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Modular Phosphole-Methano-Bridged-Phosphine(Borane) Ligands. Application to Rhodium-Catalyzed Reactions

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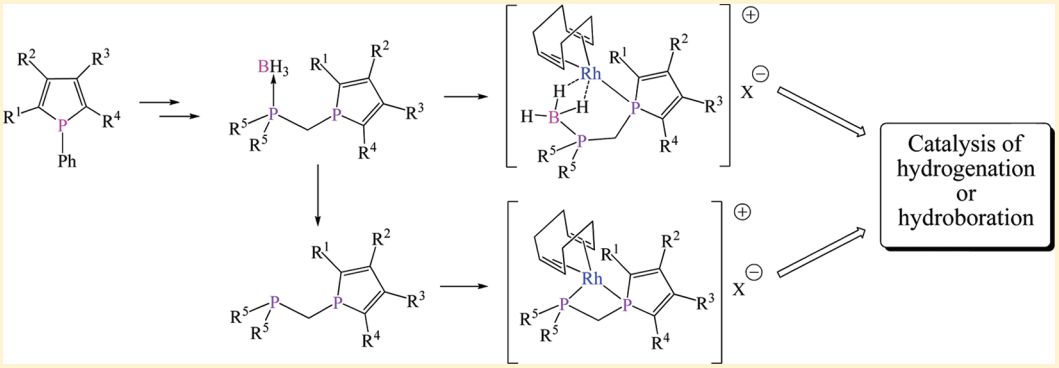
Supporting Information



ABSTRACT: The synthesis of the phospholyl(phosphinoborane)methane air- and moisture-stable hybrid ligands **4a−f**, starting from 1-phenylphospholes **1a−d**, was performed via P−C bond coupling on the methano bridge. Two strategies were investigated, according to the phospholyl moiety used as a nucleophilic or an electrophilic reagent. In the first pathway, the phospholyl anions react with the easily available (chloromethyl)diphenylphosphine−borane **3** to afford ligands **4a−d** in 29−67% isolated yields. In the second pathway, the phospholyl(dicyclohexylphosphinoborane)methane ligands **4e**,**f** were synthesized in 18−23% yields, through a nucleophilic substitution on the cyanophosphole. Removal of the BH_3 moiety on **4a−c** assisted by DABCO leads to the hybrid phospholyl(diphenylphosphino)methanes **5a−c**. Compounds **4** and **5** were fully characterized by multinuclear NMR spectroscopy (^1H, ^{31}P, ^{13}C, ^{11}B), mass spectrometry, and elemental analysis, and the X-ray crystal structures of **4a**,**c** and **5a**,**b** have been established. Ligands **5a**,**b** were used to prepare the cationic rhodium complexes $[Rh(\eta^4\text{-COD})(\mathbf{5a})]^+$ (**8a′**), $[Rh(\eta^4\text{-COD})(\mathbf{5b})]^+$ (**8b**), $[Rh(\mathbf{5a})_2]^+$ (**9a′**), and $[Rh(\mathbf{5b})_2]^+$ (**9b**), containing four-membered chelate rings with BF_4^- or $CF_3SO_3^-$ as counterions. Ligands **4a−f** were also used to synthesize the $[Rh(\eta^4\text{-COD})(\mathbf{4})]^+$ chelate complexes **10a−f**, resulting from coordination of the phospholyl part and the BH_3 group via a η^2 mode with two bridging B−H−Rh 3c−2e bonds, as shown by the X-ray crystal structures of the complexes **10b**,**c**. Rhodium complexes **8** and **10** isolated or formed in situ with ligands **4** and **5** were studied for catalytic hydrogenation of methyl 2-(acetamidomethyl)acrylate (**11**) and hydroboration of styrene (**13**) with catecholborane. In both reactions, the catalytic systems prepared either from the phospholyl(phosphinoborane)methane ligands **4** or the corresponding free ligands **5**, gave good to excellent conversions. In addition, the regioselectivity of the catalyzed hydroboration is slightly influenced using these ligands. Finally, the use of hybrid phospholyl(phosphinoborane)methanes as ligands offers a new, efficient way to improve catalytic processes, for designing both the structure and the electronic properties of the catalyst, or still to implement it without removing the borane protecting group.

INTRODUCTION

Bidentate phosphorus-containing ligands display a widespread use in coordination catalysis.[1] One subclass is small-bite-angle diphosphines in which the two phosphorus centers are separated only by a single-atom linker unit, the archetypical example being 1,1-bis(diphenylphosphino)methane (dppm).[2] This diphosphinomethane ligand family is well-established for giving flexible coordination modes, being monodentate or bidentate in either chelating (resulting in highly strained four-membered metallacycles) or bridging geometries (including A-frame complexes).[1a]

Such unusual coordination behavior of these small-bite-angle diphosphines has been recently exploited in a range of catalytic processes. Indeed, diphosphinomethane complexes have been shown to be excellent precursors for the polymerization and

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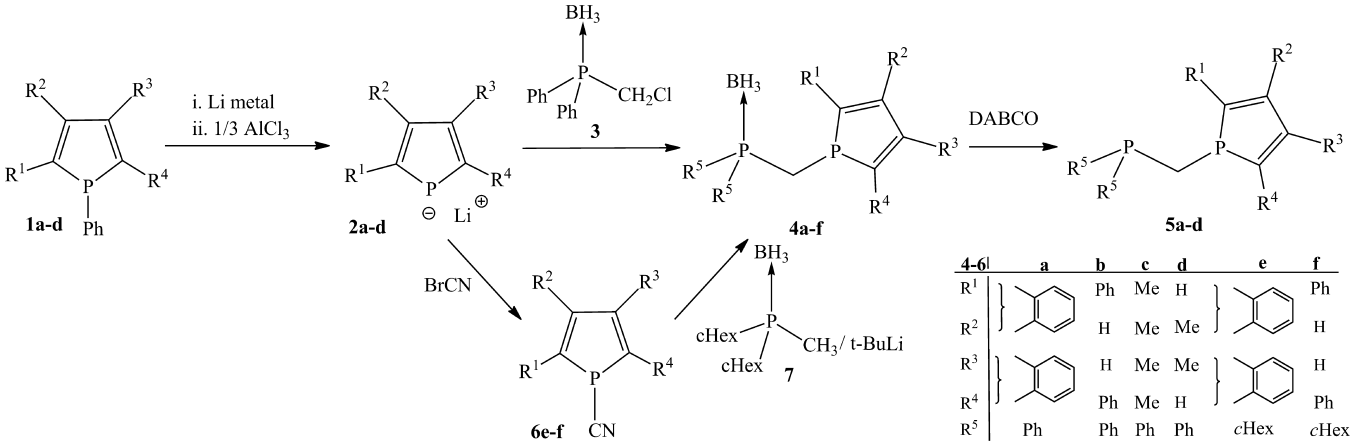
Scheme 1. Reaction Pathways for Synthesis of Ligands 4a−f and 5a−d



oligomerization of ethylene,[3] hydrogenation of a broad range of substrates,[4] hydrosilylation of simple ketones,[5] and C−C bond coupling reactions.[6]

The reactivity and catalytic properties of diphosphinomethane complexes depend largely on the substituents on the phosphino groups.[7] Especially bulky substituents, in particular alkyl, are better σ-donors toward the metal center than diphosphine ligands bearing smaller substituents and consequently stabilize four-membered chelate structures.[8] It is worth noting that the stereoselective synthesis of P-chirogenic diphosphinomethane ($RR'PCH_2PRR'$) ligands has been recently described, as well as their use for enantioselective metal-catalyzed reactions,[9] chiral-cluster chemistry,[10] and coordination polymers.[11]

However, unsymmetrical diphosphinomethane ($R_2PCH_2PR'_2$) compounds possessing chemically and electronically different phosphorus atoms have attracted less attention, and to the best of our knowledge, their catalytic activity has been only investigated in hydrogenation.[12] A priori, a hemilabile behavior could be envisaged with such ligands.[12c] In order to extend the chemistry of the unsymmetrical dppm-type ligands, we considered their synthesis with one phospholyl moiety on the methano bridge. Phosphole ligands are sterically and electronically different from phosphines and are also efficient in promoting homogeneous transition-metal catalysis.[13] Such a synthesis is challenging, since both phosphorus moieties with their different donation/back-donation abilities can introduce steric and electronic dissymmetry in the coordination sphere of the metal center. Therefore, the design of such ligands is a powerful tool for stereochemically controlling the substrates and reagents in the coordination sphere of the metal during the catalytic cycle.

As part of our ongoing program on organophosphorus synthesis using phosphine−borane chemistry,[14] we investigated the synthesis of phospholylphosphinomethane ligands by P−C bond formation on the methano bridge, using electrophilic or nucleophilic phosphine−borane building blocks. In a preliminary work, we reported the first synthesis of dibenzophospholyl(diphenylphosphinoborane)methane ligand through a Pd-catalyzed reaction of (chloromethyl)-diphenylphosphine−borane with the dibenzophospholyl anion.[15] Using this methodology and a second new one, we describe in this full paper the synthesis of several substituted phospholyl(phosphinoborane)methanes and the corresponding free modified dppm. The applications of both kinds of ligands were investigated in catalyzed hydrogenation or hydroboration reactions with cationic rhodium complexes.

RESULTS AND DISCUSSION

1. Synthesis of Phospholyl(phosphino)methane Ligands. The synthesis of phospholyl(diphenylphosphino)-methane ligands was performed following two strategies starting from 1-phenylphospholes **1a−d**, depending on whether the phospholyl reagent is a nucleophilic or an electrophilic species, as shown in Scheme 1.

In the first pathway, the reductive cleavage of the exocyclic phosphorus−phenyl bond of **1a−d** with an excess of metallic lithium, followed by neutralization of PhLi using $AlCl_3$ ($^1/_3$ equiv), led quantitatively to the lithium phospholide reagents **2a−d**. Their reaction with the easily available (chloromethyl)-diphenylphosphine−borane **3** affords the corresponding hybrid phospholyl(phosphinoborane)methane **4a−d** by chloride substitution.

The nucleophilic substitution of chloroalkyl derivatives with the lithium phospholide is relatively rare,[16] because this anion is a poor nucleophilic reagent due to the delocalization of the negative charge within the heterocycle. Moreover, the chloro substituent is also a poor leaving group. Indeed, the direct reaction of the anions **2a−d** (1 equiv) with the (chloromethyl)-phosphine−borane **3** in THF at room temperature over 48 h resulted in low yields (<10%) in each case. Better results (32−52%) were obtained using catalytic conditions with the palladium complex [$Pd(OAc)_2$(dppf)].[17] However, in spite of these conditions, the complete conversion of **3** was not achieved and small amounts of methyldiphenylphosphine−borane,[18] dppf−diborane adducts,[19] and free phospholyl-(phosphino)methane **5** were observed.[20] Complete conversion was achieved by reaction of 2 equiv of **2a−d** with **3** even in the absence of Pd(II), in THF at room temperature during 48 h, affording compounds **4a−d** in high isolated yields (29−67%).

In the second pathway, the phospholyl-(dicyclohexylphosphinoborane)methane **4e,f** were obtained in 18 and 23% yields, respectively, by reaction of the α-carbanion resulting from the deprotonation of the dicyclohexylmethyl-phosphine−borane **7** with the corresponding cyanophosphole **6** (Scheme 1).

Compounds **4** were generally isolated as air- and moisture-stable solids and were fully characterized by conventional NMR techniques (^{31}P, ^1H, ^{13}C, ^{11}B), mass spectrometry, elemental analysis, and single-crystal X-ray analyses. $^{31}P\{^1H\}$ NMR

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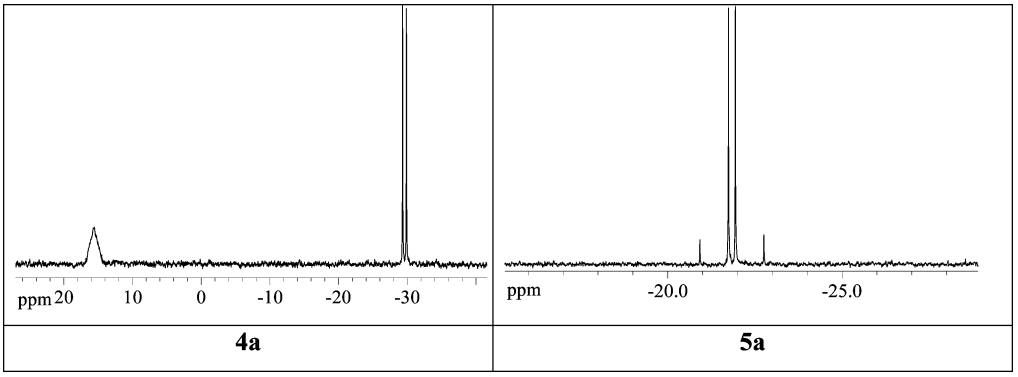

Figure 1. $^{31}P\{^{1}H\}$ NMR spectra of **4a** and **5a**.

