# The Reaction of Rhenium(V) Cores with a Tetradentate Schiff Base. The Isolation of '3+3' and '4+0' Complexes of Rhenium(V)

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The reaction of the potentially tetradentate  $N_4$ -donor ligand  $N_iN'$ -bis[(2-aminophenyl)methylidene]ethane-1,2-diamine (H<sub>2</sub>ane) with various rhenium(V) precursors led to the formation of different rhenium(V) complexes. With *trans*-[ReOBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>], the unusual '3+3' complex cation [Re(tnn)(Htnn)]<sup>2+</sup> (H<sub>2</sub>tnn = N-(2-aminophenylmethylidene)ethane-1,2-diamine) was isolated. With *trans*-[ReO<sub>2</sub>(py)<sub>4</sub>]Cl, the complex [ReO(dne)] was found (H<sub>3</sub>dne =  $N^1$ -2-aminobenzyl- $N^2$ -2-aminobenzylideneethane-1,2-diamine), and the cationic complex [ReO(ane)]<sup>+</sup> was formed from *cis*-[ReO<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]. These products were characterized by <sup>1</sup>H NMR and IR spectroscopy, and by X-ray diffraction.

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#### Introduction

There is currently considerable interest in the coordination chemistry of rhenium, mainly because of the potential applications of its <sup>186/188</sup>Re radionuclides in radiotherapy.<sup>[1,2]</sup> The main focus is on the +I (d<sup>6</sup>) and +V (d<sup>2</sup>) oxidation states of the metal, since they are stabilized by a large variety of ligands and can be easily accessed by a large variety of synthons.

Tetradentate Schiff base complexes of rhenium(V) have been well studied. However, the majority of the ligands in these complexes were of the N<sub>2</sub>O<sub>2</sub> donor atom set, and were based on the salicylaldehyde-amine (e.g. N,N'ethylenebis(salicylaldimine) - sal2en) and the acetylacetone derived (e.g. N,N'-ethylenebis(acetylacetoneimine) - acac2en) Schiff base ligands.<sup>[3–8]</sup> The first monomeric and dimeric oxorhenium(V) complexes were reported in 1979 for both the salicylaldehyde and acetylacetone based ligands, but their characterization was limited to elemental analysis and IR spectroscopy.<sup>[6]</sup> It was found that the four donor atoms of the tetradentate Schiff bases of the sal2en type do not all coordinate in equatorial positions (to the oxo oxygen) in complexes of the '4+1' type [ReOCl(sal2en)], but rather with an asymmetric coordination of the two N,O-units, with a phenolate oxygen trans to the oxo group.<sup>[7]</sup> With the acac<sub>2</sub>en type ligands the [ReOX(acac2en)] complexes were prepared with different substituents X (H<sub>2</sub>O, ReO<sub>4</sub><sup>-</sup>, MeO<sup>-</sup>, Cl<sup>-</sup>) coordinated trans to the oxo group.<sup>[8]</sup>

In this account the reactions of the new potentially tetradentate ligand N,N'-bis[(2-aminophenyl)methylidene]ethane-1,2diamine (H<sub>2</sub>ane) (Scheme 1) with the rhenium(V) precursors *trans*-[ReOBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>], *trans*-[ReO<sub>2</sub>(py)<sub>4</sub>]Cl, and *cis*-[ReO<sub>2</sub>I(PPh<sub>3</sub>)<sub>2</sub>] are reported. In all three reactions, different



Scheme 1. Line structure and labelling of H<sub>2</sub>ane.



rhenium(V) complexes were isolated. In the reaction of H<sub>2</sub>ane with *trans*-[ReOBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] in ethanol, the highly unusual '3+3' complex double cation [Re(tnn)(Htnn)]Br<sub>2</sub> was isolated, in which tnn is coordinated as a tridentate imido-imino-amine, and Htnn is present as a tridentate monoanionic amido-imino-amine chelate (H<sub>2</sub>tnn = N-(2-aminophenylmethylidene)ethane-1,2-diamine). With *trans*-[ReO<sub>2</sub>(py)<sub>4</sub>]Cl as starting material, the neutral complex [ReO(dne)] was found (Scheme 2), in which the tetradentate chelate dne acts as a triamido-imine. The reaction of *cis*-[ReO<sub>2</sub>I(PPh<sub>3</sub>)<sub>2</sub>] with H<sub>2</sub>ane led to the formation of the monocationic complex salt [ReO(ane)]PF<sub>6</sub>, with ane acting as a tetradentate diamionic diamidodiimine.

