Dalton Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 10215

www.rsc.org/dalton

PAPER

Studies of the reactions of tripodal pyridine-containing ligands with $Re(CO)_5Br$ leading to rheniumtricarbonyl complexes with potential biomedical applications†

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Received 31st May 2011, Accepted 15th July 2011
DOI: 10.1039/c1dt11020a

The complexes formed from the reaction of *N*-acylated tris-(pyridin-2-yl)methylamine (LH) with $[Re(CO)_5Br]$ depend on the structure of the ligand and the reaction conditions. Thus, while *N*-[1,1,1-tris-(pyridin-2-yl)methyl]acetamide coordinates through the three pyridine nitrogens to give a stable cationic complex $[LHRe(CO)_3Br]$, the analogous *N*-benzoyl ligand reacts under similar conditions to give a neutral complex $[LRe(CO)_3]$ with coordination through two pyridine nitrogens and a deprotonated amide. To try to explain these different outcomes, the reactions of some structurally related *N*-acylated [1,1-bis(pyridin-2-yl)]methylamines (L′H) with $[Re(CO)_5Br]$ have been studied and the reaction pathways identified. These studies indicate that a neutral complex $[L'HRe(CO)_3Br]$ is initially formed in which the amide portion of the ligand is uncoordinated, but that this complex under appropriate conditions then rearranges to give a cationic complex $[L'HRe(CO)_3]Br$ in which the coordinated amide nitrogen either remains protonated or is present in its imidic acid tautomeric form. Elimination of HBr from these complexes either thermally or in the presence of base then gives stable neutral complexes $[L'Re(CO)_3]$. The impact of the *N*-acyl group and any substituent at the apex of the tripodal ligands (L″H) on the relative stabilities of intermediate complexes on the reaction pathway helps provide an explanation for the observed difference in behaviour of the *N*-acylated tris(pyridin-2-yl)methylamines (LH).

Introduction

The development of convenient methods for forming rhenium(I) tricarbonyl complexes[1] for use in radiopharmaceutical applications has meant there is renewed interest in tridentate chelates that are capable of coordinating in a facial manner.[2] Since we had previously used tripodal *N*-acylated 1,1,1-tris(pyridin-2-yl)methylamine ligands to form metal complexes with both copper and zinc in which coordination occurs facially *via* the three pyridine nitrogen atoms,[3] it was a logical extension to see whether such tripodal systems might prove suitable for applications in radiopharmaceutical imaging and therapy agents. The rationale was that if coordination to the rhenium could be achieved *via* the three pyridine rings then functionalisation of the uncoordinated amide limb in the resulting rheniumtricarbonyl complex would potentially provide a means for controlling its targeting and biodistribution.

However, in a preliminary study[4] of the reaction of $[Re(CO)_5Br]$ with the parent tripodal tris(pyridin-2-yl)methylamine ligand (tpmaH) **1a** and its *N*-benzoylated derivative (tpmbaH) **1b**, we had found that both systems showed a preference for the formation of rhenium complexes where coordination occurs through two pyridine rings and the aliphatic nitrogen atom.

In contrast, when the *N*-acetylated tris(pyridin-2-yl)-methylamine ligand **1c** was used, a cationic complex formed in which coordination to the rhenium centre had occurred *via* the three pyridine rings.[5] It is now clear from our studies that the nature of the complexes isolated in the reaction of *N*-substituted tris(pyridin-2-yl)methylamine ligands with $[Re(CO)_5Br]$ is dependent on both the reaction conditions and the nature of the *N*-substituent. To better understand the factors that influence the nature and stability of the rhenium complexes formed we have now broadened the scope of these studies to include the use of ligands based on the bis(pyridin-2-yl)methylamine system (bpmaH) **2a** and its phenyl substituted analogue (Ph-bpmaH) **2a′** (Fig. 1).

The phenyl substituted ligands **2a′**–**c′** were chosen to mimic more closely the steric bulk of the corresponding tris(pyridin-2-yl)methylamine ligands **1a–c** while maintaining the donor set found in the bis(pyridin-2-yl)methylamine ligands **2a–c**. It was hoped that a comparison of the complexing behaviour of these three sets of ligands would enable us to get a better understanding of the factors that influence the course of their reactions with $[Re(CO)_5Br]$.

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† CCDC reference numbers 733190, 821715–821721. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11020a

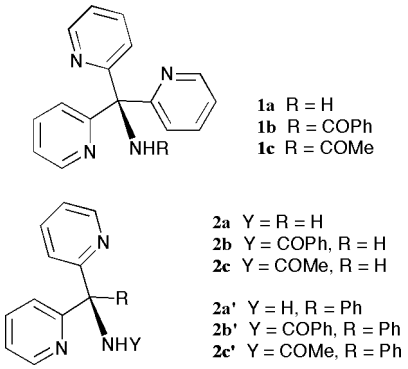


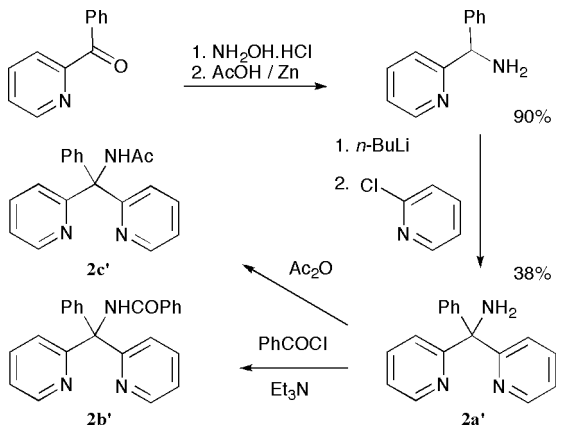
Fig. 1 Ligand structures.

Results and discussion

Ligand synthesis

We have previously reported the preparation of ligands **1a–c** and **2a–b**. For the present study we required the *N*-acetylated ligand **2c** which was prepared by the action of acetic anhydride on 1,1-bis(pyridin-2-yl)methylamine **2a**.

The corresponding phenyl substituted ligands **2a′–c′** were prepared from 2-benzoylpyridine as shown in Scheme 1.

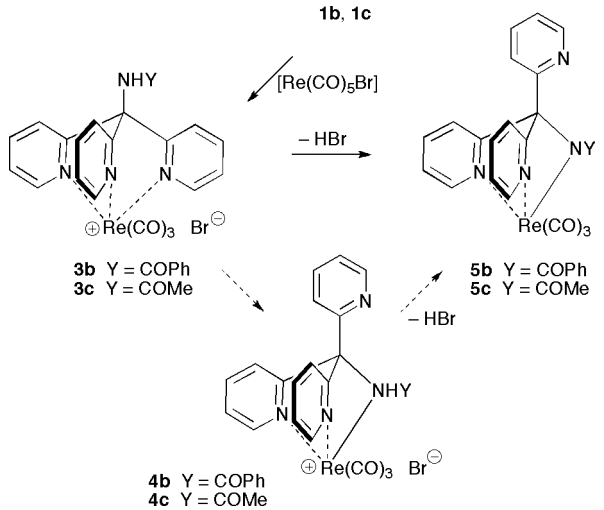


Scheme 1 Synthesis of ligands **2a′–c′** from 2-benzoylpyridine.

Comparison of the reactions of tpmbaH 1b, bpmbaH 2b and Ph-bpmbaH 2b′ with [Re(CO)$_5$Br]

In our earlier studies of the copper complexes of the tris(pyridin-2-yl)methylamine ligands[3] we had shown that it was possible to prevent coordination at the aliphatic nitrogen in these ligands by acylation of the primary amine group. However, as noted earlier, the product isolated from the reaction of the *N*-benzoylated ligand (tpmbaH) **1b** with [Re(CO)$_5$Br] in toluene was a neutral complex [(tpmba)Re(CO)$_3$] **5b** in which the coordination had occurred *via* two of the pyridine nitrogens and a deprotonated amide group.[4]

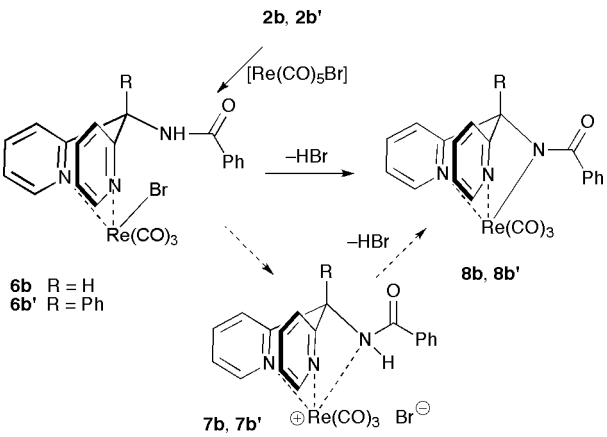
More recently[5] we have shown that the complex **5b** is formed *via* the rearrangement of an initially formed complex **3b** in which coordination occurs *via* the three pyridine rings. Moreover, this rearrangement of the complex **3b** occurs under mild conditions, since it occurred when attempts were made to crystallise the complex **3b** by the slow evaporation of a solution of this material in methylene chloride at room temperature. Since there are no strongly basic centres present in the cationic system **3b** to deprotonate the uncoordinated amide, it would seem likely that deprotonation of the amide nitrogen occurs after its coordination to the rhenium and hence that **4b** lies on the pathway between **3b** and **5b** (Scheme 2).



Scheme 2 Proposed reaction pathway to the benzoylated complex **5b**.

The facile formation of complex **5b** containing an uncoordinated pyridine ring, then posed the question whether a similarly coordinated complex might be formed from the corresponding *N*-benzoylated bis(pyridin-2-yl)methylamine ligand (bpmbaH) **2b**. This would be advantageous since with metal-based radiopharmaceuticals it is desirable to keep the size of the metal complex attached to the targeting vehicle as small as possible. Moreover, if the basic ligand structure can be kept small this increases the scope for subsequent modification to improve targeting.

However, the complex that precipitated from solution when the bispyridyl system bpmbaH **2b** was heated with [Re(CO)$_5$Br] in toluene was the neutral complex [(bpmbaH)Re(CO)$_3$Br] **6b** (Scheme 3), in which no coordination of the amide group to the rhenium had occurred.



Scheme 3 Proposed reaction pathway to the benzoylated complexes **8b** and **8b′**.

The X-ray structure of the neutral complex **6b**, shown in Fig. 2, confirms that the molecule has adopted a distorted octahedral

Table 1 Crystallographic parameters for **6b**, **8b**,[5] **8b′.HBr** and **8b′**

Complex	[(bpmbaH)Re(CO)$_3$Br] **6b**	[Re(CO)$_3$(Ph-bpmbaH)]Br **8b′·HBr**	[Re(CO)$_3$(Ph-bpmba)] **8b′**	[(bpmba)Re(CO)$_3$] **8b**
Formula	$C_{21}H_{15}BrN_3O_4Re\cdot MeCN$	$C_{27}H_{18}N_3O_4Re\cdot HBr$	$C_{27}H_{18}N_3O_4Re$	$C_{21}H_{14}N_3O_4Re\cdot MeCN$
M_r (Da)	680.52	715.56	634.64	579.56
T (K)	160(2)	120(2)	120(2)	120(2)
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	$P1$	$Pcab$	$Pc2_1n$	$P1$
a (Å)	7.602(3)	17.395(2)	11.0493(2)	10.7023(1)
b (Å)	12.208(8)	13.956(2)	12.7288(2)	12.8618(2)
c (Å)	13.094(5)	20.464(2)	16.2947(2)	15.0542(1)
α (°)	74.81(4)	90	90	109.990(1)
β (°)	80.92(4)	90	90	95.392(1)
γ (°)	94.31(6)	90	90	91.556(1)
V (Å^3)	1149.4(10)	4967.9(10)	2291.76(6)	91.556(1)
D_{Calc} (g cm^{-3}) (Z)	1.966(2)	1.913(8)	1.839(4)	1.954(4)
μ_{Mo} (mm^{-1})	7.062	6.540	5.343	6.316
Crystal size (mm^3)	0.38 × 0.30 × 0.15	0.16 × 0.06 × 0.03	0.26 × 0.14 × 0.12	0.48 × 0.30 × 0.18
Index ranges for h, k, l	0/9, −14/14, −15/15	−21/21, −17/12, −25/25	−14/14, −16/16, −21/20	−13/13, −16/16, −19/19
No. of reflections collected	4336	25325	23097	40952
No. of reflections unique (R_{int})	4005 (0.0272)	4955 (0.0897)	5186 (0.0442)	8865 (0.0373)
No. of reflections observed	3529	3630	4791	8280
$T_{max/min}$	0.4173 and 0.1744	0.8280 and 0.4209	0.5665 and 0.3372	0.3960 and 0.1515
Data/restraints/parameters	4005/0/291	4955/0/298	5186/1/292	8865/0/541
Goodness-of-fit (GOF)	1.024	1.096	1.097	1.113
R_1, wR_2 [$I > 2\sigma(I)$]	0.0309, 0.0773	0.0841, 0.1816	0.0248, 0.0476	0.0237, 0.0553
(all data)	0.0403, 0.0799	0.1182, 0.2033	0.0286, 0.0488	0.0264, 0.0563
Largest diff. peak and hole (e/Å^{-3})	1.829 and −2.056	3.136 and −2.048	0.716 and −1.159	0.750 and −1.935