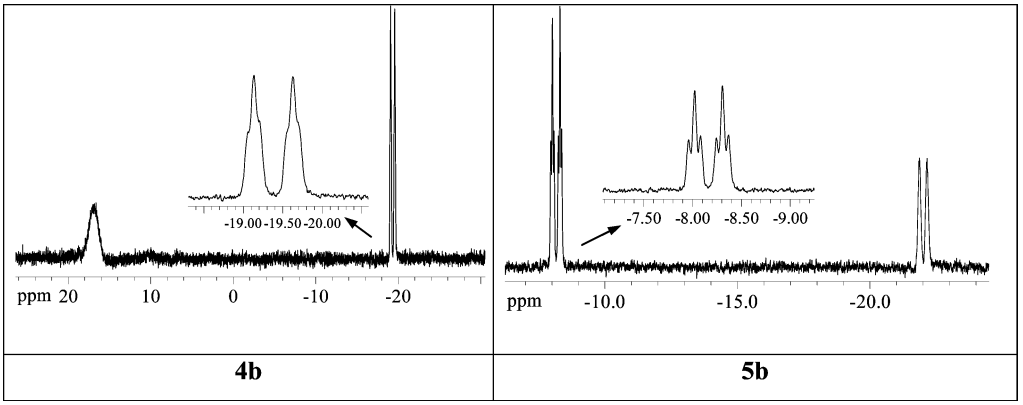

Figure 2. ^{31}P NMR spectra of **4b** and **5b**.[21]

spectra showed two groups of signals: a doublet for the phosphorus atom of the phospholyl part P(1) and a broad lower field signal for that of the phosphino group P(2), which is consistent with bonding to the quadrupolar boron atom (Figure 1). In the ^{31}P NMR spectrum of **4b**, the phosphole phosphorus atom P(1) resonated as an enlarged pseudotriplet due to the coupling with two equivalent protons of the heterocycle and the phosphine phosphorus atom (Figure 2).

Interestingly, the ^{31}P chemical shifts of **4a**−**d** lie systematically at high field relative to both **1a**−**d** and **3** (δ +23.7 ppm), around 20 and 8 ppm away for phospholyl-P(1) and phosphino-P(2), respectively (see the Supporting Information). The more basic $P(cHex)_2$ moiety induces a displacement of chemical shifts of P(1) toward lower field (2 ppm for **4e** with respect to **4a** and 6 ppm for **4f** vs **4b**). The presence of the BH_3 moiety to the P(2) atom results in larger H−P(2) coupling constants (ca. 10 Hz) than for H−P(1) (∼2 Hz) (see the Supporting Information).

Suitable crystals for X-ray analysis were obtained by recrystallization from CH_2Cl_2/*n*-pentane at −20 °C. The molecular view of the BH_3-protected ligand **4a** has already been reported.[15] The crystal structure of **4c** is shown in Figure 3. A selection of relevant bond lengths and angles of **4a,c** is given in the Supporting Information. The two X-ray crystal structures of **4a**[15] and **4c** clearly reveal the presence of the BH_3 group coordinated to PPh_2 with P(2)−B(1) bond lengths of 1.9085(17) and 1.9152(19) Å, respectively.

The phosphorus atom of the phosphino group adopts a tetrahedral geometry, as confirmed by the angles about the P(2) atom in the range of 104−114°. The P(1)−C(5)−P(2) angles of 110.20(7)° for **4a** and 109.48(8)° for **4c** are close to

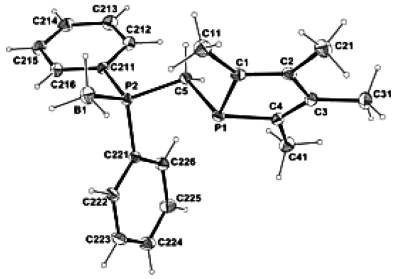

Figure 3. Molecular view of **4c** with the atom-labeling scheme. Ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

the corresponding value reported for the bis(diphenylphosphino)methane−borane ligand (dppm·BH_3).[22] These angles around the bridging carbon atom are consistent with a tetrahedral geometry at the methylene carbon atom. In both ligands, the phosphole ring is slightly bent with respect to the P(1)−C(5)−P(2) plane, making dihedral angles of 83.06(4)° for **4a** and 82.44(7)° for **4c**. The distances and angles in the phosphole ring are similar to those previously reported for common phosphole compounds.[23] In each case, the phosphorus P(1) of the phosphole ring is slightly out of the C(1)C(2)C(3)C(4) plane by 0.140(1) and 0.262(3) Å, respectively, as already observed in phosphole ligands.[24]

In the last step, the BH_3 decomplexation reaction was performed using DABCO, as previously described[25] (Scheme 1). Phospholyl(diphenylphosphino)methane ligands **5a**−**c** were quantitatively isolated and fully characterized by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy, mass spectrometry (DCI), elemental

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analyses, and single-crystal X-ray analyses. The $^{31}P\{^{1}H\}$ NMR spectra display AX systems for the two nonequivalent phosphorus atoms, except for ligand **5a**, which exhibits an AB system (Figure 1), consistent with two phosphorus atoms in close electronic environments. It is worth mentioning that the loss of BH_3 results not only in resonances of P(2) at higher field but also in a significant displacement of the P(1) chemical shifts to lower field (around 10 ppm), revealing a lower electron density and thus an electron transfer toward the PPh_2 moiety. In addition, the ^{31}P spectrum of **5b** shows the resonance of the P(1) atom at δ −8.17 ppm, displayed as a doublet of sharp triplets as previously observed for **4b** ($J_{HP(1)}$ = 10.2 Hz, $J_{P(1)P(2)}$ = 46.0 Hz; Figure 2). The molecular structures of **5a,b** have been established by single-crystal X-ray diffraction studies.

The molecular view of **5a** is shown in Figure 4 (for **5b** see the Supporting Information). The lone pairs of the two phosphorus atoms point away from each other, as indicated by the lone pair−P(1)−C(5)−P(2) torsion angles of 132° for **5a** and 160° for **5b** (the lone pair has been figured as a virtual H position). The phosphorus geometry of the two P(1) and P(2) atoms is pyramidal in both ligands **5a,b** with the sum of the three C−P−C angles lying between 290 and 304°.

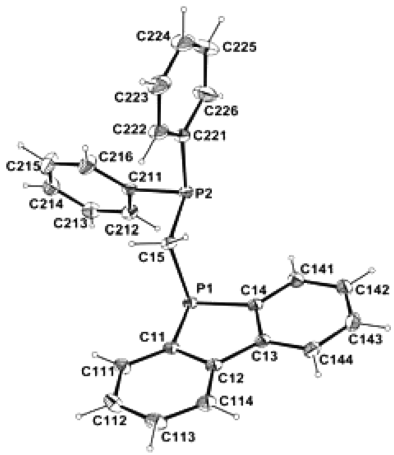


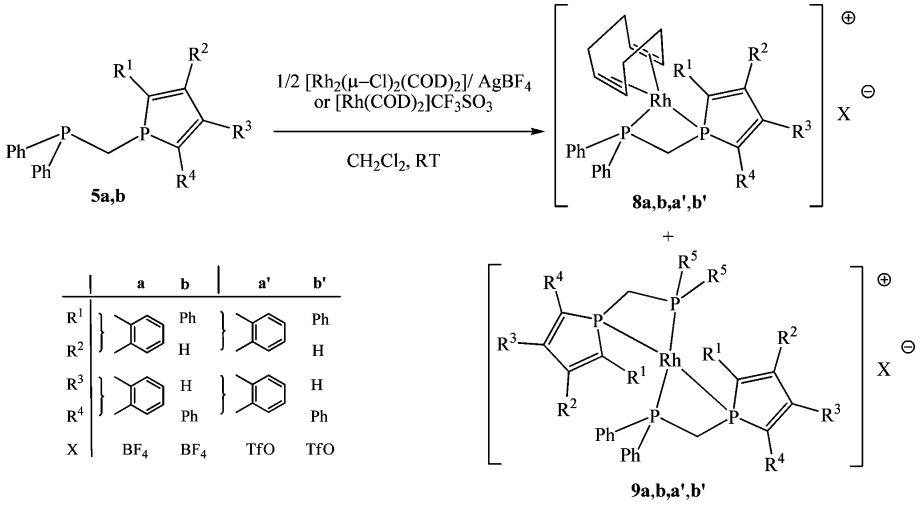
Figure 4. Molecular view of **5a** (only one molecule represented) with the atom-labeling scheme. Ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

As for the two BH_3 protected ligands **4a,c**, the bridging carbon atom is tetrahedral and the P(1)−C(5)−P(2) plane is slightly bent with respect to the phosphole ring (dihedral angles of 77.67(8)° [74.65(8)°] for **5a** and 86.5(6)° for **5b**). The P(1)−C(5)−P(2) angles (109° for **5a** and 117.7(6)° for **5b**) are higher than the corresponding value (106°) reported for the dppm ligand,[26] presumably related to the steric bulk of the phospholyl moiety. The BH_3 deprotection does not influence the bond lengths within the phospholyl(diphenylphosphino)-methane framework in **5a,b**, and even the bond angles are not significantly affected. Indeed, all bond lengths and bond angles of the phosphole rings compare favorably to those of other common phosphole compounds, and the P(1) atom is slightly out of the C(1)C(2)C(3)C(4) planes by 0.082(1) and 0.19(2) Å, respectively.

2. Synthesis of Rhodium Complexes. The reaction of $[Rh_2(\mu-Cl)_2(\eta^4\text{-COD})_2]$ with 2 equiv of **5a,b** in dichloromethane at −90 °C, using $AgBF_4$ as a halide abstracting agent and warming slowly to room temperature, yielded the cationic rhodium complexes $[Rh(\eta^4\text{-COD})(\mathbf{5})][BF_4]$ (**8a,b**, respectively) (Scheme 2). An alternative synthesis was also developed using the cationic precursor $[Rh(\eta^4\text{-COD})_2][CF_3SO_3]$ with a stoichiometric amount of **5a,b** under similar conditions.

Complexes **8a′,b** gave yellow moderately air-stable powders after evaporating the solvent. As all attempts at purification failed, they were identified in solution by ^{1}H and ^{31}P NMR spectroscopy and mass spectrometry. FAB-MS spectra in positive mode displayed a strong ion peak of m/z 593 for **8a′** and 645 for **8b**, corresponding to the $[Rh(\eta^4\text{-COD})$-(phospholyl(diphenylphosphino)methane)$]^+$ fragment. The $^{31}P\{^{1}H\}$ NMR spectra of **8a′,b** consisted of two groups of sharp doublet of doublets due to the P−P and P−Rh couplings (see the Supporting Information), represented by the cross peaks on the COSY 2D $^{31}P\{^{1}H\}$−$^{31}P\{^{1}H\}$ spectrum and interpreted as an AMX spin system (see the Supporting Information). The higher field doublet of doublets pattern can be assigned to the P(2) atom of the diphenylphosphino group and the lower field doublet of doublets to the P(1) atom of the phospholyl group, via ^{1}H−$^{31}P\{^{1}H\}$ HMQC experiments. Moreover, the high-field chemical shift signals observed for

Scheme 2



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both P(1) and P(2) atoms with respect to the free ligands **5a,b** are typical of a four-membered chelate ring.[27]

In all cases, traces of $[Rh(\mathbf{5})_2]X$ complexes **9a′,b** were also observed by $^{31}P\{^1H\}$ NMR. Complexes **9a′,b** were independently prepared from the $[Rh_2(\mu\text{-}Cl)_2(\eta^4\text{-}COD)_2]$ or $[Rh(\eta^4\text{-}COD)_2][CF_3SO_3]$ precursors. After evaporation of the solvent, complexes **9a′,b** were isolated as yellow air-sensitive powders and all attempts to isolate them failed. They were identified in solution by ^1H and ^{31}P NMR and mass spectrometry. The positive ion FAB-MS spectra display a strong ion peak of m/z 867 for **9a′** and 971 for **9b**, which correspond to the $[Rh\{phospholyl(diphenylphosphino)methane\}_2]^+$ fragment.

The $^{31}P\{^1H\}$ NMR spectrum of **9a′** consisted of two groups of signals, each one containing eight sharp lines derived from an AA′MXX′ spin system (M = Rh, Figure 5). This is consistent

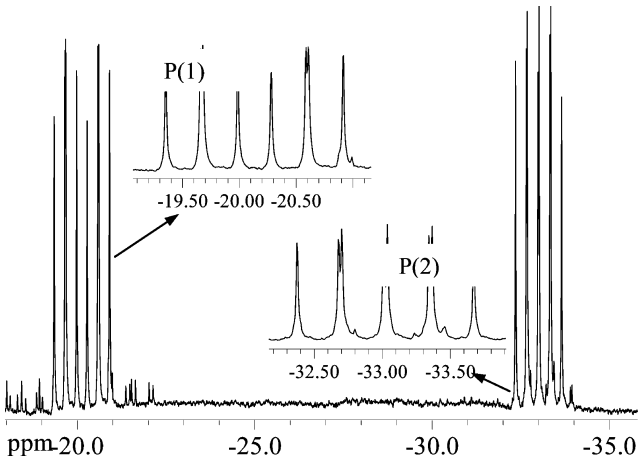


Figure 5. $^{31}P\{^1H\}$ NMR spectrum of **9a′**.

with a centrosymmetric structure in which one phosphorus atom A is coupled to the other one A′ trans to the rhodium center and to the two other phosphorus atoms in a trans configuration as well (X and X′). Of the two eight-line patterns, that at lower field is assigned to the *P*-dibenzophospholyl group and that at higher field to the PPh_2 group.

