

Electronic Supplementary Information

Rhodium(I) complexes with *N*-heterocyclic carbenes bearing a 2,3,4,5-tetraphenylphenyl and its higher dendritic frameworks

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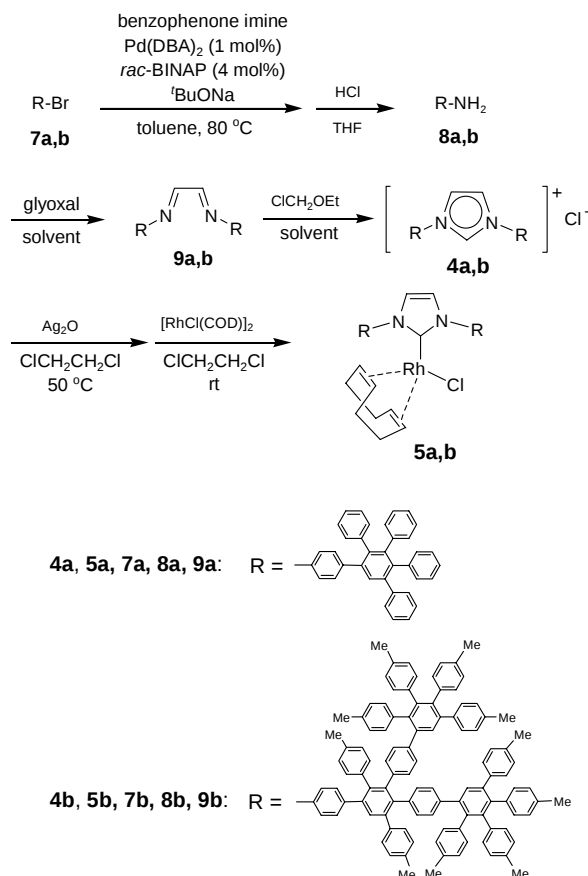
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General procedure and materials.

All manipulations were performed under an argon atmosphere using standard Schlenk-type glasswares on a dual-manifold Schlenk line. The reagents and the solvents for catalytic reactions were dried and purified before use by usual procedures.¹ ¹H NMR and ¹³C{¹H} NMR spectra were measured with a Bruker ARX-400, a JEOL ECX-400 or a JEOL ECA-600 spectrometers. MALDI-TOF mass spectra were measured with a Bruker Autoflex instrument. FD mass spectra were measured with a JEOL JMS-SX102A instrument at the GC-MS & NMR Laboratory of Faculty of Agriculture, Hokkaido University. ESI mass spectra were measured with a JEOL JMS-HX110 instrument at the Center for Instrumental Analysis, Hokkaido University. Elemental analyses were also carried out at the same center. Preparative recycling gel permeation chromatography (GPC) was performed with a JASCO LC9104. GC analysis was carried out using Shimadzu GC-17A

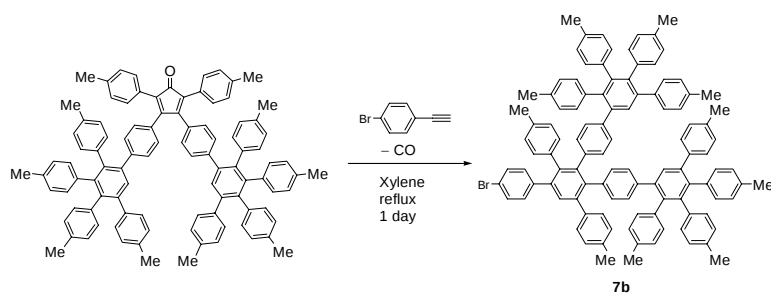
equipped with Shimadzu CPB1 (25 m length, 0.25 mm i.d.) or CPB10 (25 m length, 0.25 mm i.d.) columns.

Scheme 1S shows the preparation methods of **5a** and **5b**. **5c**,² **6a-d**³ and 4-Bromo-(2',3',4',5'-tetraphenylphenyl)biphenyl (**7a**)⁴ were prepared according to the literatures.