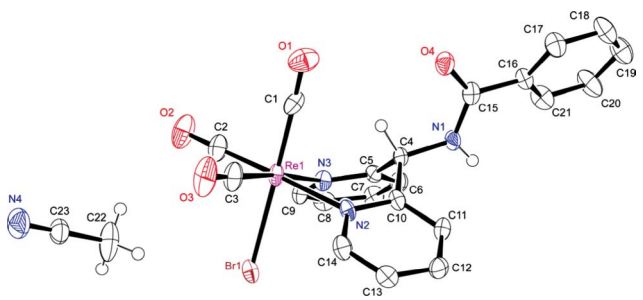


Fig. 2 X-Ray crystal structure of the neutral complex **6b·MeCN**.

arrangement around the rhenium with the amide portion of the bispyridyl ligand orientated away from the coordinated bromide ligand. Crystallographic parameters for **6b** are presented in Table 1 and selected bond lengths and angles are shown in Table 2.

Although in the solid state the plane of the benzoyl phenyl group is slightly rotated relative to the adjacent carbonyl group [O(4)–C(15)–C(16)–C(17) dihedral angle 29.03°], the NMR data for **6b** in solution shows a symmetrical complex with the two pyridine rings having the same chemical shifts. The presence of the amide N–H proton is also clearly visible at low field (δ_H 10.23 ppm) showing a strong coupling of 10 Hz to the adjacent CH (δ_H 7.16 ppm), this being consistent with their approximately coplanar arrangement (H–N–C–H dihedral angle = −175.28°) in the X-ray structure (Fig. 2).[6]

Although the amide nitrogen is inappropriately orientated to coordinate to the rhenium in the neutral complex **6b**, it proved possible to facilitate coordination of the amide group and loss of HBr to give the neutral complex **8b** if the neutral complex **6b** was dissolved in DMF and the resulting solution heated at *ca.* 118 °C for an extended period. This clearly indicates that dissociation and reorientation of the ligand is occurring during this process. It should also be noted that if the ligand **2b** is heated with [Re(CO)$_5$Br] in DMF the complex **6b** does not precipitate from solution and only the formation of the final product **8b** is observed.[5] Since the conversion of **6b** to **8b** can be achieved in the absence of base, this process probably involves the intermediate formation of the complex **7b** where coordination to the amide NH occurs prior to loss of HBr.

Support for this view comes from a study of the corresponding phenyl substituted *N*-benzoylated bis(pyridin-2-yl)methylamine ligand (Ph-bpmbaH) **2b′** which was chosen to mimic the steric bulk of the tris(pyridin-2-yl)methylamine ligand (tpmbaH) **1b** while maintaining the donor atom set present in the bis(pyridin-2-yl)methylamine ligand (bpmbaH) **2b**. When the ligand **2b′** was heated with [Re(CO)$_5$Br] in toluene at 105–110 °C, the product that precipitated was shown by NMR to be the intermediate cationic complex **7b′** where the amide nitrogen is coordinated to the rhenium as an N–H. Thus, the ^{1}H NMR spectrum for this complex in $CDCl_3$ clearly showed an acidic N–H proton resonance at δ_H 11.55 ppm, at significantly lower field than the uncoordinated amide group in the free ligand [δ_H ($CDCl_3$) 10.19 ppm]. The presence of two sets of pyridine ring signals also reflected the unsymmetrical nature of the complex.

It is interesting to note that the ^{1}H NMR spectrum of **7b′** has a number of unusual features, the interpretation of which required extensive use of ^{1}H-^{1}H and ^{1}H-^{13}C 2D correlation spectra. In particular the two *ortho* protons on one of the phenyl rings gave broad resonances at quite different chemical shifts (δ_H 7.96 and 8.93 ppm) indicating restricted rotation of this phenyl group. Since the *ortho* protons on the other phenyl ring (δ_H 8.58 ppm) were shown to have a long range coupling to the amide carbonyl carbon it was clear that it was the phenyl ring at the apex of the tripodal

Table 2 Selected bond lengths and angles for **6b**, **8b**,[5] **8b′.HBr** and **8b′**

	[(bpmbaH) Re-$(CO)_3$Br] **6b**	[(Ph-bpmbaH)Re-$(CO)_3$]Br **8b′·HBr**	[(Ph-bpmba)Re-$(CO)_3$] **8b′**	[(bpmba)Re$(CO)_3$] **8b**[5]	
Bond lengths (*Å*)			[a]	*Bond lengths* (*Å*)	[b]
Re(1)–C(1)	1.902(6)	1.890(17)	1.918(4)	Re(1)–C(1)	1.923(3)
Re(1)–C(2)	1.898(6)	1.934(16)	1.925(5)	Re(1)–C(2)	1.92(3)
Re(1)–C(3)	1.902(6)	1.924(18)	1.910(4)	Re(1)–C(3)	1.914(3)
Re(1)–N(1)	—	2.280(11)	2.159(3)	Re(1)–N(2)	2.1975(3)
Re(1)–N(2)	2.198(4)	2.169(13)	2.198(3)	Re(1)–N(1)	2.1825(3)
Re(1)–N(3)	2.215(4)	2.166(14)	2.173(2)	Re(1)–N(3)	2.1565(3)
C(1)–O(1)	1.135(7)	1.182(19)	1.153(6)	C(1)–O(1)	1.153(4)
C(2)–O(2)	1.161(7)	1.152(19)	1.150(5)	C(2)–O(2)	1.1505(4)
C(3)–O(3)	1.156(7)	1.17(2)	1.160(5)	C(3)–O(3)	1.1585(4)
N(1)–C(4)	1.437(7)	1.459(19)	1.492(5)	N(3)–C(9)	1.473(4)
N(1)–C(15)	1.363(7)	1.446(19)	1.383(6)	N(3)–C(15)	1.3455(4)
O(4)–C(15)	1.224(6)	1.225(18)	1.233(5)	O(4A)–C(15A)	1.249(4)
Bond angles (°)				*Bond angles* (°)	
C(1)–Re(1)–C(2)	87.9(3)	87.2(6)	87.62(18)	C(1)–Re(1)–C(2	89.4(14)
C(1)–Re(1)–C(3)	86.7(3)	85.9(7)	89.95(15)	C(1)–Re(1)–C(3)	89.62(14)
C(2)–Re(1)–C(3)	88.9(2)	89.9(6)	93.98(17)	C(2)–Re(1)–C(3)	89.77(14)
C(1)–Re(1)–N(1)	—	169.9(6)	168.23(13)	C(1)–Re(1)–N(1)	98.085(12)
C(1)–Re(1)–N(2)	94.4(2)	98.3(6)	98.21(16)	C(1)–Re(1)–N(2)	94.08(12)
C(1)–Re(1)–N(3)	98.1(2)	99.0(6)	95.38(15)	C(1)–Re(1)–N(3)	166.815(12)
C(2)–Re(1)–N(1)	—	100.5(5)	98.33(16)	C(2)–Re(1)–N(1)	92.185(11)
C(2)–Re(1)–N(2)	176.43(18)	171.5(6)	172.41(16)	C(2)–Re(1)–N(2)	173.27(11)
C(2)–Re(1)–N(3)	93.9(2)	93.2(6)	93.88(19)	C(2)–Re(1)–N(3)	101.535(12)
C(3)–Re(1)–N(1)	—	100.6(5)	99.70(14)	C(3)–Re(1)–N(1)	172.04(12)
C(3)–Re(1)–N(2)	93.9(2)	96.9(6)	90.89(14)	C(3)–Re(1)–N(2)	95.99(12)
C(3)–Re(1)–N(3)	174.6(2)	174.3(5)	170.68(19)	C(3)–Re(1)–N(3)	97.52(12)
N(1)–Re(1)–N(2)	—	73.4(4)	75.08(12)	N(1)–Re(1)–N(2)	81.64(10)
N(1)–Re(1)–N(3)	—	74.2(5)	74.18(14)	N(1)–Re(1)–N(3)	74.545(10)
N(2)–Re(1)–N(3)	83.17(16)	79.6(5)	80.80(16)	N(2)–Re(1)–N(3)	74.335(10)
C(4)–N(1)–C(15)	130.0(5)	115.8(12)	114.7(3)	C(9)–N(3)–C(15)	114.7(3)
Torsion angles (°)				*Torsion angles* (°)	
Re(1)–N(1)–C(4)–C(5)	—	−55.7(10)	−56.5(3)	O(4)–C(15)–N(3)–Re(1)	
Re(1)–N(1)–C(4)–C(10)	—	56.0(10)	50.7(3)	O(4)–C(15)–N(3)–C(9)	
Re(1)–N(1)–C(4)–C(22)	—	−175.7(8)	−177.4(2)		
Re(1)–N(1)–C(15)–C(16)	—	72.7(12)	73.7(4)		
Re(1)–N(1)–C(15)–O(4)	—	−104.4(13)	−108.2(4)		
Re(1)–N(2)–C(10)–C(4)	8.7(6)	6.2(18)	−5.8(4)		
Re(1)–N(3)–C(5)–C(4)	−4.5(6)	−8.0(13)	−0.1(4)		
O(4)–C(15)–N(1)–C(4)	—	9.6(18)	12.2(6)		
O(4)–C(15)–C(16)–C(17)	29.2(7)	−164.8(10)	−151.5(3)		
N(1)–C(15)–C(16)–C(17)	−152.0(7)	18.2(16)	26.8(5)		
N(1)–C(4)–C(22)–C(23)	—	3.0(14)	73.7(3)		

[a] Atom numbering is that shown in Fig. 4, this differs from cif file which shows inverse structure; [b] Average values from the two conformations present.

ligand that was exhibiting slow rotation on the NMR timescale. The corresponding *ortho* carbon resonances on the other hand, while showing the expected broadening, exhibited a less significant chemical shift difference (*cf.* δ_C 131.9 to 133.1 ppm) consistent with there being smaller changes in magnetic anisotropy nearer to the axis of rotation.

If we assume that both the ligands **2b** and **2b′** follow the same basic reaction pathway in their reaction with [$Re(CO)_5Br$] (see Scheme 3), then the precipitation of **7b′** rather than **6b′** in the latter case suggests that the concentration of **7b′** builds up more quickly than that of **6b′**. If so, this would suggest that the presence of the phenyl substituent is encouraging **6b′** to adopt a conformation that facilitates an interaction between the amide nitrogen atom and the metal centre. It is interesting to speculate whether a similar conformational effect in the structurally related trispyridyl ligand **1b** helps to explain the relative ease of formation of the neutral complex **5b** from the initially formed cationic complex **3b**.[5]

It is also interesting to note that while the solution NMR spectra of the complex formed from the reaction of the ligand **2b′** with [$Re(CO)_5Br$] clearly identified it as being **7b′**, the X-ray structure determined for the same crystals suggests that in the solid state it dissociates to give the neutral complex **8b′** and HBr. Both components are clearly visible in the crystal structure shown in Fig. 3. We must conclude that this dissociation permits more favourable packing in the crystalline state since these two molecules clearly readily re-associate to give **7b′** when returned to the solution state. It is, however, interesting to note that the ATR infrared spectrum of the complex shows a weak band at 2568 cm^{-1} typical of $H–N^+$ bonds and suggesting that some degree of protonation of the amide nitrogen is present even in the solid phase.

