Catalysed aerobic dehydrogenation of amines and an X-ray crystal structure of a bis(benzylamine) ruthenium(II) porphyrin species

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The complex *trans*-[Ru^{VI}(tmp)(O)$_2$] 1 (tmp = dianion of 5,10,15,20-tetramesitylporphyrin) catalytically dehydrogenates primary and secondary amines in the presence of air; possible reaction steps involve a disproportionation reaction that generates a Ru^{II} intermediate, as evidenced by the isolated bis(benzylamine) complex [Ru^{II}(tmp)(PhCH$_2$NH$_2$)$_2$] 2 which is characterised crystallographically.

The use of transition-metal porphyrin complexes as catalytic oxidants is well known.[1] While there are a few examples of metalloporphyrin oxo species that dehydrogenate or dealkylate amines,[2,3] there are no reports hitherto on the use of such porphyrin complexes to oxidise (*i.e.* dehydrogenate) organic amines catalytically under O$_2$ (air). Non-porphyrin systems can effect such catalytic dehydrogenations although often forcing conditions are required, for example RuCl$_3$ (at a concentration of 2.5×10^{-2} mol dm^{-3} in toluene) is effective at 3 atm O$_2$ and 100 °C.[4]

We report here on such a process using the dioxo porphyrin complex *trans*-[Ru^{VI}(tmp)(O)$_2$] **1** to oxidatively dehydrogenate a variety of primary and secondary amines. In the process of an investigation of such a reaction with benzylamine as the substrate, **2**, the bis(amine) complex [Ru^{II}(tmp)(PhCH$_2$NH$_2$)$_2$], was isolated and characterised crystallographically. The studies relate to our recent report on the [Ru^{VI}(tmp)(O)$_2$]-catalysed aerobic oxidation of alcohols.[5]

Complex **1** was generated by *in situ* oxidation of [Ru^{II}(tmp)CO] (typically 10 mg, 0.01 mmol) by excess *m*-chloroperbenzoic acid (20 mg, 0.1 mmol) in a benzene solution (5 ml); the excess peracid was removed by chromatography on neutral alumina (activity 1) by elution with benzene.[6] The concentration of **1** in the benzene eluate was determined by UV–VIS spectroscopy. Various amines were then added (20 equiv.) and the reaction mixtures, containing 1 ml of the eluate, heated at 50 °C for 24 h in sealed vials under air. The results of the catalytic oxidations are summarised in Table 1. Primary amines with –CH$_2$NH$_2$ functionalities were oxidised to nitriles in 100% yields, water being the coproduct; the intermediate imines (–CH=NH) are presumably readily dehydrogenated. Primary amines with CHNH$_2$ groups and secondary amines gave imines, and sometimes other products presumably resulting from imine decomposition (particularly from hydrolysis). No oxidation of tertiary amines (*e.g.* pyridine) was detected even after 5 d in benzene at 50 °C. The yields and catalytic turnovers were determined by GC or GCMS. In the absence of **1** no amine dehydrogenation was observed. Complex **1** decomposes slowly under the reaction conditions and its concentration is considerably diminished after 24 h, judging by the fact that with a recharge of an additional 20 equiv. of amine a maximum of only 5 turnovers can be achieved.

During investigations of the benzylamine system at higher concentrations of amine, brown crystals of **2** were isolated from the reaction mixture. X-Ray analysis of **2** shows a structure with an inversion centre (Fig. 1);† the essentially octahedral Ru is surrounded by six nitrogens, with the metal in the porphyrin plane. The benzylamine ligands are not quite perpendicular to the porphyrin ring with N′(1)–Ru–N(11) and N(1)–Ru–N(11) bond angles of 93.43 and 86.57° respectively. The Ru–N bond lengths of the axial benzylamine ligands (2.129 Å) are longer than those in the porphyrin plane (av. 2.039 Å). The dimensions of the Ru(tmp) moiety are essentially the same as those found earlier.[5,6a] In the unit cell there are two solvent benzylamines, each hydrogen-bonded to a coordinated benzylamine, and a half-occupancy benzene solvate.

