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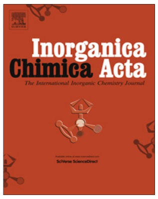

The synthesis and characterization of rhenium nitrosyl complexes. The X-ray crystal structures of [$ReBr_2(NO)(NCMe)_3$], [$Re(NO)(N_5)$](BPh_4)$_2$] and [$ReBr_2(NO)(NCMe)$ {py-CH_2-NH∼CH_2CH_2-N(CH_2-py)$_2$}]

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ABSTRACT

Reactions of low oxidation state rhenium–nitrosyl complexes with polyamine ligands have been examined. Rhenium(II)–nitrosyl complexes gave an array of unstable products that were difficult to isolate cleanly. The rhenium(I)–nitrosyl complex [$ReBr_2(NO)(NCMe)_3$] gave multiple products which were more easily isolated.

The major product from the reaction of [$ReBr_2(NO)(NCMe)_3$] with the potentially pentadentate ligand N_1,N_1,N_2-tris(2-pyridinylmethyl)-1,2 ethanediamine was the dicationic species [$Re(NO)(N5)]^{2+}$, which was isolated as the bis-tetraphenylborate salt. The other major product [$ReBr_2(NO)(NCMe)$ {py-CH_2NH∼CH_2CH_2N(CH_2-py)$_2$}], was separated from a number of other neutral species via chromatography. This species contains the same potentially pentadentate ligand, only here it is coordinated through only two of its amine functional groups. Left dangling is the secondary amine and both of its pyridyl groups.

Both amine complexes are diamagnetic and both display their respective parent ions in the ESI(+) mass spectra. The dication [$Re(NO)(N5)]^{2+}$ shows its half mass parent peak at 275 *m/z* while [$ReBr_2(NO)(NCMe)${py-CH_2NH∼CH_2CH_2N(CH_2-py)$_2$}] shows its parent peak at 751 *m/z*. The infrared spectrum of [$ReBr_2(NO)(NCMe)${py-CH_2NH∼CH_2CH_2N(CH_2-py)$_2$}] displays its ν(N=O) at 1676 cm^{-1}. And the infrared spectrum of [Re(NO)(N5)](BPh_4)$_2$ displays its ν(N=O) at 1714 cm^{-1}.

1. Introduction

We recently reported on the difficulties encountered when examining the coordination chemistry of technetium–nitrosyl complexes with polyamine and phosphine-amine ligands [1,2]. The starting material initially used in these reactions was the anionic Tc(II) complex (Bu_4N)[$TcNOCl_4$] [3]. This highly reactive species was shown to be easily reduced to Tc(I) under ambient reaction conditions, generating a host of products as determined by infrared spectroscopy, greatly complicating even simple substitution reactions. However, when the Tc(I) nitrosyl complex [$TcCl_2(NO)(HOMe)(PPh_3)_2$] [4] was employed as starting material, the number of by-products was greatly diminished, allowing the major products to be more easily isolated and fully characterized.

Here we report similar difficulties employing the dianionic Re(II) nitrosyl complex (Me_4N)$_2$[$ReNOBr_5$] [5]. Multiple products were obtained as determined chromatographically, many with limited solution stability when this precursor was reacted with the same set of polyamine ligands used in the technetium reactions. The rhenium(I) nitrosyl complex [$ReBr_2(NO)(NCMe)_3$] [6] gave more easily isolable products with these polyamine ligands, but simple substitution reactions again gave a surprisingly large number of products under ambient reaction conditions.

2. Experimental

Reagents and solvents were used as received unless otherwise stated. Routine infrared spectra were obtained on a Perkin Elmer Spectrum One FTIR Spectrometer. ^{1}H NMR spectra were collected on a Bruker (600 mHz) spectrometer. Mass spectra were obtained on a Bruker Daltonics APEXII 3 Tesla Fourier Transform Mass Spectrometer (Ion Cyclo-tron Resonance Mass Spectrometer).