Scheme 1S. Preparation of **5a** and **5b**

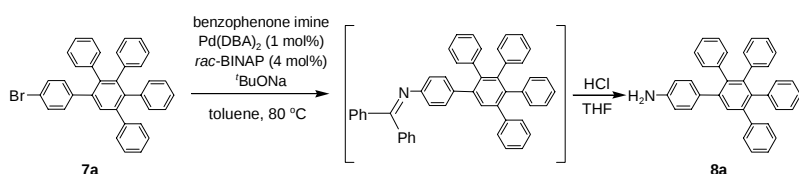
Synthesis of **7b**:



In a 300-cm³ flask under an argon atmosphere, a solution of 2,5-bis(*p*-tolyl)-3,4-bis{4-[2',3',4',5'-tetra(*p*-tolyl)]biphenyl}cyclopentadienone⁵ (8.4 g, 6.5 mmol)

and 4-bromo-1-ethynylbenzene (1.5 g, 8.2 mmol) in degassed *o*-xylene (150 cm³) was refluxed for 1 d. After a removal of the solvent, a residue was purified by silica gel chromatography using hexane/toluene (2/3) as an eluent. Removal of volatiles gave a white powder. Yield 5.3 g (57%). ¹H NMR (400 MHz, CDCl₃) δ 7.444 (s, 1H, Ar₅C₆H), 7.436(s, 1H, Ar₅C₆H), 7.40 (s, 1H, Ar₅C₆H), 6.94-7.04 (m, 12H, Ph), 6.56-6.75 (m, 36H, Ph), 6.51 (d, 2H, *J* = 8.0 Hz, C₆H₄Br), 6.44 (d, 2H, *J* = 8.0 Hz, C₆H₄Br), 2.30 (s, 3H, Me), 2.26 (s, 6H, Me), 2.19 (s, 3H, Me), 2.15 (s, 6H, Me), 2.11 (s, 12H, Me). ¹³C NMR (100 MHz, CDCl₃) δ 141.8, 141.5, 141.0, 140.7, 140.52, 140.50, 140.3, 139.5, 139.3, 139.21, 139.15, 139.12, 139.10, 139.0, 138.91, 138.86, 137.6, 137.2, 137.0, 135.5, 134.6, 134.3, 131.6, 131.55, 131.50, 131.3, 131.2, 131.03, 130.96, 130.7, 129.9, 129.8, 128.7, 128.5, 128.3, 128.2, 127.8, 127.6, 127.4, 127.3, 21.2, 21.13, 21.10, 21.05, 21.03. MALDI-TOF-MS (matrix: dithranol) *m/z* = 1437 [M+H]⁺. Anal. Calcd. For C₁₀₆H₈₅Br: C, 88.49; H, 5.95. Found C, 88.40; H, 5.95.

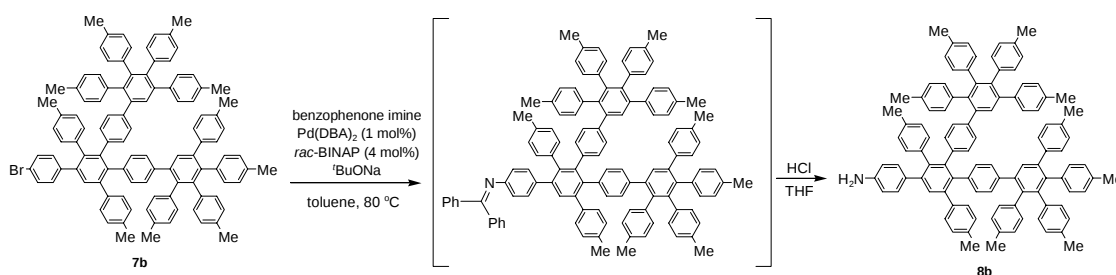
Synthesis of 8a:



In a 300-cm³ two-neck flask under an argon atmosphere, benzophenone imine (3.5 cm³, 21 mmol) was added to a suspension of **7a** (10 g, 18.7 mmol), *rac*-BINAP (466 mg, 0.75 mmol), Pd(DBA)₂ (95 mg, 0.19 mmol) and ^tBuONa (2.7 g, 28 mmol) in degassed toluene (100 cm³) at 80 °C. The mixture was stirred at 80 °C under argon for 2 d. After removal of the solvent, a crude product was purified by silica gel column chromatography using CH₂Cl₂ as an eluent. Removal of volatiles gave the *N*-arylated imine as a yellow solid. It was dissolved in THF (500 cm³) and 1N HCl aq. (150 cm³) was added to the solution. The mixture was stirred at room temperature for 15 h. An aqueous saturated solution of NaHCO₃ (300 cm³) was added to the reaction mixture and the organic layer was separated after vigorous shaking. The aqueous layer was extracted with AcOEt