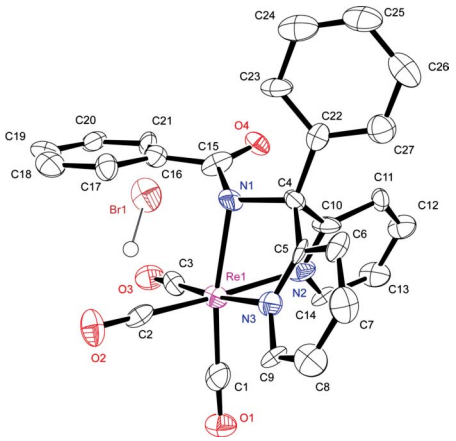


Fig. 3 X-Ray crystal structure suggesting the cationic complex **7b′** dissociates into **8b′·HBr** in the solid state.

Selected bond lengths and angles from the X-ray crystal structure of the complex formed from the reaction of the ligand **2b′** with $[Re(CO)_5Br]$ (*i.e.* **8b′·HBr**) are shown in Table 2 and other crystallographic parameters are presented in Table 1.

We earlier noted that the extended heating of a solution of the neutral complex **6b** in DMF resulted in loss of HBr and formation of the neutral complex **8b**. The complex **8b′·HBr**, formed from the reaction of the ligand **2b′** with $[Re(CO)_5Br]$, behaves similarly under comparable conditions resulting in formation of **8b′**.

The X-ray structure of the neutral complex **8b′** is shown in Fig. 4. Its crystallographic parameters are presented in Table 1 with selected bond lengths and angles in Table 2. The most obvious change between this structure and that of **8b′·HBr** is the orientation of the uncoordinated phenyl ring in **8b′**, which is rotated through *ca.* 71° relative to the case when the molecule of HBr is present. However there are also significant changes in the orientation of the benzoyl C–N bond relative to the axis of the apical phenyl group and the orientation of the adjacent benzoyl ring [$\Delta°_{\mathbf{8b'\cdot HBr-8b''}}$ for C(15)–N(1)–C(4)–C(22) = 10.39 and for N(1)–C(15)–C(16)–C(17) = –8.53]. As anticipated the structure adopted by **8b′** is also very similar to the analogous complex from the *N*-benzoylated tris(pyridin-2-yl)methylamine ligands **1b**.[5]

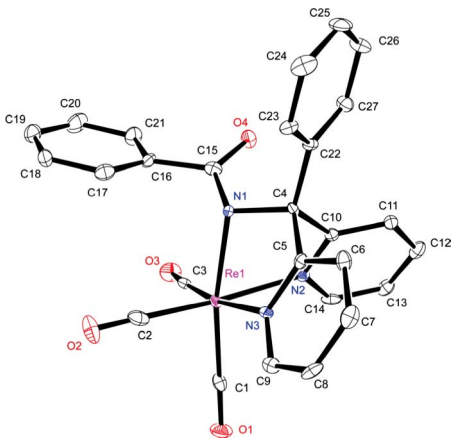


Fig. 4 X-Ray crystal structure of the neutral complex **8b′**.

In contrast to the NMR spectrum of **7b′**, it is interesting to note that the NMR spectra of the neutral complex **8b′** shows the two coordinated pyridine rings as being magnetically equivalent. Moreover, in the analogous tris(pyridyl)methylamine complex **5b** we had observed restricted rotation of the uncoordinated pyridine ring. This had led to exceptional broadening of the 3-H proton resonances of the coordinated pyridine rings to the point that they were not readily apparent at ambient temperatures.[5] No such effects were observed with the corresponding complex **8b′**, where the uncoordinated pyridine ring in **5b** has been replaced by a phenyl group. This clearly confirms our earlier suspicions that the presence of the uncoordinated pyridine nitrogen atom does have a significant impact on the conformational behaviour of **5b** on the NMR timescale, and that the unsymmetrical nature of the rotating pyridine ring is also responsible for the exceptional broadening of the 3-H proton resonances observed in this compound.

We were also able to confirm that the neutral complex **8b′** does reform the cationic complex **7b′** in solution in the presence of HBr. Thus, bubbling a little HBr into the NMR solution of the neutral complex **8b′** produced changes in the NMR spectrum of the resulting solution consistent with the formation of the cationic complex **7b′**.

As expected the conversion of **7b′** to **8b′** can be carried out much more quickly (<45 min) and at room temperature if a base, such as triethylamine, is added to facilitate the deprotonation. This ready deprotonation of **7b′** in the presence of base also helps explain why no evidence for the formation of the intermediate cationic complex **4b** is observed from the trispyridyl ligand **1b** when a solution of the initially formed complex **3b** is warmed (see Scheme 2). The cationic complex **4b** can be viewed as containing a built-in base (the uncoordinated pyridine ring) and this would be expected to facilitate the rapid removal of the amide N–H to give the observed final complex **5b**.

Comparison of the reactions of tpmaaH 1c, bpmaaH 2c and Ph-bpmaaH 2c′ with $[Re(CO)_5Br]$

We next investigated the impact of changing the substituent on the amide nitrogen from benzoyl to acetyl. We have already commented on the marked difference in the behaviour of the *N*-substituted tris(pyridin-2-yl)methylamine ligands **1b** and **1c** in their reaction with $[Re(CO)_5Br]$[5] and it was hoped that a study of the corresponding *N*-substituted bis(pyridin-2-yl)methylamine ligands **2c** and **2c′** might help shed some light on the main factors involved.

The previously unreported X-ray structure of the *N*-acetylated trispyridyl complex **3c** (Fig. 5) is shown in Fig. 6 and related data is shown in Table 3. The structure shows some disorder about the acetyl group but the bond lengths of the C–N and the C═O bonds (1.387 and 1.222 Å, respectively) are consistent with those expected for a normal amide and similar to those found in the free ligand (1.350 and 1.228 Å, respectively).[7]

It is interesting to note that while the corresponding benzoyl complex **3b** had readily undergone rearrangement and loss of HBr on heating in solution (Scheme 2),[5] the *N*-acetylated complex **3c** had proved resistant to rearrangement. We had earlier speculated that this possibly reflected the greater acidity of the N–H proton in **3b**, thus facilitating its removal and encouraging coordination of the deprotected amide group.[5] However, it is interesting to note that we have subsequently shown that the acetylated compound **3c** failed to rearrange to give the neutral complex **5c** even when heated

Table 3 Crystallographical parameters, selected bond lengths and angles for **3c**, [(tpmaaH)Re(CO)$_3$]Br

Formula	$C_{21}H_{16}BrN_4O_4Re{\cdot}H_2O$	*Bond lengths (Å)*	
M_r (Da)	672.50	Re(1)–C(1)	1.902(15)
T (K)	120(2)	Re(1)–C(2)	1.921(18)
Crystal system	Trigonal	Re(1)–C(3)	1.930(18)
Space group	$R\bar{3}$	Re(1)–N(1)	2.168(11)
a (Å)	29.8269(16)	Re(1)–N(2)	2.207(13)
b (Å)	29.8269(16)	Re(1)–N(3)	2.166(12)
c (Å)	15.6504(11)	C(1)–O(1)	1.168(18)
α (°)	90	C(2)–O(2)	1.13(2)
β (°)	90	C(3)–O(3)	1.14(2)
γ (°)	120	N(4)–C(4)	1.44(2)
V (Å^3)	12057.9(12)	N(4)–C(15)	1.39(2)
D_{Calc} (g cm^{-3}) (Z)	1.667(18)	O(4)–C(15)	1.22(2)
μ_{Mo} (mm^{-1})	6.060		
Crystal size (mm^3)	0.11 × 0.10 × 0.04	*Bond angles* (°)	
Index ranges for h, k, l	–25/35,–26/35,–19/19	C(1)–Re(1)–C(2)	88.4(7)
No. of reflections collected	19587	C(1)–Re(1)–C(3)	88.6(6)
No. of reflections unique (R_{int})	5025 (0.0550)	C(2)–Re(1)–C(3)	88.4(8)
No. of reflections observed	3987	C(1)–Re(1)–N(1)	175.1(5)
$T_{max/min}$	0.7936 and 0.5553	C(1)–Re(1)–N(2)	93.2(5)
Data/restraints/parameters	5025/0/303	C(1)–Re(1)–N(3)	95.3(5)
Goodness-of-fit (GOF)	1.211	C(2)–Re(1)–N(1)	96.4(6)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0820, 0.1731	C(2)–Re(1)–N(2)	177.3(6)
(all data)	0.01045, 0.1822	C(2)–Re(1)–N(3)	95.0(7)
Largest diff. peak and hole (e/Å^{-3})	2.877 and –1.852	C(3)–Re(1)–N(1)	92.5(5)

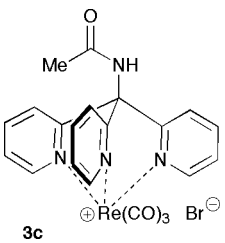


Fig. 5 Structure of the cationic complex **3c**.

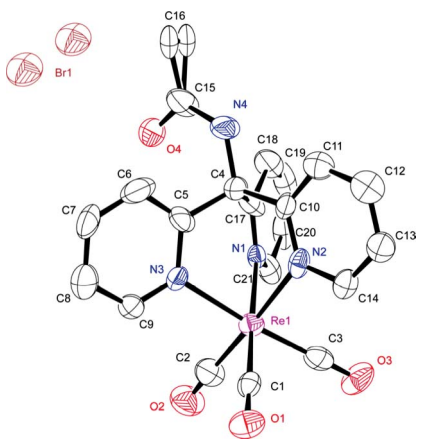


Fig. 6 X-Ray crystal structure of the cationic complex **3c·H$_2$O** (the water molecule has been omitted).

with triethylamine in DMSO for 16 h at 70 °C. The greater steric bulk of the benzoyl group relative to the acetyl group therefore appears to have a more significant role in determining whether rearrangement of the initially formed complex **3** occurs.

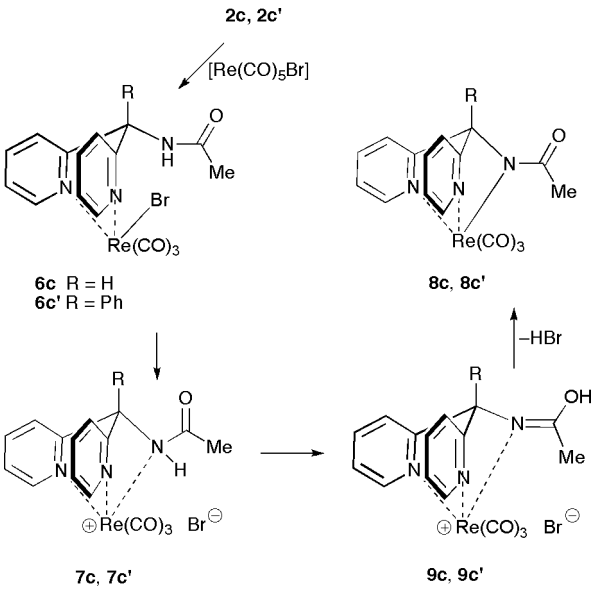
In view of this it was of interest to compare the coordination behaviour of the *N*-acetylated bis(pyridin-2-yl)methylamine ligands **2c** and **2c′** with those of the corresponding *N*-benzoylated ligands **2b** and **2b′** investigated earlier.

To maximise the chances of seeing reaction intermediates, the reaction of [Re(CO)$_5$Br] with the bispyridyl ligand **2c** was initially investigated under mild conditions in toluene. However, because [Re(CO)$_5$Br] is not particularly soluble in toluene at room temperature, the reaction had to be carried out at about 80 °C. After heating at this temperature for about 20 min the reaction mixture was shown by NMR spectroscopy to contain three pyridine-containing compounds in a ratio of *ca.* 0.7 : 1 : 1. These were subsequently identified as the starting ligand **2c**, the neutral complex **6c** [(bpmaaH)Re(CO)$_3$Br] and a cationic complex **9c** (Scheme 4). By repeating the reaction under more vigorous conditions (heating under reflux for 5 h) it was possible to demonstrate that **6c**, the initially formed complex, undergoes rearrangement to give the cationic complex **9c**.