The $^{31}P\{^1H\}$ NMR spectrum of **9b** is more complex than that of **9a′** and is interpreted as an A_2B_2X spin system (X = Rh), due to the proximity of the two chemical shifts rather than an AA′BB′X system, as shown by the two experimental and simulated $^{31}P\{^1H\}$ NMR spectra (see the Supporting Information). As previously mentioned for **8**, the upfield ^{31}P resonance for the phosphorus atoms P(1) and P(2) with respect to those of the ligands **5a,b** is typical of a four-membered chelating ring.[27] All chemical shifts and coupling constants are displayed in the Supporting Information. The $^{31}P\{^1H\}$ NMR spectra are consistent with the formation of the pure *trans*-[Rh(phospholyl(diphenylphosphino)methane)$_2$] diastereoisomeric complex in both cases.

The phospholyl(phosphinoborane)methane **4a−c,e,f** act as chelating P-(η^2-BH_3) ligands toward the rhodium center, affording air- and moisture-stable complexes as already described.[15] Thus, the reaction of $[Rh_2(\mu\text{-}Cl)_2(\eta^4\text{-}COD)_2]$ with 2 equiv of ligand **4** in dichloromethane, using $AgBF_4$, afforded the rhodium complexes $[Rh(\eta^4\text{-}COD)\{(\eta^2\text{-}BH_3\text{-}phosphine)(\kappa^1\text{-}phosphole)\}][BF_4]$ (**10a−c,e,f**) in excellent yields (61−91%) (Scheme 3). It is worth noting that an excess of **4a** added to **10a** at room temperature does not displace the COD ligand. Alternatively, using the cationic precursor $[Rh(\eta^4\text{-}COD)_2][CF_3SO_3]$ with a stoichiometric amount of **4a−c** in dichloromethane provided the complexes $[Rh(\eta^4\text{-}COD)\{(\eta^2\text{-}BH_3\text{-}phosphine)(\kappa^1\text{-}phosphole)\}][CF_3SO_3]$ (**10a′−c′**) in very good yields. Complexes **10a−f** were fully characterized by NMR spectroscopy, mass spectrometry, elemental analysis, and single-crystal X-ray determinations. The BF_4^- metathesis of **10a** with the bulky BPh_4^- anion gave **10a″**, whose crystals were suitable for an X-ray structure determination, as previously reported.[15] However for **10b,c**, monocrystals were grown by slow diffusion of diethyl ether into dichloromethane solutions at −20 °C.

The molecular structure of the rhodium complex **10b** is displayed in Figure 6 (for **10c** see the Supporting Information).

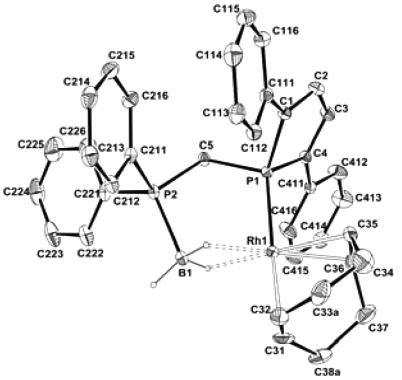
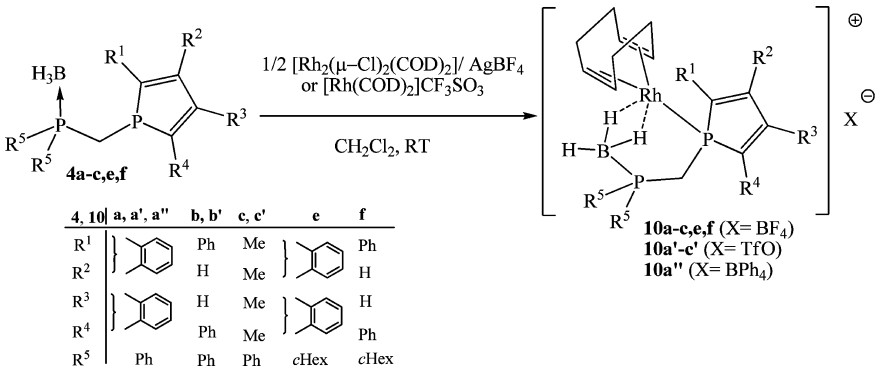


Figure 6. Molecular view of complex **10b** with the atom-labeling scheme. Ellipsoids are drawn at the 30% probability level. For the sake of clarity, only H atoms attached to boron were represented as small spheres of arbitrary radii. H bonds are shown as dashed lines.

Scheme 3



4, 10	a, a′, a″	b, b′	c, c′	e	f
R^1	}	Ph	Me	}	Ph
R^2		H	Me		H
R^3	}	H	Me	}	H
R^4		Ph	Me		Ph
R^5	Ph	Ph	Ph	*c*Hex	*c*Hex

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In all complexes, the phospholyl(phosphinoborane)methane ligands **4** bind to the metal center through the phosphorus atom of the phosphole moiety (P(1)) and the BH_3 group in a η^2 mode. The latter involves two B−H−Rh three-center−two-electron bonds, as observed in [Rh(η^4-COD){(η^2-BH_3-phosphine)(κ^1-dibenzophosphole)methane}][BPh_4] (**10a″**).[15] The Rh center has a square-planar geometry defined by the two centroids of the two C═C bonds of the COD ligand, the P(1), and the Rh−B(1) direction. However, the geometry of **10** could also be viewed as a trigonal bipyramid with one centroid and the H(1) and H(2) atoms in the equatorial plane.

A similar pentacoordination has been observed previously in [(η^4-COD)Rh{(η^2-H_3B)$Ph_2PCH_2PPh_2$}][BPh_4].[28] The bidentate coordination mode of BH_3, with a 3c−2e bond, has also been observed in [8,8-η^2-{η^2-(BH_3)·dppm}-*nido*-8,7-$RhSB_9H_{10}$] and [9,9-η^2-{η^2-(BH_3)·dppm}-*nido*-9,7,8-$RhC_2B_8H_{11}$].[29] The Rh−H and B−H distances are in good agreement, within experimental error, the shortest B−H distance corresponding to the noncoordinated H atom. The selected relevant bond lengths and angles are given in Table 1.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 10a″,b,c[a]

	10b	10c	10a″[15]
Rh−P(1)	2.280(1)	2.2598(8)	2.24532(16)
Rh−B(1)	2.364(5)	2.302(4)	2.331(2)
Rh−B(1)−P(2)	110.7(2)	113.61(17)	113.48(9)
Rh−P(1)−C(5)	112.66(13)	111.55(10)	111.561(5)
Rh−H(1)	1.83(5)	1.80(3)	1.85(3)
Rh−H(2)	2.06(5)	1.89(3)	1.96(3)
B(1)−H(1)	1.18(5)	1.17(3)	1.24(3)
B(1)−H(2)	1.09(5)	1.14(3)	1.13(3)
B(1)−H(3)	1.05(5)	0.97(3)	1.00(3)

[a] P(1) = *P*-phosphole, P(2) = PPh_2.

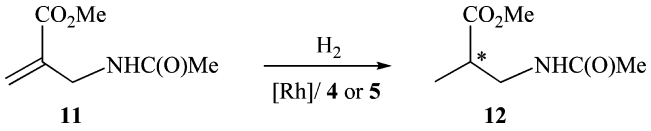
The coordination brings back the phosphorus into the plane of the phosphole ring, as already observed in phosphole-ligated rhodium complexes; the deviations of the P(1) atom from the C(1)−C(2)−C(3)−C(4) mean plane are 0.0081 and 0.1076 for **10b,c**, respectively (vs 0.262(3) Å for **4c**; see the Supporting Information).

As observed previously for **10a**, NMR monitoring at 188 K of **10b** confirms that the molecular structure described above is maintained in solution. In the $^1H\{^{11}B,^{31}P\}$ NMR spectrum, a singlet[30] at δ −1.23 corresponding to 2H of BH_3 was observed, the third proton of BH_3 probably being included in the massif (2.0−2.6 ppm) of the CH_2 protons of the COD ligand. By 1D ^1H EXSY experiment with broad-band decoupling of ^{11}B and ^{31}P, two singlets[29] for the three protons of BH_3 at 2.08 ppm (1H) and −1.23 ppm (2H) were observed and assigned to the terminal B−H and to the two bridging Rh−H−B bonds, respectively. The variable-temperature $^1H\{^{11}B,^{31}P\}$ NMR spectra, from 183 to 298 K, show that these two singlets collapsed (T_c = 233 K, $\Delta G^{\ddagger}$ = 42.3 ± 1 kJ/mol). At room temperature, a pseudodoublet at −0.06 ppm ($J_{HRh} \approx 11$ Hz) was observed, consistent with three equivalent BH_3 protons. This suggests that the BH_3 group is fluxional in solution, as observed in other rhodium complexes,[22,28,29,31] due to the rapid exchange of the three B−H bonds, their bonding to the Rh center occurring through rotation around the P−B bond according to the mechanism proposed by Barton.[29] Therefore, the η^2-BH_3 binding motif determined in the solid state is not maintained in solution. T_1 measurements, obtained by the conventional inversion−recovery method, have been carried out also for **10b**. At any temperature, an average T_1 for the three protons of BH_3 was observed showing a fast exchange on the T_1 relaxation time scale, even at 183 K, where the exchange is slow on the NMR time scale (see the Supporting Information).[15] The remaining observed ^{31}P, ^{11}B, and ^{13}C resonances are entirely consistent with the solid-state structure. The boron chemical shift downfield of that of ligand **4** is similar to that of Weller's Rh complex.[28] In the $^{31}P\{^1H\}$ NMR spectra, the doublet of doublets for P(1) and the broad signal for P(2) are shifted to lower fields. All representative NMR data of **10a″,b,c,e,f** are collected in the Supporting Information.

3. Investigation of the Catalytic Properties of the Rhodium Complexes. As cationic rhodium complexes are good precursors for the hydrogenation of C═C double bonds,[32] we explored in a first approach the catalytic activity of the rhodium complexes containing ligands **4** and **5** in the hydrogenation of methyl 2-(acetamidomethyl)acrylate (**11**). This preliminary investigation is devoted to the performance of the catalytic system under mild conditions. We extended this study to the hydroboration of styrene **13** operating with catecholborane **14**, this catalysis using BH_3-protected ligands having been hardly explored.[33,34]

3a. Hydrogenation Catalysis. The catalytic performances of the new ligands **4** and **5** were explored in the hydrogenation reaction of (**11**) (Scheme 4). In the first set of experiments, the

Scheme 4. Hydrogenation of Methyl 2-(Acetamidomethyl)acrylate 11



11 **12**

rhodium complexes generated in situ by addition of ligands **5** to the [Rh(η^4-COD)$_2$][CF_3SO_3] precursor have been investigated (Table 2).

Table 2. Rh-Catalyzed Hydrogenation of Methyl 2-(Acetamidomethyl)acrylate 11

entry	ligand	substrate/Rh	P_{H_2}	yield (%)
1	**5a**[a]	50	20	100
2	**5a**[a]	100	20	3
3	**5b**[a]	50	20	100
4	**5b**[a]	100	20	80
5	**5a**[b]	100	20	100
6	**5b**[b]	100	20	100
7	**5b**[b]	200	20	100
8	**5b**[b]	400	20	91
9	**5b**[b]	100	10	100
10	**4a**[b]	100	40	17
11	**4b**[b]	50	40	100
12	**4b**[b]	100	40	85

[a] Experimental conditions: [Rh(η^4-COD)$_2$][CF_3SO_3], solvent MeOH, t = 20 h, T = 25 °C, [P]/[Rh] = 2. [b] Experimental conditions: formation of the precatalyst during 3 h in the absence of H_2.

The addition of 1 equiv of ligands **5a,b** to [Rh(η^4-COD)$_2$]$^+$ presumably provides the complexes [Rh(η^4-COD)(**5**)]$^+$ (**8a′,b′**) and then the solvated derivatives [Rh(**5**)(MeOH)$_2$]$^+$,

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by hydrogenation of the COD in methanol.[35] When the **11**/[Rh] ratio is 50/1, the substrate is quantitatively hydrogenated at 20 bar in 20 h (entries 1 and 3), whereas for a 100/1 ratio, the product **12** is obtained in 3% yield for **5a** and 80% yield for **5b**, indicating that rhodium complex **8b′** with a 2,5-diphenylphospholyl moiety is catalytically more active than **8a′** with a dibenzophospholyl moiety (entries 2 and 4). This difference in reactivity is presumably due to the pronounced electronic dissymmetry shown by the ligand **5b**.

