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FULL PAPER

Ruthenate(VI)-catalysed dehydrogenation of primary amines to nitriles, and crystal structures of *cis*-$[Ru(bipy)_2(NH_2CH_2Ph)_2]$-$[PF_6]_2\cdot 0.5MeOH$ and *cis*-$[Ru(bipy)_2(NCPh)_2][PF_6]_2\cdot CH_2Cl_2$ †

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Catalytic dehydrogenation of benzylic and other primary amines RCH_2NH_2 to the corresponding nitriles RCN by the system *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ has been investigated. The complex *cis*-$[Ru(bipy)_2(NH_2CH_2Ph)_2]^{2+}$ and the new *cis*-$[Ru(bipy)_2(NH_2CH_2R)_2]^{2+}$ (R = *o*-, *m*- or *p*-ClC_6H_4, *o*-MeC_6H_4, *o*- or *p*-$MeOC_6H_4$); *cis*-$[Ru(phen)_2(NH_2CH_2R)_2]^{2+}$ (R = Ph or *p*-$MeOC_6H_4$) and *cis*-$[Os(bipy)_2(NH_2CH_2Ph)_2]^{2+}$ have been made, and dehydrogenation of the co-ordinated amine in the ruthenium complexes to the corresponding nitriles in *cis*-$[Ru(L–L)_2(NCR)_2]^{2+}$ (L–L = bipy or phen) by peroxodisulfate demonstrated. The crystal structures of *cis*-$[Ru(bipy)_2(NH_2CH_2Ph)_2][PF_6]\cdot 0.5MeOH$ and *cis*-$[Ru(bipy)_2(NCPh)_2][PF_6]_2\cdot CH_2Cl_2$, the latter a product of co-ordinated amine dehydrogenation by peroxodisulfate to give *cis*-$[Ru(bipy)_2(NH_2CH_2Ph)_2]^{2+}$, were determined. Raman, infrared and ^{1}H NMR data for the complexes have been measured; the latter suggest that the *cis* configurations of the amine complexes are retained in solution.

As part of our continuing studies on the application of oxoruthenates and other ruthenium complexes as catalysts for the oxidation of alcohols,[2–4] alkyl halides and nitro compounds,[3] sulfides,[5] alkenes and alkanes[6] we have extended and developed our earlier brief observations[7] that benzylamine is dehydrogenated to benzonitrile by the catalytic *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ reagent. We find that the latter is effective for the catalytic dehydrogenation (or oxidative dehydrogenation) of primary aromatic and some primary aliphatic amines RCH_2NH_2 to nitriles RCN, and in some cases it will further catalyse the hydration of nitriles to amides $RCONH_2$. The use of other oxoruthenate systems to effect these conversions has been studied, and a study made of the stoichiometric dehydrogenation of amine complexes *cis*-$[Ru(L–L)_2(NH_2CH_2R)_2]^{2+}$ (L–L = bipy or phen) to $[Ru(L–L)_2(NCR)_2]^{2+}$ by peroxodisulfate. A number of new amine and nitrile complexes have been isolated.

Relatively few reagents are known for the catalytic conversion of amines into nitriles; there are a number of stoichiometric procedures, *e.g.* the use of hypochlorite[8] or silver(II) compounds.[9] The best catalytic system hitherto reported is a nickel(II) sulfate–peroxodisulfate reagent in 0.4 M aqueous base; this gives good yields and selectivities but is slow, taking a day for most reactions.[10] The copper(I) chloride–pyridine–dioxygen system is also slow and requires higher temperatures (60 °C).[11] The complex *trans*-$[Ru^{VI}O_2(tmp)]$ (tmp = dianion of 5,10,15,20-tetramesitylporphyrin) in benzene aerobically catalyses dehydrogenation of benzylamine and of *n*-butylamine quantitatively to the corresponding nitriles at 50 °C over a 24 h period;[12] $RuCl_3\cdot nH_2O$ in toluene dehydrogenates these substrates to a mixture of the nitriles and amides at 100 °C under 2 atm (atm = 101 325 Pa) of dioxygen,[13] and $[Ru(PPh_3)_2(NH_2CH_2Ph)_2Cl_2]$ has been shown to catalyse the aerobic conversion of benzylamine into benzonitrile at 80 °C.[14] Apart then from the slow nickel system, none of these catalytic reagents operates efficiently at room temperatures.

† Studies on transition-metal nitrido and oxo complexes. Part 18.[1]

Results and discussion

(a) Dehydrogenation of amines to nitriles by *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$

This reagent comprised of 1×10^{-4} M Ru (initially as $RuCl_3\cdot nH_2O$ or $RuO_2\cdot nH_2O$), 0.1 M sodium peroxodisulfate and molar aqueous potassium hydroxide, is an efficient catalyst for the conversion of a wide range of primary benzylic amines into the corresponding nitriles at room temperatures, and we have optimised the reaction conditions giving good yields and selectivities over relatively short periods of time (1–2 h; Table 1). With primary aliphatic amines however the system is more capricious: *n*-hexylamine and *n*-octylamine gave reasonable yields of the nitriles but took much longer (24 h) to react than did the aromatic amines; *n*-butylamine gave butyric acid, perhaps due to hydrolysis at the high pH of the reagent. None of these reactions occurs to any appreciable extent in the absence of ruthenium. As with most other oxidations involving ruthenate as a catalyst[2,7] these are self-indicating: the orange *trans*-$[Ru(OH)_2O_3]^{2-}$ turns dark green on addition of the amine, the orange ruthenate colour returning when the reactions are complete. The GC-MS studies show that in most cases only the nitriles are present after the reaction with traces of aldehyde and amide side-products; only in the case of benzylamine were significant quantities of the imine $PhCH_2N{=}CHPh$ and benzaldehyde also formed (*ca.* 28 and 5% respectively as determined by GC-MS). The purity of all the nitrile products was checked by their melting or boiling points as appropriate, and their ^{1}H NMR and GC-MS spectra measured.

