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Article

First Dibenzophospholyl(diphenylphosphino)methane−Borane Hybrid P−(η^2-BH_3) Ligand: Synthesis and Rhodium(I) Complex

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The first dibenzophospholyl(diphenylphosphino)methane−borane hybrid ligand has been prepared from a Pd-catalyzed reaction of (chloromethyl)diphenylphosphine−borane with the dibenzophospholyl anion. This borane precursor is readily synthesized using a promising new reaction of diphenylphosphine−borane with dichloromethane, under phase transfer catalysis (PTC) conditions. The dibenzophospholyl(diphenylphosphino)methane−borane acts as a chelating P−(η^2-BH_3) ligand to afford an air-stable Rh(I) complex. The X-ray crystal structure of this complex shows complexation of both benzophospholyl and borane moieties.

Recently the reaction of phosphine−boranes with transition-metal complexes has attracted particular attention, owing to their possible dehydrogenation under mild catalytic conditions,[1] making it as a promising H_2 source. In addition, phosphine−boranes could also be used without previous decomplexation to prepare various transition-metal complexes by ligand exchange or by a reaction with the corresponding metal salts.[2,3] Using this methodology, phosphine−boranes allow one to prepare chiral or achiral complexes with phosphorus ligands which cannot be prepared by alternative approaches or purified in their trivalent form.[2,3] On the other hand, phosphine−boranes carry out the complexation by their BH_3 group with the formation of three-center−two-electron M−H−B bonds, as illustrated by the complexes [Mn(η^5-C_5H_5)(η^1-$H_3B\cdot PMe_3$)$(CO)_2$] (**1**),[4] [(Rh(η^2-$H_3B\cdot$dppm)(η^4-C_8H_{12})][PF_6] (**2**),[5] and [Ru(η^5-C_5H_5)(η^1-$H_3B\cdot$dppm)]PF_6] (**3**)[6] (Figure 1).

Bis(diphenylphosphino)methane−borane (dppm·BH_3) stabilizes the labile M···H_3B bond toward its η^1 or η^2 coordination mode, but until to date only dppm−borane has been reported so far.[5−8]

In order to extend the chemistry of these complexes, we were interested in the design and synthesis of modulable chelating phosphine−borane ligands by introduction of a phosphole group[9] which possesses different steric and electronic effects with respect to the phosphine. As part of our ongoing program on phosphine−borane derivatives used as electrophilic or nucleophilic building blocks,[10] we investigated the synthesis of phospholyl(diphenylphosphino)-methane ligands using a promising new reaction producing a methano bridge via the formation of a P−C bond, starting from a (chloromethyl)diphenylphosphine−borane as precursor.

We report herein the synthesis of the first dibenzophospholyl(diphenylphosphino)methane−borane and its use for the preparation of a new hybrid P−(η^2-BH_3)−rhodium(I) complex.

Results and Discussion

The hybrid dibenzophospholyl(diphenylphosphino)methane−borane ligand **7** is prepared from the reaction of the

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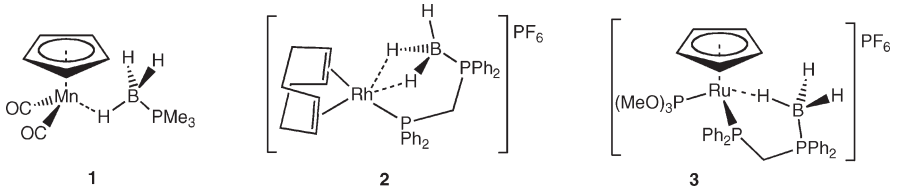
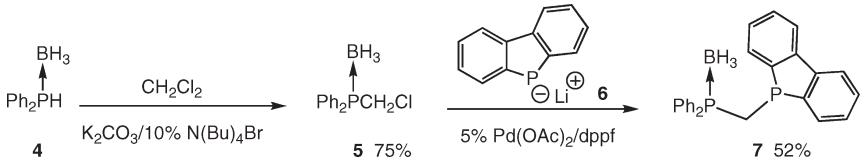


Figure 1. Drawings of **1**−**3**.