The UV–VIS spectrum of **2** in benzene [λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1}): 408 (220) and 504 (37)] is significantly different from that of **1** [422 (280), 514 (28)]. The IR spectrum (KBr) shows strong bands at 3028 and 1495 cm^{-1}, assigned to ν(N–H) and δ(N–H), respectively, and an 'oxidation-state marker'

Table 1 Dehydrogenation of amines catalysed by *trans*-[Ru(tmp)(O)$_2$] **1** under air

Substrate	Product(s)	Yield (%) (turnover)[a]
Benzylamine	Benzonitrile	100 (20)
n-Butylamine	Butyronitrile	100 (20)
α-Methylbenzylamine	1-Phenylethanimine (PhCMe=NH)	90 (18)
Isopropylamine	2-Propanimine (Me$_2$C=NH)	20 (6)
	Acetone	10
Cyclohexylamine	Cyclohexanol	10 (2)
	Cyclohexanone	13
Dibenzylamine	*N*-Benzylidenebenzylamine (PhCH=NCH$_2$Ph)	76 (15)
	Benzonitrile	11
	Benzaldehyde	13
Diethylamine	*N*-Ethylideneethylamine (MeCH=NEt)	10 (2)
	Ethanol	3
	Acetonitrile	2
Di(*n*-octyl)amine	*N*-Octylideneoctylamine (C$_7$H$_{15}$CH=NC$_8$H$_{17}$)	12 (2)
	Octanal	10
	Octanonitrile	10

[a] Turnovers are quoted for 24 h at 50 °C in benzene for the primary oxidation product only; [Ru] 1×10^{-3} mol dm^{-3}, [amine] 2×10^{-2} mol dm^{-3}.

band[3,7] (a strong sharp band at 1000 cm^{-1}) consistent with Ru in the +2 oxidation state.

The ^{1}H NMR spectrum of **2** (200 MHz, C_6D_6, 20 °C) shows resonances for tmp in a diamagnetic species, δ (all singlets): 8.41 (8H, pyrrole-H), 7.12 (8H, *m*-H), 2.35 (12H, *p*-Me), 2.26 (24H, *o*-Me); and resonances for the coordinated benzylamine ligands, δ: a multiplet at *ca.* 6.8 (10H, C_6H_5), and two triplets at −5.11 (4H, CH_2) and −1.92 (4 H, NH_2).

Possible reaction steps are proposed in Scheme 1. The initial step involves a two-electron oxidation of benzylamine to *N*-benzylideneamine by **1**, which is then reduced to the monooxo species [Ru^{IV}(tmp)(O)] **3**, observed and characterised by its distinctive ^{1}H NMR spectrum.[7] Complex **3** is known to disproportionate in solution[7,8] (steps **d** in Scheme 1) to reform **1** and the [Ru^{II}(tmp)] species **4** previously reported to be very reactive toward O_2.[9] Complex **1** or possibly species **3**[1a] presumably effects the second dehydrogenation of the imine to the nitrile. Complex **2** must be formed *via* a competitive reaction of the amine with **4**.

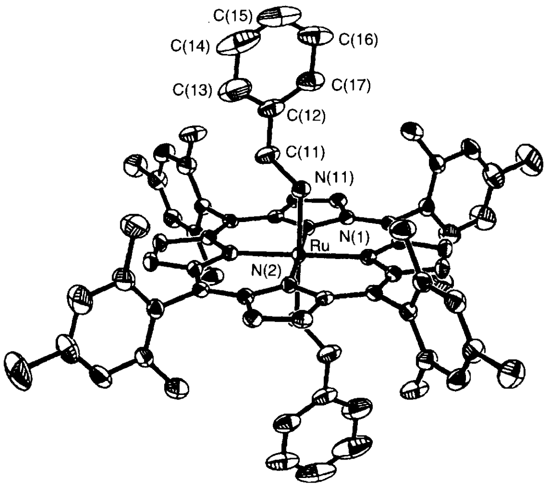
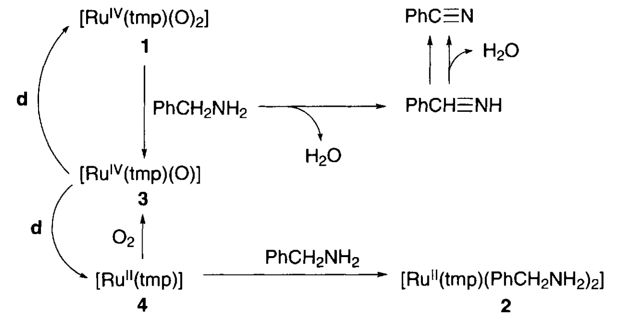