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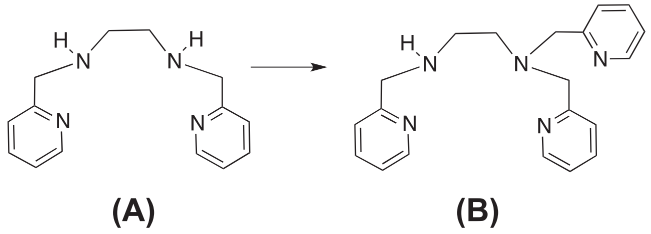


Scheme 1. Addition of a pyridyl arm to the linear tetradentate ligand.

3. X-ray crystal structure determination

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å).

The structures were solved by direct methods using SHELXS [7] and refined against F^2 on all data by full-matrix least squares with SHELXL-97 [8] following established refinement strategies [9]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups and hydroxyl hydrogen atoms).

4. Synthesis

4.1. N_1,N_2-Bis(2-pyridinyl-methyl)-1,2-ethanediamine [A]

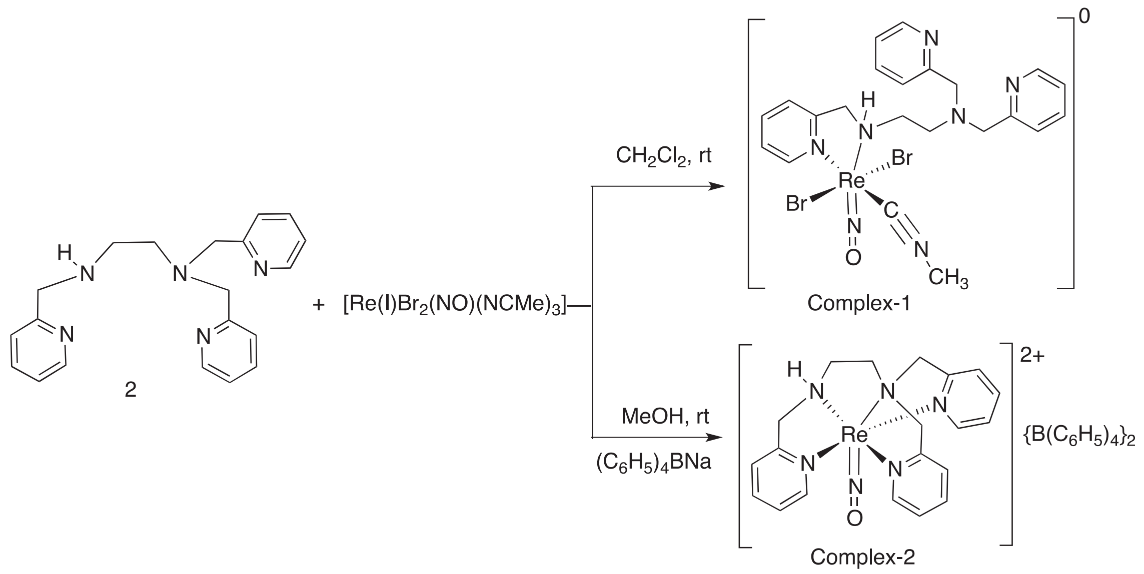
The procedure was adapted from published literature [10]. A solution of ethane-1,2-diamine (1.2 g, 20 mmol) in dry EtOH (30 mL) was added dropwise to a solution of pyridine-2-carbaldehyde (4.28 g, 40 mmol) in dry EtOH (100 mL). The mixture was refluxed for 12 h and after cooling to room temperature the solvent was removed. The resulting residue was redissolved in methanol, followed by addition of $NaBH_4$ (1.5 g, 40 mmol) and stirred overnight. The solvent was evaporated, following extraction with dichloromethane and water. The dichloromethane extract was concentrated and purified by a silica gel chromatography using 3–6% methanolic NH_3 (7 M NH_3 in methanol)/97–94% CH_2Cl_2 as eluent, to yield the desired product, as a yellow oil (60%). ^{1}H NMR ($CDCl_3$, 600 MHz): 8.49 (dd, 2H, Ar), 7.59 (m, 2H, Ar), 7.27 (d, 2H, Ar), 7.11 (m, 2H, Ar), 3.87 (s, 4H, CH_2), 3.78 (s, 4H, CH_2).