Scheme 1



dibenzophospholyllithium reagent **6**[11] with (chloromethyl)-diphenylphosphine−borane **5**. The compound **5** was previously prepared in 75% yield, by the new reaction of diphenylphosphine−borane **4** with dichloromethane, under phase transfer catalysis (PTC) conditions (Scheme 1). Noteworthy the direct reaction of the anion **6** with the (chloromethyl)phosphine−borane **5** results in low yield (< 10%). Conversely, in the presence of 5% $Pd(OAc)_2$/dppf, the desired ligand **7** is obtained in 52% isolated yield (Scheme 1).

The white solid dibenzophospholyl(diphenylphosphino)-methane−borane ligand **7** is both air- and moisture-stable and is fully characterized by conventional NMR techniques (^{31}P, ^{1}H, ^{13}C, ^{11}B), mass spectrometry, and elemental analysis. The $^{31}P\{^{1}H\}$ NMR spectrum displays a doublet at δ −29.7 ppm ($^{2}J_{PP}$ = 68.0 Hz) and a lower field broad signal at δ 15.6 ppm, the latter being assigned to the PPh_2 group coordinated to borane. It is noteworthy that the BH_3 group does not migrate from the PPh_2 moiety to the phospholyl group during the reaction between $BH_3 \cdot P(CH_2Cl)Ph_2$ and $LiP(C_6H_4)_2$. The BH_3 group appears as a doublet at δ 1.34 ppm ($^{2}J_{HP(1)}$ = 15.9 Hz) in $^{1}H\{^{11}B\}$ NMR, whereas the ^{11}B NMR spectrum displays a single broad resonance at δ −38.3 ppm, characteristic of a phosphine−borane chemical shift.[12] Finally, the ^{1}H NMR spectrum exhibits a doublet of doublet at δ 2.63 ppm ($^{2}J_{HP(1)}$ = 10.8 Hz, $^{2}J_{HP(2)}$ = 2.1 Hz) corresponding to the methylene bridge. The X-ray crystal structure of the hybrid ligand **7** is shown in Figure 2 along with selected bond distances and angles. The P(1)−B(1) bond length is 1.9085(17) Å. The H atoms attached to the boron atom were idealized with distances of 0.98 Å and treated as riding on the B atom. The P(1)−C(11)−P(2) angle is 110.20(7)°. The C(21), C(22), C(23), and C(24) atoms of the dibenzophosphole residue are planar, with the largest deviation from the mean plane being 0.044(2) Å. The P(2) atom deviates from this plane by 0.140(1) Å, as already observed for other dibenzophosphole compounds.[13] All bond lengths and bond angles compare favorably to those of other common dibenzophospholes.[13]

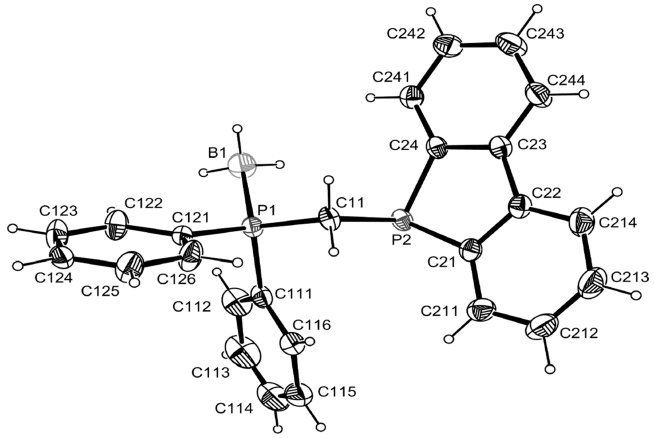
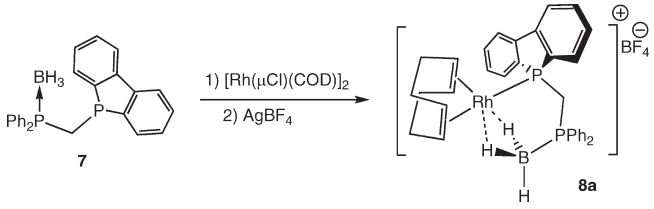


Figure 2. X-ray crystal structure of the hybrid ligand **7**. Selected bond lengths (Å) and angles (deg):P(1)−B(1), 1.9085(17); P(1)−C(11), 1.8106(13); P(1)−C(111), 1.8053(15); P(1)−C(121), 1.8014(14); P(2)−C(11), 1.8624(13); P(2)−C(21), 1.8169(14); P(2)−C(24), 1.8088(14); P(1)−C(11)−P(2), 110.20(7); C(24)−P(2)−C(21), 89.70(6).