#### **Results and Discussion**

# Synthesis and Characterization of [Re(tnn)(Htnn)]Br<sub>2</sub>·EtOH (**1**·EtOH)

The reaction of the potentially tetradentate N4-donor ligand N, N'-bis[(2-aminophenyl)methylidene]ethane-1,2-diamine (H<sub>2</sub>ane) with trans-[ReOBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] led to the decomposition of the ligand molecule to produce [Re(tnn)(Htnn)]Br<sub>2</sub> (1)  $(H_2 tnn = N - (2 - aminophenylmethylidene) ethane - 1, 2 - diamine)).$ Although an explanation for the decomposition of the ligand would be speculative, it could be achieved by hydrolysis of one of the HC=N bonds of H2ane (to form the amine H2tnn and 2-aminobenzaldehyde) after initial coordination to the metal, since water will be produced as a by-product after imido formation and coordination. Metal-enhanced hydrolysis has been noted for lanthanides.<sup>[9]</sup> Decomposition is typically initiated by nucleophilic attack by solvent molecules on the electropositive methine carbon atom of the Schiff base. These fragments of the hydrolyzed Schiff base can lead to complex formation, e.g. a rhenium(III) complex with a chelated dehydroacetate was formed from the reaction with a tetradentate N2O2-donor Schiff base.[10]

Complex 1 is soluble in a wide variety of solvents such as alcohols, acetone, DMF, and DMSO. It is stable in air and is a 1:2 electrolyte in methanol. The infrared spectrum is characterized by the presence of a strong absorption at  $1074 \text{ cm}^{-1}$ , assigned to the Re=N stretching frequency. The Re-N stretches occur as medium intensity peaks in the  $425-495 \text{ cm}^{-1}$  range. The sharp bands at 1586 and 1609 cm<sup>-1</sup> are assigned to the C=N stretching modes of the Schiff base ligands of the tnn and Htnn moieties. The <sup>1</sup>H NMR spectrum shows that the H(7) and H(16) methine protons are magnetically equivalent, with a two-proton singlet at 9.05 ppm. Due to the deshielding interaction of the rhenium(V) ion, a two-proton singlet far downfield at 12.95 ppm is assigned to the amine protons  $N(6)H_2$ , which occupies the site *trans* to the imido nitrogen N(4). The aromatic region (6.80-7.80 ppm) consists of four two-proton signals: a doublet (at 7.68 ppm); a triplet (7.61 ppm); a doublet (at 7.02 ppm); and a triplet at 6.81 ppm. These signals correspond to the eight aromatic protons on the two phenyl rings of the ligands tnn and Htnn, and show that the corresponding protons on the two aromatic rings are magnetically equivalent. The electronic nature of the donor atoms N(3) and N(6) has therefore no influence on the magnetic character of the phenyl rings. The broad singlet at 4.33 ppm integrates for the four protons of the two amines. In the UV-vis spectrum there is an intraligand transition  $(\pi \rightarrow \pi^*)$  of the coordinated ligand at 369 nm. The band at 533 nm is assigned to a ligand-to-metal charge transition, and a d-d transition occurs at 733 nm.

The X-ray structure determination of the title compound reveals that the rhenium(V) atom is surrounded by six nitrogen atoms originating from the tnn and Htnn chelates in a distorted octahedral geometry (Fig. 1). The distortion originates from geometric constraints imposed by the chelating ligands. The N(2)-Re-N(5) bond angle of 174.5(2)° is relatively close to linearity, but the trans angles N(1)-Re-N(3) and N(4)-Re-N(6) [158.0(2) and  $158.6(2)^{\circ}$ , respectively] deviate considerably (Table 1). There is a large variation in the *cis* angles of a nitrogen-donor atom of one chelate with the donor atoms of the other chelate, for example, N(1)-Re-N(4) =  $102.3(2)^{\circ}$ , N(1)-Re-N(5) =  $95.7(2)^{\circ}$ , N(1)-Re-N(6) = 86.2(2)°, N(4)-Re-N(2) = 101.2(2)°, and N(4)- $\text{Re-N}(3) = 95.5(2)^\circ$ . The bite angles of the two tnn and Htnn are noticeably different: N(1)-Re- $N(2) = 86.5(2)^{\circ}$ , N(2)- $\text{Re-N}(3) = 77.3(2)^\circ$ , N(4)-Re-N(5) = 83.2(2)^\circ, and N(5)-Re- $N(6) = 76.3(2)^{\circ}$ . The obvious reason for these differences is that



Fig. 1. *ORTEP* view of 1. The bromides, ethanol solvent of crystallization, and hydrogen atoms have been omitted for clarity.

