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Synthesis and reactivity of *N,N,N',N'*-tetramethyldiaminomethane complexes of tricarbonylrhenium(I). X-ray molecular structures of $[\text{ReBr}(\text{CO})_3(\text{TMDM})]$ and $[\{\text{Re}(\text{bipy})(\text{CO})_3\}_2(\mu\text{-OH})][\text{SbF}_6]$

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Abstract

N,N,N',N'-Tetramethyldiaminomethane (TMDM) is known to act as a source of Me_2NCH in carbonyl substitution reactions, but the reaction of TMDM with the neutral halogenopentacarbonylrhenium(I) compounds gave unexpectedly *fac*- $[\text{ReX}(\text{CO})_3(\text{TMDM})]$ ($\text{X} = \text{Cl}, \text{Br}$ or I), in which the intact TMDM ligand acts in a chelating fashion. The complexes are stable both in the solid-state and in solution, but rapidly decompose on dehalogenation, yielding Re metal. Under anaerobic conditions, the reaction of TMDM with $[\text{Re}(\text{CO})_3(\text{bipy})]^+$ also leads to decomposition. In the presence of oxygen the system is stable. Three $\text{Re}(\text{bipy})$ containing species were identified in the reaction mixture: $[\{\text{Re}(\text{CO})_3(\text{bipy})\}_2(\mu\text{-OH})][\text{SbF}_6]$ (**1**), which was characterised by X-ray crystallography, $[\{\text{Re}(\text{CO})_3(\text{bipy})\}_2(\mu\text{-OH}_2)][\text{SbF}_6]_2$ (**2**) and $[\text{Re}(\text{OH})(\text{CO})_3(\text{bipy})]$ (**3**).

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Keywords: Tricarbonylrhenium (I) complexes; Tetramethyldiaminomethane; Dimethylamine; X-ray crystallography

1. Introduction

The ability of ethylenediamine (en) and *N,N,N',N'*-tetramethylethylenediamine (tmen) to act as both chelating and bridging ligands is well known [1], but few complexes of the analogous ligand *N,N,N',N'*-tetramethyldiaminomethane ($\text{Me}_2\text{NCH}_2\text{NMe}_2$, TMDM) have been reported [2]. TMDM is an effective reagent for the introduction of the dimethylaminocarbene moiety, Me_2NCH , into transition metal complexes by carbonyl substitution reactions [3–5] and also acts as a source of dimethylamine [6,7]. Reaction of TMDM with $[\text{PtXMe}_3]_4$ ($\text{X} = \text{Cl}, \text{Br}$ or I) or $[\text{PtMe}_3(\text{bipy})]^+$ (bipy = 2,2'-bipyridine) yields the dimethylamine complexes $[\text{PtXMe}_3(\text{Me}_2\text{NH})]_2$ and $[\text{PtMe}_3(\text{bipy})(\text{Me}_2\text{NH})]^+$, re-

spectively, and formic acid [7]. Similarly, the reaction of $[\text{Re}_2(\text{CO})_8\text{H}_2]$ with TMDM in chloroform gives $[\text{Re}_2(\text{CO})_8(\text{Me}_2\text{NH})\text{Cl}(\mu\text{-H})]$ [6].

TMDM is believed to act in chelating fashion in $[\text{MCl}_4(\text{TMDM})]$ ($\text{M} = \text{Ti}$ or Sn) [8] and $[\text{MMe}_3(\text{TMDM})]$ ($\text{M} = \text{B}, \text{Al}$ or Ga) [9,10], and probably has a bridging role in $[(\text{MMe}_3)_2(\text{TMDM})]$ ($\text{M} = \text{B}, \text{Al}$ or Ga) [10]. The only complexes of TMDM that have been characterised crystallographically are $[\text{Co}(\text{TMDM})(3,6\text{-DBQ})_2]$ (DBQ = di-*tert*-butyl-1,2-benzoquinone) [11], $[\text{CoCl}_2(\text{TMDM})]_2$ [12] and $[\text{FeCl}_2(\text{TMDM})]_2$ [12], in which TMDM acts in a chelating fashion.

The (*bis*)phosphine ligands $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$ ($n = 1$ or 2) are known to act in both a chelating and bridging fashion towards the tricarbonylrhenium(I) moiety [13–15]. It is therefore of interest to investigate the mode of action of TMDM towards tricarbonylrhenium(I) to see if it behaves in analogous fashion to the (*bis*)phosphine ligands or as a source of either Me_2NCH or Me_2NH . The results of this investigation are reported here.

