Electronic Supplementary Information for Dalton Transactions

Supplementary Information for

A new route for substitution of the bridging acetate on the oxo-centered triruthenium acetate cluster

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General.

All reactions were carried out under N_2 atmosphere. $[Ru_3O(OAc)_6(Mepy)_3]$ was prepared according to ref 1 replacing pyridine with Mepy. All solvents except THF were used without distillation; THF was distilled from sodium/benzophenone ketyl. ^{1}H NMR spectra (δ relative to internal TMS at 0) were measured on a Bruker Avance II 600 spectrometer at 600 MHz and ^{19}F NMR spectra (δ relative to external C_6F_6 in $CHCl_3$ at -162.9) were on a Bruker ARX300 at 282.4 MHz. UV-vis spectra were recorded on a Jasco V-570 spectrometer. Mass spectra were recorded on a Hitachi M-2500 mass spectrometer.

Preparation of $[Ru_3O(OAc)_6(Mepy)_2(CN$*t*$-Bu)]$ 1

A solution of $[Ru_3O(OAc)_6(Mepy)_3]$ (763 mg, 0.80 mmol) and *tert*-butylisocyanide (0.10 mL, 0.88 mmol) in THF (80 mL) was refluxed for 1 h. After removal of the volatiles *in vacuo*, the residue was chromatographed on a silica-gel column with ethyl acetate. The first yellow band was discarded and the second blue band was collected and evaporated to dryness. Yield 594 mg (0.63 mmol, 79 %). ^{1}H NMR ($CDCl_3$): δ 9.30 (d, J = 6.4 Hz, 4H), 7.77 (d, J = 6.4 Hz, 4H), 2.76 (s, 6H), 2.07 (s, 12H), 1.85 (m, 9H+6H). UV/Vis (CH_2Cl_2): λ_{max} (log ε) 248 (4.45), 341 (3.92), 671 (3.68), 816 nm (3.64). IR (Nujol, cm^{-1}): 2047 [ν(C≡N). MS (SI): *m/z* 943 [M^+]. Anal. Calc. for $C_{29}H_{41}N_3O_{13}Ru_3$: C, 36.94; H, 4.38; N, 4.46. Found: C, 37.29; H, 4.54; N, 4.39 %.

Synthesis of $[Ru_3O(OAc)_5(\mu$-Cl$)(Mepy)_2(CN$*t*$-Bu)]$ 2a

A solution of **1** (188 mg, 0.20 mmol) and acetyl chloride (0.20 ml) in THF (10 ml) was refluxed for 1 h. The resulting solution was filtered through a bed of alumina-gel. The eluent was purified by silica-gel column chromatography with ethyl acetate. The greenish-blue eluent was collected and evaporated to dryness. Yield 54 mg (0.059 mmol, 30%). Replacing acetyl chloride with triethylsilyl chloride the same procedure afforded **2a** in a 36 % yield. ^{1}H NMR ($CDCl_3$): δ 9.24 (d, J = 5.0 Hz, 2H), 9.07 (d, J = 5.0 Hz, 2H), 7.82 (d, J = 6.4 Hz, 2H), 7.71 (d, J = 6.4 Hz, 2H), 2.79 (s,

3H), 2.75 (s, 3H), 2.58 (s, 3H), 2.11 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H), 1.82 (s, 3H), 1.78 (s, 9H). UV/Vis (CH_2Cl_2): λ_{max} (log ε) 247 (4.41), 345 (3.94), 641 (3.68), 810 nm (3.53). IR (Nujol, cm^{-1}): 2048 [ν(C≡N)]. MS (SI): *m/z* 920 [M^+]. Anal. Calc. for $C_{27}H_{38}ClN_3O_{11}Ru_3$: C, 35.28; H, 4.17; N, 4.57. Found: C, 35.39; H, 4.20; N, 4.58 %.

Synthesis of [$Ru_3O(OAc)_5(\mu$-OEt)(Mepy)$_2$(CN*t*-Bu)] 3

A solution of **2a** (103 mg, 0.112 mmol) and sodium acetylacetonate monohydrate (96 mg, 0.69 mmol) in EtOH (9 mL) was stirred for 2 d at rt. After removal of the volatiles *in vacuo*, the residue was extracted with chloroform, and chromatographed by silica-gel column with ethyl acetate. Yield 40 mg (0.043 mmol, 38 %). ^{1}H NMR (C_6D_6): δ 9.85 (d, *J* = 6.3 Hz, 2H), 9.50 (d, *J* = 6.3 Hz, 2H), 7.17 (d, *J* = 5.6 Hz, 2H), 7.14 (d, *J* = 5.6 Hz, 2H), 2.75 (s, 3H), 2.24 (s, 3H), 2.21 (s, 3H), 2.12 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.56 (s, 9H), 1.00 (m, 2H), 0.93 (t, *J* = 6.9 Hz, 3H). UV/Vis (CH_2Cl_2): λ_{max} (log ε) 247 (4.47), 356 (3.96), 654 (3.75), 807 nm (3.65). IR (Nujol, cm^{-1}): 2033 [ν(C≡N)]. MS (SI): *m/z* 930 [M^+]. Anal. Calc. for $C_{29}H_{45}N_3O_{13}Ru_3$ (= **3**·H_2O): C, 36.79; H, 4.79; N, 4.44. Found: C, 36.61; H, 4.72; N, 4.54%.

