Electronic supplementary information

Rhodium(III) complexes with a bidentate *N*-heterocyclic carbene ligand bearing flexible dendritic frameworks

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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. Reagents and solvents were dried and purified before use by usual procedures.[1] ^{1}H NMR and ^{13}C{^{1}H} NMR, H-H COSY, and HSQC 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.

N-Methylimidazole was purchased from Wako. Fréchet-type polybenzylether dendrimer bromides, G_1-Br and G_2-Br, were prepared by a reported method.[2] G_0-Im (*N*-benzylimidazole: **1a**),[3] $[(G_0)(C_3H_3N_2)CH_2(C_3H_3N_2)(G_0)]I_2$ (**2a**)[4] and $[Me(C_3H_3N_2)CH_2(C_3H_3N_2)Me]I_2$ (**2d**)[5] were prepared according to previous reports.

G_1-Im (1b). A mixture of imidazole (2.0 g, 30 mmol), G_1-Br (11.5 g, 30 mmol), K_2CO_3 (4.2 g, 30 mmol), KOH (1.7 g, 30 mmol) and tetra(*n*-butyl)ammonium bromide (0.72 g, 1.5 mmol) in degassed toluene (200 cm^3) was refluxed under Ar for 19 h. After cooling at room temperature, the suspension was filtered with a celite pad and the filtrate was evaporated to dryness. The residue was dissolved in $CHCl_3$ and the solution was purified with silica gel column chromatography. The fraction eluted with 2% MeOH-$CHCl_3$ was corrected and removal of volatiles under vacuum gave a white solid. Yield 6.2 g (57%). Found: C, 77.85; H, 6.03; N, 7.55. $C_{24}H_{22}N_2O_2$ requires C, 77.81; H, 5.99; N, 7.56. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H, Im), 7.37–7.28 (m, 10H, Ph), 7.07 (s, 1H, Im), 6.86 (s, 1H, Im), 6.54 (t, *J* = 2.0 Hz, 1H, Ph), 6.34 (d, *J* = 2.0 Hz, 2H, Ph), 5.00 (s, 2H, CH_2Im), 4.96 (s, 4H, CH_2Ph). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.3, 138.5, 137.5, 136.4, 129.8, 128.6, 128.1, 127.5, 119.3, 106.3, 101.5, 70.1 (CH_2Ph), 50.7 (CH_2-Im). FD-MS: *m/z* = 370 ($[M]^+$).

G_2-Im (1c). This compound was prepared with G_2-Br (6 mmol scale) by the similar method used for **1b**. Yield 2.0 g (42%). Found: C, 78.12; H, 5.97; N, 3.34. $C_{52}H_{46}N_2O_6$ requires C, 78.57; H, 5.83; N, 3.52. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H, Im), 7.43–7.31 (m, 20H, Ph), 7.09(s, 1H, Im), 6.87 (s, 1H, Im), 6.65 (d, *J* = 2.0 Hz, 4H, Ph), 6.58 (t, *J* = 2.2 Hz, 2H, Ph), 6.53 (t, *J* = 2.0 Hz, 1H, Ph), 6.34 (d, *J* = 2.0 Hz, 2H, Ph), 5.02 (s, 8H, CH_2Ph), 4.99 (s, 2H, CH_2Im), 4.91 (s, 4H, CH_2Ph). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.2, 160.0, 138.8, 138.5, 137.4, 136.6, 129.8, 128.5, 127.9, 127.5, 119.3, 106.3, 106.2, 101.5, 101.4, 70.0 (CH_2Ph), 69.9 (CH_2Ph), 50.6 (CH_2-Im). FD-MS: *m/z* = 794 ($[M]^+$).

$[(G_1)(C_3H_3N_2)CH_2(C_3H_3N_2)(G_1)]I_2$ (2b). A solution of G_1-Im (**1b**) (3.7 g, 10 mmol) and CH_2I_2 (1.4 g, 5 mmol) in toluene (20 cm^3) was refluxed under Ar for 19 h. The white precipitate was collected by filtration, washed with cold toluene, and dried under vacuum.

Yield 3.1 g (61%). Found: C, 58.21; H, 4.61; N, 5.55. $C_{49}H_{46}I_2N_4O_4$ requires C, 58.34; H, 4.60; N, 5.55. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 2H, Im), 8.62 (s, 2H, Im), 7.39 (s, 2H, Im), 7.32–7.22 (m, 20H, Ph), 6.99 (s, 2H, Im-C*H*$_2$-Im), 6.63 (d, *J* = 2.0 Hz, 4H, Ph), 6.51 (t, *J* = 2.0 Hz, 2H, Ph), 5.19 (s, 4H, C*H*$_2$Im), 4.95 (s, 8H, C*H*$_2$Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.5, 137.7 (Im), 136.3, 133.5, 128.6, 128.1, 127.7, 122.9 (Im), 121.9 (Im), 108.4, 103.4, 70.4, 57.4, 54.1. FD-MS: *m/z* = 881 ([M-I]$^+$).

