Supporting Information

Diphosphene with a Phosphineborane Tether and Its Rhodium Complex

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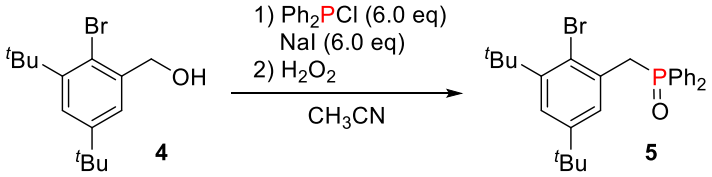
1. Experimental

General. All anaerobic and/or moisture-sensitive manipulations were carried out with conventional Schlenk techniques under a nitrogen atmosphere or with glovebox techniques under an argon atmosphere. Analytical thin-layer chromatography (TLC) was performed using Silicagel 70 F_{254} TLC Plate-Wako. The developed chromatogram was viewed under a UV lamp (254 nm). Silica gel column chromatography was performed with Wako-gel® 60N (Wako, 150–425 μm, irregular) or Silica Gel 60 (Nacalai Tesque Inc., spherical, neutral) under an argon atmosphere. Preparative thin-layer chromatography (PTLC) was performed using Silicagel 70 PF_{254} TLC Plate-Wako. ^{1}H NMR (400 or 500 MHz), ^{13}C NMR (100 or 125 MHz), ^{31}P NMR (162 MHz), ^{11}B NMR (129 MHz), and ^{19}F NMR (378 MHz) spectra were measured in $CDCl_3$ and CD_2Cl_2 with a JEOL JNM-ECS400 or JEOL JNM-ECZ500R spectrometer. Signals of tetramethylsilane (0.0 ppm) in $CDCl_3$ and $CHDCl_2$ (5.32 ppm) in CD_2Cl_2 in the ^{1}H NMR spectra; and $CDCl_3$ (77.16 ppm) and CD_2Cl_2 (53.84 ppm) in the ^{13}C NMR spectra were used as internal references. ^{31}P, ^{11}B, and ^{19}F NMR chemical shifts were externally referenced to 85% H_3PO_4 (0 ppm), $BF_3{\cdot}OEt_2$ (0 ppm), and $CFCl_3$ (0 ppm), respectively. Chemical shifts are reported in ppm downfield. Low- and high-resolution mass spectra were recorded on a JEOL JMS-700 spectrometer in the FAB (3-nitrobenzyl alcohol) mode or a Bruker micrOTOF II time-of-flight mass spectrometer (ESI). IR samples were prepared by the KBr plate method (JASCO Tablet Master), and IR spectra were measured on a JASCO FT/IR-4100 spectrometer. All melting points were determined on a Yanaco micro melting point apparatus (MP-J3) and were uncorrected. The melting points of phosphine **3'**, dichlorophosphine **2**, diphosphene–phosphineborane ligand **1**, and diphosphene–rhodium complex **7** were measured under an argon atmosphere in a sealed tube.

Reagents. Acetonitrile, dichloromethane, Et_2O, THF, toluene, 1,4-dioxane (Wako, super dehydrated grade), and 1,2-dichloroethane (Aldrich, anhydrous) were purchased and used as received. $CDCl_3$ (CIL) and CD_2Cl_2 (CIL) used in a glovebox were dried over calcium hydride, degassed by freeze-pump-thaw cycles, distilled in a vacuum line, and stored in a glovebox. Sodium iodide (Aldrich), chlorodiphenylphosphine (Wako), hydrogen peroxide in aqueous solution (Wako), triethoxysilane (TCI), titanium(IV) tetraisopropoxide (Wako), borane–tetrahydrofuran complex (1.03 M in THF; Aldrich), *n*-butyllithium (1.6 M in hexane; Mitsuwa), and *tert*-butyllithium (1.55 M in pentane; Kanto) were purchased and used as received. Phosphorus trichloride was distilled from calcium hydride prior to use. *N*-Methylpyrrolidine, triethylamine, *N*,*N*,*N*,*N*-tetramethylethylenediamine (tmeda), and pyridine (py) were distilled from sodium hydroxide prior to use. 2-Bromo-3,5-di-*tert*-butyl-1-(hydroxymethyl)benzene (**4**),[S1] 2-bromo-1-bromomethyl-3,5-di-*tert*-butyl-benzene (**6**),[S1] $Ph_2PH{\cdot}BH_3$,[S2] $^{t}Bu(Me_3Si)NH$,[S3] $Mes^{*}PH_2$,[S4] and $[Rh(cod)_2]BF_4$[S5] were synthesized according to the reported procedures.

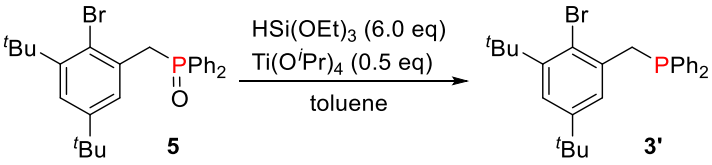
Synthesis of (2-bromo-3,5-di-*tert*-butylphenyl)methyldiphenylphosphine oxide (5).



This compound was prepared according to the similar method to the reported procedure.[S6] To a solution of 2-bromo-3,5-di-*tert*-butyl-1-(hydroxymethyl)benzene (**4**, 9.81 g, 32.8 mmol) and sodium iodide (24.6 g, 164 mmol) in CH_3CN (80 mL) was added chlorodiphenylphosphine (36.2 g, 164 mmol). After the reaction mixture was stirred at reflux for 14 h, H_2O_2 aq. was added dropwise at 0 ºC. The reaction mixture was stirred at room temperature for 10 min, and then quenched with Na_2SO_3 aq. The organic layer was separated, and then the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered through a pad of Celite, and then evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane/ethyl acetate = 1/1 (R_f = 0.45) to give **5** as a colorless solid (13.3 g, 27.5 mmol, 84%).

Mp. 181-182 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.21 (s, 9H, ^{t}Bu), 1.42 (s, 9H, ^{t}Bu), 4.05 (d, J = 14.4 Hz, 2H, CH_2), 7.30 (dd, J = 2.5, 2.5 Hz, 1H, aromH), 7.31 (dd, J = 2.5, 2.5 Hz, 1H, aromH), 7.38-7.43 (m, 4H, Ph), 7.47-7.51 (m, 2H, Ph), 7.63-7.68 (m, 4H, Ph); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 30.2 (CH_3), 31.2 (CH_3), 34.7 (C), 37.6 (C), 39.5 (d, J = 66.5 Hz, CH_2), 123.3 (d, J = 7.7 Hz, C), 124.1 (d, J = 2.8 Hz, CH), 127.2 (d, J = 4.8 Hz, CH), 128.5 (d, J = 11.6 Hz, CH), 131.5 (d, J = 8.7 Hz, CH), 131.8 (d, J = 2.9 Hz, CH), 132.2 (d, J = 98.3 Hz, C), 132.8 (d, J = 6.8 Hz, C), 147.9 (d, J = 1.9 Hz, C), 149.4 (d, J = 2.9 Hz, C); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 30.5 (P=O); HRMS (FAB) *m/z* found: 483.1459 ([M+H]$^+$), calcd for $C_{27}H_{33}{}^{79}BrOP$ 483.1452.

Synthesis of (2-bromo-3,5-di-*tert*-butylphenyl)methyldiphenylphosphine (3').

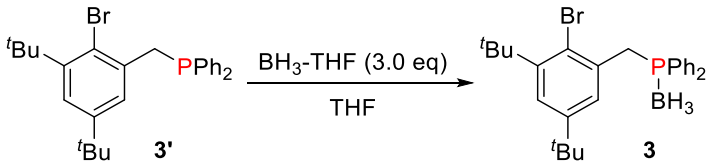


To a solution of **5** (500 mg, 1.03 mmol) in toluene (10 mL) was added triethoxysilane (1.14 mL, 6.21 mmol) and titanium(IV) tetraisopropoxide (0.15 mL, 0.52 mmol). After the reaction mixture was stirred at reflux for 1 h, the volatiles were removed under reduce pressure. The residue was chromatographed on silica gel with hexane/benzene = 5/1 (R_f = 0.60) in a glovebox under an argon atmosphere to give **3'** as a colorless solid (461 mg, 0.99 mmol, 95%).

Mp. 84.5-85.3 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.05 (s, 9H, ^{t}Bu), 1.55 (s, 9H, ^{t}Bu), 3.65 (s, 2H, CH_2), 6.44 (dd, J =2.3, 2.3 Hz, 1H, aromH), 7.26 (dd, J = 2.1, 2.1 Hz, 1H, aromH), 7.31-7.34 (m, 6H, Ph), 7.39-7.44 (m, 4H, Ph); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 30.4 (CH_3), 31.1 (CH_3), 34.5 (C), 37.6 (C), 38.8 (d, J = 16.4 Hz, CH_2), 122.5 (d, J = 4.8 Hz, C), 123.4 (d, J = 1.9 Hz, CH), 126.7 (d, J = 5.8 Hz, CH), 128.5 (d, J = 5.8 Hz, CH), 128.8 (CH), 133.3 (d, J = 18.3 Hz, CH), 137.9 (d, J = 5.8 Hz, C), 138.5 (d, J = 16.4 Hz, C), 147.8 (d, J = 2.0 Hz, C), 148.7 (d, J = 1.9 Hz, C); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ =

−13.2 (PPh_2); HRMS (FAB) *m/z* found: 466.1420 ($[M]^+$), calcd for $C_{27}H_{32}{}^{79}BrP$ 466.1425.

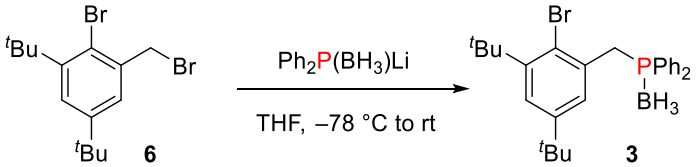
Synthesis of (2-bromo-3,5-di-*tert*-butylphenyl)methyldiphenylphosphine-borane (3).



To a solution of **3'** (200 mg, 0.427 mmol) in THF (6 mL) was added dropwise borane–tetrahydrofuran complex (1.03 M in THF; 1.90 mL, 1.96 mmol) at 0 ºC. After the reaction mixture was stirred at room temperature for 2 h, the volatiles were removed under reduce pressure. The residue was chromatographed on silica gel with hexane/AcOEt = 10/1 (R_f = 0.50) to give **3** as a colorless solid (165 mg, 0.343 mmol, 80%).

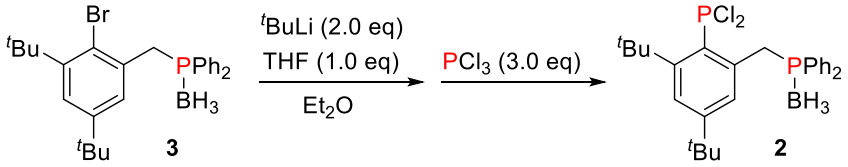
Mp. 137-138˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.6-1.4 (br, 3H, BH_3), 1.20 (s, 9H, ^{t}Bu), 1.40 (s, 9H, ^{t}Bu), 3.99 (d, *J* = 11.5 Hz, 2H, CH_2), 7.14 (dd, *J* = 2.3, 2.3 Hz, 1H, aromH), 7.32 (dd, *J* = 2.0, 2.0 Hz, 1H, aromH), 7.35-7.40 (m, 4H, Ph), 7.44-7.49 (m, 2H, Ph), 7.55-7.61 (m, 4H, Ph); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 30.2 (CH_3), 31.2 (CH_3), 34.7 (C), 35.3 (d, *J* = 31.8 Hz, CH_2), 37.5 (C), 123.4 (d, *J* = 5.8 Hz, C), 124.3 (d, *J* = 1.9 Hz, CH), 127.3 (d, *J* = 3.9 Hz, CH), 128.3 (d, *J* = 53.9 Hz, C), 128.6 (d, *J* = 9.6 Hz, CH), 131.3 (d, *J* = 1.9 Hz, CH), 133.1 (d, *J* = 8.7 Hz, CH), 133.5 (d, *J* = 4.8 Hz, C), 147.8 (d, *J* = 2.0 Hz, C), 149.3 (d, *J* = 1.9 Hz, C); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 19.3 (br d, *J* = 43.6 Hz, PBH_3). ^{11}B {^{1}H} NMR (129 MHz, $CDCl_3$) δ = −39.1 (br d, *J* = 34.4 Hz); HRMS (FAB) *m/z* found: 481.1833 ($[M+H]^+$), calcd for $C_{27}H_{36}B^{79}BrP$ 481.1831.

Synthesis of phosphineborane 3 from 2-bromo-1-bromomethyl-3,5-di-*tert*-butyl-benzene (6).



To a solution of $Ph_2PH{\cdot}BH_3$ (3.97 g, 19.8 mmol) in THF (40 mL) was added dropwise ^{n}BuLi (1.6 M in hexane; 12.4 mL, 19.8 mmol) at −78 ºC. After the reaction mixture was stirred at −78 ºC for 20 min, a solution of **6** (7.54 g, 20.8 mmol) in THF (8 mL) was added. The reaction mixture was gradually warmed to room temperature, and then stirred for 1 h. The reaction was quenched with sat. NH_4Cl aq. The organic layer was separated, and then the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over $MgSO_4$, filtered through a pad of Celite, and then evaporated under reduced pressure. The residue was washed with hexane to give **3** as a colorless solid (7.35 g, 15.3 mmol, 77%).

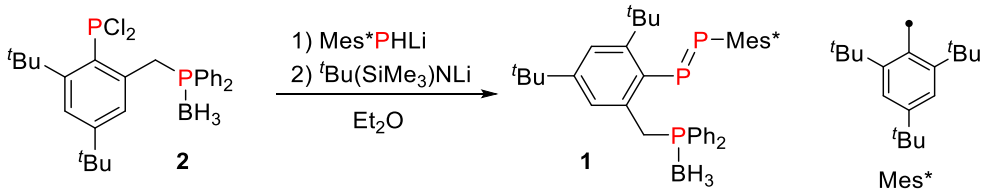
Synthesis of (3,5-di-*tert*-butyl-2-dichlorophosphinophenyl)methyldiphenylphosphine-borane (2).



To a solution of **3** (1.00 g, 2.08 mmol) and THF (168 μL, 2.08 mmol) in Et_2O (40 mL) was added dropwise ^{t}BuLi (1.55 M in pentane; 2.68 mL, 4.16 mmol) at −105 ºC. After the reaction mixture was stirred at −105 ºC for 15 min, PCl_3 (0.91 mL, 10.4 mmol) was added. The reaction mixture was gradually warmed to room temperature, and then stirred for 2 h. The volatiles were removed under reduced pressure. The precipitate was filtered off by passing though a pad of Celite under a nitrogen atomosphere. The volatiles of the filtrate was removed under reduced pressure. The residue was washed with hexane to give **2** (429 mg, 0.85 mmol, 41%) as a pale yellow solid.

Mp. 101 ˚C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.12 (s, 9H, ^{t}Bu), 1.52 (d, J = 1.6 Hz, 9H, ^{t}Bu), 4.51 (d, J = 11.7 Hz, 2H, CH_2), 7.32 (d, J = 6.7 Hz, 1H, aromH), 7.36-7.41 (m, 5H, aromH and Ph), 7.43-7.48 (m, 2H, Ph), 7.57-7.62 (m, 4H, Ph); The BH_3 signal could not be assigned likely due to the line-broadening around 1 ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 30.8 (CH_3), 32.4 (dd, J = 33.7, 3.9 Hz, CH_2), 34.2 (d, J = 22.2 Hz, CH_3), 35.3 (C), 37.6 (d, J = 3.9 Hz, C), 122.0 (d, J = 8.7 Hz, CH), 128.5 (d, J = 6.8 Hz, CH), 128.8 (d, J = 10.6 Hz, CH), 129.3 (d, J = 54.9 Hz, C), 131.3 (d, J = 1.9 Hz, CH), 133.0 (d, J = 8.7 Hz, CH), 133.2 (dd, J = 85.7, 5.8 Hz, C), 140.9 (dd, J = 3.8, 2.9 Hz, C), 155.3 (C), 156.0 (d, J = 36.6 Hz, C); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 20.7 (br d, J = 47.9 Hz, PBH_3), 159.4 (PCl_2); ^{11}B {^{1}H} NMR (129 MHz, $CDCl_3$) δ = −38.2 (br); HRMS (FAB) *m/z* found: 503.1757 ([M+H]$^+$), calcd for $C_{27}H_{36}BCl_2P_2$ 503.1762.

Synthesis of diphosphene–phosphineborane ligand 1.

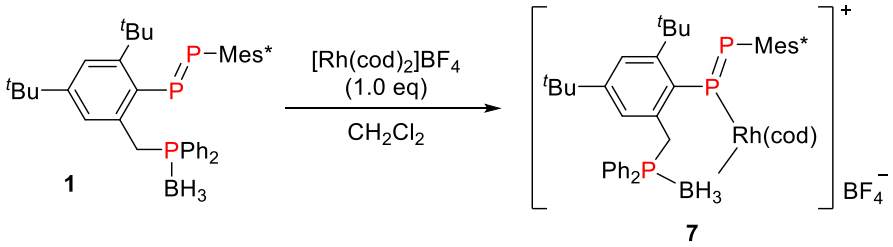


To a solution of Mes*PH_2 (96.7 mg, 0.347 mmol) in Et_2O (3 mL) was added ^{n}BuLi (1.55 M in hexane; 231 μL, 0.365 mmol) dropwise at room temperature in a glovebox filled with argon. After stirring for 30 min, the mixture was added to **2** (174.7 mg, 0.347 mmol) in Et_2O (30 mL) dropwise. After the mixture was stirred for 1.5 h, ^{t}Bu(Me_3Si)NLi in a Et_2O solution was added dropwise, which was prepared by the reaction of ^{t}Bu(Me_3Si)NH (80.6 μL, 420 μmol) with *n*-BuLi (1.55 M in hexane; 231 μL, 365 μmol) in a Et_2O solution (3 mL) at room temperature for 2 h. After the reaction mixture was stirred for 3.5 h, the volatiles were removed under reduce pressuere to give an orange solid. The residue was filtered though a pad of Celite with hexane, and then the solvent of the filtrate was removed under reduced pressure. The residue was chromatographed on silica gel with hexane/toluene = 5/1 (R_f = 0.10) to 2/1 (R_f = 0.20) under argon atmosphere to give **1** as an orange solid (74.4 mg, 0.109 mmol, 30%).

Mp. 137 ˚C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.16 (s, 9H, ^{t}Bu), 1.34 (s, 9H, ^{t}Bu), 1.36 (s, 9H, ^{t}Bu), 1.37 (s, 18H, ^{t}Bu), 4.05 (d, J = 11.5 Hz, 2H, CH_2), 7.11 (dd, J = 2.1, 2.1 Hz, 1H, aromH), 7.31-7.36 (m, 5H, aromH and Ph), 7.41 (s, 2H, Mes*-*m*-aromH), 7.41-7.45 (m, 2H, Ph), 7.48-7.54 (m, 4H, Ph); The BH_3 signal could not be assigned likely due to the line-broadening around 1 ppm; ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 1.16 (s, 9H, ^{t}Bu), 1.34 (s, 9H, ^{t}Bu), 1.360 (s, 9H, ^{t}Bu), 1.363 (s, 18H, ^{t}Bu), 4.04 (d, J = 11.5 Hz, 2H, CH_2), 7.06 (dd, J = 1.8, 1.8 Hz, 1H, aromH), 7.35-7.39 (m, 4H, Ph), 7.41 (dd, J = 1.8, 1.8 Hz, 1H, aromH), 7.44 (s, 2H, Mes*-*m*-aromH), 7.45-7.53 (m, 6H, Ph); The BH_3 signal could not be assigned likely due to the line-broadening around 1 ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 31.1 (CH_3), 31.5 (CH_3), 33.1 (br, CH_3), 34.1 (br, CH_3), 34.7 (C), 35.0 (C), 36.4 (d, J = 29.9 Hz, CH_2), 38.0 (C), 38.8 (C), 122.5 (CH), 123.0 (d, J = 2.0 Hz, CH), 126.3 (d, J = 5.7 Hz, CH), 128.7 (d, J = 9.6 Hz, CH), 128.8 (d, J = 53.2 Hz, C), 131.2 (d, J = 1.9 Hz, CH), 133.1 (d, J = 9.6 Hz, CH), 134.6 (br, C), 137.6 (dd, J = 67, 12 Hz, C),*1) 139.5 (d, J = 61 Hz, C),*1) 149.8 (C), 150.6 (C), 153.7 (d, J = 4.8 Hz, C), 154.0 (C); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 528.9 (d, $^1J_{PP}$ = 579 Hz, P=PAr), 479.2 (d, $^1J_{PP}$ = 579 Hz, P=PAr), 21.1 (br, PBH_3); ^{11}B {^{1}H} NMR (129 MHz, $CDCl_3$) δ = −35.9 (br). HRMS (ESI) *m/z* found: 709.4396 ([M+H]$^+$), calcd for $C_{45}H_{65}BP_3$ 709.4392. IR (KBr) ν_{max}/cm^{-1} 2965, 2401 (BH), 2368 (BH), 1596, 1361, 1237, 1060.

*1) The signals were tentatively assigned due to their low intensities.

Synthesis of diphosphene–rhodium complex 7.

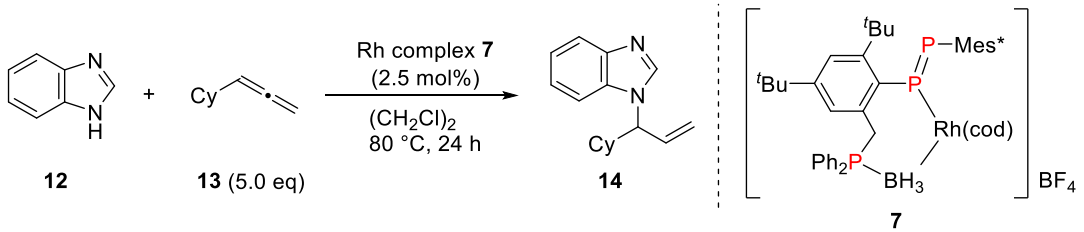


To a solution of $[Rh(cod)_2]BF_4$ (40.5 mg, 99.7 μmol) in CH_2Cl_2 (2.5 mL) was added dropwise a solution of diphosphene–phosphineborane ligand **1** (74.4 mg, 105 μmol) in CH_2Cl_2 (2.5 mL). After stirring at room temperature for 1.5 h, the reaction mixture was filtered through a pad of Celite to remove a black precipitate. The solvent of the filtrate was removed under reduce pressuere. The residue was washed with hexane and then reprecipitated with CH_2Cl_2/hexane to give **7** as red crystals (84.5 mg, 83.9 μmol, 80%).

Mp. 151 ˚C (decomp). ^{1}H NMR (500 MHz, CD_2Cl_2) δ = −0.56 (br, d, J = 105 Hz, 3H, BH_3), 0.99 (s, 9H, ^{t}Bu), 1.38 (s, 9H, ^{t}Bu), 1.43 (s, 9H, ^{t}Bu), 1.54 (s, 9H, ^{t}Bu), 1.66-1.74 (m, 1H, cod), 1.82 (s, 9H, ^{t}Bu), 1.85-1.97 (m, 2H, cod), 2.10-2.15 (m, 2H, cod), 2.15-2.20 (m, 1H, cod), 2.29 (dd, J = 15.1, 6.9 Hz, 1H, cod), 2.58 (dtd, J = 16.0, 10.0, 6.9 Hz, 1H, cod), 2.80-2.84 (m, 1H, cod), 3.81-3.86 (m, 1H, cod), 3.97 (dd, J = 17.7, 14.0 Hz, 1H, CH_2), 4.34 (dd, J = 14.0, 8.1 Hz, 1H, CH_2), 4.86-4.91 (m, 1H, cod), 5.60 (dd, J = 7.8, 7.8 Hz, 1H, cod), 6.31 (dd, J = 1.9, 1.9 Hz, 1H, aromH), 7.02 (ddd, J = 12.0, 8.2, 1.3 Hz, 2H, Ph), 7.33 (ddd, J = 8.0, 8.0, 2.7 Hz, 2H, Ph), 7.40 (d, J = 1.6 Hz, 1H, aromH), 7.49-7.53 (m, 1H, Ph), 7.56 (d, J = 1.9 Hz, 2H, aromH), 7.68-7.71 (m, 2H, Ph), 7.75-7.79 (m, 3H, Ph); ^{13}C {^{1}H} NMR (126 MHz, CD_2Cl_2) δ = 25.0 (CH_2), 30.5 (CH_2), 30.8 (CH_3), 31.5 (CH_3), 31.7 (CH_2), 33.3 (d, J = 33.8 Hz, CH_2), 34.0 (br, CH_3), 34.5 (br, CH_3), 34.6 (CH_3), 34.8 (C), 35.3 (C), 37.8 (CH_2), 38.8 (×2C), 39.4 (C), 75.8 (CH), 75.9 (CH),

106.0 (CH), 109.5 (CH), 122.9 (CH), 123.9 (CH), 124.6 (d, J = 51.9 Hz, C), 125.2 (d, J = 54.3 Hz, C), 125.7 (br, CH), 128.0 (br, CH), 129.5 (d, J = 10.9 Hz, CH), 130.1 (d, J = 9.6 Hz, CH), 132.5 (d, J = 7.2 Hz, CH), 133.3 (d, J = 9.7 Hz, CH), 133.5 (CH), 133.9 (br, C), 153.5 (C), 153.9 (d, J = 3.6 Hz, C), 155.5 (C), 156.1 (d, J = 10.8 Hz, C), 156.3 (d, J = 10.8 Hz, C). The ^{13}C signals bound to the phosphorus atoms could not be assigned due to their low intensities; ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 439.8 (d, $^{1}J_{PP}$ = 544 Hz, $^{2}J_{PRh}$ = 18 Hz, Mes*P=P), 348.7 (dd, $^{1}J_{PP}$ = 544 Hz, $^{1}J_{PRh}$ = 149 Hz, P=P[Rh]Ar), 4.6 (br q, J = 114 Hz, PBH_3); ^{11}B {^{1}H} NMR (129 MHz, CD_2Cl_2) δ = −3.1 (BF_4), −36.6 (br, BH_3); HRMS (ESI) m/z found: 919.4301 ([M−BF_4]$^+$), calcd for $C_{53}H_{76}BP_3Rh$ 919.4308. IR (KBr) ν_{max}/cm^{-1} 2955, 2432 (B−H), 2075 (Rh−H), 2008 (Rh−H), 1594, 1438, 1058.