(300 cm³ × 2) and the washing liquid was combined with the organic layer, which was dried over anhydrous MgSO₄. After removal of volatiles, a crude product was obtained. It was dissolved in CH₂Cl₂ (20 cm³) and the solution was poured into MeOH (600 cm³). The product **8a** was collected by filtration as a white precipitate, washed with MeOH and dried *in vacuo*. Yield 7.9 g (96%). ¹H NMR (400 MHz, THF-d₈) δ 7.46 (s, 1H, Ar₅C₆H), 6.77-7.14 (m, 22H, Ph), 6.35 (d, 2H, *J* = 8.3 Hz, C₆H₄NH₂), 4.34 (s, 2H, NH₂). ¹³C NMR (100 MHz, THF-d₈) δ 147.8, 143.1, 142.6, 142.2, 141.8, 141.7, 141.6, 141.4, 139.9, 139.2, 132.49, 132.47, 132.4, 132.1, 131.3, 130.73, 130.69, 128.23, 127.61, 127.56, 127.3, 126.7, 126.1, 126.0, 125.8. FD-MS *m/z* = 474 [M]⁺. Anal. Calcd. For C₃₆H₂₇N: C, 91.30; H, 5.75; N, 2.96. Found: C, 91.44; H, 5.62; N, 2.95.

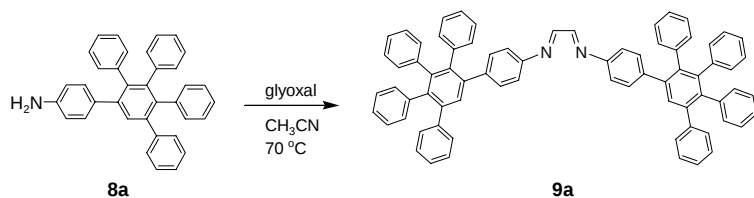
Synthesis of **8b**:



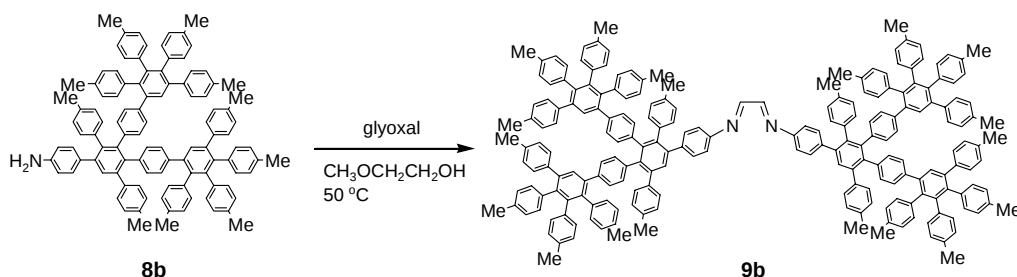
In a 100-cm³ two-neck flask under an argon atmosphere, benzophenone imine (0.42 cm³, 2.5 mmol) was added to a suspension of **7b** (3.2 g, 2.2 mmol), *rac*-BINAP (55 mg, 89 μmol), ^tBuONa (327 mg, 3.4 mmol) and Pd(DBA)₂ (12 mg, 24 μmol) in degassed toluene (25 cm³) at 80 °C. The mixture was stirred at 80 °C for 20 h. After removal of the solvent, a residue was purified by silica gel column chromatography using hexane/CH₂Cl₂ (from 2/1 to 1/1) as eluents. Removal of volatiles gave the *N*-arylated imine as a yellow solid. It was dissolved in THF (100 cm³) and 1N HCl aq. (50 cm³) was added to the solution. The mixture was stirred at room temperature for 1 h. An aqueous saturated solution of NaHCO₃ (100 cm³) was added to the reaction mixture and the organic layer was separated after vigorous shaking. The aqueous layer was extracted with diethyl ether (100 cm³ × 2) and the washing liquid was combined with the organic layer, which was dried over anhydrous MgSO₄. After removal of volatiles, a crude product was obtained. It was