Table	1.	Selected	bond	lengths	[Å]	and	angles	[°]	in
		[Re(1	tnn)(Htr	nn)]Br <sub>2</sub> .Et	OH (1	•EtOH	I)		

Re-N(1)	1.944(4)	Re-N(4)	1.776(4)
Re-N(2)	2.073(4)	Re-N(5)	2.097(4)
Re-N(3)	2.169(4)	Re-N(6)	2.182(4)
N(2)-C(7)	1.300(7)	N(5)-C(16)	1.297(6)
N(2)-C(8)	1.491(7)	N(5)-C(17)	1.483(7)
N(1)-Re-N(3)	158.0(2)	N(4)-Re-N(6)	158.6(2)
N(2)-Re-N(5)	174.5(2)	N(1)-Re-N(6)	86.2(2)
C(7)-N(2)-C(8)	118.3(4)	C(16)-N(5)-C(17)	116.7(4)
N(1)-Re-N(2)	86.5(2)	N(4)-Re-N(5)	83.3(2)
N(2)-Re-N(3)	77.3(2)	N(5)-Re-N(6)	76.3(2)
N(2)-C(8)-C(9)	108.0(4)	N(5)-C(16)-C(15)	126.4(4)

the nitrogen-donor atoms are coordinated in different electronic forms, such as amino, imino, amido, and imido.

The coordinating modes of the chelates are indicated by Re-N bond distances. For the chelate tnn, the Re-N(4) length of 1.776(4) Å is in the range found for Re(V)-N(imido) bonds, which typically occur in the range 1.72(1)-1.78(1) Å.<sup>[11–13]</sup> The Re-N(5) [2.097(4) Å] and Re-N(6) [2.182(4) Å] bond lengths are typical for rhenium(V)-imino<sup>[12–14]</sup> and rhenium(V)-amino bonds, respectively.<sup>[10–15]</sup> The tnn ligand thus acts as a dianionic imido[N(4)]-imino[N(5)]-amino[N(6)] chelate. The Re-N(4)-C(10) bond angle is  $144.3(3)^{\circ}$ , indicating (due to its deviation from linearity) that N(4) is doubly, rather than triply, bonded to the metal. The Re-N(6)-C(18) angle of  $111.5(3)^{\circ}$  indicates sp<sup>3</sup>-hybridization of the amino nitrogen N(6). The N(5)-C(16) bond length [1.297(6) Å] illustrates its double bond character, and the C(16)-N(5)-C(17) bond angle of  $116.7(4)^{\circ}$  is lower than would be expected from a sp<sup>2</sup>-hybridized nitrogen atom.

D-H···A	D-H	H···A	D· · ·A	D-H···A
$\overline{O(1)-H(1B)\cdots Br(2)}$	0.84	2.45	3.18(2)	146
$N(3)-H(3A)\cdots Br(1)$	0.92	2.75	3.596(4)	153
$N(3)-H(3B)\cdots Br(2)$	0.92	2.46	3.369(4)	172
$N(6)-H(6A)\cdots Br(1)$	0.92	2.36	3.260(4)	168
$N(6)-H(6B)\cdots Br(2)$	0.92	2.61	3.388(4)	143

Table 2. Hydrogen-bond parameters [Å, °] for [Re(tnn)(Htnn)]Br2·EtOH (1·EtOH)

For the Htnn ligand, the Re-N(1) bond distance of 1.944(4) Å is consistent with those found in the literature for Re-N (amido) bonds.<sup>[14–19]</sup> The Re-N(2) [2.073(4) Å] and Re-N(3) [2.169(4) Å] lengths are consistent with their imino and amino character, respectively.<sup>[11–19]</sup> The C(7)-N(2)-C(8) angle of 118.3(4)° is slightly higher than that in tnn. All the other bond lengths and angles in the complex are normal.

The two bromide counter-ions and the ethanol solvent of crystallization (O(1)H) are involved in a series of hydrogenbonds (Table 2). Br(1) forms hydrogen-bonds with N(3)-H(3A) and N(6)-H(6A), while Br(2) is involved with O(1)-H(1B) of an ethanol solvent of crystallization, and with N(3)H(3B) and N(6)H(6B).