Scheme 2



The $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ and $[Rh(COD)_2][CF_3SO_3]$ precursors were used to synthesize the corresponding complexes with the hybrid ligand **7**. The reaction of $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ with 0.5 equiv of **7** in dichloromethane, using $AgBF_4$ as a halide abstracting agent, gave the rhodium complex $[Rh(COD)\{(\eta^2\text{-}BH_3\text{-phosphine})(\kappa^1\text{-phosphole})\}]BF_4$ (**8a**) in excellent yield (86% isolated), which is an air- and moisture-stable solid (Scheme 2). An alternative synthesis was also developed using the cationic precursor $[Rh(COD)_2]^+$ (as its $CF_3SO_3^-$ salt) with a stoichiometric amount of **7** in dichloromethane. Indeed, the reaction led to the complex $[Rh(COD)\{(\eta^2\text{-}BH_3\text{-phosphine})(\kappa^1\text{-phosphole})\}][CF_3SO_3]$ (**8b**) in a very good

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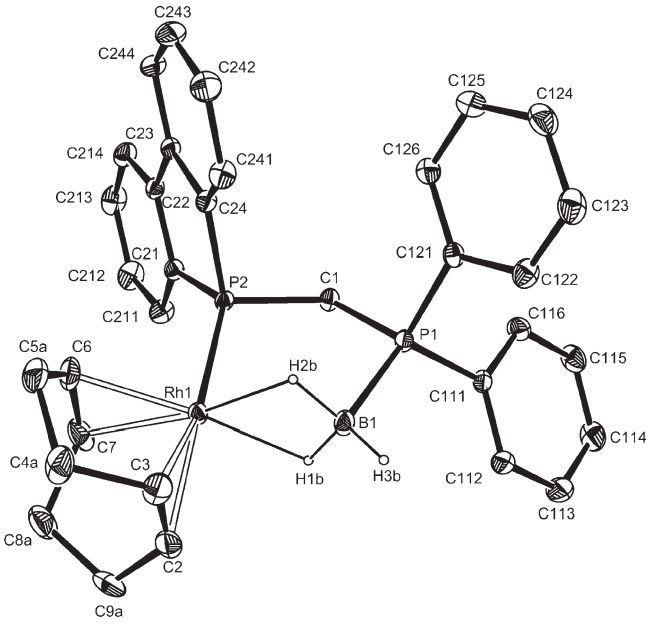

Figure 3. X-ray crystal structure of the cationic part of complex **8**. Selected bond lengths (Å) and angles (deg): P(1)−B(1), 1.928(2); P(1)−C(1), 1.8102(4); P(2)−C(1), 1.8377; Rh(1)−B(1), 2.331(2); Rh(1)−H(1b), 1.96(3); Rh(1)−H(2b), 1.85(3); B(1)−H(1b), 1.13(3); B(1)−H(2b), 1.24(3); B(1)−H(3b), 1.00(3); Rh(1)−P(2), 2.24532(16); P(2)−C(1), 1.8377; Rh(1)−C(2), 2.27157(17); Rh(1)−C(3), 2.25416(17); Rh(1)−C(6), 2.121(2); Rh(1)−C(7), 2.120(2); P(1)−C(1)−P(2), 112.743(14).

yield (92%). The complex **8a** was fully characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. The $[BF_4]^-$ metathesis with the bulky $[BPh_4]^-$ anion afforded crystals of **8c** suitable for the X-ray diffraction study.