dissolved in CH_2Cl_2 and the solution was poured into MeOH. The product **8b** was collected by filtration as a white powder, washed with MeOH and dried *in vacuo*. Yield 3.0 g (96%). ^1H NMR (400 MHz, CDCl_3) δ 7.48 (s, 1H, $\text{Ar}_5\text{C}_6\text{H}$), 7.46 (s, 1H, $\text{Ar}_5\text{C}_6\text{H}$), 7.42 (s, 1H, $\text{Ar}_5\text{C}_6\text{H}$), 6.93-7.05 (m, 12H, Ph), 6.88 (d, 2H, $J = 7.9$ Hz, $\text{C}_6\text{H}_4\text{NH}_2$), 6.58-6.75 (m, 32H, Ph), 6.52 (d, 2H, $J = 7.9$ Hz, $\text{C}_6\text{H}_4\text{NH}_2$), 6.451 (d, 2H, $J = 7.5$ Hz, $\text{Ar}_2\text{C}_6\text{H}_4$), 6.450 (d, 2H, $J = 7.5$ Hz, $\text{Ar}_2\text{C}_6\text{H}_4$), 3.54 (br, 2H, NH_2), 2.29 (s, 3H, Me), 2.26 (s, 6H, Me), 2.18 (s, 3H, Me), 2.13 (s, 6H, Me), 2.11 (s, 12H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 141.8, 141.2, 140.7, 140.5, 140.4, 139.2, 139.1, 139.0, 138.92, 138.86, 138.7, 138.3, 138.1, 137.7, 137.6, 137.2, 137.1, 137.0, 135.6, 135.5, 134.7, 134.6, 134.3, 132.4, 132.3, 131.6, 131.3, 131.15, 131.06, 130.8, 130.03, 129.98, 129.8, 128.7, 128.3, 128.2, 127.6, 127.4, 127.3, 21.2, 21.2, 21.0. MALDI-TOF-MS (matrix: dithranol) $m/z = 1374$ $[\text{M}+\text{H}]^+$. Anal. Calcd. For $\text{C}_{106}\text{H}_{87}\text{N}$: C, 92.60; H, 6.38; N, 1.02. Found C, 92.64; H, 6.55; N, 1.08.

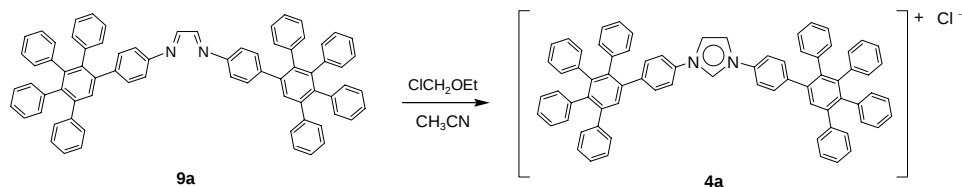
Synthesis of 9a:



In a 100- cm^3 flask, glyoxal (40 wt% in water, 0.4 cm^3 , 3.5 mmol) was added to a solution of **8a** (3.0 g, 6.3 mmol) in CH_3CN (45 cm^3) at 70 $^\circ\text{C}$. The mixture was stirred at 70 $^\circ\text{C}$ for 6.5 h. A yellow solid formed and was collected by filtration, washed with CH_3CN and dried *in vacuo*. Yield 2.2 g (73%). ^1H NMR (400 MHz, THF-d_8) δ 8.32 (s, 2H, $\text{C}_2\text{H}_2\text{N}_2$), 7.55 (s, 2H, $\text{Ar}_5\text{C}_6\text{H}$), 7.21 (d, 4H, $J = 8.7$ Hz, $\text{C}_6\text{H}_4\text{N}$), 7.08-7.14 (m, 12H, Ph), 6.80-6.90 (m, 32H, Ph). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 160.0, 142.2, 142.1, 141.9, 141.2, 140.8, 140.5, 140.4, 140.3, 139.9, 139.7, 131.87, 131.84, 131.78, 131.4, 131.3, 130.3, 127.9, 127.3, 127.2, 126.9, 126.7, 126.1, 126.0, 125.7, 121.0. FD-MS $m/z = 968$ $[\text{M}]^+$. Anal. Calcd. For $\text{C}_{74}\text{H}_{52}\text{N}_2$: C, 91.70; H, 5.41; N, 2.89. Found: C, 91.42; H, 5.55; N, 2.81.

