Supporting Information for

Inversion of Axial Chirality in Coordinated Bis-β-diketonato Ligands

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Figure S1. The HPLC chromatogram for the fraction containing [Ru(acac)$_2$(baetH)]. The mixture was eluted on a silica gel column (Inertsil, GL Science Inc., Japan) with a solvent of 95:5 (v/v) benzene-acetonitrile at a flow rate of 1.0 ml/min. The absorbance of the eluate was monitored at 600 nm. Peaks F$_{10}$ at 9.8 min and F$_{11}$ at 10.5 min (as denoted in the figure) were assigned to the two diastereomers (see text). The other small peaks were impurities.
Figure S2. The HPLC chromatogram for the fraction containing [Ru(acac)₂(baet)Ru(acac)₂]. The mixture was eluted on a silica gel column (Inertsil, GL Science Inc. (Japan)) with a solvent of 8:2 (v/v) benzene-acetonitrile at a flow rate of 0.5 ml/min. The absorbance of the eluate was monitored at 600 nm. Peaks F₉ at 27.4 min, F₁₁ at 34.9 min and F₁₂ at 36.7 min (as denoted in the figure) were assigned to the meso-type, a racemic and the other racemic dinuclear complexes, respectively (see text).
The $^1$H NMR spectra (400 MHz, CDCl$_3$) and mass analyses of free ligands and fractions B$_{11}$, B$_{12}$, B$_{31}$, B$_{32}$ and B$_{33}$.

dabeH$_2$ as HL-LH

dabeH$_2$: $\delta$ = 2.0 (s, 6H, CH$_3$), 5.9 (s, 2H, CH), 7.0–8.0 (m, 10H, arom.); $m/z$ = 322 (calc. 322).

B$_{11}$: [Ru(acac)$_2$(dabeH)]. $\delta$ = -12.18 (3H, CH$_3$), -10.88 (3H, CH$_3$), -8.69 (3H, CH$_3$), 1.19 (3H, CH$_3$), 3.95 (3H, CH$_3$), 4.55 (2H, arom.), 5.49 (2H, arom.), 6.34 (1H, arom.), 6.65 (2H, arom.), 9.03 (1H, arom.), 9.98 (2H, arom.), 15.66 (1H, OH); $m/z = 620$ (calc. for $^{102}$Ru: 621).

B$_{12}$: [Ru(acac)$_2$(dabeH)]. $\delta$ = -10.48 (3H, CH$_3$), -8.85 (3H, CH$_3$), -5.87 (3H, CH$_3$), -2.07 (3H, CH$_3$), 0.71 (3H, CH$_3$), 0.77 (3H, CH$_3$), 4.65 (2H, arom.), 5.77 (2H, arom.), 6.23 (1H, arom.), 6.74 (2H, arom.), 8.91 (1H, arom.), 9.64 (2H, arom.), 15.49 (1H OH); $m/z = 620$ (calc. for $^{102}$Ru: 621).

B$_{31}$: ΔΛ-[Ru(acac)$_2$(dabe)Ru(acac)$_2$]. $\delta$ = -34.20 (2H, CH), -17.61 (2H, CH), -14.30 (3H, CH$_3$), -12.70 (3H, CH$_3$), -11.59 (3H, CH$_3$), -11.03 (3H, CH$_3$), -9.70 (3H, CH$_3$), -6.52 (3H, CH$_3$), 0.12 (3H, CH$_3$), 2.28 (3H, CH$_3$), 3.77 (3H, CH$_3$), 4.52 (2H, arom.), 4.67 (2H, arom.), 5.47 (3H, CH$_3$), 8.02 (2H, arom.), 8.34 (4H, arom.); $m/z = 918$ (calc. for $^{102}$Ru: 920).

B$_{32}$: ΔΔ-(or ΛΛ)-[Ru(acac)$_2$(dabe)Ru(acac)$_2$]. $\delta$ = -35.10 (2H, CH), -16.10 (2H, CH), -15.3 (6H, CH$_3$), -10.13 (6H, CH$_3$), -6.90 (6H, CH$_3$), 0.77 (6H, CH$_3$), 4.01 (4H, arom.), 4.70 (6H, CH$_3$), 6.26 (4H, arom.), 7.58 (2H, arom.); $m/z = 918$ (calc. for $^{102}$Ru: 920).

