10.5 Hz, 9 H, P-C-(CH_3)$_3$), 1.91, 2.06 (2 m, 8 H, CH_2 of COD), 3.88 (m, 4 H, C*H* of COD), 5.32 (d, $^4J_{HP}$ = 10.5 Hz, 1 H, H_4), 6.95−7.04, 7.18−7.30 (2 m, 10 H, C*H* of phenyls). ^{13}C NMR ($CDCl_3$): 27.70 (d, $^2J_{CP}$ = 13 Hz, P-C-(CH_3)$_3$), 31.33 (bs, CH_2 of COD), 42.34 (d, $^2J_{CP}$ = 39 Hz, P-*C*-(CH_3)$_3$), masked by solvent peak (*C*H of COD), 80.23 (d, $^1J_{CP}$ = 17 Hz, $^1J_{CRh}$ = 4.0 Hz, C_2-Ph), 87.91 (d, $^3J_{CP}$ = 5 Hz, C_4H), 119.91 (dd, $^2J_{CP}$ = 6 Hz, $^1J_{CRh}$ = 3 Hz, C_3-Ph), 125.03 (d, $^4J_{CP}$ = 2 Hz, $C_{meta}H$ of α-phenyls), 127.19 (s, $C_{para}H$ of α-phenyls), 127.32, 128.01, 130.60 (3 s, *C*H of β-phenyls), 131.28 (d, $^3J_{CP}$ = 12 Hz, $C_{ortho}H$ of α-phenyls), 140.82 (s, C_{ipso} of β-phenyls), 143.26 (d, $^2J_{CP}$ = 24 Hz, C_{ipso} of α-phenyls). ^{31}P NMR ($CDCl_3$): −3.53 (d, $^2J_{PRh}$ = 9.0 Hz).

X-ray Structural Determination. Yellow blocks of complex **5** crystallized by slow evaporation of a saturated solution in hexanes. Orange needles of complex **6** were obtained by diffusing hexanes into a dichloromethane solution of the

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complex **6**. Data were collected on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.71070 Å) X-ray source and a graphite monochromator at 150 K. Experimental details are described in Table 1. The crystal structures were solved using SIR 97[32] and SHELXL-97.[33] ORTEP drawings were made using ORTEP III for Windows.[34] 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 CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

General Procedure for Styrene Hydroformylation. To a solution of styrene (243 μL, 2.11 mmol) in toluene (5 mL) was added the catalyst **5** or **6** (7 mg, 0.01 mmol) 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 (20 bar). After reaction time, the autoclave was cooled to room temperature and depressurized, then the reaction mixture was analyzed by GC with internal standard and correction factors.

General Procedure for Cyclohexene Hydroformylation. To a solution of cyclohexene (810 μL, 8 mmol) in toluene (3 mL) was added the catalyst **6** (1.9 μmol, 64 μL of a solution of the complex in toluene, c = 0.03 mol·L^{-1}) under nitrogen. The solution was placed in the high-pressure apparatus, which was then charged with CO (10 bar) and then H_2 (20 bar). After reaction time, the autoclave was cooled to room temperature and depressurized, then 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 (3.57 mL, 30 mmol) in toluene (3 mL) was added the catalyst **6** (20 mg, 0.03 mmol) under nitrogen. The solution was placed in the high-pressure apparatus, which was then charged with CO (10 bar) and then H_2 (20 bar). After reaction time, the autoclave was cooled to room temperature and depressurized, then the reaction mixture was analyzed by GC with internal standard and correction factors. Aldehyde selectivity ≥ 99%, regioselectivity ≥ 99%.

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Supporting Information Available: Tables of crystal data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen coordinates, and ORTEP views of one molecule of compounds **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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