Electronic Supporting Information

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Synthesis and catalytic alcohol oxidation and ketone transfer hydrogenation activity of donor-functionalized mesoionic triazolylidene ruthenium(II) complexes

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1. Synthetic details

Synthesis of 1-mesityl-4-(methyl carboxylate)triazole. This compound has been reported previously, yet incompletely.[S1] Mesityl azide (387 mg, 2.4 mmol) and methyl propiolate (222 mg, 2.64 mmol) were added to a mixture of water (4 mL) and *tert*-BuOH (8 mL). To the previous mixture copper sulphate (1 N, 1.2 mL) and copper powder (150 mg) were added and the mixture was irradiated in a Biotage microware reactor at 100 ºC for 120 minutes. The copper powder was filtered off, dichloromethane (10 mL) added and the mixture was washed with aqueous NH_3 to remove copper salts. The mixture was extracted with dichloromethane (2 × 50 mL). The combined organic phases were washed with water (2 × 30 mL), brine (1 × 50 mL), dried over $MgSO_4$ and solvent evaporation. The residue was washed with pentane (50 mL), 1-mesityl-4-(methyl carboxylate)triazole was obtained as an off white solid (498 mg, 85 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 1H, H_{trz}), 7.00 (s, 2H, H_{mes}), 4.00 (s, 3H,

S1 V. V. R. Rao, B. E. Fulloon, P. V. Bernhardt, R. Koch and C. Wentrup, *J. Org. Chem.,* 1998, 63, 5779–5786.

OCH_3), 2.36 (s, 3H, CH_3), 1.96 (s, 6H, CH_3). $^{13}C\{1H\}$ NMR (125 MHz, CDCl3): δ 161.3 ($COOCH_3$), 140.7 (C_{mes}), 134.9 (C_{trz}), 132.8 (C_{mes}), 129.7 (CH_{trz}), 129.4 (CH_{mes}), 129.0 (C_{mes}), 52.4 ($COOCH_3$), 21.2 (CH_3), 17.3 (2·CH_3). IR (KBr): ν = 1730 cm^{-1} (s; C=O). Anal. Calc for $C_{13}H_{15}N_3O_2$ (245.28): C, 63.66; H, 6.16; N, 17.13. Found: C, 63.41; H, 6.16; N, 16.97.

Alcohol deprotection from 2e. Complex **2e** (14.3 mg, 0.022 mmol) was dissolved in $CDCl_3$ (1.0 mL) then Bu_4NF (22 μL, 1.0 M in THF, 0.022 mmol) was added. The reaction mixture was stirred at 40 °C for 18 h. ^1H NMR ($CDCl_3$ 400 MHz): δ 7.02 (s, 2H, H_{ar}), 5.09, 4.76 (2 × d, $^3J_{HH}$ = 5.6 Hz, 2H, H_{cym}), 4.61 (s, 2H, CH_2O), 4.21 (s, 3H, NCH_3), 3.32 (m, 8H, NCH_2), 2.28 (s, 3H, $ArCH_3$), 2.18 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, $CHMe_2$), 2.19 (s, 6H, $ArCH_3$), 1.87 (s, 3H, C_{cym}–CH_3), 1.60 (m, 8H, NCH_2CH_2), 1.41 (m, 8H, $NCH_2CH_2CH_2$), 1.08 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH–CH_3), 0.97 (m, 12H, $NCH_2(CH_2)_2CH_3$), 0.90 (s, 9H, SiC–CH_3), 0.14 (s, $^3J_{HF}$ = 7.5 Hz, 6H, Si–CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 168.6 (C_{trz}–Ru), 166.8 (C_{trz}–CH_2O), 146.9, 140.6, 136.5, 129.1 (4 × C_{Mes}), 100.5, 93.9, 83.5, 83.1 (4 × C_{cym}), 59.1 (NCH_2), 54.6 (CH_2O), 36.9 (NCH_3), 31.7 ($CHMe_2$), 25.3 (C–CH_3), 24.3 (NCH_2CH_2), 23.1 ($CHCH_3$), 21.2 ($ArCH_3$), 19.9 ($NCH_2CH_2CH_2$), 18.5 (C_{cym}–CH_3), 18.1 ($ArCH_3$), 18.0 (Si–CMe_3), 13.8 ($NCH_2(CH_2)_2CH_3$), –4.5 (Si–CH_3, $^2J_{CF}$ = 14.9 Hz).