The X−ray crystal structure of **8c** was determined at 180 K (Figure 3). The ligand binds to the metal center through the phosphorus atom of the phosphole moiety and in a η^2 mode through the BH_3 group, formally as two three-center−two-electron bonds. All hydrogen atoms on the borane were located and refined. The two bridging hydrogens exhibit similar Rh−H distances within experimental error (Rh−H(1b) = 1.96(3) Å; Rh−H(2b) = 1.85(3) Å). These distances compare well to those reported for other crystallographically characterized rhodium−dppm(borane) complexes.[5,7] Due to these Rh···H−B interactions, the corresponding B−H bond distances (B−H(1b) = 1.13(3) Å; B−H(2b) = 1.24(3) Å) are slightly longer than that found for the terminal B−H(3b) distance (1.00(3) Å). The Rh···B interatomic distance of 2.332 Å is longer than the sum of the combined covalent radii of Rh and B (2.27 Å) and is similar to those found in the rhodium complex **2** (2.313(3) Å), which is consistent with the absence of a direct Rh−B interaction. The Rh metal center has a square-planar geometry defined by the two centroids of the COD ligand and the P(2) and the B(1) atoms. Moreover, the geometry of **8** can be viewed as a trigonal bipyramid with one centroid and the H(1) and H(2) atoms in the equatorial plane, the H(1)−Rh−H(2) angle being small (60.7(12)°) (Figure 3).

The differences observed for the Rh−COD bond lengths reveal a differentiated *trans* influence for the benzophospholyl and BH_2 moeties. The Rh−Cg1 distance (C(2)−C(3) = 2.1752 (2) Å) *trans* to the benzophospholyl moiety is significantly longer than those that are *trans* to the BH_2 fragment, i.e. Rh−Cg2 (C(6)−C(7) = 2.0012 (2) Å). The coordination of ligand **7** to the rhodium induces a slight variation of the P(1)−C−P(2) angle (110.20(7)° *versus* 112.743(14)° for **7** and **8**, respectively). Surprisingly, the deviation of the P(2) atom from the C(21), C(22), C(23), C(24) mean plane increased (0.140(1) Å for **7** *versus* 0.1855(4) Å for **8**), whereas the phosphorus coordination normally brings the phosphorus back in the plane of the central *cycle*, as already observed in dibenzophosphole−rhodium complexes.[14]

The ^{1}H NMR spectral data at 188 K of the Rh complex **8a** confirm the molecular structure described above. In the $^1H\{^{11}B,^{31}P\}$ NMR spectrum, a singlet[15] at δ −1.41 ppm corresponding to 2H of BH_3 is observed, the third proton of BH_3 being included in a massif centered at 2.26 ppm with four protons of the COD ligand. By 1D ^{1}H EXSY experiment with broadband decoupling of ^{11}B and ^{31}P, two singlets[15] for the three protons of BH_3 (2.26 (1H) and −1.41 ppm (2H)) could be observed and assigned to the terminal B−H and to the bridging Rh−H−B, respectively.

The variable-temperature $^1H\{^{11}B,^{31}P\}$ NMR spectra, with heating from 188 to 298 K, show that these two singlets collapsed (T_c = 238 K, $\Delta G^{\ddagger} = 41.4 \pm 1$ kJ/mol) into a doublet at −0.09 ppm (J_{HRh} = 15.0 Hz). As the three protons of the BH_3 group are equivalent, the η^2-BH_3 binding motif observed in the solid state is not maintained in solution at room temperature. This suggests that the BH_3 group is fluxional in solution at room temperature, as observed in other rhodium complexes,[4−8] 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.[7]

T_1 measurements, obtained by the conventional inversion recovery method, have been carried out. At all temperatures, we observed an average T_1 for the three protons of BH_3, showing that the exchange is fast on the T_1 relaxation time scale, even at 188 K where the exchange is slow on the spectral time scale.

The remaining observed ^{31}P, ^{11}B, and ^{13}C resonances are entirely consistent with the solid-state structure. The boron chemical shift at δ −26.03 ppm (d, J_{BP} = 85.1 Hz), downfield of that of ligand **7** (δ −38.31 ppm), is similar to Weller's Rh complex.[5] In ^{31}P NMR spectra, the doublet of doublet at δ 47.52 ppm (dd, $J_{P(1)Rh}$ = 139.7 Hz, $J_{P(1)P(2)}$ = 68.9 Hz) and the broad signal at δ 20.66 ppm, corresponding to the phosphine−borane group, are shifted to lower fields. Moreover, the ^{31}P−^{103}Rh HMQC NMR spectrum at 298 K allows the assignment of the doublet at δ −8258.4 ppm to the Rh metal center.