Synthesis of 9b:

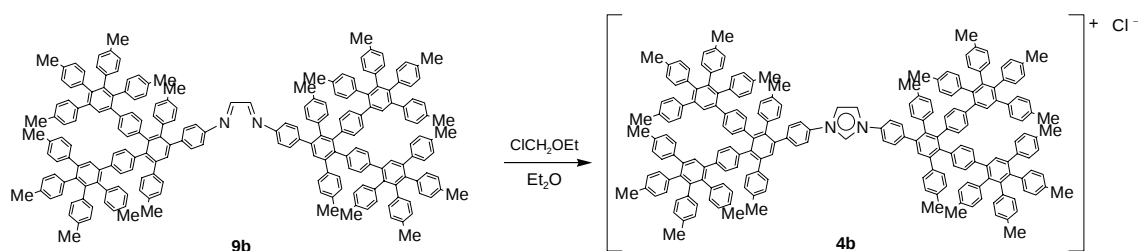
In a 30-cm^3 flask, a solution of glyoxal (40 wt% in water, 0.021 cm^3 , 0.19 mmol) in 2-methoxyethanol (1 cm^3) was added to a solution of **8b** (512 mg , 0.37 mmol) in 2-methoxyethanol (4 cm^3) at $50\text{ }^\circ\text{C}$. The mixture was stirred at $50\text{ }^\circ\text{C}$ for 17 h. After cooling with an ice bath, a yellow suspension was filtered on a Celite and washed with cold 2-methoxyethanol. The yellow material was dissolved in diethyl ether and evaporation of the solvent gave **9b** as a yellow powder. Yield 479 mg (93%). ^1H NMR (400 MHz, CDCl_3) δ 8.33 (s, 2H, $\text{C}_2\text{H}_2\text{N}_2$), 7.45 (s, 4H, $\text{Ar}_5\text{C}_6\text{H}$), 7.41 (s, 2H, $\text{Ar}_5\text{C}_6\text{H}$), 6.84–7.16 (m, 28H, Ph), 6.44–6.73 (m, 76H, Ph), 2.30 (s, 6H, Me), 2.27 (s, 12H, Me), 2.18 (s, 6H, Me), 2.15 (s, 12H, Me), 2.12 (s, 24H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 141.8, 140.5, 140.4, 139.1, 138.92, 138.86, 137.6, 137.2, 137.1, 137.0, 136.7, 135.5, 134.7, 134.6, 134.3, 131.6, 131.3, 131.2, 131.1, 130.0, 129.8, 128.7, 128.4, 128.2, 127.6, 127.4, 127.3, 21.12, 21.09, 21.04, 21.02. MALDI-TOF-MS (matrix: dithranol) $m/z = 2770\text{ [M+H]}^+$. ESI-MS-HR Calcd. For $\text{C}_{214}\text{H}_{172}\text{N}_2\text{Na}$: 2792.3418, Found: $m/z = 2792.3484$.

Synthesis of 4a:

In a 5-cm^3 flask, **9a** (1.0 g , 1.0 mmol) was added to ClCH_2OEt (2 cm^3 , 22 mmol) at room temperature with vigorous stirring. After **9a** was completely dissolved in ClCH_2OEt (in ca. 1 min), CH_3CN (2.5 cm^3) was added and the mixture was stirred for 30 min. After removal of volatiles, a

residue was purified by silica gel column chromatography. Materials eluted with CH_2Cl_2 were discarded and a fraction eluted with $\text{MeOH}/\text{CH}_2\text{Cl}_2$ (1/9) was collected. Evaporation of the fraction *in vacuo* gave a crude product as a pale-brown solid. Further purification was performed with a preparative recycling GPC to afford a white powder. Yield 733 mg (69%). ^1H NMR (400 MHz, CDCl_3) δ 11.51 (s, 1H, NCHN), 7.90 (d, 4H, $J = 8.7$ Hz, $\text{C}_6\text{H}_4\text{Im}$), 7.69 (s, 2H, NCH=CHN), 7.50 (s, 2H, $\text{Ar}_5\text{C}_6\text{H}$), 7.37 (d, 4H, $J = 8.7$ Hz, $\text{C}_6\text{H}_4\text{Im}$), 6.78-6.93 (m, 40H, Ph). ^{13}C NMR (100 MHz, CDCl_3) δ 144.4, 142.1, 141.3, 141.1, 140.2, 139.9, 139.7, 139.4, 139.2, 138.6, 135.1, 132.4, 132.0, 131.43, 131.41, 131.36, 131.1, 129.9, 127.7, 127.3, 127.0, 126.7, 126.0, 125.8, 125.5, 121.1, 120.8. FD-MS $m/z = 981$ $[\text{M}-\text{Cl}]^+$. ESI-MS-HR Calcd. For $\text{C}_{75}\text{H}_{53}\text{N}_2$: 981.4209, Found: $m/z = 981.4197$.