Compound 1 is unusual since it contains the ReN<sub>6</sub> chromophore, which is rare for rhenium(V). We have previously reacted the potentially tridentate Schiff base *N*-(2-aminobenzylidene)benzene-1,2-diamine (H<sub>2</sub>L) with *trans*-[ReO<sub>2</sub>(py)<sub>4</sub>]Cl to produce the '3+3' complex salt [Re(L)<sub>2</sub>] (ReO<sub>4</sub>), in which each ligand L acts as a diamido-imine.<sup>[20]</sup> Mononuclear double cations of rhenium(V) are also rare. Two of the few examples in the literature are [ReO(OH)(cyclam)](ClO<sub>4</sub>)<sub>2</sub> (cyclam = 1,4,8,11-tetraazacyclotetradecane)<sup>[21]</sup> and [ReOCl(OH<sub>2</sub>)<sub>2</sub>(L)]Cl<sub>2</sub> (L = 2-hydrazinobenzimidazole).<sup>[22]</sup>

#### Synthesis and Characterization of [ReO(dne)] (2)

The reaction of H<sub>2</sub>ane with *trans*-[ReO<sub>2</sub>(py)<sub>4</sub>]Cl led to the formation of [ReO(dne)] (**2**), where the tetradentate dne chelate acts as a triamido-imine (H<sub>3</sub>dne = N-(2-aminobenzyl)-N'-[(2-aminophenyl)methylidene]ethane-1,2-diamine). This reaction is represented by the equation

#### $[\text{ReO}_2(\text{py})_4]\text{Cl} + \text{H}_2\text{ane} \rightarrow 2 + \text{H}_2\text{O} + 3\text{py} + [\text{pyH}]\text{Cl}$

Complex 2 is a non-electrolyte in DMF. It is soluble in polar solvents and is stable for months in the solid state and for days in solution. The IR spectrum is characterized by an intense absorption at  $909 \text{ cm}^{-1}$ , ascribed to the asymmetric Re=O stretching mode, which is within the range  $(895-1020 \text{ cm}^{-1})$  expected for this vibration.<sup>[11–19]</sup> The  $\nu$ (C=N) of the coordinated dne ligand is observed at 1609 cm<sup>-1</sup> and the N-H stretches are indicated by medium intensity peaks at 3397 and  $3280 \text{ cm}^{-1}$ . The medium intensity peaks at 466 and 502 cm<sup>-1</sup> are due to  $\nu$ (Re-N). In the <sup>1</sup>H NMR spectrum, the one-proton signal due to the methine proton (H(7)) appears as a sharp singlet at 9.50 ppm. The three multiplets in the aromatic region integrate for the eight protons of the aromatic rings of the dne chelate. The singlet at 5.20 ppm is assigned to the two protons of C(10) and the two broad oneproton singlets at 4.32 and 3.75 ppm are due to the protons on the amide nitrogens N(1) and N(4), respectively. In the UV-vis spectrum, two absorption bands are observed: an intraligand transition at 355 nm and a ligand-to-metal charge transfer band at 419 nm, due to the  $[p_{\pi}(NH^{-}) \rightarrow d_{\pi}^{*}(Re)]$  transition.

The structure of the title compound comprises of two independent and similar molecules. An *ORTEP* view of the asymmetric unit is shown in Fig. 2, and selected bond distances and angles are given in Table 3. The rhenium(V) is five-coordinated and sits in a square-pyramidal geometry, with the oxo group occupying the apical position. The rhenium atom lies 0.64 Å above the plane defined by the four nitrogen-donor atoms of dne, which is the result of the steric repulsion between these atoms and the oxo oxygen, with the angles O(1)-Re(1)-N(1) = 108.5(2)°, O(1)-Re(1)-N(2) = 108.0(2)°, O(1)-Re(1)-N(3) = 107.9(2)°, and O(1)-Re(1)-N(4) = 111.1(2)°. The corresponding values for the second molecule denoted by Re(2) are very different, with O(2)-Re(2)-N(5) = 112.6(2)°, O(2)-Re(2)-N(6) = 103.1(2)°, O(2)-Re(2)-N(7) = 112.6(2)°, and O(2)-Re N(8) = 107.0(2)°.

The average Re=O distance of 1.717(4) Å is typical, but at the higher end of the range observed for square-pyramidal monoxorhenium(V) complexes.<sup>[11,23–25]</sup> This corresponds with the observed lower value for  $\nu$ (Re=O).