In summary, we have described the synthesis of the first dibenzophospholyl(diphenylphosphino)methane−borane hybrid ligand prepared starting from (chloromethyl)diphenylphosphine−borane. This compound acting as a building block was easily prepared by the new reaction of diphenylphosphine−borane with dichloromethane under PTC conditions, which offers a promising route for the synthesis of modified dppm's. Dibenzophospholyl(diphenylphosphino)-methane−borane acts as a P−(η^2-BH_3) chelating ligand

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(15) The ^{1}H−Rh coupling could not be observed at low temperature.

affording a stable Rh(I) complex, with coordination of both the dibenzophospholyl and the borane moieties. Using this methodology, the synthesis of P-chirogenic phospholyl-(diphenylphosphino)methane−borane ligands and their Rh(I) complex derivatives are currently in progress for application in asymmetric catalysis.

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, P_2O_5 for CH_2Cl_2, and CaH_2 for *n*-pentane. 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 1D and 2D NMR spectra data were recorded on Bruker DRX 300 or Advance 300−500 spectrometers with TMS as internal reference for ^1H and ^{13}C, 85% phosphoric acid as external reference for ^{31}P, $BF_3 \cdot Et_2O$ as external reference for ^{11}B, and $Rh(acac)_3$ as external reference for ^{103}Rh. T_1 relaxation times were mesured by the conventional inversion recovery method. Mass spectral analyses were performed on Bruker ESI micro-TOF-Q (HR) and TSQ 7000 Thermoquest instruments (DCI). The *m*/*z* value of the major peak is given with the intensity as a percentage of the base peak shown in brackets. Elemental analyses were measured with a precision superior to 0.3% at the Microanalysis Laboratory of the LCC at Toulouse. Commercially available palladium(II) acetate, dppf, $[Rh(COD)_2]$-CF_3SO_3, silver trifluoroborate, and tetraphenylborate were used as received. 1-Phenyldibenzophosphole,[16] $[Rh(\mu\text{-Cl})(COD)]_2$,[17] and diphenylphosphine[18] were prepared as described.

Diphenylphosphine−Borane (4).[19] This compound was freshly prepared before use. In a round-bottom flask at room temperature were introduced THF (20 mL), diphenylphosphine (2.0 g, 10.7 mmol, 1 equiv), and then $BH_3 \cdot SMe_2$ (1.2 mL, 12.8 mmol). After it was stirred for 3 h, the mixture was hydrolyzed with H_2O (10 mL) and extracted with 3 × 10 mL of AcOEt. The organic phases were dried over $MgSO_4$, and the solvent was evaporated. The crude product was purified by flash chromatography over silica gel using AcOEt/petroleum ether (1/3) as eluent, affording pure **4** (1.85 g; yield 86%) as a white solid. ^1H NMR (298 K, $CDCl_3$, 300.13 MHz; δ (ppm)): 7.66−7.72 (m, 4H, *H* arom), 7.44−7.57 (m, 6H, *H* arom), 6.33 (qd, 1H, $^1J_{PH}$ = 379 Hz, $^3J_{HH}$ = 7 Hz, PH), 0.50−1.50 (br q, 3H, $^1J_{BH}$ = 87 Hz, B*H*$_3$). ^{31}P NMR (298 K, $CDCl_3$, 121.489 MHz; δ (ppm)): 1.3 (m).

(Chloromethyl)diphenylphosphine−Borane (5).[20] In a round-bottom flask at room temperature were introduced diphenylphosphine−borane **4**[17] (54 mg, 0.25 mmol, 1 equiv), tetrabutylammonium bromide (8 mg, 0.025 mmol, 10 mol %), dichloromethane (0.4 mL), finely crushed potassium carbonate (70 mg, 0.5 mmol, 2 equiv), and finally 25 μL of H_2O. After the mixture was stirred for 12 h, the end of the reaction was controlled by ^{31}P no lock NMR and the salts were removed by filtration over silica using dichloromethane as solvent. The solvent was evaporated and the crude product purified by flash chromatography over silica gel using toluene as eluent, affording pure **5** (yield 78%) as a white oil. R_f = 0.65 (toluene). ^1H NMR (298 K, $CDCl_3$, 300.13 MHz; δ (ppm)): 7.63−7.67 (m, 4H, *H* arom), 7.42−7.48 (m, 6H, *H* arom), 4.02 (d, 2H, J = 3.3 Hz, C*H*$_2$), 0.50−1.50 (m, 3H, B*H*$_3$). ^{31}P NMR (298 K, $CDCl_3$, 121.489 MHz; δ (ppm)): 23.7 (m). HRMS (ESI): calcd for $C_{13}H_{14}BClP$ ($M^+ - H$) 247.0615, found 247.0638.