[(G$_2$)(C$_3$H$_3$N$_2$)CH$_2$(C$_3$H$_3$N$_2$)(G$_2$)]I$_2$ (2c). A solution of G$_2$-Im (**1c**) (4.0 g, 5 mmol) and CH_2I_2 (0.7 g, 2.5 mmol) in toluene (20 cm^3) was refluxed under Ar for 24 h. The reaction mixture was evaporated to dryness. The residue was purified with silica gel column chromatography by using $CHCl_3$ as an eluent. A colorless fraction eluted with 10% MeOH-$CHCl_3$ was collected. Removal of volatiles under vacuum gave a white solid. Yield 1.3 g, (28%). Found: C, 66.45; H, 5.18; N, 3.14. $C_{105}H_{94}I_2N_4O_{12}\cdot(CHCl_3)_{0.5}$ requires C, 66.09; H, 4.97; N, 2.92. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 2H, Im), 8.54 (s, 2H, Im), 7.32–7.22 (m, 42H, Ph + Im), 6.85 (s, 2H, Im-C*H*$_2$-Im), 6.60 (8H, Ph), 6.58 (4H, Ph), 6.48 (m, 6H, Ph), 5.06 (s, 4H, C*H*$_2$Im), 4.90 (s, 16H, C*H*$_2$Ph), 4.88 (s, 8H, C*H*$_2$Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.4, 160.0, 138.8, 137.6 (Im), 136.6, 133.4, 128.5, 127.9, 127.6, 122.9 (Im), 121.8 (Im), 108.2, 106.5, 103.5, 101.4, 70.1, 70.0, 57.2, 54.1. FD-MS: *m/z* = 1731 ([M-I]$^+$).

RhI$_2$(OAc)[(G$_0$)(C$_3$H$_2$N$_2$)CH$_2$(C$_3$H$_2$N$_2$)(G$_0$)] (3a). A mixture of $[RhCl(COD)]_2$ (200 mg, 0.4 mmol), $[(G_0)(C_3H_3N_2)CH_2(C_3H_3N_2)(G_0)]I_2$ (**2a**) (467 mg, 0.8 mmol), KI (332 mg, 2 mmol), and KOAc (392 mg, 4 mmol) was stirred in CH_3CN (20 cm^3) at 65 ^{o}C for 16 h. After cooling at room temperature, insoluble materials were removed by filtration and the filtrate was evaporated to dryness. The crude product was dissolved in CH_2Cl_2 and the solution was passed through a silica gel column (2×15 cm, solvent: CH_2Cl_2). The second orange band eluted with CH_2Cl_2-acetone (5:1, v/v) was collected and evaporated to dryness. The residue was re-dissolved in a small amount of CH_2Cl_2 and precipitated by adding *n*-pentane. The orange precipitate was collected by filtration, washed with *n*-pentane, and dried under vacuum. Yield 170 mg (29%). Found: C, 37.29; H, 3.15; N, 7.78. $C_{23}H_{23}I_2N_4O_2Rh$ requires C, 37.12; H, 3.12; N, 7.53. ^1H NMR (600 MHz, DMSO-d_6) δ 7.57–7.56 (m, 6H, Im + Ph), 7.37–7.29 (m, 8H, Ph), 6.18 (s, 2H, NHC-C*H₂*-NHC), 5.60 (s, 4H, CH_2Ph), 1.78 (s, 3H, CH_3CO). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 187.0 (CH_3*C*O), 151.5 (d, $J_{Rh\text{-}C}$ = 41.6 Hz, N*C*N), 137.2, 129.0, 128.4, 127.9, 123.2 (NHC), 122.6 (NHC), 62.2 (NHC-*C*H_2-NHC), 52.8 (*C*H_2Ph), 24.3 (*C*H_3CO). FD-MS: *m/z* = 744 ($[M-H]^+$).

