

Electronic Supplementary Information

Dendrimer *N*-heterocyclic carbene complexes with rhodium (I) at the core

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General Procedures 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 were dried and purified before use by usual procedures.¹ ¹H NMR and ¹³C{¹H} NMR spectra were measured with a JEOL ECX-400 or a JEOL ECA-600 spectrometers. FD mass spectra were recorded on a JEOL JMS-SX102A instrument at the GC-MS & NMR Laboratory of Faculty of Agriculture, Hokkaido University. Elemental analyses were carried out at the Center for Instrumental Analysis, Hokkaido University. Preparative recycling gel permeation chromatography (GPC) was performed with a JASCO LC9104. Cyclic voltammograms were recorded at room temperature by using an ALS model 606B electrochemical analyzer. The working and the counter electrodes were a glassy carbon and a Pt wire, respectively. The reference electrode was an Ag/AgNO₃ (Ag/Ag⁺). A Fc/Fc⁺ couple was observed at +0.22 V in the present condition. The sample solutions in CH₂Cl₂ containing *n*-Bu₄NClO₄ were deoxygenated by Ar flow.

Fréchet polybenzyl ether dendrimer bromides, G₁-Br, G₂-Br and G₃-Br, were prepared by

reported methods.² $(G_0)_2(C_3H_3N_2)Br$ (**1a**),³ $Me_2(C_3H_3N_2)I$ (**1e**),⁴ and $(Mes)_2(C_3H_3N_2)Cl$ (**1f**),⁵ $RhCl(COD)[Me_2(C_3H_2N_2)]$ (**2e**),⁴ and $RhCl(COD)[(Mes)_2(C_3H_2N_2)]$ (**2f**)⁵ were prepared according to previous reports. $RhCl(COD)[(G_0)_2(C_3H_2N_2)]$ (**2a**) was synthesized by the similar method that was used for **2b-d**.

$(G_1)_2(C_3H_3N_2)Br$ (1b): A suspension of imidazole (0.4 g, 6 mmol), G_1-Br (4.6 g, 12 mmol) and CsF-celite (1.2 g)⁶ in CH_3CN (50 cm³) was refluxed under Ar for 12 h. After the filtration of the suspension, filtrate and washings were concentrated to dryness. The resulting oil was purified by silica gel column chromatography. Materials eluted with $CHCl_3$ were discarded and the product eluted with 5-10% MeOH- $CHCl_3$ was collected. Removal of volatiles under vacuum gave a colorless solid. Yield 1.9 g (42%). Found: C, 68.85; H, 5.74; N, 3.54. Calcd. for $C_{45}H_{41}N_2O_4Br \cdot 2H_2O$: C, 68.44; H, 5.74; N, 3.55. ¹H NMR (400 MHz, $CDCl_3$): δ 10.55 (s, 1H, Im), 7.32–7.22 (m, 20H, Ph), 6.97 (s, 2H, Im), 6.62 (d, $J = 2.2$ Hz, 4H, Ph), 6.51 (t, $J = 2.2$ Hz, 2H, Ph), 5.32 (s, 4H, CH_2Im), 4.95 (s, 8H, CH_2Ph). ¹³C{¹H} NMR (100 MHz, $CDCl_3$): δ 160.4, 137.1 (Im, NCN), 136.3, 134.7, 128.5, 128.0, 127.6, 121.4 (Im), 107.9, 102.9, 70.2, 53.4 (CH_2-Im). FD-MS: $m/z = 673$ ($[M-Br]^+$).

$(G_2)_2(C_3H_3N_2)Br$ (1c): This salt was prepared with G_2-Br (6 mmol) by the similar method used for **1b**. Yield 2.4 g (50%). Found: C, 75.00; H, 5.63; N, 1.71. Calcd. for $C_{108}H_{89}N_2O_{12}Br$: C, 75.69; H, 5.60; N, 1.75. ¹H NMR (400 MHz, $CDCl_3$): δ 10.74 (s, 1H, Im), 7.34–7.21 (m, 40H, Ph), 6.83 (s, 2H, Im), 6.61 (d, $J = 2.2$ Hz, 8H, Ph), 6.56 (d, $J = 2.2$ Hz, 4H, Ph), 6.49 (4H+2H, Ph), 5.27 (s, 4H, CH_2Im), 4.93 (s, 16H, CH_2Ph), 4.90 (s, 8H, CH_2Ph). ¹³C{¹H} NMR (100 MHz, $CDCl_3$): δ 160.3, 160.0, 138.8, 137.4 (NCN, Im), 136.6, 134.7, 128.5, 127.9, 127.5, 121.3 (Im), 107.7, 106.4, 102.9, 101.5, 70.0, 69.9, 53.3 (CH_2-Im). FD-MS: $m/z = 1523$ ($[M-Br]^+$).