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2. Results and discussion

Reaction of the halogenopentacarbonylrhenium(I) compounds, $[\text{ReX}(\text{CO})_5]$ ($\text{X} = \text{Cl}, \text{Br}$ or I) with TMDM yields air-stable, white crystalline solids, soluble in common polar organic solvents. The infrared spectra of the products display three bands in the carbonyl stretching region ($1850\text{--}2100\text{ cm}^{-1}$) and up to six bands each due to the $\text{Re}\text{--}\text{C}$ stretching and deformation modes, characteristic of a *fac*-octahedral tricarbonyl metal moiety [16]. Bands below 1500 cm^{-1} are characteristic of TMDM [17], and no $\text{N}\text{--}\text{H}$ stretching bands are observed. Infrared data therefore indicate that the intact TMDM ligand co-ordinates to the metal in a bidentate chelate fashion. The fast atom bombardment (FAB) mass spectra of the complexes exhibit intense peaks due to the species $[\text{M}\text{--}\text{X}]^+$: observed and calculated isotope patterns are consistent with the formulated species, as are the elemental analytical figures. Data, reported in Table 1, are therefore consistent with the formation of the complexes $[\text{ReX}(\text{CO})_3(\text{TMDM})]$ ($\text{X} = \text{Cl}, \text{Br}$ or I).

The solution ^1H NMR spectra of the complexes each exhibit two singlets ($\delta \approx 2.9\text{--}3.5$) and an AB quartet ($\delta \approx 4.4\text{--}4.8$; $^2J_{\text{HH}} \approx 11\text{ Hz}$), assignable to the $\text{N}\text{--}\text{Me}$ and methylene hydrogens, respectively. This indicates that the plane of symmetry bisecting the $(\text{Me})\text{C}\text{--}\text{N}\text{--}\text{C}(\text{Me})$ angles is lost while that bisecting the $\text{N}\text{--}\text{C}(\text{H}_2)\text{--}\text{N}$ angle is retained. This is consistent with the intact TMDM ligand acting in a bidentate chelate fashion. NMR data are reported in Table 2.

The X-ray molecular structure of $[\text{ReBr}(\text{CO})_3(\text{TMDM})]$ was obtained to confirm the unusual bidentate co-ordination mode of TMDM, indicated by analytical and spectroscopic data. A suitable crystal was obtained by recrystallisation of the bromo complex from a dichloromethane/hexane mixture at $-20\text{ }^\circ\text{C}$. A view of the molecule, showing the atom numbering scheme is shown in Fig. 1. Crystal data, collection data and refinement parameters are given in Table 3. Selected bond lengths and angles are reported in Table 4. Fig. 1 shows clearly that the metal moiety has the expected *fac*-octahedral geometry with the intact TMDM ligand chelating. The geometry at Re deviates somewhat from that of an idealised octahedron because of the small bite angle of TMDM: $\text{N}(1)\text{--}\text{Re}\text{--}\text{N}(2) = 63.4(1)^\circ$, similar to the corresponding angles in the $[\text{MCl}_2(\text{TMDM})]_2$ ($\text{M} = \text{Co}$ or Fe) complexes [12], but less than that found in $[\text{Co}(\text{TMDM})(3,6\text{-DBQ})_2]$ (71.8°) [11]. The ReNCN chelate ring is essentially planar; maximum deviation from the mean plane is 0.16 \AA [C(4)]. The dihedral angle between the planes ReNCN and $\text{C}(1)\text{ReC}(2)$ is 8.7° . The $\text{Re}\text{--}\text{N}$ ($\approx 2.27\text{ \AA}$), $\text{Re}\text{--}\text{C}$ ($\approx 1.88\text{ \AA}$) and $\text{Re}\text{--}\text{Br}$ (2.62 \AA) lengths are similar to those measured in other Re^{I} complexes [18–20] and, apart from the smaller bite angle of TMDM, the complex is structurally very similar to the analogous tetramethylethylenediamine (tmen) and dimethylethylenediamine (dmen) complexes, $[\text{ReBr}(\text{CO})_3(\text{tmen})]$ [21], $[\text{ReF}(\text{CO})_3(\text{tmen})]$ [22] and $[\text{ReBr}(\text{CO})_3(\text{dmen})]$ [23].