$RhI_2(OAc)[(G_1)(C_3H_2N_2)CH_2(C_3H_2N_2)(G_1)]$ (3b). A mixture of $[RhCl(COD)]_2$ (50 mg, 0.1 mmol), $[(G_1)(C_3H_3N_2)CH_2(C_3H_3N_2)(G_1)]I_2$ (**2b**) (202 mg, 0.2 mmol), KI (83 mg, 0.5 mmol), and KOAc (98 mg, 1 mmol) was stirred in CH_3CN (50 cm^3) at 65 °C for 16 h. After cooling at room temperature, insoluble materials were removed by filtration and the residue was washed with hot CH_3CN. Removal of the solvent gave orange solids. The solids were collected by filtration, washed with a mixed solvent of CH_3CN and *n*-pentane (1:3, v/v), and dried under vacuum. Yield 105 mg (45%). Found: C, 52.67; H, 4.16; N, 5.74. $C_{51}H_{47}I_2N_4O_6Rh\cdot CH_3CN$ requires C, 52.62; H, 4.17; N, 5.79. ^1H NMR (600 MHz, $CDCl_3$) δ 7.43–7.27 (m, 20H, Ph), 6.92 (d, *J* = 1.8 Hz, 2H, Im), 6.84 (d, *J* = 1.8 Hz, 2H, Im), 6.83 (d, *J* = 2.4 Hz, 4H, Ph), 6.58 (t, *J* = 2.4 Hz, 2H, Ph), 5.95 (s, 2H, NHC-C*H₂*-NHC), 5.59 (s, 4H, C*H₂*Ph), 5.05 (s, 8H, C*H₂*Ph), 1.94 (s, 3H, CH_3CO). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 188.9 (CH_3*C*O), 160.2, 155.0 (d, $J_{Rh\text{-}C}$ = 41.6 Hz, N*C*N), 138.3, 136.8, 128.5, 127.9, 127.6, 123.0 (NHC), 120.6 (NHC), 108.5, 102.5, 70.3 (*C*H_2Ph), 63.3 (NHC-*C*H_2-NHC), 54.5 (*C*H_2Ph), 24.8 (*C*H_3CO). FD-MS: *m/z* = 1168 ($[M-H]^+$).

RhI$_2$(OAc)[(G$_2$)(C$_3$H$_2$N$_2$)CH$_2$(C$_3$H$_2$N$_2$)(G$_2$)] (3c). A mixture of [RhCl(COD)]$_2$ (50 mg, 0.1 mmol), [(G$_2$)(C$_3$H$_3$N$_2$)CH$_2$(C$_3$H$_3$N$_2$)(G$_2$)]I$_2$ (**2c**) (371 mg, 0.2 mmol), KI (83 mg, 0.5 mmol), and KOAc (98 mg, 1 mmol) was stirred in CH$_3$CN (20 cm^3) at 65 ^{o}C for 2 days. After cooling at room temperature, the insoluble materials were removed by filtration and the filtrate was evaporated to dryness. The crude product was dissolved in CH$_2$Cl$_2$ and passed through a silica gel column (2×15 cm, solvent CH$_2$Cl$_2$). The orange band eluted with CH$_2$Cl$_2$-acetone (5:1, v/v) was collected and evaporated to dryness. The residue was re-dissolved in a small amount of CH$_2$Cl$_2$ and precipitated by adding *n*-pentane. The orange powder was collected by filteration, washed with *n*-pentane, and dried under vacuum. Yield 223 mg (55%). Found: C, 63.69; H, 4.87; N, 2.71. C$_{107}$H$_{95}$I$_2$N$_4$O$_{14}$Rh requires C, 63.40; H, 4.75; N, 2.78. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.41–7.30 (m, 40H, Ph), 6.69–6.65 (m, 14H, Ph + Im), 6.61 (s, 2H, Im), 6.54–6.53 (m, 6H, Ph), 5.58 (m, 6H, NHC-CH_2-NHC + CH_2Ph), 4.99 (24H, CH_2Ph), 1.91 (s, 3H, CH_3CO). ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ 188.9 (CH$_3$*C*O), 160.0, 159.9, 154.8 (d, $J_{\text{Rh-C}}$ = 41.7 Hz, N*C*N), 139.3, 138.4, 136.7, 128.6, 128.0, 127.6, 122.9 (NHC), 120.6 (NHC), 107.9, 106.4, 102.6, 101.4, 70.1 (*C*H$_2$Ph), 69.9 (*C*H$_2$Ph), 63.1 (NHC-*C*H$_2$-NHC), 54.3 (*C*H$_2$Ph), 24.8 (*C*H$_3$CO). FD-MS: *m/z* = 2018 ([M+H]$^+$).