Dibenzophospholyl(diphenylphosphino)methane−Borane (7). To a solution of 1-phenyldibenzophosphole (0.573 g, 2.2 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. After removal of the unreacted lithium, the dark red solution was cooled at −20 °C and anhydrous $AlCl_3$ (0.8 mmol, 0.11 g) was added to neutralize PhLi. The reaction mixture was warmed to room temperature and stirred again for 30 min to afford the dibenzophospholyl anion **6**. To the anion was added at −78 °C a solution of (chloromethyl)diphenylphosphine−borane **5** (0.50 g, 2.0 mmol) in THF (10 mL) and then a solution of $Pd(OAc)_2$ (0.1 mmol, 0.022 g) and dppf (0.2 mmol, 0.11 g) in THF (10 mL). After it was stirred for 48 h, the yellow reaction mixture was concentrated to 5 mL and quenched with degassed H_2O (20 mL). The residue was extracted with dichloromethane (3 × 30 mL), and the combined extracts were dried over $MgSO_4$ and then evaporated to afford a yellow solid. Purification by silica gel column chromatography (eluent CH_2Cl_2/*n*-hexane (50/50 or 40/60)) yielded 0.41 g (52%) of ligand **7** as a white solid. Crystals suitable for an X-ray diffraction study were obtained by recrystallization from an CH_2Cl_2/*n*-pentane solution at −20 °C. ^1H NMR (298 K, $CDCl_3$, 300.13 MHz; δ (ppm)): 7.88 (dd, $^4J_{HH}$ = 0.6 Hz, $^3J_{HH}$ = 7.5 Hz, 2H(3,3′) of phosphole), 7.75 (m, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 8.4 Hz, J_{HP} = 1.5 Hz, 4H, CH, Ph), 7.40−7.58 (m, 10H, 4H(3,3′,5,5′) of phosphole and 6H of Ph), 7.25 (t, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 1.0 Hz, 1H, H(4 or 4′) of phosphole), 7.24 (t, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 1.0 Hz, 1H, H(4 or 4′) of phosphole), 2.63 (dd, $^2J_{HP(2)}$ = 2.1 Hz, $^2J_{HP(1)}$ = 10.8 Hz, 2H, CH_2), 1.34 (brq, $^1J_{HB}$ = 88.5 Hz, 3H, BH_3). $^1H\{^{11}B\}$ NMR (298 K, $CDCl_3$, 300.13 MHz; selected δ (ppm)): 1.34 (d, $^1J_{HP(1)}$ = 15.9 Hz, 3H, BH_3). $^{31}P\{^1H\}$ NMR (298 K, $CDCl_3$, 121.495 MHz; δ (ppm)): +15.58 (br, P(1), PBH_3), −29.70 (d, P(2), $^2J_{PP}$ = 68.0 Hz). $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$, 75.468 MHz; δ (ppm)): 143.53 (d, J_{CP} = 1.8 Hz, C(2 or 2′) of phosphole), 142.85 (t, J_{CP} = 7.3 Hz, C(2 or 2′) of phosphole), 132.45 (d, J_{CP} = 8.7 Hz, Ph), 131.95 (d, J_{CP} = 2.4 Hz, Ph), 130.58 (d, J_{CP} = 22.4 Hz, C(6,6′) of phosphole), 129.81 (d, J_{CP} = 55.3 Hz, Ph), 129.78 (d, J_{CP} = 55.2 Hz, Ph), 129.0 (s, C(5,5′) of phosphole), 128.93 (d, J_{CP} = 10.1 Hz, Ph), 127.59 (d, J_{CP} = 7.3 Hz, CH(4,4′) of phosphole), 121.33 (s, CH(3,3′) of phosphole), 27.82 (dd, J_{CP} = 33.0, J_{CP} = 40.4 Hz, CH_2). $^{11}B\{^1H\}$ NMR (298 K, $CDCl_3$, 96.294 MHz; δ (ppm)): −38.44 (d, 1B, J_{BP} = 40.7 Hz). MS (DCI, NH_3; *m*/*z* (%)): 397.2 (100%) $[M + H]^+$. Anal. Calcd for $BC_{25}H_{23}P_2$: C, 75.79; H, 5.85. Found: C, 75.61; H, 5.99.