Coupling reaction of benzimidazole (12) with cyclohexylallene (13).[S7]



Diphosphene–rhodium complex **7** (2.0 mg, 2.0 μmol), benzimidazole (9.3 mg, 79 μmol), cyclohexylallene (58 μL, 397 μmol), and 1,2-dichloroethane (0.32 mL) was successively charged in a 5 mL screw vial in a glovebox filled with argon and sealed. The reaction mixture was stirred at 80 ℃ for 24 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by PTLC on silica gel to give **14** as a yellow oil (6.7 mg, 28 μmol, 35%).

^{1}H and ^{13}C NMR spectral data are identical to those in the literature.[S7] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.85-0.94 (m, 1H, Cy), 0.99-1.10 (m, 1H, Cy), 1.10-1.21 (m, 2H, Cy), 1.22-1.31 (m, 1H, Cy), 1.31-1.39 (m, 1H, Cy), 1.62-1.69 (m, 2H, Cy), 1.78-1.84 (m, 1H, Cy), 1.90-2.05 (m, 2H, Cy), 4.50 (dd, J = 8.7, 7.5 Hz, 1H, NCHCy), 5.18 (d, J = 17.0 Hz, 1H, CH=CH_2), 5.28 (d, J = 10.3 Hz, 1H, CH=CH_2), 6.17 (ddd, J = 17.0, 10.3, 7.5 Hz, 1H, CH=CH_2), 7.25-7.30 (m, 2H, aromH), 7.38-7.43 (m, 1H, aromH), 7.79-7.84 (m, 1H, aromH), 7.92 (s, 1H, imidazoleH); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 25.7 (CH_2), 25.8 (CH_2), 26.1 (CH_2), 29.7 (CH_2), 30.4 (CH_2), 41.3 (CH), 64.8 (CH), 110.6 (CH), 119.0 (CH_2), 120.5 (CH), 122.1 (CH), 122.7 (CH), 133.6 (C), 134.6 (CH), 142.0 (CH), 143.9 (C).

Synthesis of [Rh(tmeda)(cod)]BF_4 (tmeda = *N*,*N*,*N*,*N*-tetramethylethylenediamine).[S8]

To a solution of [Rh(cod)$_2$]BF_4 (60.9 mg, 0.150 mmol) in CH_2Cl_2 (1 mL) was added dropwise *N*,*N*,*N*,*N*-tetramethylethylenediamine (169 mg, 1.45 mmol). After stirring at room temperature for 15 min, Et_2O (5 mL) was added. The resulting precipitate was filtered and washed with Et_2O to give [Rh(tmeda)(cod)]BF_4 as a yellow solid (60.3 mg, 0.146 mmol, 97%).

Mp. 168 ˚C (decomp). ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 1.84-1.89 (m, 4H, cod), 2.43-2.49 (m, 4H, cod), 2.55 (s, 12H, NCH_3), 2.59 (s, 4H, NCH_2), 3.95 (br s, 4H, cod); ^{13}C {^{1}H} NMR (126 MHz, CD_2Cl_2) δ = 30.2 (CH_2), 49.2 (CH_3), 61.1 (CH_2), 83.9 (d, J = 13.3 Hz, CH); ^{19}F NMR (378 MHz, CD_2Cl_2) δ = −152.4; ^{11}B {^{1}H} NMR (129 MHz, CD_2Cl_2) δ = −2.1. HRMS (ESI) m/z found: 327.1310 ([M−BF_4]$^+$), calcd for

$C_{14}H_{28}N_2Rh$ 327.1308.

Synthesis of $[Rh(py)_2(cod)]BF_4$ (15, py = pyridine).[S8]

To a solution of $[Rh(cod)_2]BF_4$ (60.9 mg, 0.150 mmol) in CH_2Cl_2 (1 mL) was added dropwise pyridine (236 mg, 2.98 mmol). After stirring at room temperature for 15 min, Et_2O (5 mL) was added. The resulting precipitate was filtered and washed with Et_2O to give **15** as a yellow solid (57.0 mg, 0.125 mmol, 83%).
Mp. 162 ˚C (decomp). ^1H NMR (500 MHz, CD_2Cl_2) δ = 1.99-2.08 (m, 4H, cod), 2.63-2.70 (m, 4H, cod), 4.18 (br s, 4H, cod), 7.40-7.43 (m, 4H, py), 7.77 (tt, J = 7.7, 1.7 Hz, 2H, py), 8.72-8.73 (m, 4H, py); ^{13}C $\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ = 30.9 (CH_2), 85.7 (d, J = 12.1 Hz, CH), 126.5 (CH), 139.0 (CH), 150.6 (CH); ^{19}F NMR (378 MHz, CD_2Cl_2) δ = −152.6; ^{11}B $\{^1H\}$ NMR (129 MHz, CD_2Cl_2) δ = −1.9. HRMS (ESI) *m/z* found: 369.0838 ($[M-BF_4]^+$), calcd for $C_{18}H_{22}N_2Rh$ 369.0838.

2. Spectral Data

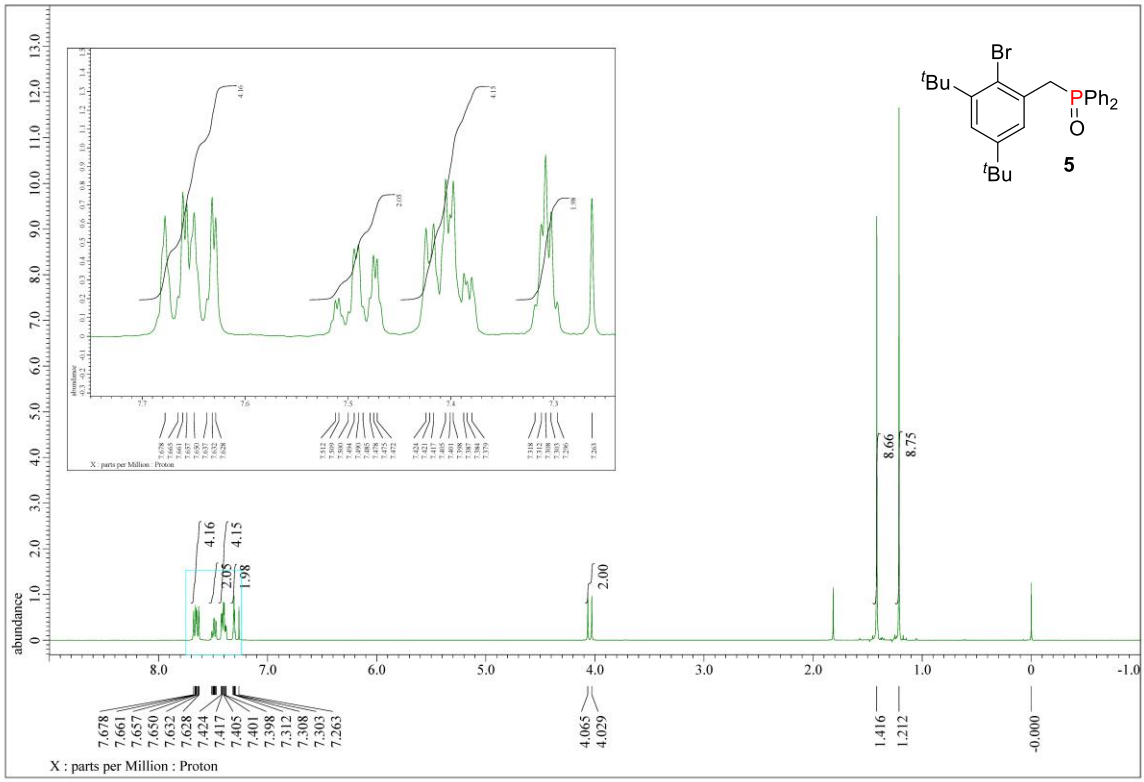


Fig. S1 ^{1}H NMR Spectrum of 5.

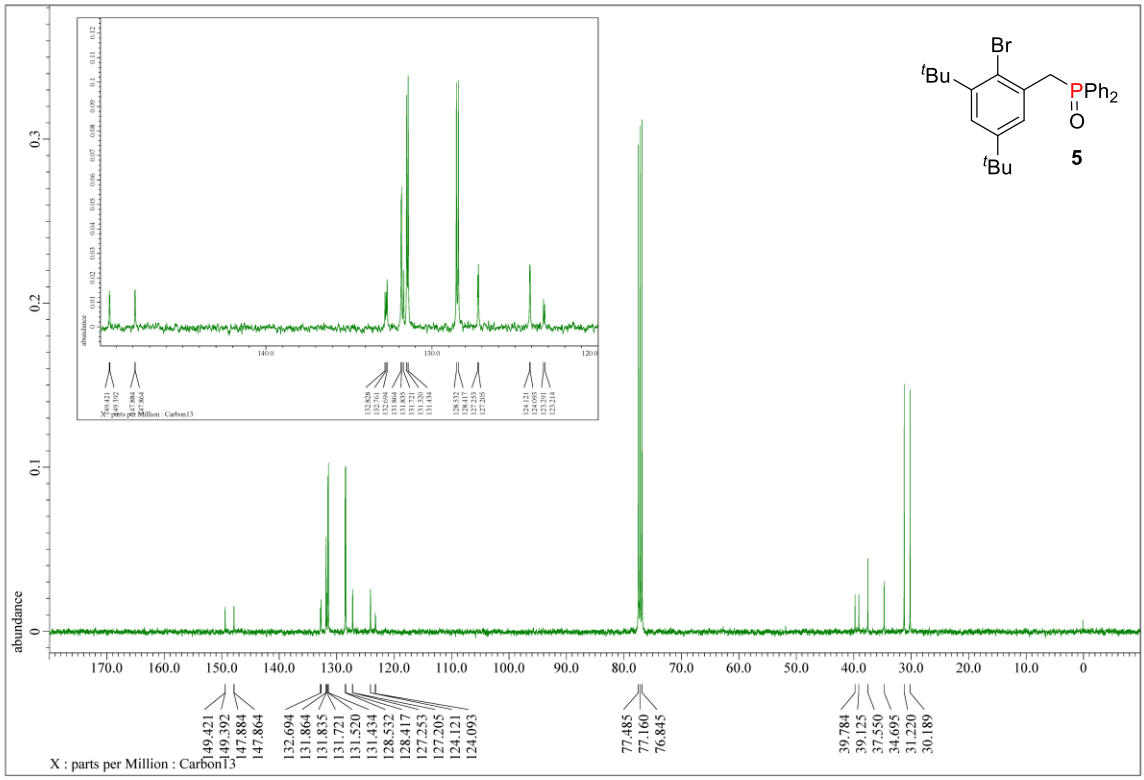


Fig. S2 ^{13}C NMR Spectrum of 5.

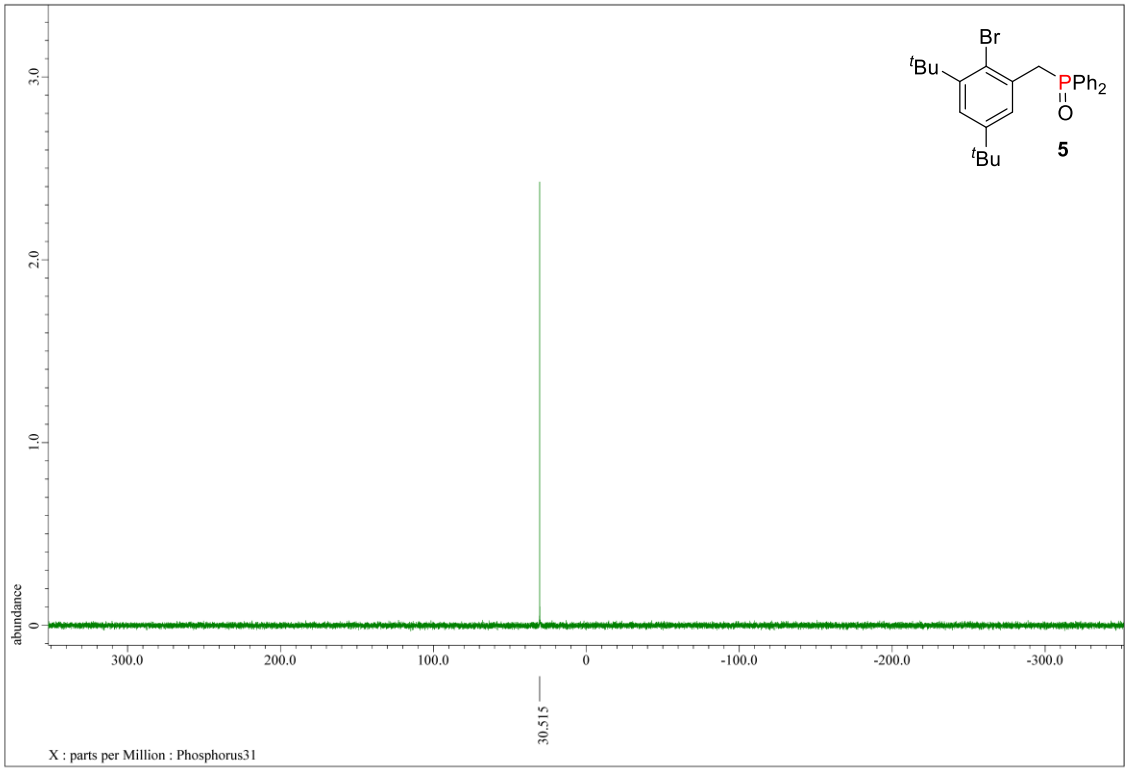


Fig. S3 ^{31}P NMR Spectrum of 5.

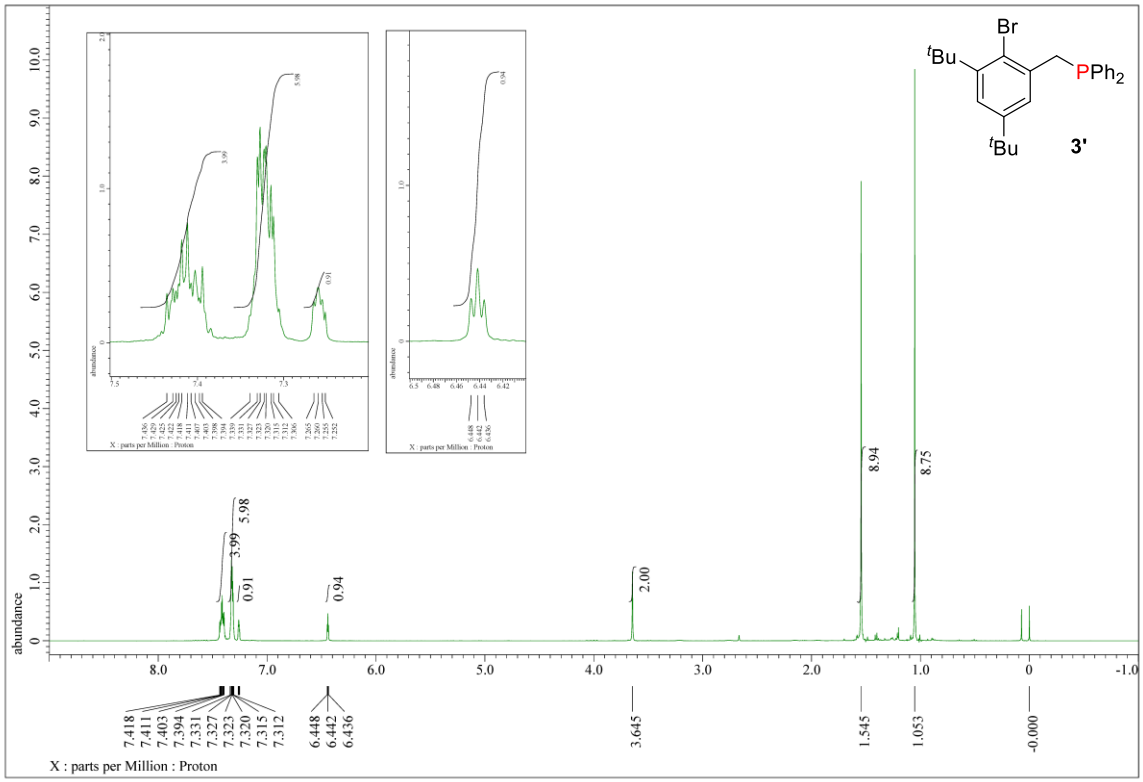


Fig. S4 ^{1}H NMR Spectrum of 3'.

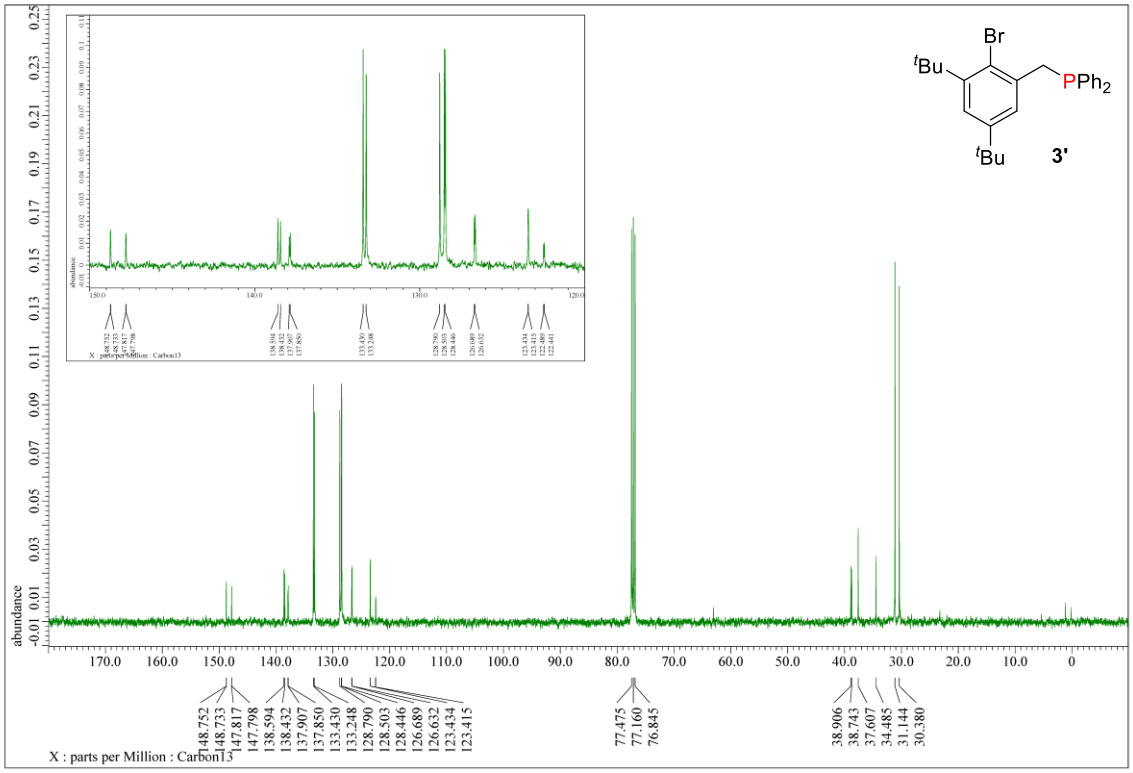


Fig. S5 ^{13}C NMR Spectrum of 3'.

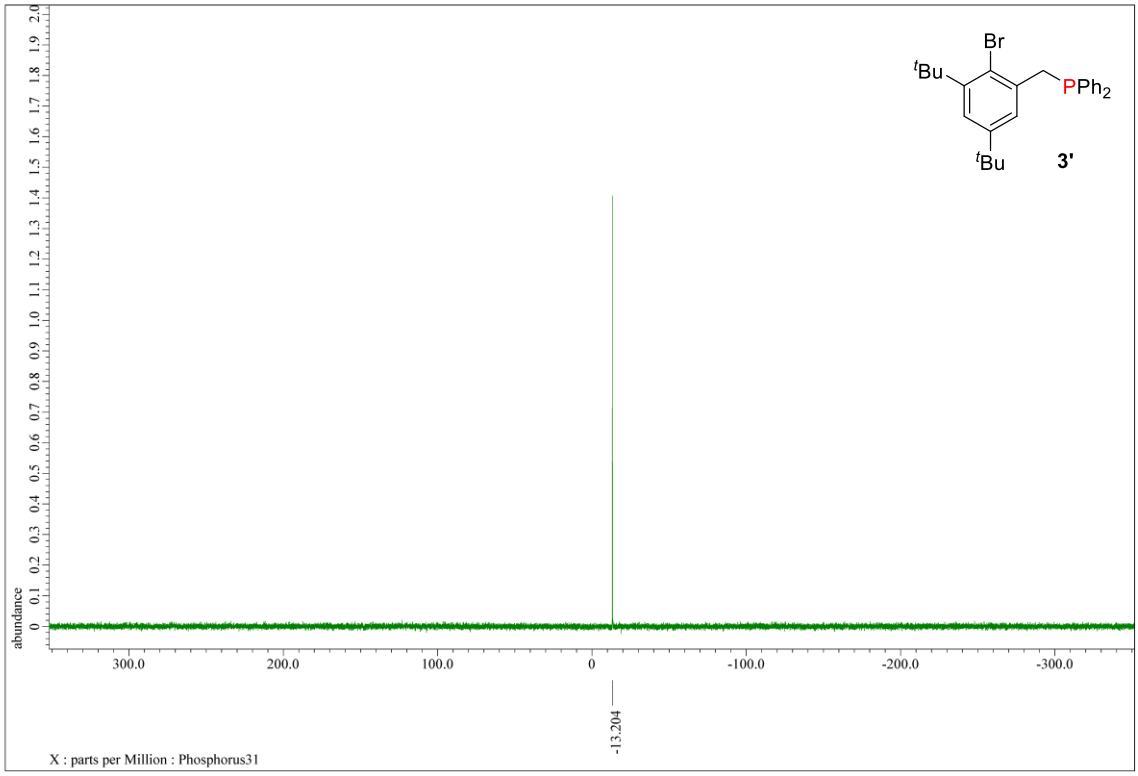


Fig. S6 ^{31}P NMR Spectrum of 3'.

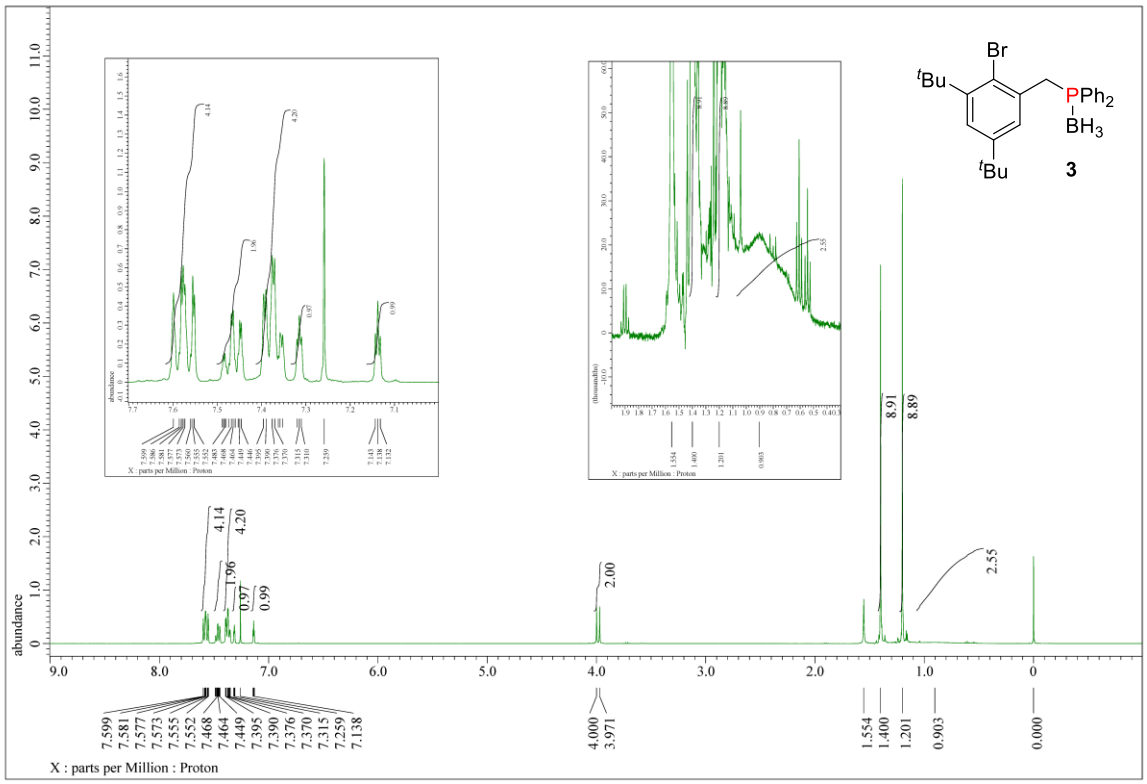


Fig. S7 ^{1}H NMR Spectrum of 3.

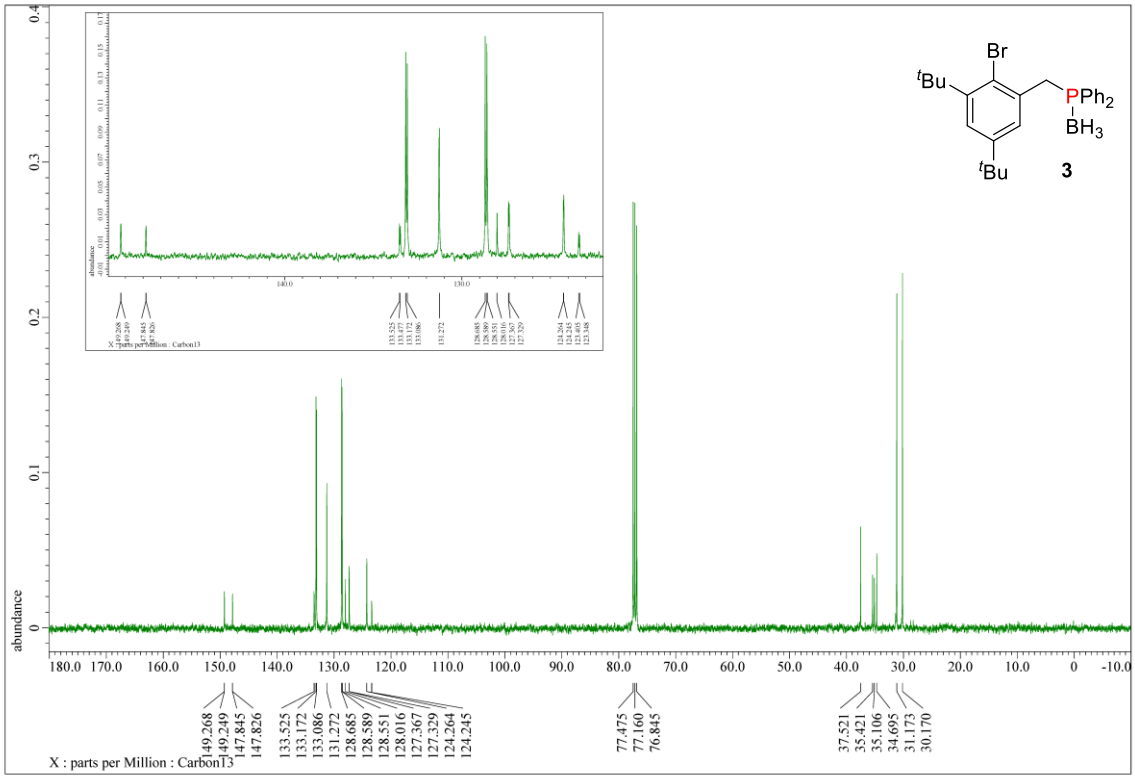


Fig. S8 ^{13}C NMR Spectrum of 3.