(G₃)₂(C₃H₃N₂)Br (1d): This salt was prepared with G₃-Br (3 mmol) by the similar method (but in THF) used for **1b**. After the purification by silica gel column chromatography, the product was further purified by preparative recycling GPC. Removal of volatiles under vacuum gave a colorless solid. Yield (44%). Found: C, 74.44; H, 5.60; N, 0.80. Calcd. for C₂₁₃H₁₈₅N₂O₂₈Br·CHCl₃: C, 75.15; H, 5.48; N, 0.82. ¹H NMR (600 MHz, CDCl₃): δ 10.94 (s, 1H, Im), 7.33~7.21 (m, 80H, Ph), 6.71 (s, 2H, Im), 6.62~6.47 (m, 42H, Ph), 5.19 (s, 4H, CH₂Im), 4.94~4.78 (m, 56H, CH₂Im). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ 160.3, 160.0, 159.9, 139.2, 138.9, 137.6 (NCN, Im), 136.7, 134.8, 128.5, 127.9, 127.5, 121.2 (Im), 107.6, 106.4, 106.3, 102.9, 101.6, 101.5, 70.0, 70.0, 69.9, 53.3 (CH₂-Im). FD-MS: *m/z* = 3221 ([M-Br]⁺).

RhCl(COD)[(G₁)₂(C₃H₂N₂)] (2b): A suspension of (G₁)₂(C₃H₃N₂)Br (**1b**) (150 mg, 0.2 mmol) and silver oxide (24 mg, 0.1 mmol) in 1,2-dichloroethane (20 cm³) was stirred at 50 °C for 12 h under Ar. After cooling to room temperature, [RhCl(COD)]₂ (50 mg, 0.1 mmol) and an excess amount of *n*-Bu₄NCl (100 mg, 0.36 mmol) were added to the reaction mixture. The resulting mixture was stirred at room temperature for 24 h under Ar. The suspension was filtered through Celite to remove insoluble materials, then the filtrate was concentrated to dryness. The residue was dissolved in CH₂Cl₂ and the solution was passed through a silica gel column. The first band eluted with CH₂Cl₂ contained [RhCl(COD)]₂ and was discarded. The second yellow band eluted with 5% acetone-CH₂Cl₂ (v/v) was collected and volatiles were evaporated to dryness. The crude product was dissolved in a small amount of CH₂Cl₂ and crystallized by adding *n*-pentane. The pale-yellow crystalline compound was collected by filtration, washed with *n*-pentane, and dried under vacuum. Yield 133 mg (72%). Found: C, 68.71; H, 5.85; N, 3.00. Calcd. for C₅₃H₅₂ClN₂O₄Rh: C, 69.24; H, 5.70; N, 3.05.

^1H NMR (600 MHz, CDCl_3): δ 7.34–7.26 (m, 20H, Ph), 6.63 (d, $J = 2.1$ Hz, 4H, Ph), 6.57 (s, 2H, NHC), 6.51 (t, $J = 2.1$ Hz, 2H, Ph), 5.87 (d, $J = 14.8$ Hz, 2H, $\text{CH}_2\text{-NHC}$), 5.50 (d, $J = 14.8$ Hz, 2H, $\text{CH}_2\text{-NHC}$), 5.01 (br, 2H, COD), 4.98–4.97 (m, 8H, CH_2Ph), 3.24 (br, 2H, COD), 2.28 (br, 4H, COD), 1.84 (br, 4H, COD). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 183.3 (d, $J_{\text{Rh-C}} = 50.8$ Hz, NCN), 160.2, 138.8, 136.7, 128.5, 127.9, 127.6, 120.9 (NHC), 107.3, 101.8, 98.8 (d, $J_{\text{Rh-C}} = 6.7$ Hz, COD), 70.1, 68.4 (d, $J_{\text{Rh-C}} = 14.3$ Hz, COD), 54.6 ($\text{CH}_2\text{-NHC}$), 32.9 (COD), 28.8 (COD). FD-MS: $m/z = 918$ ($[\text{M}]^+$).