Preforming the rhodium catalyst by mixing $[Rh(\eta^4\text{-COD})_2]^+$ with 1 equiv of **5a,b** (P/Rh = 2) and a large excess of substrate **11** at room temperature for 3 h, in the absence of H_2, gives more satisfactory results. A 100% hydrogenation yield is reached for either a **11**/[Rh] ratio of 100 with **5a**, and with a ratio of 100 or 200 with **5b** (entries 5−7). As already observed, the rhodium catalyst bearing the 2,5-diphenylphospholyl substituent (**5b**) is more active. Thus, increasing the **11**/[Rh] ratio to 400 with **5b** still provides the product **12** in 91% yield (entry 8). Higher reactivity with the preformed Rh species could be consistent with the formation of the rhodium−substrate complex $[Rh(\mathbf{5})(\mathbf{11})]^+$ under such conditions. This preformed species should then react directly with dihydrogen to produce $[Rh(H)_2(\mathbf{5b})(\mathbf{11})]^+$ going along the catalytic cycle. Thus, reducing the H_2 pressure to 10 bar for a **11**/[Rh] ratio of 100 still allows complete conversion (entry 9). Similar activities were reported for rhodium cationic complexes containing chiral diphosphine ligands,[36] including 1,2-bis-(alkylmethylphosphino)methane[4a] for the hydrogenation reaction of methyl 2-(acetamidomethyl)acrylate (**11**).

Interestingly, phospholyl(phosphinoborane)methane ligands **4a,b** give Rh catalytic systems that are active in the hydrogenation of **11**. With **4b**, complete conversion is achieved for a **11**/[Rh] ratio of 50 and 85% conversion for a ratio of 100, under a higher pressure of H_2 (40 bar, entries 11 and 12). For **4a**, the results are less spectacular, although a moderate yield of 17% is still observed (entry 10). Catalytic activities of the phospholyl(phosphinoborane)methane−rhodium systems are lower than those observed with the deprotected ligands **5a,b**. Presumably, this reactivity difference means that the dihydrogen oxidative addition is the rate-determining step in this catalytic hydrogenation, directly connected to the electron density on the metal center. It is worth noting that these results demonstrate the possibility to use the phosphine−borane ligand in Rh-catalyzed hydrogenation without removing the borane-protecting group. Moreover, the phospholyl-(phosphinoborane)methane seems to really act as a bidentate ligand.[37]

3b. Catalysis of Hydroboration. The catalyzed hydroboration reaction is a powerful method for the chemo-, regio-, and stereoselective synthesis of organoborane compounds, from which numerous functional derivatives can be prepared.[38,39] The use of rhodium phosphine complexes in the reaction of catecholborane with olefins favors Markovnikov addition and, therefore, the formation of branched products. In some cases, the regioselectivity of the addition is sensitive to the oxidation of the catalytic system.[38] We investigated herein the use of ligands **4** and **5** in the hydroboration catalysis of styrene **13** with catecholborane **14** (Scheme 5). The catalytic reactions were performed using either the previously isolated complexes **10** or species prepared in situ (1 mol %) in THF by mixing the precursor $[Rh(\eta^4\text{-COD})_2][BF_4]$ and **4** or **5**. The reactions were carried out at room temperature for 22 h, and then the crude organoborane mixtures were oxidized into the corresponding alcohols. After workup, the conversion and the regioselectivities were determined by ^{1}H NMR spectroscopy. The results are reported in Table 3.

Scheme 5. Hydroboration of Styrene 13 with Catechol Borane 14

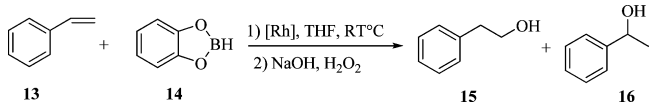
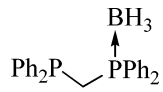


Table 3. Rhodium-Catalyzed Hydroboration of Styrene[a]

entry	cat.	Rh/L	conversn (%)[b]	**15**/**16**[b]
1	no cat.		16	100/0
2	[Rh]/dppm	1/1	95	23/77
3	[Rh]/**17**	1/1	80	69/31
4	**10g**		83	64/36
5	[Rh]/**5a**	1/1	92	46/54
6	[Rh]/**5b**	1/1	90	46/54
7	**10a**		84	51/49
8	**10b**		87	43/57
9	**10e**		60	48/52
10	**10f**		57	35/65
11	[Rh]/**17**	1/2	69	43/57
12	[Rh]/**4a**	1/2	50	55/45
13	[Rh]/**4b**	1/2	63	53/47

[a]Experimental conditions: [Rh] = $[Rh(\eta^4\text{-COD})_2][BF_4]$ (1 mol %), T = 25 °C, t = 22 h; solvent THF (2 mL), styrene (1 mmol), catecholborane (1 mmol). [b]Determined by ^{1}H NMR.

First, hydroboration with no rhodium catalyst gives a low conversion and leads regiospecifically to the linear alcohol **15** (entry 1). When the reaction is catalyzed by a rhodium complex, the conversions are good to excellent (50−95%) and a mixture of linear/branched alcohols **15**/**16** in ratios ranging from 23/77 to 64/36 are obtained, depending on the ligands used (entries 2−13). The catalyst generated by mixing $[Rh(\eta^4\text{-COD})_2][BF_4]$ and 1 equiv of dppm in THF for 30 min leads to the alcohols with a linear/branched **15**/**16** ratio of 23/77 (entry 2). On the other side, using the dppm·BH_3 ligand **17** produces higher quantities of the linear isomer with a **15**/**16** ratio of 69/31 (entry 3). It is worth noting that when the rhodium complex $[Rh(\eta^4\text{-COD})(\mathbf{17})][BF_4]$ (**10g**) is directly introduced, the catalyzed hydroboration induces roughly the same regioselectivity: i.e., 64/36 vs 69/31 (entries 3 and 4).



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The rhodium complexes prepared in situ from **5a,b** afford the alcohol mixture with excellent conversions (90−92%) and with similar **15**/**16** ratios of 46/54 (entries 5 and 6). No significant differences in terms of regioselectivity are observed with isolated complexes **10a** (**15**/**16** = 51/49, entry 7) or **10b** (**15**/**16** = 43/57, entry 8) in comparison to Rh catalysts formed in situ from the corresponding free ligands **5a,b**. In addition, unlike the case for the rhodium-bound dppm complex giving higher branched regioslectivity than with **5a,b** (entries 2, 5, 6), complex **10g** containing the chelating dppm·BH_3 ligand generates less branched isomer **16** than **10a,b** (entry 4). It is

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worth noting that in spite of the lower conversions observed with both **10e,f** containing the more basic $P(cHex)_2$ moiety (57−60%), in comparison with **10a,b,g** (83−87%), the best branched regioselectivity is obtained with the Rh complex **10f** (**15**/**16** = 35/65, entry 10).

The influence of the [Rh]/ligand ratio on the catalytic reactivity has been studied as well. In fact, adding 2 equiv of dppm·BH_3 (**17**) results in both a lower conversion and the reverse linear/branched **15**/**16** ratio with respect to 1 equiv added in the reaction: i.e. 43/57 vs 69/31 (entries 3 and 11). Similarly, introducing 2 equiv of ligands **4a,b** to the rhodium precursor also induces a lower conversion (50−63%) (entries 12 and 13). However, the **15**/**16** ratios seem to be not strongly affected, with values of 51/49 vs 55/45 for **4a** (entries 7 and 12) and 43/57 vs 53/47 for **4b** (entries 8 and 12), slightly in favor of the formation of the linear isomer **15**.

Therefore, in the absence of a catalyst, the hydroboration of styrene provides after oxidation and workup the linear alcohol. Introduction of a rhodium cationic catalyst containing one of the hybrid phosphine−phosphole ligands of this study allows us to increase the yields and to produce the branched alcohol with selectivities ranging from 31 to 65%. The selectivity is somewhat better when a BH_3-protected ligand is used to generate the catalyst.

CONCLUSION

We have prepared hybrid phospholyl(phosphino)methane ligands, and their monoborane protected forms, with a methylene bridge between the phospholyl and phosphino moieties. Two synthetic pathways have been used to graft the phosphorus blocks onto the CH_2 motif by P−C bond formation. The first pathway involves the nucleophilic attack of a phospholyl anion on the (chloromethyl)-diphenylphosphine−borane as the key step. In the second case, the synthesis is based on the nucleophilic substitution of an electrophilic phospholyl species by a dicyclohexyl-(phosphino)methylenic anion. Both synthetic strategies allow us to obtain phospholylphosphinomethane derivatives with various aryl or alkyl substituents.

The two types of phospholylphosphinomethane ligands, complexed to a borane or not, have been used for the preparation of rhodium(I) cationic complexes. Both kinds of rhodium complexes are active in the catalyzed hydrogenation and hydroboration reactions. Particularly interesting results have been gained with the hybrid phospholyl-(phosphinoborane)methane ligands, which act as chelating P-(η^2-BH_3) entities toward the rhodium center and present good reactivity in hydrogenation and, more especially, promising activity and regioselectivity in hydroboration.

This study shows that the use of hybrid phospholyl-(phosphinoborane)methanes as ligands offers a new way to improve a catalytic process, for designing both its structure and its electronic properties, or still to implement the catalyst without removing the borane protecting group before use.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an argon atmosphere in dried glassware. Solvents were dried and freshly distilled under an argon atmosphere over sodium/benzophenone for THF and diethyl ether, P_2O_5 for CH_2Cl_2, CaH_2 for *n*-pentane, and sodium for toluene. Thin-layer chromatography was performed on silica gel (60 F_{254}) and visualized by UV, iodine, or permanganate treatment. Flash chromatography was performed on silica gel (35−70 μm). All NMR spectral data were recorded on Bruker DRX 300 or Avance 300−500 spectrometers with TMS as internal reference for ^1H and ^{13}C, 85% phosphoric acid as external reference for ^{31}P, and $BF_3{\cdot}Et_2O$ for ^{11}B. Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropiate. T_1 relaxation times were mesured by the conventional inversion−recovery method. Simulated spectra were obtained using the gNMR v 4.1 program (Cherwell Scientific Ltd). Mass spectral analyses were performed on a Bruker ESI microTOF-Q (HR) apparatus and on a TSQ 7000 Thermoquest instrument (DCI). The major *m*/*z* peak was reported with the intensity as a percentage of the base peak in brackets. Elemental analyses were measured with a precision superior to 0.3% at the Microanalysis Laboratory of the LCC at Toulouse. X-ray structures were determined on an Oxford Diffraction Xcalibur CCd diffractometer. Commercially available diphenylphosphine, palladium(II) acetate, 1,1-bis(diphenylphosphino)methane, 1,1′-bis-(diphenylphosphino)ferrocene, $[Rh(\eta^4\text{-}COD)_2][CF_3SO_3]$, $[RhCl(\eta^4\text{-}COD)]_2$, silver tetrafluoroborate, and tetraphenylborate were used as received. The ligands 1-phenyldibenzophosphole (**1a**),[40] 1,2,5-triphenylphosphole (**1b**),[41] 1-phenyl-2,3,4,5-tetramethylphosphole (**1c**),[42] 1-phenyl-3,4-dimethylphosphole (**1d**),[43] 1-cyanodibenzophosphole (**6a**), 1-cyano-2,5-diphenylphosphole (**6b**),[44] (chloromethyl)diphenylphosphine−borane (**3**),[45] dicyclohexylmethylphosphine−borane (**7**),[46] and dppm·BH_3[47] were prepared according to the literature.

General Procedure for the Synthesis of the Hybrid Phospholyl(diphenylphosphinoborane)methane Ligands 4a−d. To a solution of 1-phenylphosphole **1** (4.8 mmol) in THF (40 mL) was added at 0 °C metallic lithium in excess (0.20 g). The reaction mixture was vigorously stirred for 1 h at 0 °C and then for 3 h at room temperature to afford the phospholyl anion **2** and PhLi. After removal of the unreacted lithium, the dark red solution was cooled to −20 °C and anhydrous $AlCl_3$ (0.8 mmol) was added. The reaction mixture was warmed to room temperature and stirred again for 30 min. To the resulting solution of **2** was added at −78 °C a solution of (chloromethyl)diphenylphosphine−borane (**3**; 2.4 mmol) in THF (10 mL). The obtained solution was warmed to room temperature and stirred for 48 h. The solution mixture was concentrated to 5 mL and quenched with degassed H_2O (20 mL), and the aqueous phase was extracted with dichloromethane (3 × 30 mL). The combined extracts were dried over $MgSO_4$ and evaporated under reduced pressure to afford a yellow residue. Successive purifications of the yellow crude products by chromatography on a silica gel column (eluent CH_2Cl_2/*n*-hexane, 50/50 or 40/60) and recrystallization in a CH_2Cl_2/*n*-pentane mixture at −20 °C gave the pure compounds **4**. For **4d,** which was partially oxidized during chromatography (see the Supporting Information), pure compound was obtained by repeated crystallization with a CH_2Cl_2/Et_2O mixture at −20 °C.