RhI$_2$(OAc)[Me(C$_3$H$_2$N$_2$)CH$_2$(C$_3$H$_2$N$_2$)Me] (3d). This complex was prepared with [Me(C$_3$H$_3$N$_2$)CH$_2$(C$_3$H$_3$N$_2$)Me]I$_2$ (**2d**) (0.4 mmol) by the similar method used for **3a**. Yield 35 mg (15%). Found: C, 22.41; H, 2.56; N, 9.30. C$_{11}$H$_{15}$I$_2$N$_4$O$_2$Rh requires C, 22.32; H, 2.55; N, 9.46. ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 7.57 (d, *J* = 2.4 Hz, 2H, Im), 7.54 (d, *J* = 2.4 Hz, 2H, Im), 6.10 (s, 2H, NHC-CH_2-NHC), 3.92 (s, 6H, NHC-CH_3), 1.82 (s, 3H, CH_3CO). ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ 186.5 (CH$_3$*C*O), 151.3 (d, $J_{\text{Rh-C}}$ = 43.1 Hz, N*C*N), 125.0 (NHC), 121.5 (NHC), 62.0 (NHC-*C*H$_2$-NHC), 37.5 (NHC-*C*H$_3$), 24.2 (*C*H$_3$CO).

Calculation

An optimized structure of **3c** was obtained by ONIOM[6] calculations by using an initial structure generated with CAChe[7]/CONFLEX[8]/MM3[9]. In the ONIOM calculation, the molecular system of **3c** was divided into two layers. The high layer was assigned to **3c** with a $RhI_2(OAc)[(C_3H_2N_2)CH_2(C_3H_2N_2)]$ core for B3LYP[10]/LANL2DZ[11] calculation. The low layer contains the rest dendritic frameworks of **3c** for molecular mechanics calculation using UFF force field.[12] All calculations were performed with the Gaussian 03 program[10] on a HIT HPC-IA642/SS 1.3/3D-4G.

X-ray Diffraction Study. A summary of crystal structure refinements of $RhI_2(OAc)[(G_0)(C_3H_2N_2)CH_2(C_3H_2N_2)(G_0)]\cdot C_4H_8O$ (**3a**·THF), $RhI_2(OAc)[(G_1)(C_3H_2N_2)CH_2(C_3H_2N_2)(G_1)]\cdot CH_3CN$ (**3b**·CH_3CN) and $RhI_2(OAc)[Me(C_3H_2N_2)CH_2(C_3H_2N_2)Me]$ (**3d**) was given in Table S1. Single crystals of (**3a**·THF) suitable for X-ray diffraction study were obtained by diffusion of *n*-pentane into **3a** in THF. Single crystals of **3b**·CH_3CN and **3d** were obtained by slow evaporation of **3b** or **3d** in CH_3CN. Data were collected on a Rigaku/Saturn70 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) at 113 K, and processed using CrystalClear (Rigaku). The structures were solved by a heavy-atom Patterson method (SHELX97) and refined by full-matrix least-square refinement on F^2. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on the calculated positions and not refined. All calculations were performed using the CrystalStructure software package. CCDC Numbers 633257, 633258 and 633259.

Table S1. Crystallographic Data of $RhI_2(OAc)[(G_0)(C_3H_2N_2)CH_2(C_3H_2N_2)(G_0)]\cdot THF$ (**3a**·THF), $RhI_2(OAc)[(G_1)(C_3H_2N_2)CH_2(C_3H_2N_2)(G_1)]\cdot CH_3CN$ (**3b**·CH_3CN) and $RhI_2(OAc)[Me(C_3H_2N_2)CH_2(C_3H_2N_2)Me]$ (**3d**).

	3a·THF	**3b**·CH_3CN	**3d**
empirical formula	$C_{23}H_{23}I_2N_4O_2Rh\cdot C_4H_8O$	$C_{51}H_{47}I_2N_4O_6Rh\cdot C_2H_3N$	$C_{11}H_{15}I_2N_4O_2Rh$
formula weight	816.28	1209.72	591.98
temp / K	113	113	113
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	Cc (#5)
a / Å	12.126(5)	9.338(4)	9.685(2)
b / Å	14.786(6)	13.972(6)	13.321(3)
c / Å	15.987(6)	20.243(8)	12.691(3)
α / deg	90	72.083(12)	90
β / deg	92.446(6)	85.57(1)	94.340(2)
γ / deg	90	78.379(9)	90
V / Å^3	2863(2)	2461(2)	1632.6(7)
Z	4	2	4
ρ_{cacd}/g cm^{-3}	1.893	1.632	2.408
unique reflections	6455	10345	2075
observed reflections	5511, $I>2\sigma(I)$	8789, $I>2\sigma(I)$	2074, $I>2\sigma(I)$
GOF	0.993	1.072	1.088
$R1$, $wR2$ (all data) [a]	0.042, 0.098 [b]	0.043, 0.102 [c]	0.019, 0.059 [d]

[a] $R1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$, $wR2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$, [b] $w = 1/[\sigma(F_o^2)]/(4F_o^2)$, [c] $w = 1/[0.002F_o^2 + \sigma(F_o^2)]/(4F_o^2)$, [d] $w = 1/[0.0005F_o^2 + 0.2\sigma(F_o^2)]/(4F_o^2)$.

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