Two large-scale oxidations were carried out: thus 6.8 g (0.05 mol) of *p*-methoxybenzylamine gave 3.2 g (0.03 mol) of *p*-methoxybenzonitrile when treated with 0.1 g of $RuCl_3\cdot 3H_2O$ (3.8×10^{-4} mol) in 500 cm^3 of 1 M aqueous KOH containing 10.4 g (0.04 mol) of $K_2S_2O_8$ for 24 h. Under the same conditions 5.4 g (0.05 mol) of benzylamine gave 2.6 g (0.025 mol) of benzonitrile. When the reaction is conducted stoichiometrically the ruthenium-containing product is RuO_2, so that 2 mol of ruthenate should dehydrogenate 1 mol of amine (*i.e.* an overall four-electron reaction). Stoichiometrically, solid barium ruthenate (0.34 g, 1.0 mmol) dehydrogenated 0.07 g (0.58

Table 1 Catalytic oxidation* of amines to nitriles by *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$

Substrate	Product	Stirring time/h	Yield (%)
Benzylamine	Benzonitrile	1.5	61
o-Chlorobenzylamine	*o*-Chlorobenzonitrile	1.0	70
m-Chlorobenzylamine	*m*-Chlorobenzonitrile	1.0	60
p-Chlorobenzylamine	*p*-Chlorobenzonitrile	1.0	60
o-Methylbenzylamine	*o*-Methylbenzonitrile	1.0	81
m-Methylbenzylamine	*m*-Methylbenzonitrile	1.0	98
p-Methylbenzylamine	*p*-Methylbenzonitrile	1.5	70
o-Methoxybenzylamine	*o*-Methoxybenzonitrile	0.5	68
p-Methoxybenzylamine	*p*-Methoxybenzonitrile	0.75	90
o-Bromobenzylamine hydrochloride	*o*-Bromobenzonitrile	1.5	83
m-Bromobenzylamine hydrochloride	*m*-Bromobenzonitrile	1.5	75
n-Butylamine	Butyric acid	24	9
n-Hexylamine	Hexanenitrile	24	15
n-Octylamine	Octanenitrile	24	50

* Oxidations were carried out with 2 mmol substrate, 0.1 mmol $RuCl_3 \cdot 3H_2O$ and an excess of $K_2S_2O_8$ (2.8 g) in 1 M KOH solution (25 cm^3).

mmol) of *p*-methoxybenzylamine to give 0.065 g (0.049 mmol) of *p*-methoxybenzonitrile, corresponding to a 3.8 electron change, in reasonable agreement with the expected four electron change.

The use of a phase-transfer catalyst, $(NBu^n_4)OH$ (following the effective use of $(NBu^n_4)HSO_4$ for the stoichiometric oxidations of amines to nitriles by hypochlorite[8]), was attempted but did not improve yields or turnovers; and likewise sonication or heating the solution to 50 °C gave little improvement.

Other ruthenium-containing systems were also used but were inferior to the *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ reagent. Surprisingly, the use of perruthenate (in the catalytic $[RuO_4]^-/BrO_3^-$ system), known to be effective for oxidation of alcohols, halides and nitro compounds,[2] was completely ineffectual, as was $[RuO_4]^-/S_2O_8^{2-}$; however, this latter system is known not to function as a catalyst for alcohol oxidations.[2] No amine dehydrogenation was observed with the $[RuO_4]^-/BrO_3^-$ system, suggesting that peroxodisulfate is necessary for the reaction. However, $[NPr^n_4][RuO_4]$, with *N*-methylmorpholine *N*-oxide as cooxidant,[4] which has been shown recently to be an effective and clean reagent for conversion of secondary amines $R^1CH_2NHR^2$ into the corresponding imine $R^1CH{=}NR^2$,[15] does convert benzylic amines into nitriles over 3 h periods at room temperatures, but substantial quantities of aldehyde and other side-products are also formed.

Over a 24 h period, the amines are dehydrogenated and then hydrated in relatively small yields to the corresponding amides $RCONH_2$ (*ca.* 10% for benzylamine and *p*-methoxybenzylamine) as we noted earlier;[16] this does not occur in the absence of peroxodisulfate. The stoichiometric hydration of amines to nitriles in the presence of $[Ru^{II}(NH_3)_5(H_2O)]^{2+}$ has been noted.[17] It is clear that the platinum(II) phosphinito complexes recently reported are much better nitrile hydration catalysts.[18]

(b) Oxidations of co-ordinated primary amines to co-ordinated nitriles by peroxodisulfate

We find that when aromatic amines are added to the *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ reagent or to a pure solution of *trans*-$[Ru(OH)_2O_3]^{2-}$ in aqueous base a green species is formed, probably an amine complex such as $[Ru(OH)_2O_3(NH_2CH_2R)]^{2-}$. No such colour is formed with the corresponding nitrile. Attempts to isolate this green species have failed, and no ^1H NMR spectrum could be measured owing to the paramagnetism of *trans*-$[Ru(OH)_2O_3]^{2-}$ and/or the complex. Direct reaction of amines with solid *trans*-$Ba[Ru(OH)_2O_3]$ or solid *trans*-$K_2[Ru(OH)_2O_3]$ or of *trans*-$[Ru(OH)_2O_3]^{2-}$ in solution in the absence or presence of stabilising coligands such as pyridine or 2,2′-bipyridyl did not give identifiable products. The intermediacy of such an amine complex seems likely, however: Bailey and James[12] found, during their work on *trans*-$[Ru^{VI}O_2(tmp)]$ with benzylamine, that *trans*-$[Ru^{II}(tmp)(NH_2CH_2Ph)_2]$ is formed when the amine is present in excess.