Because the neutral complex **6c** slowly underwent conversion to give the cationic complex **9c** in solution it was not possible to isolate a pure sample of **6c** for NMR analysis, although sufficient data could be obtained to show it shared the characteristic features observed in the spectra of the *N*-benzoylated complex **6b**. Thus, for example, **6b** exhibited an amide proton resonance at δ_H 10.23 ppm showing coupling to the bridgehead methyne proton (d, J_{HH} 10 Hz), and the complex assigned to **6c** gave a similar resonance at δ_H 10.25 ppm (d, J_{HH} 10.5 Hz).

It is interesting to note that while the cationic complex [(Ph-bpmbaH)Re(CO)$_3$]Br **7b′**, derived from the phenyl-substituted *N*-benzoylated ligand **2b′**, had shown the amide nitrogen coordinated as an N–H, the X-ray structure of the cationic complex **9c** (Fig. 7) shows the amide portion of the ligand to be coordinated to the rhenium *via* its imidate form.

The presence of an acidic hydroxyl group in **9c** is supported by the ^{1}H NMR spectrum of the complex in $CDCl_3$, which shows a broad low field signal at *ca.* δ_H 13.5 ppm. Coordination of the amide nitrogen *via* its imidic acid tautomer means that the complex



Scheme 4 Proposed reaction pathway to the benzoylated complexes **8c** and **8c′**.

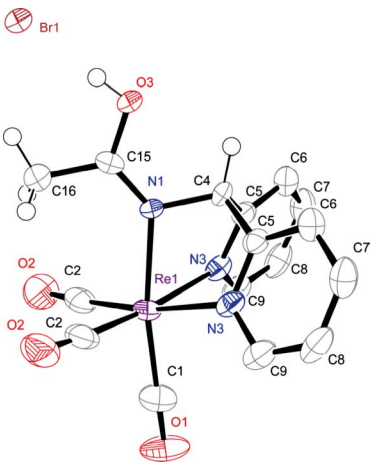


Fig. 7 X-Ray crystal structure of the cationic complex **9c**.

remains cationic with the bromide counterion hydrogen-bonding to the 'imidic acid' proton. This tautomerism also explains why the 'amide' carbon–nitrogen bond length of 1.288 Å is shorter in **9c** than that observed in the trispyridyl system **5b** (1.361 Å) or the bispyridyl systems **7c′**/**8c** (1.442/1.340 Å), and likewise the length of the 'amide' C–O bond is longer in **9c** (1.312 Å) than in the carbonyl groups in **5b** (1.242 Å) or **7c′**/**8c** (1.196/1.249 Å). We were unable to find another example of this type of tautomerisation of an acetyl group in a rhenium complex, although there are rare examples of the coordination of an acetyl group *via* its imidic acid tautomer in palladium,[8] platinum,[9,10] cobalt[11] and iridium[12] complexes. Fortunately, limited X-ray crystallographic data is available for two of these complexes, **10**[8] and **11**[12] to support the proposed structures (Fig. 8). For the palladium complex **10** it is interesting to note that the length of the C═N bond is 1.288 Å, the same length as that seen for the corresponding bond in **9c**, while in the iridium complex **11** the C═N bond (1.260 Å) is slightly shorter and the C–O bond (1.321 Å) slightly longer than those observed in **9c**. Further selected bond lengths and

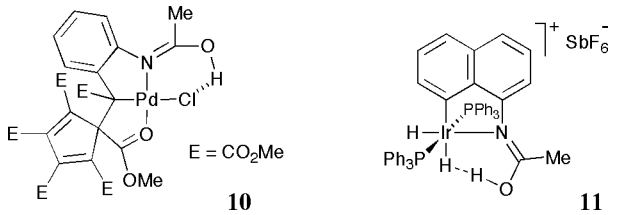


Fig. 8 Complexes with the acetyl group in its imidic acid tautomeric form.

angles for the cationic complex **9c** are shown in Table 5 and other crystallographic parameters are presented in Table 4.

No spectral evidence for the formation of the intermediate cationic complex **7c** was observed during the conversion of **6c** into **9c**.

Treatment of the complex **9c** with triethylamine in chloroform at room temperature resulted in the removal of HBr and formation of the neutral complex **8c**. The X-ray structure of **8c** is shown in Fig. 9, selected bond lengths and angles are shown in Table 5 and other crystallographic parameters are presented in Table 4. As noted earlier the 'amide' bond lengths in **8c** are typical of the values seen in other complexes containing C–N and C═O bonds such as **5b** and **7c′**.

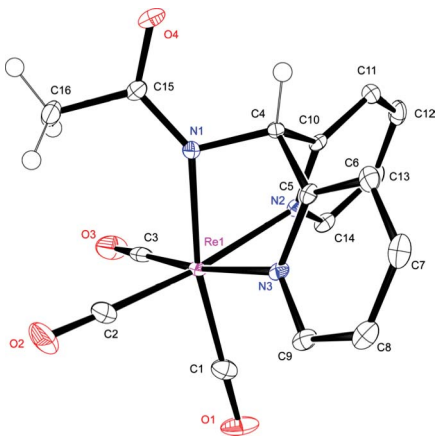


Fig. 9 X-Ray crystal structure of the neutral complex **8c**.

Having established that the *N*-acetylated bispyridyl ligand **2c** reacts with [Re(CO)$_5$Br] in the presence of base to give the neutral complex **8c** *via* a reaction pathway involving the intermediate complexes **6c** and **9c**, it was of interest to see how the presence of an additional phenyl group, as in **2c′**, would affect the reaction pathway and the relative stabilities of the intermediate complexes.

Heating the ligand **2c′** with [Re(CO)$_5$Br] in toluene under reflux led to the formation of a precipitate that was shown to be the cationic complex **7c′** (Fig. 10). Selected bond lengths and angles for this complex are shown in Table 5 and other crystallographic parameters are presented in Table 4. Interestingly, in this complex the amide portion of the original ligand has been coordinated to the rhenium as an NH without tautomerising to its imidate form.

This is supported by the NMR data in $CDCl_3$ which shows the presence of an acidic N–H resonance at δ_H 11.4 ppm analogous to the chemical shift value seen in **7b′** (δ_H 11.4 ppm). Addition of a little d_4-MeOD to the solution of **7c′** in $CDCl_3$ was found to improve the appearance of the spectrum and aid interpretation.

Table 4 Crystallographical parameters for **7c′**, **8c**, **8c′** and **9c**

Complex	[(Ph-bpmaaH)Re(CO)$_3$]Br **7c′**	[(bpmaa)Re(CO)$_3$] **8c**	[(Ph-bpmaa)Re(CO)$_3$] **8c′**	[(Re(CO)$_3$(bpmaaH)]Br **9c**
Formula	$C_{22}H_{17}BrN_3O_4Re$	$C_{16}H_{12}N_3O_4Re$	$C_{22}H_{16}N_3O_4Re{\cdot}CH_2Cl_2$	$C_{16}H_{13}BrN_3O_4Re$
M_r (Da)	653.50	496.49	615.04	577.40
T (K)	120(2)	120(2)	120(2)	120(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	C2/c	P1	P2/n	Pnma
a (Å)	17.8235(5)	8.6598(1)	14.2033(7)	12.2711(4)
b (Å)	17.5400(3)	8.7143(1)	11.9057(5)	10.3063(3)
c (Å)	16.1051(4)	11.5640(2)	26.0996(12)	14.6466(5)
α (°)	90	77.870(1)	90	90
β (°)	120.057 (1)	88.862(1)	92.1430(10)	90
γ (°)	90	70.192(1)	90	90
V (Å^3)	4357.79(18)	801.452(19)	4410.4(4)	1852.35(10)
D_{Calc} (g cm^{-3}) (Z)	1.992 (8)	2.057 (2)	1.853 (8)	2.070 (4)
μ_{Mo} (mm^{-1})	7.445	7.606	5.666	8.742
Crystal size (mm^3)	0.22 × 0.16 × 0.05	0.80 × 0.38 × 0.28	0.40 × 0.20 × 0.12	0.18 × 0.04 × 0.03
Index ranges for h, k, l	−23/22, −22/21, −20/20	−11/10, −11/11, −15/14	−17/17, −14/14, −32/32	−15/15, −13/12, −18/18
No. of reflections collected	24328	18270	19785	21095
No. of reflections unique (R_{int})	5003 (0.0555)	3673 (0.0389)	7984 (0.0385)	2242 (0.0439)
No. of reflections observed	4280	3620	7173	2018
$T_{max/min}$	0.7072 and 0.2912	0.2246 and 0.0643	0.5496 and 0.2102	0.7794 and 0.3021
Data/restraints/parameters	5003/0/273	3673/0/219	7984/13/547	2242/0/129
Goodness-of-fit (GOF)	1.059	1.124	1.060	1.115
R_1, wR_2 [$I > 2\sigma(I)$]	0.0334, 0.0688	0.0162, 0.0388	0.0480, 0.1324	0.0248, 0.0492
(all data)	0.0435, 0.0728	0.0166, 0.0390	0.0532, 0.1392	0.0311, 0.0521
Largest diff. peak and hole (e/Å^{-3})	1.675 and −1.309	0.817 and −1.058	2.966 and −2.303	1.317 and −1.033

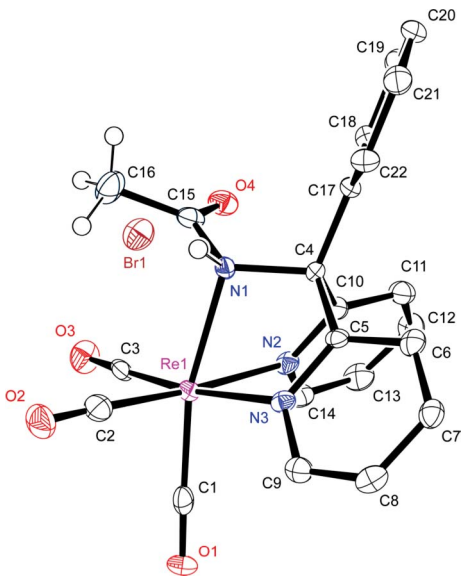


Fig. 10 X-Ray crystal structure of the cationic complex **7c′**.

However, even so, the signals in the ^{1}H and ^{13}C NMR spectra of **7c′** were broadened, reflecting the presence of an NMR exchange process. Careful analysis of these NMR spectra showed effects very similar to those previously discussed for the corresponding benzoyl analogue **7b′**. In particular the *ortho* protons on the phenyl ring at the apex of the tripod in **7c′** were again non-equivalent (δ_H 8.35 and 7.82 ppm) indicating that the rotation of this phenyl group around its axis was again very slow on the NMR timescale.

It is interesting to note that the IR spectrum of **7c′** obtained with an ATR accessory shows a broad band at ν_{max} 2594 cm^{-1} consistent with the presence of an N$^+$–H bond which also explains the absence of an amide N–H band in the region 3100–3600 cm^{-1}. The adjacent C═O had also been moved to higher wavenumber (ν_{max} 1759 cm^{-1}) relative to its position in the free ligand **2c′** (ν_{max} 1675 cm^{-1}), this being consistent with an increase in the electronegativity of the substituent on the carbonyl group. With this in mind the situation shown in Fig. 11, with the major contribution coming from the resonance structure on the right, would appear to be a better representation of **7c′** than that shown in Scheme 3.

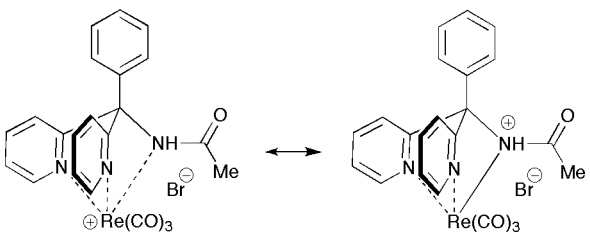


Fig. 11 Improved representation of the cationic complex **7c′**.

As previously noted, the IR spectrum of the corresponding benzoyl system **7b′** also showed some evidence for the presence of N$^+$–H bonds although the movement of the C═O band to higher wavenumber in the complex relative to the free ligand was much less marked in the case of **7b′** ($\Delta\nu_{max}$ 48 cm^{-1}) than observed for **7c′** ($\Delta\nu_{max}$ 84 cm^{-1}). This is also consistent with our earlier conclusion that there is significant dissociation of **7b′** into **8b′** and HBr in the solid phase.