B$_{33}$: ΔΔ-(or ΛΛ)-[Ru(acac)$_2$(dabe)Ru(acac)$_2$]. $\delta$ = < -40 (2H, CH), -14.30 (6H, CH$_3$), -6.90 (6H, CH$_3$), 0.77 (6H, CH$_3$), 4.01 (4H, arom.), 4.70 (6H, CH$_3$), 6.26 (4H, arom.), 8.92 (4H, arom.); $m/z = 918$ (calc. for $^{102}$Ru: 920).

baetH$_2$ as HL-LH

baetH$_2$: $\delta$ = 0.91 (d, 12H, CH$_3$), 1.98 (s, 6H, COCH$_3$), 2.11 (d, 4H, CH$_2$), 2.1–2.2 (m, 2H, CH), 17.05 (s, 2H, OH); $m/z = 282$ (calc. 282).

B$_{11}$: [Ru(acac)$_2$(baetH)]. $\delta$ = -33.7 (1H, CH), -23.3 (1H, CH), -12.40 (1H, COCH$_2$), -10.92 (1H, COCH$_2$), -10.36 (3H, CH$_3$), -5.59 (3H, CH$_3$), -2.96 (3H, CH$_3$), -0.32 (3H, CH$_3$), 0.34 (3H, CH$_3$), 0.46 (3H, CH$_3$), 0.85 (3H, CH$_3$), 1.75 (3H, CH$_3$), 2.1 (1H, CHMe$_2$), 2.40 (3H, COCH$_3$), 2.45 (2H, COCH$_2$), 9.68 (1H, CHMe$_2$), 15.66 (1H, OH); $m/z = 580$ (calc. for $^{102}$Ru: 581).

B$_{12}$: [Ru(acac)$_2$(baetH)]. $\delta$ = -32.6 (1H, CH), -22.6 (1H, CH), -11.32 (1H, COCH$_2$), -10.72 (3H, CH$_3$), -10.08 (1H, COCH$_2$), -9.34 (3H, CH$_3$), -4.48 (3H, CH$_3$), -2.90 (3H, CH$_3$), -1.16 (3H, CH$_3$), -0.32 (d, 3H, CH$_3$), 0.60 (d, 3H, CH$_3$), 1.14 (d, 3H, CH$_3$), 1.20 (d, 3H, CH$_3$), 1.20 (3H, COCH$_3$), 1.57 (2H, COCH$_2$), 8.36 (1H, CHMe$_2$), 15.47 (1H, OH); $m/z = 580$ (calc. for $^{102}$Ru: 581).

B$_{31}$: ΔΛ-[Ru(acac)$_2$(baet)Ru(acac)$_2$]. $\delta$ = -29.8 (1H, CH), -28.5 (1H, CH), -22.7 (1H, CH), -22.1 (1H, CH), -19.59 (1H, COCH$_2$), -18.29 (1H, COCH$_2$), -15.67 (1H, COCH$_2$), -14.96 (1H, COCH$_2$), -13.73 (3H), -13.01 (3H), -7.88 (3H), -7.37 (3H), -3.87 (3H), -3.46 (3H), -2.84 (3H), -2.83 (3H), -1.07 (3H), -0.62 (3H), 0.08 (3H), 0.44 (3H), 0.93 (3H), 0.94 (3H), 9.67 (2H); $m/z = 879$ (calc. for $^{102}$Ru: 880).
\[ \begin{align*}
\textbf{B32: } & \Delta \Delta - [\text{Ru(acac)}_2(\text{baet})\text{Ru(acac)}_2]. \quad \delta = -28.3 \ (2H, \text{CH}), -24.4 \ (2H, \text{CH}), -16.91 \ (2H, \text{COCH}_2), -16.44 \ (2H, \text{COCH}_2), -13.07 \ (6H), -7.27 \ (6H), -3.95 \ (6H), -3.02 \ (6H), -1.09 \ (6H), -0.63 \ (6H), \\
& 1.59 \ (6H), 10.05 \ (2H, \text{CHMe}_2); \ m/z = 879 \ (\text{calc. for } ^{102}\text{Ru}: 880). \\
\textbf{B33: } & \Delta \Delta - [\text{Ru(acac)}_2(\text{baet})\text{Ru(acac)}_2]. \quad \delta = -31.9 \ (2H, \text{CH}), -20.2 \ (2H, \text{CH}), -15.16 \ (2H, \text{COCH}_2), -14.73 \ (2H, \text{COCH}_2), -11.85 \ (6H), -8.37 \ (6H), -5.08 \ (6H), -2.93 \ (6H), -1.81 \ (6H), 1.53 \ (12H), \\
& 7.37 \ (2H, \text{CHMe}_2); \ m/z = 879 \ (\text{calc. for } ^{102}\text{Ru}: 880). \\
\end{align*} \]