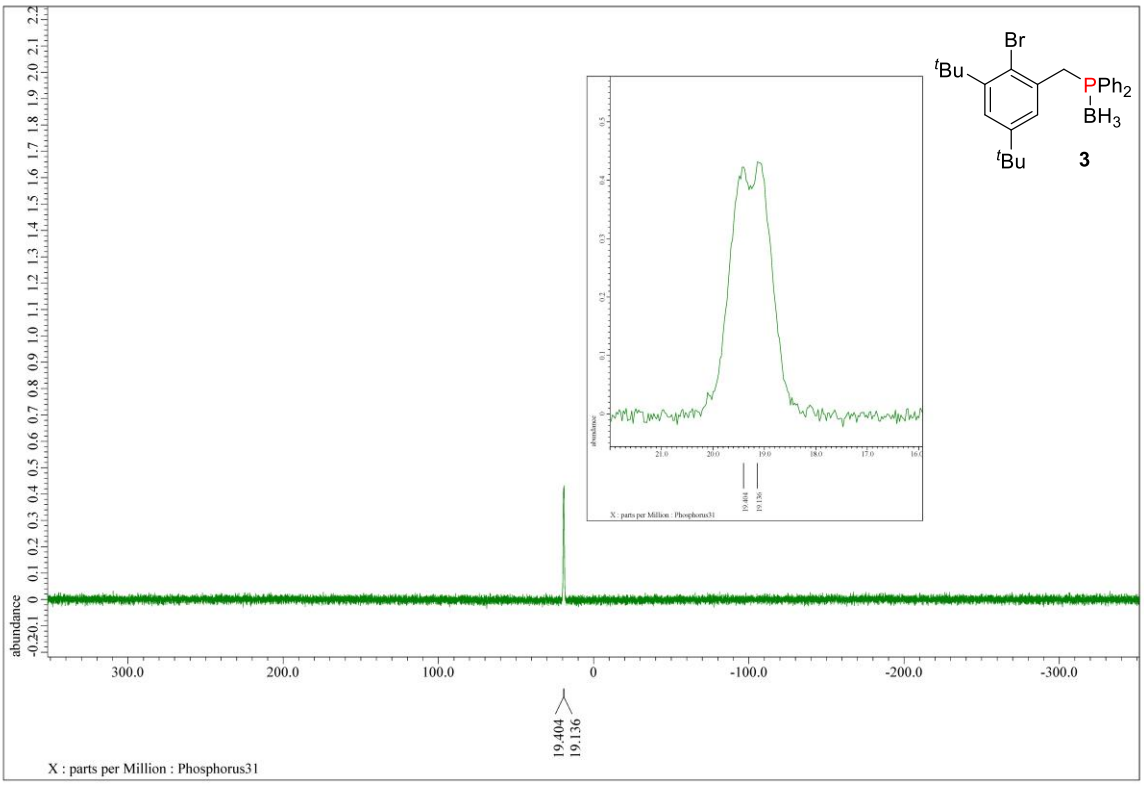


Fig. S9 ^{31}P NMR Spectrum of 3.

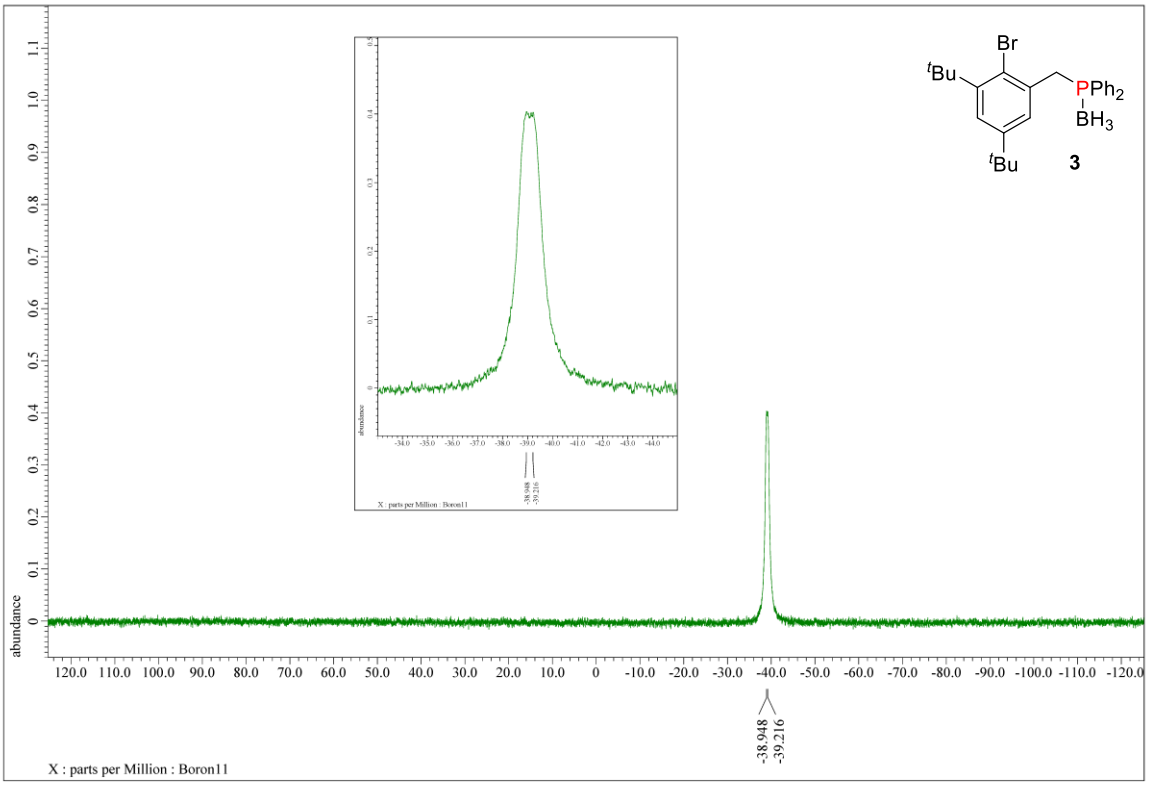


Fig. S10 ^{11}B NMR Spectrum of 3.

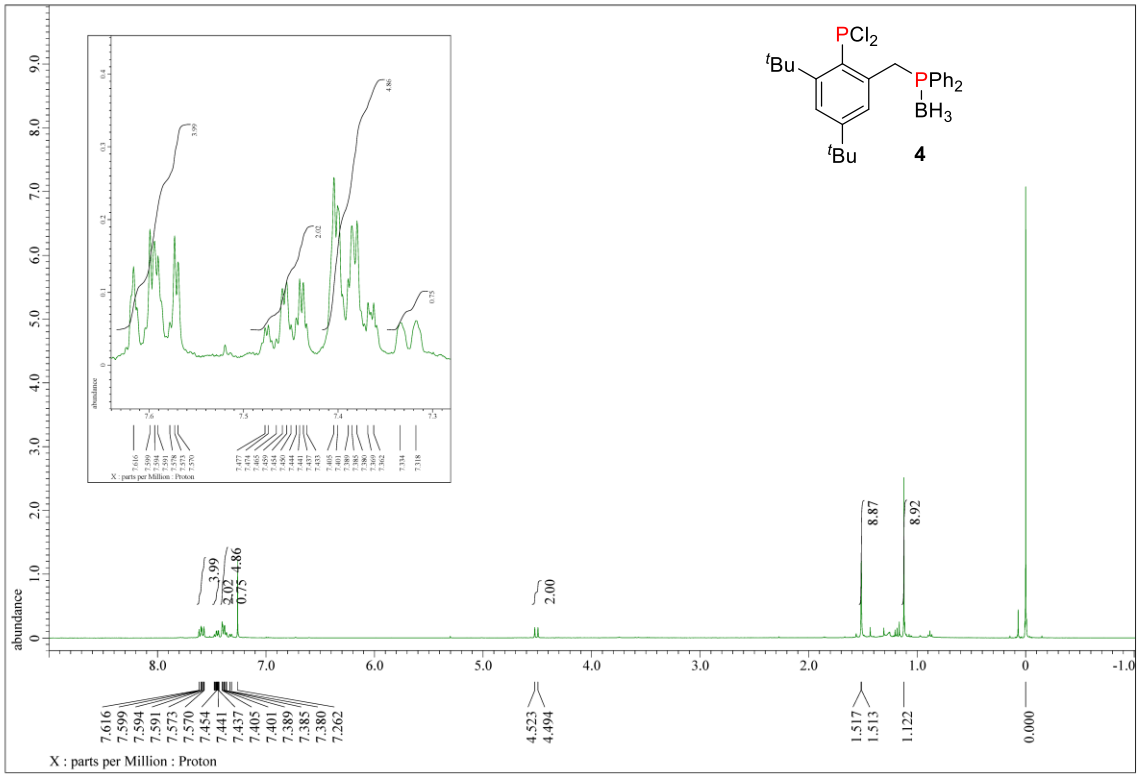


Fig. S11 ^{1}H NMR Spectrum of 4.

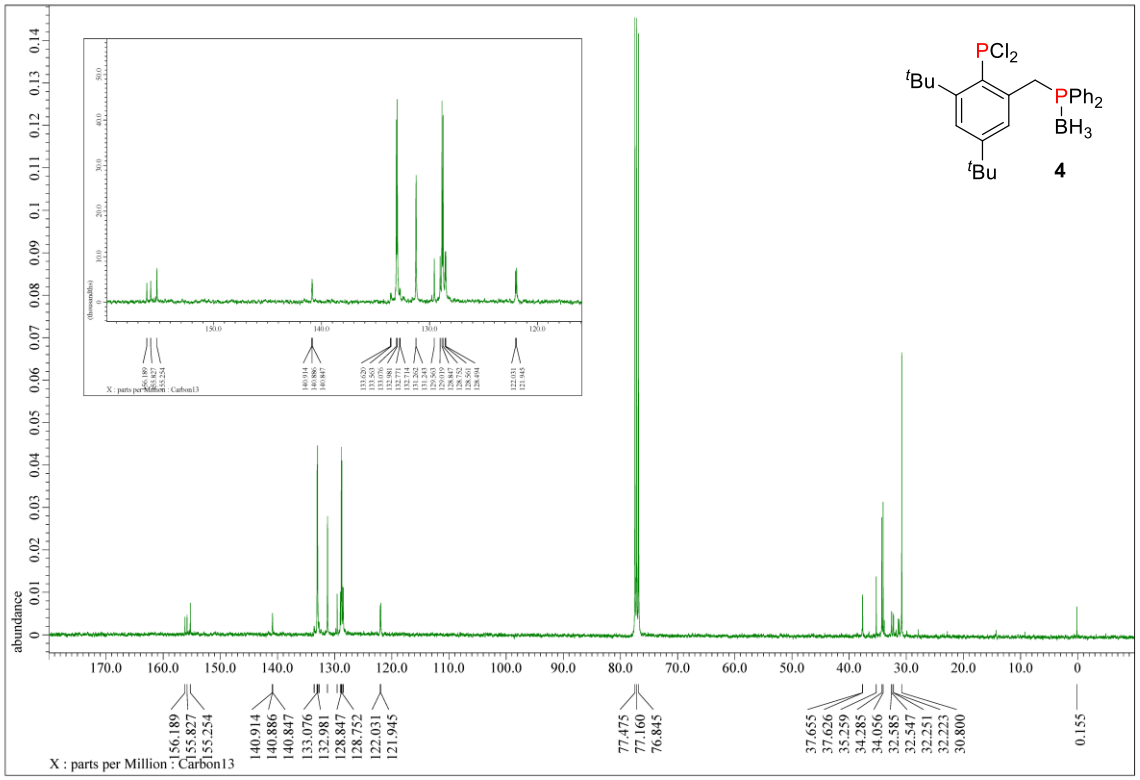


Fig. S12 ^{13}C NMR Spectrum of 4.

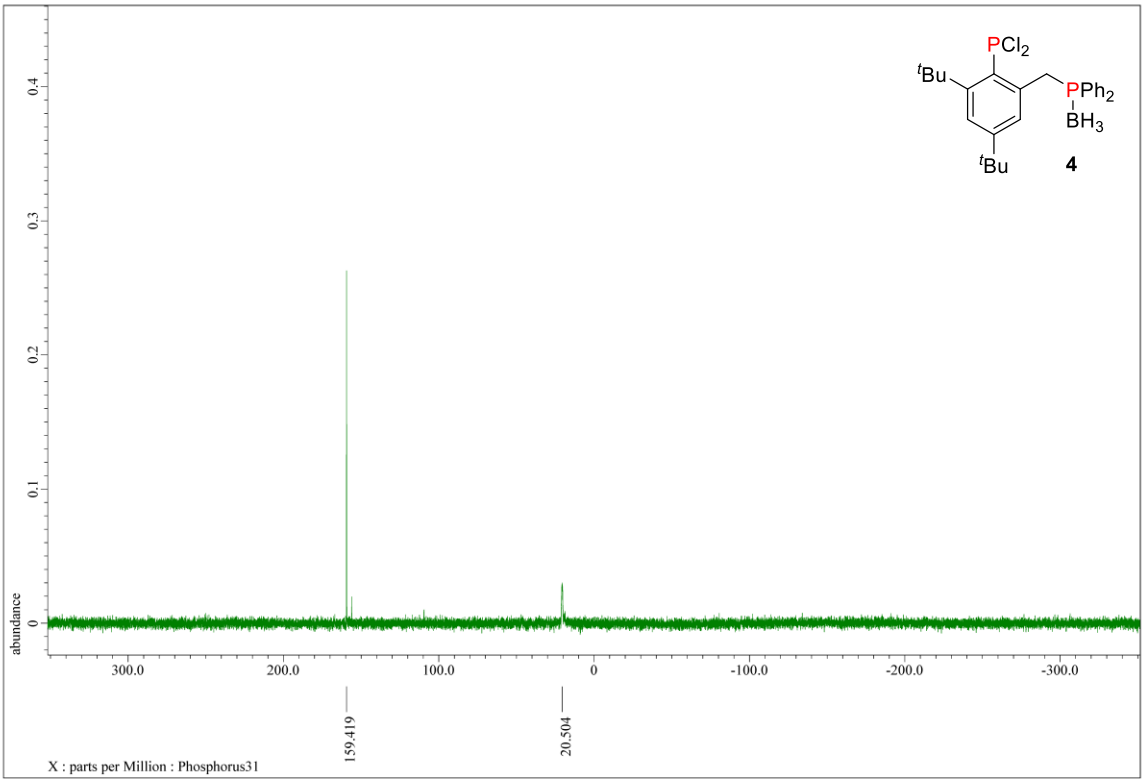


Fig. S13 ^{31}P NMR Spectrum of 4.

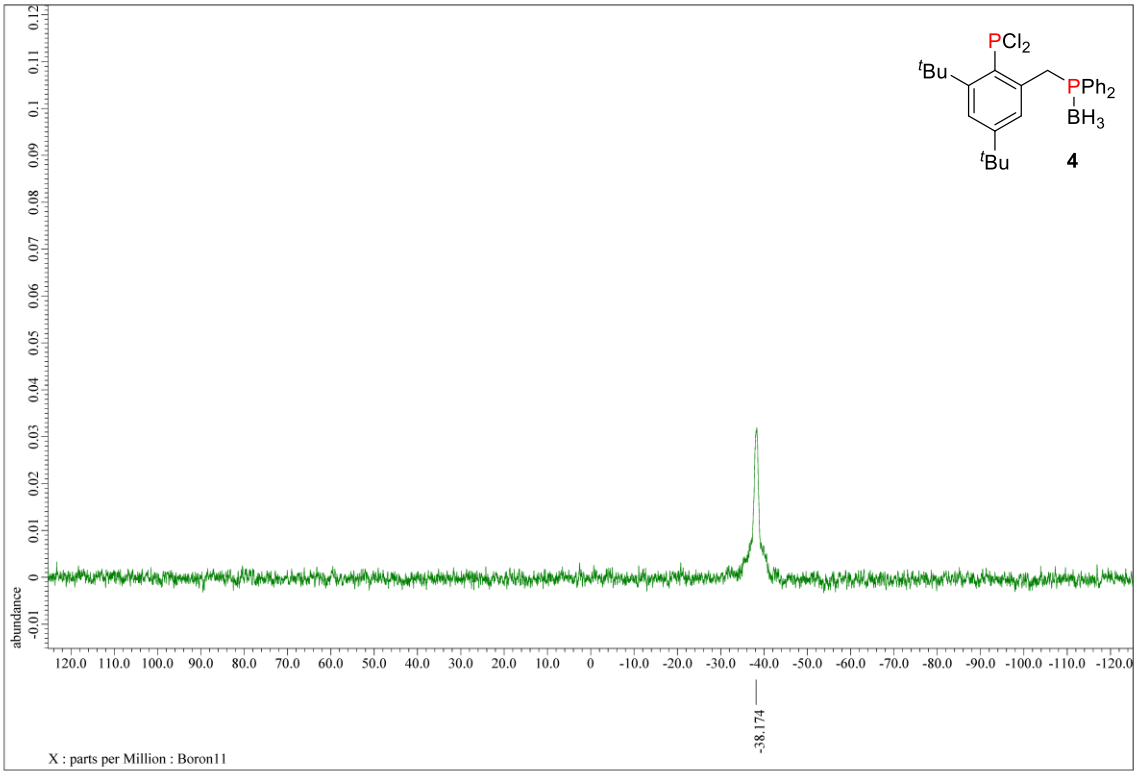


Fig. S14 ^{11}B NMR Spectrum of 4.

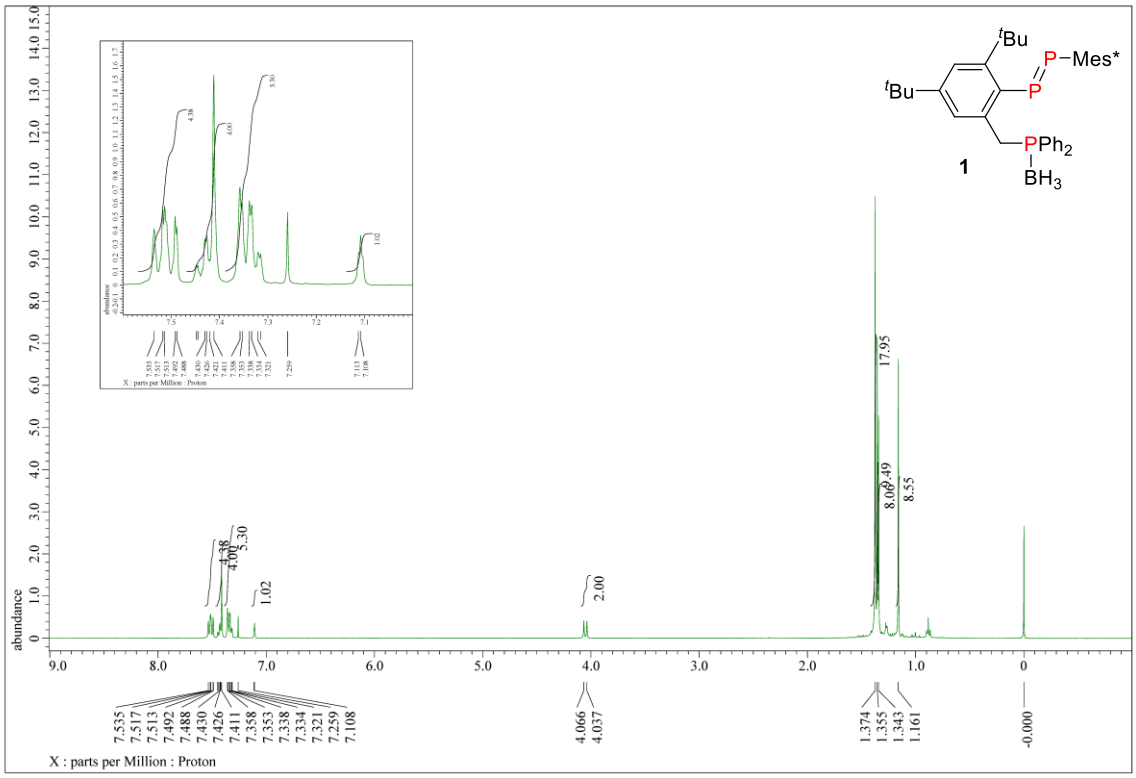


Fig. S15 ^{1}H NMR Spectrum of 1 in $CDCl_3$.

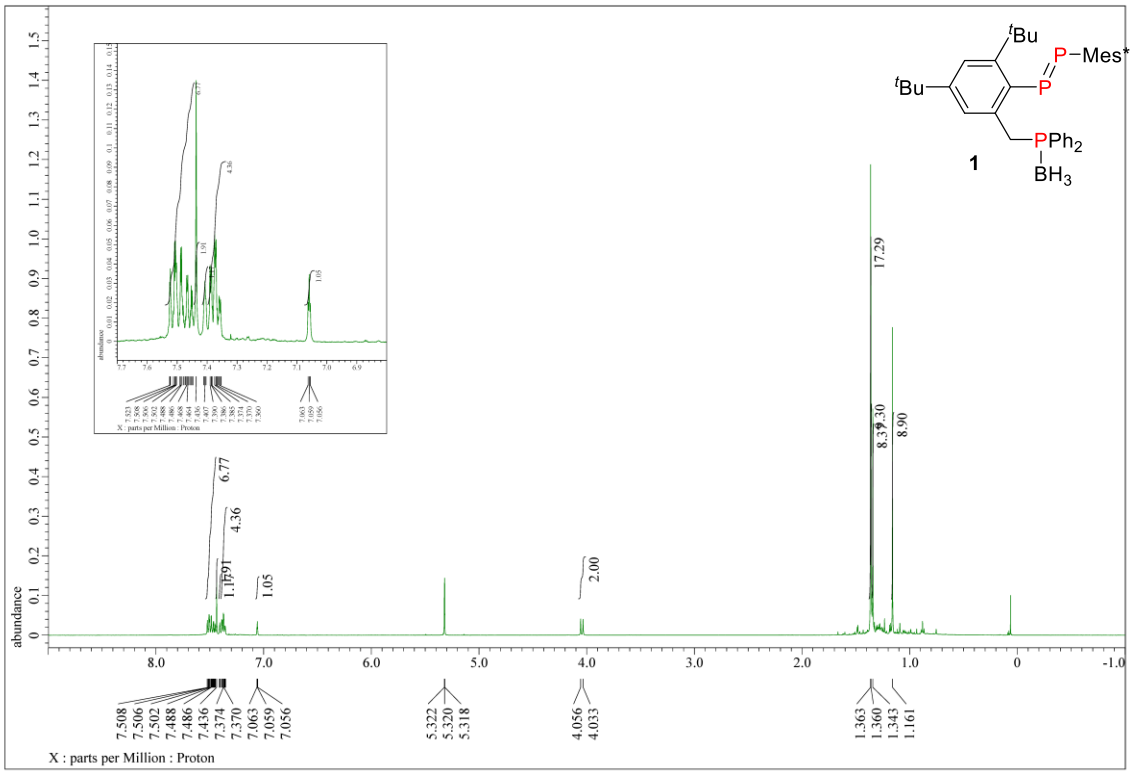


Fig. S16 ^{1}H NMR Spectrum of 1 in CD_2Cl_2.

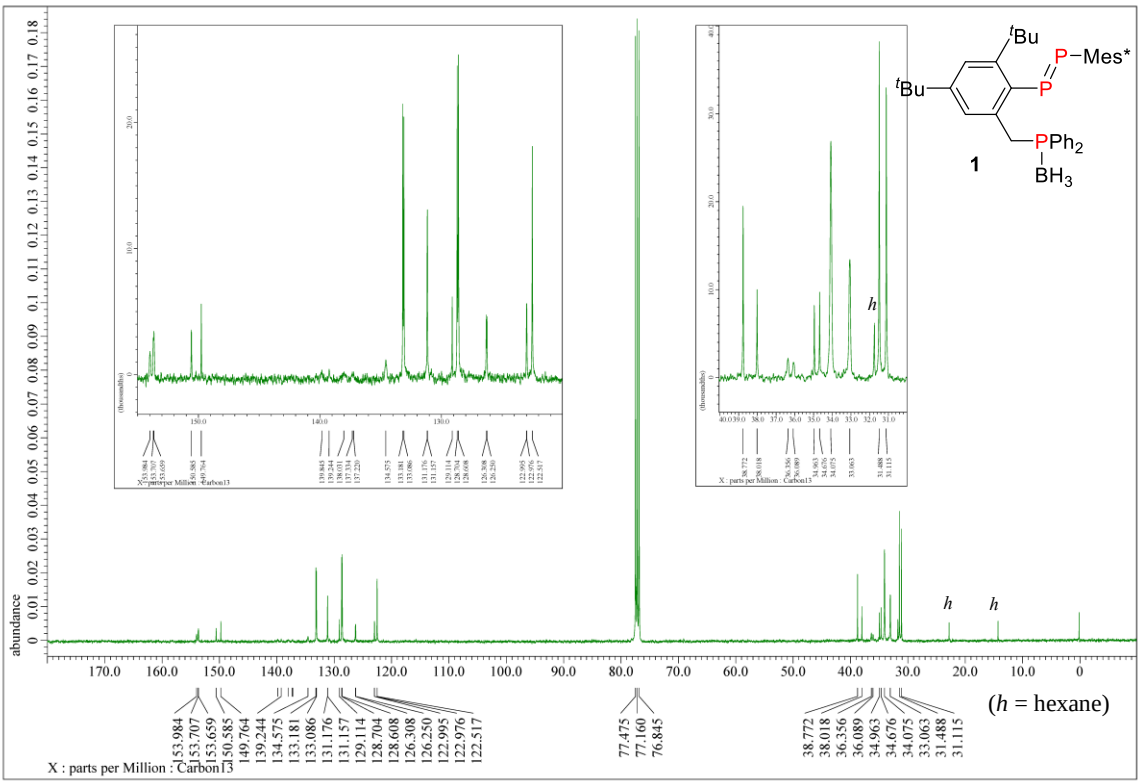


Fig. S17 ^{13}C NMR Spectrum of 1.

