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Tunable single-site ruthenium catalysts for efficient water oxidation

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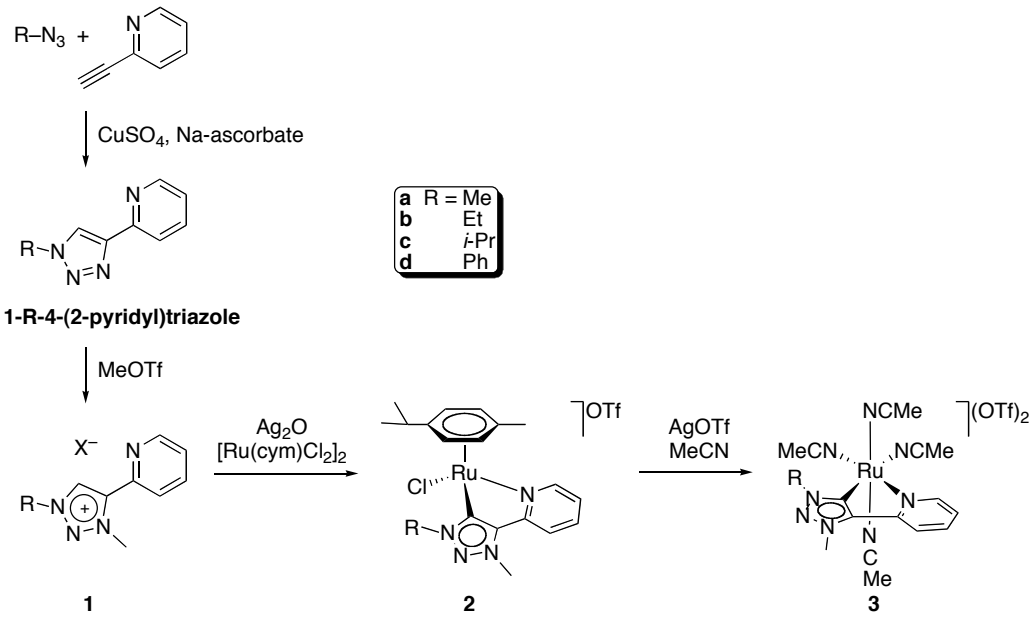
Content

1. Synthetic procedures

General remarks

1-Phenyl-4-(2-pyridyl)triazole was reported previously and has been prepared in slight modification of the published procedure.[1] The synthesis of the ruthenium complexes **6** and **7** will be reported elsewhere. All other chemicals were commercially available and used as received. Thin layer chromatography was performed on Merck silica gel 60 F_{254} glass plates. All NMR spectra were recorded on a Varian 500 spectrometer and referenced by the resonance due to residual protio solvent (δ in ppm, J in Hz). Microanalyses were performed by the Microanalytical laboratory of University College Dublin.



Scheme S1

Synthesis of the triazoles

Synthesis of 1-methyl-4-(2-pyridyl)triazole. A suspension of MeI (500 mg, 3.52 mmol) and NaN_3 (687 mg, 10.6 mmol) in H_2O/THF (20 mL 1:1 v/v) was stirred at room temperature for 16 h. Subsequently, 2-ethynylpyridine (436 mg, 4.23 mmol), $CuSO_4.5H_2O$ (52 mg, 0.21 mmol) and sodium ascorbate (420 mg, 2.1 mmol) were added and the mixture was irradiated in a Biotage microwave reactor at 100 ºC for 30 minutes. The solvents were removed under reduced pressure and the residue was suspended in CH_2Cl_2 (60 mL) and washed with 10% $NH_{3\ aq}$ (2 × 100 mL), water (2 × 100 mL), and brine (2 × 100 mL). After drying over $MgSO_4$

and solvent evaporation, 1-methyl-4-(2-pyridyl)triazole was obtained as an off-white powder (460 mg, 82%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.58 (m, 1H, H_{py}), 8.17 (m, 1H, H_{py}), 8.12 (s, 1H, H_{trz}), 7.77 (m, 1H, H_{py}), 7.22 (m, 1H, H_{py}), 4.15 (s, 3H, NCH_3). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 150.2, 149.3, 148.6, 136.8, 122.9 (C_{trz}–H), 122.7, 120.1, 36.7 (NCH_3). Anal. calcd for $C_8H_8N_4$ (160.18): C, 59.99; H, 5.03; N, 34.98; found: C, 59.83; H, 4.91; N, 34.77.

Synthesis of 1-ethyl-4-(2-pyridyl)triazole. According to the procedure described for 1-methyl-4-(2-pyridyl)triazole yet starting from EtI (700 mg, 4.49 mmol), NaN_3 (875 mg, 13.5 mmol) in H_2O/THF (30 mL), followed by addition of $CuSO_4{\cdot}5H_2O$ (28 mg, 0.11 mmol), sodium ascorbate (222 mg, 1.1 mmol) and 2-ethynylpyridine (289 mg, 2.81 mmol), 1-ethyl-4-(2-pyridyl)triazole was isolated as yellow oil (740 mg, 95%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.57 (m, 1H, H_{py}), 8.17 (m, 2H, H_{py} + H_{trz}), 7.77 (m, 1H, H_{py}), 7.22 (m, 1H, H_{py}), 4.48 (q, $^{3}J_{HH}$ = 7.4 Hz, 2H, NCH_2), 1.60 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 150.37 (C_{py}), 149.31 (C_{py}), 148.36 (C_{trz}–C), 136.83 (C_{py}), 122.72 (C_{py}), 121.27 (C_{py}), 120.13 (C_{trz}–H), 45.38 (NCH_2), 15.38 (CH_3).

Synthesis of 1-isopropyl-4-(2-pyridyl)triazole. According to the procedure for 1-methyl-4-(2-pyridyl)triazole, yet starting from *i*-PrI (500 mg, 2.94 mmol) and NaN_3 (574 mg, 8.82 mmol) in H_2O/THF (60 mL), and upon addition of $CuSO_4{\cdot}5H_2O$ (12.2 mg, 0.049 mmol), sodium ascorbate (97 mg, 0.49 mmol), and 2-ethynylpyridine (126 mg, 1.23 mmol), 1-ethyl-4-(2-pyridyl)triazole was obtained as yellow solid (940 mg, 90%).

^{1}H NMR (CD_3CN, 500 MHz): δ 8.58 (ddd, $^{3}J_{HH}$ = 4.9 Hz, $^{4}J_{HH}$ = 1.7 Hz, $^{5}J_{HH}$ = 1.0 Hz, 1H, H_{py}), 8.19 (dt, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.0 Hz, $^{5}J_{HH}$ = 1.0 Hz, 1H, H_{py}), 8.18 (s, 1H, H_{trz}), 7.77 (td, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.7 Hz, 1H, H_{py}), 7.22 (ddd, $^{3}J_{HH}$ = 7.8, $^{3}J_{HH}$ = 4.9 Hz, $^{5}J_{HH}$ = 1.0 Hz, 1H, H_{py}), 4.91 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, $CHMe_2$), 1.63 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, C–CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$), 125 MHz: δ 150.57 (C_{py}), 149.34 (C_{py}), 148.15 (C_{trz}–C), 136.91 (C_{py}), 122.74 (C_{py}), 120.19 (C_{py}), 119.40 (C_{trz}–H), 53.13 ($CHMe_2$), 23.09 (CH_3).