2. ORTEP plot of 1f

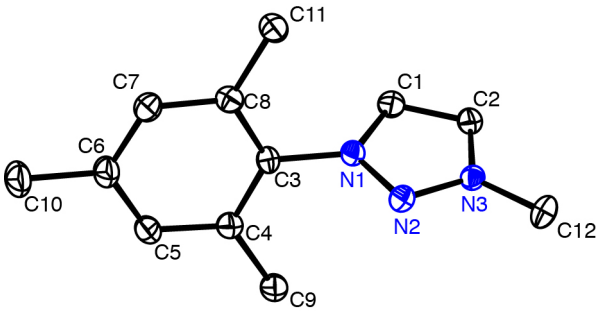
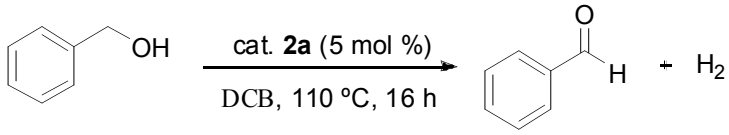


Figure S1 ORTEP representation of **1f** (50% probability, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): C1–C2 1.366(2), C1–N1 1.3515(19), C2–N3 1.3411(19), N1–N2 1.3260(17), N2–N3 1.3181(17), N1–C3 1.4451(18); N1–C1–C2 105.27(13), C1–C2–N3 105.37(13), C2–N3–N2 113.27(12), N3–N2–N1 103.56(11), N2–N1–C1 112.51(12), C1–N1–C3 127.21(13), N2–N3–C12 120.17(12).

3. Catalytic details

Table S1. Time-dependent monitoring of the catalytic alcohol oxidation of benzyl alcohol with complex **2a**. [a]



entry	time (h)	conversion (%)[b]	TON
1	0	0	---
2	2	36	7
3	4	55	11
4	6	68	14
5	8	75	15
6	16	77	15
7	24	82	16

[a] Reaction conditions: Benzyl alcohol (0.2 mmol), anisole (0.2 mmol), **2a** (5 mol%) 1,2-dichlorobenzene (2 mL), at 110 °C; [b]Determined by ^{1}H NMR spectroscopy (anisole as a standard).

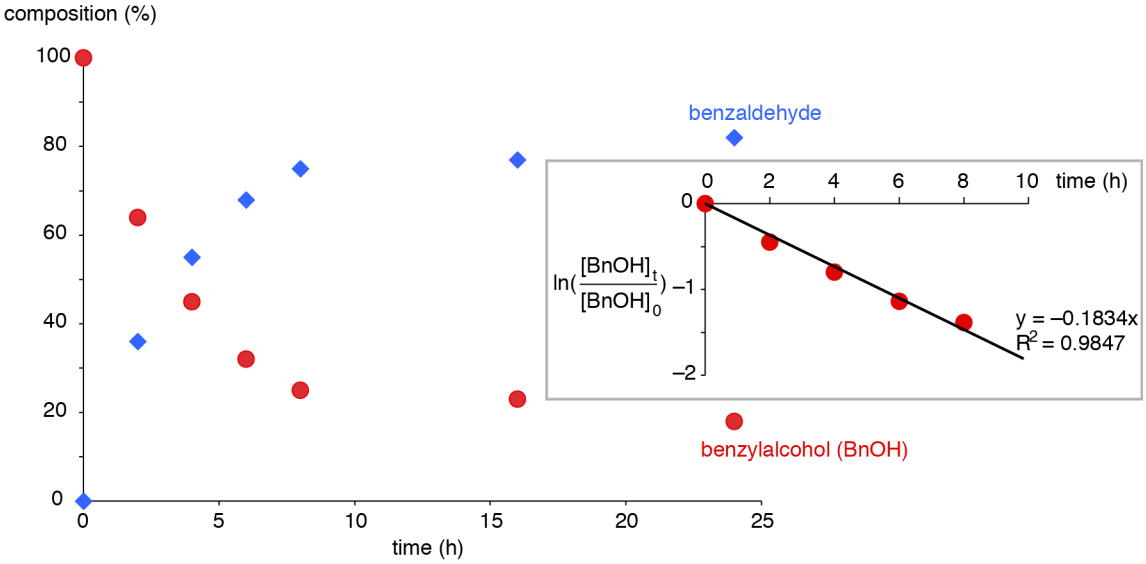
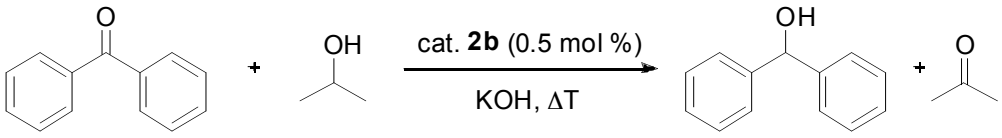


Figure S2 Reaction profile of a representative catalytic alcohol oxidation using **2a** (5 mol%) and featuring the oxidation of benzylalcohol (●) to benzaldehyde (◆); inset shows the first-order kinetics for benzylalcohol (BnOH) consumption. The linear fit allows the 50% conversion time to be determined accurately, $TOF_{50} = 2.7\ h^{-1}$.