*Dibenzophospholyl(diphenylphosphinoborane)methane (**4a**).* White solid. Yield: 67%. ^1H NMR (298 K, $CDCl_3$, 300.13 MHz, ppm): δ 7.88 (dd, 2H, =CH−, $^4J_{HH}$ = 0.6 Hz, $^3J_{HH}$ = 7.5 Hz, phosphole), 7.75 (m, 4H, =CH−, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 8.4 Hz, J_{HP} = 1.5 Hz, Ph), 7.40−7.58 (m, 4H of phosphole and 6H of Ph, =CH−), 7.25 (t, 1H, =CH−, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 1.0 Hz, phosphole), 7.24 (t, 1H, =CH−, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 1.0 Hz, phosphole), 2.63 (dd, 2H, >CH_2, $^2J_{HP(1)}$= 2.1 Hz, $^2J_{HP(2)}$ = 10.8 Hz, P(1)CH_2P(2)), 1.34 (br q, 3H, $^1J_{HB}$ = 88.5 Hz, BH_3). $^1H\{^{11}B\}$ NMR (298 K, $CDCl_3$, 300.13 MHz, ppm): δ selected 1.34 (d, 3H, $^1J_{HP(2)}$ = 15.9 Hz, BH_3). $^{31}P\{^1H\}$ NMR (298 K, $CDCl_3$, 121.495 MHz, ppm): δ +15.58 (br, P(2), $Ph_2P{\cdot}BH_3$), −29.70 (d, P(1), $^2J_{PP}$ = 68.0 Hz, phosphole). $^{11}B\{^1H\}$ NMR (298 K, $CDCl_3$, 96.294 MHz, ppm): δ −38.44 (d, 1B, J_{BP} = 40.7 Hz, BH_3). $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$, 75.468 MHz, ppm): δ 143.53 (d, >C=, J_{CP} = 1.8 Hz, phosphole), 142.85 (t, >C=, J_{CP} = 7.3 Hz, phosphole), 132.45 (d, J_{CP} = 8.7 Hz, Ph), 131.95 (d, J_{CP} = 2.4 Hz, Ph), 130.58 (d, >C=, J_{CP} = 22.4 Hz, phosphole), 129.81 (d, J_{CP} = 55.3 Hz, Ph), 129.78 (d, J_{CP} = 55.2 Hz, Ph), 129.0 (s, >C=, phosphole), 128.93 (d, J_{CP} = 10.1 Hz, Ph), 127.59 (d, =CH−, J_{CP} = 7.3 Hz, phosphole), 121.33 (s, =CH−, phosphole), 27.82 (dd, J_{CP} = 33.0, 40.4 Hz, P(1)CH_2P(2)). MS (DCI, NH_3): *m*/*z* (%) 397.2 (100) $[M + H]^+$. Anal. Calcd for $C_{25}H_{23}BP_2$: C, 75.79; H, 5.85. Found: C,

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75.61; H, 5.99. Crystals suitable for an X-ray diffraction study were obtained by recrystallization from CH_2Cl_2/*n*-pentane solution at −20 °C.

*2,5-Diphenylphospholyl(diphenylphosphinoborane)methane (**4b**).* Yellow solid. Yield: 51%. ^{1}H NMR (298 K, $CDCl_3$, 300.13 MHz, ppm): δ 7.49 (m, 4H, =CH−, J_{HH} = 1.5, 7.6 Hz, J_{HP} = 9.0 Hz), 7.36 (tt, 6H, =CH−, J_{HH} = 1.5, 6.3 Hz, −Ph, phosphole), 7.18−7.28 (m, 10H, =CH−), 7.11 (dd, =CH−, J_{HP} = 1.5, 9.9 Hz, phosphole), 2.68 (dd, >CH_2, $J_{HP(1)}$ = 3.0 Hz, $J_{HP(2)}$ = 11.1 Hz, P(1)CH_2P(2)), 1.17 (br, 3H, BH_3). ^{1}H{^{11}B} (298 K, $CDCl_3$, 300.13 MHz, ppm): δ selected 1.17 (d, 3H, J_{HP} = 16.0 Hz, BH_3). ^{31}P{^{1}H} NMR (298 K, $CDCl_3$, 121.495 MHz, ppm): δ +16.79 (br, P(2), $Ph_2P{\cdot}BH_3$), −19.33 (d, P(1), $J_{P1P(2)}$ = 60.8 Hz, phosphole). ^{11}B{^{1}H} NMR (298 K, $CDCl_3$, 96.294 MHz, ppm): δ −38.33 (br, BH_3). ^{13}C{^{1}H} NMR (298 K, $CDCl_3$, 75.468 MHz, ppm): δ 152.17 (d, >C=, J_{CP} = 6.2 Hz), 152.10 (d, >C=, J_{CP} = 6.0 Hz), 136.01 (d, >C=, J_{CP} = 17.4 Hz), 132.73 (d, 2C, =CH−, J_{CP} = 8.7 Hz, phosphole), 132.14 (d, =CH−, J_{CP} = 9.4 Hz), 131.20 (=CH−, phosphole), 131.17 (=CH−, phosphole), 129.65 (d, >C=, J_{CP} = 54.8 Hz), 129.62 (d, >C=, J_{CP} = 54.9 Hz), 128.78 (=CH−, phosphole), 128.55 (d =CH−, J_{CP} = 10.0 Hz), 127.20 (=CH−, phosphole), 126.96 (d, =CH−, J_{CP} = 9.6 Hz), 21.07 (dd, >CH_2, J_{CP} =31.6, 33.9 Hz, P(1)CH_2P(2)). MS (DCI, NH_3): *m*/*z* (%) 449.2 (100) [M + H]$^+$. Anal. Calcd for $C_{29}H_{27}BP_2$: C, 77.70; H, 6.07. Found: C, 77.46; H, 6.23.

*2,3,4,5-Tetramethylphospholyl(diphenylphosphinoborane)-methane (**4c**).* White solid. Yield: 60%. ^{1}H NMR (298 K, $CDCl_3$, 300.13 MHz, ppm): δ 7.75 (m, 4H-*o*, =CH−; J_{HH} = 1.5, 6.3 Hz), 7.49 (m, 4H-*m* and 2H-*p*, =CH−), 2.53 (dd, 2H, >CH_2, $J_{HP(1)}$ = 2.4 Hz, $J_{HP(2)}$ = 10.2 Hz, P(1)CH_2P(2)), 1.85 (d, 6H, −CH_3, $^4J_{HP}$ = 2.1 Hz, phosphole), 1.79 (d, 6H, −CH_3, J_{HP} = 10.2 Hz, phosphole), 1.13 (3H, BH_3, $J_{HP(2)}$ = 16.0 Hz, BH_3). ^{31}P{^{1}H} NMR (298 K, $CDCl_3$, 161.976 MHz, ppm): δ +16.10 (br, P(2), $Ph_2P{\cdot}BH_3$), −8.25 (d, P(1), $J_{P1P(2)}$ = 55.2 Hz, phosphole). ^{31}P NMR (298 K, CD_2Cl_2, 161.976 MHz, ppm): δ +15.77 (br, P(2), $H_3B{\cdot}PPh_2$), −23.43 (q, P(1), J_{P1H} = 40.8 Hz, $J_{P1P(2)}$ = 43.4 Hz, phosphole). ^{11}B{^{1}H} NMR (298 K, $CDCl_3$, 96.294 MHz, ppm): δ −38.03 (d, J_{BP} = 56.9 Hz, BH_3). ^{13}C{^{1}H} NMR (298 K, $CDCl_3$, 75.468 MHz, ppm): δ 143.19 (d, >C=, J_{CP} = 11.3 Hz), 134.28 (d, >C=, J_{CP} = 6.8 Hz), 134.25 (d, >C=, J_{CP} = 6.8 Hz), 132.48 (d, 4C, =CH−, J_{CP} = 9.8 Hz), 131.22 (d, 2C, =CH−, J_{CP} = 3.0 Hz), 128.68 (d, 4C, =CH−, J_{CP} = 9.8 Hz), 19.69 (dd, >CH_2, J_{CP} = 38.2, 32.6 Hz, P(1)CH_2P(2)), 13.90 (d, 2C, −CH_3, J_{CP} = 2.6 Hz, phosphole), 12.69 (d, 2C, −CH_3, J_{CP} = 22.3 Hz, phosphole). MS (DCI, NH_3): *m*/*z* (%) 353.2 (100) [M + H]$^+$. Anal. Calcd for $C_{21}H_{27}BP_2$: C, 71.62; H, 7.73. Found: C, 71.70; H, 7.71. Crystals suitable for an X-ray diffraction study were obtained by recrystallization in diethyl ether at −20 °C.

*3,4-Dimethylphospholyl(diphenylphosphinoborane)methane (**4d**).* White solid. Yield: 29%. ^{1}H NMR (298 K, $CDCl_3$, 400.13 MHz, ppm): δ 7.73 (m, 4H-*o*, =CH−, J_{HH} = 6.8 Hz, −Ph), 7.51 (m, 2H-*p*, =CH−, J_{HH} = 7.2 Hz, J_{HP} = 1.6 Hz, −Ph), 7.46 (td, 4H-*m*, =CH−, J_{HH} = 7.6 Hz, J_{HP} = 2.0 Hz, −Ph), 6.16 (d, 2H, =CH−, J_{HP} = 39.2 Hz, phosphole), 2.53 (d, 2H, >CH_2, $J_{HP(2)}$ = 10.4 Hz, P(1)CH_2P(2)), 2.00 (d, 6H, −CH_3, J_{HP} = 2.8 Hz, phosphole), 1.12 (br, 3H, BH_3). ^{1}H{^{11}B} NMR (298 K, $CDCl_3$, 300.13 MHz, ppm): δ selected 1.12 (d, 3H, J_{HP} = 15.6 Hz, BH_3). ^{31}P{^{1}H} NMR (298 K, $CDCl_3$, 161.976 MHz, ppm): δ +15.82 (br, P(2), $Ph_2P{\cdot}BH_3$), −23.51 (d, P(1), $J_{P(2)P(1)}$ = 44.4 Hz, phosphole). ^{11}B{^{1}H} NMR (298 K, $CDCl_3$, 96.294 MHz, ppm): δ −38.38 (d, J_{BP} = 46.2 Hz, BH_3). ^{13}C{^{1}H} NMR (298 K, $CDCl_3$, 100.613 MHz, ppm): δ 149.42 (d, >C=, J_{CP} = 7.65 Hz), 132.37 (d, =CH−*o*, J_{CP} = 9.3 Hz, −Ph), 131.31 (d, =CH−*p*, J_{CP} = 2.3 Hz, −Ph), 130.00 (t, J_{CP} = 6.2 Hz, =CH−, phosphole), 129.89 (d, >C=, J_{CP} = 55.4 Hz, −Ph), 129.87 (d, >C=, J_{CP} = 55.2 Hz, −Ph), 128.70 (d, =CH−*m*, J_{CP} = 10.1 Hz, −Ph), 21.14 (dd, >CH_2, $J_{CP(1)}$ = 31.8, 35.4 Hz, P(1)CH_2P(2)), 17.67 (d, −CH_3, J_{CP} = 3.6 Hz, phosphole).

General Procedure for the Synthesis of Phospholyl-(dicyclohexylphosphinoborane)methanes 4e,f. To a solution of dicyclohexylmethylphosphine−borane (**7**; 0.44 mmol), previously prepared according to the literature procedure,[46] in THF (2 mL) was added dropwise *t*-BuLi (0.49 mmol) at 0 °C. After the mixture was stirred for 30 min at 0 °C and then for 90 min at room temperature, a solution of cyanophosphole **6** (0.49 mmol) in THF (5 mL) was added at 0 °C and the solution was stirred at room temperature overnight. The reaction mixture was hydrolyzed with water (5 mL), and the aqueous phase was extracted with methylene chloride (3 × 5 mL). The combined organic phases were dried over $MgSO_4$ and filtered and the solvent removed in vacuo to give a residue, which was purified by chromatography on a silica gel column using toluene as eluent.