Synthesis of 1-phenyl-4-(2-pyridyl)triazole. A mixture of PhN_3 (450 mg, 3.78 mmol), 2-ethynylpyridine (390 mg, 3.78 mmol), $CuSO_4.5H_2O$ (47 mg, 0.19 mmol) and sodium ascorbate (374 mg, 1.9 mmol) in H_2O/THF (20 mL 1:1 v/v) was heated to 100 °C under microwave irradiation for 30 minutes. Purification as described above yielded 1-phenyl-4-(2-

pyridyl)triazole as a white solid. (780 mg, 93%). The spectroscopic data are in agreement with the literature.[1,3]

Synthesis of the triazolium salts (1a–d).

Synthesis of 1a. A suspension of 1-methyl-4-(2-pyridyl)triazole (400 mg, 2.50 mmol) and MeOTf (450 mg, 2.75 mmol) in CH_2Cl_2 (5 mL) was stirred at 0° C for 30 min. After addition of Et_2O (30 mL), the precipitate was separated and the tan oily residue was washed repetitively with Et_2O. The residual mixture was separated by preparative thin layer chromatography (TLC) using MeCN/CH_2Cl_2 (1:3 v/v) for elution. The desired compound was at the front and isolated by suspension of the silica fraction in MeOH and MeCN and filtration through a pad of Celite. The solvent was removed and the product was redissolved into a minimum amount of MeCN and filtered again through Celite. The solvent was removed and the residue dried under high vacuum to afford **1a** as a white solid (177 mg, 22%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.41 (s, 1H, H_{trz}), 8.74 (ddd, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.7 Hz, $^5J_{HH}$ = 1.0 Hz, 1H, H^6_{py}), 8.10 (dt, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.0 Hz, $^5J_{HH}$ = 1.0 Hz, 1H, H^3_{py}), 7.95 (td, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H^4_{py}), 7.49 (ddd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, H^5_{py}), 4.64 (s, 3H, NCH_3), 4.45 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 149.7, 142.8, 140.8, 138.3, 130.8 (C_{trz}–H), 125.8, 125.2, 41.1 (NCH_3), 40.5 (NCH_3). ^{19}F{^{1}H} NMR (CD_3CN, 282 MHz): δ –80 (s). Anal. calcd for $C_{10}H_{11}F_3N_4O_3S$ (324.28) C, 37.04; H, 3.42; N, 17.28; found: C, 36.79; H, 3.35; N, 17.02.

Synthesis of 1b. According to the procedure described for **1a**, 1-ethyl-4-(2-pyridyl)triazole (740 mg, 4.25 mmol) and MeOTf (835 mg, 5.09 mmol) in CH_2Cl_2 (6 mL) gave, after preparative TLC purification, **1b** as a white solid (382 mg, 25%).

^{1}H NMR (CD_3CN, 500 MHz): δ 8.85 (s, 1H, H_{trz}), 8.84 (m, 1H, H_{py}), 8.07 (td, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H_{py}), 7.92 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, H_{py}), 7.62 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, H_{py}), 4.68 (q, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2), 4.56 (s, 3H, NCH_3), 1.68 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 150.411 (C_{trz}–H), 143.37 (C_{py}), 141.18 (C_{trz}–C), 138.38 (C_{py}), 128.69 (C_{py}), 126.06 (C_{py}), 124.74 (C_{py}), 49.79 (NCH_2), 40.75 (NCH_3), 13.76 (CH_2CH_3). ^{19}F{^{1}H} NMR (CD_3CN, 282 MHz): δ –79 (s). Anal. calcd for $C_{11}H_{13}F_3N_4O_3S$ (338.07): C 39.05, H 3.87, N 16.56; found: C 39.03, H 3.77, N 16.30.

Synthesis of 1c. According to the procedure described for **1a**, 1-isopropyl-4-(2-pyridyl)triazole (1000 mg, 2.84 mmol) and MeOTf (0.48 mL, 4.3 mmol) in CH_2Cl_2 (4 mL) afforded, after preparative TLC purification, **1c** as white solid (536 mg, 28%).
^{1}H NMR (CD_3CN, 500 MHz): δ 8.85 (s, 1H, H_{trz}), 8.84 (m, 1H, H_{py}), 8.08 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H_{py}), 7.92 (m, 1H, H_{py}), 7.63 (ddd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, H_{py}), 5.09 (sept, $^3J_{HH}$ = 6.7 Hz, 1H, $CHMe_2$), 4.55 (s, 3H, NCH_3), 1.72 (d, $^3J_{HH}$ = 6.7 Hz, 6H, C–CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN, 125 MHz): δ 150.40 (C_{trz}–H), 143.45 (C_{py}), 141.09 (C_{trz}–C), 138.37 (C_{py}), 127.35 (C_{py}), 126.04 (C_{py}), 124.67 (C_{py}), 58.65 ($CHMe_2$), 40.78 (NCH_3), 21.47 (C–*C*H_3). $^{19}F\{^1H\}$ NMR (CD_3CN, 282 MHz): δ –79 (s). Anal. calcd for $C_{12}H_{15}F_3N_4O_3S$ (352.08): C 40.91, H 4.29, N 15.90; found: C 40.95, H 4.21, N 15.83.

Synthesis of 1d. According to the procedure described for **1a**, 1-phenyl-4-(2-pyridyl)triazole (460 mg, 2.07 mmol) and MeOTf (0.408 mg, 2.48 mmol) in CH_2Cl_2 (3 mL) yielded after preparative TLC compound **1d** as off-white solid (200 mg, 26%).
^{1}H NMR ($CDCl_3$, 500 MHz): 9.98 (s, 1H, H_{trz}), 8.74 (d, $^3J_{HH}$ = 4.1 Hz, 1H, H_{py}), 8.34 (d, $^3J_{HH}$ = 7.4 Hz, 1H, H_{py}), 8.07 (m, 2H, H_{ar}), 7.88 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H_{py}), 7.60 (m, 3H, H_{ar}), 7.45 (m, 1H, H_{py}), 4.79 (s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 149.6, 142.6, 141.8, 138.3, 134.6, 132.0, 130.4, 127.4 (C_{trz}–H), 125.9, 125.7, 121.3, 41.8 (NCH_3). $^{19}F\{^1H\}$ NMR($CDCl_3$, 282 MHz): –79 (s). Anal. calcd for $C_{15}H_{13}F_3N_4O_3S$ (386.35) C, 46.63; H, 3.39; N, 14.50; found: C, 46.53; H, 3.38; N, 14.31.

Synthesis of the complexes [Ru(cym)(trz-py)Cl]OTf (2a–d).

Synthesis of 2a. A mixture of **1a** (100 mg, 0.31 mmol), Ag_2O (71 mg, 0.31 mmol) and $[Ru(cym)Cl_2]_2$ (94 mg, 0.154 mmol) in dry MeCN was stirred at room temperature for 40 h. After filtration through Celite and solvent evaporation, the residue was washed with Et_2O and purified by flash chromatography (SiO_2, pentane, then acetone/CH_2Cl_2 1:1). The yellow band was collected and concentrated to about 1 mL. Addition of excess Et_2O caused the precipitation of yellow solid that was separated and died in vacuo (76 mg, 42 %).
^{1}H NMR (CD_3CN, 500 MHz): δ 9.39 (d, $^3J_{HH}$ = 5.6 Hz, H_{py}, 1H), 8.07 (td, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H_{py}), 7.93 (m, 1H, H_{py}), 7.47 (m, 1H, H_{py}), 6.08 (d, $^3J_{HH}$ = 6.3 Hz, 2H, H_{cym}), 5.84 (d, $^3J_{HH}$ = 6.3 Hz, 1H, H_{cym}), 5.49 (d, $^3J_{HH}$ = 6.3 Hz, 1H, H_{cym}), 4.46 (s, 3H, NCH_3) 4.42 (s, 3H, NCH_3), 2.42 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, C_{cym}–$CHMe_2$), 2.08 (s, 3H, C_{cym}–CH_3), 0.94, 0.93 (2 × d, $^3J_{HH}$ = 6.9 Hz, 3H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (CD_3CN, 125 MHz): δ 174.13 (C_{trz}–