4.2. (N_1,N_1,N_2-Tris(2-pyridinylmethyl)-1,2-ethanediamine) [B]

[B] was synthesized following a modified literature procedure [11]. A solution of 3.8 g (15.9 mmol) of [A] and 1.7 g (15.9 mmol) of 2-pyridinecarboxaldehyde in 10 mL Et_2O was stirred at room temperature with $CaCl_2$ protection for 16 h. The resulting white precipitate was isolated by filtration and washed with Et_2O to afford the intermediate compound (2,2′-((2-pyridin-2-yl)imidazollidine-1,3-diyl)bis(methylene)))dipyridine) (4.5 g, 13.8 mmol, 86% yield). To a solution of 1.0 g (3.04 mmol) of this intermediate in 50 mL MeOH was added 0.19 g (3.02 mmol) of $NaBH_3CN$ and 0.46 mL (5.98 mmol) of CF_3CO_2H. The solution was stirred at room temperature with $CaCl_2$ protection for 18 h. A 15% NaOH solution (30 mL) was added and after stirring for 3 h, the solution was extracted three times with 50 mL of CH_2Cl_2 and the combined organic layers were dried (Na_2SO_4). Evaporation of the solvent afforded 0.70 g (2.13 mmol) of [B]. See Scheme 1 below (70% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.45 (dd, 1H, Ar), 8.43 (dd, 2H, Ar), 7.58–7.54 (overlapped m, 3H, Ar), 7.43 (d, 2H, Ar), 7.28 (d, 1H, Ar), 7.09 (m, 1H, Ar), 7.06 (m, 2H, Ar), 3.82 (s, 2H, CH_2), 3.79 (s, 4H, CH_2), 2.78 (m, 4H, CH_2) [11].

4.3. [$ReBr_2(NO)(NCMe)_3$]

[$ReBr_2(NO)(NCMe)_3$] was prepared as described in [12] and purified with column chromatography, eluting with 5% methanol in dichloromethane. The only mobile component was an orange band which was collected, concentrated via rotary evaporation and recrystallized by slow evaporation at room temperature to yield large, dark orange crystals. IR(neat): ν(N=O) at 1686 cm^{-1}. The X-ray crystallography has been reported previously, however a second unit cell/crystallographic solution was discovered and is reported here. See Table 3.



Scheme 2. Synthetic approach to synthesizing the 2 complexes which incorporate the potentially pentadentate ligand. Complex **1** only utilizes 2 of the 5 available amine groups while complex **2** is fully encapsulated by the pentadentate ligand.

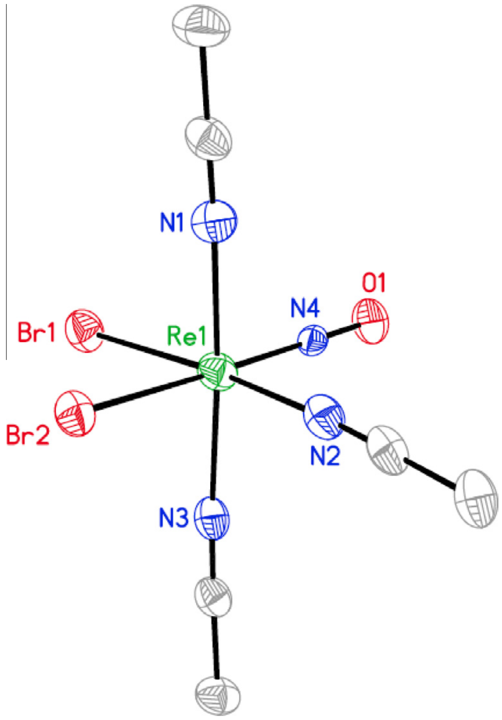


Fig. 1. An ORTEP diagram of [ReBr$_2$(NO)(NCMe)$_3$], showing non-carbon atoms labeled. Hydrogen atoms have been omitted for clarity.