On dehalogenation under anaerobic conditions (reaction with Ag^+) the complexes decompose immediately, giving a black solid. The addition of TMDM to the

Table 1
Synthetic and analytical data for $[\text{ReX}(\text{CO})_3(\text{TMDM})]$ ($\text{X} = \text{Cl}, \text{Br}$ or I) and complexes 1–3

Complex	Yield ^a (%)	Infrared ^b (cm^{-1})				Analysis ^c (%)			Mass spectral data (m/z)
		CO	Re–C	TMDM	OH	C	H	N	
$[\text{ReCl}(\text{CO})_3(\text{TMDM})]$	54	1874; 1907; 2019	473; 484; 529; 539; 636; 658	867; 961; 989; 1036; 1226; 1459		23.63 (23.56)	3.34 (3.46)	6.77 (6.87)	408 $[\text{M}]^+$; 373 $[\text{M}\text{--}\text{Cl}]^+$
$[\text{ReBr}(\text{CO})_3(\text{TMDM})]$	50	1879; 1910; 2021	473; 485; 528; 637; 655	868; 963; 990; 1037; 1226; 1466		21.33 (21.24)	3.00 (3.12)	6.05 (6.19)	452 $[\text{M}]^+$ 373 $[\text{M}\text{--}\text{Br}]^+$
$[\text{ReI}(\text{CO})_3(\text{TMDM})]$	42	1893; 1930; 2020	474; 485; 528; 634; 653	867; 958; 989; 1036; 1236; 1468		19.33 (19.24)	2.81 (2.82)	5.32 (5.61)	500 $[\text{M}]^+$ 373 $[\text{M}\text{--}\text{I}]^+$
(1)	32	1882; 1925; 2027			3447br	28.44 (28.24)	1.85 (1.55)	4.98 (5.07)	871 $[\text{M}\text{--}\text{SbF}_6]^+$; 235 ^d $[\text{SbF}_6]^-$
(2)	28	1894; 1944; 2032			3438br	23.56 (23.26)	1.34 (1.35)	4.03 (4.17)	871 $[\text{M}\text{--}\text{H}\text{--}2\text{SbF}_6]^+$; 428 $[\text{Re}(\text{CO})_3(\text{bpy})]^+$; 235 ^d $[\text{SbF}_6]^-$
(3)	65	1898; 1917; 2023			3421br	33.57 (33.37) ^e	2.28 (2.07) ^e	5.27 (5.77) ^e	428 $[\text{M}\text{--}\text{OH}]^+$

^a Yield quoted relative to $[\text{ReX}(\text{CO})_5]$ or $[\text{ReBr}(\text{CO})_3(\text{bpy})]$.

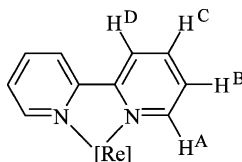
^b Infrared spectra recorded as KBr discs.

^c Calculated values in parentheses.

^d Negative ion MS.

^e Calculated analytical figures include 0.5 mol of dichloromethane (which is observed in the ^1H NMR spectra).

Table 2
Hydrogen-1 NMR data^a for [ReX(CO)₃(TMDM)] (X = Cl, Br or I) and complexes 1–3



Complex	δ (Me)	δ (CH ₂) ^b	δ (pyridine-H) ^c			
			H _A	H _B	H _C	H _D
[ReCl(CO) ₃ (TMDM)]	2.92; 3.32	4.55; 4.65 (~11)				
[ReBr(CO) ₃ (TMDM)]	3.02; 3.36	4.64; 4.71 (~11)				
[ReI(CO) ₃ (TMDM)]	3.20; 3.42	4.74; 4.79 (~11)				
(1)			8.88	7.59	8.19	8.26
(2)			8.70	7.51	8.17	8.20
(3)			9.03	7.56	8.11	8.23

^a Spectra recorded in CDCl₃ {[ReX(CO)₃(TMDM)]} or CD₂Cl₂ {complexes 1–3}. Chemical shifts reported in ppm relative to tetramethylsilane as an internal standard.

^b ²J_{HH}/Hz given in parentheses.

^c Scalar couplings do not vary significantly between complexes: ³J_{AB} ~ 5.5; ⁴J_{AC} ~ 1.6; ³J_{BC} ~ 7.6; ⁴J_{BD} ~ 1.6; ³J_{CD} ~ 8.1 Hz.