Ru), 157.65 (C_{py}), 149.02 (C_{py}), 143.70 (C_{trz}–C), 139.34 (C_{py}), 125.00 (C_{py}), 121.71 (C_{py}), 104.72, 104.68 (2 × C_{cym}–C), 90.77, 88.21, 86.09, 81.59 (4 × C_{cym}–H), 40.37 (NCH_3), 38.92 (NCH_3), 31.19 ($CHMe_2$), 21.65, 21.57 (2 × CH–CH_3), 18.29 (C_{cym}–CH_3). $^{19}F\{^1H\}$ NMR (CD_3CN, 282 MHz): δ –79 (s). Anal. calcd for $C_{20}H_{24}ClF_3N_4O_3RuS$ (594.01): C, 40.44; H, 4.07; N, 9.43; found: C, 40.40; H, 3.98; N, 9.33.

Synthesis of 2b. According to the procedure described for **2a**, a mixture of **1b** (135 mg, 0.399 mmol), $[Ru(cym)Cl_2]_2$ (122 mg, 0.199 mmol) and Ag_2O (93 mg, 0.399 mmol) in dry MeCN (6 mL) yielded **2b** as an orange solid (93 mg, 38%).
^1H NMR (CD_3CN, 500 MHz): δ 9.42 (ddd, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 1.2 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, H_{py}), 8.10 (td, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H_{py}), 7.96 (dt, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, H_{py}), 7.51 (ddd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, H_{py}), 6.07 (d, $^3J_{HH}$ = 6.5 Hz, 1H, H_{cym}), 6.05 (d, $^3J_{HH}$ = 6.0 Hz, 1H, H_{cym}), 5.84 (d, $^3J_{HH}$ = 6.5 Hz, 1H, H_{cym}), 5.46 (d, $^3J_{HH}$ = 6.0 Hz, 1H, H_{cym}), 4.83 (m, 2H, NCH_2), 4.42 (s, 3H, NCH_3), 2.43 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, C_{cym}–$CHMe_2$) 2.13 (s, 3H, C_{cym}–CH_3), 1.68 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_2CH_3), 0.96, 0.95 (2 × d, $^3J_{HH}$ = 6.9 Hz, 3H, $CHCH_3$). $^{13}C\{^1H\}$ NMR (CD_3CN, 125 MHz): δ 172.87 (C_{trz}–Ru), 157.52, 148.93 (2 × C_{py}), 143.66 (C_{trz}–C), 139.12, 124.94, 121.21 (3 × C_{py}), 104.77, 104.22 (2 × C_{cym}–C), 90.76, 88.83, 85.41, 81.16 (4 × C_{cym}–H), 49.10 (NCH_2), 39.01 (NCH_3), 30.63 (C_{cym}–$CHMe_2$), 21.24 ($CHCH_3$), 18.06 (C_{cym}–CH_3), 14.49 (CH_2CH_3). $^{19}F\{^1H\}$ NMR (CD_3CN, 282 MHz): δ –79 (s). Anal. calcd for $C_{21}H_{26}ClF_3N_4O_3RuS$ (656.08): C 41.48, H 4.31, N 9.21; found: C 41.46, H 4.26, N 9.50.

Synthesis of 2c. According to the procedure described for **2a** from **1c** (100 mg, 0.284 mmol), $[Ru(cym)Cl_2]_2$ (87 mg, 0.142 mmol), and Ag_2O (66 mg, 0.284 mmol) in MeCN (6 mL) afforded **2c** as an orange solid (70 mg, 40%).
^1H NMR (CD_3CN, 500 MHz): δ 9.43 (ddd, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 1.9 Hz, $^5J_{HH}$ = 1.0 Hz, 1H, H_{py}), 8.10 (td, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.9 Hz, 1H, H_{py}), 7.97 (dt, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, H_{py}), 7.50 (ddd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, H_{py}), 6.06, 6.05, 5.84, 5.45 (4 × d, $^3J_{HH}$ = 6.7 Hz, 1H, H_{cym}), 5.26 (sept, $^3J_{HH}$ = 6.7 Hz, 1H, $NCHMe_2$), 4.42 (s, 3H, NCH_3), 2.43 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, C_{cym}–$CHMe_2$), 2.10 (s, 3H, C_{cym}–CH_3), 1.91 (d, $^3J_{HH}$ = 6.9 Hz, 3H, C_{cym}–$CHCH_3$), 1.50 (d, $^3J_{HH}$ = 6.9 Hz, 3H, C_{cym}–$CHCH_3$), 0.96, 0.95 (2 × d, $^3J_{HH}$ = 6.9 Hz, 6H, $NCHCH_3$). $^{13}C\{^1H\}$ NMR (CD_3CN, 125 MHz): δ 172.44 (C_{trz}–Ru), 157.51, 148.75 (2 × C_{py}), 142.90 (C_{trz}–C), 139.40, 124.80, 121.29 (3 × C_{py}), 105.14, 104.28 (2 × C_{cym}–

C), 91.10, 88.63, 85.86, 81.35 (4 × C_{cym}–H), 57.73 ($NCHMe_2$), 38.95 (NCH_3), 31.28 (C_{cym}–*C*HMe_2), 23.44 ($NCHCH_3$), 21.66, 21.61 (2 × C_{cym}–$CHCH_3$), 21.49 ($NCHCH_3$), 18.35 (C_{cym}–*C*H_3). $^{19}F\{^1H\}$ NMR (CD_3CN, 282 MHz): δ –79 (s). Anal. calcd for $C_{22}H_{28}ClF_3N_4O_3RuS$ (622.06) × 0.25CH_2Cl_2: C 41.54, H 4.47 N 8.71 found: C 41.69, H 4.31, N 8.75.

Synthesis of 2d. According to the procedure described for **2a** from **1d** (120 mg, 0.31 mmol), $[Ru(cym)Cl_2]_2$ (96 mg, 0.155 mmol), and Ag_2O (72 mg, 0.31 mmol) in MeCN (6 mL) afforded **2d** as a yellow solid (110 mg, 54%).
^1H NMR (CD_3CN, 500 MHz): δ 9.35 (m, 1H, H_{py}), 8.06 (m, 4H, H_{py} + H_{ph}), 7.70 (m, 3H, H_{py} + H_{ph}), 7.44 (m, 1H, H_{py}), 5.49 (m, 1H, H_{cym}), 5.43 (m, 1H, H_{cym}), 5.27 (m, 1H, H_{cym}), 4.87 (m, 1H, H_{cym}), 4.64 (s, 3H, NCH_3), 2.53 (m, 1H, $CHMe_2$), 2.01 (s, 3H, C_{cym}–CH_3), 2.07 (d, $^3J_{HH}$ = 6.9 Hz, 3H, $CHCH_3$), 1.00 (d, $^3J_{HH}$ = 6.9 Hz, 3H, $CHCH_3$). ^{13}C NMR (CD_3CN, 125 MHz): δ 174.04 (C_{trz}–Ru), 156.88 (C_{py}), 148.88 (C_{py}), 143.99 (C_{trz}–C), 139.41 (C_{py}), 138.20 (C_{ph}), 131.18 (C_{py}), 129.79 (C_{ph}), 125.22 (C_{ph}), 125.17 (C_{py}), 122.07 (C_{ph}), 109.16, 102.29 (2 × C_{cym}–C), 89.76, 86.98, 85.98, 83.02 (4 × C_{cym}–H), 39.44 (NCH_3), 31.14 ($CHMe_2$), 22.87, 21.51 (2 × C_{cym}–$CHCH_3$), 18.74 (C_{cym}–*C*H_3). ^{19}F NMR (CD_3CN, 282 MHz): δ –79 (s). Anal. calcd for $C_{25}H_{26}ClF_3N_4O_3RuS$ (656.04): C 45.77, H 3.99, N 8.54; found: C 45.39, H 3.67, N 8.40.