dpeH\textsubscript{2} as HL-LH

\[ \begin{align*}
dpeH\textsubscript{2}: \delta = 1.12 \ (t, \ 6H, \text{CH}_3), 2.01 \ (s, \ 6H, \text{COCH}_3), 2.30 \ (q, \ 4H, \text{CH}_2), 16.87 \ (s, \ 2H, \text{OH}); \ m/z = 226 \ (\text{calc. 226}). \\
\end{align*} \]

\[ \begin{align*}
\textbf{B11: } & [\text{Ru(acac)}_2(\text{dpeH})]. \quad \delta = -12.57 \ (1H, \text{COCH}_2), -10.78 \ (3H, \text{CH}_3), -9.95 \ (3H, \text{CH}_3), -8.48 \ (1H, \\
& \text{COCH}_2), -6.43 \ (3H, \text{CH}_3), -3.31 \ (3H, \text{CH}_3), 0.68 \ (3H, \text{CH}_3), 2.37 \ (3H), 3.58 \ (2H, \text{CH}_2), 16.01 \ (1H, \text{OH}). \quad \text{Some signals in 1.0-1.8 ppm were obscured due to overlap with the signal of residual water in the solvent; } \ m/z = 524 \ (\text{calc. for } ^{102}\text{Ru: 525}). \\
\textbf{B12: } & [\text{Ru(acac)}_2(\text{dpeH})]. \quad \delta = -12.46 \ (3H, \text{CH}_3), -9.85 \ (3H, \text{CH}_3), -8.41 \ (1H, \text{COCH}_2), -8.05 \ (3H, \text{CH}_3), -5.44 \ (1H, \text{CH}_2), -1.56 \ (3H, \text{CH}_3), 1.89 \ (3H), 3.90 \ (2H, \text{CH}_2), 16.08 \ (1H, \text{OH}). \quad \text{Some signals in 1.0-1.8 ppm were obscured due to overlap with the signal of residual water in the solvent; } \ m/z = 524 \ (\text{calc. for } ^{102}\text{Ru: 525}). \\
\textbf{B31: } & \Delta \Lambda - [\text{Ru(acac)}_2(\text{dpe})\text{Ru(acac)}_2]. \quad \delta = -12.07 \ (3H, \text{CH}_3), -11.40 \ (3H, \text{CH}_3), -11.02 \ (2H, \text{COCH}_2), -10.95 \ (3H, \text{CH}_3), -10.23 \ (2H, \text{COCH}_2), -8.95 \ (3H, \text{CH}_3), -7.29 \ (3H, \text{CH}_3), -5.00 \ (3H, \text{CH}_3), -2.81 \ (3H, \text{CH}_3), -0.47 \ (3H, \text{CH}_3), 0.59 \ (3H, \text{CH}_3), 2.72 \ (3H, \text{CH}_3), 3.69 \ (3H, \text{CH}_3), 4.41 \ (3H, \text{CH}_3); \ m/z = 822 \ (\text{calc. for } ^{102}\text{Ru: 824}). \\
\textbf{B32: } & \Delta \Delta - (or \Lambda \Lambda) - [\text{Ru(acac)}_2(\text{dpe})\text{Ru(acac)}_2]. \quad \delta = -11.51 \ (12H, \text{CH}_3), -11.16 \ (2H, \text{COCH}_2), -10.19 \ (2H, \text{COCH}_2), -7.31 \ (6H, \text{CH}_3), -0.99 \ (6H, \text{CH}_3), 2.40 \ (6H, \text{CH}_3), 4.01 \ (6H, \text{CH}_3); \ m/z = 822 \ (\text{calc. for } ^{102}\text{Ru: 824}). \\
\textbf{B33: } & \Delta \Delta - (or \Lambda \Lambda) - [\text{Ru(acac)}_2(\text{dpe})\text{Ru(acac)}_2]. \quad \delta = -11.66 \ (4H, \text{COCH}_2), -10.46 \ (6H, \text{CH}_3), -9.70 \ (6H, \text{CH}_3), -5.53 \ (6H, \text{CH}_3), -2.78 \ (6H, \text{CH}_3), 0.50 \ (6H, \text{CH}_3), 3.07 \ (6H, \text{CH}_3); \ m/z = 822 \ (\text{calc. for } ^{102}\text{Ru: 824}). \\
\end{align*} \]
Figure S3. The HPLC chromatograms for ΔΛ-[Ru(acac)_2(dabe)Ru(acac)_2] (top), ΔΛ-[Ru(acac)_2(baet)Ru(acac)_2] (middle) and ΔΛ-[Ru(acac)_2(dpe)Ru(acac)_2] (bottom). Each racemate was eluted on a chiral column (4 mm (i.d.) × 25 cm) packed with an ion-exchange adduct of Δ-[Ru(phen)_3]^{2+} (phen = 1,10-phenanthroline) and synthetic hectorite at a flow rate of 0.5 ml/min. The eluting solvent was a mixture of methanol and chloroform. The absorbance of the eluate was monitored at 600 nm.