Each tetradentate chelate contributes three negative charges to the [ReO]<sup>3+</sup> centre in order to maintain electroneutrality. The Re(1)-N(1) [2.017(4)Å], Re(1)-N(4) [1.951(5)Å], Re(2)-N(5) [1.995(4) Å], and Re(2)-N(8) [1.956(4) Å] bond lengths are similar to those found for rhenium(V)-amide bonds [average = 1.989 Å] in a large variety of complexes.<sup>[14-19]</sup> The Re(1)-N(2) [2.038(4) Å] and Re(2)-N(6) [2.075(4) Å] distances, coupled with the N(2)-C(7) [1.304(6)Å] and N(6)-C(23) [1.291(6)Å] lengths intimate that N(2) and N(6)are neutral imino nitrogen atoms, which are sp<sup>2</sup>-hybridized  $[C(7)-N(2)-C(8) = 115.7(4)^{\circ}, C(23)-N(6)-C(24) = 119.7(4)^{\circ}].$ The bond angles around N(3)  $[C(9)-N(3)-C(10) = 111.0(4)^{\circ}]$ and N(7)  $[C(25)-N(7)-C(26) = 109.0(3)^{\circ}]$  illustrate their sp<sup>3</sup>hybridization, and the Re(1)-N(3) and Re(2)-N(7) distances [1.934(4) and 1.936(4)Å] show that they are coordinated as amides (deprotonated secondary amines). The three bite angles in each molecule of the complex  $[N(1)-Re(1)-N(2) = 86.2(2)^{\circ}, N(2)-Re(1)-N(3) = 78.8(2)^{\circ},$  $N(3)-Re(1)-N(4) = 88.4(2)^{\circ}, N(5)-Re(2)-N(6) = 85.2(2)^{\circ}, N(6) Re(2)-N(7) = 78.6(2)^{\circ}$ ,  $N(7)-Re(2)-N(8) = 88.8(2)^{\circ}$ ] clearly show the influence of the different nature of the nitrogen-donor atoms N(2) and N(3), and N(6) and N(7), on the six-membered metallocycles in which they are involved. The dne chelate is thus coordinated as a tetradentate triamido-imine.

There are only two intermolecular hydrogen-bonds between the two molecules of the complex in the asymmetric unit: between N(1)-H(1) $\cdots$ O(2) and N(5)-H(5) $\cdots$ O(1).

Neutral oxorhenium(V) complexes containing trianionic tetradentate ligands are well known in the literature. Most of the research was based on the common chelating agents bis(aminoethanethiol) (BAT), diamidodithiol (DADT), and their derivatives with N<sub>2</sub>S<sub>2</sub> and N<sub>3</sub>S donor sets.<sup>[26]</sup> It was found that the reaction of HSCH<sub>2</sub>CONH(CH<sub>2</sub>)<sub>n</sub>NCH(2-HOC<sub>6</sub>H<sub>4</sub>) (H<sub>3</sub>L; N<sub>2</sub>OS donor set) with *trans*-[ReO<sub>2</sub>(py)<sub>4</sub>]Cl in methanol yielded the five-coordinate neutral complex [ReO(L)] (for n = 2) and the six-coordinate [ReO(py)(L) (for n = 3, 4).<sup>[27]</sup>

The reduction of one of the -CH=N- bonds of H<sub>2</sub>ane to -CH<sub>2</sub>-NH- of H<sub>3</sub>dne is not a common reaction, and it may be a possible intermediate en route to the cleavage of the C=N bond as observed in the formation of **1**. We can offer no plausible explanation for this phenomenon. An elegant study by Francesconi et al. has shown that an oxorhenium(V) BAT-imine



Fig. 2. ORTEP diagram of the asymmetric unit of 2. Hydrogen atoms have been omitted for clarity.

Table 3. Selected bond lengths [Å] and angles [°] in [ReO(dne)] (2)

Re(1)-O(1)	1.716(4)	Re(2)-O(2)	1.718(3)
Re(1)-N(1)	2.017(4)	Re(2)-N(5)	1.995(4)
Re(1)-N(2)	2.038(4)	Re(2)-N(6)	2.075(4)
Re(1)-N(3)	1.934(4)	Re(2)-N(7)	1.936(4)
Re(1)-N(4)	1.951(5)	Re(2)-N(8)	1.956(4)
N(2)-C(7)	1.304(6)	N(6)-C(23)	1.291(6)
N(3)-C(10)	1.443(7)	N(7)-C(26)	1.445(6)
N(3)-C(9)	1.456(8)	N(7)-C(25)	1.484(7)
N(1)-Re(1)-N(2)	86.2(2)	N(5)-Re(2)-N(6)	85.2(2)
N(2)-Re(1)-N(3)	78.8(2)	N(6)-Re(2)-N(7)	78.6(2)
N(3)-Re(1)-N(4)	88.4(2)	N(7)-Re(2)-N(8)	88.8(2)
C(7)-N(2)-C(8)	115.7(4)	C(23)-N(6)-C(24)	119.7(4)
C(9)-N(3)-C(10)	111.0(4)	C(25)-N(7)-C(26)	109.0(3)
O(1)-Re(1)-N(1)	108.5(2)	O(2)-Re(2)-N(5)	112.6(2)
O(1)-Re(1)-N(2)	108.0(2)	O(2)-Re(2)-N(6)	103.1(2)
O(1)-Re(1)-N(3)	107.9(2)	O(2)-Re(2)-N(7)	112.6(2)
O(1)-Re(1)-N(4)	111.1(2)	O(2)-Re(2)-N(8)	107.0(2)