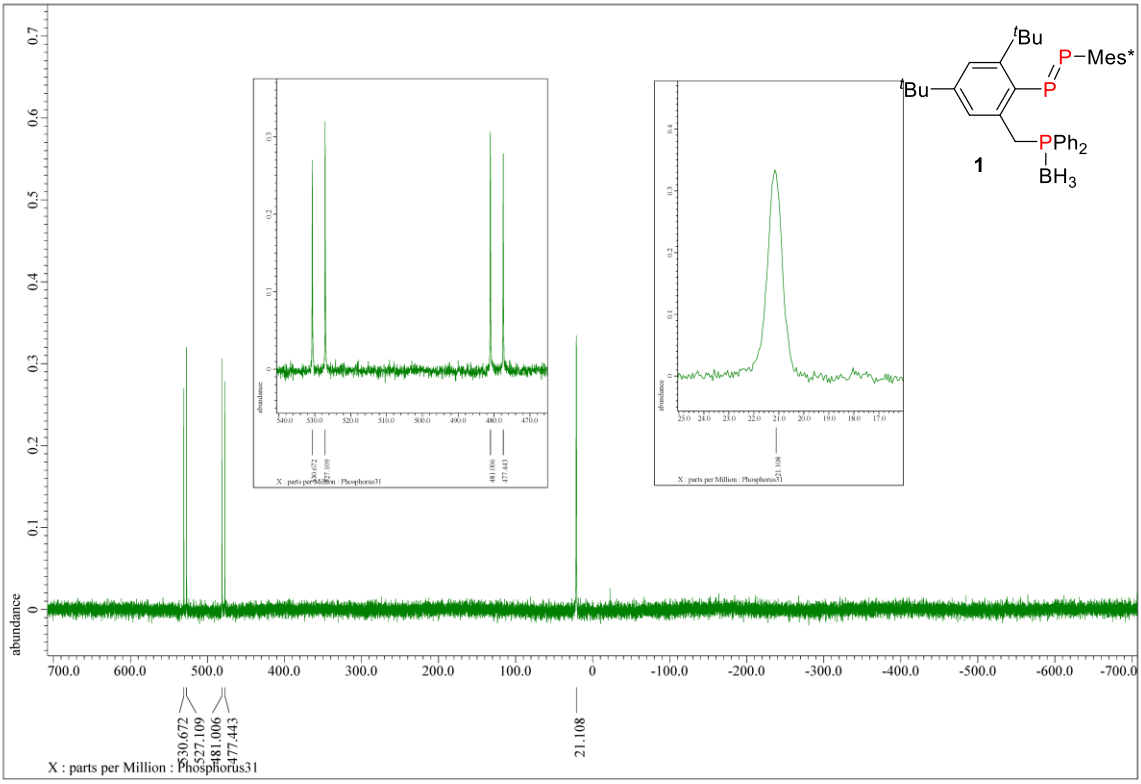


Fig. S18 ^{31}P NMR Spectrum of 1.

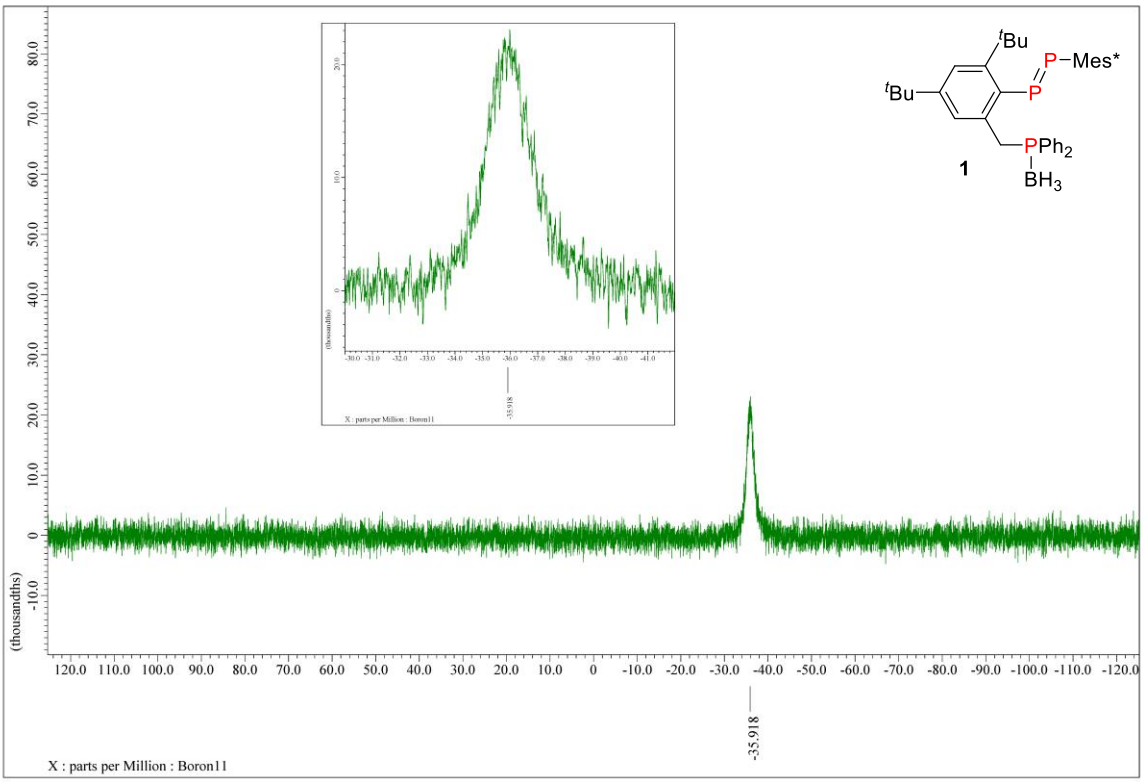


Fig. S19 ^{11}B NMR Spectrum of 1.

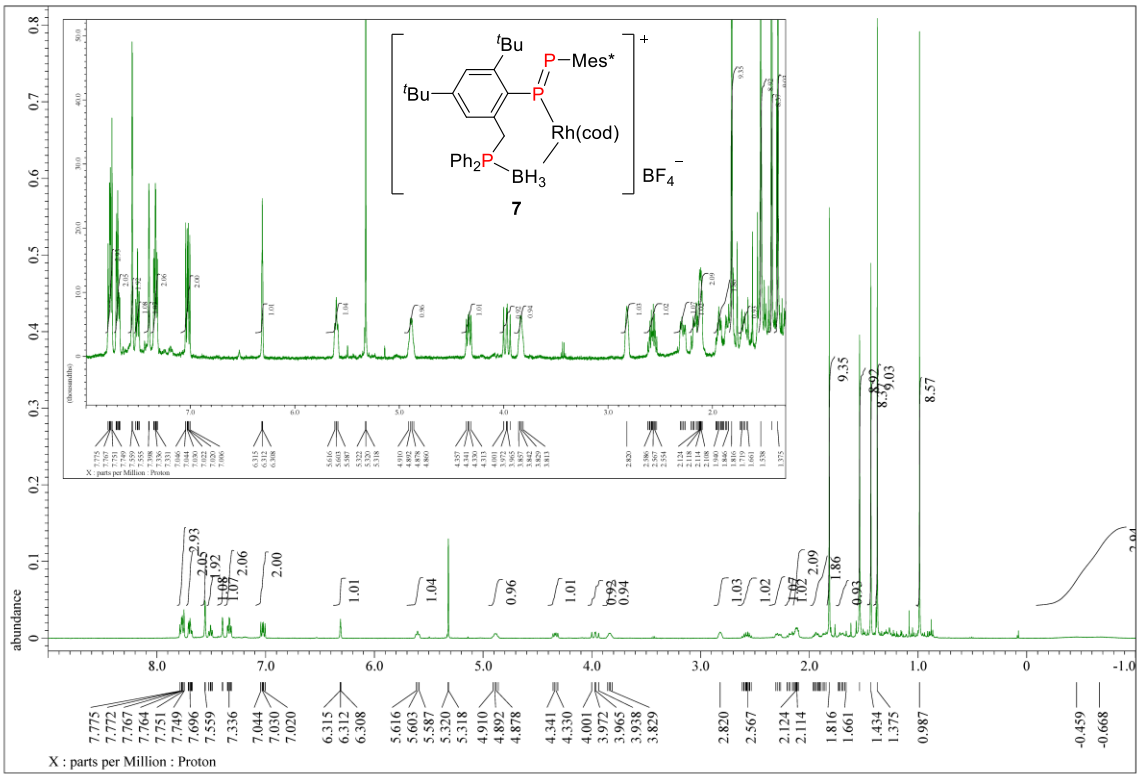


Fig. S20 ^{1}H NMR Spectrum of 7.

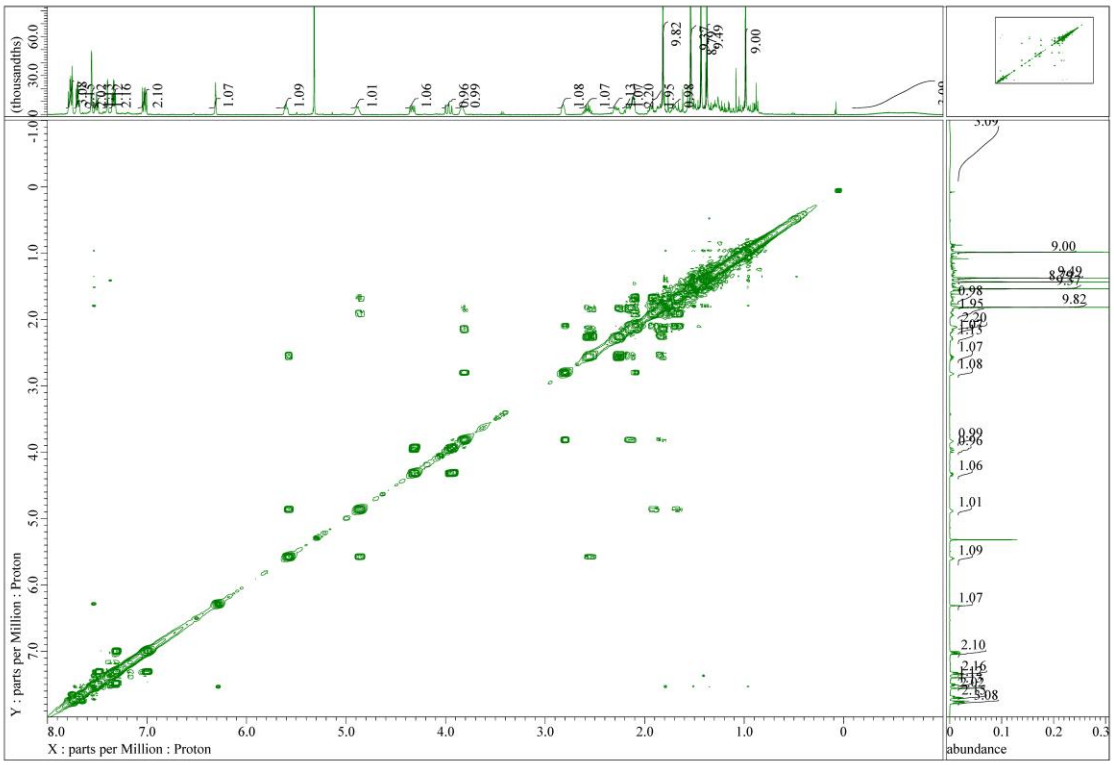


Fig. S21 ^{1}H-^{1}H COSY Spectrum of 7.

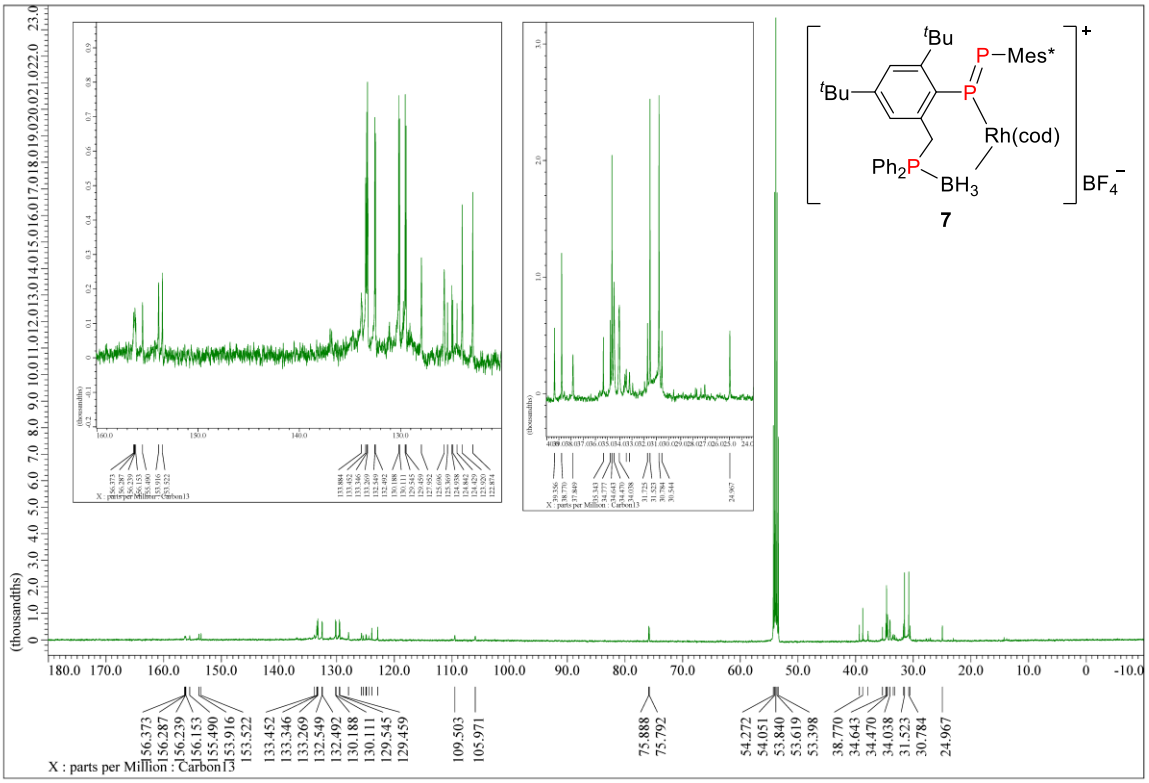


Fig. S22 ^{13}C NMR Spectrum of 7.

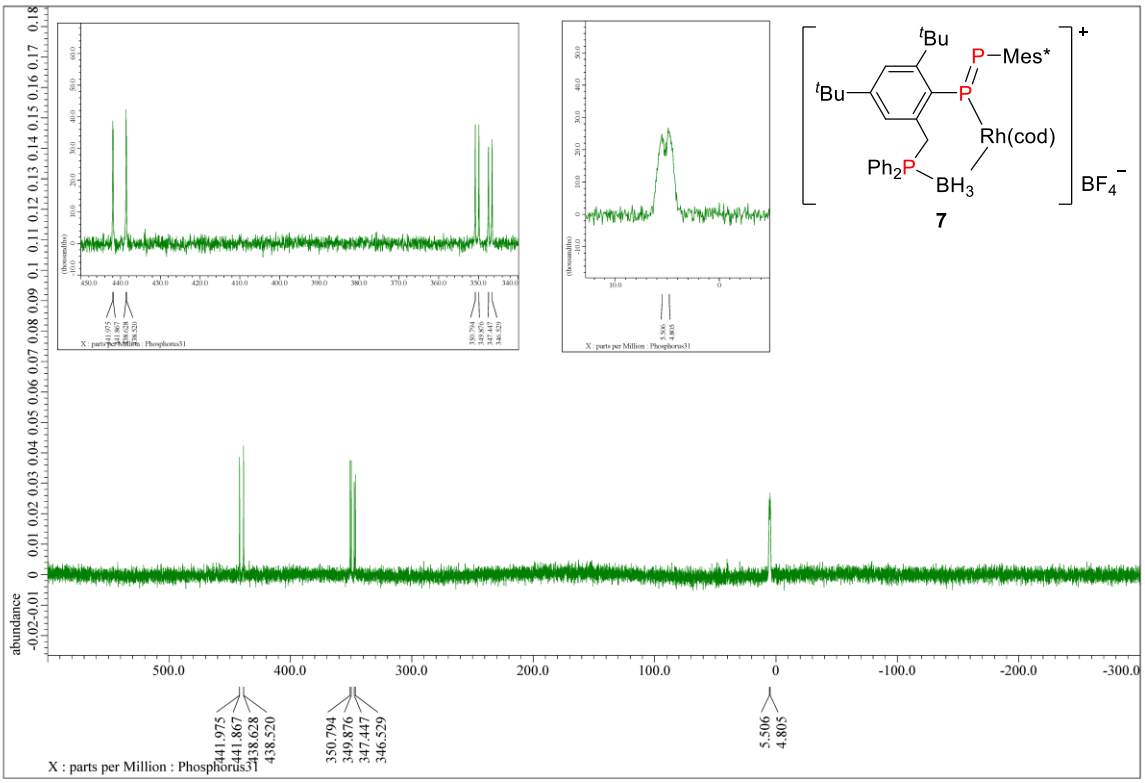


Fig. S23 ^{31}P NMR Spectrum of 7.

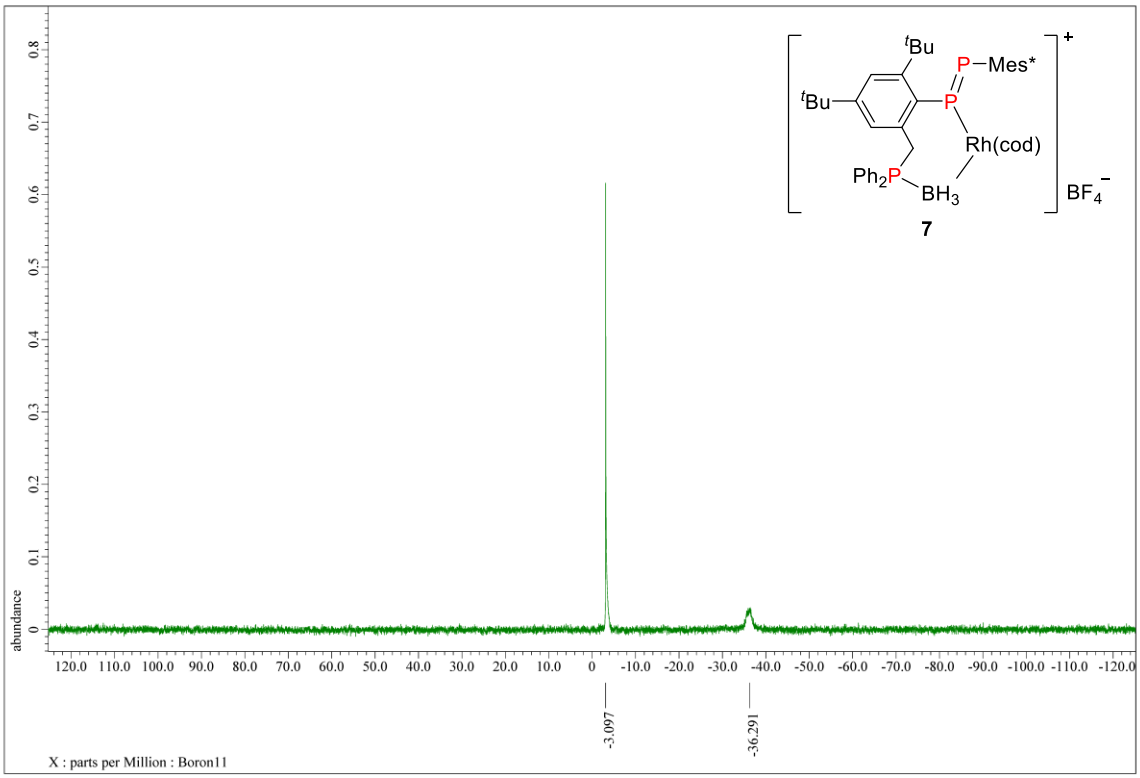


Fig. S24 ^{11}B NMR Spectrum of 7.

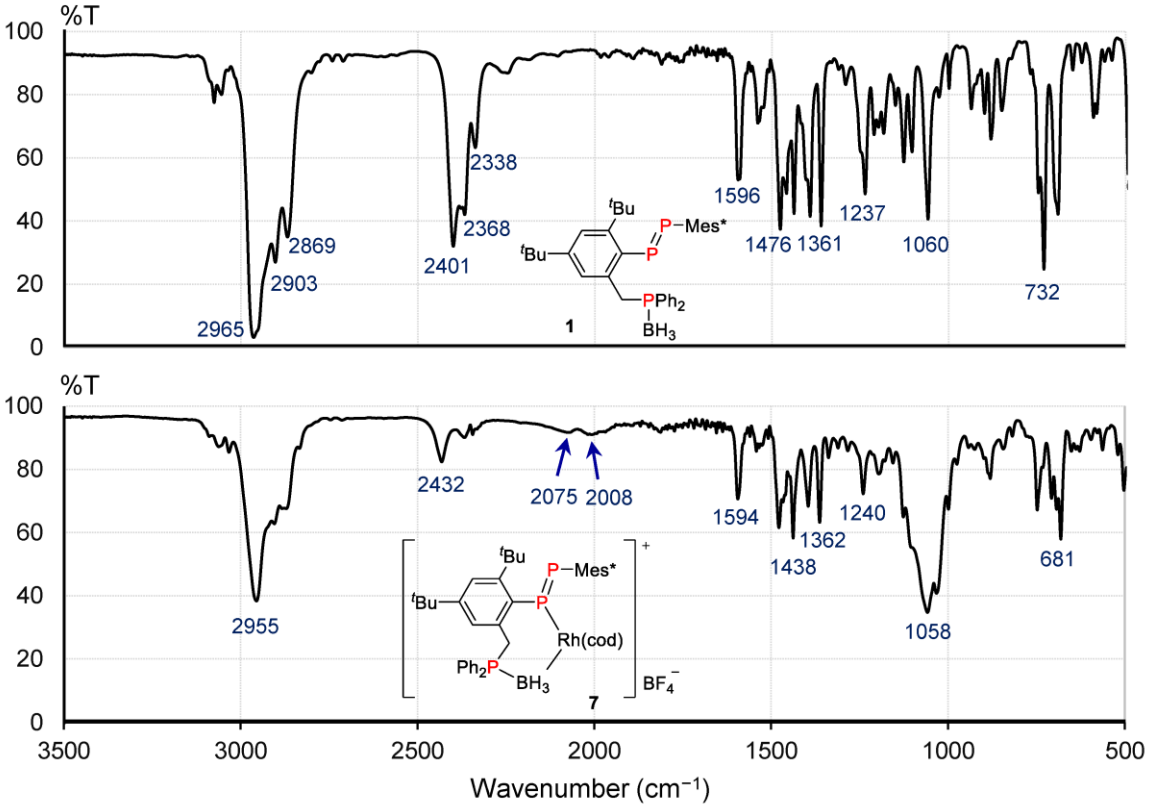


Fig. S25 IR Spectra of 1 and 7.

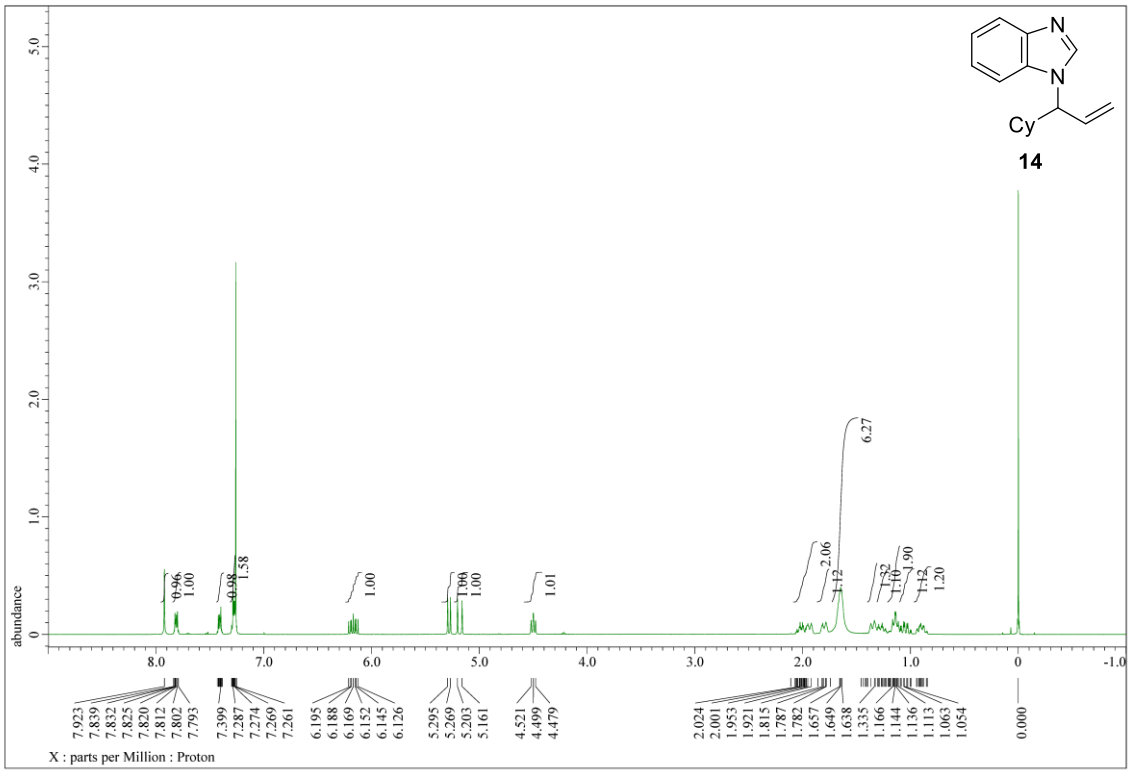


Fig. S26 ^{1}H NMR Spectrum of 14.

