Experimental Section

General
All manipulations were carried out in the argon-filled glove box (Miwa MFG) unless otherwise noted. The $^1$H, $^{11}$B ($^1$H), $^{13}$C ($^1$H), and $^{31}$P ($^1$H) NMR spectra were recorded on 500 MHz spectrometers with residual protiated solvent for $^1$H, deuterated solvent for $^{13}$C ($^1$H), an external BF$_3$·OEt$_2$ for $^{11}$B ($^1$H), and an external 85% H$_2$PO$_4$ for $^{31}$P ($^1$H) used as reference. Elemental analyses were performed by A Rabbit Science Co., Ltd. using yanaco CHN corder MT-5. X-ray crystallographic analyses were recorded on a Rigaku Mercury CCD or VariMax Saturn CCD diffractometer. Melting points were measured on a MPA100 Optimelt Automated Melting Point System and are uncorrected. CH$_2$Cl$_2$ and $n$-hexane were purified by passing through a solvent purification system (Grass Contour). Anhydrous $n$-pentane and benzene (Kanto Chemical Co., Inc.), PtCl$_2$ (Tanaka Kikinzoku Kogyo), AgOTf (Aldrich), AgNTf$_2$ (Aldrich), and Karstedt's cat (Aldrich) were purchased and used without purification. 1-decene (Tokyo Chemical Industry Co., Ltd.: TCI), $n$-dodecane (TCI), and HSiEt$_3$ were degassed by three-cycles of freeze-pump-thaw before the use. Argon were purchased from Suzuki Shokan Co., Ltd. Hydroborane precursor 1, Pt(cod)Cl$_2$, and AgBAR$_4$ were synthesized according to literature procedures.

Preparation of [PBP]PtCl (2). A solution of 1 (0.750 g, 1.73 mmol) in CH$_2$Cl$_2$ (15 mL) was added Pt(cod)Cl$_2$ (0.508 g, 1.36 mmol) and the resulting solution was stirred at room temperature for 24 h to give a yellow solution. Volatiles were removed from the solution and reprecipitation from CH$_2$Cl$_2$ & $n$-hexane twice. Volatiles was removed from the filtrate gave white powder of 2 (0.493 g, 0.743 mmol, 55%). Single crystals suitable for X-ray analysis were obtained from CH$_2$Cl$_2$ solution diffused by $n$-pentane vapor at −35 °C. $^1$H NMR (C$_6$D$_6$, 500 MHz) δ 1.31 (vt, $^3$J$_{PH}$ = 7 Hz, 36H), 3.65 (vt, $^3$J$_{PH}$ = 2 Hz, $^3$J$_{PP}$ = 10 Hz, 4H), 6.95 (dd, $J_6$ = 6, 2 Hz, 2H), 7.13 (dd, $J_6$ = 6, 2 Hz, 2H); $^{31}$P NMR (C$_6$D$_6$, 202 MHz) δ 90.2 (s, $^3$J$_{PP}$ = 3140 Hz); $^{11}$B NMR (C$_6$D$_6$, 160 MHz) δ 33.4 (brs); $^{13}$C NMR (C$_6$D$_6$, 126 MHz) δ 29.5 (vt, $^3$J$_{PC}$ = 3 Hz, CH$_3$), 36.7 (vt, $^3$J$_{PC}$ = 10 Hz, 4°), 40.5 (vt, $^3$J$_{PC}$ = 19 Hz, CH$_2$), 109.4 (CH), 119.0 (CH), 139.5 (vt, $^3$J$_{PC}$ = 7 Hz, 4°); mp: 300.1-328.7 °C (dec.); Anal. calcd. for C$_{24}$H$_{34}$BClN$_3$P$_2$Pt: C, 43.42; H, 6.68; N, 4.22. Found: C, 43.46; H, 6.96; N, 4.15.
Preparation of [PBP]PtH (3). A suspension of 2 (80.0 mg, 0.120 mmol) and NaBH₄ (10.6 mg, 0.281 mmol) in THF (2.5 mL) was stirred at room temperature for 30 min. Triethylamine (0.839 mL, 6.02 mmol) was added to the suspension and stirred at 70 °C for 2 h. Then, volatiles were removed and n-hexane (20 mL) was added to the residue. The resulting suspension was filtered through a pad of Celite® and volatiles were removed from the filtrate to give a white solid of 3 (64.8 mg, 85.7%). Single crystals suitable for X-ray analysis were obtained from benzene solution at room temperature. 

