Supplementary Information

Structural Diversity of Bimetallic Rhodium and Iridium Half Sandwich Dithiolato Complexes

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1. Experimental Procedures

1.1 Synthesis of 1

To a solution of $RhCl_3 \cdot 3H_2O$ (5.00 g, 18.9 mmol) in MeOH (50 mL) was added 1,2,3,4,5-pentamethylcyclopentadiene (3.22 g, 3.70 mL, 23.7 mmol) and the reaction refluxed for 48 hrs. A red precipitate was filtered and the filtrate put on ice for 1 hr to allow more product to form. The combined filtrands were washed with EtOH (100 mL) then ether (100 mL) and dried under vacuum (5.36 g, 8.67 mmol, 92%). Crystals suitable for X-ray work were obtained from 1,2-dichloroethane. Anal. calcd. for $C_{20}H_{30}Cl_4Rh_2$ (615.92 g mol^{-1}): C, 38.96; H, 4.90. Found: C, 38.89; H, 4.90. IR (KBr): ν_{max}/cm^{-1} 2972w (ν_{Ar-H}), 2918m (ν_{C-H}), 1466s, 1371s, 1027s, 452w. Raman (glass capillary): ν_{max}/cm^{-1} 2968w (ν_{Ar-H}), 2912s (ν_{C-H}), 1426w, 593s, 452s, 270m (ν_{Rh-Cl}), 196m (ν_{Rh-Cl}). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.62 (15 H, s, Cp-C$\underline{H}_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 94.1 (C_q, d, $^1J_{CRh}$ = 9.5 Hz, $\underline{C}$-CH_3), 9.4 (C-$\underline{C}H_3$) MS (ES+): *m/z* 577.00 (M − Cl_2+OMe, 60%), 546.98 (M − Cl_2+H, 100).

1.2 Synthesis of 2

This was prepared as per compound **1** using $IrCl_3 \cdot 3H_2O$ (5.00 g, 14.2 mmol) and 1,2,3,4,5-pentamethylcyclopentadiene (2.91 g, 3.34 mL, 21.3 mmol). **2** was obtained as a yellow solid (4.64 g, 5.82 mmol, 82%). Crystals suitable for X-ray work were obtained from 1,2-dichloroethane. Anal. calcd. for $C_{20}H_{30}Cl_4Ir_2$ (796.03 g mol^{-1}): C, 30.14; H, 3.78. Found: C, 30.11; H, 3.82. IR (KBr): ν_{max}/cm^{-1} 2987m (ν_{Ar-H}), 2916m (ν_{C-H}), 1450s, 1373s, 1033s, 466w. Raman (glass capillary): ν_{max}/cm^{-1} 2970m (ν_{Ar-H}), 2917s (ν_{C-H}), 1424m, 590s, 542m, 461m, 449s, 286m (ν_{Ir-Cl}). ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.58 (15 H, s, Cp-C$\underline{H}_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 86.2 (C_q, $\underline{C}$-CH_3), 9.3 (C-$\underline{C}H_3$). MS (ES+): *m/z* 747.21 (M – CH_2Cl, 100%).

1.3 Synthesis of 3a

$[Cp^*RhCl_2]_2$ (100 mg, 0.16 mmol) was added to THF (25 mL) followed by **H_2a** (75 mg, 0.52 mmol) and the reaction refluxed for 2 hrs; during which time the solution turned purple. The solvent was removed under vacuum and the crude product heated to 60 °C under vacuum to remove excess ligand. The purple solid was purified by column chromatography (silica/CH_2Cl_2) resulting in a purple solid (101 mg, 0.13 mmol, 84%). Crystals suitable for X-ray work were obtained from CH_2Cl_2. Anal. calcd. for $C_{32}H_{38}Rh_2S_4$ (756.70 g mol^{-1}): C, 50.79; H, 5.06. Found: C, 50.70; H, 5.13. IR (KBr): ν_{max}/cm^{-1} 3042w (ν_{Ar-H}), 2915m (ν_{C-H}), 1561m, 1438s, 1377s, 1239m, 1021s, 762s, 740s. Raman (glass capillary): ν_{max}/cm^{-1} 2907m (ν_{C-H}), 1539m, 1439m, 1090s, 1020m, 613m (ν_{C-S}), 494m, 431m. ***Mono complex*** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.85 (2 H, dd, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 3.3 Hz, Ar-$\underline{H}$), 7.08 (2 H, dd, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 3.3 Hz, Ar-$\underline{H}$), 2.04 (15 H, s, C-C$\underline{H}_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.5 (C_q, Ar-$\underline{C}$), 130.0 (CH, Ar-$\underline{C}$), 122.5 (CH, Ar-$\underline{C}$), 98.4 (C_q, d, $^1J_{CRh}$ = 7.1 Hz, $\underline{C}$-CH_3), 10.7 (C-$\underline{C}H_3$). ***Dimeric Complex*** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (2 H, d, $^3J_{HH}$ = 7.6 Hz, Ar-$\underline{H}$), 7.13 – 7.07 (2 H, m, Ar-$\underline{H}$), 6.83 (2 H, t, $^3J_{HH}$ = 7.6 Hz, Ar-$\underline{H}$), 6.64 (2 H, t, $^3J_{HH}$ = 7.6 Hz, Ar-$\underline{H}$), 1.27 (30 H, s, C-C$\underline{H}_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.2 (C_q, Ar-$\underline{C}$), 139.0 (C_q, Ar-$\underline{C}$), 130.8 (CH, Ar-$\underline{C}$), 128.8 (CH, Ar-$\underline{C}$), 125.2 (CH, Ar-$\underline{C}$), 120.2 (CH, Ar-$\underline{C}$), 96.6 (C_q, d, $^1J_{CRh}$ = 5.7 Hz, $\underline{C}$-CH_3), 8.1 (C-$\underline{C}H_3$). MS (ES+): *m/z* 378.00 (½M, 100%), 400.99 (M+Na, 10).

1.4 Synthesis of 4a

This was prepared as per complex **3a** using $[Cp^*IrCl_2]_2$ (150 mg, 0.18 mmol) and **H_2a** (85 mg, 0.60 mmol). **4a** was obtained as a purple solid (101 mg, 0.13 mmol, 84%). Crystals suitable for X-ray work were obtained from CH_2Cl_2. Anal. calcd. for $C_{16}H_{19}IrS_2$ (467.67 g mol^{-1}): C, 41.03; H, 4.09. Found: C, 41.23; H, 4.15. IR (KBr): ν_{max}/cm^{-1} 2918w (ν_{C-H}), 1439m, 1382m, 1029m, 761s. Raman (glass capillary): ν_{max}/cm^{-1} 3028w (ν_{Ar-H}), 2912m (ν_{C-H}), 1542s, 1441m, 1091s, 1019m, 669m (ν_{C-S}), 428s, 179s. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05 (2 H, dd, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 3.2 Hz, Ar-H), 7.03 (2 H, dd, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 3.2 Hz, Ar-H), 2.15 (15 H, s, C-CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.0 (C_q, Ar-C), 129.6 (CH, Ar-C), 122.9 (CH, Ar-C), 91.8 (C_q, C-CH_3), 10.6 (C-CH_3). MS (ES+): *m/z* 468.05 (M, 100%), 491.04 (M+Na, 10).