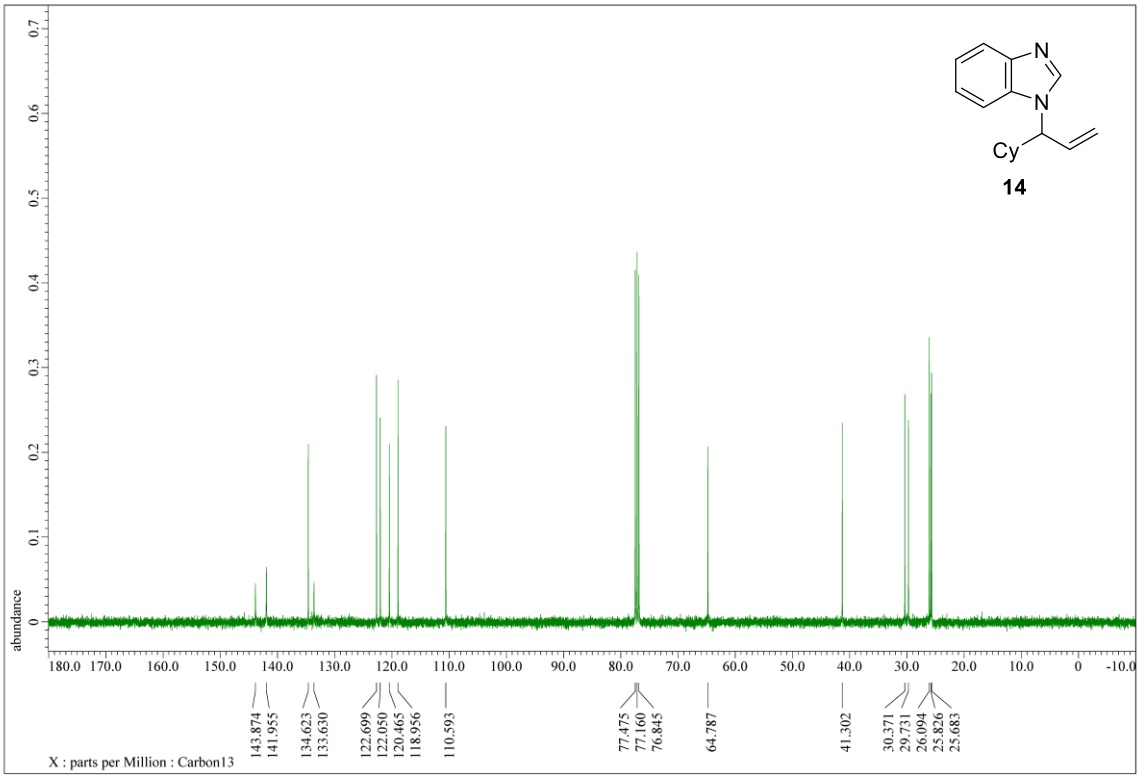


Fig. S27 ^{13}C NMR Spectrum of 14.

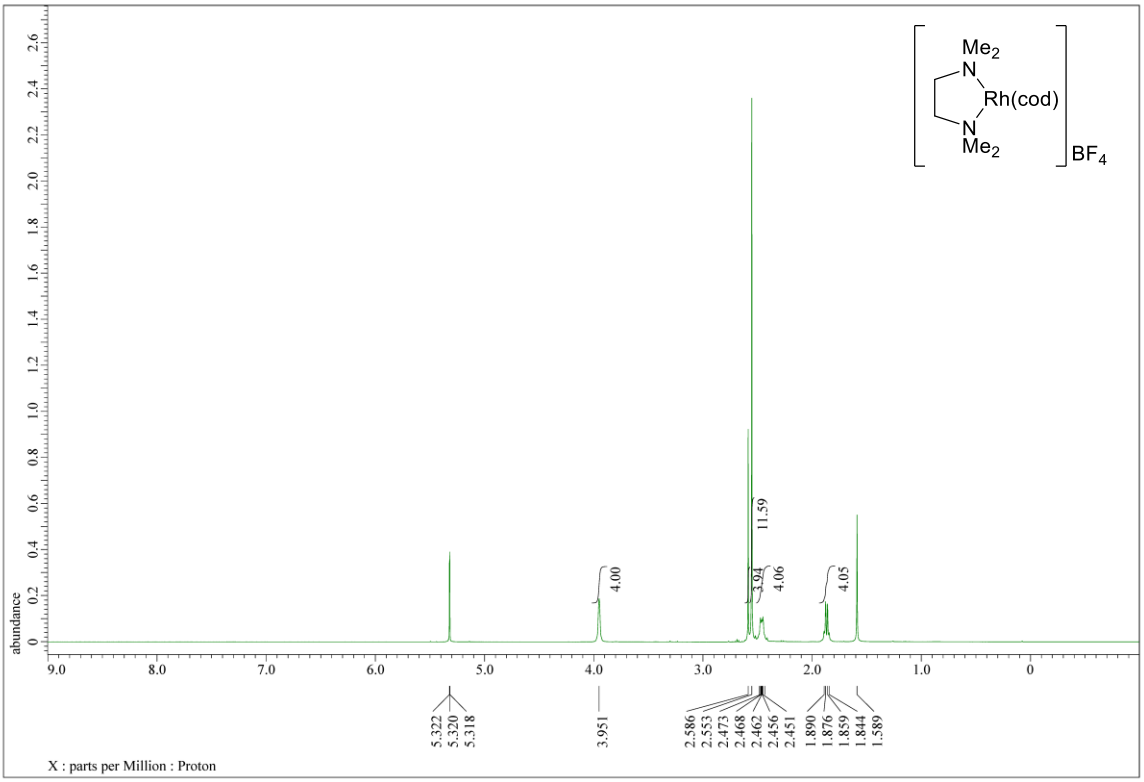


Fig. S28 ^{1}H NMR Spectrum of [Rh(tmeda)(cod)]BF$_4$.

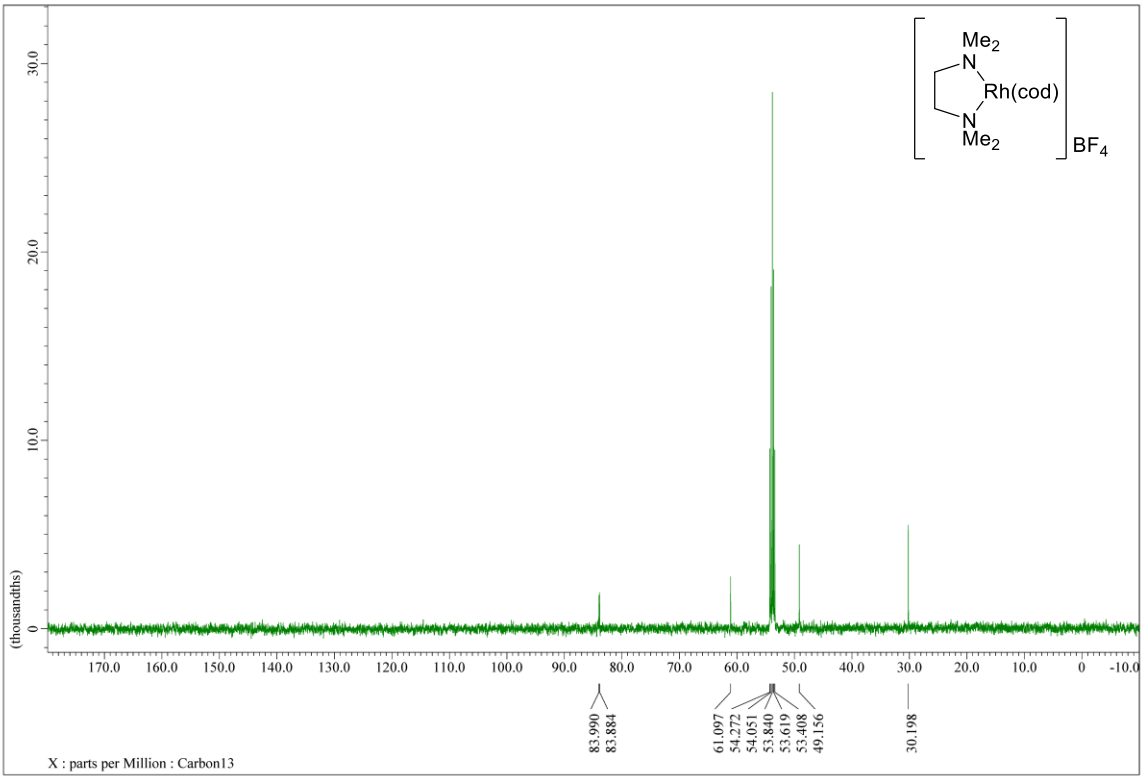


Fig. S29 ^{13}C NMR Spectrum of [Rh(tmeda)(cod)]BF_4.

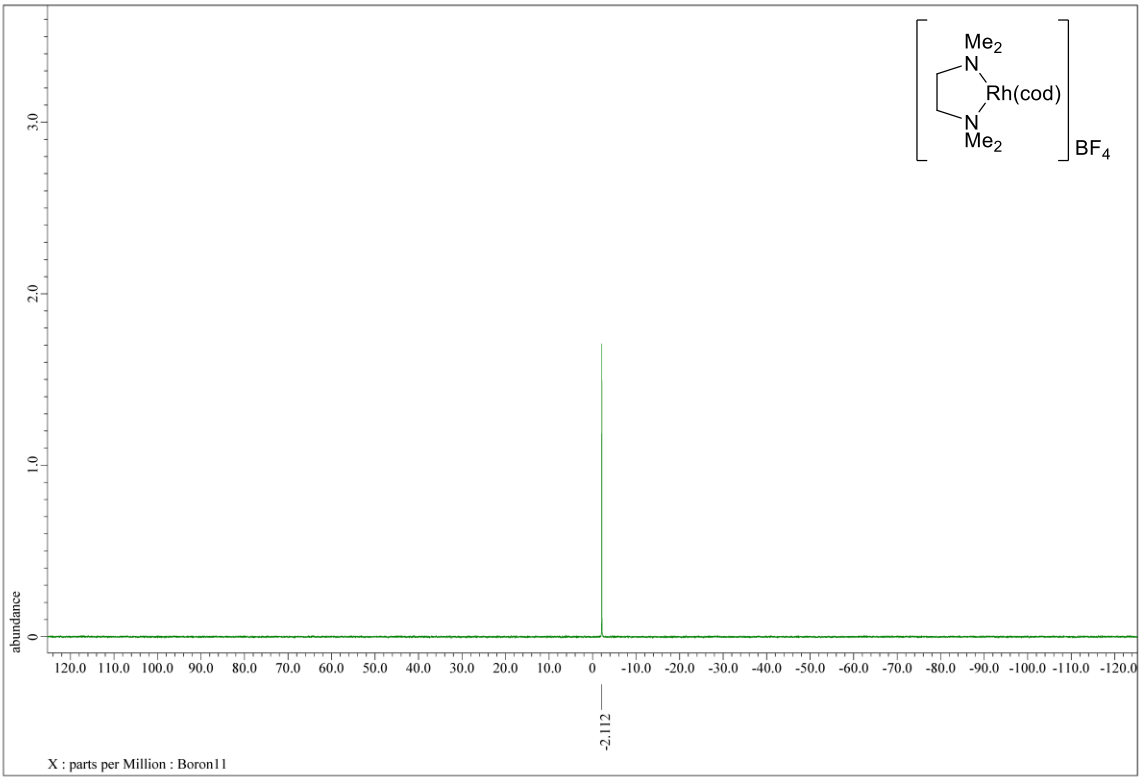


Fig. S30 ^{11}B NMR Spectrum of [Rh(tmeda)(cod)]BF_4.

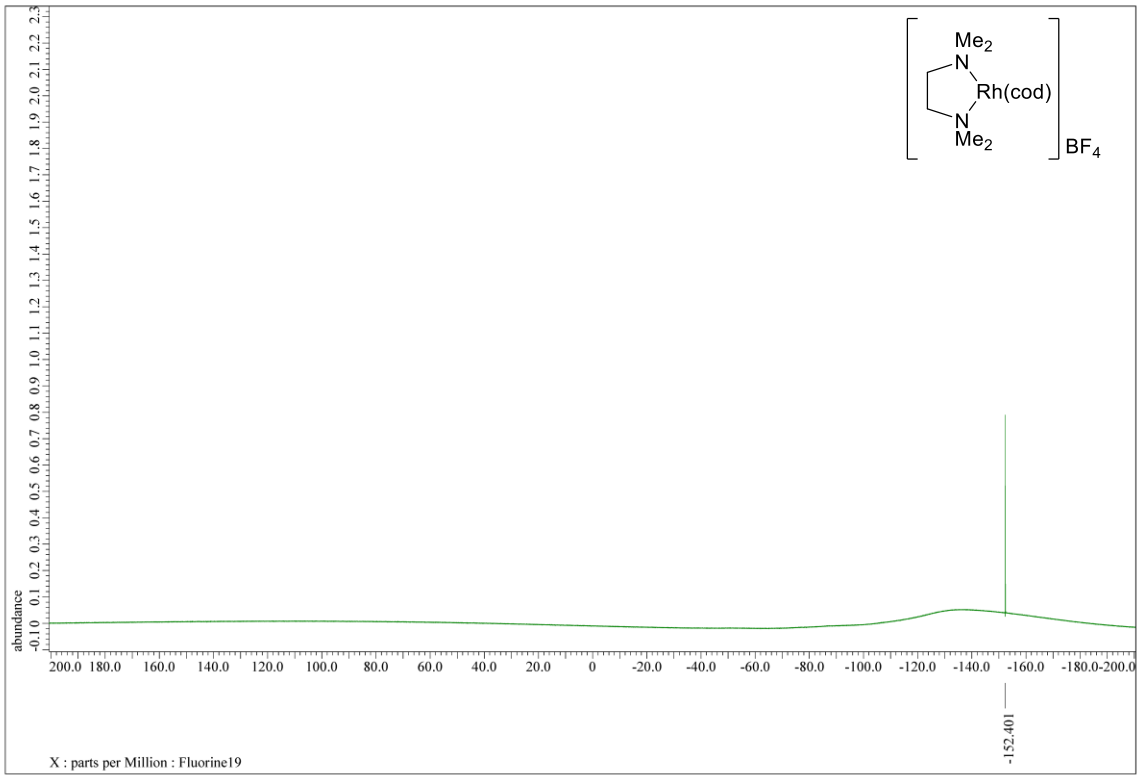


Fig. S31 ^{19}F NMR Spectrum of [Rh(tmeda)(cod)]BF_4.

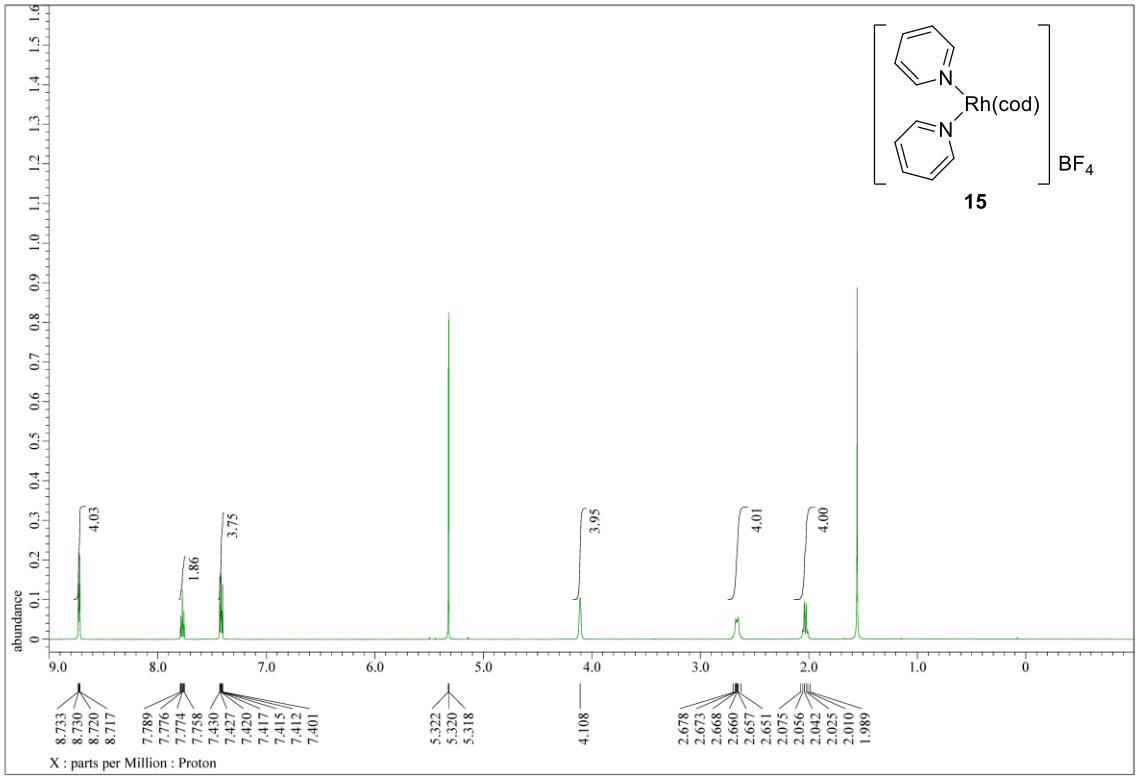


Fig. S32 ^{1}H NMR Spectrum of 15.

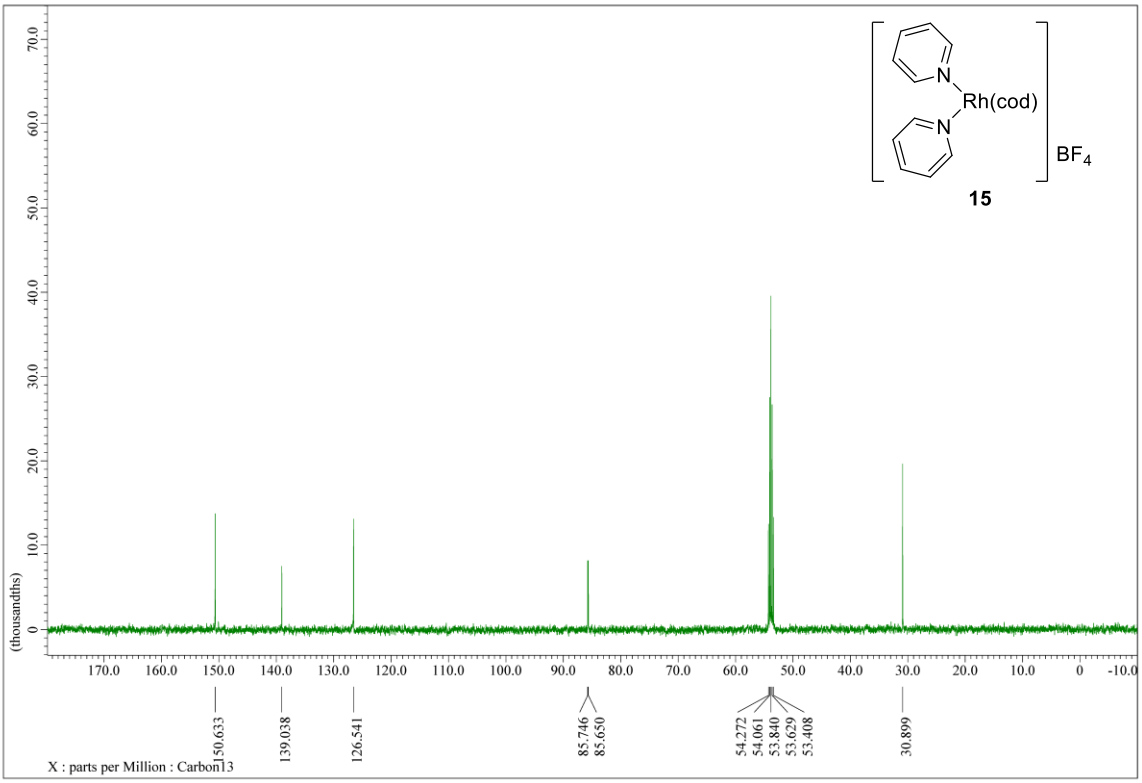


Fig. S33 ^{13}C NMR Spectrum of 15.

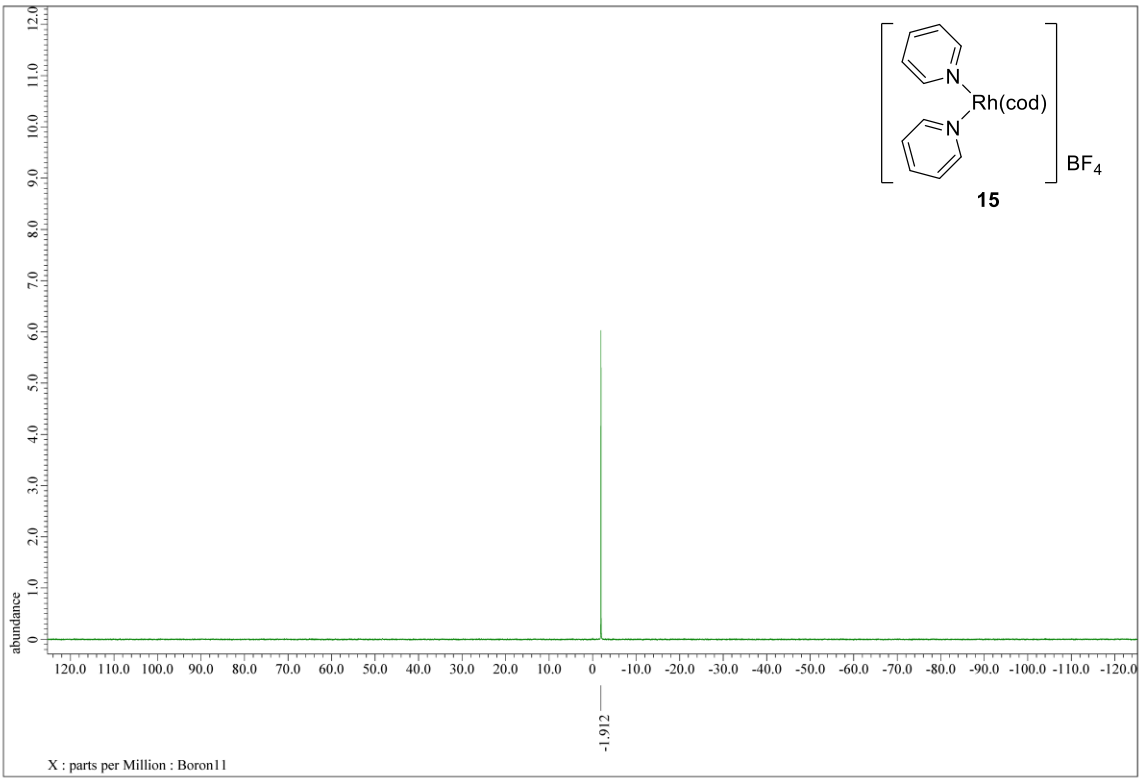


Fig. S34 ^{11}B NMR Spectrum of 15.

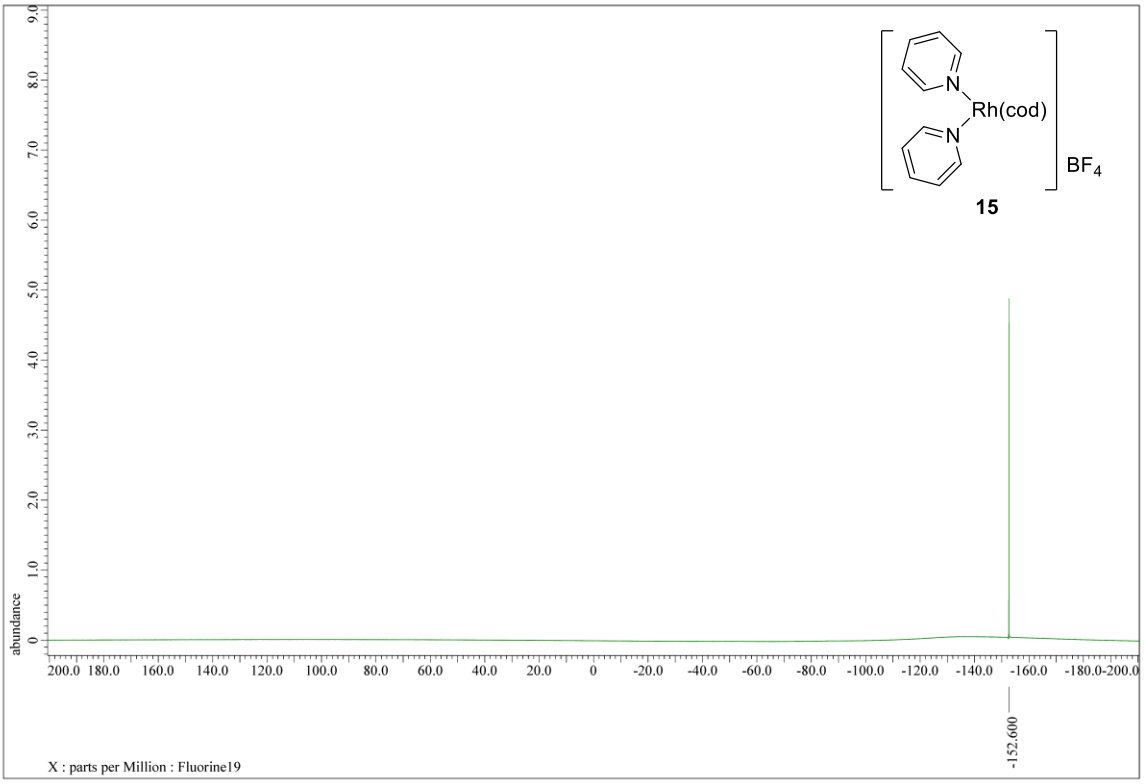


Fig. S35 ^{19}F NMR Spectrum of 15.