Rhodium Complex (8). A solution of the ligand **7** (0.059 g, 0.149 mmol) in CH_2Cl_2 (10 mL) was added to a solution of $[Rh_2(\mu\text{-Cl})_2(COD)_2]$ (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 and 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 and concentrated, and *n*-pentane was added to afford **8a** as a yellow-green solid. Workup with diethyl ether (3 × 10 mL) give the clean product (0.089 g, 86%). ^1H NMR (298 K, CD_2Cl_2, 500.33 MHz; δ (ppm)): 7.97 (dd, J_{HH} = 7.8 Hz, $^3J_{HP}$ = 0.9 Hz, 1H, CH (3 or 3′) of phosphole), 7.96 (dd, J_{HH} = 7.8 Hz, $^3J_{HP}$ = 0.9 Hz, 1H, CH-(3 or 3′) of phosphole), 7.70−7.75 (m, $^3J_{HH}$ = 6.2 Hz, J_{HP} = 1.1 Hz, 6H, $4H_{ortho} + 2H_{para}$, Ph), 7.66 (td, J_{HP} = 1.4 Hz, J_{HH} = 8.7 Hz, 1H, CH (4 or 4′) of phosphole), 7.64 (td, J_{HP} = 1.4 Hz, J_{HH} = 8.7 Hz, 1H, CH (4 or 4′) of phosphole), 7.58−7.62 (m, J_{HH} = 7.5 Hz, $4H_{meta}$, Ph), 7.39 (d, J_{HH} = 7.7 Hz, 1H, CH-(6 or 6′) of phosphole), 7.38 (d, J_{HH} = 7.1 Hz, 1H, CH(6 or 6′) of phosphole), 7.33 (td, J_{HP} = 4.0 Hz, J_{HH} = 1.0, 7.5 Hz, 1H, CH-(5 or 5′) of phosphole), 7.32 (td, J_{HP} = 4.0 Hz, J_{HH} = 1.0, 7.5 Hz, 1H, CH(5 or 5′) of phosphole), 5.88 (br, 2H, CH, COD), 3.30 (br, 2H, CH, COD), 2.82 (t, $J_{HP(1)} = J_{HP(2)}$ = 11.8 Hz, 2H, P(1)CH_2P(2)), 2.39−2.45 (m, 2H, CH_2, COD), 2.23−2.30