As a model for our postulated amine complex we treated *cis*-$[Ru(bipy)_2(NH_2CH_2Ph)_2]^{2+}$ with an excess of aqueous peroxodisulfate to establish whether it was dehydrogenated to a co-ordinated benzonitrile complex. No such conversions with peroxodisulfate have been reported, though Meyer and co-workers[19] have shown that *cis*-$[Ru(bipy)_2(NH_2CH_2Ph)_2]^{2+}$ is converted electrochemically into *cis*-$[Ru(bipy)_2(NH_2CH_2Ph)(NCPh)]^{2+}$ and *cis*-$[Ru(bipy)_2(NCPh)_2]^{2+}$, and Taube and co-workers[20] aerobically dehydrogenated $[Ru(NH_3)_5(NH_2CH_2Ph)]^{2+}$ to $[Ru(NH_3)_5(NCPh)]^{2+}$. We find that *cis*-$[Ru(bipy)_2(NH_2CH_2Ph)_2]^{2+}$ is indeed converted into *cis*-$[Ru(bipy)_2(NCPh)_2]^{2+}$ by an excess of aqueous peroxodisulfate; *i.e.* co-ordinated benzylamine is oxidised to co-ordinated benzonitrile. The constitutions of these two complexes as their hexafluorophosphate salts **1** and **2** have been unambiguously established by X-ray crystallography (see below). We have made a number of new amine complexes of ruthenium *cis*-$[Ru(L{-}L)_2(NH_2CH_2R)_2]^{2+}$ (L–L = bipy or phen) and find that they too are converted into salts of the corresponding new nitrile complexes $[Ru(bipy)_2(NCR)_2]^{2+}$ by an excess of aqueous peroxodisulfate at room temperatures (Table 2). Although peroxodisulfate is an effective stoichiometric oxidant for such conversions, it is surprising that bromate, which we have previously shown[3] to function as an effective cooxidant with *trans*-$[Ru(OH)_2O_3]^{2-}$, does not oxidise these amine complexes. Neither peroxodisulfate nor bromate will oxidise the co-ordinated amine ligands in $[Os(bipy)_2(NH_2CH_2Ph)_2]^{2+}$, $[Ru(CO)_2Cl_2(NH_2CH_2Ph)_2]$ or $[Ru(NH_2CH_2Ph)_6]Cl_2$.

(c) X-Ray crystallography

(i) Crystal structure of *cis*-$[Ru(bipy)_2(NH_2CH_2Ph)_2][PF_6]_2 \cdot 0.5MeOH$ 1. Orange-red crystals of the complex were prepared by reaction of *cis*-$[Ru(bipy)_2Cl_2]$ and benzylamine under reflux with subsequent addition of NH_4PF_6, and recrystallised from methanol.

The X-ray structural analysis of complex **1** (Fig. 1) confirms it to have the expected *cis*-configuration for the benzylamine ligands. The co-ordination geometry at ruthenium is slightly distorted octahedral, with angles in the ranges 78.7(2) to 98.9(3)° and 169.3(2) to 175.6(2)°, the marked contractions in the *cis* angles being due to the bite of the 2,2′-bipyridyl ligands. The six Ru–N bond lengths (Table 3) clearly emphasise their differing chemical natures, those to the two benzylamine ligands being noticeably longer at 2.166(6) [N(2)] and 2.174(7) Å [N(1)] than those to the chelating 2,2′-bipyridyl ligands [ranging between 2.041(6) and 2.075(6) Å]. These differences reflect the sp^3 and sp^2 nature of the respective co-ordinated nitrogen centres. The two N–C (benzyl) distances (average 1.43

Table 2 Analytical and spectroscopic data for *cis*-$[Ru(L–L)_2(NH_2CH_2R)_2]^{2+}$ and *cis*-$[Ru(L–L)_2(NCR)_2]^{2+}$ complexes