A suspension of 2 (100 mg, 0.151 mmol) and AgOTf (40.2 mg, 0.156 mmol) in benzene (1.5 mL) was stirred at room temperature for 30 minutes. The resulting suspension was filtered through a pad of Celite® and volatiles were removed from the filtrate under reduced pressure. Recrystallization from benzene/ n-hexane at room temperature gave colorless crystals of 4 (24.5 mg, 31.5 mmol, 32%). 1H NMR (C₆D₆, 500 MHz) δ 1.20 (vt, 3J_PtH = 7 Hz, 36H), 3.90 (vt, J_PtH = 2 Hz, 3J_PtH = 8 Hz, 4H), 7.07 (dd, J = 6, 2 Hz, 2H), 7.18 (dd, J = 6, 2 Hz, 2H), 7.92 (vt, J_PtH = 14 Hz, 3J_PtH = 488.9 Hz, 1H); 31P NMR (C₆D₆, 202 MHz) δ 114.5 (s, J_PtP = 3043 Hz); 11B NMR (C₆D₆, 160 MHz) δ 51.4 (brs); 13C NMR (C₆D₆, 126 MHz) δ 29.6 (vt, 2J_PtC = 3 Hz, CH₃), 35.3 (vt, 1J_PtC = 10 Hz, 4°), 42.5 (vt, 1J_PtC = 9 Hz, CH₂), 109.7 (CH), 118.5 (CH), 140.3 (vt, 3J_PtC = 7 Hz, 4°); mp: 224.3-230.0 °C (dec.); IR (KBr), ν_PtH = 1735 cm⁻¹; Anal. calcd. for C₂H₄₅N₂O₂P₂PtC: C, 45.79; H, 7.21; N, 4.45. Found: C, 45.80; H, 6.95; N, 4.27.

Preparation of [PBP]PtOTf (4). A suspension of 2 (120 mg, 0.181 mmol) and AgOTf (40.2 mg, 0.156 mmol) in benzene (1.5 mL) was stirred at room temperature for 30 minutes. The resulting suspension was filtered through a pad of Celite® and volatiles were removed from the filtrate under reduced pressure. Recrystallization from benzene/ n-hexane at room temperature gave colorless crystals of 4 (24.5 mg, 31.5 mmol, 32%). 1H NMR (C₆D₆, 500 MHz) δ 1.20 (vt, 3J_PtH = 7 Hz, 36H), 3.90 (vt, J_PtH = 2 Hz, 3J_PtH = 10 Hz, 4H), 6.95 (dd, J = 6, 2 Hz, 2H), 7.13 (dd, J = 6, 2 Hz, 2H); 31P NMR(C₆D₆, 202 MHz) δ 94.3 (s, J_PtP = 3170 Hz); 11B NMR (C₆D₆, 160 MHz) δ 33.4 (brs); 13C NMR (C₆D₆, 126 MHz) δ 29.3 (vt, 2J_PtC = 3 Hz, CH₃), 36.5 (vt, 1J_PtC = 10 Hz, 4°), 39.4 (vt, 1J_PtC = 19 Hz, CH₂), 109.5 (CH), 119.5 (CH), 121.0 (q, 1J_CF = 326 Hz, CF₃), 138.7 (vt, 3J_PtC = 7 Hz, 4°); 19F NMR (C₆D₆, 470 MHz) δ −78.8 (s); mp: 200-240 °C (dec.); Anal. calcd. for C₂₅H₄₉BF₃N₂O₂P₂PtS: C, 38.62; H, 5.70; N, 3.60. Found: C, 38.60; H, 5.82; N, 3.46.

Preparation of [PBP]PtNTf₂ (5). A suspension of 2 (120 mg, 0.181 mmol) and AgNTf₂ (40.2 mg, 0.156 mmol) in benzene (1.5 mL) was stirred at room temperature for 30 minutes. The resulting suspension was filtered through a pad of Celite® and volatiles were removed from the filtrate under reduced pressure. Recrystallization from benzene & n-hexane gave white solid of 5 (75.6mg, 83.2 mmol, 46%). Single crystals suitable for X-ray analysis were obtained from benzene solution diffused by n-hexane vapor at room temperature. 1H NMR (THF-d₈, 500 MHz) δ 1.20 (vt, 3J_PtH = 7 Hz, 36H), 3.49 (vt, J_PtH = 3 Hz, 3J_PtH = 10 Hz, 4H), 6.95 (dd, J = 6, 2 Hz, 2H), 7.13 (dd, J = 6, 2 Hz, 2H); 31P NMR(THF-d₈, 202 MHz) δ 96.9 (s, J_PtP = 3100 Hz); 11B NMR (THF-d₈, 160 MHz) δ 20.9 (brs); 13C NMR (THF-d₈, 126 MHz) δ 29.5 (vt, 2J_PtC = 3 Hz, CH₃), 37.2 (vt, 1J_PtC = 10 Hz, 4°), 39.7 (vt, 1J_PtC = 19 Hz, CH₂), 109.9 (CH), 121.0 (q, 1J_CF = 322 Hz, CF₃), 119.8 (CH), 138.6 (vt, 3J_PtC = 7 Hz, 4°); 19F NMR (THF-d₈, 471 MHz) δ −81.6 (s); mp: 72-85°C (dec.); Anal. calcd. for C₂₆H₄₁BF₆N₃O₂P₂PtS₂: 0.5C₆H₆ C, 36.75; H, 5.00; N, 4.43. Found: C, 36.35; H, 4.85; N, 4.35.
Procedure for entries 1-4, 7, 8, and 10 in Table 1. A mixture of substrate 1-decene and dodecane (0.368 mL, 1.51 mmol, \([1\text{-decene}]/[\text{dodecane}] = 4.47\)) was added to a solution of Pt complex (2, 1.0 mg, 1.5 µmol for entries 1-4; 3, 1.2 mg, 1.5 µmol for entry 7; 4, 1.4 mg, 1.5 µmol for entry 8; 3, 1.0 mg, 1.5 µmol for entry 10) in 0.200 mL of solvent (toluene for entries 1, 7, and 8; THF for entry 2, chlorobenzene for entry 3, DMF for entry 4). Triethylsilane (0.241 mL, 1.51 mmol) was syringed to the reaction mixture and the resulting mixture was stirred at 100 °C for 21 h. After the reaction mixture was cooled down to room temperature and was diluted with ether, an aliquot of the diluted solution was analyzed by GC.