RhCl(COD)[(G₂)₂(C₃H₂N₂)] (2c): The complex was synthesized with (G₂)₂(C₃H₃N₂)Br (**1c**) (0.2 mmol) by the similar method used for **2b**. After the purification of silica gel column chromatography, removal of volatiles under vacuum gave a yellow solid. Yield 261 mg (73%). Found: C, 74.06; H, 5.79; N, 1.57. Calcd. for C₁₀₉H₉₆ClN₂O₁₂Rh: C, 74.03; H, 5.70; N, 1.58. ^1H NMR (600 MHz, CDCl_3): δ 7.38–7.28 (m, 40H, Ph), 6.63 (8H, Ph), 6.56 (4H, Ph), 6.54 (s, 2H, NHC), 6.51 (4H, Ph), 6.51 (2H, Ph), 5.82 (d, $J = 14.8$ Hz, 2H, $\text{CH}_2\text{-NHC}$), 5.55 (d, $J = 14.8$ Hz, 2H, $\text{CH}_2\text{-NHC}$), 5.01 (br, 2H, COD), 4.97 (16H, CH_2Ph), 4.94–4.92 (8H, CH_2Ph), 3.22 (br, 2H, COD), 2.26 (br, 4H, COD), 1.82 (br, 4H, COD). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 183.4 (d, $J_{\text{Rh-C}} = 50.7$ Hz, NCN), 160.0, 160.0, 139.2, 139.0, 136.7, 128.6, 127.9, 127.6, 121.1 (NHC), 106.9, 106.3, 101.8, 101.5, 98.8 (d, $J_{\text{Rh-C}} = 6.7$ Hz, COD), 70.0, 69.9, 68.4 (d, $J_{\text{Rh-C}} = 14.3$ Hz, COD), 54.4 ($\text{CH}_2\text{-NHC}$), 32.9 (COD), 28.8 (COD). FD-MS: $m/z = 1768$ ($[\text{M}]^+$).

RhCl(COD)[(G₃)₂(C₃H₂N₂)] (2d): The complex was synthesized with (G₃)₂(C₃H₃N₂)Br (**1d**) (0.1 mmol) by the similar method used for **2b**. After the purification of silica gel column chromatography, removal of volatiles under vacuum gave a yellow solid. Yield 248 mg (71%). Found: C, 76.52; H, 5.81; N, 0.76. Calcd. for C₂₂₁H₁₉₆ClN₂O₂₈Rh: C, 76.58; H,

5.70; N, 0.81. ^1H NMR (600 MHz, CDCl_3): δ 7.40–7.31 (m, 80H, Ph), 6.67–6.51 (m, 42H, Ph), 6.58 (s, 2H, NHC), 5.90 (d, $J = 14.7$ Hz, 2H, $\text{CH}_2\text{-NHC}$), 5.49 (d, $J = 14.7$ Hz, 2H, $\text{CH}_2\text{-NHC}$), 5.06 (br, 2H, COD), 5.05~4.76 (m, 56H, CH_2Ph), 3.22 (br, 2H, COD), 2.27 (br, 4H, COD), 1.83 (br, 4H, COD). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 183.3 (d, $J_{\text{Rh-C}} = 47.6$ Hz, NCN), 160.0, 160.0, 159.9, 139.3, 139.1, 136.8, 136.7, 128.5, 127.8, 127.4, 121.0 (NHC), 106.9, 106.4, 106.3, 101.7, 101.5, 101.4, 98.6 (COD), 69.9, 69.9, 69.8, 68.4 (COD), 54.3 ($\text{CH}_2\text{-NHC}$), 32.8 (COD), 28.7 (COD). FD-MS: $m/z = 3466$ ($[\text{M}]^+$).

X-ray Diffraction Study.

Single crystals suitable for X-ray diffraction study were grown by slow diffusion of dichloromethane/*n*-pentane. Data of $\mathbf{2b}\cdot\text{CH}_2\text{Cl}_2$ were collected on a Rigaku/Saturn70 CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71070$ Å) at 113 K, and processed with CrystalClear program (Rigaku). The structures were solved by a direct method (SIR92),⁷ and refined by full-matrix least-square refinement on F^2 . The non-hydrogen atoms were refined anisotropically. All hydrogen atoms without those of a solvated dichloromethane molecule were located on the calculated positions and not refined. All calculations were performed using the CrystalStructure software package.⁸

Crystal data for $\text{RhCl}(\text{COD})[(\text{G}_1)_2(\text{C}_3\text{H}_2\text{N}_2)]\cdot\text{CH}_2\text{Cl}_2$ ($\mathbf{2b}\cdot\text{CH}_2\text{Cl}_2$): $\text{C}_{54}\text{H}_{54}\text{Cl}_3\text{N}_2\text{O}_4\text{Rh}$, $M = 1004.30$, $T = 113$ K, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.936(8)$, $b = 12.458(9)$, $c = 17.56(1)$ Å, $\alpha = 98.94(2)$, $\beta = 101.480(10)$, $\gamma = 91.966(11)^\circ$, $U = 2310(3)$ Å³, $Z = 2$, $\mu(\text{Mo } K\alpha) = 5.92$ cm⁻¹, Observed reflections 12898 ($I > 3\sigma(I)$), $R1$, $wR2 = 0.062$, 0.159. GOF = 1.013. Relatively large residual electron density peak (3.54 eÅ⁻³) was located near the position of Rh(1). CCDC Number 269270.

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