4.4. [ReBr$_2$(NO)(NCMe){py-CH$_2$NH$\sim$CH$_2$CH$_2$N(CH$_2$-py)$_2$}], complex **1**

Table 1
Selected bond lengths and angles for complex **1**, [ReBr$_2$(NO)(NCMe){py-CH$_2$NH$\sim$CH$_2$CH$_2$N(CH$_2$-py)$_2$}].

Re1–Br1	2.564(1)
Re1–Br2	2.558(1)
Re1–N6	1.737(8)
Re1–N1	2.060(7)
Re1–N3	2.127(6)
Re1–N4	2.220(7)
N6–O1	1.21(1)
N6–Re1–N1	95.4(3)
N6–Re1–N3	95.3(3)
N1–Re1–N3	169.2(3)
N6–Re1–N4	171.2(3)
N1–Re1–N4	93.4(3)
N3–Re1–N4	75.9(3)
N6–Re1–Br2	96.3(3)
N1–Re1–Br2	89.3(3)
N3–Re1–Br2	89.2(2)
N4–Re1–Br2	84.5(2)
N6 Re1 Br1	93.3(3)
N1–Re1–Br1	88.2(2)
N3–Re1–Br1	91.5(2)
N4–Re1–Br1	86.2(2)
Br2–Re1–Br1	170.24(3)
O1–N6–Re1	174.4(7)

A 49 mg sample of [ReBr$_2$(NO)(NCMe)$_3$] was combined with 33 mg of N5 ligand [B] and 45 mL of dichloromethane and stirred at RT. The golden colored solution darkened to golden-brown overnight. After 72 h at RT, the solvent was removed and the residue chromatographed on a silica preparatory plate, eluting with 3% methanol in dichloromethane. The major mobile band was bright orange and was isolated, concentrated via rotary evaporation and recrystallized by slow evaporation of a methanol–dichloromethane mixture. See Scheme 2 below for a diagram depicting the synthesis of complex **1**. The infrared spectrum of this product displays a ν(N═O) at 1676 cm^{-1}. ESI(+) mass spectrum: 751 *m/z* = [ReBr$_2$(NO)(NCMe)(N5)]$^+$. ^{1}H NMR (CDCl$_3$, 600 MHz) δ: 8.41 (d, 2H, Ar), 8.13 (d, 1H, Ar), 7.56 (m, 2H, Ar), 7.43 (d, 2H, Ar), 7.17–7.09 (overlapped m, 4H, Ar), 6.95 (d, 1H, Ar), 5.40 (m(br), 1H, NH), 5.24 (d, 1H, CH), 4.22 (dd, 1H, CH), 3.89