*Dibenzophospholyl(dicyclohexylphosphinoborane)methane (**4e**).* White solid. Yield: 18%. ^{1}H NMR (298 K, $CDCl_3$, 300.13 MHz, ppm): δ 7.98−7.96 (m, 2H, =CH−, phosphole), 7.93 (d, 2H, =CH−, *J* = 7.6 Hz, phosphole), 7.50 (td, 2H, =CH−, *J* = 1.1 Hz, *J* = 7.7 Hz, phosphole), 7.40 (tdd, 2H, =CH−, *J* = 1.0 Hz, 3.0 Hz, *J* = 7.4 Hz, phosphole), 2.00 (dd, 2H, >CH_2, $J_{HP(1)}$ = 2.0 Hz, $J_{HP(2)}$ = 9.7 Hz, P(1)CH_2P(2)), 2.01−1.86 (m, 10H, cHex), 1.50−1.45 (m, 4H, cHex), 1.33−1.27 (m, 8H, cHex), 0.71 (m, 3H, BH_3). ^{31}P{^{1}H} NMR (298 K, $CDCl_3$, 121.495 MHz, ppm): δ +25.48 (br, P(2), $(cHex)_2P{\cdot}BH_3$), −27.70 (d, P(1), $^2J_{PP}$ = 47.5 Hz, phosphole). ^{13}C{^{1}H} NMR (298 K, $CDCl_3$, 75.468 MHz, ppm): δ 143.52 (dd, J_{CP} = 5.6 Hz, J_{CP} = 7.7 Hz, phosphole), 143.40 (d, J_{CP} = 2.1 Hz, phosphole), 130.74 (d, J_{CP} = 22.0 Hz, phosphole), 128.94 (s, phosphole), 127.62 (d, J_{CP} = 6.9 Hz, phosphole), 121.36 (s, phosphole), 32.80 (dd, >CHP, J_{CP} = 3.2, 31.1 Hz, cHex), 27.15 (s, >CH_2, cHex), 27.00 (t, >CH_2, J_{CP} = 2.0 Hz, cHex), 26.92 (s, >CH_2, cHex), 26.85 (s, >CH_2, cHex), 25.97 (s, >CH_2, cHex), 20.91 (dd, >CH_2, J_{CP} = 26.8, 39.9 Hz, P(1)CH_2P(2)). MS (ESI): *m*/*z* (%) 431.2 (100) [M + Na]$^+$.

*2,5-Diphenylphospholyl(dicyclohexylphosphinoborane)methane (**4f**).* Yellow solid. Yield: 23%. ^{1}H NMR (298 K, C_6D_6, 300.13 MHz, ppm): δ 7.77−7.74 (m, 4H, =CH−, Ph), 7.33−7.29 (m, 4H, =CH−, Ph), 7.18−7.13 (m, 2H, =CH−, Ph), 6.97 (dd, 2H, =CH−, *J* = 1.0 Hz, *J* = 9.3 Hz, phosphole), 2.08 (dd, 2H, >CH_2, $J_{HP(1)}$ = 3.4 Hz, $J_{HP(2)}$ = 9.8 Hz, P(1)CH_2P(2)), 1.71−1.68 (m, 4H, >CHP and >CH_2, cHex), 1.57−1.49 (m, 8H, >CH_2, cHex), 1.35−1.26 (m, 4H, >CH_2, cHex), 0.84−1.00 (m, 6H, >CH_2, cHex), 1.35 (m, 3H, BH_3). ^{31}P{^{1}H} NMR (298 K, C_6D_6, 121.495 MHz, ppm): δ +32.99 (br, P(2), $(cHex)_2P{\cdot}BH_3$), −13.10 (d, P(1), $^2J_{PP}$ = 39.4 Hz, phosphole). ^{13}C{^{1}H} NMR (298 K, C_6D_6, 75.468 MHz, ppm): δ 153.68 (d, J_{CP} = 5.4 Hz, phosphole), 153.61 (d, J_{CP} = 5.5 Hz, phosphole), 137.28 (d, =CH−, J_{CP} = 17.4 Hz, Ph, phosphole), 123.16 (d, =CH−, J_{CP} = 8.4 Hz, phosphole), 129.28 (s, Ph, phosphole), 127.84 (s, Ph, phosphole), 127.76 (s, Ph, phosphole), 33.14 (dd, >CHP, J_{CP} = 2.0, 30.1 Hz, cHex), 27.17 (s, >CH_2, cHex), 27.11 (s, >CH_2, cHex), 26.80 (d, >CH_2, J_{CP} = 3.6 Hz, cHex), 26.65 (d, >CH_2, J_{CP} = 3.3 Hz, cHex), 25.98 (d, >CH_2 J_{CP} = 0.9 Hz, cHex), 15.89 (dd, >CH_2, J_{CP} = 24.9, 33.4 Hz, P(1)CH_2P(2)). MS (ESI): *m*/*z* (%) 483.2 (100) [M + Na]$^+$.

General Procedure for Decomplexation. The decomplexation reaction was performed as previously described. The reaction mixture of 1 equiv of phospholyl(diphenylphosphinoborane)methane **4** and 5 equiv of DABCO in toluene (5 mL) was heated at 50 °C under an argon atmosphere for 14 h. The resulting solution was filtered through a neutral alumina column with the use of degassed AcOEt/toluene (1/9) as eluent. After removal of the solvents, the free phosphole−phosphino methane compounds **5** were obtained in 80−90% yield. Suitable crystals for X-ray structure determinations were obtained by recrytallization in diethyl ether at −20 °C.

*Dibenzophospholyl(diphenylphosphino)methane (**5a**).* White solid. Yield: 84%. ^{1}H NMR (298 K, $CDCl_3$, 400.13 MHz, ppm): δ 7.92 (d, 2H, =CH−, J_{HH} = 8.0 Hz, phosphole), 7.66 (dd, 2H, =CH−, J_{HH} = 7.4 Hz, J_{HP} = 3.6 Hz, phosphole), 7.40−7.50 (m, 6H, =CH−, Ph), 7.25−7.38 (m, 8H, =CH−), 2.54 (t, 2H, >CH_2, J_{HP} = 1.2 Hz, P(1)CH_2P(2)). ^{31}P{^{1}H} NMR (298 K, $CDCl_3$, 121.495 MHz, ppm): δ −21.2 (d, P(1), $J_{P(1)P(2)}$ = 99.5 Hz, phosphole), −22.45 (d, P(2), $J_{P(2)P(1)}$ = 99.5 Hz, PPh_2). ^{13}C{^{1}H} NMR (298 K, $CDCl_3$, 75.468 MHz, ppm): δ 143.58 (s, >C=), 143.31 (t, >C=, J_{CP} = 4.3 Hz), 138.80 (d, >C=, J_{CP} = 10.3 Hz), 138.77 (d, >C=, J_{CP} = 10.3 Hz), 132.96 (d, =CH−, J_{CP} = 4.3 Hz), 132.75 (d, =CH−, J_{CP} = 4.4 Hz), 132.17 (d, =CH−, J_{CP} = 18.3 Hz), 128.77(s, =CH−, phosphole), 128.61 (s, =CH−, phosphole), 128.44 (d, =CH−, J_{CP} = 5.4 Hz), 127.18 (d, =CH−, J_{CP} = 1.4 Hz), 127.09 (d, =CH−, J_{CP} = 1.4 Hz), 121.30 (s, =CH−), 29.17 (dd, >CH_2, J_{CP} = 28.0, 55.5 Hz, P(1)

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$CH_2P(2)$). MS (DCI, NH_3): m/z (%) 383.1 (100) $[M + H]^+$. Anal. Calcd for $C_{25}H_{20}P_2$: C, 78.53; H, 5.27. Found: C, 78.27; H, 5.29.

*2,5-Diphenylphospholyl(diphenylphosphino)methane (**5b**).* Yellow solid. Yield: 87%. ^{1}H NMR (298 K, CD_2Cl_2, 300.13 MHz, ppm): δ 7.46 (m, 4H, =CH−, J_{HH} = 5.7 Hz), 7.34 (t, 4H, =CH−, J_{HH} = 5.4 Hz), 7.28−7.22 (m, 4H, =CH−), 7.17 (m, 10H, =CH−), 2.62 (bd, 2H, >CH_2, J_{HP} = 1.5 Hz, P(1)CH_2P(2)). ^{31}P NMR (298 K, CD_2Cl_2, 161.976 MHz, ppm): δ −8.17 (dt, P(1), $J_{HP(1)}$ = 10.2 Hz, $J_{P1P(2)}$ = 46.0 Hz, phosphole), −22.03 (d, P(2), $J_{P(2)P(1)}$ = 50.0 Hz, PPh_2). ^{31}P{^{1}H} NMR (298 K, CD_2Cl_2, 161.976 MHz, ppm): δ −8.16 (d, P(1), $J_{P(1)P(2)}$ = 46.3 Hz, phosphole), −22.03 (d, P(2), $J_{P(2)P(1)}$ = 46.3 Hz, PPh_2). ^{13}C{^{1}H} NMR (298 K, CD_2Cl_2, 100.613 MHz, ppm): δ 151.31 (d, >C=, J_{CP} = 1.9 Hz), 151.24 (d, >C=, J_{CP} = 1.9 Hz), 136.67 (d, >C=, J_{CP} = 16.9 Hz), 139.08 (d, >C=, J_{CP} = 3.8 Hz), 138.91 (d, >C=, J_{CP} = 3.7 Hz), 132.50 (d, =CH−, J_{CP} = 19.9 Hz), 131.98 (d, =CH−, J_{CP} = 8.95 Hz), 128.66 (s, =CH−), 128.51 (s, =CH−), 128.08 (d, =CH−, J_{CP} = 6.7 Hz), 127.01 (s, =CH−), 126.42 (d, =CH−, J_{CP} = 9.9 Hz), 21.37 (dd, >CH_2, J_{CP} = 21.7, 32.60 Hz, P(1)CH_2P(2)). MS (DCI, NH_3): m/z (%) 435.1 (100) $[M + H]^+$. Anal. Calcd For $C_{29}H_{24}P_2$: C, 80.17; H, 5.57. Found: C, 80.32; H, 5.67.

*2,3,4,5-Tetramethylphospholyl(diphenylphosphino)methane (**5c**).* Colorless oil liquid. Yield: 92%. ^{1}H NMR (298 K, $CDCl_3$, 300.13 MHz, ppm): δ 7.32−7.41 (m, 10H, =CH−, Ph), 2.52 (dd, 2H, >CH_2, $J_{HP(1)}$ = 2.1 Hz, $J_{HP(2)}$ = 0.90 Hz, P(1)CH_2P(2)), 1.89 (d, 6H, −CH_3, J_{HP} = 7.8 Hz, phosphole), 1.87 (s, 6H, −CH_3, phosphole). ^{31}P NMR (298 K, $CDCl_3$, 121.495 MHz, ppm): δ + 1.97 (d, P(1), $J_{P(1)P(2)}$ = 36.1 Hz, phosphole), −22.32 (d, P(2), $J_{P(2)P(1)}$ = 36.21 Hz, PPh_2). ^{13}C NMR (298 K, $CDCl_3$, 75.468 MHz, ppm): δ 143.04 (d, =C<, J_{CP} = 11.0 Hz), 134.03 (d, =C<, J_{CP} = 6.6 Hz), 132.95 (d, =CH−, J_{CP} = 14.4 Hz, Ph), 128.47 (d, =CH−, J_{CP} = 6.9 Hz, Ph), 128.19 (d, =CH−, J_{CP} = 6.6 Hz, Ph), 20.48 (dd, >CH_2, $J_{CP(1)}$ = 31.4 Hz, $J_{CP(2)}$ = 26.3 Hz, P(1)CH_2P(2)), 13.78 (d, −CH_3, J_{CP} = 2.9 Hz, phosphole), 13.11 (d, −CH_3, J_{CP} = 21.4 Hz, phosphole), 13.07 (d, −CH_3, J_{CP} = 21.5 Hz, phosphole). MS (DCI, NH_3): m/z (%) 339.1 (100%) $[M + H]^+$. Anal. Calcd for $C_{21}H_{24}P_2$: C, 74.54; H, 7.15. Found: C, 74.87; H, 7.90.

General Procedure for Rhodium Complex 8. *Method A.* To a solution of $[Rh(\mu\text{-Cl})(\eta^4\text{-COD})]_2$ (0.081 mmol, 0.04 g) in CH_2Cl_2 (15 mL) was slowly added a solution of 2 equiv of phospholyl(diphenylphosphino)methane ligand **5** (0.162 mmol) in CH_2Cl_2 (10 mL) with stirring at −90 °C. The reaction mixture was kept at the same temperature for 15 min, and then $AgBF_4$ (0.032 g, 0.164 mmol) was introduced. The resulting mixture was warmed slowly to room temperature and stirred for 2 h. The final solution was filtered and evaporated to dryness. Since the purification of this yellow residue was not successful, the crude product was directly characterized by NMR spectroscopy.

Method B. To a solution of $[Rh(\eta^4\text{-COD})_2][CF_3SO_3]$ (0.028 mmol, 0.013 g) in CH_2Cl_2 (10 mL) was added a solution of phospholyl(diphenylphosphino)methane ligand **5** (0.028 mmol) in CH_2Cl_2 (5 mL) at −90 °C. The reaction mixture was stirred for 15 min at this temperature and then warmed to room temperature, at which the yellow solution was stirred for a further 2 h. The resulting solution was finally evaporated to dryness.