Figure S4. (left) The electronic spectra of methanol solutions of ΔΛ-[Ru(acac)_2(baet)Ru(acac)_2] (black line) and ΔΛ-[Ru(acac)_2(dpe)Ru(acac)_2] (red line).
(right) The electronic spectra of methanol solutions of the two diastereomers of [Ru(acac)_2(dabeH)], \textbf{B}_{11} (red line) and \textbf{B}_{12} (black line).
Figure S5. (left) The ECD spectra of methanol/chloroform solutions of the first (black) and the second (red) fractions when the diastereomer of \([\text{Ru(acac)}_2(\text{dabeH})]\)(B\text{12}) was eluted on the chiral column; (right) The ECD spectrum of a methanol solution of the first fraction when the diastereomer of \([\text{Ru(acac)}_2(\text{dabeH})]\), B\text{11}, was eluted on the chiral column (red). For comparison, the ECD spectrum of the first fraction for B\text{12} is also included (black).

Figure S6. The ECD (left) and VCD (right) spectra of \(\Delta\Delta\)- (dotted line) or \(\Lambda\Lambda\)- (solid line) \([\text{Ru(acac)}_2(\text{baet})\text{Ru(acac)}_2]\).
Figure S7. The change of the $^1$H NMR spectra of the two diastereomers of $\Delta$-[Ru(acac)$_2$(dabeH)] with time. The reactions started from B$_{11}$ (left) and B$_{12}$ (right), respectively; (a) 0, (b) 2, (c) 5, (d) 8, (e) 16 and (f) 25 hours. The solvents were CDCl$_3$.

Figure S8. The optimized structures of $\Delta$-[Ru(acac)$_2$(S-dabeH)] (left) and $\Delta$-[Ru(acac)$_2$(R-dabeH)] (right) by the DFT calculation (see text). The total energy of each diastereomer is calculated as below:

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<th>diastereomer</th>
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<td>$\Delta$-[Ru(acac)$_2$(S-dabeH)]</td>
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