Synthesis of the complexes [Ru(trz-py)(MeCN)$_4$](OTf)$_2$ (3a–d).

Synthesis of 3a. Complex **2a** (135 mg, 0.227 mmol) and AgOTf (88 mg, 0.341 mmol) in dry MeCN (15 mL) were stirred at reflux for 18 h. The mixture was filtered through Celite and all volatiles were evaporated under reduced pressure. The residue was washed with Et_2O and purified by flash chromatography (SiO_2, pentane then acetone/MeCN 1:1). The yellow band was collected and concentrated to about 1 mL. Addition of Et_2O induced precipitation of the product as a yellow solid, which was collected and dried in vacuo (150 mg, 89%). Analytically pure material was obtained from recrystallization (MeCN/Et_2O or CH_2Cl_2/Et_2O).
^1H NMR (CD_3CN, 500 MHz): δ 9.09 (ddd, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 1.3 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, H_{py}), 8.05 (m, 1H, H_{py}), 8.00 (m, 1H, H_{py}), 7.49 (ddd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H_{py}), 4.48, 4.37 (2 × s, 3H, NCH_3), 2.56 (s, 3H, CH_3CN), 2.18 (s, 6H, CH_3CN). $^{13}C\{^1H\}$ NMR (CD_3CN, 125 MHz): δ 176.29 (C_{trz}–Ru), 155.05 (C_{py}), 152.56 (C_{py}), 146.45 (C_{trz}–C), 138.41, 124.00 (2 × C_{py}), 121.02 ($^1J_{CF}$ 322 Hz, CF_3SO_3), 120.81 (C_{py}), 124.3 (MeCN), 122.66, 120.05 (MeCN), 39.91, 38.65 (2 × NCH_3), 3.64, 3.16, (2 × *C*H_3CN).

$^{19}F\{^{1}H\}$ NMR (CD_3CN, 282 MHz): δ –79 (s). Anal. calcd for $C_{19}H_{22}F_6N_8O_6RuS_2$ (737.62): C, 30.94; H, 3.01; N, 15.19. C, 30.86; H, 2.91; N, 15.10.

Synthesis of 3b. From complex **2b** (53 mg, 0.087 mmol) and AgOTf (34 mg, 0.13 mmol) according to the procedure described for **3a**, complex **3b** was isolated as a greenish solid (49 mg, 75%).

^{1}H NMR (CD_3CN, 500 MHz): δ 9.09 (d, J = 5.7 Hz, 1H, H_{py}), 8.06 (t, J = 7.9 Hz, 1H, H_{py}), 8.00 (d, J = 7.9 Hz, 1H, H_{py}), 7.49 (m, 1H, H_{py}), 4.71 (q, $^{3}J_{HH}$ = 7.3 Hz, 2H, NCH_2), 4.49 (s, 3H, NCH_3), 2.57 (s, 3H, CH_3CN), 2.13 (s, 6H, CH_3CN), 2.00 (s, 3H, CH_3CN), 1.64 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, CH_2CH_3). $^{13}C\{^{1}H\}$ NMR (CD_3CN, 125 MHz): δ 174.52 (C_{trz}–Ru), 155.10 (C_{py}), 152.57 (C_{py}), 146.32 (C_{trz}–C), 138.47, 124.30, 120.76 (3 × C_{py}), 48.83 (NCH_2), 38.73 (NCH_3), 15.63 (CH_2CH_3), 3.66, 3.12 (2 × CH_3CN). $^{19}F\{^{1}H\}$ NMR (CD_3CN, 282 MHz): δ –79 (s). Anal. calcd for $C_{20}H_{24}F_6N_8O_6RuS_2$ (752.02) × $0.5CH_2Cl_2$: C 31.01, H 3.17, N 14.11; found: C 31.17, H 2.97, N 14.29.

Synthesis of 3c. From complex **2c** (100 mg, 0.16 mmol) and AgOTf (63 mg, 0.24 mmol) according to the procedure described for **3a,** complex **3c** was obtained as an orange solid (91 mg, 74%).

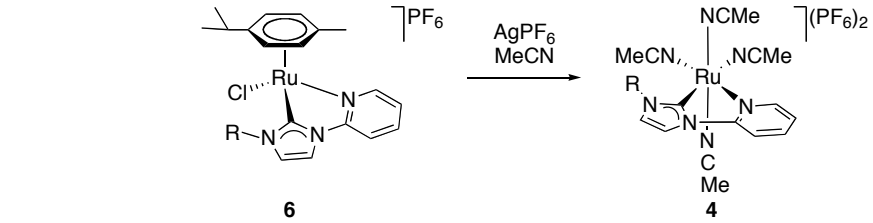
^{1}H NMR (CD_3CN, 500 MHz): δ 9.10 (dd, $^{3}J_{HH}$ = 5.3 Hz, $^{3}J_{HH}$ = 0.6 Hz, 1H, H_{py}), 8.06 (m, 1H, H_{py}), 7.99 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H_{py}), 7.49 (ddd, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{HH}$ = 5.3 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1H, H_{py}), 5.11 (sept, $^{3}J_{HH}$ = 6.7 Hz, 1H, $NCHMe_2$), 4.49 (s, 3H, NCH_3), 2.57 (s, 3H, CH_3CN), 2.12 (s, 6H, CH_3CN), 2.00 (s, 3H, CH_3CN), 1.74 (d, $^{3}J_{HH}$ = 6.7 Hz, 6H, $CHCH_3$). $^{13}C\{^{1}H\}$ NMR (CD_3CN, 125 MHz): δ 172.29 (C_{trz}–Ru), 155.04 (C_{py}), 152.56 (C_{py}), 145.74 (C_{trz}–C), 138.46, 124.25, 120.64 (3 × C_{py}), 56.69 ($NCHMe_2$), 38.76 (NCH_3), 22.09 ($NCHCH_3$), 3.63, 3.13 (2 × CH_3CN). $^{19}F\{^{1}H\}$ NMR (CD_3CN, 282 MHz): δ –79 (s). Anal. calcd for $C_{21}H_{26}F_6N_8O_6RuS_2$ (766.04) × $0.25CH_2Cl_2$: C 32.43, H 3.39, N 14.24; found: C 32.42, H 3.18, N 13.94.

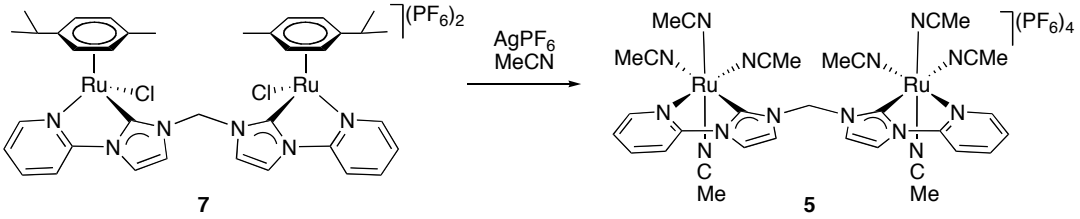
Synthesis of 3d. According to the procedure described for **3a**, reaction of complex **2d** (60 mg, 0.091 mmol) and AgOTf (35 mg, 0.14 mmol) yielded **3d** as a pale green solid (62 mg, 73%).