Table S2. Catalytic transfer hydrogenation of benzophenone with complex **2b**. [a]



entry	time (min)	conversion (%)[b]	TON
1	5	31	62
2	10	52	104
3	15	69	138
4	20	78	156
5	30	91	182
6	45	96	192
7	60	98	196
8	90	99	198
9	120	99	198

[a] Reaction conditions: Benzophenone (1 mmol), KOH (0.1 mmol) (substrate / base 10:1), **2b** (0.5 mol %), *i*PrOH (5 mL), reflux temperature; [b]Determined by ^{1}H NMR spectroscopy.

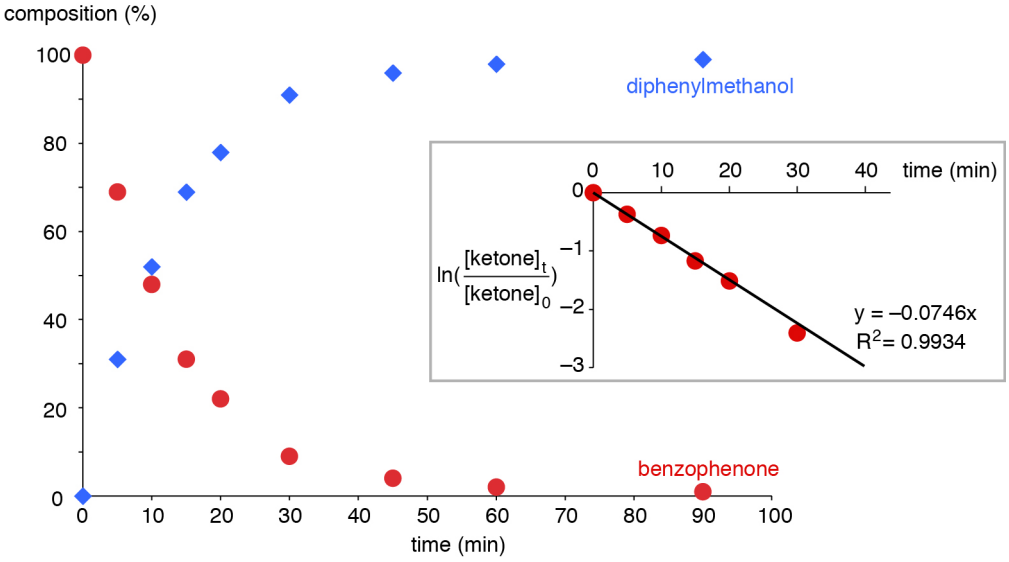


Figure S3 Reaction profile of a representative transfer hydrogenation using **2b** (0.5 mol%) and featuring the reduction of benzophenone (●) to diphenylmethanol (◆); inset shows the first-order kinetics for substrate consumption. The linear fit allows the 50% conversion time to be determined accurately, $TOF_{50} = 680\ h^{-1}$.

4. Crystallographic Tables

Table S3 Crystal data and structure refinement for **1f**.

CCDC No.	968359	
Empirical formula	$C_{12}H_{16}N_3Cl$	
Molecular formula	$[C_{12}H_{16}N_3]^+[Cl]^-$	
Formula weight	237.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$ (#14)	
Unit cell dimensions	a = 6.3174(2) Å	α = 90°
	b = 19.8791(6) Å	β = 91.123(4)°
	c = 9.8572(3) Å	γ = 90°
Volume	1237.67(7) $Å^3$	
Z	4	
Density (calculated)	1.276 Mg m^{-3}	
Absorption coefficient	0.286 mm^{-1}	
F(000)	504	
Crystal size	0.1769 × 0.1254 × 0.0530 mm^3	
Theta range for data collection	2.91 to 29.48°	
Index ranges	–8<=h<=8, –27<=k<=27, –13<=l<=13	
Reflections collected	12299	
Independent reflections	3062 [R(int) = 0.0310]	
Completeness to θ = 27.00°	99.0 %	
Absorption correction	Analytical	
Max. and min. transmission	0.986 and 0.961	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	3062 / 0 / 149	
Goodness–of–fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.0897	
R indices (all data)	R1 = 0.0485, wR2 = 0.0949	
Largest diff. peak and hole	0.266 and –0.219 e $Å^{-3}$	

Table S4 Crystal data and structure refinement for **2c**.