Synthesis of [$Ru_3O(OAc)_5(\mu$-O_2CEt)(Mepy)$_2$(CN*t*-Bu)] 4a

A solution of **2a** (84 mg, 0.091 mmol) and sodium propionate (61 mg, 0.64 mmol) in EtOH (8 mL) was stirred for 2 d at rt. After removal of the volatiles *in vacuo*, the residue was extracted with chloroform, and chromatographed by silica-gel column with chloroform. Yield 21 mg (0.022 mmol, 26 %). ^{1}H NMR ($CDCl_3$): δ 9.36 (d, *J* = 6.4 Hz, 2H), 9.18 (d, *J* = 6.4 Hz, 2H), 7.70 (m, 4H), 2.80 (s, 3H), 2.74 (s, 3H), 2.27 (m, 2H), 2.04 (s, 3H), 2.02 (s, 6H), 1.85 (s, 9H), 1.84 (s, 3H), 1.81 (s, 3H), 0.72 (t, *J* = 7.5 Hz, 3H). UV/Vis (CH_2Cl_2): λ_{max} (log ε) 248 (4.44), 344 (3.92), 672 (3.67), 814 nm (3.63). MS (SI): *m/z* 957 [M^+]. Anal. Calc. for $C_{31.2}H_{45.8}N_3O_{13}Ru_3$ (= **4a**·0.2hexane): C, 38.47; H, 4.74; N, 4.31. Found: C, 38.34; H, 4.86; N, 4.33%

Synthesis of [$Ru_3O(OAc)_5(\mu$-O_2CCF_3)(Mepy)$_2$(CN*t*-Bu)] 4b

A solution of **2a** (55 mg, 0.060 mmol) and sodium trifluoroacetate (44 mg, 0.32 mmol) in EtOH (5 mL) was stirred for 3 d at rt. After removal of the volatiles *in vacuo*, the residue was extracted with chloroform, and chromatographed by silica-gel column with benzene/ethyl acetate (*v/v*, 1:1). Yield 13 mg (0.013 mmol, 22 %). ^{1}H NMR ($CDCl_3$): δ 9.27 (d, *J* = 6.2 Hz, 2H), 9.12 (d, *J* = 6.2 Hz, 2H), 7.80 (d, *J* = 6.1 Hz, 2H), 7.70 (d, *J* = 6.1 Hz, 2H), 2.81 (s, 3H), 2.77 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H), 1.83 (m, 9H+3H), 1.82 (s, 3H). ^{19}F NMR ($CDCl_3$): δ -76.1 (s). UV/Vis (CH_2Cl_2): λ_{max} (log ε) 248 (4.44), 336 (3.98), 666 (3.67), 806 nm (3.63). MS (SI): *m/z* 997[M^+]. Anal. Calc. for $C_{29}H_{38}F_3N_3O_{13}Ru_3$: C, 34.94; H, 3.84; N, 4.22. Found: C, 35.11; H, 4.01; N, 4.19%.

Synthesis of $[Ru_3O(OAc)_5(\mu\text{-}SEt_2)(Mepy)_2(CN\textit{t}\text{-}Bu)](CF_3SO_3)$ 5

A solution of **2a** (74 mg, 0.080 mmol), diethyl sulfide (0.10 ml) and thallium(I) trifluoromethanesulfonate (60.5 mg) in THF (8 mL) was refluxed for 2 h. After removal of the volatiles *in vacuo*, the residue was extracted with $CHCl_3$, and chromatographed by silica-gel column with $CHCl_3$/acetone (*v*/*v*, 3:1). Yield 44 mg (0.039 mmol, 49 %). ^{1}H NMR ($CDCl_3$): δ 8.97 (d, *J* = 6.3 Hz, 2H), 8.94 (d, *J* = 6.3 Hz, 2H), 7.95 (d, *J* = 6.4 Hz, 2H), 7.83 (d, *J* = 6.4 Hz, 2H), 2.92 (s, 3H), 2.85 (s, 3H), 2.56–2.45 (m, 4H), 2.44 (s, 3H), 2.31 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.83 (s, 3H), 1.64 (s, 9H), 1.08 (t, *J* = 6.6 Hz, 3H), 1.02 (t, *J* = 7.5 Hz, 3H). UV/Vis (CH_2Cl_2): λ_{max} (log ε) 229 (4.42), 323 (4.03), 602 (3.74), 878 nm (3.37). MS (SI): *m/z* 975 $[(M–CF_3SO_3)^+]$. Anal. Calc. for $C_{33}H_{50}F_3N_3O_{15}Ru_3S$ (= **5**·0.5hexane): C, 35.36; H, 4.50; N, 3.75. Found: C, 35.25; H, 4.51; N, 3.77%.