	Analytical data[a] (%)			Vibrational data[b]/cm^{-1}				^1H NMR[c] (δ)	
Complex	C	H	N	$\nu_{asym}(NH_2)$	$\nu_{sym}(NH_2)$	ν(CN)	$\delta(NH_2)$	CH_2	NH_2
$[Ru(bipy)_2(NH_2CH_2Ph)_2][PF_6]_2$	44.3 (44.5)	3.8 (3.7)	8.8 (9.2)	3316m	3188w	–	1600m	3.2 (m), 3.8 (m)	4.6 (t), 4.8 (t)
$[Ru(bipy)_2(NCPh)_2][PF_6]_2$	44.3 (44.9)	3.1 (2.9)	8.8 (9.2)			2240w *2245s*, *2240w*			
$[Ru(bipy)_2(NH_2CH_2C_6H_4Cl\text{-}o)_2][PF_6]_2\cdot H_2O$	41.3 (40.7)	3.3 (3.4)	8.6 (8.4)	3320m	3244w	–	1617m	3.4 (m), 3.7 (m)	4.4 (t), 4.8 (t)
$[Ru(bipy)_2(NCC_6H_4Cl\text{-}o)_2][PF_6]_2$	41.5 (41.8)	3.4 (2.5)	8.6 (8.6)			2240w *2245s*			
$[Ru(bipy)_2(NH_2CH_2C_6H_4Cl\text{-}m)_2][PF_6]_2\cdot H_2O$	40.7 (40.7)	3.4 (3.3)	8.5 (8.2)	3314m	3134m	–	1615m	3.2 (m), 3.8 (m)	4.4 (t), 4.7 (t)
$[Ru(bipy)_2NCC_6H_4Cl\text{-}m)_2][PF_6]_2\cdot H_2O$	41.3 (41.0)	2.3 (2.6)	8.5 (8.4)			2230w *2241s*			
$[Ru(bipy)_2(NH_2CH_2C_6H_4Me\text{-}o)_2][PF_6]_2$	45.3 (45.7)	3.7 (4.0)	8.8 (8.9)	3311m *3260m*	3266m *3160w*	–	1603m	3.3 (m), 3.6 (m)	4.6 (t), 4.8 (t)
$[Ru(bipy)_2(NCC_6H_4Me\text{-}o)_2][PF_6]_2$	46.3 (46.1)	3.5 (3.2)	8.9 (9.0)			2235w			
$[Ru(bipy)_2(NH_2CH_2C_6H_4OMe\text{-}o)_2][PF_6]_2\cdot H_2O$	43.5 (43.4)	4.2 (4.1)	8.3 (8.4)	3320m	3217m	–	1620m	3.4 (m), 3.7 (m)	4.4 (t), 4.7 (t)
$[Ru(bipy)_2(NCC_6H_4OMe\text{-}o)_2][PF_6]_2\cdot 2H_2O$	43.5 (43.0)	3.5 (3.4)	8.7 (8.4)			2240w			
$[Ru(bipy)_2(NH_2CH_2C_6H_4OMe\text{-}p)_2][PF_6]_2$	44.5 (44.2)	4.2 (3.9)	8.8 (8.6)	3330m	3233m	–	1618m	3.5 (m), 3.8 (m)	4.3 (t), 4.8 (t)
$[Ru(bipy)_2(NCC_6H_4OMe\text{-}p)_2][PF_6]_2$	44.5 (44.6)	3.5 (3.1)	8.7 (8.7)			2241w			
$[Ru(phen)_2(NH_2CH_2Ph)_2][PF_6]_2\cdot H_2O$	46.8 (46.4)	3.4 (3.7)	8.5 (8.5)	3287m	3244m	–	1622m	3.2 (m), 3.8 (m)	4.4 (t), 4.9 (t)
$[Ru(phen)_2(NCPh)_2][PF_6]_2$	47.5 (47.6)	2.8 (2.9)	8.6 (8.8)			2242w			
$[Ru(phen)_2(NH_2CH_2C_6H_4OMe\text{-}p)_2][PF_6]_2\cdot H_2O$	45.3 (46.0)	3.6 (3.9)	8.0 (8.0)	3280m	3212m	–	1623m	3.3 (m), 3.7 (m)	4.4 (t), 4.8 (t)
$[Ru(phen)_2(NCC_6H_4OMe\text{-}p)_2][PF_6]_2\cdot H_2O$	46.3 (46.4)	3.2 (3.1)	8.0 (8.1)			2236w *2244s*			

[a] Calculated values in parentheses. [b] Raman data italicised. [c] In $(CD_3)_2CO$ *vs.* $SiMe_4$; resonances due to bipy/phen and phenyl omitted.

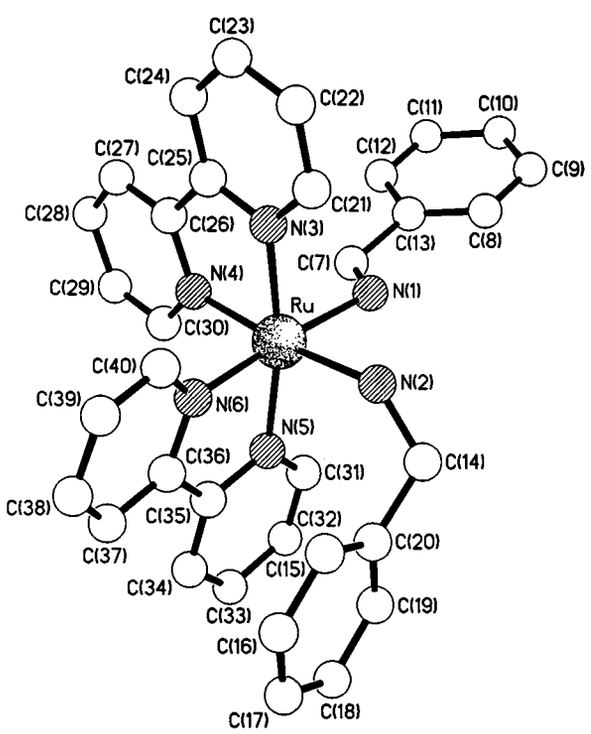

Fig. 1 The molecular structure of the cation in complex **1**, showing the overlap between one of the benzylamine ligands and one of the 2,2′-bipyridyl units.

Å) are unexceptional, reflecting their single-bond character; the angles at the benzylamine nitrogen atoms are sightly enlarged at 121.7(7) [N(1)] and 124.6(6)° [N(2)].

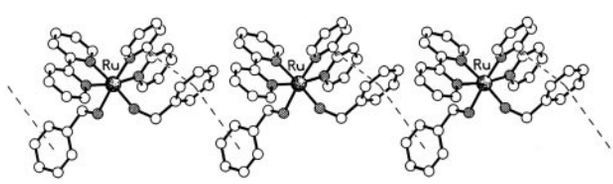

Fig. 2 Part of one of the aromatic–aromatic edge-to-face linked chains of cations present in the crystals of complex **1**.

An interesting feature of the conformation of the cation is the adoption of a *gauche* geometry about the N–CH_2 bond in one benzylamine ligand [N(2)], whereas in the other [N(1)] the geometry is *anti*. The former conformation is stabilised by an intramolecular π–π stacking interaction between the benzyl ring and adjacent bipyridyl ligand (mean interplanar separation *ca.* 3.2 Å). The opposite face of the benzyl ring is involved in an intermolecular aromatic–aromatic edge-to-edge interaction with the phenyl ring of the other benzylamine ligand (centroid–centroid separation 4.78 Å). The combined effect of these two interactions is to produce loosely linked chains of molecules that extend in the crystallographic *a* direction (Fig. 2). Centrosymmetrically related pairs of chains are cross-linked by additional T type aromatic–aromatic edge-to-edge interactions between the face of the N(1) benzylamine and the edge of the N(5) pyridine ring and *vice versa* (centroid–centroid separation 4.93 Å).