Procedure for entries 5 and 6 in Table 1. After a solution of AgOTf (7.55 mM in toluene, 0.200 mL, 1.51 µmol) was added to a solid of \([\text{PBP}]\text{PtCl}\) (1.0 mg, 1.5 µmol), a mixture of substrate 1-decene and dodecane (0.368 mL, 1.51 mmol, \([1\text{-decene}]/[\text{dodecane}] = 4.47\)) and triethylsilane (0.241 mL, 1.51 mmol) were added to the resulting suspension of platinum. The resulting mixture was stirred at 100 °C for 21 h. After the reaction mixture was cooled down to room temperature and was diluted with ether, an aliquot of the diluted solution was analyzed by GC.

Procedure for entry 9 in Table 1. A mixture of substrate 1-decene and dodecane (0.368 mL, 1.51 mmol, \([1\text{-decene}]/[\text{dodecane}] = 4.47\)) was added to a suspension of \([\text{PBP}]\text{PtCl}\) (1.0 mg, 1.5 µmol) and AgBARF\(_4\) (1.5 mg, 1.5 µmol) in toluene (0.200 mL). Triethylsilane (0.241 mL, 1510 mmol) was syringed into the mixture and the resulting mixture was stirred at 100 °C for 21 h. After the reaction mixture was cooled down to room temperature and was diluted with ether, an aliquot of the diluted solution was analyzed by GC.

Procedures for entries 11-13 in Table 1. To a solution of silver salt (1.51 µmol) in toluene (0.200 mL), a mixture of substrate 1-decene and dodecane (0.368 mL, 1.51 mmol, \([1\text{-decene}]/[\text{dodecane}] = 4.47\)) was added. Triethylsilane (0.241 mL, 1.51 mmol) was syringed into the mixture and the resulting mixture was stirred at 100 °C for 21 h. After the reaction mixture was cooled down to room temperature and was diluted with ether, an aliquot of the diluted solution was analyzed by GC.

Procedure for entry 14 in Table 1. To a solution of Karstedt’s cat. (1.51 µmol, 2%Pt in Xylene, 33.9 µL) in toluene (0.200 mL), a mixture of substrate 1-decene and dodecane (0.368 mL, 1.51 mmol, \([1\text{-decene}]/[\text{dodecane}] = 4.47\)) and triethylsilane (0.241 mL, 1510 mmol) were added and the resulting mixture was stirred at 100 °C for 21 h. After the reaction mixture was cooled down to room temperature and was diluted with ether, an aliquot of the diluted solution was analyzed by GC.
Details for X-ray crystallography

The numbers for Cambridge Structural Database, details of the crystal data, and a summary of the intensity data collection parameters for 2-5 are listed in Table S1. In each case a suitable crystal was mounted with a mineral oil to the glass fiber and transferred to the goniometer of a Rigaku Mercury CCD or VariMax Saturn CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). The structures were solved by direct methods with (SIR-97) and refined by full-matrix least-squares techniques against F² (SHELXL-97). The intensities were corrected for Lorentz and polarization effects or NUMABS program (Rigaku 2005). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. All the procedure of analyzing was performed by using Yadokari-XG software. All the resulting CIF files and their checkCIF files are also attached as supporting information.

Table S1. Crystallographic data and structure refinement details for 2-5

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Computational Details.

Structure optimization and vibrational calculation (B3LYP//LANL2DZ for Pt//cc-pvdz for others) for 3 were performed by the Gaussian 09 program\textsuperscript{S08} running on a Hitachi SR16000 system at Research Center for Computational Science in National Institutes of Natural Sciences. Visualizing was performed by using Yadokari-XG software.\textsuperscript{S07}

**Figure S1.** Optimized structure of 3 with description of vibrational mode (red arrows) at 1728 cm\textsuperscript{-1}.

Cartesian coordinate of the optimized 3

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