^{1}H NMR (CD_3CN, 500 MHz): δ 9.13 (d, $^{3}J_{HH}$ = 5.6 Hz, 1H, H_{py}), 8.17–8.06 (m, 7.8 Hz, 2H, H_{py}), 7.85–7.81 (m, 2H, H_{ph}), 7.78–7.66 (m, 3H, H_{ph}), 7.54 (ddd, $^{3}J_{HH}$ = 8.4 Hz, $^{3}J_{HH}$ = 5.6

Hz, $^{4}J_{HH}$ = 2.7 Hz, 1H, H_{py}), 4.60 (s, 3H, NCH_3), 2.17 (s, 6H, NCH_3), 2.01 (s, 3H, NCH_3). $^{13}C\{^{1}H\}$ NMR (CD_3CN, 100 MHz): δ 168.35 (C_{trz}–Ru), 155.22 (C_{py}), 152.41 (C_{py}), 146.48.17 (C_{trz}–C), 138.88 (C_{ph}–N), 138.60 (C_{py}), 131.18 (C_{ph}–H), 129.81 (C_{ph}–H), 126.48 (C_{ph}–H), 124.64 (C_{py}), 121.13 (C_{py}), 39.06 (NCH_3), 3.30, 3.22 (2 × CH_3CN). $^{19}F\{^{1}H\}$ NMR (CD_3CN, 282 MHz): δ –79 (s). Anal. calcd for $C_{24}H_{24}F_6N_8O_6RuS_2$ (800.02) × 0.5CH_2Cl_2: C 34.94, H 2.99, N 13.31; found: C 34.82, H 2.79, N 13.29.

Synthesis of mono- and dimetallic normal carbene complexes 4 and 5





Synthesis of 4. A solution of complex **6** (288 mg, 0.5 mmol) and $AgPF_6$ (126 mg, 0.5 mmol) in MeCN (20 mL) was stirred at reflux for 16 h. The solution was filtered through a pad of SiO_2 and eluted with MeCN. After solvent evaporation, complex **4** was obtained as a yellowish powder (340 mg, 95 %).

^{1}H NMR (CD_3CN, 500 MHz): δ 8.84 (d, $^{3}J_{HH}$ = 5.8 Hz, 1H, H_{py}), 8.08 (td, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, H_{py}), 7.97 (d, $^{3}J_{HH}$ = 2.2 Hz, 1H, H_{imid}), 7.79 (d, $^{3}J_{HH}$ = 7.9, 1H, H_{py}), 7.42 (dd, $^{3}J_{HH}$ = 5.8, $^{4}J_{HH}$ = 0.8, 1H, H_{py}), 7.35 (d, $^{3}J_{HH}$ = 2.2, 1H, H_{imid}), 4.03 (s, 3H, NCH_3), 2.50 (s, 6H, $NCCH_3$), 2.09 (s, 6H, $NCCH_3$). $^{13}C\{^{1}H\}$ NMR (CD_3CN, 125 MHz): δ 189.7 (C_{imid}–Ru), 156.2, 154.2, 141.7 (3 × C_{py}), 127.6 (MeCN), 127.0 (C_{imid}–H), 126.7, 125.8 (2 × MeCN), 123.5 (C_{py}), 118.3 (C_{imid}–H), 112.8 (C_{py}), 38.3 (NCH_3), 4.5, 4.4 (2 × $NCCH_3$). ESI-MS: 425.0910 (calcd for $[C_{17}H_{21}N_7Ru]^{2+}$: 425.0902). Anal. calcd for $C_{17}H_{21}F_{12}N_7P_2Ru$ (714.39): C 28.58, H 2.96, N 13.72; found: C 28.56, H 2.98, N 13.71.

Synthesis of 5. According to the procedure described for **4**, complex **5** was obtained from **7** (57 mg, 0.05 mmol) and $AgPF_6$ (25 mg, 0.1 mmol) in MeCN (20 mL) as a pale yellow powder (68 mg, 95%).

^{1}H NMR (CD_3CN, 400 MHz): δ 8.96 (d, $^3J_{HH}$ = 5.6 Hz, 2H, H_{py}), 8.15 (td, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, H_{py}), 8.11 (d, $^3J_{HH}$ = 2.2 Hz, 2H, H_{imid}), 7.88 (d, $^3J_{HH}$ = 8.0, 2H, H_{py}), 7.54 (ddd, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = $^5J_{HH}$ = 0.9 Hz, 2H, H_{py}), 7.45 (d, $^3J_{HH}$ = 2.2 Hz, 2H, H_{imid}), 6.83 (s, 2H, NCH_2N), 2.53 (s, 12H, $NCCH_3$), 2.21, 2.16 (2 × s, 6H, $NCCH_3$). $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz): δ 192.5 (C_{imid}–Ru), 155.8, 154.4, 142.2 (3 × C_{py}), 129.2, 127.1, 126.4 (3 × MeCN), 124.2 (C_{py}), 124.0, 120.8 (2 × C_{imid}–H), 113.4 (C_{py}), 63.2 (NCH_2N), 5.1, 4.7, 4.4 (3 × $NCCH_3$). Anal. calcd for $C_{17}H_{21}F_{12}N_7P_2Ru$ (1412.75): C 28.06, H 2.71, N 13.88; found: C 28.03, H 2.88, N 13.94

2. Electrochemical data

Electrochemical studies were carried out using an Metrohm Autolab Potentiostat Model PGSTAT101 employing a gas-tight three electrode cell under an argon atmosphere. A platinum disks with 7.0 mm^2 surface area was used as the working electrode and was polished before each measurement. The reference electrode was Ag/AgCl, the counter electrode was a Pt foil. In all experiments, Bu_4NPF_6 (0.1 M) was used as supporting electrolyte with analyte concentrations of approximately 1 mM. Measurements were performed at 100 mV s^{-1} scan rates. The redox potentials were referenced to ferrocenium/ferrocene (Fc^+/Fc; $E_{1/2}$ = 0.46 V *vs*. SCE in CH_2Cl_2, +0.35 V *vs*. SCE in $MeNO_2$)[2] as internal standard.

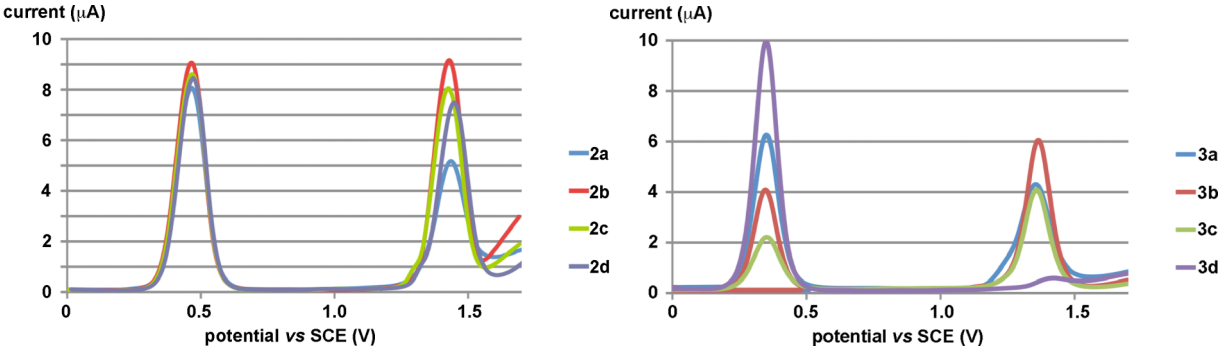


Figure S1. Differential pulse voltammograms upon potential increase from 0 to 1.7 V (scan rate 25 mV s^{-1}) for complexes **2** (left) and **3** (right), using and Ag/AgCl reference electrode and platinum working and counter electrodes, Bu_4NPF_6 as supporting electrolyte and ferrocene as internal standard (Fc/Fc^+ calibrated to +0.46 V *vs* SCE in CH_2Cl_2 for complexes **2** and to +0.34 V *vs* SCE in $MeNO_2$).