Reference

1) J. A. Baumann, D. J. Salmon, S. T. Wilson, T. J. Meyer and W. E. Hatfield, *Inorg. Chem.,* 1978, **17**, 3342.

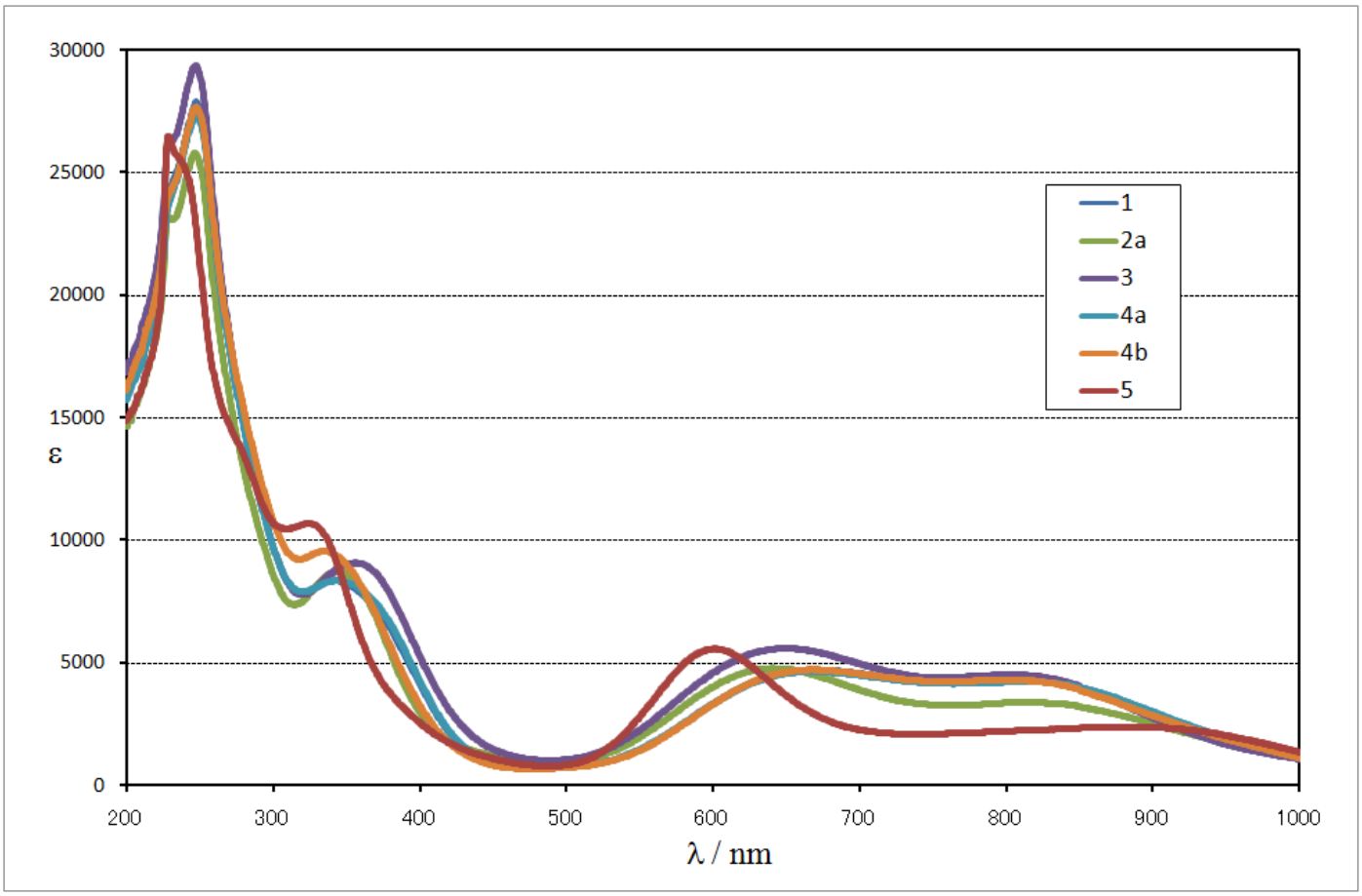

Figure S1. UV/Vis spectra of **1, 2a, 3, 4a, 4b** and **5**