3. Temperature-Dependent ^{1}H NMR Spectra

Temperature-dependent ^{1}H NMR spectra (500 MHz) of diphosphene–rhodium complex **7** were measured in CD_2Cl_2 with a JEOL JNM-ECZ500R spectrometer. The solution was prepared and charged into an NMR tube with a J. Young valve in a glovebox under an argon atmosphere. The spectra were measured at 20 °C, 0 °C, −20 °C, and every 10 °C from −20 °C to −90 °C. The observed NMR spectra are shown in Fig. S36.

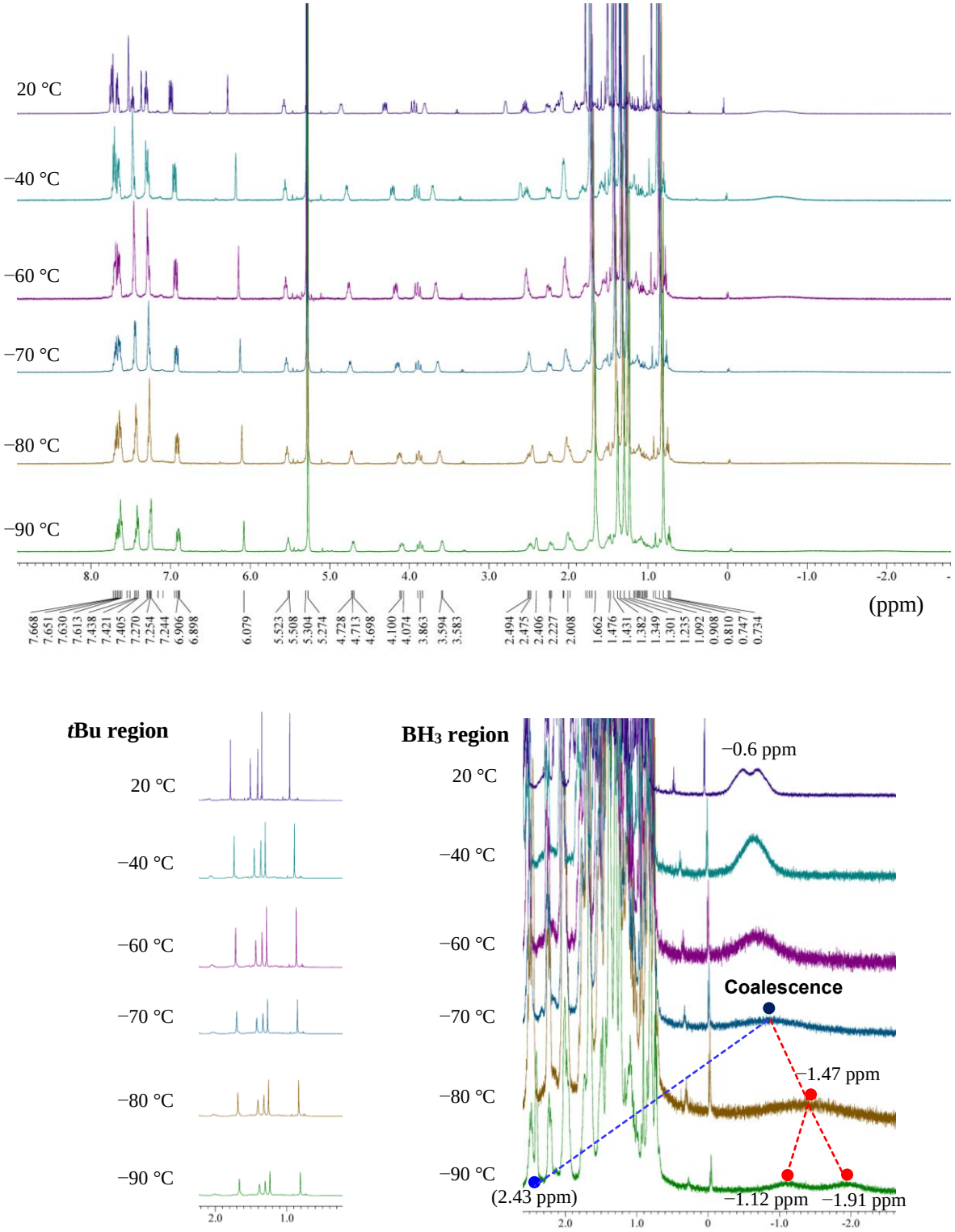


Fig. S36 Temperature-dependent ^{1}H NMR spectra of **7** in CD_2Cl_2.

4. Ligand Exchange Reactions of Diphosphene−Rhodium Complex 7

4-1. Reaction of 7 with *N*-donor reagent (20 eq.) in CD_2Cl_2

A solution of rhodium complex **7** (2.0 mg, 2.0 μmol) in CD_2Cl_2 (0.7 mL) was charged into an NMR tube equipped with a J. Young valve under an argon atmosphere, and *N*-donor reagent (20 eq.) was added. The reaction was monitored by measuring the ^{1}H NMR spectra. The results are summarized in Figs. S37 to S41.

4-2. Reaction of diphosphene–phosphineborane ligand 1 with $[Rh(py)_2(cod)]BF_4$ (15) in CD_2Cl_2

Diphosphene–phosphineborane ligand **1** (2.1 mg, 3.0 μmol) and **15** (1.3 mg, 2.9 μmol) were charged into an NMR tube equipped with a J. Young valve under an argon atmosphere, and CD_2Cl_2 (0.7 mL) was added. The reaction was monitored by measuring the ^{1}H NMR spectra. The results are summarized in Figs. 3c and S40c.

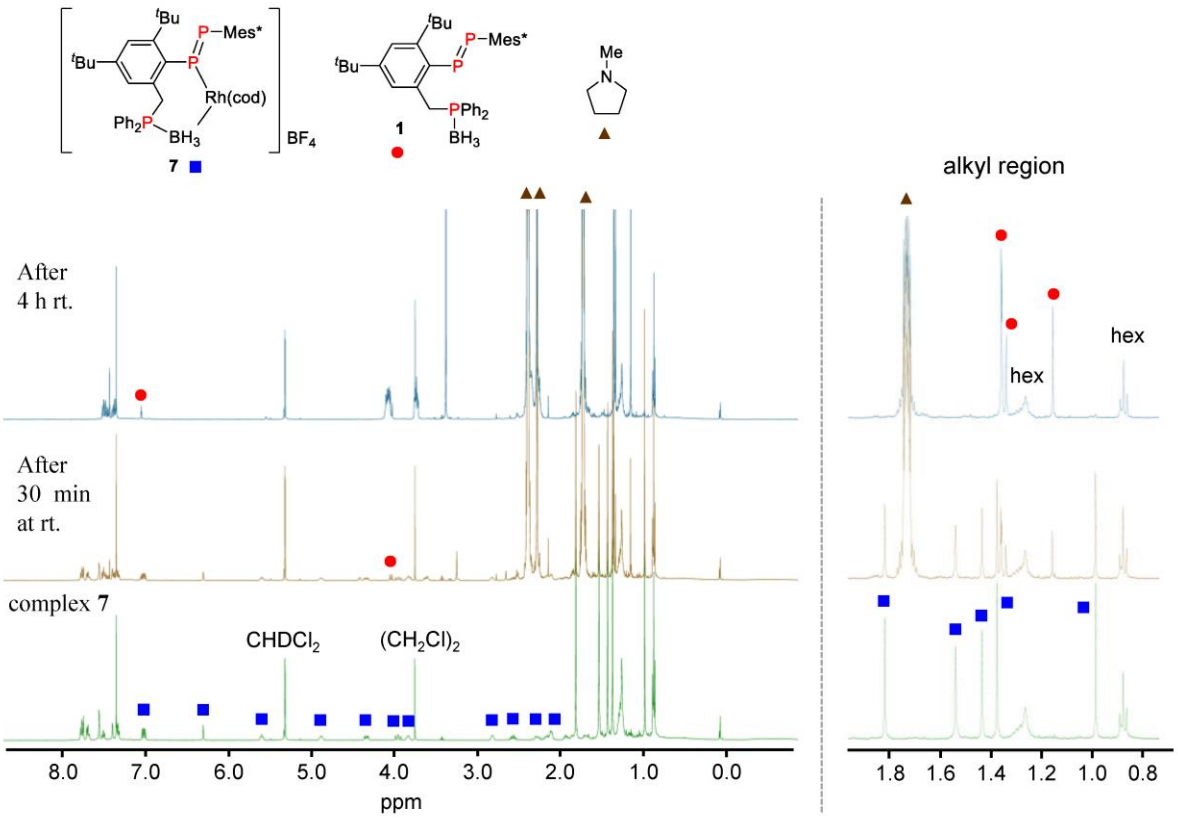


Fig. S37 Reaction of **7** with *N*-methylpyrrolidine (20 eq.) at room temperature monitored by ^{1}H NMR spectra in CD_2Cl_2.

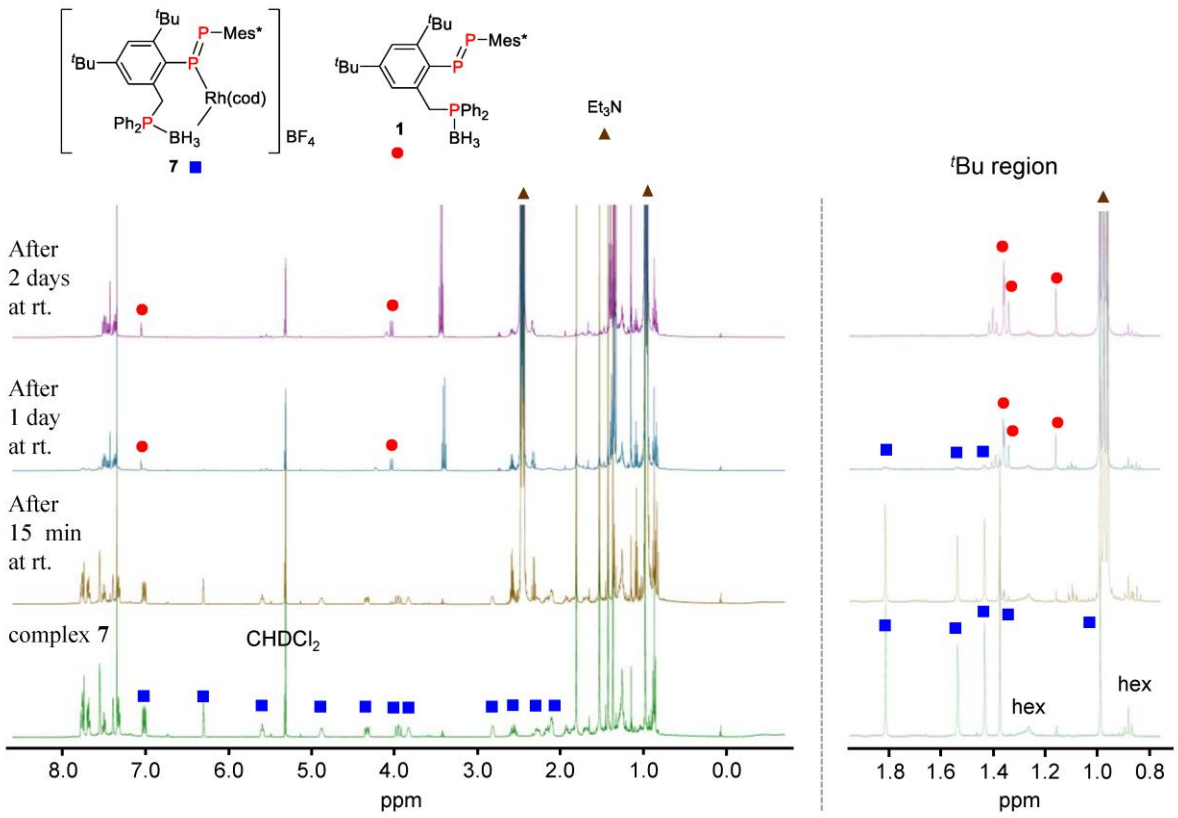


Fig. S38 Reaction of **7** with Et_3N (20 eq.) at room temperature monitored by ^1H NMR spectra in CD_2Cl_2.

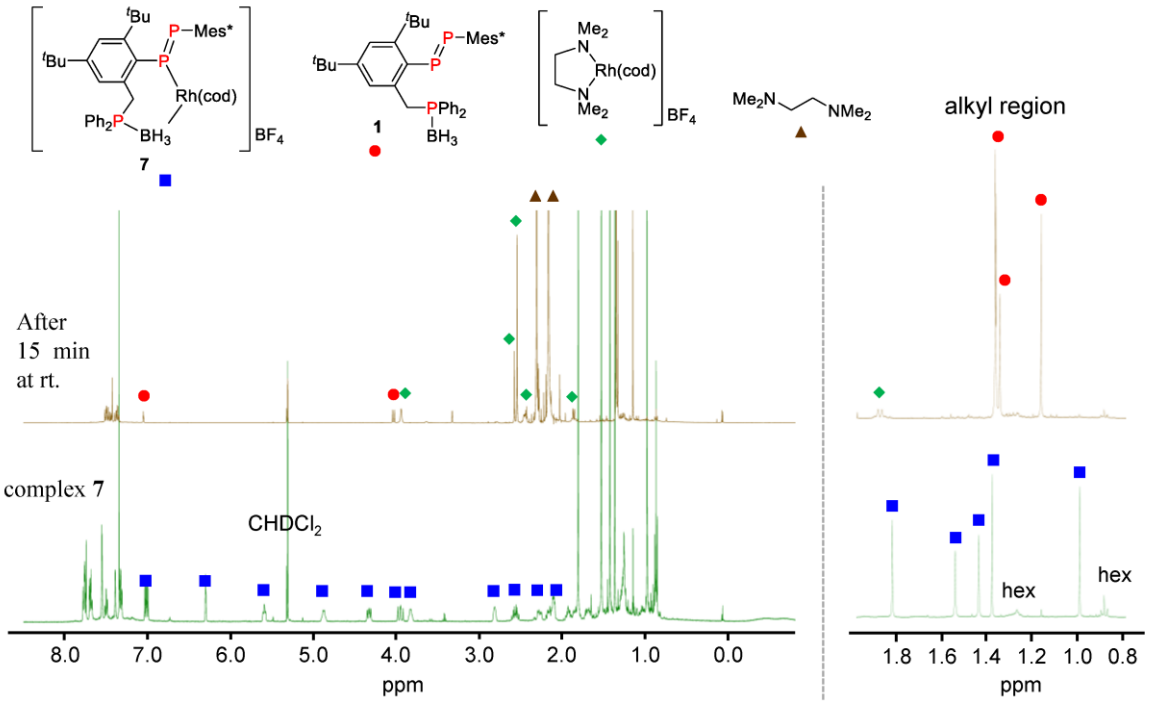


Fig. S39 ^1H NMR spectum of the crude mixture of the reaction of **7** with TMEDA (20 eq.) at room temperature.

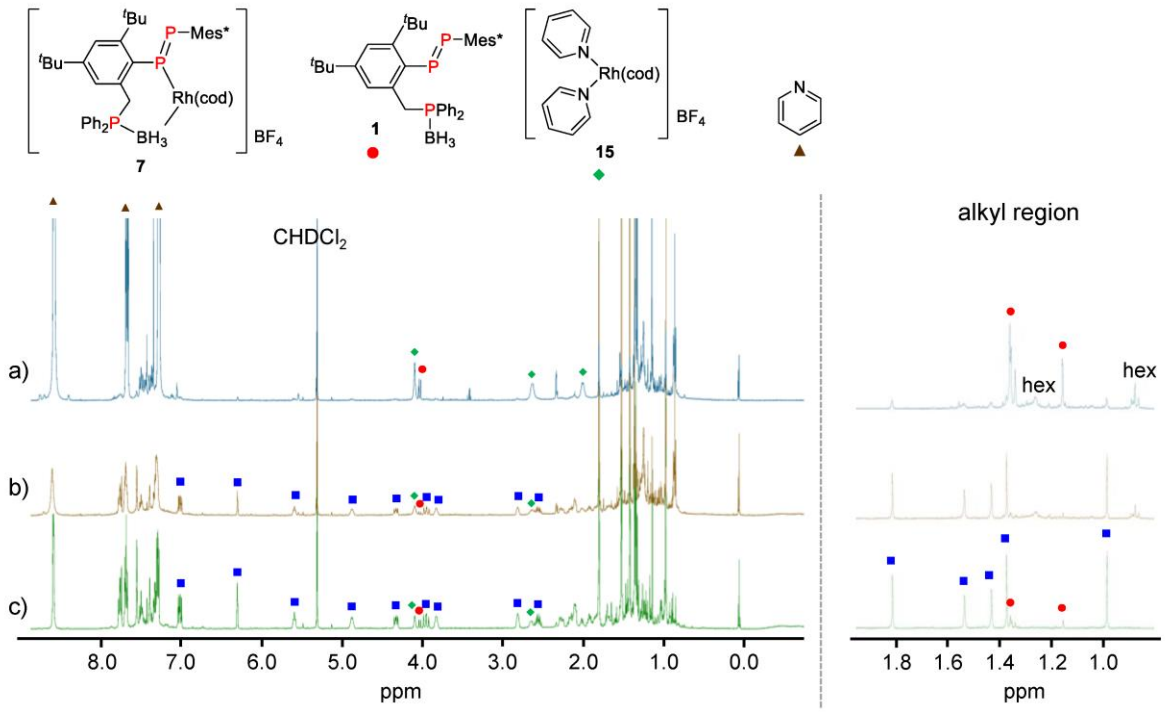


Fig. S40 ^{1}H NMR spectra measured in CD_2Cl_2 (a) after the reaction of rhodium complex **7** with pyridine (20 eq.); (b) after removal of unreacted pyridine from the reaction mixture; (c) after the treatment of **1** with $[Rh(py)_2(cod)]BF_4$ (**15**, 1 eq.).

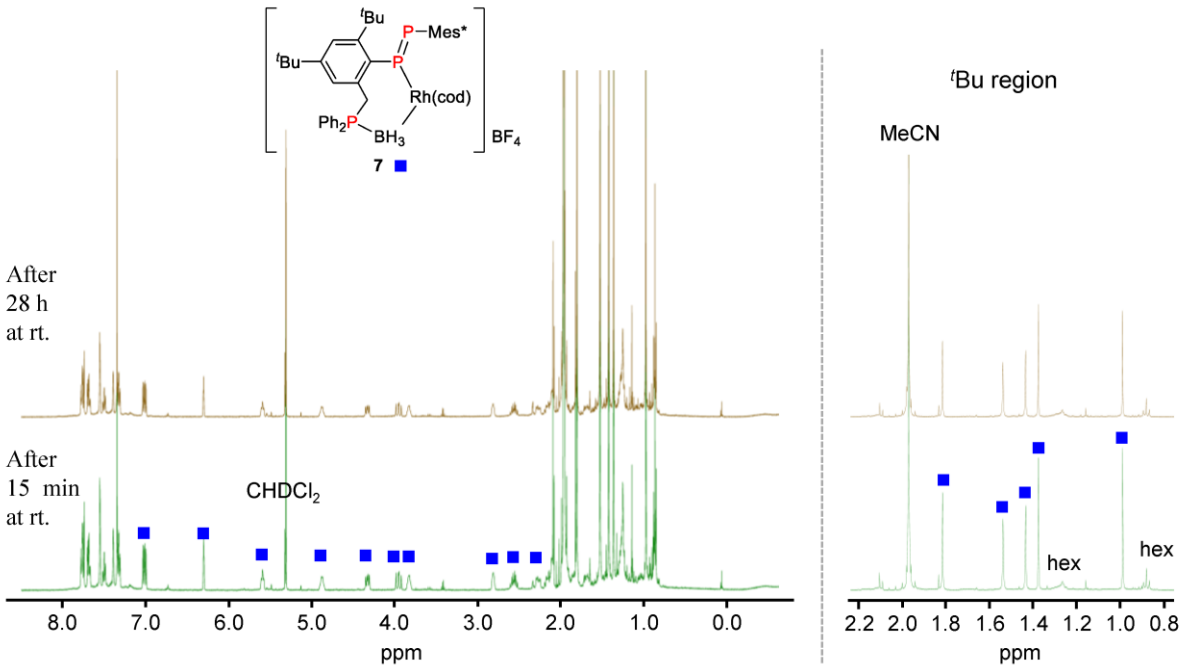


Fig. S41 Reaction of **7** with MeCN (20 eq.) at room temperature monitored by ^{1}H NMR spectra in CD_2Cl_2.

4-3. Titration of pyridine into a solution of diphosphene–rhodium complex 7 in CD_2Cl_2

Diphosphene–rhodium complex **7** (2 mg, 2 μmol), CD_2Cl_2 (0.70 mL), and 1,4-dioxane (0.196 M in CD_2Cl_2; 5.1 μL, 1.0 μmol) were charged into an NMR tube equipped with a J. Young valve under an argon atmosphere. Pyridine (0.996 M in CD_2Cl_2) was added, and ^{1}H NMR (500 MHz) spectra were measured. The integrals of the doublet of doublets signal of **7** at 6.31 ppm (1H), the multiplet signal of pyridine around 8.6 ppm (2H), the doublet signal of **1** at 4.05 ppm (2H), the multiplet signal of **15** around 4.1 ppm (4H), and the singlet signal of 1,4-dioxane at 3.65 ppm (8H; 1.0 μmol) as the internal standard were used.

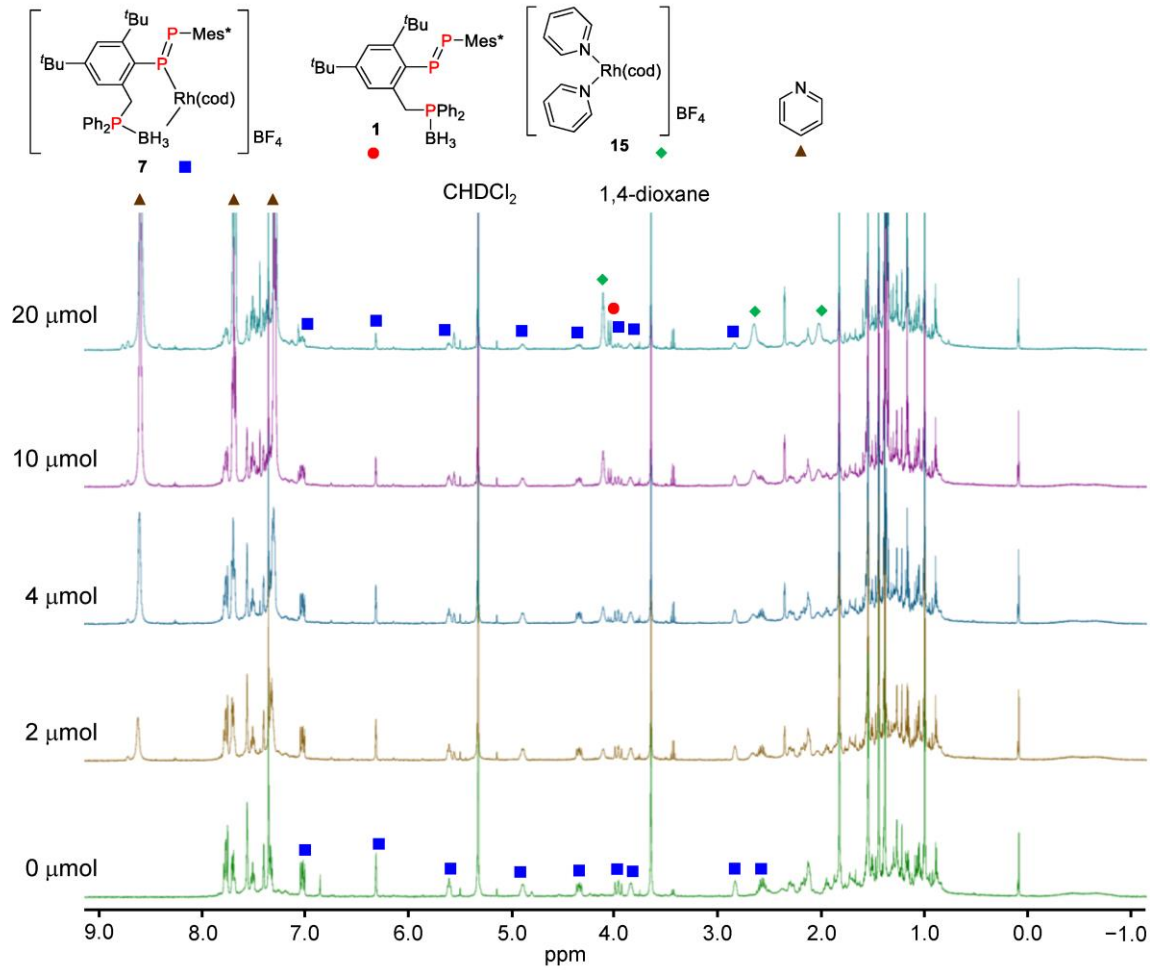
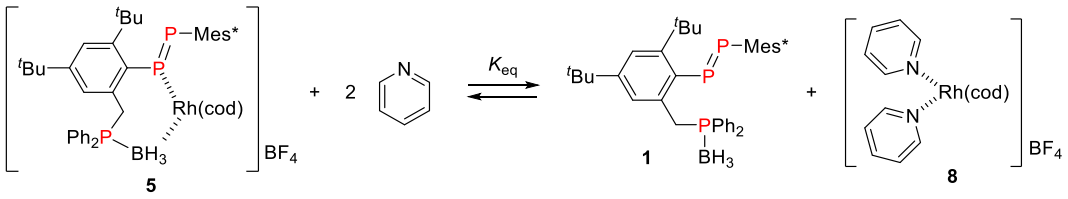


Fig. S42 ^{1}H NMR spectra of the titration of pyridine (0.996 M in CD_2Cl_2) into diphosphene–rhodium complex **7** in CD_2Cl_2.

Table S1 Integral intensities, amounts (μmol), and concentrations (mol L^{-1}) of diphosphene–rhodium complex **7**, pyridine (py), diphosphene–phosphineborane ligand **1**, and $[Rh(py)_2(cod)]BF_4$ (**15**) after titration with pyridine (0.996 M in CD_2Cl_2).