3. Catalytic procedures

Catalytic water oxidation was performed in 2mL of a 0.1M triflic acid solution (pH 1.0) at 298K using the corresponding catalyst (1 mM) and $[Ce(NO_3)_6](NH_4)_2$ (100 mM). The reaction was continuously monitored by manometric methods for determining TON and TOF values, and by on-line mass spectrometry to determine the relative ratios of O_2 and CO_2 (Fig. S2–S4).

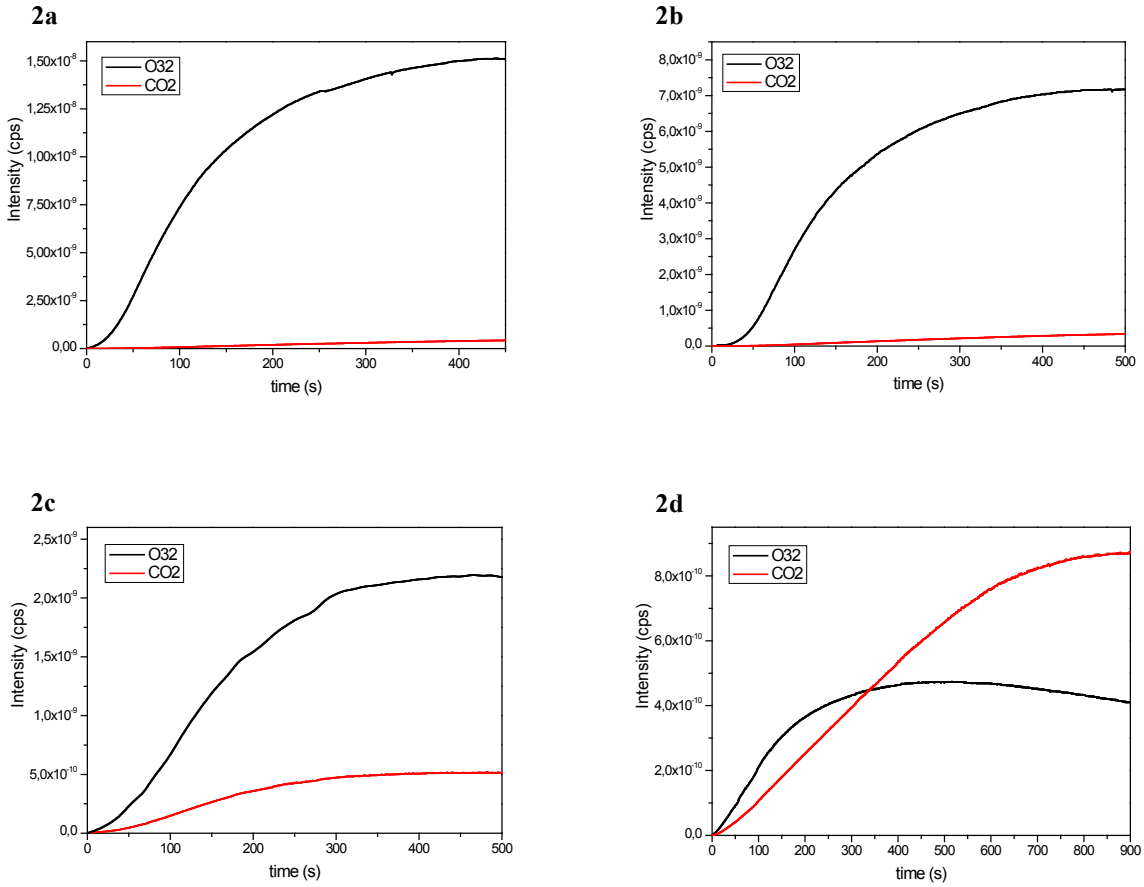


Figure S2. On-line mass spectra obtained for complexes **2a-2d** as described in Table 1 of the main text. The black line represents O_2 evolution while the red line represents CO_2 generation.

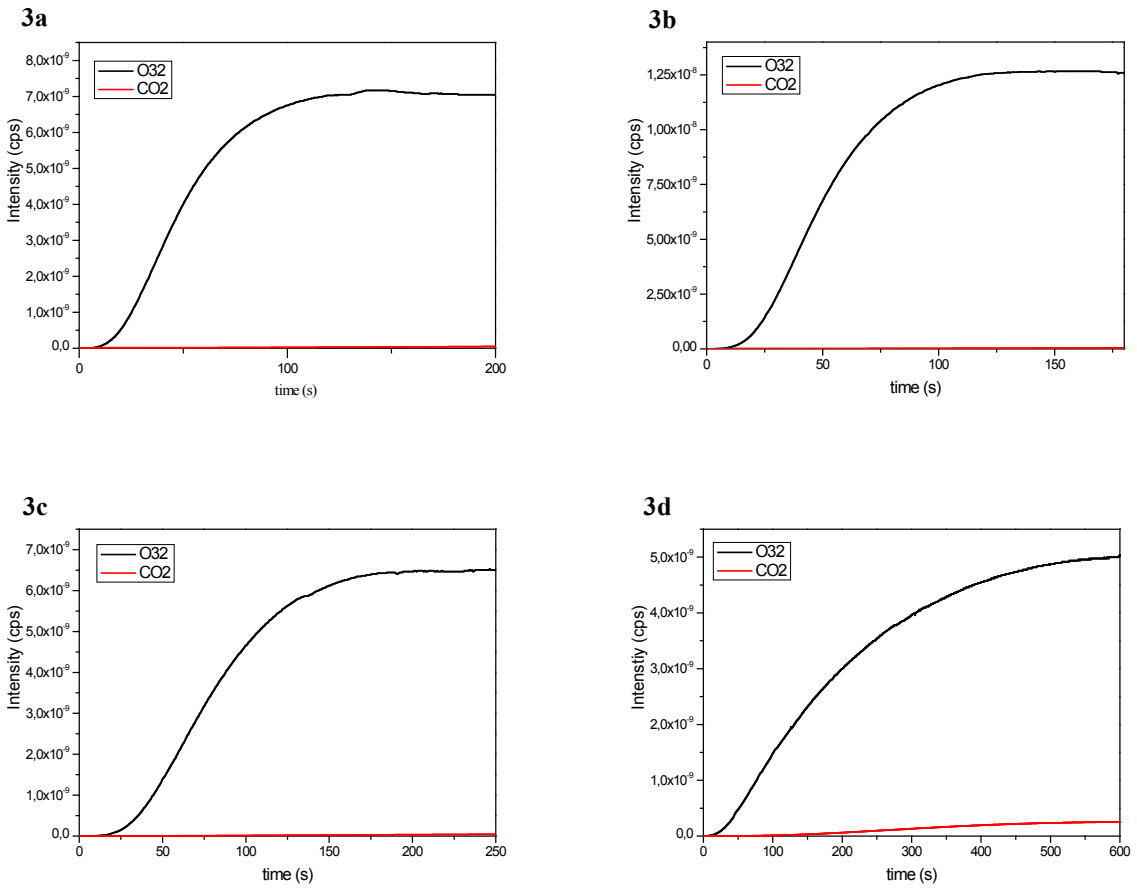


Figure S3. On-line mass spectra obtained for complexes **3a-3d** as described in Table 1 of the main text. The black line represents O_2 evolution while the red line represents CO_2 generation.