(ii) Crystal structure of *cis*-$[Ru(bipy)_2(NCPh)_2][PF_6]_2\cdot CH_2Cl_2$ 2. An aqueous solution of *cis*-$[Ru(bipy)_2(NH_2CH_2Ph)_2]^{2+}$ was treated with an excess of aqueous peroxodisulfate and the yellow product, *cis*-$[Ru(bipy)_2(NCPh)_2][PF_6]_2$, was isolated by addition of NH_4PF_6. It was recrystallised from dichloromethane as yellow crystals.

Table 3 Selected bond lengths (Å) and angles (°) for complex **1**

Ru–N(1)	2.174(7)	Ru–N(2)	2.166(6)	Ru–N(3)	2.075(6)
Ru–N(4)	2.058(6)	Ru–N(5)	2.063(6)	Ru–N(6)	2.041(6)
N(1)–C(7)	1.401(13)	N(2)–C(14)	1.454(11)		
N(6)–Ru–N(4)	92.2(2)	N(6)–Ru–N(5)	78.7(2)	N(4)–Ru–N(5)	92.7(2)
N(6)–Ru–N(3)	94.9(2)	N(4)–Ru–N(3)	78.8(2)	N(5)–Ru–N(3)	169.3(2)
N(6)–Ru–N(2)	89.3(2)	N(4)–Ru–N(2)	173.4(2)	N(5)–Ru–N(2)	93.9(2)
N(3)–Ru–N(2)	94.6(2)	N(6)–Ru–N(1)	175.6(2)	N(4)–Ru–N(1)	91.6(3)
N(5)–Ru–N(1)	98.9(3)	N(3)–Ru–N(1)	87.9(3)	N(2)–Ru–N(1)	87.2(3)
C(7)–N(1)–Ru	121.7(7)	C(14)–N(2)–Ru	124.6(6)		

Table 4 Selected bond lengths (Å) and angles (°) for complex **2**

Ru–N(1)	2.032(4)	Ru–N(2)	2.045(4)	Ru–N(3)	2.064(4)
N(1)–C(1)	1.140(6)	C(1)–C(7)	1.415(6)		
N(1)–Ru–N(1′)	91.9(2)	N(1)–Ru–N(2)	89.2(2)	N(1)–Ru–N(2′)	175.1(2)
N(2)–Ru–N(2′)	90.2(2)	N(1)–Ru–N(3)	87.7(2)	N(2)–Ru–N(3)	78.9(2)
N(1)–Ru–N(3′)	96.3(2)	N(2)–Ru–N(3′)	96.9(2)	N(3)–Ru–N(3′)	174.2(2)
C(1)–N(1)–Ru	177.6(4)	N(1)–C(1)–C(7)	178.0(6)		

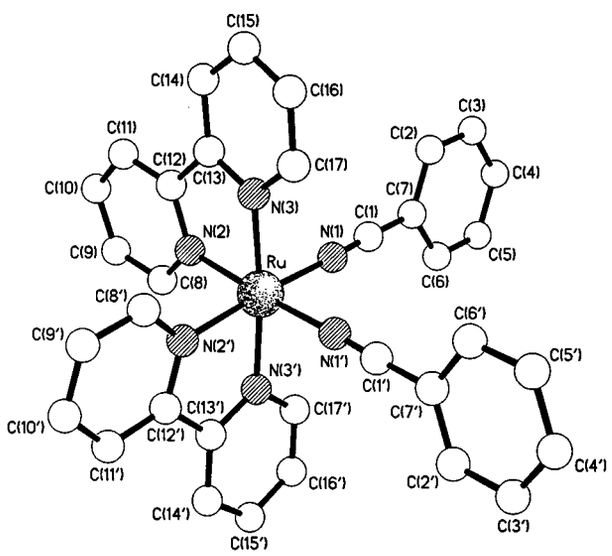

Fig. 3 The molecular structure of the C_2-symmetric cation in complex **2**.

The X-ray structural analysis of complex **2** (Fig. 3) confirms that the expected stoichiometric oxidation from co-ordinated benzylamine to benzonitrile has occurred. The two benzylamine ligands present in **1** have retained their *cis* relationship in the oxidised product **2**, the N(1)–Ru–N(1′) angle being 91.9(2)°. The complex possesses crystallographic C_2 symmetry about an axis passing through the ruthenium centre and bisecting the two benzonitrile ligands. The co-ordination geometry at ruthenium is slightly distorted octahedral, with angles in the ranges 78.9(2) to 96.9(2) and 174.2(2) to 175.1(2)°, the marked contractions observed in the *cis* angles being as expected due to the bite of the 2,2′-bipyridyl ligands. The independent Ru–N bond lengths (Table 4) clearly reflect their differing chemical natures, with those to the benzonitrile ligands [2.032(4) Å] being noticeably shorter than those to the 2,2′-bipyridyl ligands (see above). The corresponding bonds to the benzylamine ligands in **1** are longer [at 2.166(6) and 2.174(7) Å], consistent with the change from an sp^3 hybridisation in **1** to sp in **2**. The bond distances to the sp^2 hybridised 2,2′-bipyridyl ligands are essentially the same in both structures [2.041(6) to 2.075(6) Å in **1** and 2.045(4) and 2.064(4) Å in **2**] being, as expected, intermediate with respect to those to the sp^3 and sp hybridised benzylamine and benzonitrile ligands in **1** and **2**. The oxidation of the benzonitrile ligand in **1** is clearly demonstrated in **2** by the unambiguous triple-bond character for N(1)–C(1) [1.140(6) Å] and the linear geometries at C(1) and N(1) [178.0(6) and 177.6(4)° respectively]. The orientation of the terminal phenyl rings of the benzonitrile ligands is such that they lie virtually coplanar with their associated *trans* 2,2-bipyridyl ligands. There is, surprisingly, a marked absence of any intramolecular π–π interactions. The only intermolecular interactions of any note are weak cation–anion C–H···F interactions between C(11) and C(14) of one of the PF_6 anions (the H···F distances are 2.49 and 2.36 Å with C–H–F angles of 173 and 165° respectively).