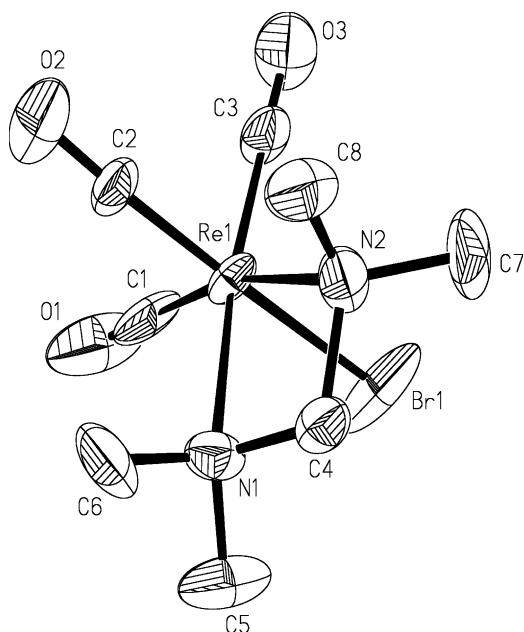


Fig. 1. X-ray molecular structure of [ReX(CO)₃(TMDM)], showing the atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

[Re(CO)₃]⁺ cation (obtained by dissolving [NEt₄]₂[ReBr₃(CO)₃] in water [24]) gave an identical result, indicating that Re^I is the active agent, rather than Ag⁺. To investigate this further, the reaction of TMDM with the stable cation [Re(CO)₃(bipy)]⁺ (bipy = 2,2'-bipyridine) [25] was studied.

On addition of TMDM to an anaerobic THF solution of [Re(CO)₃(bipy)(THF)][SbF₆], the orange solution decolourises immediately and a black solid, presumably

Re metal, is precipitated. Under aerobic conditions, the THF solution initially became yellow then slowly decolourised with the concomitant deposition of the same black solid. If oxygen is bubbled through the solution decomposition is retarded significantly, and three Re containing species were thus identified (see below). These results suggest that either TMDM itself, or a by-product is undergoing oxidation: in the absence of oxygen, Re^I must act as the oxidising agent, being reduced to Re black, which is deposited.

Concentration of the oxygenated THF solution yielded an orange–yellow solid. The ¹H NMR spectrum of the crude product indicates the presence of three Re(bipy) containing species; only bipyridine-H signals were observed. The crude solid was extracted with cold (0 °C) CH₂Cl₂, from which orange crystals of **1**, suitable for X-ray crystallography, were obtained on further cooling (–20 °C). A pure sample of a second species, **2**, insoluble in cold CH₂Cl₂ was also isolated. After the separation of the crystals of **1** from the dichloromethane solution, ¹H NMR showed the mother liquor to contain a mixture of **1** and, a third species, **3**, which could not be separated.

The infrared spectrum of **1** displays three bands in the region 1850–2050 cm^{–1}, assignable to carbonyl stretching modes and a broad band at 3447 cm^{–1} ($\Delta\sigma_{1/2} \approx 300$ cm^{–1}), assignable to an O–H stretching mode. The positive ion FAB mass spectrum displays an intense set of peaks centred on *m/z* 871 and the negative ion FAB mass spectrum displays a peak at *m/z* 235, due to SbF₆. These data, along with the elemental analytical figures (Table 1) suggest **1** is the dimeric species [{Re(CO)₃(bi-

Table 3
X-ray data for [ReBr(CO)₃(TMDM)] and [{Re(CO)₃(bpy)}₂(μ-OH)][SbF₆]

	[ReBr(CO) ₃ (TMDM)]	[{Re(CO) ₃ (bpy)} ₂ (μ-OH)][SbF ₆]
Empirical formula	C ₈ H ₁₄ BrN ₂ O ₃ Re	C ₂₆ H ₁₇ F ₆ N ₄ O ₇ Re ₂ Sb
Formula weight	452.32	1105.59
Crystal size (mm)	0.75 × 0.73 × 0.48	0.76 × 0.74 × 0.38
Crystal system	monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	7.964 (2)	12.837 (3)
<i>b</i> (Å)	12.342 (2)	18.312 (4)
<i>c</i> (Å)	13.330 (3)	13.904 (3)
α (°)	90	90
β (°)	97.23 (3)	108.71 (3)
γ (°)	90	90
<i>V</i> (Å ³)	1299.8 (5)	3095.7 (12)
<i>D</i> _{calc} (Mg m ⁻³)	2.311	2.372
<i>Z</i>	4	4
Absorption coefficient (mm ⁻¹)	12.413	8.753
<i>F</i> (0 0 0)	840	2048
θ Range for data collection (°)	2.83–25.05	2.71–25.07
Reflections collected	2456	5474
Independent reflections	2283 (<i>R</i> _{int} = 0.0315)	5474 (<i>R</i> _{int} = 0.0000)
No. of parameters	137	415
Goodness-of-fit	1.019	1.062
Extinction coefficient	0.0091 (8)	0.0091 (8)
Final <i>R</i> ₁ , <i>wR</i> ₂ indices [<i>I</i> > 2σ(<i>I</i>)]	0.0520, 0.1361	0.0661, 0.1791
<i>R</i> ₁ , <i>wR</i> ₂ indices (all data)	0.0645, 0.1656	0.0839, 0.1998
Largest difference peak and hole (e Å ⁻³)	3.037 and -2.403	2.495 and -2.066