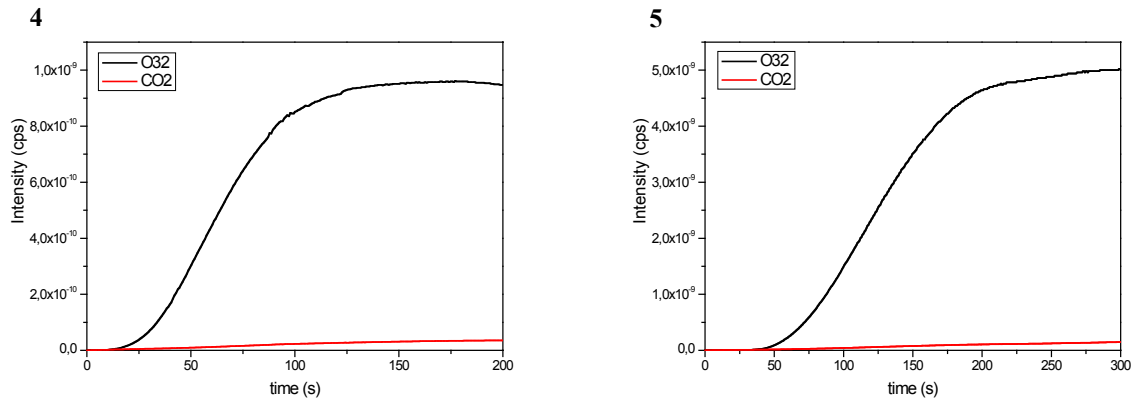


Figure S4. On-line mass spectra obtained for complexes **4** and **5** as described in Table 1 of the main text. The black line represents O_2 evolution while the red line represents CO_2 generation.

4. Crystallographic analyses

The molecular structures of all complexes confirmed the *C,N*-bidentate chelation of the ligand as deduced from solution studies. While the Ru–C bond lengths fall within the expected 2.0–2.1 Å range,[4] subtle differences have been noted. In the dicationic complexes **3**, the Ru–C bond distance is 1.999(6) Å and hence significantly shorter than in the monocationic complexes **2** (Ru–$C_{triazolylidene}$ 2.028(7) Å). Likewise, the Ru–pyridine distance shrinks from 2.129(7) Å in **2** to 2.092(3) Å in **3**. As a consequence of these bond length variations, the ligand bite angle is slightly larger (78.6(12) in **3** *vs* 76.59(6) in **2**), though it remains rather acute. In complexes **3**, the Ru–N_{MeCN} bond lengths *trans* to the triazolylidene ligand average to 2.114(7) Å and are thus about 0.08 Å longer than the analogous bonds *trans* to the pyridine ligand (Ru–N 2.032(2) Å), reflecting the markedly stronger *trans* influence of the triazolyidene ligand as compared to pyridine

Table S1. Selected bond lengths and angles of complexes 2a–2c

Complex	**2a**	**2b**	**2c**
Ru– $C_{carbene}$	2.0318(12)	2.031(3)	2.0201(16)
Ru– $N_{pyridyl}$	2.1260(11)	2.136(2)	2.1236(14)
Ru–Cl	2.4036(3)	2.4082(8)	2.4007(4)
$C_{carbene}$–Ru–$N_{pyridyl}$	76.53(4)	76.65(10)	76.58(6)
Cl–Ru–$C_{carbene}$	84.27(3)	85.56(8)	84.24(5)
Cl–Ru– $N_{pyridyl}$	85.26(3)	84.61(7)	84.47(4)

Table S2. Selected bond lengths and angles of complexes 3a–3d, 4 and 5 [a]

Complex	**3a**	**3b**	**3c**	**3d'**	**4**
Ru– $C_{carbene}$	1.9922(13)	2.0024(14)	2.002(2)	1.999(3)	1.990(7)
Ru– $N_{pyridyl}$	2.0954(11)	2.0893(11)	2.0913(17)	2.086(3)	2.043(5)
Ru–N_{MeCN} *trans*	2.1166(12)	2.1061(12)	2.1196(17)	2.096(3)	2.095(2)
Ru–N_{MeCN} *cis*	2.0315(11)	2.0343(12)	2.0298(18)	2.022(3)	2.061(2)
Ru–N_{MeCN} *apical*	2.0331(12)	2.0164(12)	2.0266(18)	2.014(3)	2.021(2)
Ru–N_{MeCN} *apical*	2.0206(11)	2.0158(12)	2.0217(18)	2.015(3)	2.025(2)
$C_{carbene}$–Ru–$N_{pyridyl}$	78.34(5)	78.76(5)	78.61(7)	78.77(14)	78.70(15)
$N_{pyridyl}$–Ru– N_{MeCN} *cis*	178.23(4)	177.21(4)	174.34(6)	177.94(11)	177.60(16)

[a] *trans* and *cis* refer to position relative to the triazolylidene ligand.

Crystallization of complex **3d** invariably resulted in crystalline material that was not suitable for X-ray diffraction. Single crystals of sufficient quality were obtained upon exchanging the non-coordinating anion from OTf^- to BPh_4^- (**3d'**). All crystallographic discussion included the structure of **3d'**.

Crystals of **4** showed a strong disorder of the *C,N*-bidentate ligand in **4** and revealed about equal occupancy of the ligand position with the carbene fragement and the pyridyl moiety. As a consequence of this disorder *trans* influences are difficult to discuss as they reflect an average of the *trans* influence of pyridine and the triazolylidene.

The crystals of **3c** showed rapid decomposition by solvent loss when taken out of their mother liquor under normal conditions. Hence one specimen was selected at low temperature as first described by Kottke and Stalke.[5] The oil on the slide was at –20°C when the crystals were put in, and the temperature was not monitored afterwards. Crystal data for **3d'** were collected on a Bruker SMART APEX CCD diffractometer. A full sphere of reciprocal space was scanned by phi-omega scans. A pseudo-empirical absorption correction based on redundant reflections was performed by the program SADABS.[6] Crystal data for all other compounds were collected using an Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector. Crystals were measured with Mo-K_α (0.71073 Å). At least one complete dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical absorption correction based on the shape of the crystal was performed for all these crystals.[7]

The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares on F^2 for all data using SHELXL-97.[8] Hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic temperature factors were fixed to 1.2 times (1.5 times for methyl groups) the equivalent isotropic displacement parameters of the carbon atom the H-atom is attached to. Anisotropic thermal displacement parameters were used for all non-hydrogen atoms. In **3d'** the solvent could not be modeled in terms of atomic sites. The procedure SQUEEZE, implemented in Platon,[9] was used to remove the spread electron density. The number of electrons was assigned to acetonitrile and diethylether, and these molecules are included in the formula, calculated density, absorption coefficient and molar mass.

Refinement of the data set for complex **5** was deteriorated by strongly disordered PF_6 anions and did not converge satisfactorily. However, the cationic portion is sufficiently well resolved to confirm the connectivity pattern.