*[Rh(η⁴-COD)(dibenzophospholyl(diphenylphosphino)methane)][CF₃SO₃] (**8a′**).* ^{1}H NMR (298 K, CD_2Cl_2, 400.13 MHz, ppm): δ selected 4.26 (td, 2H, >CH_2, $J_{HP(1)}$ = $J_{HP(2)}$ = 10.2 Hz, J_{HRh} = 2.0 Hz, P(1)CH_2P(2)). ^{31}P{^{1}H} NMR (298 K, CD_2Cl_2, 161.976 MHz, ppm): AMX, δ −31.42 (dd, $J_{P(2)P(1)}$ = 85.0 Hz, $J_{P(2)Rh}$ = 128.5 Hz, phosphole), −37.36 (dd, $J_{P(1)P(2)}$ = 85.0 Hz, $J_{P(1)Rh}$ = 130.7 Hz, −PPh_2). MS (FAB, MNBA): m/z (%) 593 (100) $[M]^+$.

*[Rh(η⁴-COD)(2,5-diphenylphospholyl(diphenylphosphino)methane)][BF₄] (**8b**).* ^{1}H NMR (298 K, CD_2Cl_2, 300.13 MHz, ppm): δ selected 5.72 (br s, 2H, =CH−, COD), 5.26 (br s, 2H, =CH−, COD), 4.13 (td, 2H, >CH_2, $J_{HP(1)}$ = $J_{HP(2)}$ = 10.7 Hz, J_{HRh} = 1.2 Hz, P(1)CH_2P(2)), 2.16−2.60 (m, >CH_2, COD). ^{31}P{^{1}H} NMR (298 K, CD_2Cl_2, 161.976 MHz, ppm): AMX, δ −36.64 (dd, $J_{P(1)P(2)}$ = 77.8 Hz, $J_{P(1)Rh}$ = 116.4 Hz, phosphole), −40.74 (dd, $J_{P(2)P(1)}$ = 77.8 Hz, $J_{P(2)Rh}$ = 124.4 Hz, −PPh_2). MS (FAB, MNBA): m/z (%) 645 (100) $[M]^+$.

General procedure for Trans Rhodium Complex 9. *Method A.* Starting from $[Rh(\mu\text{-Cl})(\eta^4\text{-COD})]_2$, complex **9** has been synthesized as described for **8**, except that 4 equiv of ligands **5** was added.

Method B. The reaction was carried out using $[Rh(\eta^4\text{-COD})_2]$-$[CF_3SO_3]$ and 2 equiv of ligands **5** under the same conditions as described above for complexes **8**.

*trans-[Rh(dibenzophospholyl(diphenylphosphino)methane)₂]-[CF₃SO₃] (**9a′**).* ^{1}H NMR (298 K, CD_2Cl_2, 300.13 MHz, ppm): δ selected 3.28 (dd, >CH_2, $J_{HP(1)}$ = 14.1 Hz, $J_{HP(2)}$ = 12.3 Hz, P(1)CH_2P(2)). ^{31}P{^{1}H} NMR (298 K, CD_2Cl_2, 121.495 MHz, ppm): spin system AA′XX′M, δ −20.14 (ddd, A, J_{AX} = 37.7 Hz, JAX′ = 40.1 Hz, J_{AM} = 113.0 Hz), −33.03 (ddd, B, J_{XA} = 37.7 Hz, $J_{XA'}$ = 40.1 Hz, J_{XM} = 80.2 Hz). MS (FAB, MNBA): m/z (%) 867 (100) $[M]^+$.

*trans-[Rh(2,5-diphenylphospholyl(diphenylphosphino)-methane)₂][BF₄] (**9b**).* ^{1}H NMR (298 K, CD_2Cl_2, 300.13 MHz, ppm): δ 8.18 (d, 6H, −CH=, J_{HH} = 7.5 Hz), 7.48 (m, 4H, −CH=, J_{HP} = 8.7 Hz), 7.37 (m, 8H, −CH=, J_{HH} = 7.5 Hz), 7.20−7.32 (m, 10H, −CH=), 7.14 (t, 10H, −CH=, J_{HH} = 7.7 Hz), 7.02 (t, 6H, −CH=, J_{HH} = 7.7 Hz), 4.32 (m, 4H, >CH_2, P(1)CH_2P(2)).^{31}P{^{1}H} NMR (298 K, CD_2Cl_2, 121.495 MHz, ppm): spin system AABBX, δ −31.73 (J_{AB} = 25.0 Hz, J_{AX} = J_{BX} = 108.0 Hz), −31.93 (J_{AB} = 25.0 Hz, J_{AX} = J_{BX} = 110 Hz); MS (FAB, MNBA): m/z (%) 971 (100) $[M]^+$.

General Procedure for Synthesis of the Rhodium Complexes 10. To a solution of ligands **4** (0.149 mmol) in CH_2Cl_2 (10 mL) was added a solution of $[Rh_2(\mu\text{-Cl})_2(\eta^4\text{-COD})_2]$ (0.037 g, 0.075 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was stirred at this temperature for 15 min, then $AgBF_4$ (0.032 g, 0.164 mmol) was introduced, and the resulting mixture was warmed to room temperature and stirred for 14 h. The solution was filtered through a Celite column and concentrated, and *n*-pentane was added to afford **10** as a yellow-green solid. Workup with diethyl ether (3 × 10 mL) gave the clean product (yields 61−94%).

*[Rh(η⁴-COD)(η²-BH₃-phosphino)(κ¹-dibenzophospholyl)-methane][BPh₄] (**10a″**).* Complex **10a″** was synthesized by metathesis of a dichloromethane solution of **10a** with $NaBPh_4$ in excess. ^{1}H NMR (298 K, CD_2Cl_2, 300.13 MHz, ppm): δ 7.97 (dd, 2H, =CH−, J_{HH} = 7.7 Hz, J_{HP} = 0.9 Hz, phosphole), 7.67 (m, 8H, =CH−), 7.56 (m, 4H, =CH−, J_{HH} = 7.8 Hz, J_{HP} = 3.6 Hz), 7.41 (bm, 8H-*o*, =CH−, J_{HH} = 7.8 Hz, BPh_4), 7.25−7.33 (m, 4H, =CH−), 7.09 (t, 8H-*m*, =CH−, J_{HH} = 7.3 Hz, BPh_4), 6.95 (t, 4H-*p*, =CH−, J_{HH} = 7.2 Hz, BPh_4), 5.93 (br s, 2H, =CH−, COD), 3.32 (br s, 2H, =CH−, COD), 2.64 (t, 2H, >CH_2, $J_{HP(1)}$ = $J_{HP(2)}$ = 11.71 Hz, P(1)CH_2P(2)), 2.12−2.54 (m, 8H, >CH_2, COD), −0.04 (b, 3H, J_{HP} = 11.4 Hz, BH_3). ^{31}P{^{1}H} NMR (298 K, CD_2Cl_2, 121.495 MHz, ppm): δ +47.42 (dd, P(1), $J_{P(1)Rh}$ = 139.5 Hz, $J_{P(1)P(2)}$ = 68.2 Hz, phosphole), 20.13 (br, P(2), PPh_2·BH_3). ^{11}B{^{1}H} NMR (298 K, $CDCl_3$, 96.294 MHz, ppm): δ −6.51 (s, BPh_4), −26.00 (d, $J_{BP(2)}$ = 77.0 Hz, BH_3). ^{13}C{^{1}H} NMR (298 K, CD_2Cl_2, 75.468 MHz, ppm): δ 164.78 (d, >C=, J_{CP} = 49.3 Hz), 163.47 (d, >C=, J_{CP} = 49.3 Hz), 142.57 (d, >C=, J_{CP} = 9.9 Hz), 136.02 (bs, =CH−*o*, BPh_4), 133.50 (d, =CH−, J_{CP} = 2.5 Hz), 132.97 (d, =CH−, J_{CP} = 1.2 Hz), 132.32 (d, =CH−, J_{CP} = 10.6 Hz), 131.00 (d, =CH−, J_{CP} = 14.8 Hz), 130.00 (d, =CH−, J_{CP} = 11.5 Hz), 130.24 (d, >C=, J_{CB} = 4.5 Hz, BPh_4), 129.20 (d, =CH−, J_{CP} = 11.1 Hz), 125.67 (br, =CH−*m*, BPh_4), 124.65 (d, >C=, J_{CP} = 64.68 Hz, PPh_2), 124.59 (d, >C=, J_{CP} = 64.8 Hz, PPh_2), 122.40 (d, =CH−, J_{CP} = 6.2 Hz, phosphole), 121.74 (s, =CH−*p*, BPh_4), 106.86 (dd, =CH, J_{CRh} = 10.2 Hz, $J_{CPtrans}$ = 6.1 Hz, COD), 74.90 (dd, J_{CRh} = 13.1 Hz, J_{CP} = 0.9 Hz), 33.51 (s, >CH_2, COD), 33.47 (s, >CH_2, COD), 28.60 (dd, $J_{CP(1)}$ = 42.5 Hz, $J_{CP(2)}$ = 11.3 Hz, P(1)CH_2P(2)), 28.25 (s, >CH_2, COD). MS (FAB, MNBA): m/z (%) 607 (100) $[M]^+$. Anal. Calcd for $C_{57}B_2H_{55}P_2Rh$: C, 73.89; H, 5.98. Found: C, 73.83; H, 5.83. Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of the concentrated dichloromethane solution at room temperature.

*[Rh(η⁴-COD)(η²-BH₃-phosphino)(κ¹-2,5-diphenylphospholyl)-methane][BF₄] (**10b**).* Yellow solid. Yield: 94%. ^{1}H NMR (298 K, CD_2Cl_2, 300.13 MHz, ppm): δ 7.95 (m, 4H, =CH−, J_{HH} = 2.1, 7.8 Hz, Ph), 7.50 (m, 6H, =CH−, J_{HH} = 7.5 Hz, Ph), 7.34−7.42 (m, 10H, =CH−, Ph), 7.31 (dd, 2H,, =CH−, J_{HP} = 1.2, 27.0 Hz, phosphole),

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6.02 (d, 2H, =CH−, J_{HP} = 1.8 Hz, COD), 3.70 (s, =CH−, 2H, COD), 2.71 (t, 2H, >CH_2, J_{HP} = 11.4 Hz, P(1)CH_2P(2)), 2.47−2.65 (m, 2H, >CH_2, COD), 2.24−2.44 (m, 6H, >CH_2, COD), −0.06 (br, 3H, BH_3). ^{1}H{^{11}B} NMR (298 K, $CDCl_3$, 300.13 MHz, ppm): δ selected −0.06 (t, 3H, J_{HP} = 10.5 Hz, BH_3). ^{11}B{^{1}H} NMR (298 K, CD_2Cl_2, 96.294 MHz, ppm): δ −27.66 (d, J_{BP} or J_{BRh} = 82.8 Hz, BH_3). ^{31}P{^{1}H} NMR (298 K, CD_2Cl_2, 121.495 MHz, ppm): δ +52.97 (dd, P(1), J_{PRh} = 130.36 Hz, $J_{P(1)P(2)}$ = 81.6 Hz, phosphole), 28.63 (br, P(2), $H_3B{\cdot}PPh_2$). ^{13}C{^{1}H} NMR (298 K, CD_2Cl_2, 75.468 MHz, ppm): δ 143.08 (d, >C=, J_{CP} = 43.0 Hz, phosphole), 143.02 (d, >C=, J_{CP} = 43.1 Hz, phosphole), 136.38 (d, =CH−, J_{CP} = 14.3 Hz, phosphole), 132.97 (d, =CH−, J_{CP} = 2.6 Hz, Ph), 132.22 (d, >C=, J_{CP} = 14.4 Hz, −Ph, phosphole), 131.79 (d, =CH−, J_{CP} = 10.7 Hz, Ph), 129.59 (d, =CH−, J_{CP} = 11.5 Hz, −Ph), 129.25 (s, =CH−, −Ph, phosphole), 129.05 (s, =CH−, −Ph, phosphole), 127.08 (d, =CH−, J_{CP} = 7.0 Hz, −Ph), 124.76 (d, >C=, J_{CP} = 65.0 Hz, −Ph), 124.68 (d, >C=, J_{CP} = 65.1 Hz, −Ph), 106.04 (dd, =CH−, $J_{CPphosphole}$ = 6.7 Hz, J_{CRh} = 9.0 Hz, COD), 77.46 (d, =CH−, J_{CRh} = 13.0 Hz, COD), 33.56 (s, >CH_2, COD), 33.52 (s, >CH_2, COD), 28.58 (s, >CH_2, COD), 28.56 (s, >CH_2, COD), 22.18 (dd, >CH_2, $J_{CP(1)}$ = 15.6, 43.88 Hz, P(1)CH_2P(2)). MS (FAB, MNBA): m/z (%) 659 (100) $[M]^+$. Anal. Calcd for $C_{37}H_{39}B_2F_4P_2Rh$: C, 59.56; H, 5.27. Found: C, 60.59; H, 5.30. Yellow crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a concentrated solution of **10b** in CH_2Cl_2 at −20 °C.