species can be converted quantitatively to the BAT-amine species by a ligand-based reduction reaction with NaBH<sub>4</sub> in ethanol.<sup>[28]</sup>

#### Synthesis and Characterization of $[ReO(ane)]PF_6$ (3)

The reaction of cis-[ReO<sub>2</sub>I(PPh<sub>3</sub>)<sub>2</sub>] with two equivalents of H<sub>2</sub>ane resulted in the formation of the cationic complex [ReO(ane)]<sup>+</sup>. The complex was isolated by recrystallization

from an ethanol/dichloromethane mixture in the presence of  $NH_4PF_6$ , and the reaction is given by the equation

$$[\text{ReO}_2\text{I}(\text{PPh}_3)_2] + \text{H}_2\text{ane} + \text{NH}_4\text{PF}_6$$
  

$$\rightarrow \mathbf{3} + \text{H}_2\text{O} + 2\text{PPh}_3 + \text{NH}_4\text{I}$$

Complex 3 is soluble in alcohols and other polar solvents, which include acetonitrile, N,N-dimethylformamide, and dichloromethane. It is stable in solution for days, but undergoes slow oxidation to  $[ReO_4]^-$  in air. The infrared spectrum indicates the presence of the Re=O core as a medium intensity absorption at 985 cm<sup>-1</sup>. An intense and broad absorption for  $\nu$ (C=N) is observed at 1609 cm<sup>-1</sup>, which has shifted to a lower frequency relative to that of the free H<sub>2</sub>ane ligand, occurring at  $1635 \text{ cm}^{-1}$ The Re-N stretches are indicated by medium intensity peaks at 494 and 465 cm<sup>-1</sup>. The P-F stretch occurs as a broad and intense peak at  $805 \text{ cm}^{-1}$ . The <sup>1</sup>H NMR spectrum emphasizes the symmetry within the molecule. The corresponding protons on each half of the chelate exhibit magnetic equivalence. The amido protons' signal occurs as a two proton singlet at 7.95 ppm. Due to the coordination to the central metal atom, the imine protons' singlet is shifted downfield (compared with the free ligand) to 13.12 ppm. The eight protons of the two phenyl rings appear as four two-proton signals as a doublet, triplet, doublet, and a triplet. The band at 364 nm in the electronic spectrum is assigned to an intraligand transition associated with the coordinated ligand. A ligand-to-metal charge transfer band  $[p_{\pi}(NH^{-}) \rightarrow d_{\pi}^{*}(Re)]$  is found at 425 nm.

The molecular structure of the title compound is illustrated in Fig. 3, and selected bond lengths and angles are



Fig. 3. ORTEP view of 3. The disordered  $PF_6^-$  counter-ion and hydrogen atoms have been omitted.

Table 4. Selected bond lengths [Å] and angles [°] for [ReO(ane)]  $\mathrm{PF}_{6}$  (3)

Re-N(1)	1.967(5)	Re-N(4)	1.970(6)
Re-N(2)	2.064(5)	Re-N(3)	2.046(5)
C(7)-N(2)	1.296(8)	C(10)-N(3)	1.299(8)
Re-O	1.672(4)	C(8)-N(2)	1.491(7)
O-Re-N(1)	109.7(2)	O-Re-N(4)	107.3(2)
O-Re-N(2)	107.2(2)	O-Re-N(3)	111.5(2)
N(1)-Re-N(2)	86.3(2)	N(3)-Re-N(4)	86.3(2)
N(2)-Re-N(3)	78.1(2)	N(1)-Re-N(3)	138.6(2)
C(7)-N(2)-C(8)	119.4(5)	C(9)-N(3)-C(10)	117.7(5)

listed in Table 4. The rhenium(V) is five-coordinate with a square-pyramidal geometry, with the oxo group occupying the apical position. The metal is lifted out of the mean equatorial  $N_4$ -plane by 0.65 Å towards the oxo oxygen. The repulsion of the latter with the equatorial nitrogens is reflected in the angles O-Re-N(1) = 109.7(2)°, O-Re-N(2) = 107.2(2)°, O-Re-N(3) = 111.5(2)°, and O-Re-N(4) = 107.3(2)°.