Heating a solution of the complex **7c′** in DMF at 120 °C for a protracted period resulted in loss of HBr and formation of the neutral complex **8c′**. This conversion can also be carried out at room temperature in the presence of a base such as triethylamine. Crystallisation of the complex **8c′** from a DCM/hexane mixture gave crystals of formula [(Ph-bpmaa)Re(CO)$_3$]·0.5CH_2Cl_2 suitable for X-ray analysis.

Table 5 Selected bond lengths and angles for **7c′**, **8c**, **8c′** and **9c**

			[(Ph-bpmaa)Re(CO)$_3$] **8c′**		[(Re(CO)$_3$(bpmaaH)]Br **9c**	
	[(Ph-bpmaaH)Re-(CO)$_3$]Br **7c′**	[(bpmaa)Re-(CO)$_3$] **8c**	**A**	**B**		
Bond lengths (*Å*)					*Bond lengths* (*Å*)	
Re(1)–C(1)	1.912(5)	1.929(3)	1.919(8)	1.925(7)	Re(1)–C(1)	1.942(6)
Re(1)–C(2)	1.936(5)	1.919(3)	1.923(7)	1.924(7)	Re(1)–C(2)	1.914(4)
Re(1)–C(3)	1.916(5)	1.920(3)	1.932(8)	1.931(8)	Re(1)–C(2)#	1.914(4)
Re(1)–N(1)	2.227(4)	2.139(2)	2.159(6)	2.173(5)	Re(1)–N(1)	2.151(4)
Re(1)–N(2)	2.173(4)	2.194(2)	2.160(6)	2.147(5)	Re(1)–N(3)	2.195(3)
Re(1)–N(3)	2.176(4)	2.190(2)	2.205(6)	2.203(6)	Re(1)–N(3)#	2.195(3)
C(1)–O(1)	1.157(6)	1.151(3)	1.152(10)	1.147(9)	C(1)–O(1)	1.140(7)
C(2)–O(2)	1.154(6)	1.151(4)	1.154(9)	1.152(9)	C(2)–O(2)	1.157(5)
C(3)–O(3)	1.157(6)	1.153(4)	1.147(10)	1.152(9)	C(2)#–O(2)#	1.157(5)
N(1)–C(4)	1.524(5)	1.474(3)	1.504(9)	1.490(9)	N(1)–C(4)	1.468(6)
N(1)–C(15)	1.442(6)	1.340(3)	1.377(9)	1.352(9)	N(1)–C(15)	1.288(6)
O(4)–C(15)	1.197(6)	1.249(3)	1.236(8)	1.239(8)	O(3)–C(15)	1.312(6)
Bond angles (°)					*Bond angles* (°)	
C(1)–Re(1)–C(2)	87.3(2)	90.57(12)	87.8(3)	86.8(3)	C(1)–Re(1)–C(2)	90.50(18)
C(1)–Re(1)–C(3)	89.52(19)	87.72(11)	89.5(3)	89.3(3)	C(1)–Re(1)–C(2)#	90.50(17)
C(2)–Re(1)–C(3)	91.4(2)	90.04(13)	91.1(3)	89.9(3)	C(2)–Re(1)–C(2)#	88.7(2)
C(1)–Re(1)–N(1)	166.78(16)	168.73(10)	168.0(3)	167.9(3)	C(1)–Re(1)–N(1)	170.2(2)
C(1)–Re(1)–N(2)	97.74(17)	97.02(10)	95.4(3)	95.3(3)	C(1)–Re(1)–N(3)	97.97(16)
C(1)–Re(1)–N(3)	96.02(16)	96.68(9)	98.5(3)	98.2(3)	C(1)–Re(1)–N(3)#	97.97(16)
C(2)–Re(1)–N(1)	100.62(17)	97.46(10)	101.4(3)	102.4(3)	C(2)–Re(1)–N(1)	96.48(13)
C(2)–Re(1)–N(2)	174.40(16)	172.26(10)	171.8(3)	172.3(3)	C(2)–Re(1)–N(3)	95.31(15)
C(2)–Re(1)–N(3)	95.71(17)	96.51(11)	90.8(3)	92.0(3)	C(2)–Re(1)–N(3)#	170.58(13)
C(3)–Re(1)–N(1)	100.71(16)	100.12(10)	98.0(3)	98.5(3)	C(2)#–Re(1)–N(1)	96.48(13)
C(3)–Re(1)–N(2)	91.03(17)	91.76(10)	96.5(3)	97.5(3)	C(2)#–Re(1)–N(3)	170.58(13)
C(3)–Re(1)–N(3)	171.19(17)	172.05(9)	171.9(3)	172.3(3)	C(2)#–Re(1)–N(3)#	95.31(15)
N(1)–Re(1)–N(2)	73.95(13)	74.81(8)	74.5(2)	74.6(2)	N(1)–Re(1)–N(3)	74.63(10)
N(1)–Re(1)–N(3)	72.86(13)	74.62(8)	73.9(2)	73.9(2)	N(1)–Re(1)–N(3)#	74.63(10)
N(2)–Re(1)–N(3)	81.47(14)	81.15(8)	81.1(2)	80.4(2)	N(3)–Re(1)–N(3)#	79.51(15)
C(4)–N(1)–C(15)	116.7(4)	117.3(3)	115.0(6)	115.5(5)	C(4)–N(1)–C(15)	120.0(4)
Torsion angles (°)					*Torsion angles* (°)	
Re(1)–N(1)–C(4)–C(5)	−55.5(3)	−56.52(19)	−58.7(5)	59.5(5)	Re(1)–N(1)–C(15)–O(3)	180.0
Re(1)–N(1)–C(4)–C(10)	53.7(3)	57.96(19)	51.9(5)	−51.5(5)	Re(1)–N(1)–C(4)–H(4)	180.0
Re(1)–N(1)–C(4)–C(17)	−179.4(2)	—	170.5(4)	−169.2(4)	Re(1)–N(1)–C(15)–C(16)	0.000(1)
Re(1)–N(1)–C(15)–C(16)	89.6(4)	6.0(4)	−62.0(7)	56.6(7)	O(3)–C(15)–N(1)–C(4)	0.000(1)
Re(1)–N(1)–C(15)–O(4)	−90.7(4)	−174.78(19)	121.9(6)	−125.8(6)		
Re(1)–N(2)–C(10)–C(4)	−0.9(5)	6.7(2)	−7.3(7)	6.9(7)		
Re(1)–N(3)–C(5)–C(4)	3.4(4)	−0.8(2)	−11.2(7)	12.6(7)		
O(4)–C(15)–N(1)–C(4)	24.8(6)	−1.7(4)	−3.6(9)	1.0(9)		
N(1)–C(4)–C(17)–C(18)			−21.6(7)	27.9(6)		

The presence of one solvent molecule to two of the complex resulted in the presence of two conformations of the complex (A and B). The structure of **8c′A** is shown in Fig. 12 and that of **8c′B** in Fig. 13. Selected bond lengths and angles for both conformations are shown in Table 5 and other crystallographic parameters are presented in Table 4.

The torsion angles shown in Table 5 indicate that the two conformations **8c′A** and **8c′B** have an approximate mirror image relationship, although there is a significant difference in the extent of rotation of the phenyl group relative to the N(1)–C(4) bond in these conformations. In solution the molecule is conformationally mobile since the NMR spectra show only an averaged spectrum with the two pyridine rings magnetically equivalent. Neither the ^{1}H or ^{13}C NMR spectra show any evidence for restricted rotation around the apical phenyl group.

Conclusions

Our studies of the reactions of *N*-acetylated bispyridylmethylamine ligands **2** with [Re(CO)$_5$Br] have provided a much clearer insight into the factors that influence the nature of the complexes formed with this ligand system and the related *N*-acetylated trispyridylmethylamine ligand system. These studies had been initiated following the unexpected observation that quite different rhenium tricarbonyl complexes were formed from the reaction of [Re(CO)$_5$Br] with *N*-[1,1,1-tris(pyridin-2-yl)methyl]benzamide, tpmbaH, **1b** than when using *N*-[1,1,1-tris(pyridin-2-yl)methyl]acetamide, tpmaaH, **1c**.[5] This was significant in the context of our efforts to develop rhenium-based agents for nuclear medicine where it was essential to be able to predict the nature of the final complex. In particular, we wanted

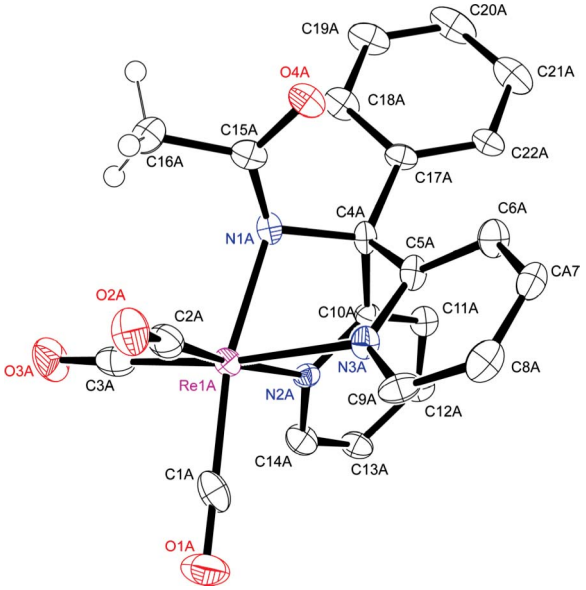


Fig. 12 X-Ray crystal structure of the neutral complex **8c′A.(0.5)DCM** with the DCM molecule omitted.

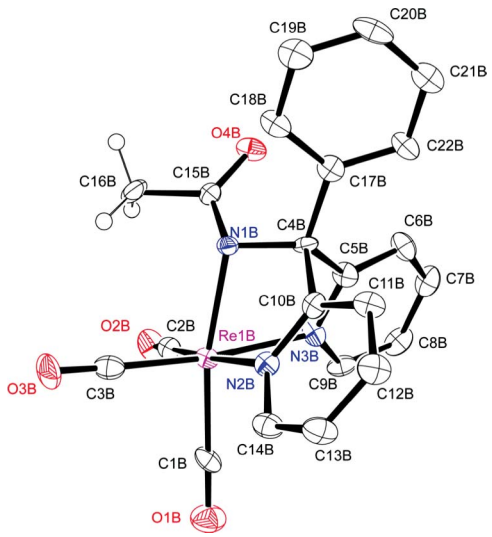


Fig. 13 X-Ray crystal structure of the neutral complex **8c′B.(0.5)DCM** with the DCM molecule omitted.

to investigate why the *N*-acetylated trispyridylmethylamine ligand (tpmaaH) **1c** formed a stable cationic octahedral complex $[(tpmabaH)Re(CO)_3]^+$ Br^- **3c** while the analogous complex from the *N*-benzoylated ligand **1b** readily rearranged to give a neutral octahedral complex $[(tpmba)Re(CO)_3]$ **5c** in which one of the pyridine rings was uncoordinated.

We have now established that under appropriate conditions bispyridyl ligands **2**, structurally related to the *N*-acylated trispyridylmethylamine ligands **1b** and **1c** studied earlier, can form neutral octahedral complexes analogous to **5c** *via* a reaction pathway (see Schemes 2 and 3) involving several intermediate complexes. The nature of these intermediates and their relative stabilities has been shown to depend on the substituents on the bispyridine ligand. Having a phenyl group at the apex of the tripodal ligand facilitates the interaction of the amide nitrogen with the rhenium centre, so that while the unsubstituted ligands **2b** and **2c** showed the initial formation of the neutral complexes **6b** and **6c**, the corresponding phenyl substituted ligands **2b′** and **2c′** quickly produced the cationic complexes **7b′** and **7c′**. All four of these rhenium complexes could be converted to the corresponding neutral complexes **8** simply by heating although in some cases the conditions required were rather vigorous. However, if a base was added to the reaction mixture, much milder conditions could be used to bring about these same conversions.