*[Rh(η^4-COD)(η^2-BH_3-phosphino)(κ^1-2,3,4,5-tetramethylphospholyl)methane][BF_4] (**10c**).* Yellow solid. Yield: 90%. ^{1}H NMR (298 K, CD_2Cl_2, 300.13 MHz, ppm): δ 7.80 (m, 4H-*o*, =CH−, J_{HH} = 0.9, 8.4 Hz, J_{HP} = 12.3 Hz, Ph), 7.59−7.72 (m, 4H-*m* and 2H-*p*, =CH−, J_{HP} = 2.1 Hz, Ph), 5.75 (s, 2H, =CH−, COD), 3.43 (br, 2H, J_{HP} = 3.0 Hz, =CH−, COD), 2.58 (t, $J_{HP(1)}$ = $J_{HP(2)}$ = 11.7 Hz, P(1)CH_2P(2)), 2.37−2.46 (m, 4H, >CH_2, COD), 2.20−2.32 (m, 4H, >CH_2, COD), 1.93 (d, 6H, −CH_3, J_{HP} = 0.6 Hz, phosphole), 1.69 (d, 6H, −CH_3, J_{HP} = 12.6 Hz, phosphole), −0.43 (brq, 3H, J_{HB} = 108.9 Hz, BH_3). ^{1}H{^{11}B} NMR (298 K, CD_2Cl_2, 300.13 MHz, ppm): selected δ −0.43 (t, J_{HP} = J_{HRh} = 11.4 Hz, BH_3). ^{31}P{^{1}H} NMR (298 K, CD_2Cl_2, 121.495 MHz, ppm): δ +66.23 (dd, P(1), $J_{P(1)P(2)}$ = 63.5 Hz, $J_{P(1)Rh}$ = 128.9 Hz, phosphole), 24.32 (br, P(2), $Ph_2P{\cdot}BH_3$). ^{11}B NMR (298 K, CD_2Cl_2, 96.294 MHz, ppm): δ −26.02 (t, J_{BH} = J_{BP} (or J_{BRh}) = 91.5 Hz, BH_3), −1.12 (s, BF_4). ^{13}C{^{1}H} NMR (298 K, CD_2Cl_2, 75.468 MHz, ppm): δ 149.15 (d, 2C, >C=, J_{CP} = 16.6 Hz, −Ph), 133.23 (d, 2C, =CH−*p*, J_{CP} = 3.0 Hz, −Ph), 132.24 (d, 4C, =CH−*o*, J_{CP} = 10.6 Hz, −Ph), 129.87 (d, 4C, =CH−*m*, J_{CP} = 11.3 Hz, −Ph), 126.74 (d, 1C, >C=, J_{CP} = 46.8 Hz, phosphole), 126.69 (d, 1C, >C=, J_{CP} = 46.0 Hz, phosphole), 125.55 (d, 1C, >C=, J_{CP} = 64.1 Hz, phosphole), 125.49 (d, 1C, >C=, J_{CP} = 64.1 Hz, phosphole), 105.16 (ddd, 1C, =CH−, $J_{CP(1)}$ = 6.0 Hz, J_{CRh} = 9.8 Hz, J_{CB} or $J_{CP(2)}$ = 1.5 Hz, COD), 74.65 (d, 1C, =CH−, $J_{CP(1)}$ or J_{CRh} = 13.6 Hz, COD), 33.84 (d, 2C, >CH_2, J_{CP} = 2.9 Hz, COD), 28.21 (d, 4C, >CH_2, J_{CP} = 1.2 Hz, COD), 23.04 (dd, 1C, >CH_2, $J_{CP(1)}$ = 11.8, 44.6 Hz, P(1)CH_2P(2)), 13.85 (d, 2C, −CH_3, J_{CP} = 10.5 Hz, phosphole), 11.62 (d, 2C, −CH_3, J_{CP} = 16.8 Hz, phosphole). MS (FAB, MNBA): m/z (%) 563 (100) $[M]^+$. Anal. Calcd for $C_{29}H_{39}B_2F_4P_2Rh$: C, 53.58; H, 6.05: Found: C, 53.75; H, 6.40. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into concentrated solution of **10c** in CH_2Cl_2 at −20 °C.

*[Rh(η^4-COD)(η^2-BH_3-dicyclohexylphosphino)(κ^1-dibenzophospholyl)methane][BF_4] (**10e**).* Yellow-brown solid. Yield: 61%. ^{1}H NMR (298 K, CD_2Cl_2, 300.13 MHz, ppm): δ 8.00 (d, 2H, =CH−, J = 7.7 Hz, phosphole), 7.85 (t, 2H, =CH−, J = 8.2 Hz, phosphole), 7.73 (t, 2H, =CH−, J = 7.7 Hz, phosphole), 7.63−7.60 (m, 2H, =CH−, phosphole), 5.79 (sl, 2H, =CH−, COD), 3.16 (sl, 2H, =CH−, COD), 2.39−2.37 (m, 2H, >CHP, cHex), 2.28−2.16 (m, 4H, >CH_2, COD), 2.14−2.04 (m, 4H, >CH_2, COD), 2.04 (t, 2H, >CH_2, $^2J_{HP(1)}$ = $^2J_{HP(2)}$ = 10.9 Hz, P(1)CH_2P(2)), 1.94−1.83 (m, 10H, >CH_2, cHex), 1.40−1.31 (m, 10H, >CH_2, cHex), −0.85 (m, 3H, BH_3). ^{31}P{^{1}H} NMR (298 K, CD_2Cl_2, 121.495 MHz, ppm): δ +52.28 (dd, P(1), $^1J_{PRh}$ = 140.4 Hz, J_{PP} = 58.7 Hz, phosphole), 40.88 (br, P(2), $(cHex)_2P{\cdot}BH_3$). MS (ESI): m/z (%) 619.3 (100) $[M]^+$.

*[Rh(η^4-COD)(η^2-BH_3-dicyclohexylphosphino)(κ^1-2,5-diphenylphospholyl)][BF_4] (**10f**).* Yellow solid. Yield: 64%. ^{1}H NMR (298 K, CD_2Cl_2, 300.13 MHz, ppm): δ 8.08−8.07 (m, 4H, =CH−, Ph, phosphole), 7.59−7.53 (m, 6H, =CH−, Ph, phosphole), 7.25 (d, 2H, =CH−, J = 12.9 Hz, phosphole), 5.93 (sl, 2H, =CH−, COD), 3.66 (sl, 2H, =CH−, COD), 2.56−2.44 (m, 4H, >CH_2, COD), 2.33−2.28 (m, 4H, >CH_2, COD), 1.86 (t, 2H, >CH_2, $^2J_{HP(1)}$ = $^2J_{HP(2)}$ = 5.4 Hz, P(1)CH_2P(2)), 1.72−1.62 (m, 12H, >CHP and >CH_2, cHex), 1.12−0.98 (m, 12H, >CH_2, cHex), −0.83 (m, 3H, BH_3). ^{31}P{^{1}H} NMR (298 K, CD_2Cl_2, 121.495 MHz, ppm): δ +57.91 (dd, P(1), $^1J_{PRh}$ = 131.3 Hz, J_{PP} = 55.8 Hz, phosphole), 45.96 (br, P(2), $(cHex)_2P{\cdot}BH_3$). MS (ESI): m/z (%) 671.3 (100) $[M]^+$.

*[Rh(η^4-COD)(η^2-BH_3-diphenylphosphinoborane)-{(diphenylphosphino)methane}][BF_4] (**10g**).* Yellow solid. Yield: 68%. ^{1}H NMR (298 K, CD_2Cl_2, 300.13 MHz, ppm): δ 7.63−7.60 (m, 4H, =CH−, Ph), 7.56−7.50 (m, 6H, =CH−, Ph), 7.49−7.47 (m, 2H, =CH−, Ph), 7.43−7.40 (m, 8H, =CH−, Ph), 5.84 (sl, 2H, =CH−, COD), 3.34 (sl, 2H, =CH−, COD), 3.28 (t, 2H, J = 11.7 Hz, >CH_2, $Ph_2PCH_2PPh_2{\cdot}BH_3$), 2.52−2.49 (m, 4H, >$CH_2$, COD), 2.32−2.27 (m, 4H, >CH_2, COD), −0.25 (m, 3H, BH_3). ^{31}P{^{1}H} NMR (298 K, CD_2Cl_2, 121.495 MHz, ppm): δ +46.65 (dd, J_{PRh} = 140.9 Hz, J_{PP} = 70.3 Hz, $Ph_2PCH_2PPh_2{\cdot}BH_3$), 19.57 (br, $Ph_2PCH_2PPh_2{\cdot}BH_3$). MS (ESI): m/z: (%) 696.1 (100%) $[M]^+$.

General Experimental Procedure for Hydrogenation. *Method A.* Into glassware was added a mixture of [Rh(η^4-COD)$_2$]-[CF_3SO_3] (3.0 mg, 0.0064 mmol), ligands **4** and **5** (0.0064 mmol), substrate (50−400 equiv), and MeOH (10 mL). The glassware was placed in a stainless steel autoclave. Hydrogenation was performed at the desired temperature (25−40 °C) under hydrogen pressure (10−40 bar) for 20 h. After the autoclave was cooled, the hydrogen pressure was slowly released. Solvent was removed under vacuum, and conversion was determined by ^{1}H NMR.

Method B. Precatalysts were prepared by mixing [Rh(η^4-COD)$_2$]-[CF_3SO_3] (3.0 mg, 0.0064 mmol), ligands **4** and **5** (0.0064 mmol), and substrate (50−400 mol equiv) under an argon atmosphere in a Schlenk tube. MeOH (10 mL) was added, and the solution was stirred for 3 h at room temperature. The reaction solution was transferred into glassware. The hydrogenation procedure was performed as described in method A.

General Procedure for Catalyzed Hydroboration Reactions. *Method A (Using Isolated Rhodium Complexes).* Rhodium complexes **10** (10 μmol) in dry THF (2 mL) were placed under argon in a Schlenk tube. Catecholborane (1 M in THF, 1 mL, 1 mmol) was added, and the light brown solution was stirred for 5 min at room temperature. Styrene (0.11 mL, 1 mmol) was then injected and the reaction mixture was stirred for 22 h at room temperature. The reaction mixture was then cooled to 0 °C, and ethanol (2 mL) was added followed by NaOH (1 M, 6 mL) and H_2O_2 (6 mL). The ice bath was removed, and the solution was stirred for 1 h at room temperature. The reaction mixture was transferred to a separatory funnel, and diethyl ether (10 mL) was added. The organic layer was washed with NaOH (1 M, 10 mL) and brine (10 mL) and dried over $MgSO_4$. The solution was filtered, and the solvent was removed in vacuo to give the hydroborated product. Conversion and regioselectivity were determined by ^{1}H NMR.

Method B (Using in Situ Prepared Rhodium Complexes). [Rh(η^4-COD)$_2$][BF_4] (10 μmol) and the ligand (11 or 22 μmol) in dry THF (2 mL) were placed under argon in a Schlenk tube and stirred for 30 min at room temperature. Catecholborane (1 M in THF, 1 mL, 1 mmol) was added, and the light brown solution was stirred for 5 min at room temperature. Styrene (0.11 mL, 1 mmol) was then injected and the reaction mixture was stirred for 22 h at room temperature. Treatment of the reaction mixture was carried out as described above for method A.

1-Phenylethanol. ^{1}H NMR (298 K, $CDCl_3$, 300.13 MHz, ppm): δ 7.42−7.28 (m, 5H, =CH−, Ph), 4.93 (q, 1H, J = 6.4 Hz, >CH−), 1.52 (d, 3H, J = 6.4 Hz, −CH_3).

2-Phenylethanol. ^{1}H NMR (298 K, $CDCl_3$, 300.13 MHz, ppm): δ 7.27−7.14 (m, 5H, =CH−, Ph), 3.78 (t, 2H, J = 6.6 Hz, CH_2O), 2.79 (t, 2H, J = 6.6 Hz, CH_2Ph).

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X-ray Structure Determination. A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a glass fiber and cooled in the cryostream of either an Oxford-Diffraction XCALIBUR CCD diffractometer for **4a**, **5a,b**, and **10b,c** or a Bruker APEX2 diffractometer for **4c**. Data were collected using monochromatic Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods (SIR97)[48] and refined by least-squares procedures on F^2 using SHELXL-97.[49]All H atoms attached to carbon were introduced in calculations in idealized positions and treated as riding models. The coordinates of H atoms attached to the boron for compounds **4a,c** were refined using similar distance restraints (SADI within SHELXL-97[49]) and overall isotropic thermal parameters, whereas for **10b,c**, the H coordinates were freely refined. In compound **10b**, the COD ligand was partially disordered over two positions. This disorder was modelized using the tools available in SHELXL-97.[49] The data for compound **5b** were of very bad quality, and thus the refinement gave very poor results, even if there is no doubt about the structure itself. The drawing of the molecules was realized with the help of ORTEP-32.[50]

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 804802−804807. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving molecular views of **4a**, **5b**, and **10b** and NMR spectra and crystal data and refinement parameters for compounds **4a,c**, **5a,b**, and **10b,c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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