CCDC No.	968356	
Empirical formula	$C_{47}H_{58}N_6O_4Cl_4Ru_2$	
Molecular formula	$(C_{23}H_{28}N_3O_2ClRu)_2 \times CH_2Cl_2$	
Formula weight	1114.93	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4/ncc (#130)	
Unit cell dimensions	a = 24.4639(2) Å	α = 90°
	b = 24.4639(2) Å	β = 90°
	c = 16.2815(2) Å	γ = 90°
Volume	9744.19(16) $Å^3$	
Z	8	
Density (calculated)	1.520 Mg m^{-3}	
Absorption coefficient	0.888 mm^{-1}	
F(000)	4560	
Crystal size	0.3285 × 0.1822 × 0.1353 mm^3	
Theta range for data collection	2.92 to 29.61°	
Index ranges	–31<=h<=33, –31<=k<=33, –22<=l<=22	
Reflections collected	99946	
Independent reflections	6521 [R(int) = 0.0222]	
Completeness to θ = 28.00°	99.8 %	
Absorption correction	Analytical	
Max. and min. transmission	0.926 and 0.818	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	6521 / 124 / 415 [a)]	
Goodness–of–fit on F^2	1.209	
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.0686	
R indices (all data)	R1 = 0.0357, wR2 = 0.0696	
Largest diff. peak and hole	0.761 and –1.035 e $Å^{-3}$	

[a)] DELU restraints were applied to all disordered atoms. The sum of the three disorder parts was restrained to be 1 using SUMP.

Table S5 Crystal data and structure refinement for **2f**.

CCDC No.	968358	
Empirical formula	$C_{22}H_{29}N_3Cl_2Ru$	
Formula weight	507.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P–1 (#2)	
Unit cell dimensions	a = 12.2789(2) Å	α = 82.000(2)°
	b = 12.7985(3) Å	β = 87.781(2)°
	c = 14.8101(5) Å	γ = 86.692(2)°
Volume	2299.83(10) $Å^3$	
Z	4	
Density (calculated)	1.466 Mg m^{-3}	
Absorption coefficient	0.926 mm^{-1}	
F(000)	1040	
Crystal size	0.1970 × 0.1297 × 0.0337 mm^3	
Theta range for data collection	2.78 to 29.59°	
Index ranges	–16<=h<=16, –17<=k<=16, –20<=l<=18	
Reflections collected	42281	
Independent reflections	11333 [R(int) = 0.0318]	
Completeness to θ = 27.00°	99.4 %	
Absorption correction	Analytical	
Max. and min. transmission	0.971 and 0.873	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	11333 / 0 / 519	
Goodness–of–fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0256, wR2 = 0.0555	
R indices (all data)	R1 = 0.0307, wR2 = 0.0580	
Largest diff. peak and hole	0.585 and –0.608 e $Å^{-3}$	

Table S6 Crystal data and structure refinement for **3a**.

CCDC No.	968357	
Empirical formula	$C_{24}H_{24}N_7O_3F_3SRu$	
Molecular formula	$[C_{23}H_{24}N_7Ru]^+[CF_3SO_3]^-$	
Formula weight	648.63	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P–1 (#2)	
Unit cell dimensions	a = 7.83027(7) Å	α = 106.7712(9)°
	b = 11.5481(1) Å	β = 101.9190(8)°
	c = 15.7934(2) Å	γ = 93.1348(8)°
Volume	1327.90(2) $Å^3$	
Z	2	
Density (calculated)	1.622 Mg m^{-3}	
Absorption coefficient	0.731 mm^{-1}	
F(000)	656	
Crystal size	0.2278 × 0.1606 × 0.1106 mm^3	
Theta range for data collection	2.68 to 29.51°	
Index ranges	–10<=h<=10, –15<=k<=14, –21<=l<=21	
Reflections collected	58626	
Independent reflections	7038 [R(int) = 0.0456]	
Completeness to θ = 28.00°	99.6 %	
Absorption correction	Analytical	
Max. and min. transmission	0.943 and 0.887	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	7038 / 0 / 357	
Goodness–of–fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0275, wR2 = 0.0533	
R indices (all data)	R1 = 0.0350, wR2 = 0.0566	
Largest diff. peak and hole	0.597 and –0.618 e $Å^{-3}$	