Table 4
Selected bond lengths (Å) and selected bond angles (°) for [ReBr(CO)₃(TMDM)]

<i>Bond lengths</i> (Å)			
Re–C(2)	1.868(12)	Re–N(1)	2.267(10)
Re–C(1)	1.875(14)	Re–N(2)	2.279(10)
Re–C(3)	1.893(13)	Re–Br(1)	2.619(2)
N(1)–C(4)	1.50(2)	N(2)–C(4)	1.48(2)
<i>Angles</i> (°)			
N(1)–Re–N(2)	63.4(4)	C(1)–Re–C(3)	88.0(7)
C(4)–N(1)–Re	92.5(7)	C(2)–Re–Br	175.4(4)
C(4)–N(2)–Re	92.7(7)	C(2)–Re–N(1)	95.4(5)
N(2)–C(4)–N(1)	106.8(9)	C(2)–Re–N(2)	94.5(5)
N(1)–Re–Br	88.6(3)	C(2)–Re–C(1)	89.9(6)
N(2)–Re–Br	89.3(3)	C(2)–Re–C(3)	86.4(6)
C(1)–Re–Br	87.0(5)	C(3)–Re–Br	90.0(4)
C(1)–Re–N(1)	102.4(5)	C(3)–Re–N(1)	169.5(5)
C(1)–Re–N(2)	165.5(5)	C(3)–Re–N(2)	106.1(5)

Estimated standard deviations given in parentheses.

py)₂(μ-OH)][SbF₆]. This is confirmed by X-ray crystallography.

The molecular structure of [{Re(CO)₃(bipy)}₂(μ-OH)]⁺, **1**–[SbF₆], is shown in Fig. 2 and crystal data, collection data and refinement parameters are reported in Table 3. Selected bond lengths and angles are given in Table 5. The molecular structure of the cation consists

of two chemically identical [Re(CO)₃(bipy)] units linked by a single, unsupported hydroxide bridge; there are no interactions with the counter ion (SbF₆⁻). The Re–O(H)–Re angle, 135.1(5)°, is significantly opened out, presumably because of the steric requirements of the two [Re(CO)₃(bipy)] moieties. The two (equatorial) planes containing the bipyridine ligands are essentially staggered; the torsion angles N(1)Re(1)Re(2)N(3) and N(2)Re(1)Re(2)N(4) are 37.0 and 39.4°, respectively. The dihedral angle between the equatorial planes is 27.8° and the shortest distance between the two rings is 3.38 Å. The two Re–O distances are 2.146(9) Å and 2.176(8) Å, similar to those reported in other Re–OH species [26–29]. The Re–C and Re–N lengths and associated angles are unremarkable [18–20]. Although hydroxy-bridged rhenium(I) complexes are well known [26–29] as far as we are aware, this is the first example of a single, unsupported hydroxy-bridged rhenium(I) complex.

The cation in **1** is probably formed from deprotonation (by either TMDM or dimethylamine) of the aquo species, [Re(CO)₃(bipy)(OH₂)]⁺ and subsequent dimerisation with the solvent adduct, [Re(CO)₃(bipy)(THF)]⁺. The most likely source of water is the TMDM sample: TMDM is prepared in aqueous solution [30,31].