		Compound					
Addition		**7**	py	**1**	**15**	dioxane[a]	K_{eq}[b]
0 μL	Integral	0.954	–	–	–	8.0	
(0 μmol)	Amount (μmol)	0.954	–	–	–	1.0	
	Conc. (mol L^{-1})	1.35×10^{-3}	–	–	–		
1 μL	Integral	1.03	1.09	n.d.[c]	0.632	8.0	
(1 μmol)	Amount (μmol)	1.03	0.547	–	0.158	1.0	
	Conc. (mol L^{-1})	1.45×10^{-3}	7.75×10^{-4}	–	2.24×10^{-4}		–
2 μL	Integral	0.996	3.37	0.034	0.737	8.0	
(2 μmol)	Amount (μmol)	0.996	1.69	0.017	0.184	1.0	
	Conc. (mol L^{-1})	1.41×10^{-3}	2.39×10^{-3}	2.40×10^{-5}	2.61×10^{-4}		0.78
4 μL	Integral	0.910	7.42	0.144	1.19	8.0	
(4 μmol)	Amount (μmol)	0.910	3.71	0.072	0.297	1.0	
	Conc. (mol L^{-1})	1.28×10^{-3}	5.23×10^{-3}	1.02×10^{-4}	4.19×10^{-4}		1.21
7 μL	Integral	0.830	14.3	0.318	1.65	8.0	
(7 μmol)	Amount (μmol)	0.830	7.14	0.159	0.414	1.0	
	Conc. (mol L^{-1})	1.17×10^{-3}	1.00×10^{-2}	2.23×10^{-4}	5.81×10^{-4}		1.11
10 μL	Integral	0.690	21.3	0.531	2.01	8.0	
(10 μmol)	Amount (μmol)	0.690	10.6	0.266	0.503	1.0	
	Conc. (mol L^{-1})	9.65×10^{-4}	1.49×10^{-2}	3.71×10^{-4}	7.04×10^{-4}		1.23
15 μL	Integral	0.536	35.0	0.752	2.77	8.0	
(15 μmol)	Amount (μmol)	0.536	17.5	0.376	0.692	1.0	
	Conc. (mol L^{-1})	7.44×10^{-4}	2.43×10^{-2}	5.22×10^{-4}	9.61×10^{-4}		1.14
20 μL	Integral	0.455	44.8	0.919	3.10	8.0	
(20 μmol)	Amount (μmol)	0.455	22.4	0.460	0.775	1.0	
	Conc. (mol L^{-1})	6.28×10^{-4}	3.09×10^{-2}	6.34×10^{-4}	1.07×10^{-3}		1.13
25 μL	Integral	0.353	57.4	1.05	3.49	8.0	
(25 μmol)	Amount (μmol)	0.353	28.7	0.527	0.874	1.0	
	Conc. (mol L^{-1})	4.83×10^{-4}	3.93×10^{-2}	7.21×10^{-4}	1.20×10^{-3}		1.15

a) Internal standard. b) Equilibrium constant, $K_{eq} = ([\mathbf{1}]\cdot[\mathbf{15}])/([\mathbf{7}]\cdot[py]^2)$. c) Not determined owing to the low intensity.

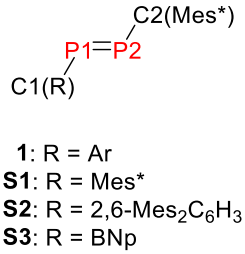
5. X-ray Crystallographic Analysis

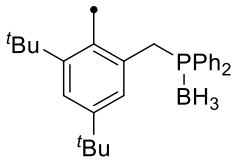
Orange crystals of diphosphene–phosphineborane ligand **1** and red-orange crystals of diphosphene–rhodium complex **7** were grown by slow evaporation of hexane solution (for **1**) and recrystallization from 1,2-dichloroethane/diisopropyl ether at −25 °C in a glovebox under an argon atmosphere. X-ray data of **1** were collected on a Rigaku Saturn diffractometer with VariMax multi-layer mirror monochromated Mo-Kα radiation (λ = 0.71073 Å) at −170 °C. The data were corrected for Lorentz and polarization effects. An empirical absorption correction based on multiple measurements of equivalent reflections was applied using the REQABS program in CrystalClear software. X-ray data of **7** were collected on an XtaLAB Synergy four-circle diffractometer (Rigaku Oxford Diffraction) with a HyPix-6000HE hybrid pixel two-dimensional detector and a PhotonJet monochromated Cu-Kα radiation (λ = 1.5418 Å) at −173 °C. An empirical absorption correction was applied using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm in CrysAlisPro (1.171.42.72a) software. The structures were solved by direct methods (SIR2014[S9] for **1** and SHELXS2013[S10] for **7**) and refined by the full-matrix least squares method against F^2 using all data. Non-hydrogen atoms were refined anisotropically, whereas all hydrogen atoms were generated by AFIX instructions. Hydrogen atoms of BH_3 in diphosphene–rhodium complex **7** were located from difference Fourier maps and refined isotropically. All calculations were performed using the Yadokari-XG 2009[S11] software package except for refinement, which was performed using SHELXL-2013.[S12]

Crystal data for **1** (CCDC-2301466): Crystal Size, 0.17 × 0.15 × 0.10 mm; Molecular formula; $C_{45}H_{64}BP_3$; Molecular weight, M = 708.68; T = −170 °C; triclinic; P-1 (#2); a = 9.875(4) Å, b = 12.159(4) Å, c = 19.275(7) Å, α = 102.317(4)°, β = 101.497(4)°, γ = 100.4456(13)°, V = 2154.2(13) Å^3, Z = 2, D_{calc} = 1.093 g cm^{-3}, μ = 0.167 cm^{-1}, $2\theta_{max}$ = 55.0°, 22513 measured reflections, 9741 independent reflections [R_{int} = 0.0353], 526 refined parameters, Completeness to θ = 99.1%, R_1 = 0.0437 [I>2σ(I)], wR_2 = 0.1197 (all data), GOF = 1.053, largest diff. peak/hole 0.419/−0.229 e.Å^{-3}.

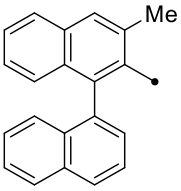
Crystal data for **7** (CCDC-2301467): Crystal Size, 0.18 × 0.15 × 0.05 mm; Molecular formula; $C_{59}H_{88}B_2Cl_6F_4P_3Rh$; Molecular weight, M = 1303.43; T = −173 °C; triclinic; P-1 (#2); a = 10.4512(2) Å, b = 13.8345(3) Å, c = 23.1447(4) Å, α = 97.4885(16)°, β = 96.6648(17)°, γ = 101.8517(17)°, V = 3211.78(11) Å^3, Z = 2, D_{calc} = 1.348 g cm^{-3}, μ = 5.531 cm^{-1}, $2\theta_{max}$ = 156.0°, 45374 measured reflections, 13105 independent reflections [R_{int} = 0.0561], 704 refined parameters, Completeness to θ = 99.9%, R_1 = 0.0527 [I>2σ(I)], wR_2 = 0.1378 (all data), GOF = 1.022, largest diff. peak/hole 1.827/−1.248 e.Å^{-3}.

Table S2 Selected structural parameters of Mes*-substituted diphosphenes and rhodium complex **7**.

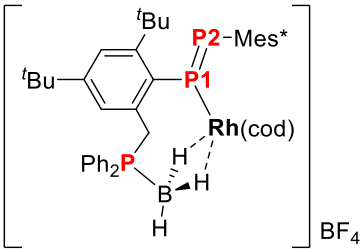




Ar



BNp

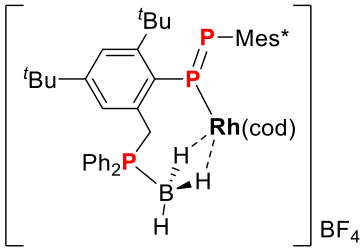


7

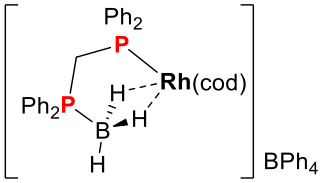
structural parameter					
	1	**7**	**S1**[c]	**S2**[d]	**S3**[e]
d(P1=P2) /Å	2.0406(8)	2.0414(11)	2.034(2)	2.0240(13)	2.0323(6)
d(P1−C1) /Å	1.8598(15)	1.850(3)	1.862(2)	1.846(3)	1.8523(13)
d(P2−C2) /Å	1.8593(15)	1.852(3)	–	1.860(3)	1.8565(13)
d(P−B) /Å	1.924(2)	1.927(4)	–	–	–
deg(C1−P1−P2) /°	100.39(6)	101.80(10)	102.8(1)	101.19(11)	98.59(4)
deg(P1−P2−C2) /°	98.73(5)	106.15(10)		97.99(11)	103.07(4)
(CPP)−(R) /° [a]	65.2	76.5	63.9[f]	82.5[f]	77.0
(CPP)−(Mes*) /° [b]	75.7	82.9	–	84.1[f]	89.1

[a] Dihedral angles between the CPP plane containing the C1 atom and its benzene ring of substituent R. [b] Dihedral angles between the CPP plane containing the C2 atom and the benzene ring of the Mes* groups. [c] Ref S13. [d] Ref S14. [e] Ref S15. [f] Reinvestigated from information in the deposited cif files.

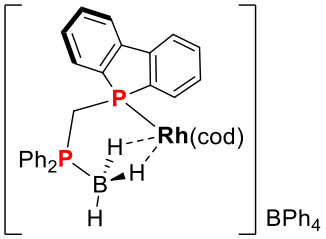
Table S3 Selected structural parameters of rhodium complexes **7**, **8c**, and **9c** with bidentate ligand including a phosphinoborane moiety.



7

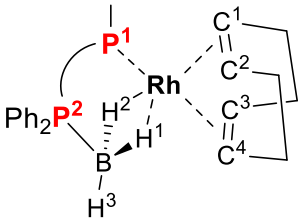


8c



9c

structural parameter			
	7	**8c**[a]	**9c**[b]
d(Rh−P1) /Å	2.2694(8)	2.2743(7)	2.2483(4)
d(Rh···B) /Å	2.348(4)	2.313(3)	2.331(2)
d(Rh−C1) /Å	2.161(3)	2.124(3)	2.120(2)
d(Rh−C2) /Å	2.126(3)	2.126(3)	2.120(2)
d(Rh−C3) /Å	2.234(3)	2.249(3)	2.264(2)
d(Rh−C4) /Å	2.274(3)	2.271(3)	2.271(2)
d(Rh−H1) /Å	1.98(4)	1.82(4)	1.96(3)
d(Rh−H2) /Å	2.04(3)	1.91(3)	1.85(3)
d(P2−B) /Å	1.927(4)	1.923(3)	1.928(3)
d(B−H1) /Å	1.13(4)	1.16(3)	1.13(3)
d(B−H2) /Å	1.19(3)	1.16(3)	1.24(3)
d(B−H3) /Å	1.06(6)	1.09(3)	1.00(3)
deg(P1−Rh−B) /°	92.97(9)	87.26(8)	87.35(4)



[a] Ref S16. [b] Ref S17.

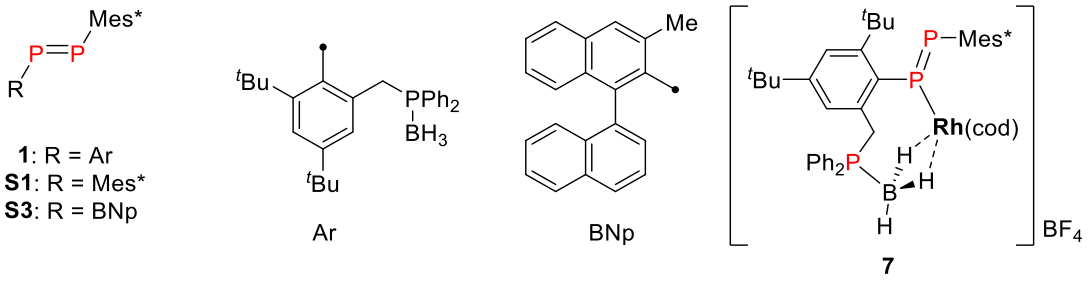
6. UV-vis Spectra

UV-vis spectra of **1** and **7** were measured on a JASCO V-670 spectrophotometer in dichloromethane solution (ca. 2×10^{-4} M) at room temperature with a 1 mm quartz cell equipped with a screw cap filled with argon. Dichloromethane (Nacalai Tesque Inc., spectral grade solvent) was dried over calcium hydride, degassed by freeze-pump-thaw cycles, distilled in a vacuum line, and stored in a glovebox. The results are shown in Fig. 3a and Table S4.

Table S4 UV-vis spectral data of **1**, **7** and related diphosphenes.

Compound	λ / nm (ε / M^{-1} cm^{-1})		
1	464 (400)	338[a] (4190)	276 (10670)
7		398[a] (3840)	300[a] (13900)
S1[b]	460 (1360)	340 (7690)	284 (15660)
S3[c]	455 (500)	334 (7060)	275 (22300)

[a] Observed as a shoulder. [b] Ref S13. [c] Ref S15.



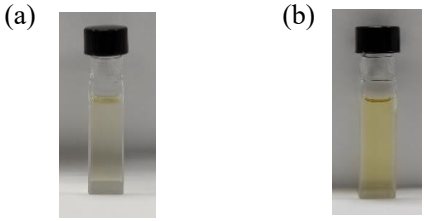


Fig. S43 Photographs of dichloromethane solutions of (*a*) **1** and (*b*) **7**.

7. Theoretical Calculations

All theoretical calculations were performed using the Gaussian 09[S18] program on an NEC LX 110Rh-1 system of the Research Center for Computational Science, Japan. All structures were optimized without any symmetry assumptions. Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated from the gas-phase studies. Harmonic vibration frequency calculations at the same level were performed to verify all stationary points as local minima (with no imaginary frequency). The structures of **1**, the cation moieties of **7**, **7'**, and **8c**, and cations **10** and **11** were optimized using M06[S19] functional with the basis set of SDD[S20] (Rh) and 6-31G(d) (other atoms) level. NBO calculations[S21] were carried out using PBE0 functional[S22] with the basis set of SDD (Rh) and 6-311+G(d) (other atoms) level. TD–DFT calculations of **1** and the cation moiety of **7** were performed at M06/SDD (Rh) and 6-311+G(2d,p) (other atoms) level in conjunction with the PCM model (dichloromethane)[S23] to evaluate solvation effects.

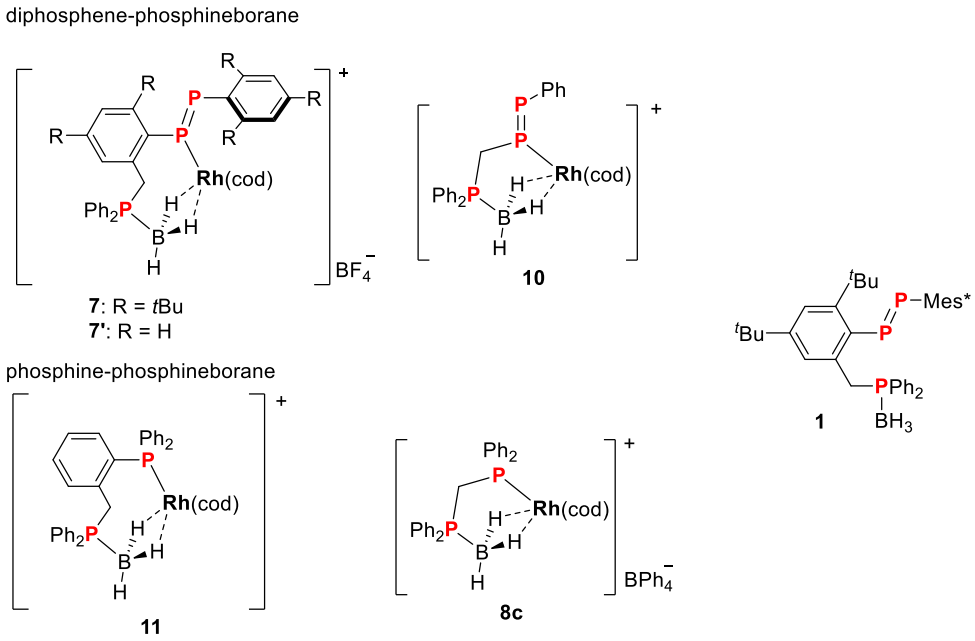
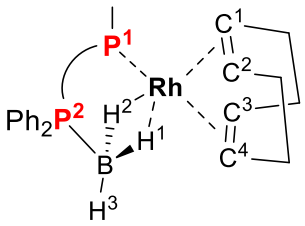


Table S5 Uncorrected and thermal-corrected (298 K) energies of stationary points (Hartree).[a]

	E	*E* + *ZPE*	*H*	G
1	-2800.76167967	-2799.781339	-2799.726872	-2799.865429
7	-3222.96068351	-3221.793828	-3221.730714	-3221.885013
7'	-2437.35583442	-2436.753538	-2436.716494	-2436.823154
8c	-2096.65444604	-2096.042796	-2096.007439	-2096.108610
10	-2206.48069235	-2205.959836	-2205.927365	-2206.024793
11	-2327.51461814	-2326.820790	-2326.780756	-2326.892353

[a] *E*: electronic energy; *ZPE*: zero-point energy; *H* (= $E + ZPE + E_{vib} + E_{rot} + E_{trans} + RT$): sum of electronic and thermal enthalpies; *G* (= $H - TS$): sum of electronic and thermal free energies.

Table S6 Selected structural parameters of rhodium complexes of bidentate ligand with a phosphinoborane moiety.



structural parameter					
	7	**7'**	**10**	**11**	**8c**
d(P1−P2) /Å	2.051	2.043	2.043	–	–
d(Rh−P1) /Å	2.345	2.294	2.310	2.390	2.324
(WBI)[a]	(0.509)[a]	(0.558)[a]	(0.551)[a]	(0.501)[a]	(0.532)[a]
d(Rh···B) /Å	2.394	2.392	2.404	2.375	2.375
d(Rh−C1) /Å	2.139	2.154	2.166	2.142	2.140
d(Rh−C2) /Å	2.172	2.169	2.161	2.156	2.152
d(Rh−C3) /Å	2.286	2.282	2.275	2.285	2.282
d(Rh−C4) /Å	2.238	2.258	2.252	2.263	2.261
d(Rh−H1) /Å	2.021	2.046	2.133	1.955	2.059
d(Rh−H2) /Å	2.036	2.012	1.919	2.093	1.941
d(P2−B) /Å	1.929	1.932	1.939	1.919	1.939
d(B−H1) /Å	1.246	1.242	1.236	1.256	1.244
d(B−H2) /Å	1.240	1.249	1.261	1.237	1.254
d(B−H3) /Å	1.208	1.208	1.203	1.208	1.203
deg(P1−Rh−B) /º	93.9	92.3	84.6	96.1	86.9

[a] Wiberg bond index.

Table S7 Natural bond orbital analysis selected for the Rh−P moiety.

(Occupancy) Bond orbital / Coefficients / Hybrids

7

78. (1.59910) LP (1) P2 s(74.82%)p 0.34(25.16%)d 0.00(0.03%)

0.0000	0.0000	0.8648	-0.0141	0.0000
0.0000	0.0000	-0.2092	-0.0018	-0.0005
-0.0018	0.0000	0.0000	0.2554	0.0185
0.0000	0.0005	-0.0002	0.0000	0.3758
0.0314	-0.0002	0.0007	0.0000	0.0024
0.0012	0.0122	-0.0074	0.0071	

7'

59. (1.95121) BD (1) Rh 1 - P2

(33.82%) 0.5816*Rh 1 s(14.60%)p 0.02(0.23%)d 5.83(85.17%)

0.0000	0.3820	-0.0055	0.0058	-0.0003
-0.0002	0.0000	0.0031	0.0082	0.0002
0.0010	0.0000	-0.0003	-0.0040	0.0011
0.0002	0.0000	-0.0467	-0.0051	0.0034
0.0001	0.2144	0.0098	0.0057	-0.2229
-0.0147	-0.0138	0.1598	0.0026	0.0085
-0.2858	-0.0072	-0.0119	0.8029	0.0249
0.0523				

(66.18%) 0.8135* P 2 s(42.99%)p 1.32(56.93%)d 0.00(0.08%)

0.0000	0.0000	0.6546	0.0372	-0.0052
0.0007	0.0000	0.0000	0.1688	0.0083
0.0066	-0.0031	0.0000	0.0000	0.0122
-0.0027	0.0018	0.0000	-0.0003	0.0000
-0.7349	-0.0198	-0.0032	-0.0039	-0.0005
-0.0153	-0.0041	-0.0026	-0.0068	0.0213

10

52. (1.60305) LP (1) P2 s(77.58%)p 0.29(22.37%)d 0.00(0.05%)

0.0000	0.0000	0.8806	0.0184	0.0002
0.0006	0.0000	0.0000	-0.3253	-0.0130
-0.0002	-0.0036	-0.0001	0.0000	-0.3159
-0.0275	-0.0010	-0.0026	-0.0001	0.0000
0.1296	0.0175	0.0068	-0.0024	-0.0004
0.0005	-0.0021	-0.0173	-0.0123	0.0046

11

59. (1.93925) BD (1)Rh1- P2

(33.82%) 0.5816*Rh 1 s(13.78%)p 0.01(0.16%)d 6.25(86.06%)

0.0000	0.3711	-0.0068	-0.0055	-0.0021
0.0005	0.0000	-0.0003	0.0044	0.0000
0.0006	0.0000	-0.0345	-0.0063	-0.0024
-0.0005	0.0000	-0.0144	-0.0097	0.0019
0.0000	0.1802	0.0036	0.0090	0.0493
-0.0001	0.0043	0.4747	0.0132	0.0299
-0.7612	-0.0196	-0.0415	0.1315	0.0160
0.0079				

(66.18%) 0.8135* P 2 s(32.23%)p 2.10(67.70%)d 0.00(0.07%)

0.0000	0.0000	0.5671	-0.0271	0.0003
0.0000	0.0000	-0.0962	0.0080	0.0000
-0.0004	-0.0002	0.0000	-0.6412	0.0482
0.0022	-0.0010	0.0004	0.0000	-0.5036
0.0240	0.0018	0.0013	0.0003	0.0050
0.0015	0.0198	-0.0158	0.0016	

8c

53. (1.94500) BD (1)Rh 1 - P2
(36.82%) 0.6068*Rh 1 s(11.99%)p 0.01(0.15%)d 7.33(87.87%)
0.0000 0.3461 -0.0046 0.0051 -0.0020
-0.0009 0.0000 0.0144 0.0075 0.0001
0.0007 0.0000 -0.0155 -0.0031 0.0012
0.0004 0.0000 -0.0309 0.0008 -0.0010
-0.0002 -0.4279 -0.0164 -0.0250 -0.4935
-0.0160 -0.0273 0.3948 0.0101 0.0263
-0.3521 -0.0165 -0.0180 0.4104 0.0103
0.0196
(63.18%) 0.7948* P 2 s(32.83%)p 2.04(67.08%)d 0.00(0.09%)
0.0000 0.0000 0.5722 0.0289 0.0001
0.0000 0.0000 0.3574 -0.0144 -0.0001
0.0022 -0.0001 0.0000 -0.4207 0.0271
0.0009 0.0008 0.0005 0.0000 -0.6029
0.0403 0.0023 -0.0012 0.0004 -0.0110
-0.0162 0.0204 -0.0054 0.0110

Table S8. Transition energies, wavelengths, and oscillator strengths (*f*) of the transitions of **1** and **7** longer than 290 nm (8 states for **1** and 19 states for **7**).

1: The 192nd orbital is the HOMO, and the 193rd orbital is the LUMO.

Excited State 1: Singlet-A
2.4665 eV 502.67 nm f=0.0281
191 -> 193 0.17702
192 -> 193 0.67351
Excited State 2: Singlet-A
3.2650 eV 379.74 nm f=0.0630
188 -> 193 -0.10286
189 -> 193 -0.12482
190 -> 193 -0.36717
191 -> 193 0.56411
192 -> 193 -0.10478
Excited State 3: Singlet-A
3.4416 eV 360.26 nm f=0.0974
186 -> 193 0.10596
187 -> 193 0.10243
188 -> 193 0.21483
190 -> 193 0.52311
191 -> 193 0.34458
192 -> 193 -0.15739
Excited State 4: Singlet-A
3.5457 eV 349.67 nm f=0.0237
187 -> 193 0.10584
188 -> 193 0.14442
189 -> 193 0.64994
190 -> 193 -0.17635
Excited State 5: Singlet-A
3.5844 eV 345.90 nm f=0.0152
188 -> 193 0.64305
189 -> 193 -0.18694
190 -> 193 -0.20033
Excited State 6: Singlet-A
3.9105 eV 317.05 nm f=0.0190
183 -> 193 -0.10257
185 -> 193 0.13539
186 -> 193 0.44066
187 -> 193 0.45565
189 -> 193 -0.13173
191 -> 193 -0.12547
Excited State 7: Singlet-A
4.2002 eV 295.19 nm f=0.3242
192 -> 194 0.22704
192 -> 195 0.49943
192 -> 197 -0.39972
Excited State 8: Singlet-A
4.2525 eV 291.56 nm f=0.0031
183 -> 193 0.13586
186 -> 193 -0.45398
187 -> 193 0.50501

7: The 230th orbital is the HOMO, and the 231st orbital is the LUMO.