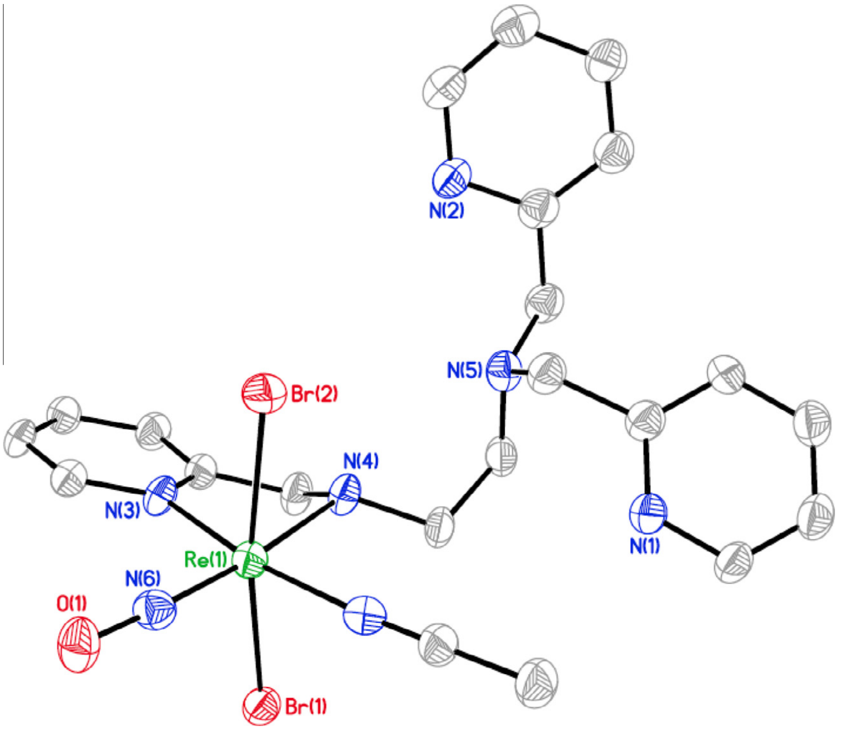


Fig. 2. An ORTEP diagram of complex **1**, [ReBr$_2$(NO)(NCMe){py-NH$\sim$N(py)$_2$}], showing only non-carbon atoms labeled. Hydrogen atoms have been omitted for clarity.

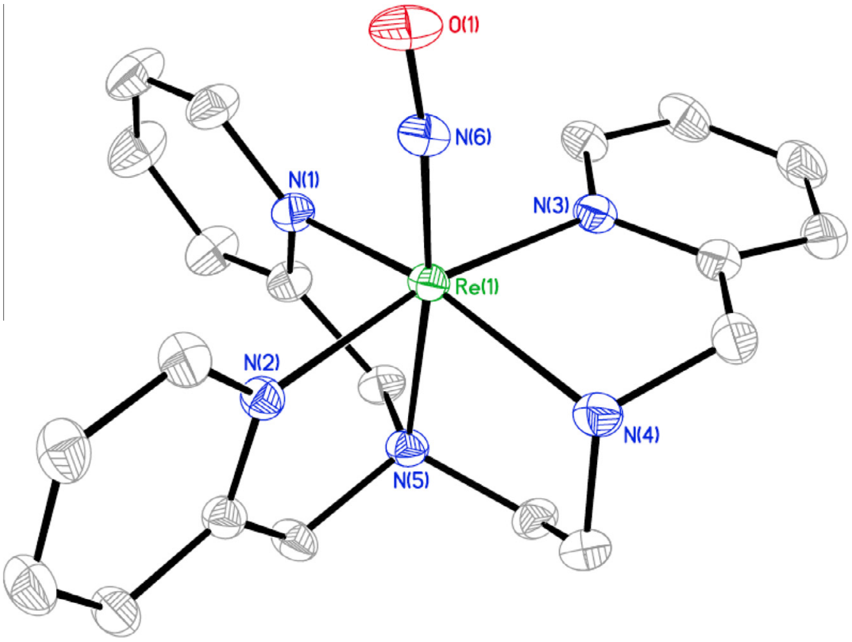


Fig. 3. An ORTEP diagram of complex **2**, the dication [Re(NO){py-NH∼N(py)$_2$}]$^{2+}$, showing only non-carbon atoms labeled. Hydrogen atoms have been omitted for clarity.

(overlapped d, 2H, CH$_2$), 3.69 (d, 2H, CH$_2$), 3.45 (m, 1H, CH), 2.97 (m, 1H, CH), 2.99 (s, 3H, CH$_3$), 2.86 (m, 1H, CH), 2.65 (m, 1H, CH).