Although the concentrations of the three species observed differ, the solution ¹H NMR spectrum of **1** is

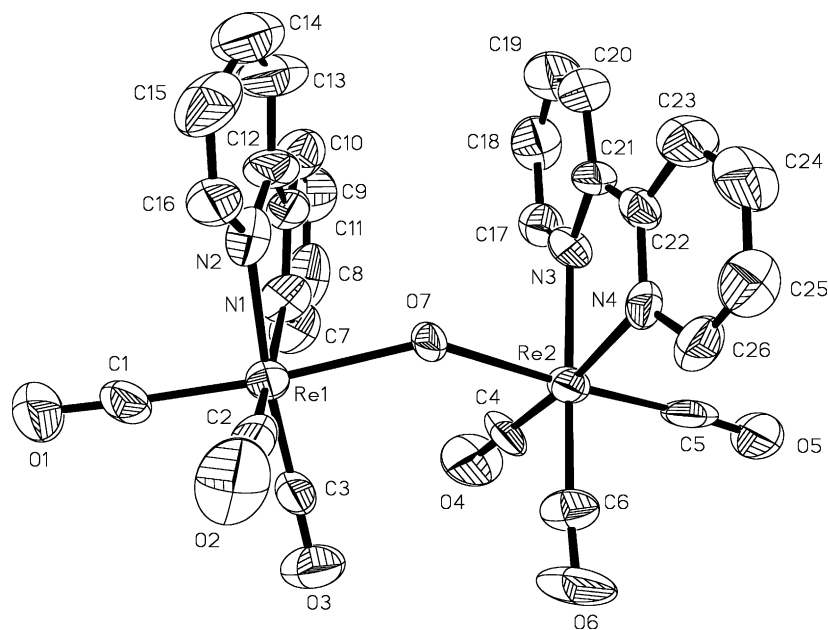


Fig. 2. X-ray molecular structure of $[\{\text{Re}(\text{CO})_3(\text{bipy})\}_2(\mu\text{-OH})]^{2+}$, showing the atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

Table 5
Selected bond lengths (Å) and selected bond angles (°) for $[\{\text{Re}(\text{CO})_3(\text{bpy})\}_2(\mu\text{-OH})][\text{SbF}_6]$

Bond lengths (Å)			
Re(1)–C(1)	1.88(2)	Re(1)–N(1)	2.162(13)
Re(1)–C(2)	1.91(2)	Re(1)–N(2)	2.133(14)
Re(1)–C(3)	1.84(2)	Re(2)–N(3)	2.153(12)
Re(2)–C(4)	1.89(2)	Re(2)–N(4)	2.134(12)
Re(2)–C(5)	1.90(2)	Re(1)–O(7)	2.146(9)
Re(2)–C(6)	1.93(2)	Re(2)–O(7)	2.176(8)
Angles (°)			
Re(1)–O(7)–Re(2)	135.1(5)	N(4)–Re(2)–N(3)	74.0(4)
N(2)–Re(1)–N(1)	75.2(5)	N(3)–Re(2)–O(7)	84.0(4)
O(7)–Re(1)–N(1)	82.2(5)	N(4)–Re(2)–O(7)	80.7(4)
N(2)–Re(1)–O(7)	80.0(4)	C(4)–Re(2)–N(3)	98.2(6)
C(1)–Re(1)–N(1)	93.1(6)	C(4)–Re(2)–N(4)	172.2(7)
C(1)–Re(1)–N(2)	96.0(6)	C(4)–Re(2)–O(7)	98.1(5)
C(1)–Re(1)–C(2)	90.0(8)	C(4)–Re(2)–C(5)	86.5(7)
C(1)–Re(1)–O(7)	174.4(5)	C(4)–Re(2)–C(6)	86.9(7)
C(2)–Re(1)–N(1)	170.4(7)	C(5)–Re(2)–N(3)	94.0(5)
C(2)–Re(1)–N(2)	95.4(7)	C(5)–Re(2)–N(4)	94.6(6)
C(2)–Re(1)–O(7)	94.2(6)	C(5)–Re(2)–O(7)	175.2(5)
C(3)–Re(1)–N(1)	99.2(6)	C(5)–Re(2)–C(6)	87.9(7)
C(3)–Re(1)–N(2)	173.0(6)	C(6)–Re(2)–N(3)	174.7(6)
C(3)–Re(1)–O(7)	95.2(5)	C(6)–Re(2)–N(4)	100.9(6)
C(3)–Re(1)–C(1)	88.4(7)	C(6)–Re(2)–O(7)	93.7(5)
C(3)–Re(1)–C(2)	90.0(8)		