Excited State 1: Singlet-A
2.4924 eV 497.45 nm f=0.0084
228 -> 231 -0.13286
228 -> 232 -0.15575
229 -> 231 0.11818
230 -> 231 0.57648
230 -> 232 0.30891
Excited State 2: Singlet-A
2.6425 eV 469.19 nm f=0.0033
228 -> 231 -0.16697
228 -> 232 -0.15791
229 -> 231 -0.37717
230 -> 231 -0.26908
230 -> 232 0.45301
Excited State 3: Singlet-A
2.8159 eV 440.31 nm f=0.0113

228 -> 231 0.29679
228 -> 232 -0.18241
229 -> 231 0.43986
229 -> 232 0.11651
230 -> 231 -0.23136
230 -> 232 0.29172
Excited State 4: Singlet-A
2.9060 eV 426.65 nm f=0.0326
219 -> 232 -0.10328
223 -> 232 0.14406
227 -> 231 -0.14761
227 -> 232 -0.12050
228 -> 231 0.44636
228 -> 232 0.20619
229 -> 231 -0.12008
229 -> 232 -0.32102
230 -> 232 0.12243
Excited State 5: Singlet-A
3.0682 eV 404.10 nm f=0.0085
219 -> 232 -0.12988
223 -> 232 0.18079
226 -> 231 0.21609
226 -> 232 0.16882
227 -> 231 0.41091
227 -> 232 0.21947
228 -> 231 -0.12687
228 -> 232 0.27965
Excited State 6: Singlet-A
3.1452 eV 394.21 nm f=0.0487
223 -> 231 -0.14469
223 -> 232 -0.27097
226 -> 231 0.13175
227 -> 231 0.26854
227 -> 232 0.17617
228 -> 231 0.32784
228 -> 232 -0.23158
229 -> 231 -0.23555
230 -> 231 0.10155
230 -> 232 -0.11009
Excited State 7: Singlet-A
3.2298 eV 383.87 nm f=0.0488
218 -> 232 -0.11817
223 -> 231 0.14482
223 -> 232 0.22555
224 -> 231 -0.10594
224 -> 232 -0.11727
225 -> 231 -0.20538
225 -> 232 -0.12334
227 -> 231 -0.11879
227 -> 232 0.23784
228 -> 231 0.11963
229 -> 231 -0.22220
229 -> 232 0.36637
Excited State 8: Singlet-A
3.3527 eV 369.80 nm f=0.0023
223 -> 231 -0.16066
224 -> 231 0.16169
225 -> 231 0.23240
226 -> 232 0.24238
227 -> 231 -0.33986
227 -> 232 0.39020
228 -> 232 0.10521
Excited State 9: Singlet-A
3.4227 eV 362.24 nm f=0.0022
224 -> 231 -0.14846
225 -> 231 -0.11846
226 -> 231 0.60085
227 -> 231 -0.30300
Excited State 10: Singlet-A
3.4970 eV 354.54 nm f=0.0649
218 -> 232 -0.10664
223 -> 231 -0.10212
223 -> 232 0.23199
224 -> 231 0.27023
225 -> 231 0.42808
225 -> 232 -0.15987
226 -> 231 0.20265
226 -> 232 -0.10288
227 -> 232 -0.13832
229 -> 232 0.16637
Excited State 11: Singlet-A
3.5587 eV 348.39 nm f=0.0019
223 -> 231 0.59368
223 -> 232 -0.12925
224 -> 231 0.26100
228 -> 232 -0.11028
Excited State 12: Singlet-A
3.5887 eV 345.49 nm f=0.0022
223 -> 231 -0.15091
224 -> 231 0.52665
225 -> 231 -0.42433
Excited State 13: Singlet-A
3.8110 eV 325.33 nm f=0.0333
228 -> 233 -0.13770
230 -> 233 0.56723
230 -> 237 0.23566
Excited State 14: Singlet-A
3.9643 eV 312.75 nm f=0.1898
223 -> 232 -0.18237
224 -> 232 0.14146
225 -> 232 0.19572
228 -> 232 0.37062
229 -> 232 0.30624
230 -> 232 0.23447
Excited State 15: Singlet-A
3.9962 eV 310.26 nm f=0.0053
217 -> 231 0.18366
218 -> 231 0.26447
219 -> 231 0.32764
220 -> 231 0.27944
221 -> 231 0.29522
222 -> 231 0.22369
223 -> 232 0.10055
Excited State 16: Singlet-A
4.0729 eV 304.41 nm f=0.0327
217 -> 231 0.15459
218 -> 231 0.35260
222 -> 231 -0.11726
223 -> 232 -0.10612
228 -> 232 0.10196
228 -> 233 -0.15154
229 -> 233 0.44030
Excited State 17: Singlet-A
4.1457 eV 299.06 nm f=0.0258
217 -> 231 0.11617
218 -> 231 0.33588

219 -> 231 -0.13835
221 -> 231 -0.12919
222 -> 231 -0.19220
228 -> 233 0.26837
229 -> 232 0.16068
229 -> 233 -0.32153

Excited State 18: Singlet-A
4.2067 eV 294.73 nm f=0.0032
216 -> 231 -0.21211
218 -> 231 0.18585
219 -> 231 -0.17663
220 -> 231 -0.20705
222 -> 231 0.51703
228 -> 233 -0.10675

Excited State 19: Singlet-A
4.2609 eV 290.98 nm f=0.1067
222 -> 231 0.18687
226 -> 232 -0.18777
227 -> 232 0.14672
228 -> 233 0.36091
229 -> 233 0.18093
230 -> 233 0.25823
230 -> 235 -0.20875
230 -> 237 -0.17122

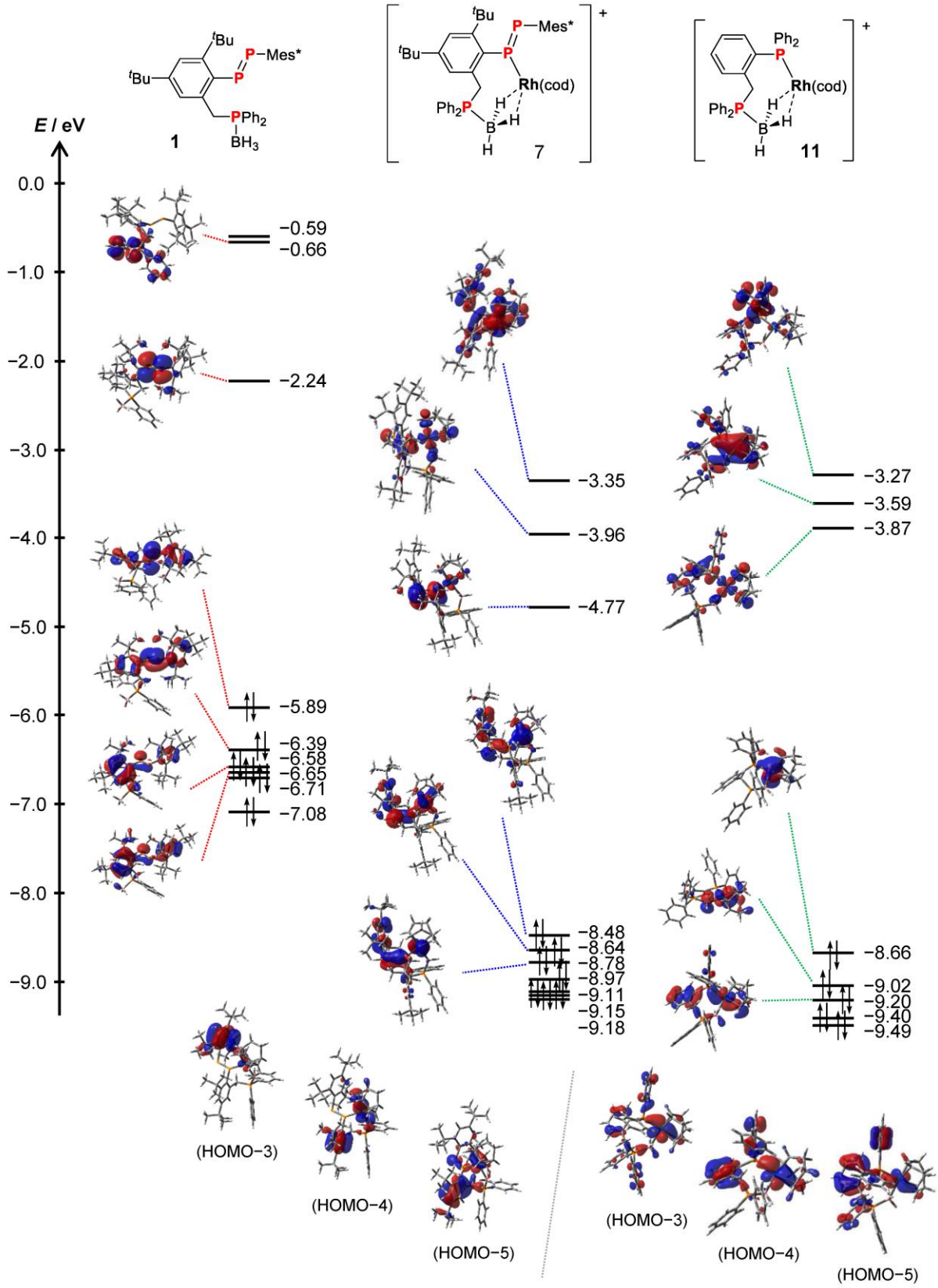
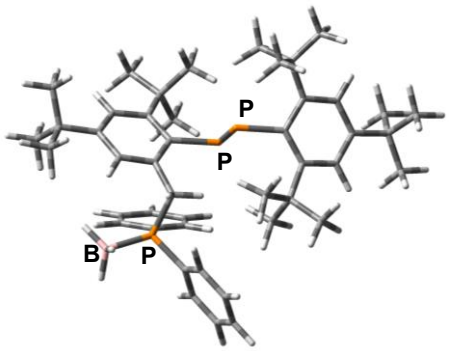


Fig. S44 Energy diagram of **1**, $\mathbf{7}^{+}$ and $\mathbf{11}^{+}$ (Isovalue = 0.03).

Table S9 Atomic coordinates of the optimized structures.

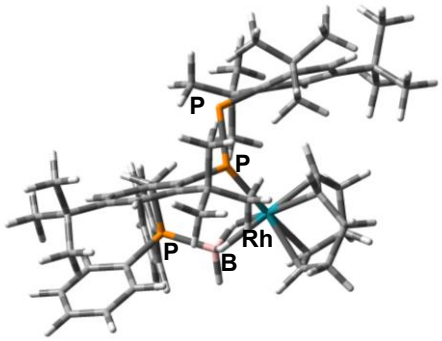
1



P	1.10794900	-0.95508300	-1.36284600
P	0.27268600	-0.79989000	0.51064500
P	-2.85940600	2.26910100	-0.31968300
C	2.87558500	-0.53563400	-0.93038700
C	-1.49373600	-1.21021000	0.06706200
C	-2.19764700	-0.37342200	-0.82541600
C	4.47892500	0.94570600	0.10781300
H	4.75677600	1.94733700	0.42056100
C	4.98937800	-1.35625800	-0.09889500
H	5.69109800	-2.17093300	0.05109700
C	-1.77038600	1.02659300	-1.17199000
H	-1.86815400	1.21517000	-2.25173200
H	-0.73774900	1.25042000	-0.89033300
C	-3.41566200	-2.67449400	0.05640700
H	-3.92715600	-3.55807200	0.42638900
C	3.81356000	-1.60534400	-0.79964700
C	-4.06587100	-1.92064800	-0.92460600
C	-3.44014800	-0.75696400	-1.33475300
H	-3.92394000	-0.08945700	-2.04536200
C	3.28136300	0.78207300	-0.60119800
C	-1.88954700	3.80782600	-0.42461200
C	5.31963800	-0.10741300	0.42697100
C	-5.43730700	-2.34439400	-1.43881000
C	-2.15957000	-2.36398700	0.57565700
C	-1.25383500	4.13494300	-1.62606400
H	-1.31136000	3.45917500	-2.47983800
C	2.55166600	2.08273200	-1.01474900
C	1.73909700	1.92406600	-2.30464400
H	0.87824900	1.24994300	-2.21973500
H	2.37108200	1.54433900	-3.11979200
H	1.34057500	2.90238800	-2.60906900
C	-5.91318900	-1.46832300	-2.59637900
H	-6.04038700	-0.41916900	-2.29555700
H	-6.88671500	-1.82964200	-2.95488100
H	-5.21368800	-1.50125300	-3.44352800
C	-6.45118500	-2.21910500	-0.29552000
H	-6.17998500	-2.84856000	0.56275000
H	-7.45124000	-2.52455900	-0.63575700
H	-6.51307400	-1.17833800	0.05279900
C	-5.38949800	-3.79571700	-1.92787300
H	-4.65834200	-3.91251000	-2.73951000
H	-6.37433300	-4.09740700	-2.31180600
H	-5.11877600	-4.49813000	-1.12893700
C	-1.83248600	4.70878400	0.64097600
H	-2.33923900	4.47494600	1.57686900
C	-0.54667100	5.32570500	-1.74822100
H	-0.05091900	5.56524000	-2.68800100
C	1.67092000	2.61292000	0.12250900
H	1.18828800	3.55858500	-0.16833700
H	2.27289900	2.79621100	1.02345300
H	0.88699800	1.89610900	0.39570200
C	3.64010700	-2.99320600	-1.45995900
C	-0.47676900	6.20801000	-0.67418700
H	0.07720500	7.14028000	-0.76859200
C	6.59590400	0.05962200	1.24705700
C	-1.59509200	-3.24706200	1.70581700
C	3.57310600	3.18829900	-1.34525300
H	3.03949200	4.05202000	-1.76647300
H	4.31095400	2.84810200	-2.08438400
H	4.11396200	3.55795700	-0.46614300
C	-0.30249200	-3.95500900	1.28592600
H	-0.44248100	-4.50653500	0.34502100
H	0.00240700	-4.67317600	2.06079000
H	0.53177100	-3.25771800	1.14677700
C	-1.12667900	5.90060100	0.51678400
H	-1.08539000	6.59232200	1.35619300
C	-2.83310300	1.75652400	1.42458000
C	-4.00864100	1.23958400	1.97269300
H	-4.91316300	1.21250800	1.36606100
C	-2.57171600	-4.35070100	2.12822600
H	-2.76636700	-5.06948000	1.32047400
H	-3.53199100	-3.94793800	2.47763700
H	-2.12957400	-4.91127700	2.96226500
C	-1.34979900	-2.38813000	2.95374300
H	-1.02749200	-3.02395600	3.79110100
H	-2.27046200	-1.86470400	3.24947800
H	-0.57085000	-1.63045300	2.80137700
C	2.56978800	-3.85273100	-0.77730300
H	2.74491500	-3.90729400	0.30688200
H	2.60155200	-4.87607700	-1.17871500
H	1.55363300	-3.47443300	-0.93664300
C	3.30925400	-2.82145300	-2.94953900
H	3.23758800	-3.80677600	-3.43181300
H	4.09814400	-2.25013500	-3.45780300
H	2.35494600	-2.30852300	-3.12108200
C	-1.66965200	1.79138300	2.20062800
H	-0.74426900	2.19705600	1.78864100
C	4.93680000	-3.81255600	-1.41066500
H	5.20893600	-4.10746400	-0.38828800
H	5.78502000	-3.27698300	-1.85806200
H	4.79069900	-4.73817900	-1.98252300
C	6.77077000	1.48548400	1.76514600
H	5.92247000	1.79825200	2.38964200
H	6.88144400	2.20985800	0.94645900
H	7.67798300	1.54557700	2.38139600

B	-4.61963700	2.53212800	-1.08059300
H	-5.27330700	1.52080800	-0.92543400
H	-4.36438100	2.77922400	-2.24536500
H	-5.04333000	3.48906700	-0.46366600
C	7.81253400	-0.28447100	0.37964600
H	7.86361500	0.37279700	-0.49933300
H	7.78466700	-1.32175000	0.02074300
H	8.74083600	-0.15691400	0.95517800
C	6.54854800	-0.87929800	2.45808600
H	7.46071800	-0.76724700	3.06154700
H	6.47397600	-1.93368300	2.16294300
H	5.68556900	-0.64855200	3.09745200
C	-4.02154400	0.76799500	3.28216900
H	-4.94319300	0.37047200	3.70343700
C	-1.68525500	1.32050400	3.50713600
H	-0.77429700	1.34695000	4.10257200
C	-2.86274300	0.81046600	4.04903200
H	-2.87342900	0.44187000	5.07365800

7



Rh	-0.59672700	0.48341700	1.82828200
P	-0.16747900	-0.85112800	-0.05186100
P	2.58226800	1.92273400	0.06680100
P	-1.04785500	-1.40025900	-1.82112600
C	-1.09991500	1.08331600	-3.57397800
H	-0.30488400	0.49943100	-3.09336900
H	-0.59607800	1.89373700	-4.12005600
H	-1.58385400	0.43611000	-4.31895100
C	-1.18825300	1.95198500	3.47686600
H	-0.58634700	2.82808200	3.22940500
C	2.48008700	3.61637900	-0.56964400
C	-1.41111200	2.51980900	-1.53502700
H	-2.13285900	3.05663900	-0.90207700
H	-0.75278300	3.27205900	-1.99701800
H	-0.80820700	1.89131800	-0.86453500
C	-2.12419900	1.68662100	-2.60627200
C	1.25037700	-3.84192900	0.86038000
C	-5.28788600	0.33660700	-0.97040200
C	-2.77647800	-0.73026300	-1.71857100
C	2.43358400	-0.61854900	-0.99974000
C	4.21216900	-2.27123700	-0.98664800
C	1.56240300	-1.48232300	-0.29557100
C	-3.84190600	-1.61317700	-1.34716700
C	2.04842400	-2.75657700	0.11194200
C	-4.29077600	1.14015900	-1.50256900
H	-4.48173900	2.20452000	-1.59496500
C	3.35314500	-3.09337300	-0.25924900
H	3.72869300	-4.07160900	0.02675400
C	1.94948700	5.22873800	-2.28893100
H	1.60033300	5.44926200	-3.29575400
C	4.32835400	1.59454000	0.40665300
C	-5.05242900	-1.03746900	-0.96930600
H	-5.86372100	-1.68686500	-0.65660600
C	2.10401400	0.81180600	-1.32825000
H	1.03971600	0.99216200	-1.52786600
H	2.66689700	1.13524200	-2.21533000
C	3.72216600	-1.02470300	-1.34456100
H	4.35023800	-0.32111600	-1.88915000
C	4.66382200	0.68568500	1.41381400
H	3.87923200	0.22166000	2.01275500
C	2.77285600	5.97791400	-0.14903400
H	3.06616200	6.78609700	0.51772300
C	-3.05142800	0.64847700	-1.93054400
C	5.33332700	2.18232400	-0.36871800
H	5.07443500	2.89807900	-1.14994300
C	-3.04605900	-3.70373400	-2.58332700
H	-3.12769800	-4.79861600	-2.60807500
H	-1.97404800	-3.47553700	-2.61173600
H	-3.49727100	-3.31047000	-3.50455000
C	-3.10480100	-3.66993300	-0.06032600
H	-3.67654500	-3.34653400	0.82251200
H	-2.07536600	-3.31118300	0.04886400
H	-3.07254700	-4.76941100	-0.05804100
C	0.50944600	-4.69574000	-0.17812700
H	1.22318400	-5.19666700	-0.84593200
H	-0.15963500	-4.09283500	-0.80622700
H	-0.09292500	-5.46960500	0.32011800
C	-6.63205900	0.88798000	-0.50716600
C	-3.76930000	-3.15986000	-1.34393400
C	2.02913100	3.90700100	-1.85963900
H	1.73214700	3.10901800	-2.53994200
C	-2.27698400	-0.73748700	2.46500700
H	-2.23730400	-1.69138900	1.93626500
C	2.85060200	4.66141100	0.28586400
H	3.20838200	4.44144200	1.29240100
C	-2.37909800	-0.86943800	3.97372100
H	-3.29953000	-0.38473600	4.32742100
H	-2.49138400	-1.93135000	4.22771200
C	-2.72789900	0.35546900	1.69724500
H	-2.97785200	0.14524600	0.65331300
C	2.32115500	6.26199800	-1.43587400
H	2.26148700	7.29430100	-1.77467900
C	-5.16948100	-3.79298100	-1.38925100
H	-5.76180500	-3.42397100	-2.23722700
H	-5.74248400	-3.63524000	-0.46691600
H	-5.06192700	-4.87890300	-1.50551400
C	6.66538100	1.86176000	-0.13459700
H	7.44797700	2.32343200	-0.73322400
C	5.61825300	-2.74699300	-1.33456300
C	-7.04852000	0.23814900	0.81702700

H	-6.29122700	0.40237100	1.59789200
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H	-7.99462500	0.67251300	1.16743700
C	-2.68207900	2.15283900	3.49207800
H	-3.11809600	1.66448300	4.37257000
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C	-0.52263100	0.87225100	4.03142200
H	0.54752300	0.99674900	4.21518300
C	-1.14822700	-0.32056700	4.70132600
H	-1.38761100	-0.07585100	5.75002700
H	-0.38298100	-1.10766200	4.74454300
C	6.99641600	0.95749000	0.87262300
H	8.04055200	0.71299700	1.05961400
C	0.26159300	-3.27066300	1.87500700
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H	-6.41908700	2.94869200	-1.23284000
C	6.37338400	-3.08831100	-0.04396300
H	7.39442800	-3.41747500	-0.28173800
H	5.89060100	-3.89499500	0.52270400
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H	-7.78687900	-0.50792000	-1.74256500
H	-7.41952900	1.03614200	-2.53829500
C	5.99803200	0.37077100	1.64616000
H	6.26017000	-0.32842100	2.43819400
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H	-3.58432200	2.09368500	-4.19290100
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H	-3.60389600	3.31410100	-2.90242200
C	-3.32949100	1.63750900	2.20570500
H	-3.20476200	2.39370000	1.41409900
H	-4.41978000	1.51961500	2.33826900
C	6.41702900	-1.68113000	-2.08179000
H	5.94801400	-1.41147700	-3.03846600
H	7.42027800	-2.06583700	-2.30719800
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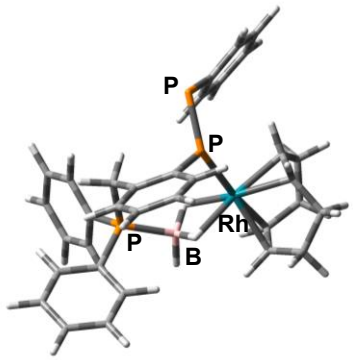

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C	-4.95741100	3.02689600	-0.86764800
C	-3.02968500	1.43263900	-2.11075700
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C	2.57625700	-3.09117600	-2.82549200
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C	-4.35390400	1.42987900	-2.56974700
C	0.22286400	-2.87718500	-2.39042500
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H	-3.35108600	3.72032200	0.39280200
C	1.30246600	-3.64836100	-2.80385900
H	1.14747500	-4.68094200	-3.10917200
C	2.67721300	4.68056700	-0.18756500
H	2.54792500	5.43844300	-0.95750500
C	3.83768700	-0.27266400	0.43507400
C	-5.31518000	2.21060100	-1.93860800
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C	1.94276600	0.45070900	-1.61902300
H	1.08936000	1.10069200	-1.85866900
H	2.82217600	0.85648600	-2.14009900
C	2.76478400	-1.76733100	-2.44435700
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C	3.25462700	4.07244300	2.07426700
H	3.57633100	4.35691900	3.07392500
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C	3.01260900	2.73714500	1.78134500
H	3.14944200	1.97739600	2.55195700
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H	-5.70881700	3.64821800	-0.38433500
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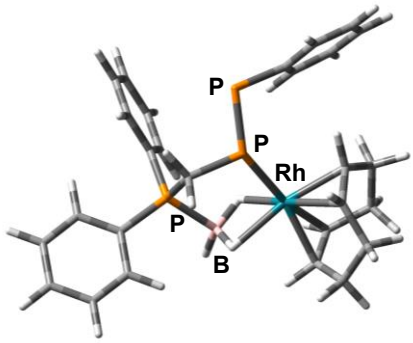

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C	1.52627900	0.13700500	-1.62019500
H	1.68721100	-0.79153700	-2.18649300
H	1.94751800	0.97483500	-2.19001400
C	-2.02892600	-2.36302200	1.90587500
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C	-3.51870900	-2.11948500	1.92315300
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H	-3.80632500	-0.02642800	1.48689600
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C	-3.05522900	-3.48024800	-0.78576300
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H	-1.66233300	2.21688000	0.99099000
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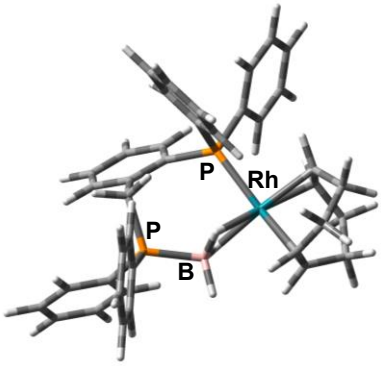

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H	-0.12953400	-3.56824900	-1.01650500
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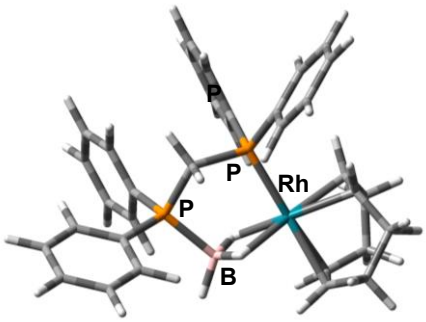

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H	-0.83251400	-1.20903000	1.89890300
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C	2.37365600	-1.33095600	-2.93174700
H	1.51101700	-1.22141900	-3.59355800
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H	3.49974600	-0.11990300	-4.27962900
H	4.48455100	-1.06377900	-3.18561900
C	3.66453200	0.75762700	-2.31682500
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C	3.23215600	0.48168100	-0.89919700
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C	3.49986200	-0.68389000	-0.14745300
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H	5.15198400	-1.46742600	-1.28509500
H	4.88480600	-2.26956100	0.24278200
C	3.54932800	-2.94845800	-1.30090600
H	3.13937000	-3.61389500	-0.52813800
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H	-4.89665800	-0.58925700	0.58027600
C	-2.87652600	0.64159100	-0.77985700
C	-3.01580700	0.73229400	-2.16881400
H	-2.59758000	-0.04355000	-2.81027400
C	-3.68882000	1.81103700	-2.73131300
H	-3.79904400	1.87717100	-3.81159700
C	-4.21574600	2.80449500	-1.91172100
H	-4.73790600	3.65110500	-2.35327500
C	-4.08189400	2.71781200	-0.52793800
H	-4.49279000	3.49599300	0.11214800
C	-3.41652200	1.63836800	0.03998000
H	-3.32090700	1.57850200	1.12468500
C	0.08528400	2.18851900	0.42496400
C	-0.39458400	3.05834200	1.41259800
C	0.10907400	2.60659200	-0.90849000
C	-0.82960200	4.33142100	1.06812700
H	-0.41480800	2.74606700	2.45796200
C	-0.34150000	3.87773000	-1.25195100
H	0.47277800	1.92189600	-1.67758000
C	-0.80295600	4.74100600	-0.26422000
H	-1.18976500	5.00870600	1.84021800
H	-0.32313300	4.19617400	-2.29234600
H	-1.14390600	5.73952100	-0.53109300
C	1.53827800	0.56428500	2.37149300
C	1.64420700	-0.57850300	3.17419700
C	2.31253300	1.68836100	2.67666100
C	2.48533100	-0.58430500	4.27939900
H	1.08290300	-1.48169600	2.92959800
C	3.15916500	1.67550600	3.78117700
H	2.25398300	2.58222600	2.05605600
C	3.24299100	0.54391100	4.58489600
H	2.55246300	-1.47395200	4.90230600
H	3.75368700	2.55648000	4.01443300
H	3.90269800	0.53763800	5.45008300

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