*4.5. [Re(NO)(N5)](BPh$_4$)$_2$, complex **2***

A 81 mg sample of [ReBr$_2$(NO)(NCMe)$_3$] was combined with 55 mg of the N5 ligand [B] in 50 mL of methanol. After 72 h at RT, the methanol was removed via rotary evaporation. The resulting brown residue was washed with dichloromethane, causing the formation of a brown oil, which was dissolved with the addition of a few mL of methanol. Excess sodium tetraphenylborate was added, which caused the formation of a dark colored precipitate. The precipitate was removed via vacuum filtration and the filtrate set aside to evaporate at RT. After 12 h, methanol was added, allowing isolation of deep red-purple crystals after 24 hours at RT. See Scheme 2 below for a diagram depicting the synthesis of complex **2**. IR(KBr) ν(N=O) at 1714 cm^{-1}. ESI(+) mass spectrum: 275 *m/z* = [Re(NO)(N5)]$^{2+}$. ^{1}H NMR (CDCl$_3$, 600 MHz) δ: 8.54 (d, 1H, Ar), 8.45 (d, 1H, Ar), 8.19 (m, 1H, Ar), 7.89 (s, 1H, Ar), 7.82 (d, 1H, Ar), 7.63 (m, 1H, Ar), 7.59–7.54 (overlapped m, 2H, Ar), 7.49–7.44 (overlapped m, 3H, Ar), 7.29[1] (m(br), Ar(TPB)), 7.014 (m, Ar(TPB)), 6.86 (m, Ar(TPB)), 6.57 (m(br), 1H, NH), 4.91 (d, 1H, CH), 4.82 (m, 2H, CH$_2$), 4.73 (m, 2H, CH$_2$), 3.97 (d, 1H, CH), 3.49 (m, 1H, CH), 3.44 (m, 1H, CH), 3.36 (m, 1H, CH), 2.74 (m, 1H, CH).

5. Discussion

The technetium(I)–nitrosyl core presents interesting chemical properties that might be found useful in radiopharmaceutical design. Of the cores currently employed in established radiopharmaceuticals, the technetium(V)-oxo core is the most versatile. It has the capacity to accommodate ligation at its available five coordination sites. This versatility is reflected in the number of established imaging agents that incorporate this core, including ^{99m}TcO-HMPAO, ^{99m}TcO-ECD, ^{99m}TcO-MAG$_3$, and ^{99m}TcO-TRODAT. The core currently receiving the most attention in the search for new imaging agents is the technetium(I)-tricarbonyl core. This lipophilic core has only three facial coordination sites available for ligand incorporation, seriously restricting the scope of potential coligands. The Tc(I)–nitrosyl core is less lipophilic than the {Tc(I)-(CO)$_3$} core and it has five coordination sites available to accommodate coligands. When this new species is more fully developed, it may prove very useful in radiopharmaceutical development.

Rhenium–nitrosyl complexes are under increased scrutiny in organometallic chemistry as hydrogenation catalysts and transfer agents [11]. In that regard, substitution reactions of Re–nitrosyl complexes such as (Me$_4$N)$_2$[Re(NO)Cl$_5$] are being examined [6]. Preliminary results of reactions of our polyamine ligands with this Re(II)–nitrosyl complex give similar results to those we obtained with the technetium(II) complex (Bu$_4$N)[TcNOCl$_4$] [1]. These reactions are greatly complicated by redox reactions competing with the intended ligand substitution reactions. Reactions with the rhenium(I) complex [ReBr$_2$(NO)(NCMe)$_3$] proved less problematic in this regard, however a number of products were formed as determined by thin layer chromatography and infrared spectroscopy. An X-ray crystallographic study of this deep red-orange complex was performed to confirm its identity. The neutral Re(I) complex displays the three acetonitrile ligands coordinated in a meridional manner, with the nitrosyl and two bromines coordinated similarly. Bonding parameters for the nitrosyl ligand are typical for linearly coordinated nitrosyl ligands of this type, {Re–N 1.823(6) Å and N–O 1.173(7) Å and Re–N–O of 179.6(9)°} with multiple bonding throughout the Re–N–O moiety. The Re–N bond lengths to the three acetonitrile ligands are similar and in the expected range. The Re–Br bond lengths too are unexceptional. The infrared spectrum of this complex displays the ν(N=O) at 1686 cm^{-1}. See Fig. 1 for an ORTEP diagram of complex **1**. For a complete list of bonding parameters see Ref. [11].