Fig. 1 X-ray crystal structure of **2** (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°) with esds in parentheses: Ru–N(porph) 2.039(av.), Ru–N(11) 2.129(2), N(11)–C(11) 1.475(4), C(11)–C(12) 1.505(5); N(2)–Ru–N(1) 89.66(9), N(2)–Ru–N′(1) 90.34(9), N(1)–Ru–N(11) 86.57(10), N′(1)–Ru–N(11) 93.43(10), N(2)–Ru–N(11) 89.89(9), N′(2)–Ru–N(11) 90.11(9), C(11)–N(11)–Ru 118.7(2), N(11)–C(11)–C(12) 114.5(3).



Scheme 1 Proposed reaction scheme for the catalytic dehydrogenation of benzylamine; **d** denotes the disproportionation reaction 2[Ru^{IV}(tmp)(O)] **3** → [Ru^{II}(tmp)] **4** + [Ru^{VI}(tmp)(O)$_2$] **1**

The catalytic oxidation of benzylamine was also carried out using either [Ru^{VI}(tdcpp)(O)$_2$][6a,10] [tdcpp = dianion of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin] or [Ru^{VI}(Cl$_8$tdcpp)(O)$_2$][11] [Cl$_8$tdcpp = dianion of 5,10,15,20-tetrakis(2,6-dichlorophenyl)-2,3,5,7,12,13,17,18-octachloroporphyrin] as catalysts. Benzonitrile was again produced in 100% yield and at faster rates (< 16 h at 50 °C) than observed using **1**; however, the chlorinated catalysts were visibly less stable under these conditions (*i.e.* some bleaching occurred).

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Footnote

† *Crystal data*: $C_{87}H_{91}N_8Ru$, M = 1349.75, triclinic, space group $P\bar{1}$, a = 11.625(1), b = 12.269(1), c = 14.009(1) Å, α = 71.063(1), β = 80.298(1), γ = 75.892(1)°, U = 1824.18(6) Å^3, Z = 1, D_c = 1.229 g cm^{-3}, μ(Mo-Kα) = 0.266 mm^{-1}, F(000) = 713. A dark brown crystal of dimensions 0.22 × 0.22 × 0.09 mm was used. Structural refinements and calculations were performed using SHELXTL-PLUS in conjunction with the new International Union of Crystallography CIF archive format. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically using absorption corrected data to give $R1$ = 0.0498, $wR2$ = 0.1170 for 6335 reflections with $I > 2\sigma(I)$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/226.

References

1 (*a*) T. Mlodnicka and B. R. James, in *Metalloporphyrin Catalysed Oxidations*, ed. F. Montanari and L. Casella, Kluwer Academic, Dordrecht, 1994, p. 121; (*b*) Y. Naruta, in *Metalloporphyrins in Catalytic Oxidations*, ed. R. A. Sheldon, Marcel Dekker Inc., New York, 1994, p. 241.
2 J. R. Lindsay Smith and D. N. Mortimer, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1743.
3 J. S. Huang, C. M. Che, Z. Y. Li and C. K. Poon, *Inorg. Chem.*, 1992, **31**, 1313.
4 R. Tang, S. E. Diamond, N. Neary and F. Mares, *J. Chem. Soc., Chem. Commun.*, 1978, 562.
5 S. Y. S. Cheng, N. Rajapakse, S. J. Rettig and B. R. James, *J. Chem. Soc., Chem. Commun.*, 1994, 2669.
6 (*a*) N. Rajapakse, B. R. James and D. Dolphin, *Stud. Surf. Sci. Catal.*, 1990, **55**, 109; (*b*) P. Dubourdeaux, M. Tavarès, A. Grand, R. Ramasseal and J.-C. Marchon, *Inorg. Chim. Acta*, 1995, **240**, 657.
7 J. T. Groves and K. H. Ahn, *Inorg. Chem.*, 1987, **26**, 3831.
8 J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, 1985, **107**, 5790.
9 M. J. Camenzind, B. R. James and D. Dolphin, *J. Chem. Soc., Chem. Commun.*, 1986, 1137.
10 C. B. Hansen, F. P. W. Agterberg, A. M. C. van Eijndhoven and W. Drenth, *J. Mol. Catal.*, 1995, **102**, 117.
11 S. Y. S. Cheng, L. Xie, B. R. James and D. Dolphin, unpublished work.

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