If we compare the structures of the trispyridyl ligands **1** with the bispyridyl ones **2** we can see that the trispyridyl ligands **1** in principle contain both elements needed to facilitate formation of neutral complexes analogous to **8**. The trispyridyl ligands **1** can be considered as being bispyridyl ligands of type **2** that have a pyridine group at the apex of the tripod. Moreover, this pyridine ring is relatively large, certainly of comparable size to the phenyl group present in **2b′** and **2c′**, and it can also function as a base. So it is reasonable to assume that both the trispyridyl ligands **1b** and **1c** should readily form the corresponding neutral complexes **5b** and **5c** given the opportunity. The reason that the acetylated ligand **1c** does not do so is probably related to the stability of the initially formed cationic complex **3c**. In contrast, in the corresponding benzoyl system **3b** we would expect increased steric crowding between the substituent at the apex of the tripod and the coordinated pyridine rings. This would increase the likelihood that one of these coordinated pyridine rings will twist and become detached from the rhenium. This in turn would then provide access to the reaction pathway seen in the bispyridyl ligands (Schemes 2 and 3) leading to the observed formation of the neutral complex **5b**. If stable complexes of type **4** are required we can therefore conclude that it is essential to ensure that the nature of the substituent placed at the apex of the tripod will contribute as little as possible to steric interactions with the coordinated pyridine rings.

Another interesting issue is why the *N*-acetyl group in the ligand **2c** forms a complex **9c** in which the ligand is bound in its imidic acid tautomeric form, whereas the corresponding phenyl substituted ligands **2c′** and **2b′** do not. We believe this is due to steric factors. In the absence of a substituent at the apex of the tripodal ligand, the imidic acid portion of the molecule **9c** can readily adopt a conformation where it is coplanar with the bond from the amide nitrogen to the rhenium, minimising its interactions with the adjacent carbonyl ligands and giving a symmetrical molecule. In contrast, a similar conformation in the analogous complexes from the substituted ligands **2c′** and **2b′** would produce a significant steric interaction between the imidic oxygen and the phenyl group at the apex of the ligand, requiring the imidic portion to adopt the amide tautomeric form so that it can rotate to reduce this interaction. Unfortunately, for the *N*-benzoylated ligand **2b** the vigorous conditions needed to get the initially formed complex **6b** to react further meant that no intermediate complexes could be observed en route to the formation of the final complex **8b** (Scheme 3). However, the *N*-benzoyl substituent in its imidic acid tautomeric form would be expected to adopt a planar arrangement to permit conjugation between the imidic acid N=C bond and the adjacent phenyl ring, so a symmetrical complex **9b** analogous to that seen in the corresponding *N*-acetylated complex **9c** is feasible providing there is no significant steric interaction between the phenyl ring and the adjacent carbonyl groups on the rhenium.

Experimental

General details

NMR (^{1}H, ^{13}C, COSY, ^{13}C-^{1}H correlated) spectra were recorded on JEOL EX-270 and Bruker AMX400, AV400 and AV600 spectrometers. ^{1}H NMR spectra in $CDCl_3$ are referenced to TMS, those in d_4-MeOD to the residual CD_2H signal at δ_H 3.31 ppm and those in d_6-DMSO to the residual CD_2H signal at δ_H 2.50 ppm unless otherwise indicated.^{13}C NMR spectra are referenced to the solvent resonance, *i.e.* $CDCl_3$ at δ_C 77.23 ppm, d_4-MeOD at δ_C 49.15 ppm or d_6-DMSO at δ_C 39.51 ppm unless otherwise indicated. *J* values are given in Hz. '*J*' indicates an apparent coupling constant in a second order spin system or in a resonance showing substantial line broadening. IR spectra were recorded using either a Shimadzu FTIR-8300 or a Perkin Elmer Spectrum 65 FT-IR spectrophotometer and selected bands are reported below. Low resolution mass spectra were obtained using a Bruker Esquire LC mass spectrometer equipped with an electrospray ionisation source. High resolution mass spectrometry was carried out by the facility at Kings College, London or the EPSRC facility at Swansea. Elemental analyses were obtained from the Department of Chemistry at UCL or Medac Limited. Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. TLC was performed with alumina backed silica gel 60 F_{254} eluting with the solvent system used for the column chromatography unless otherwise stated and the plates were visualised under UV light or developed in an iodine tank. Column chromatography used silica gel with particle size 33–50 μm and was purchased from BDH. Rheniumpentacarbonyl bromide [$Re(CO)_5Br$] was purchased from Strem Chemicals UK. All other materials were purchased from Sigma–Aldrich Ltd. and used as received unless indicated otherwise.

Ligand synthesis

The syntheses of 1,1,1-tris(pyridin-2-yl)methylamine, tpmaH, **1a**,[3] *N*-[1,1,1-tris(pyridin-2-yl)methyl]benzamide, tpmbaH, **1b**,[5] *N*-[1,1,1-tris(pyridin-2-yl)methyl]acetamide, tpmaaH, **1c**,[5] 1,1-bis(pyridin-2-yl)methylamine, bpmaH, **2a**[13,14] and *N*-[bis(pyridin-2-yl)methyl]benzamide, bpmbaH, **2b**[5] are reported elsewhere.

***N*-[Bis(pyridin-2-yl)methyl]acetamide, bpmaaH, 2c.** Acetic anhydride (0.3 g, 2.9 mmol) was added dropwise to a solution of bpmaH **2a** (0.5 g, 2.7 mmol) in DCM (2 cm^3) at room temperature and the mixture stirred for 30 min. Dichloromethane (10 cm^3) was then added and the solution washed with saturated aqueous sodium hydrogen carbonate (3 × 10 cm^3). The organic phase was then dried ($MgSO_4$), filtered and volatile components removed by warming under reduced pressure (35 °C at 10 mmHg). The resulting acetamide **2c** was then purified by chromatography on silica using mixtures of acetonitrile and acetone as the eluent. The bpmaaH **2c** was obtained as a viscous oil (0.5 g, 81%), δ_H(270 MHz, $CDCl_3$) 2.02 (3 H, s, Me), 6.16 (1 H, d, *J* 6.5, α-CH), 7.05 (2 H, ddd, *J* 7.6, 4.8 and 1, 5-H), 7.35 (2 H, d, *J* 7.7, 3-H), 7.53 (2 H, td, *J* 7.7 and 1.7, 4-H), 7.92 (1 H, d, *J* 6.5, NH), 8.44 (2 H, ddd, *J* 4.8, 1.7 and 1, 6-H); δ_C(100.63 MHz, $CDCl_3$) 22.6 (Me), 58.8 (CH), 121.6 (×2)(C-5), 121.9 (×2)(C-3), 136.3 (×2)(C-4), 148.5 (×2)(C-6), 158.6 (×2)(C-2), 169.2 (C═O); Selected IR bands ν_{max}(film, cm^{-1}) 3292 (br, NH), 1661 (C═O), 1589, 1570, 1506, 1472 (pyr); *m*/*z* (ESI) 266 (M+K^+. $C_{13}H_{13}KN_3O$ requires 266).

1-Phenyl-1,1-bis(pyridin-2yl)methylamine, Ph-bpmaH, 2a′.

a) 1-Phenyl-1-(pyridin-2-yl)methylamine. 1-Phenyl-1-(pyridin-2-yl)methylamine was prepared from 2-benzoylpyridine, hydroxylamine hydrochloride, glacial acetic acid and zinc dust using the method of Winthrop *et al.*[15] and isolated as a pale brown oil (6.6 g, 90%); δ_H(270 MHz, $CDCl_3$) 2.20 (2 H, br s, NH_2), 5.16 (1 H, s, α-CH), 6.98 (1 H, ddd, *J* 7.3, 4.9 and 0.8, 5-H), 7.10–7.18 (2 H, m, 3-H and 4′-H), 7.23 (2 H, t, *J* 8, 3′/5′-H), 7.34 (2 H, d, *J* 8, 2′/6′-H), 7.45 (1 H, dd, *J* 8 and 2, 4-H), 8.48 (1 H, br, 6-H); δ_C(67.9 MHz, $CDCl_3$) 60.6 (α-CH), 121.4 (C-5), 121.7 (C-3), 126.7 (×2)(C-3′/5′), 126.9 (C-4′), 128.3 (×2)(C-2′/6′), 136.4 (C-4), 144.2 (C-1′), 148.6 (C-6), 162.9 (C-2).

b) 1-Phenyl-1,1-bis(pyridin-2yl)methylamine, Ph-bpmaH, ***2a′***. A solution of *n*-butyl lithium in hexanes (2.5 M, 12 cm^3, 30 mmol) was added dropwise over 30 min to a stirred solution of 1-phenyl-1-(pyridin-2-yl)methylamine (5.35 g, 29 mmol) in dry THF (50 cm^3) cooled to −78 °C under dry argon. After allowing this mixture to warm slowly to room temperature it was stirred for a further 16 h. 2-Chloropyridine (3.4 g, 30 mmol) was then added dropwise and the mixture stirred for 24 h. Volatile components were removed under reduced pressure (40 °C at 15 mmHg) and water (50 cm^3) added carefully to the residue. The mixture was then extracted with dichloromethane (3 × 50 cm^3). The organic extracts were combined, dried ($MgSO_4$), filtered and the solvent evaporated under reduced pressure to leave a brown viscous oil. This product was purified by chromatography on silica using a DCM/MeOH (95 : 5) mixture as the eluent to give the Ph-bpmaH **2a′** (2.9 g, 38%) as a viscous oil, R_f 0.4; δ_H(270 MHz, $CDCl_3$) 2.98 (2 H, br s, NH_2), 7.05 (2 H, d, *J* 8.0, 3-H), 7.12 (2 H, ddd, *J* 8.0, 4.5 and 1.0, 5-H), 7.24–7.28 (5 H, m, Ph), 7.54 (2 H, td, *J* 8 and 2, 4-H), 8.59 (2 H, d, *J* 4.5, 6-H); δ_C(67.9 MHz, $CDCl_3$) 69.2 (α-C), 121.8 (×2)(C-5), 123.1 (×2)(C-3), 127.1 (C-4′), 128.2 (×2)(C-3′/5′), 128.6 (×2)(C-2′/6′), 136.1 (×2)(C-4), 146.7 (C-1′), 149.0 (×2)(C-6), 165.7 (×2)(C-2); Selected IR bands ν_{max}(ATR)/cm^{-1} 3370, 3300 (NH_2), 1584, 1570, 1490, 1462 (pyr); *m*/*z* (ESI) 262.1339 (M+H^+. $C_{17}H_{16}N_3$ requires 262.1339).

***N*-[1-Phenyl-1,1-bis(pyridin-2-yl)methyl]benzamide, Ph-bpmbaH, 2b′.** A solution of benzoyl chloride (300 mg, 2.1 mmol) in dichloromethane (2 cm^3) was added dropwise to a stirred solution of Ph-bpmaH **2a′** (330 mg 1.2 mmol) and triethylamine (0.25 g 2.5 mmol) in dichloromethane (15 cm^3) and the mixture stirred at room temperature for 3 h. Water (20 cm^3) was then added and the layers separated. The organic layer was then washed with further portions of water (2 × 20 cm^3) and then dried ($MgSO_4$) and filtered. Volatile components were removed from the filtrate under reduced pressure (35 °C at 15 mmHg) and the residue purified by chromatography on silica using a DCM/MeOH (195 : 5) mixture as the eluent. Recrystallisation of the product from a DCM/Hexane mixture gave the Ph-bpmbaH **2b′** (R_f 0.15) as fawn coloured crystals (205 mg, 37%), m.p. 229–230 °C; δ_H(400 MHz, $CDCl_3$) 7.09 (2 H, ddd, *J* 7.4, 4.8 and 0.8, 5-H), 7.14–7.22 (3 H, m, 3′/5′-H and 4′-H), 7.29 (2 H, dm, *J* 8.0, 2′/6′-H), 7.34–7.42 (3 H, m, 3″/5″-H and 4″-H), 7.43 (2 H, dt, *J* 8.0 and 0.8, 3-H), 7.54 (2 H, ddd, *J* 8, 7.4 and 1.6, 4-H), 7.90 (2 H, d, *J* 8, 2″/6″-H), 8.50 (2 H, ddd, *J* 4.8, 1.6 and 0.8, 6-H), 10.19 (1 H, br s, NH); δ_C(67.9 MHz, $CDCl_3$) 69.9 (α-C), 122.3

(×2)(C-5), 124.4 (×2)(C-3), 127.3 (C-4′), 127.5 (×2)(C-2″/6″), 127.9 (×2)(C-3′/5′), 128.6 (×2)(C-3″/5″), 129.5 (×2)(C-2′/6′), 131.6 (C-4″), 135.4 (C-1″), 136.7 (×2)(C-4), 143.4 (C-1′), 147.9 (×2)(C-6), 161.6 (×2)(C-2), 165.3 (C═O); Selected IR bands ν_{max}(ATR)/cm^{-1} 3335 (NH), 1659 (C═O), 1585, 1560, 1505, 1465 (pyr); *m*/*z* (ESI) 366.1601 (M+H$^+$. $C_{24}H_{20}N_3O$ requires 366.1601).