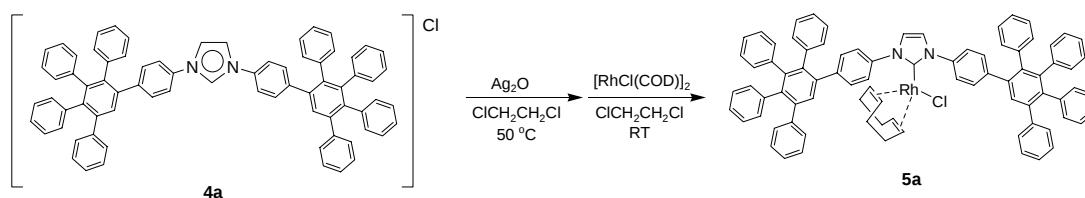
Synthesis of 4b:



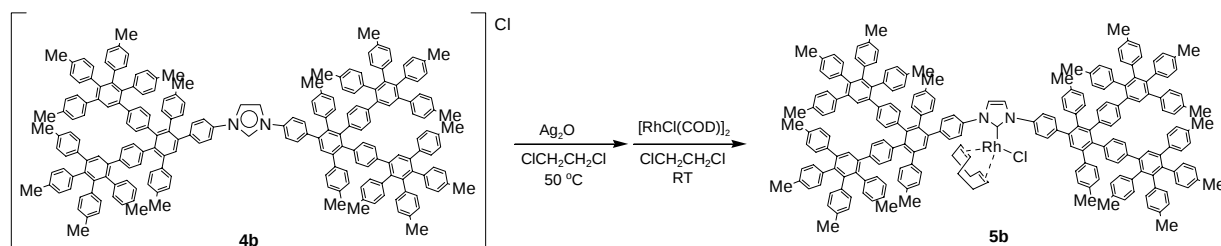
In a 50- cm^3 flask under an argon atmosphere, a solution of ClCH_2OEt (0.25 cm^3 , 2.7 mmol) in degassed diethyl ether (5 cm^3) was added at -25 $^\circ\text{C}$ to a solution of **9b** (502 mg, 0.18 mmol) in degassed diethyl ether (10 cm^3). The mixture was stirred at -25 $^\circ\text{C}$ for 19 h. After removal of volatiles, a crude product was purified by silica gel column chromatography. Materials eluted with CH_2Cl_2 , diethyl ether, and $\text{MeOH}/\text{diethyl ether}$ (2/98) was discarded. A fraction eluted with $\text{MeOH}/\text{CH}_2\text{Cl}_2$ (1/9) was collected and evaporation gave a pale-brown powder. Yield 218 mg (43%). ^1H NMR (600 MHz, CDCl_3) δ 11.15 (s, 1H, NCHN), 7.81 (d, 4H, $J = 7.2$ Hz, $\text{C}_6\text{H}_4\text{Im}$), 7.66 (s, 2H, NCH=CHN), 7.45 (s, 2H, $\text{Ar}_5\text{C}_6\text{H}$), 7.44 (s, 2H, $\text{Ar}_5\text{C}_6\text{H}$), 7.41 (s, 2H, $\text{Ar}_5\text{C}_6\text{H}$), 7.32 (d, 4H, $J = 7.2$ Hz, $\text{C}_6\text{H}_4\text{Im}$), 6.96-7.04 (m, 24H, Ph), 6.58-6.71 (m, 64H, Ph), 6.54 (d, 4H, $J = 7.2$ Hz, $\text{Ar}_2\text{C}_6\text{H}_4$), 6.46 (d, 4H, $J = 7.2$ Hz, $\text{Ar}_2\text{C}_6\text{H}_4$), 2.29 (s, 6H, Me), 2.27 (s, 12H, Me), 2.16 (s, 6H, Me),

2.15 (s, 12H, Me), 2.11 (s, 24H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 144.8, 141.8, 141.7, 140.9, 140.5, 140.3, 139.7, 139.25, 139.20, 138.92, 138.87, 138.7, 138.5, 137.6, 137.3, 137.2, 137.1, 137.0, 136.3, 135.9, 135.5, 135.3, 134.7, 134.6, 134.3, 132.3, 131.9, 131.6, 131.5, 131.3, 131.2, 131.0, 130.9, 129.9, 129.8, 128.8, 128.5, 128.3, 128.2, 128.0, 127.6, 127.4, 127.3, 121.3, 121.0, 21.19, 21.15, 21.11, 21.08, 21.06, 21.04. MALDI-TOF-MS (matrix: dithranol) m/z = 2782 $[\text{M}-\text{Cl}]^+$. ESI-MS-HR Calcd. For $\text{C}_{215}\text{H}_{173}\text{N}_2$: 2782.3599, Found: m/z = 2782.3599.