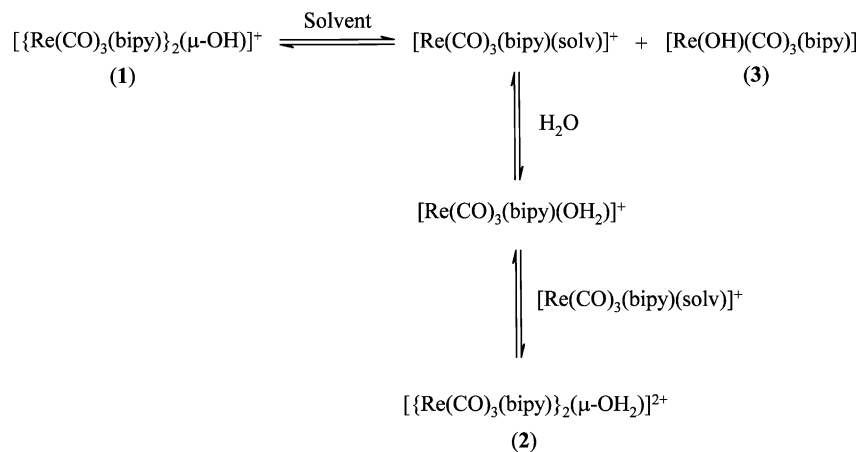
Estimated standard deviations given in parentheses.

identical to that of the crude product mixture [32]. Comparison of the NMR data with that obtained for the other two species observed (see below) enabled the sub-spectrum of **1** to be identified. The assignment of the signals (Table 2) to the different hydrogen environ-

ments of the bipy ligand were made on the basis of the scalar coupling network (COSY) and by comparison with other $[\text{Re}(\text{CO})_3(\text{bipy})]$ complexes [25,33].

The IR and (positive and negative ion) FAB mass spectra of **2** are essentially identical to those of **1**. The C:H:N ratio is similar to that in **1**, but the absolute magnitudes are considerably lower (Table 1), consistent with a dicationic, dimeric Re species. Complex **2** was thus characterised tentatively as the aquo-bridged species $[\{\text{Re}(\text{CO})_3(\text{bipy})\}_2(\mu\text{-OH}_2)][\text{SbF}_6]_2$. The solution ^1H NMR spectrum of **2** displays one set of signals in the aromatic region, which correspond to one of the three sets in the crude product, assignable to the hydrogens of the (metal co-ordinated) 2,2-bipyridine ligand. No signal due to *co-ordinated* water is observed; however, the O–H stretching mode is observed clearly in the IR spectrum [$\nu(\text{OH}) = 3438$].

The ^1H NMR spectra show clearly that **2** can be derived from **1**, but not, at least under neutral conditions, vice versa. A plausible explanation for this observation is that one of the Re–O bonds in $[\{\text{Re}(\text{CO})_3(\text{bipy})\}_2(\mu\text{-OH})]^{2+}$, breaks giving the neutral hydroxy species, $[\text{Re}(\text{OH})(\text{CO})_3(\text{bipy})]$, and $[\text{Re}(\text{CO})_3(\text{bipy})(\text{solvent})]^{2+}$, which then co-ordinates residual water in the solvent. Further reaction of aquo-adduct, $[\text{Re}(\text{CO})_3(\text{bipy})(\text{OH}_2)]^{2+}$, with $[\text{Re}(\text{CO})_3(\text{bipy})(\text{solvent})]^{2+}$ yields $[\{\text{Re}(\text{CO})_3(\text{bipy})\}_2(\mu\text{-OH}_2)]^{2+}$, **2**– $2[\text{SbF}_6]$, (Scheme 1). In the absence of any base to deprotonate the co-ordinated water molecule this is irreversible. If this hypothesis is correct, the hydroxide complex, $[\text{Re}(\text{OH})(\text{CO})_3(\text{bipy})]$, should also be present in the crude product and in solutions of **1**. It was not possible to isolate $[\text{Re}(\text{OH})(\text{CO})_3(\text{bipy})]$ from the reac-



Scheme 1. Proposed reaction for the formation of complexes (2) and (3) from (1).

tion mixtures, but there is strong evidence to suggest its presence. An explicit synthesis of $[\text{Re}(\text{OH})(\text{CO})_3(\text{bipy})]$ was carried out by adding an aqueous solution of sodium hydroxide to a THF solution of $[\text{Re}(\text{CO})_3(\text{bipy})]^+$. Analytical and spectroscopic data (Table 1) are consistent with the formation of $[\text{Re}(\text{OH})(\text{CO})_3(\text{bipy})]$. The ^1H NMR spectrum of $[\text{Re}(\text{OH})(\text{CO})_3(\text{bipy})]$ shows a single set of bipy signals with identical chemical shifts to **3**; **3** was thus assigned tentatively as the species $[\text{Re}(\text{OH})(\text{CO})_3(\text{bipy})]$.