(d) Vibrational and ^{1}H NMR spectra of amine and nitrile complexes

There are very slight differences in the elemental analyses between *cis*-$[Ru(bipy)_2(NH_2CH_2R)_2]^{2+}$ and *cis*-$[Ru(bipy)_2(NCR)_2]^{2+}$ salts, but vibrational and ^{1}H NMR spectra clearly demonstrate the presence of either NH_2CH_2R or NCR ligands. In Table 2 we list infrared, Raman and ^{1}H NMR data on the ruthenium amine and nitrile complexes isolated in this work. The NH_2 stretches $\nu(NH_2)$ and deformations $\delta(NH_2)$ are present in the spectra of the amine complexes but absent in those of the nitrile species. Bands near 2240 cm^{-1} of moderate intensity appear in the infrared spectra of the nitrile complexes and as strong bands in the Raman, clearly arising from the CN stretch ν(CN). A *cis* geometry is indicated for the $[Ru(bipy)_2(NCR)_2]^{2+}$ and $[Ru(phen)_2(NCR)_2]^{2+}$ species by the fact that the infrared and Raman bands have significantly different frequencies: in the former it is the asymmetric CN stretch ν_{asym}(CN) which is the strongest band while the symmetric stretch ν_{sym}(CN) is stronger in the Raman.

The ^{1}H NMR spectra demonstrate that a *cis* configuration for the amine complexes is retained in solution. Thus, for *cis*-$[Ru(bipy)_2(NH_2CH_2Ph)_2]$ the peaks due to bipyridyl are very complex suggesting a *cis* rather than a *trans* structure; furthermore, the amine protons appear as two multiplets (at δ 4.8 and 4.6 *vs.* $SiMe_4$); on shaking a solution of the complex with ^2H_2O these peaks disappear due to exchange with deuterium. The methylene protons also appear as two multiplets (at δ 3.2 and 3.4); for *trans*-$[Ru(bipy)_2(NH_2CH_2R)_2]^{2+}$ only one set of resonances for amine and methylene groups would be expected, but for the *cis* isomer there will be two sets since this isomer is diastereotopic.

Conclusion

We have shown that the *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ reagent is

effective for the dehydrogenation of primary amines (particularly benzylic amines) to the corresponding nitriles under ambient conditions; over longer periods of time nitrile hydration to amides occurs. The reaction may proceed *via* initial formation of a co-ordinated amine complex; as models for reaction of co-ordinated amine species with peroxodisulfate we made a number of new complexes *cis*-$[Ru(L–L)_2(NH_2CH_2R)_2]^{2+}$ (L–L = bipy or phen) and have shown that these are oxidised by an excess of peroxodisulfate to the corresponding nitrile complexes *cis*-$[Ru(L–L)_2(NCR)_2]^{2+}$. The crystal structures of two such species, *cis*-$[Ru(bipy)_2(NH_2CH_2Ph)_2][PF_6]_2\cdot 0.5MeOH$ and *cis*-$[Ru(bipy)_2(NCPh)_2][PF_6]_2\cdot CH_2Cl_2$, have been determined.

Experimental

Chemicals were from Aldrich and used without further purification. The compounds $RuCl_3\cdot nH_2O$ and $Na_2[OsCl_6]\cdot nH_2O$ were obtained from Johnson Matthey Ltd.

Preparation of the *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ reagent

The literature procedure[3] was used but with slightly different concentrations: $RuCl_3\cdot nH_2O$ (0.024 g, 0.1 mmol) was predissolved in water (5 cm^3) and an excess of $K_2S_2O_8$ (2.8 g, 0.01 mol) in aqueous molar KOH (25 cm^3) was added to give an orange solution.

Catalytic dehydrogenation of amines to nitriles

The reactions were performed at room temperature by dropwise addition of the amines (RCH_2NH_2; 2 mmol) over a period of 5 min to a vigorously stirred solution (100 cm^3) of the *trans*-$[Ru(OH)_2O_3]^{2-}/S_2O_8^{2-}$ reagent. The initial reaction mixture is dark green; when the reaction is complete the original orange colour of ruthenate reappears. The mixture was then extracted with diethyl ether (3×25 cm^3), the ether extracts dried over anhydrous $MgSO_4$ and the ether removed. Products were characterised by ^1H NMR, IR spectra and melting points where appropriate.

Hydration of nitriles to amides

Reactions were carried out as above, but for 24 h periods; benzene was used rather than diethyl ether for extracting the products.

Preparation and reactions of ruthenium amine and nitrile complexes

The complex $[Ru(bipy)_2(NH_2CH_2Ph)_2][PF_6]_2$ was made by a method based on that of Meyer and co-workers[19] but the hexafluorophosphate salt was isolated in place of the perchlorate salt. The complex *cis*-$[RuCl_2(bipy)_2]$, made by the literature method[21] (0.2 g, 0.4 mmol), was suspended in 50% aqueous methanol (30 cm^3). Benzylamine (2 g, 18.7 mmol) was added and the solution refluxed under nitrogen for 2 h. Methanol was evaporated off, the solution cooled and extracted with diethyl ether (3×20 cm^3) to remove the excess of benzylamine. The remaining aqueous solution was filtered and the complex precipitated by slow addition of a saturated solution of NH_4PF_6, and the red precipitate filtered off, washed with water, diethyl ether and then dried *in vacuo*. Yield of red crystals 0.33 g, 0.36 mmol (90%).

The methanol adduct **1** was made by recrystallisation of this material from MeOH.