***N*-[1-Phenyl-1,1-bis(pyridine-2-yl)methyl]acetamide, Ph-bpmaaH, 2c′.** A mixture of Ph-bpmaH **2a′** (500 mg, 1.9 mmol) and acetic anhydride (3 cm^3) was stirred at room temperature for 16 h. Volatile components were removed under reduced pressure (65 °C at 15 mmHg) and the residue stirred with saturated sodium bicarbonate solution (20 cm^3) for 30 min. This mixture was then extracted with DCM (3 × 15 cm^3). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure (30 °C at 15mmHg) to give a brown viscous residue. Purification of this residue by chromatography on silica gel using a mixture of DCM/MeOH (195 : 5) as the eluant gave the Ph-bpmaaH **2c′** (200 mg, 32%) as a waxy solid, R_f 0.2; δ_H(270 MHz, $CDCl_3$) 2.04 (3 H, s, Me), 7.04 (2 H, dd, *J* 7.5 and 5, 5-H), 7.15–7.23 (3 H, m, 3′/5′-H and 4′-H), 7.27 (2 H, m, 2′/6′-H), 7.34 (2 H, d, *J* 8, 3-H), 7.49 (2 H, td, *J* 8 and 1.5, 4-H), 8.46 (2 H, br d, *J* 5, 6-H), 9.11 (1 H, br s, NH); δ_C(67.9 MHz, $CDCl_3$) 24.2 (Me), 69.6 (α-C), 121.9 (×2)(C-5), 124.0 (×2)(C-3), 126.9 (C-4′), 127.5 (×2)(C-3′/5′), 129.0 (×2)(C-2′/6′), 136.2 (×2)(C-4), 143.0 (C-1′), 147.5 (×2)(C-6), 161.2 (×2)(C-2), 168.2 (C═O); Selected IR bands ν_{max}(ATR)/cm^{-1} 3325 (NH), 1675 (C═O), 1586, 1569, 1499, 1464 (pyr); *m*/*z* (ESI) 304.1447 (M+H$^+$. $C_{19}H_{18}N_3O$ requires 304.1444).

Synthesis of rhenium complexes

The reaction of [Re(CO)$_5$Br] with tpmbaH 1b. The formation of [(tpmbaH)Re(CO)3]Br **3b** and [(tpmba)Re(CO)$_3$] **5b** from the reaction of [Re(CO)$_5$Br] with bpmbaH **1b** has been described elsewhere.[5]

The reaction of [Re(CO)$_5$Br] with bpmbaH 2b.

*Formation of [(bpmbaH)Re(CO)$_3$Br] **6b**.* A stirred mixture of [Re(CO)$_5$Br] (115 mg, 0.28 mmol), bpmbaH **2b** (87 mg, 30 mol) and toluene (10 cm^3) was heated under reflux for 2 h by which time the [Re(CO)$_5$Br] had completely dissolved and had been replaced by a colourless solid. This solid was filtered off, washed with DCM (10 cm^3) and dried. Slow crystallisation of this sample from acetonitrile gave [(bpmbaH)Re(CO)$_3$Br] **6b** (140 mg, 79%) as colourless crystals suitable for X-ray crystallography, mp >250 °C, (Found: C, 40.1; H, 2.55; N, 8.0; $C_{21}H_{15}BrN_3O_4Re$. MeCN requires C, 40.59; H, 2.67; N, 8.23%). δ_H(400 MHz, DMSO-d$_6$, TMS) 7.16 (1 H, d, *J* 10, α-CH), 7.60–7.65 (4 H, m, 5-H and 3′/5′-H), 7.69 (1 H, t, *J* 8, 4′-H), 8.03 (2 H, d, *J* 8, 3-H), 8.16 (2 H, d, *J* 7.5, 2′/6′-H), 8.20 (2 H, td, *J* 7.5 and 1.5, 4-H), 9.12 (2 H, dd, *J* 5.5 and 1, 6-H), 10.23 (1 H, d, *J* 10, NH); δ_C(100.63 MHz, DMSO-d$_6$) 59.5 (α-CH), 122.0 (×2)(C-5), 125.2 (×2)(C-3), 128.0 (×2)(C-3′/5′), 128.6 (×2)(C-2′/6′), 132.3 (C-4′), 133.2 (C-1′), 140.7 (×2)(C-4), 156.9 (×2)(C-6), 157.0 (×2)(C-2), 167.0 (C═O), 189.7 (CO), 195.7 (x2)(CO); Selected IR bands ν_{max} (MeCN, cm^{-1}) 3325 (NH), 2026, 1923, 1895 (CO), 1674 (C═O); *m*/*z* (ESI) 561.0623 (M–Br$^+$. $C_{21}H_{15}N_3O_4Re$ requires 561.0620).

Heating a sample of the [(bpmbaH)Re(CO)$_3$]Br complex **6b** in DMF at 118 °C for 48 h resulted in the loss of HBr and formation of the neutral complex [(bpmba)Re(CO)$_3$] **8b** which was identified by comparison with an authentic sample.[5]

The reaction of [Re(CO)$_5$Br] with Ph-bpmbaH 2b′.

*Formation of [(Ph-bpmbaH)Re(CO)$_3$]Br **7b′**.* A mixture of Ph-bpmbaH **2b′** (103 mg, 0.28 mmol), [Re(CO)$_5$Br] (105 mg, 0.26 mmol) and dry toluene (3 cm^3) was heated at 105–110 °C for 16 h and then cooled. The resulting solid was filtered off, washed with petroleum ether (bp 40–60 °C) (20 cm^3) and then air dried (120 mg, 65%). Crystals of the cationic complex **7b′** suitable for X-ray diffraction studies were obtained from the slow evaporation of a DCM/Hexane solution of the product, mp >250 °C; δ_H (600 MHz, $CDCl_3$)[16] 7.36 (1 H, m, 5′-H), 7.42 (1 H, m, 5-H), 7.43–7.51 (4 H, m, 5′-H, 4′-H, 3″/5″-H), 7.55 (1 H, t, *J* 7, 4″-H), 7.60 (1 H, br, 3′-H), 7.76 (1 H, d, *J* 8, 3-H), 7.95 (1 H, m, 4-H), 7.96 (1 H, br, 6′-H), 8.00–8.07 (2 H, m, 3′-H, 4′-H), 8.58 (2 H, d, *J* 7, 2″/6″-H), 8.91 (1 H, d, '*J*' 5, 6′-H), 8.93 (1 H, br, 2′-H), 8.98 (1 H, d, '*J*' 4.5, 6-H), 11.55 (1 H, br s, NH); δ_C(100.64 MHz, $CDCl_3$) 79.9 (α-C), 124.5 (C-5′), 124.8 (C-3′), 125.8 (C-5), 126.6 (C-3), 127.6 (C-4′), 129.0 (×2)(C-3″/5″), 130.0 (C-1″), 130.0 (br, C-5′), 130.4 (×2)(C-2′/6′), 130.4 (br, C-3′), 131.9 (br, C-6′), 132.3 (C-1′), 133.1 (br, C-2′), 134.7 (C-4″), 140.5 (C-4′), 140.8 (C-4), 154.5 (C-6′), 154.8 (C-6), 159.5 (C-2), 160.3 (C-2′), 170.9 (C═O), 193.5 (CO), 194.1 (CO), 195.4 (CO); Selected IR bands ν_{max} (ATR)/cm^{-1} 2568 (w), 2026, 1933, 1894 (CO), 1707 (C═O), 1599, 1448, 1413 (pyr); *m*/*z* (ESI) 636.0921 (M–Br$^+$. $C_{27}H_{19}N_3O_4Re$ requires 636.0933)

*Formation of [(Ph-bpmba)Re(CO)$_3$] **8b′**.* Method 1—A mixture of the cationic complex [(Ph-bpmbaH)Re(CO)$_3$]Br **6b′** (72 mg, 0.1 mmol) and DMF (2 cm^3) was heated at 120 °C for 48 h and volatile components were then removed under reduced pressure (70 °C at 15 mmHg). The yellow residue was dissolved in dichloromethane (1 cm^3) and the resulting solution added to hexane (20 cm^3) with rapid stirring. The precipitated solid was filtered off and then crystallised by the slow evaporation of a DCM/Hexane solution. The neutral complex **8b′** (40 mg, 63%) was isolated as yellow crystals.

Method 2—Triethylamine (100 mg, 1.0 mmol) was added dropwise to a solution of the cationic complex [(Ph-bpmbaH)Re(CO)$_3$]Br **6b′** (115 mg, 0.16 mmol) dissolved in dry dichloromethane (5 cm^3) and the mixture stirred at room temperature for 45 min. Dichloromethane (5 cm^3) was added and the solution washed with water (3 × 5 cm^3). The organic layer was then dried ($MgSO_4$), filtered and solvent removed under reduced pressure to give the neutral complex **8b′** as a fawn coloured solid. Slow crystallisation of this sample from a DCM/hexane mixture gave crystals (80 mg, 78%) suitable for X-ray study.

The neutral complex [(Ph-bpmba)Re(CO)$_3$] **8b′**, mp >250 °C, gave δ_H(400 MHz, d$_6$-DMSO) 7.27 (2 H, t, *J* 7.5, 3″/5″-H), 7.32-7.37 (2 H, m, 4′-H and 4″-H), 7.38–7.46 (4 H, m, 5-H and 3′/5′-H), 7.67 (2 H, d, *J* 7.5, 2′/6′-H), 7.83 (2 H, d, *J* 7.5, 2″/6″-H), 7.87 (2 H, d, *J* 8, 3-H), 8.05 (2 H, td, *J* 8 and 1.5, 4-H), 8.93 (2 H, br d, *J* 5.5, 6-H); δ_C(100.63 MHz, d$_6$-DMSO) 82.5 (α-C), 124.0 (×2)(C-5), 124.6 (×2)(C-3), 127.1 (×2)(C-3″/5″), 127.2 (C-4′), 127.3 (×2)(C-3′/5′), 128.9 (×2)(C-2′/6′), 129.9 (C-4″), 130.4 (×2)(C-2″/6″), 138.9 (C-1″), 140.3 (×2)(C-4), 140.5 (C-1′), 153.9 (×2)(C-6), 163.8 (×2)(C-2), 175.8 (C═O), 197.7 (CO), 199.4 (×2)(CO); Selected IR bands ν_{max}(ATR)/cm^{-1} 2007, 1906, 1878 (CO), 1599 (C═O), 1564, 1460 and 1442 (pyr); *m*/*z* (ESI) 636.0918 (M+H$^+$. $C_{27}H_{19}N_3O_4Re$ requires 636.0929).

The reaction of [Re(CO)$_5$Br] with tpmaaH 1c.

Formation of [(tpmaa)Re(CO)$_3$] 3c. This complex was prepared from tpmaaH **1c** and [Re(CO)$_5$Br] as previously described. The slow evaporation of a solution of this compound in acetone gave crystals suitable for X-ray diffraction studies.[5]

Investigation of the stability of the complex [(tpmaa)Re(CO)$_3$] 5c. 1. In base: A sample of the cationic complex **3c** (10 mg, 0.015 mmol) was heated with triethylamine (15 mg, 0.15 mmol) in d$_6$-DMSO (1.5 cm^3) for 16 h at 70 °C. The solvent and triethylamine were then removed under reduced pressure. Analysis of the product by NMR spectroscopy confirmed that the complex **5c** remained unchanged.

2. Thermal stability: As previously reported,[5] no changes were observed when a solution of the complex **3c** in DMF was heated at 105–110 °C for 16 h.