The tetradentate ligand acts as a dianionic chelate, with the amino nitrogens N(1) and N(4) singly deprotonated, and N(2) and N(3) coordinated as imines. The Re-N(1) and Re-N(4) bond lengths are practically identical [average = 1.979(6) Å], and these two nitrogens are thus coordinated as amides.<sup>[23–25]</sup> The two imines N(2) and N(3) form bond lengths of 2.064(5) and 2.046(5) Å, respectively with the rhenium(V) centre,<sup>[12–14]</sup> with the C(7)-N(2)-C(8) [119.4(5)°] and C(9)-N(3)-C(10) [117.7(5)°] bond angles indicative of their sp<sup>2</sup> hybridization. The Re=O bond length [1.672(4) Å] falls in the expected range for square-pyramidal oxorhenium cations.<sup>[23–25]</sup> The two bite angles N(1)-Re-N(2) and N(3)-Re-N(4) are identical at 86.3(2)°, considerably larger than the N(2)-Re-N(3) one [78.1(2)°], due to the six-membered metallocycle. The two phenyl rings form a dihedral angle of 2.56° with each other.

There are no hydrogen-bonds involved in the packing of the molecules in the crystal. The  $PF_6^-$  counterion is disordered, and the closest contact that it has with the complex is with N(1) [3.15(1) Å] and N(4) [3.18(1) Å].

Monomeric square-pyramidal cationic monooxorhenium(V) complexes with  $N_2O_2$  and  $N_2S_2$ -donor tetradentate ligands are uncommon. The reaction of the potentially  $N_2S_2$ -donor tetradentate ligand 1,2-di(2-aminophenylthio)ethane (H<sub>2</sub>L) with (*n*-Bu<sub>4</sub>N)[ReOCl<sub>4</sub>] produced the neutral complex [ReOCl(L)], in which both amino groups are singly deprotonated in the same

manner as in complex **3**. It was intimated that the chloride is coordinated *trans* to the oxo group.<sup>[29]</sup> Also, the six-coordinate complex salt *trans*-[ReO(OH<sub>2</sub>)(acac<sub>2</sub>en)]Cl (**4**) was synthesized from [ReOCl<sub>4</sub>]<sup>-</sup>, and the further reaction of **4** with the phosphines PEt<sub>2</sub>Ph and PEt<sub>3</sub> (Y) led to the isolation of the cationic salts *cis*-[ReO(Y)(acac<sub>2</sub>en)]PF<sub>6</sub>.<sup>[30]</sup> With the tetradentate ligand HS-(CH<sub>2</sub>)<sub>2</sub>-S-CH<sub>2</sub>-CO-NH-CH(CO<sub>2</sub>CH<sub>3</sub>)CH<sub>2</sub>-SH (H<sub>2</sub>L) the neutral square-pyramidal complex [ReO(L)] was isolated.<sup>[31]</sup> The anionic square-pyramidal complex [ReO(Cl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] with the N<sub>2</sub>SO tetradentate ligand (2-HOC<sub>6</sub>H<sub>4</sub>)NH-CO-CH<sub>2</sub>-NH-CO-CH<sub>2</sub>-SH(H<sub>4</sub>ONNS).<sup>[32]</sup>

## Potential Application as Radiopharmaceuticals

With regard to the relevance of these ligands to possible radiopharmaceutical applications, we have reduced perrhenate with sodium dithionite in the presence of the ligand H<sub>2</sub>ane and hydroxide. The product has the identical spectroscopic properties and melting point to that of complex **2**, prepared from *trans*-[ReO<sub>2</sub>(py)<sub>4</sub>]Cl. It was shown previously that dithionite also reduces a variety of imines to secondary amines.<sup>[33]</sup>

#### Conclusion

The reaction of different oxorhenium(V) cores with the potentially tetradentate  $N_4$ -donor ligand H<sub>2</sub>ane led to different products. With the monooxo *trans*-[ReOBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>], the tetradentate ligand decomposed to produce a tridentate ligand in the '3+3' complex cation [Re(tnn)(Htnn)]<sup>2+</sup>. With the *trans*dioxo [ReO<sub>2</sub>(py)<sub>4</sub>]Cl, the tetradentate chelate acts as a triamidoimine in [ReO(dne)], and with the *cis*-dioxo [ReO<sub>2</sub>I(PPh<sub>3</sub>)<sub>2</sub>], the complex salt [ReO(ane)]PF<sub>6</sub> was isolated, with ane coordinated as a diamido-diimine.