Further crystallographic details are compiled in Table S3. CCDC 817668–817675 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S3. Crystallographic data for complexes

	Complex **2a**	Complex **2b**	Complex **2c**
CCDC number	817668	817669	817670
crystal size /mm^{-1}	0.12 × 0.15 × 0.22	0.04 × 0.07 × 0.12	0.13 × 0.22 × 0.25
Empirical formula	$C_{20}H_{24}ClF_3N_4O_3RuS$	$C_{21}H_{26}ClF_3N4O_3RuS$ × CH_3CN	$C_{22}H_{28}ClF_3N_4O_3RuS$ × CH_3CN
Fw	594.01	649.09	663.12
T /K	100	100	100
crystal system	Triclinic	Triclinic	Monoclinic
space group	P–1 (No. 2)	P–1 (No. 2)	$P2_1/c$ (No. 14)
unit cell			
a /Å	9.0688(2)	7.9511(2)	9.2210(1)
b /Å	9.8428(2)	11.3181(3)	10.6901(1)
c /Å	13.7787(3)	15.6143(5)	27.7904(3)
α /°	85.827(2)	83.120(2)	90
β /°	84.744(2)	75.630(2)	92.849(1)
γ /°	70.410(2)	80.116(2)	90
Volume /Å^3	1152.70(4)	1336.59(6)	2736.01(5)
Z	2	2	4
D_{calcd} /g cm^{-3}	1.711	1.613	1.610
μ /mm^{-1}	0.941	0.820	0.803
no. total reflcns	41596	22534	46079
unique reflecns	11813	5452	7126
R_{int}	0.0360	0.0612	0.0409
Absorption correction	Analytical	Analytical	Analytical
transmission range	0.854–0.925	0.935–0.974	0.853–0.918
no. parameters	303	340	350
no. restraints	0	0	0
GOF	1.06	1.06	1.09
R_1,[a] wR_2,[b] $I > 2\sigma(I)$	0.0292, 0.0632	0.0366, 0.0631	0.0271, 0.0502
R_1,[a] wR_2,[b] all data	0.0380, 0.0687	0.0566, 0.0699	0.0376, 0.0543
largest diff. peak, hole /e Å^{-3}	–1.094, 1.170	–0.529, 0.587	–0.567, 0.499

Table S3. Crystallographic data for complexes (continued)

	Complex **3a**	Complex **3b**	Complex **3c**
CCDC number	817671	817672	817673
crystal size /mm^{-1}	0.09 × 0.15 × 0.26	0.13 × 0.15 × 0.19	0.19 × 0.29 × 0.37
Empirical formula	$C_{19}H_{22}F_6N_8O_6RuS_2$	$C_{20}H_{24}F_6N_8O_6RuS_2$	$C_{21}H_{26}F_6N_8O_6RuS_2$ × 0.75 CH_3CN × 0.25 H_2O
Fw	737.64	751.66	801.16
T /K	100	100	100
crystal system	Triclinic	Monoclinic	Monoclinic
space group	P–1 (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
unit cell			
a /Å	10.8566(5)	12.2612(1)	8.5421(1)
b /Å	11.8285(4)	15.4601(2)	24.5273(2)
c /Å	12.7801(5)	16.5297(2)	16.1468(2)
α /°	71.673(3)	90	90
β /°	72.374(4)	107.760(1)	102.379(1)
γ /°	65.259(4)	90	90
Volume /Å^3	1386.76(10)	2984.03(6)	3304.34(6)
Z	2	4	4
D_{calcd} /g cm^{-3}	1.767	1.673	1.610
μ /mm^{-1}	0.807	0.752	0.686
no. total reflcns	31523	37720	32309
unique reflecns	9541	7486	8218
R_{int}	0.0311	0.0217	0.0331
Absorption correction	Analytical	Analytical	Analytical
transmission range	0.861–0.940	0.902–0.930	0.826–0.892
no. parameters	385	394	498
no. restraints	0	0	1
GOF	1.05	1.05	1.07
R_1,[a] wR_2,[b] $I > 2\sigma(I)$	0.0257, 0.0620	0.0216, 0.0507	0.0319, 0.069
R_1,[a] wR_2,[b] all data	0.0343, 0.0641	0.0243, 0.0524	0.0435, 0.0755
largest diff. hole, peak /e Å^{-3}	–0.772, 0.652	–0.503, 0.487	–0.636, 0.883

Table S3. Crystallographic data for complexes (continued)

	Complex **3d'**	Complex**4**
CCDC number	817674	817675
crystal size /mm^{-1}	0.10 × 0.20 × 0.30	0.13 × 0.18 × 0.26
Empirical formula	$C_{70}H_{64}B_2N_8Ru$ × 0.75 CH_3CN × 0.25 $C_4H_{10}O$	$C_{17}H_{21}F_{12}N_7P_2Ru$
Fw	1189.30	714.42
T /K	100	100
crystal system	Orthorhombic	Triclinic
space group	$Pna2_1$ (No. 33)	P–1 (No. 2)
unit cell		
a /Å	35.555(3)	9.1535(2)
b /Å	11.8292(9)	11.7781(3)
c /Å	14.7547(12)	12.9329(3)
α /°	90	84.914(2)
β /°	90	71.896(2)
γ /°	90	85.969(2)
Volume /Å^3	6205.6(8)	1318.72(5)
Z	4	2
D_{calcd} /g cm^{-3}	1.273	1.799
μ /mm^{-1}	0.304	0.823
no. total reflcns	93844	34786
unique reflecns	10681	6320
R_{int}	0.0648	0.0281
Absorption correction	semi-empirical from equivalents	Analytical
transmission range	0.914–0.970	0.863–0.922
no. parameters	735	531
no. restraints	221	98
GOF	1.11	1.05
R_1,[a] wR_2,[b] $I > 2\sigma(I)$	0.0389, 0.0894	0.0332, 0.0775
R_1,[a] wR_2,[b] all data	0.0409, 0.0904	0.0379, 0.0807
largest diff. hole, peak /e Å^{-3}	–1.019, 0.504	–0.698 0.780

[a] $R_1 = \Sigma||F_O|-|F_C||/\Sigma|F_O|$; [b] $wR_2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma(w(F_O^4)]^{1/2}$

5. References

1 K. Barral, A. D. Moorhouse and J. E. Moses, *Org. Lett*., 2007, **9**, 1809.

2 N. G. Connelly and W. E. Geiger, *Chem. Rev.,* 1996, **96**, 877.

3 J. T. Fletcher, B. J. Bumgarner, N. D. Engels and D. A. Skoglund, *Organometallics,* 2008, **27**, 5430.

4 See for examples: (a) J. Huang, E. D. Stevens, S. P. Nolan and J. L. Petersen, *J. Am. Chem. Soc.,* 1999, **121**, 2674; M. Poyatos, E. Mas-Marza, M. Sanau and E. Peris, *Inorg. Chem.,* 2004, **43**, 1793; L. Mercs, A. Neels and M. Albrecht, *Dalton Trans.,* 2008, 5570; C. Gandolfi, M. Heckenroth, A. Neels, G. Laurenczy and M. Albrecht, *Organometallics,* 2009, **28**, 5112; F. E. Hahn, A. R. Naziruddin, A. Hepp and T. Pape, *Organometallics,* 2010, **29**, 5283.

5 T. Kottke and D. Stalke *J. Appl. Cryst.,* 1993, **26**, 615.

6 Bruker 2001, SADABS, Bruker AXS Inc., Madison, Wisconsin, USA.

7 R. C. Clark and J. S. Reid, *Acta Cryst.,* 1995, **A51**, 887.

8 G. M. Sheldrick, *Acta Cryst.,* 2008, **A64**, 112.

9 A. L. Spek, *Acta Cryst*., 2009, **D65**, 148.