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(m, 4H, CH_2, COD), 2.12−2.18 (m, 2H, CH_2, COD), −0.11 (bd, $^1J_{HB}$ = 109.7 Hz, 3H, BH_3). $^1H\{^{11}B,^{31}P\}$ NMR (298 K, CD_2Cl_2, 500.33 MHz; selected δ (ppm)): −0.09 (d, 3H, J_{HRh} = 15.0 Hz, BH_3). EXSY-1D $^1H\{^{11}B,^{31}P\}$ NMR (188 K, CD_2Cl_2, 500.33 MHz; δ (ppm)): 2.26 (s, 1H, terminal H, BH_3), −1.41 (s, 2H, bridging H, BH_3). $^1H\{^{11}B\}$ NMR (298 K, CD_2Cl_2, 300.13 MHz; selected δ (ppm)): −0.09 (t, J_{HP} = J_{HRh} = 11.7 Hz, 3H, BH_3). $^{31}P\{^1H\}$ NMR (298 K, CD_2Cl_2, 202.537 MHz; δ (ppm)): +47.52 (dd, $^1J_{P(1)Rh}$ = 139.8 Hz, $^2J_{P(1)P(2)}$ = 68.9 Hz, P(2)), +20.66 (br, P(1)). $^{11}B\{^1H\}$ NMR (298 K, CD_2Cl_2, 160.526 MHz; δ (ppm)): −1.08 (b, BF_4^-), −26.03 (d, $^1J_{BP}$ = 85.1 Hz, BH_3). ^{103}Rh NMR (298 K, CD_2Cl_2, 15.8112 MHz; δ (ppm)): −8258.40 (d, $^1J_{RhP}$ = 73.8 Hz). $^{13}C\{^1H\}$ NMR (298 K, CD_2Cl_2, 100.613 MHz; δ (ppm)): 142.58 (d, J_{CP} = 9.8 Hz, C(2,2′) of phosphole), 133.40 (d, J_{CP} = 2.7 Hz, Ph), 132.85 (d, J_{CP} = 1.81 Hz, C(4,4′) of phosphole), 132.39 (d, J_{CP} = 10.7 Hz, Ph), 131.00 (d, J_{CP} = 15.0 Hz, C(6,6′) of phosphole), 129.91 (d, J_{CP} = 11.5 Hz, Ph), 129.10 (d, J_{CP} = 11.1 Hz, C(5,5′) of phosphole), 124.72 (d, J_{CP} = 64.7 Hz, C(1 or 1′) of phosphole), 124.67 (d, J_{CP} = 64.8 Hz, C(1 or 1′) of phosphole), 122.34 (d, J_{CP} = 6.1 Hz, C(3 or 3′), phosphole), 106.67 (dd, J_{CRh} = 10.3 Hz, J_{CP} = 6.0 Hz, CH, COD), 74.78 (d, J_{CP} = 13.1 Hz, CH, COD), 33.42 (CH_2, COD), 33.39 (CH_2, COD), 28.55 (dd, $J_{CP(1)}$ = 11.5 Hz, $J_{CP(2)}$ = 42.7 Hz, P(1)CH_2P-(2)), 28.18 (CH_2, COD), 28.17 (CH_2, COD). MS (FAB, MNBA; m/z (%)): 607 (100%) $[M]^+$. Anal. Calcd for $C_{33}B_2H_{35}F_4P_2Rh$: C, 57.10; H, 5.08. Found: C, 57.20; H, 5.98. Crystals suitable for an X-ray diffraction study were obtained by metathesis of a dichloromethane solution of **8a** with excess $NaBPh_4$, filtration, and crystallization by slow evaporation of dichloromethane to afford **8c**.

X-ray Diffraction Studies. A single crystal of each compound was mounted under inert perfluoro polyether at the tip of a glass fiber and cooled in the cryostream of an Oxford-Diffraction XCALIBUR CCD diffractometer for **7** or in the cryostream of a Bruker APEX2 CCD diffractometer for **8c**. Data were collected using monochromatic Mo Kα radiation (λ = 0.710 73 Å).

The structures were solved by direct methods (SIR97)[21] and refined by least-squares procedures on F^2 using SHELXL-97.[22] All H atoms attached to carbon were introduced in idealized positions and treated as riding on their parent atoms in the calculations. H atoms attached to boron were located in difference Fourier syntheses; their coordinates were refined using restraints, and their isotropic thermal parameters were related to the boron atom. Drawings of the molecules were realized with the help of ORTEP3.[23]

Crystal Data for 7. $C_{25}H_{23}BP$, M_w = 354.4, monoclinic, a = 10.7285(3) Å, b = 14.9875(4) Å, c = 13.2512(3) Å, V = 2122.08(10) Å^3, T = 180(2) K, space group $P2_1/c$ (No. 14), Z = 4, μ(Mo Kα) = 0.134 mm^{-1}, 18 819 reflections measured, 5266 unique reflections (R_{int} = 0.024) which were used in all calculations. The final R and $R_w(F^2)$ values were 0.0477 and 0.1028, respectively (all data).

Crystal Data for 8c. $C_{57}H_{33}B_2P_2Rh$, M_w = 926.48, triclinic, a = 11.9261(5) Å, b = 14.1919(7) Å, c = 14.6192(6) Å, α = 87.739(3)°, β = 84.475(3)°, γ = 69.165(3)°, V = 2301.78(18) Å^3, T = 180(2) K, space group $P\bar{1}$ (No. 2), Z = 2, μ(Mo Kα) = 0.479 mm^{-1}, 42 266 reflections measured, 13 334 unique reflections (R_{int} = 0.027), which were used in all calculations. The final R and $R_w(F^2)$ values were 0.0408 and 0.1039, respectively (all data).

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Supporting Information Available: A figure giving variable-temperature $^1H\{^{11}B,^{31}P\}$ NMR spectra, a table giving T_1 measurements, and CIF files giving X-ray crystallographic data for compounds **7** and **8c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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