This neutral Re(I) complex [ReBr$_2$(NO)(NCMe)$_3$] was reacted with the neutral pentadentate amine ligand N$_1$,N$_1$,N$_2$-tris(2-pyridinylmethyl)-1,2-ethanediamine [2] in dichloromethane at room temperature. The resulting crude product mixture was chromatographed in silica, with the major brownish product remaining immobile at the baseline. The most prominent mobile component

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[1] The missing ligand proton signal is buried under the tetraphenylborate aromatic signal δ 7.29. This was confirmed by a 2-D NMR spectroscopic analysis.

Table 2
Selected bond lengths and angles for complex **2**, [Re(NO)(N5)]$(BPh_4)_2$.

Re1–N6	1.758(1)
Re1–N1	2.080(1)
Re1–N2	2.103(1)
Re1–N3	2.130(1)
Re1–N4	2.166(1)
Re1–N5	2.179(1)
N6–O1	1.190(2)
N6–Re1–N1	98.24(6)
N6–Re1–N2	94.81(6)
N1–Re1–N2	89.05(6)
N6–Re1–N3	95.68(7)
N1–Re1–N3	94.42(6)
N2–Re1–N3	168.36(6)
N6–Re1–N4	102.30(7)
N1–Re1–N4	158.86(6)
N2–Re1–N4	94.15(6)
N3–Re1–N4	78.70(6)
N6–Re1–N5	172.62(6)
N1–Re1–N5	77.86(6)
N2–Re1–N5	78.97(5)
N3–Re1–N5	90.89(6)
N4–Re1–N5	82.25(6)
O1–N6–Re1	173.8(1)

was a bright orange species, complex **1**, that was isolated and crystallized by slow evaporation of the eluting solvent mixture of methanol and dichloromethane. The infrared spectrum of this complex displays a strong absorption at 1676 cm^{-1} which corresponds to the ν(N=O). The ESI(+) mass spectrum displays the parent peak $[ReBr_2(NO)(NCMe)(N5)]^+$ at 751 *m/z*. Complex **1** is diamagnetic, with the ^1H NMR spectrum data listed in Section 2 (*vide supra*).

The X-ray crystallographic structural analysis of these crystals proved them to be the neutral Re(I) complex $[ReBr_2(NO)(NCMe)\{py\text{-}CH_2NH{\sim}CH_2CH_2N(CH_2\text{-}py)_2\}]$, which contains the pentadentate polyamine ligand coordinated in a bidentate manner, with the three remaining amine moieties dangling in a pendant manner. This result suggests that under the ambient reaction conditions employed and in the non-polar solvent, the rhenium precursor is more strongly bonded to the bromide ligands and the acetonitrile ligand *cis* to the nitrosyl core than was anticipated. A similar result was reported by Berke et al. with their synthesis of $[ReCl_2(NO)(NCMe)(PR_3)_2]$ from $[ReCl_2(NO)(NCMe)_3]$ and the phosphine in acetonitrile at 70° [12]. The rhenium–nitrogen bond length to the nitrosyl nitrogen is 1.737(8) Å with the N–O bond length of the nitrosyl group at 1.210(10) Å. The Re–N–O bond angle is 174.4(7)°. The bromide ligands are in a *cis* orientation in the precursor and are mutually *trans* in this reaction product. The bidentate ligand coordination results in a very contracted bite angle of only 75.9(3)°. This large distortion from octahedral results in the remaining bond angles within the coordination sphere being somewhat distorted as well. Fig. 2 displays an ORTEP diagram from complex **1** and Table 1 lists selected bond lengths and angles.

The major product from the analogous reaction in methanol is the fully chelated dication [Re(NO)(N5)]$(BPh_4)_2$ complex **2**. This species is precipitated from the reaction mixture by addition of sodium tetraphenylborate, which causes a dark colored precipitate to form. The infrared spectrum of this complex displays the ν(N=O) at 1714 cm^{-1}. The ESI(+) mass spectrum displays the half-parent peak at 275 *m/z*, which corresponds to $[Re(NO)(N5)]^{2+}/2$. The ^1H NMR data for this diamagnetic species are listed in Section 2 (*vide supra*).