The reaction of [Re(CO)$_5$Br] with bpmaaH 2c. A mixture of bpmaaH **2c** (58 mg, 0.26 mmol), Re(CO)$_5$Br (100 mg, 0.24 mmol) and toluene (2 cm^3) was gradually heated until the Re(CO)$_5$Br dissolved. This occurred at about 80 °C, about 20 min after heating had commenced.[13]C NMR analysis of the product mixture at this time indicated the presence of three components, subsequently identified as unreacted starting material bpmaaH **2c**, and the isomeric complexes [(bpmaaH)Re(CO)$_3$Br] **6c** and [('bpmaaH')Re(CO)$_3$]Br **9c** in the ratio of 1 : 1 : 0.7. The initially formed neutral complex **6c** was observed to undergo rearrangement in solution to give the cationic complex **9c** preventing its isolation in a pure state.

The neutral complex **6c** gave δ_H(270 MHz, CDCl$_3$) 2.05 (3 H, s, CH$_3$), 7.21 (1 H, d, *J* 10.5, CH), 7.24 (2 H, m, 5-H), 7.75 (2 H, td, *J* 8 and 1, 4-H), 8.25 (2 H, d, *J* 8, 3-H), 9.17 (2 H, dd, *J* 5 and 1, 6-H), 10.25 (1 H, br d, *J* 10.5, NH); δ_C(100.63 MHz, CDCl$_3$) 23.3 (CH$_3$), 57.2 (α-CH), 123.2 (C-5), 124.6 (C-3), 140.1 (C-4), 156.5 (C-6), 158.8 (C-2), 174.3 (C═O), 189.7 (CO), 195.6 (×2)(CO).

Formation of [('bpmaaH')Re(CO)$_3$]Br 9c[17]. A mixture of bpmaaH **2c** (58 mg, 0.26 mmol), [Re(CO)$_5$Br] (100 mg, 0.24 mmol) and toluene (5 cm^3) was heated under reflux for 5 h. After cooling, the brown precipitate was filtered off and dried to give the cationic complex **9c** (98 mg, 82%) in a good state of purity. Slow crystallisation of this product from acetonitrile gave the pure complex **9c** as orange crystals suitable for X-ray crystallography, mp >250 °C (Found: C, 33.45; H, 2.25; N, 7.35. $C_{16}H_{12}BrN_3O_4Re$ requires C, 33.34; H, 2.10; N, 7.29%); δ_H(400 MHz, MeOD-d$_4$) 2.40 (3 H, s, Me), 7.38 (1 H, s, α-CH), 7.38 (2 H, ddd, J_{HH} 7.8, 5 and 1, 5-H), 8.04 (2 H, td, J_{HH} 7.8 and 1.4, 4-H), 8.20 (2 H, d, J_{HH} 7.8, 3-H), 8.82 (2 H, d, J_{HH} 5, 6-H); δ_C(100.63 MHz, d$_4$-MeOD) 24.4 (Me), 70.3 (α-CH), 124.1 (×2)(C-5), 125.8 (×2)(C-3), 142.1 (×2)(C-4), 154.6 (×2)(C-6), 158.3 (×2)(C-2), 172.3 (NC-O), 195.8 (CO), 196.3 (×2)(CO); Selected IR bands ν_{max} (KBr, cm^{-1}) 3400 (br, OH), 2025, 1911 (br) (CO), 1653 (N═C), 1533, 1474, 1437 (pyr).

Formation of [(bpmaa)Re(CO)$_3$] 8c. A mixture of [('bpmaaH')Re(CO)$_3$]Br **9c** (80 mg, 0.14 mmol), triethylamine (70 mg, 0.7 mmol) and chloroform (10 cm^3) was stirred for 3 h at room temperature. Water (30 cm^3) was added the mixture separated and the aqueous layer extracted further with chloroform (2 × 10 cm^3). The three organic extracts were combined, dried (MgSO$_4$), filtered and volatile components removed under reduced pressure (60 °C at 10 mmHg). The residue (62 mg, 89%) was shown to be the complex [(bpmaa)Re(CO)$_3$] **8c** in a good state of purity. Recrystallisation of this product from an acetonitrile/hexane mixture gave the pure complex **8c** as orange colourless crystals suitable for X-ray crystallography. (Found: C, 38.56; H, 2.40; N, 8.40%; $C_{16}H_{12}N_3O_4Re$ requires C, 38.71; H, 2.44; N, 8.46%); δ_H(400 MHz, CDCl$_3$) 2.20 (3 H, s, CH$_3$), 7.19 (2 H, ddd, *J* 8, 5 and 1, 5-H), 7.22 (1 H, s, CH), 7.64 (2 H, d, *J* 8, 3-H), 7.84 (2 H, td, *J* 8 and 1, 4-H), 8.82 (2 H, d, *J* 5, 6-H); δ_C(100.63 MHz, CDCl$_3$) 27.1 (CH$_3$), 70.7 (α-CH), 122.2 (×2)(C-3), 123.9 (×2)(C-5), 140.3 (×2)(C-4), 154.1 (×2)(C-6), 161.3 (×2)(C-2), 176.2 (C═O), 198.2 (CO), 198.5 (×2)(CO); Selected IR bands ν_{max}(ATR)/cm^{-1} 2017, 1879 (br) (CO), 1608 (C═O), 1574, 1467, 1433 (pyr).

The reaction of [Re(CO)$_5$Br] with Ph-bpmaaH 2c′.

Formation of [(Ph-bpmaaH)Re(CO)$_3$]Br 7c′. A mixture of Ph-bpmaaH **2c′** (104 mg, 0.34 mmol), [Re(CO)$_5$Br] (115 mg, 0.28 mmol) and dry toluene (3 cm^3) was heated at 105–110 °C for 16 h and then cooled. The precipitated solid was filtered off, washed with petroleum ether (bp 40–60 °C) and then air dried. This solid (162 mg, 92%) was found to be the complex **7c′** in a good state of purity. Pure crystals of **7c′** suitable for X-ray diffraction studies were obtained by the slow evaporation of a solution of the complex in DCM/Hexane; δ_H (600 MHz, CDCl$_3$/d$_4$-MeOD)[18] 7.41 (1 H, m, 5′-H), 7.48 (1 H, m, 5-H), 7.53-7.58 (2 H, m, 4′-H, 5′-H), 7.65 (1 H, br, 3′-H), 7.71 (1 H, d, '*J*'$_{HH}$ 7, 3-H), 7.82 (1 H, br, 6′-H), 7.97 (1 H, d, '*J*'$_{HH}$ 7, 3′-H), 8.00–8.07 (2 H, m, 4-H, 4′-H), 8.35 (1 H, br, 2′-H), 8.93 (1 H, d, '*J*'$_{HH}$ 3.5, 6′-H), 9.00 (1 H, d, '*J*'$_{HH}$ 4.5, 6-H); δ_C (100.63 MHz, CDCl$_3$) 25.7 (Me), 79.3 (α-C), 125.0 (br, C-3′/5′), 125.9 (br, C-5), 126.3 (br, C-3), 128.1 (br, C-4′), 130.0 (br, C-3′), 130.4 (br, C-5′), 130.5 (C-1′), 131.7 (br, C-6′), 132.0 (br, C-2′), 140.9 (br, C-4/4′), 154.8 (C-6/6′), 159.3 (C-2), 175.8 (C═O), 193.0 (CO), 195.8 (×2)(br, CO); Selected IR bands ν_{max} (ATR)/cm^{-1} 2594 (br, N$^+$–H), 2026, 1927, 1906 (CO), 1759 (C═O), 1602, 1497, 1460 (pyr); *m*/*z* (ESI) 574.0762 (M–Br$^+$. $C_{22}H_{17}N_3O_4Re$ requires 574.0777)

Conversion of 7c′ to [(Ph-bpmaa)Re(CO)$_3$] 8c′.

Thermally. A solution of the complex **7c′** (75 mg, 0.11 mmol) in DMF (2 cm^3) was heated at 120 °C for 48 h. The solvent was removed under reduced pressure (70 °C at 10 mmHg) to leave a yellow residue. This was redissolved in DCM (1 cm^3) and the solution added to hexane (20 cm^3) while rapidly stirring. The yellow solid that precipitated was filtered off and crystallised by the slow evaporation of a DCM/Hexane solution to give the complex **8c′** as a yellow crystalline solid (35 mg, 53%).

In the presence of base. Triethylamine (55 mg, 0.5 mmol) was added dropwise to a solution of complex **7c′** (112 mg, 0.17 mmol) dissolved in dry chloroform (10 cm^3) and the mixture stirred at room temperature for 16 h. The solution was then washed with water (3 × 5 cm^3), dried (MgSO$_4$), filtered and solvent evaporated under reduced pressure to leave the complex **8c′** (90 mg, 93%) in a good state of purity. Slow evaporation of a DCM/Hexane solution of **8c′** yielded yellow crystals suitable for X-ray diffraction studies, mp >250 °C; δ_H (400 MHz, DMSO-d$_6$) 1.98 (3 H, s, Me), 7.37–7.43 (3 H, m, 5-H$_2$, 4′-H), 7.44 (2 H, t, *J* 7.5, 3′/5′-H), 7.70 (2 H, d, *J* 7.5, 2′/6′-H), 7.80 (2 H, d, *J* 8, 3-H), 8.00 (2 H, td, *J* 8 and 1.5, 4-H), 8.98 (2 H, dd, *J* 5.5 and 1, 6-H); δ_C (100.63 MHz, DMSO-d$_6$) 28.3 (CH$_3$), 82.2 (α-C), 124.0 (×2)(C-5), 124.6 (×2)(C-3), 127.0 (C-4′), 127.3 (×2)(C-3′/5′), 130.3 (×2)(C-2′/6′), 139.0 (C-1′), 140.3

(×2)(C-4), 154.0 (×2)(C-6), 163.4 (×2)(C-2), 177.4 (C═O), 197.7 (CO), 200.2 (×2)(CO); Selected IR bands ν_{max} (ATR)/cm^{-1} 2008, 1863(br) (CO), 1593 (C═O), 1570, 1459, 1433 (pyr); *m/z* (ESI) 574.0760 (M+H$^+$. $C_{22}H_{17}N_3O_4Re$ requires 574.0777)

X-Ray structure determination

For all complexes, the crystals were glued to a glass fibre and mounted on the diffractometer head. Except for complex **6b**, intensity data for all crystals were collected at 120 K, using either a Bruker-Nonius Roper CCD diffractometer (**8b**, **8b′**, **8c** and **7c′**) or a Bruker-Nonius APEX II CCD diffractometer (**8b′·HBr**, **3c**, **9c** and **8c′**), both equipped with a Mo-Kα rotating anode (λ = 0.71073 Å), monochromated by graphite or confocal focusing mirrors. The crystals were positioned 30 mm from the CCD and all intensities were measured using a counting time of 20 s with 1.0° increments (ø and Ω) to fill the Ewald sphere. The unit cell parameters were determined by least-squares refinement of 25 automatically centred reflections with setting angles of $2.91 \leq 2\theta \leq 27.48°$.

For complex **6b**, the crystal was mounted the same way and intensity data were collected at 160 K on a Enraf-Nonius CAD-4 diffractometer equipped with a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å) and a graphite monochromator. The data collection method used was the same as mentioned above, except the setting angles of $10.327 \leq 2\theta \leq 12.318°$ were used to determine unit cell parameters.

All intensities were collected using the programs CAD4[19] (for complex **6b**) or COLLECT[20] Data reductions and refinements were performed using XCAD4[21] (for compound **6b**) or DENZO[22] according to Lorentz and polarisation effects. Absorption corrections were applied based on multi-scan method and were obtained using SADABS.[23] X-ray crystal structures were determined using the DirAx[24] program. The programs ORTEP-3[25] and PLATON[26] were used for drawing the molecules. WINGX[27] was used to prepare material for publication.

All structures were solved by the heavy-atom method using the DIRDIFF99[28] program and refined anisotropically (non-hydrogen atoms) by full-matrix least-squares technique against F^2 using the SHELXL-97[29] program. All H atoms were calculated geometrically and refined by a riding model.

Acknowledgements

The authors would like to thank the EPSRC UK National Crystallographic Service at Southampton and the EPSRC National Mass Spectrometry Service Centre (NMSSC) at Swansea for their help with the acquisition of some of the data presented.

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