Other $[Ru(bipy)_2(NH_2CH_2R)_2][PF_6]_2$ salts. The complex *cis*-$[RuCl_2(bipy)_2]\cdot 2H_2O$ (0.2 g, 0.38 mmol) was suspended in 50% aqueous methanol (30 cm^3). The amine (2 g) was added and the solution refluxed under nitrogen for 2 h. The methanol was evaporated off, the solution cooled and extracted with diethyl ether (3×20 cm^3) to remove the excess of amine. The remaining aqueous solution was filtered and the complex precipitated by slow addition of a saturated solution of NH_4PF_6. The precipitate was filtered off, washed with water, diethyl ether and then dried *in vacuo*.

The complexes *cis*-$[Ru(phen)_2(NH_2CH_2Ph)_2][PF_6]_2\cdot H_2O$ and *cis*-$[Ru(phen)_2(NH_2CH_2C_6H_4OMe\text{-}p)_2][PF_6]_2\cdot H_2O$ were similarly prepared, *cis*-$[RuCl_2(phen)_2]\cdot 2H_2O$ (made by the literature method[21]) (0.2 g, 0.35 mmol) replacing *cis*-$[RuCl_2(bipy)_2]\cdot 2H_2O$.

Dehydrogenation of *cis*-$[Ru(bipy)_2(NH_2CH_2Ph)_2]^{2+}$ to *cis*-$[Ru(bipy)_2(NCPh)_2][PF_6]_2$. The complex *cis*-$[RuCl_2(bipy)_2]$ (0.2 g, 0.4 mmol) was suspended in 50% aqueous methanol (30 cm^3). Benzylamine (2 g, 18.7 mmol) was added and the solution refluxed under nitrogen for 2 h. Methanol was evaporated off, the solution cooled and extracted with diethyl ether (3×20 cm^3) to remove the excess of benzylamine. The remaining aqueous solution of $[Ru(bipy)_2(NH_2CH_2Ph)_2]^{2+}$ was degassed and aqueous $K_2S_2O_8$ (3%, 10 cm^3) was added with stirring under nitrogen at room temperature for 1.5 h; the mixture changed gradually from red to orange and finally to yellow. The yellow solution was filtered and a yellow precipitate was formed by adding a saturated solution (10 cm^3, 10%) of NH_4PF_6. The precipitate of *cis*-$[Ru(bipy)_2(NCPh)_2][PF_6]_2$ was collected, washed with water, diethyl ether and dried *in vacuo*. Yield 0.33 g, 0.36 mmol (90%).

The dichloromethane adduct **2** was made by recrystallisation of this material from CH_2Cl_2.

General procedure for dehydrogenation of *cis*-$[Ru(bipy)_2(NH_2CH_2R)_2]^{2+}$ to *cis*-$[Ru(bipy)_2(NCR)_2]^{2+}$ by peroxodisulfate. The complex *cis*-$[RuCl_2(bipy)_2]\cdot 2H_2O$ (0.2 g, 0.4 mmol) was suspended in 50% aqueous methanol (30 cm^3), the amine (2 g) added and the solution refluxed under nitrogen for 2 h. Methanol was evaporated off, the solution cooled and extracted with diethyl ether (3×20 cm^3) to remove the excess of amine. The remaining aqueous solution was filtered and degassed by nitrogen, then aqueous $K_2S_2O_8$ (3%, 10 cm^3) solution added with stirring under nitrogen at room temperature for 2 h; the mixture changed gradually from red to orange and finally to yellow. The yellow solution was filtered and a yellow precipitate formed by adding a saturated solution (10 cm^3, 10%) of NH_4PF_6. The precipitate was collected, washed with water and dried *in vacuo*.

The complexes *cis*-$[Ru(phen)_2(NCPh)_2][PF_6]_2$ and *cis*-$[Ru(phen)_2(NCC_6H_4OMe\text{-}p)_2][PF_6]_2\cdot H_2O$ were similarly prepared, using *cis*-$[RuCl_2(phen)_2]\cdot 2H_2O$ (0.2 g, 0.35 mmol) in place of *cis*-$[RuCl_2(bipy)_2]\cdot 2H_2O$.

Ruthenium carbonyl complexes. A ruthenium carbonyl-containing solution using ethanol as the solvent was prepared by following the procedure of Chatt *et al.*[22] The compound $RuCl_3\cdot nH_2O$ (4.2 g) was added to ethanol (75 cm^3), heated at reflux and carbon monoxide passed into the solution. A blood red colour was formed after 5 h. This solution was used for the following reactions.

$[RuCl_2(CO)_2(NH_2CH_2Ph)_2]$. The procedure of Wilkinson and co-workers[23] was used with some modifications. Benzylamine (0.4 g, 3.7 mmol) was added slowly to the red solution (9 cm^3). After 5 min a change to green occurred and a pale green precipitate was formed. This was filtered off, washed with ethanol, diethyl ether and dried *in vacuo*. Yield 0.3 g, 0.6 mmol (67%) (Found: C, 43.5; H, 4.7; N, 6.3. Calc. for $C_{16}H_{18}Cl_2N_2O_2Ru$: C, 43.4; H, 4.1; N, 6.3%).

$[Ru(NH_2CH_2Ph)_6]Cl_2$. Benzylamine (2 g, 18.7 mmol) was added slowly to the red solution (9 cm^3); there was an immediate change to green and the reaction mixture was heated at reflux for 15 min, after which time a red crystalline precipitate was formed. The precipitate was filtered off, washed with ethanol and diethyl ether (4×25 cm^3) to remove the excess of

benzylamine and dried *in vacuo*. Yield 0.6 g, 0.73 mmol (73.7%) (Found: C, 61.5; H, 6.5; N, 10.1. Calc. for $C_{42}H_{54}Cl_2N_6Ru$: C, 61.9; H, 6.7; N, 10.3%).

Neither of the above two complexes could be oxidised to the corresponding nitrile complexes with an excess of peroxodisulfate.