The details of the reaction between the $[\text{Re}(\text{CO})_3]^+$ moiety and TMDM are not known, but it probably involves metal activated (N)C–N bond cleavage with the concomitant formation of dimethylamine [6,7]. Whilst the complexes $[\text{ReX}(\text{CO})_3(\text{Me}_2\text{NH})_2]$ ($\text{X} = \text{Cl}, \text{Br}$ or I) are known [34], our attempts to prepare dimethylamine complexes of $[\text{Re}(\text{CO})_3]^+$ were unsuccessful; addition of dimethylamine to $[\text{Re}(\text{CO})_3(\text{bipy})]^+$ led to decomposition with the deposition of a black solid. We therefore tend to the view that a dimethylamine complex is formed and that it is this species that undergoes (oxidative) decomposition. The oxidation of amines is generally complex (the products depend on the substrates and reaction conditions involved [35,36]). The organic product(s) of the reaction have yet to be determined.

3. Experimental

3.1. Starting materials

Starting materials were purchased from standard sources and used without further purification. The $[\text{ReX}(\text{CO})_5]$ ($\text{X} = \text{Cl}, \text{Br}$ or I) compounds [37], $[\text{ReBr}(\text{CO})_3(\text{bipy})]$ [25,32] and $[\text{Et}_4\text{N}]_2[\text{ReBr}_3(\text{CO})_3]$ [24] were prepared by previously published procedures.

3.2. Synthesis of $[\text{ReX}(\text{CO})_3(\text{TMDM})]$ complexes

TMDM (0.025 mg, 0.246 mmol) was added to a stirred benzene solution of $[\text{ReX}(\text{CO})_5]$ (0.246 mmol). The reactants were refluxed for approximately 8 h, then the solvent evaporated to dryness in vacuo. The solid residue was washed with hexane and crystallised from a dichloromethane/*n*-hexane mixture at -20°C .

3.3. Reaction of $[\text{Re}(\text{CO})_3(\text{bipy})]^+$ with TMDM

$[\text{Re}(\text{CO})_3(\text{bipy})(\text{THF})][\text{SbF}_6]$ was prepared in situ by the reaction of $[\text{ReBr}(\text{CO})_3(\text{bipy})]$ with AgSbF_6 . TMDM was added to the THF solution of $[\text{Re}(\text{CO})_3(\text{bipy})(\text{THF})][\text{SbF}_6]$ (which was filtered to remove AgBr) and stirred for approximately 1 h, during which time the solution was kept saturated with oxygen. The solution was filtered, and then concentrated to dryness. The resulting yellow solid was extracted with cold dichloromethane, giving an orange solution and a yellow residue of **2**. Crystals of **1** suitable for X-ray crystallography were obtained by cooling (-20°C) of the dichloromethane solution.

3.4. Synthesis of $[\text{Re}(\text{OH})(\text{CO})_3(\text{bipy})]$

An aqueous, dilute solution of NaOH was added to a THF solution of $[\text{Re}(\text{CO})_3(\text{bipy})(\text{THF})][\text{SbF}_6]$ and stirred for approximately 8 h. The solution was filtered and then evaporated to dryness in vacuo. The resulting yellow solid was washed with hexane and crystallised from a dichloromethane/*n*-hexane mixture at -20°C . Yield: 65%.

3.5. Physical methods

Hydrogen-1 NMR spectra were recorded at ambient temperature in CDCl_3 or CD_2Cl_2 solution on a Bruker DRX500 Fourier transform spectrometer operating at

500.13 MHz, using standard Bruker automation programs. Chemical shifts are quoted relative to tetramethylsilane as an internal standard. Infrared spectra were recorded as KBr discs on a Shimadzu hyper 8700 FT-IR spectrometer operating in the region 4000–400 cm^{-1} . FAB mass spectra were obtained at the London School of Pharmacy on a VG Analytical ZAB-SE4F instrument, using Xe^+ bombardment at 8 kV energy, on samples in a matrix of 3-nitrobenzyl alcohol. Elemental analyses were carried out at University College London.

The X-ray structure determinations were carried out using an automatic four-circle Nicolet R3mV diffractometer, using the $\omega-2\theta$ technique at 293(2) K. Data were recorded using routine procedures and empirical absorption corrections applied (ψ scan method). The structures were solved by direct methods and refined to convergence (least-squares; SHELXL 93) [38]. Hydrogen atoms were inserted in calculated idealised positions (r C–H = 0.96 Å) and assigned a common isotropic thermal parameter ($U = 0.08 \text{ \AA}^2$).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 198077 and 198078. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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