Synthesis of 5a:



In a 100-cm³ two-neck flask under argon atmosphere, a suspension of **4a** (329 mg, 0.32 mmol) and Ag_2O (46 mg, 0.20 mmol) in 1,2-dichloroethane (30 cm³) was stirred at 50 °C for 1 d under Ar. At room temperature, $[\text{RhCl}(\text{COD})]_2$ (96 mg, 0.20 mmol) was added to the solution and the whole mixture was stirred at room temperature under Ar for 8 h. After filtration through Celite to remove insoluble materials, a residue obtained by evaporation was purified by silica gel column chromatography using CH_2Cl_2 /hexane (1/1) as an eluent. The crude product was recrystallized from CH_2Cl_2 /diethyl ether. Yellow crystals were collected by filtration, washed with diethyl ether and dried *in vacuo*. Yield 274 mg (69%). ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, 4H, J = 8.6 Hz, $\text{C}_6\text{H}_4\text{Im}$), 7.60 (s, 2H, $\text{Ar}_5\text{C}_6\text{H}$), 7.37 (d, 4H, J = 8.6 Hz, $\text{C}_6\text{H}_4\text{Im}$), 7.16-7.21 (m, 12H, Ph), 6.79-6.96 (m, 30H, Ph), 4.88 (m, 2H, COD), 2.58 (m, 2H, COD), 1.92 (m, 2H, COD), 1.49-1.59 (m, 6H, COD). ^{13}C NMR (100 MHz, CDCl_3) δ 184.4 (d, $J_{\text{Rh}-\text{C}}$ = 48.7 Hz, NCN), 142.1, 141.6, 141.5, 141.0, 140.2, 139.8, 139.7, 139.6, 139.3, 138.5, 131.54, 131.46, 131.38, 131.32, 130.4, 129.9, 127.7, 127.2, 127.1, 126.9, 126.67, 126.62, 126.4, 125.9, 125.7, 125.4, 124.2, 122.0, 97.3 (d, $J_{\text{Rh}-\text{C}}$ = 6.7 Hz), 68.0 (d, $J_{\text{Rh}-\text{C}}$ = 14.3 Hz), 32.3, 28.6. FD-MS m/z = 1227 $[\text{M}]^+$. Anal. Calcd. For $\text{C}_{83}\text{H}_{64}\text{N}_2\text{ClRh}$: C, 81.20; H, 5.25; N, 2.28. Found C, 81.26; H, 5.32; N, 2.33.

Synthesis of 5b:

In a 100-cm³ two-necked flask under argon atmosphere, a solution of **4b** (652 mg, 0.23 mmol) and Ag₂O (33 mg, 0.14 mmol) in 1,2-dichloroethane (20 cm³) was stirred at 50 °C for 9 h under Ar. At room temperature, [RhCl(COD)]₂ (70 mg, 0.14 mmol) was added to the solution and the mixture was stirred at room temperature for 18 h. After filtration through Celite to remove insoluble materials, a residue obtained by evaporation was purified by silica gel column chromatography using CH₂Cl₂/hexane (3/7) as an eluent. Removal of volatiles gave a pale-orange solid. Yield 487 mg (70%). ¹H NMR (600 MHz, CDCl₃) δ 8.11 (d, 4H, *J* = 8.4 Hz, C₆H₄Im), 7.53 (s, 2H, NCH=CHN), 7.47 (s, 2H, Ar₅C₆H), 7.42 (s, 2H, Ar₅C₆H), 7.32 (d, 4H, *J* = 7.8 Hz, C₆H₄Im), 7.21 (s, 2H, Ar₅C₆H) 6.95-7.05 (m, 24H, Ph), 6.79-6.47 (m, 72H, Ph), 4.87 (br, 2H, COD), 2.60 (br, 2H, COD), 2.31, 2.27, 2.17, 2.16, 2.15, 2.13, 2.122, 2.119 (s, 60H, Me) 1.92 (br, 2H, COD), 1.66 (br, 2H, COD), 1.57 (br, 2H, COD), 1.52 (br, 2H, COD). ¹³C NMR (150 MHz, CDCl₃) δ 184.3 (d, *J*_{Rh-C} = 47.7 Hz, NCN), 141.9, 141.8, 141.7, 140.7, 140.53, 140.50, 140.3, 139.7, 139.25, 139.19, 139.10, 139.08, 138.96, 138.92, 138.87, 138.7, 138.6, 138.4, 137.8, 137.6, 137.5, 137.2, 137.1, 137.0, 136.8, 135.8, 135.5, 135.0, 134.7, 134.6, 134.3, 131.6, 131.3, 131.2, 131.0, 130.3, 129.9, 129.8, 128.7, 128.3, 128.2, 128.0, 127.6, 127.5, 127.3, 124.1, 121.9, 97.2 (br, COD), 68.0 (br, COD), 32.2, 28.5, 21.2, 21.14, 21.08, 21.06, 21.02. MALDI-TOF-MS *m/z* = 2992 [M-Cl]⁺. Anal. Calcd. For C₂₂₃H₁₈₄N₂ClRh: C, 88.39; H, 6.12; N, 0.92. Found C, 88.59; H, 6.29; N, 1.01.