The X-ray crystallographic analysis of this dication shows the Re–N and N–O bond lengths to be 1.7587(16) Å and 1.190(2) Å respectively, reflecting the multiple bonding throughout the nitrosyl unit. The Re–N–O bond angle is 173.83(15)°, somewhat distorted from linear. The Re–N bond lengths to the amines are such that the aliphatic amine bond lengths are longer than those to the pyridyl termini. The Re–N5 bond length is the longest of all at 2.1792(15) Å, which is a result of the *trans*-influence of the multiply-bonded nitrosyl unit pulling electrons away from the *trans*-amine ligand and lengthening its bond. Steric constraints imposed by the chelated ligand cause significant deviations from octahedral geometry. Fig. 3 displays an ORTEP diagram for complex **2** and Table 2 lists selected bond lengths and angles.

Table 3
X-ray Crystallographic Data Collection Parameters.

	$[ReBr_2(NO)(NCMe)_3]$	Complex **1**	Complex **2**
Empirical formula	$C_6H_9Br_2N_4ORe$	$C_{22}H_{26}Br_2N_7ORe$	$C_{74}H_{75}B_2N_6O_{2.50}Re$
Formula weight	499.19	782.56	1296.22
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P*2(1)/*c*	$P2_1$	*P*2(1)/*n*
Unit cell dimensions			
a (Å)	8.0641(9)	7.3668(12)	15.7874(13)
b (Å)	10.0173(12)	27.048(4)	22.2079(18)
c (Å)	15.5094(18)	13.123(2)	18.3931(15)
β (°)	97.120(2)	94.214(4)	107.466(2)
Volume ($Å^3$)	1243.2(2)	2607.8(7)	6151.4(9)
Z	4	4	4
Density (calculated) (Mg/m^3)	2.667	1.993	1.400
Absorption coefficient (mm^{-1})	16.179	7.759	2.029
F(000)	904	1512	2664
Crystal size (mm^3)	0.10 × 0.04 × 0.01	0.44 × 0.41 × 0.04	0.17 × 0.15 × 0.15
Θ range for data collection	2.43–31.51°	1.51–31.51°	2.17–31.57°
Reflections collected	56304	166395	310040
Independent reflections	4138 [R_{int} = 0.0413]	16555 [R_{int} = 0.0467]	17671 [R_{int} = 0.0409]
Absorption correction	multi scan	multi scan	multi scan
Max. and min. transmission	0.8314 and 0.4474	0.7466 and 0.1315	0.7506 and 0.7242
Data/restraints/param.	4138/66/143	17363/609/657	20470/459/876
Goodness-of-fit on F^2	1.098	1.120	1.058
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0343$, $wR_2 = 0.0802$	$R_1 = 0.0195$, $wR_2 = 0.0439$	$R_1 = 0.0248$, $wR_2 = 0.0330$
R indices (all data)	$R_1 = 0.0409$, $wR_2 = 0.0842$	$R_1 = 0.1402$, $wR_2 = 0.1422$	$R_1 = 0.0600$, $wR_2 = 0.0649$

6. Conclusion

The rhenium(I)–nitrosyl complex $[ReBr_2(NO)(NCMe)_3]$ has been shown to react with polyamine ligands to form chelate complexes such as $[Re(NO)(N5)](BPh_4)_2$ and $[ReBr_2(NO)(NCMe)\{py\text{-}CH_2\text{-}NH{\sim}CH_2CH_2N(CH_2\text{-}py)_2\}]$. Reactions utilizing rhenium(II)–nitrosyl complexes with these polyamine ligands proved problematic due to competing redox chemistry, analogous to previously reported technetium chemistry. This diverse family of polyamine ligands, which can be easily modified in both coordinating geometry and in functional donor group composition, may prove useful in the design of new radiopharmaceuticals.

Acknowledgments

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