Osmium complexes

***cis*-[$OsCl_2(bipy)_2$].** This was prepared by a variation of the literature method.[24] The salt $Na_2[OsCl_6]\cdot nH_2O$ (1 g, 2.2 mmol) and 2,2′-bipyridyl (0.72 g, 4.6 mmol) were added to ethylene glycol (50 cm^3) and the mixture was heated at reflux for 45 min under nitrogen. Since the crude reaction mixture contained both *cis*-[$OsCl_2(bipy)_2$] and *cis*-[$Os(bipy)_2Cl_2]^+$, an equal volume of saturated sodium dithionite was added to the cooled reaction mixture in order to reduce the excess of Os^{III} to Os^{II}. The purple-black precipitate formed was isolated by filtration, washed with water to remove $[Os(bipy)_3]^{2+}$ and other ionic products, and washed with a large volume of diethyl ether. Yield 0.5 g, 0.87 mmol (87%) (Found: C, 41.6; H, 2.3; N, 9.7. Calc. for $C_{20}H_{16}Cl_2N_4Os$: C, 41.9; H, 2.8; N, 9.8%).

[$Os(bipy)_2(NH_2CH_2Ph)_2$][PF_6]$_2$. The complex *cis*-[$OsCl_2$-$(bipy)_2$] (0.1 g, 0.17 mmol) was suspended in 50% aqueous ethanol (30 cm^3), benzylamine (2 g, 18.7 mmol) was added and the solution refluxed under nitrogen for 4 h. It changed from purple to dark yellow, then ethanol was evaporated off, the solution cooled and extracted with diethyl ether (3 × 20 cm^3) to remove the excess of benzylamine. The remaining aqueous solution was filtered and the complex precipitated by slow addition of a saturated solution of NH_4PF_6. The brown precipitate was filtered off, washed with water, diethyl ether and then dried *in vacuo*. Yield 0.06 g, 0.06 mmol (35%) (Found: C, 39.8; H, 3.1; N, 8. Calc. for $C_{34}H_{34}F_{12}N_6OsP_2$: C, 40.6; H, 3.4; N, 8.4%).

This complex was not oxidised by peroxodisulfate under the conditions used for the ruthenium analogue.

X-Ray crystallography

Crystal data. $[C_{34}H_{34}N_6Ru][PF_6]_2\cdot 0.5CH_3OH$ **1**, $M = 933.7$, monoclinic, space group $P2_1/c$ (no. 14), $a = 11.987(1)$, $b = 20.692(2)$, $c = 16.544(1)$ Å, $\beta = 106.73(1)°$, $U = 3929.7(4)$ Å^3, $Z = 4$, $D_c = 1.578$ g cm^{-3}, μ(Cu-Kα) = 48.4 cm^{-1}, $F(000) = 1884$, $T = 293$ K, orange-red block, 0.27 × 0.17 × 0.12 mm.

$[C_{34}H_{26}N_6Ru][PF_6]_2\cdot CH_2Cl_2$ **2**, $M = 994.5$, monoclinic, space group $C2/c$ (no. 15), $a = 13.644(1)$, $b = 26.405(2)$, $c = 11.371(1)$ Å, $\beta = 90.21(1)°$, $U = 4096.7(6)$ Å^3, $Z = 4$ (the molecule has crystallographic C_2 symmetry), $D_c = 1.612$ g cm^{-3}, μ(Mo-Kα) = 6.81 cm^{-1}, $F(000) = 1984$, $T = 293$ K, orange prism, 0.67 × 0.67 × 0.23 mm.

Data collection and processing. Data were measured on Siemens P4/PC diffractometers with graphite monochromated Cu-Kα (Mo-Kα) radiation for complex **1** (**2**) using ω scans. 5839 (3596) Independent reflections were measured [$2\theta \leqslant 120$ (50)°] of which 4278 (2780) had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz-polarisation factors, and semiempirical absorption corrections (based on ψ scans) applied; the maximum and minimum transmission factors were 0.51 and 0.39 for **1** and 0.83 and 0.71 for **2** respectively.

Structure analysis and refinement. The structures were solved by direct methods and the non-hydrogen atoms of the cationic complexes refined anisotropically. In **1** both of the hexafluorophosphate anions were disordered; in each case this disorder was resolved into two, discrete, partial occupancy orientations, with the atoms of the major occupancy orientation being refined anisotropically. The half occupancy included solvent methanol molecule in **1** was found to be distributed over three discrete sites, all of which were refined isotropically. The included dichloromethane solvent molecule in **2** was disordered over a crystallographic C_2 axis, and this was resolved into two symmetry related half occupancy orientations, both of which were refined anisotropically. The positions of the hydrogen atoms in both structures were idealised, assigned isotropic thermal parameters [$U(H) = 1.2U_{eq}(C/N)$, $U(H) = 1.5U_{eq}(O)$], and allowed to ride on their parent atoms. Refinements were by full matrix least squares based on F^2 to give $R1 = 0.062$ (0.050), $wR2 = 0.153$ (0.112) for the observed data and 537 (266) parameters for **1** (**2**) respectively. The maximum and minimum residual electron densities in the final ΔF map were 0.70 and −0.75 e Å^{-3} for **1** and 0.35 and −0.23 e Å^{-3} for **2** respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.001 and −0.031 for **1** and 0.000 and 0.000 for **2** respectively. All computations were carried out using the SHELXTL PC program system.[25]

CCDC reference number 186/1076.

Instrumentation

Infrared spectra were measured on a Perkin-Elmer series 1720 FTIR instrument, FT Raman spectra on a Perkin-Elmer series 1700 instrument with Nd-YAG laser excitation at 1064 nm and ^{1}H NMR spectra on a JEOL EX-270 spectrometer. Microanalyses were carried out by the Imperial College Microanalytical Service. The GC-MS data were obtained by Mr. John Barton on a Micromass AutoSpec, fitted with a Hewlett-Packard 5890 gas chromatograph and an SGE BPX5 column.

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