General procedure for the hydrosilylation (entry 1 in Table 1): A mixture of **5a** (0.01 mmol, 12 mg), CH₂Cl₂ (1 cm³), 2-cyclohexen-1-one (1 mmol, 9.7×10⁻² dm³), and bibenzyl (0.25 mmol, 45.6 mg) as an internal standard was placed in a 10-cm³ Schlenk tube under an Ar atmosphere and the

resulting solution was stirred for 5 min. Then, Ph_2SiH_2 (1.2 mmol, 0.22 dm^3) was added via a syringe and the reaction mixture was stirred at room temperature for 24 h. After removal of volatiles under vacuum at $-30\text{ }^\circ\text{C}$, a residue was dissolved in Et_2O (1 cm^3). The solution was further stirred for 1 h with K_2CO_3 (1 mg) and MeOH (1 cm^3). Total yield (77%) and a ratio (91/9) of cyclohexanone and 2-cyclohexen-1-ol were determined by a GC (Shimadzu CPB10 column, 25 m length, 0.25 mm i.d.).

X-ray Diffraction Study. Single crystals of $5\mathbf{a}\cdot\text{C}_5\text{H}_{12}$ suitable for X-ray diffraction study were obtained by diffusion of *n*-pentane into $5\mathbf{a}$ in CH_2Cl_2 . Data were collected on a Rigaku/Saturn70 CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71070\text{ \AA}$) at 113 K, and processed using CrystalClear (Rigaku). The structures were solved by a direct method (SIR92) and refined by full-matrix least-square refinement on F^2 . The non-hydrogen atoms except for solvated molecules were refined anisotropically. All hydrogen atoms were located on the calculated positions and not refined. All calculations were performed using the CrystalStructure software package. Crystal data for $5\mathbf{a}\cdot\text{C}_5\text{H}_{12}$: $\text{C}_{88}\text{H}_{76}\text{ClN}_2\text{Rh}$, $M = 1299.9$, $T = 113\text{ K}$, triclinic, space group $P\bar{1}$ (No. 2), $a = 14.85(2)$, $b = 20.51(2)$, $c = 25.04(2)\text{ \AA}$, $\alpha = 79.38(7)$, $\beta = 71.05(9)$, $\gamma = 81.10(10)^\circ$, $U = 7054(1)\text{ \AA}^3$, $Z = 4$, $\mu(\text{Mo } K\alpha) = 3.30\text{ cm}^{-1}$, Unique reflections 31888, Observed reflections 16076 ($I > 3\sigma(I)$), $R1$, $wR2 = 0.056$, 0.164 , $\text{GOF} = 1.01$. CCDC Number 617650.

Calculation

An optimized structure of $5\mathbf{b}$ was obtained by ONIOM⁶ calculations. In the ONIOM calculation, the molecular system of $5\mathbf{b}$ was divided into two layers. The high layer was assigned to $5\mathbf{b}$ with $\text{R} = \text{C}_6\text{H}_4$ for B3LYP⁷/LANL2DZ⁸ calculation. The low layer contains the rest dendritic frameworks of $5\mathbf{b}$ for molecular mechanics calculation using UFF force field was carried out on the layer.⁹ All calculations were performed with the Gaussian 03 program¹⁰ on a HIT HPC-IA642/SS 1.3/3D-4G.

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