### Experimental

#### Materials

All chemicals were of reagent grade, and solvents were purified by standard techniques and drying methods. *trans*- $[ReOBr_3(PPh_3)_2]$ ,<sup>[34]</sup> *trans*- $[ReO_2(py)_4]Cl$ ,<sup>[35]</sup> and *cis*- $[ReO_2I$  (PPh\_3)\_2]<sup>[35]</sup> were prepared by literature methods.

#### Physical Measurements

<sup>1</sup>H NMR spectra were recorded in *d*<sub>6</sub>-DMSO on a Bruker AX (300 MHz) spectrometer at ambient temperatures, and values are reported relative to TMS. Infrared spectra were obtained with a Digilab FTS 3100 Excalibur HE spectrophotometer with solid

	1.EtOH	2	3
CCDC deposition no.	757785	757786	757787
Empirical formula	C <sub>20</sub> H <sub>29</sub> N <sub>6</sub> OBr <sub>2</sub> Re	C <sub>16</sub> H <sub>17</sub> N <sub>4</sub> ORe	C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> ORePF <sub>6</sub>
Formula weight	715.50	467.54	611.50
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	Cc	$P2_1/c$
Unit cell dimensions			
<i>a</i> [Å]	9.5046(2)	11.1796(2)	11.9280(2)
<i>b</i> [Å]	18.4286(4)	13.3316(2)	11.4686(2)
c [Å]	14.0372(3)	20.0117(3)	14.6399(3)
γ [Å]	102.475(2)	91.856(1)	112.229(1)
Volume [Å <sup>3</sup> ]	2400.66(9)	2981.02(8)	1853.86(6)
Ζ	4	8	4
Density (calc.) [Mg m <sup>-3</sup> ]	1.980	2.083	2.191
Absorption coefficient [mm <sup>-1</sup> ]	8.414	8.160	6.715
<i>F</i> (000)	1376	1792	1168
Crystal size [mm <sup>3</sup> ]	0.11  imes 0.18  imes 0.21	0.03  imes 0.04  imes 0.15	$0.03\times0.05\times0.10$
$\theta$ range [°]	4.0-26.3	3.1-27.5	3.3-27.5
Index ranges			
h	-11/8	-14/14	-14/15
k	-22/22	-17/15	-14/14
l	-17/17	-25/25	-19/19
Reflections collected	18436	24408	30497
Independent reflections	4849	6749	4267
Observed reflections	3675	6417	3463
Data/parameters	4849/270	6749/397	4267/289
Goodness-of-fit on $F^2$	0.95	1.08	1.04
Final <i>R</i> indices $[I > 2\sigma(I)]$	$0.0283 (wR_2 = 0.0688)$	0.236 (0.0465)	0.0364 (0.0886)
Largest diff. peak/hole [e Å <sup>-3</sup> ]	2.11/-1.46	0.56/-1.33	1.52/-1.35

Table 5. Crystal and structural refinement data for the complexes

samples prepared as KBr discs. Microanalyses were obtained on a Carlo Erba EA 1108 elemental analyzer.

#### Synthesis of N,N'-Bis[(2-aminophenyl)methylidene]ethane-1,2-diamine ( $H_2$ ane)

A mass of 0.25 g of 1,2-diaminoethane (4.15 mmol) in 50 mL of ethanol was added dropwise to a solution of 1.00 g of 2aminobenzaldehyde (8.25 mmol) in 50 mL of benzene which was kept at  $-18^{\circ}$ C (with a sludge bath of liquid nitrogen/ 1,2-dichlorobenzene). After addition, the reaction mixture was allowed to warm to room temperature, and was then refluxed for 4 h. The reaction mixture was allowed to cool down to room temperature and the solvent was reduced under vacuum to afford light yellow crystals. The crystals were filtered and dried under vacuum. Yield = 90%, mp 187–189°C.  $\nu_{max}$ /cm<sup>-1</sup>  $\nu$ (N-H) 3420, 3231;  $\nu$ (C=N) 1635.  $\delta_{\rm H}$  (295 K) 8.39 (s, 2H, H(2), H(11)), 7.05–7.12 (m, 4H, H(3), H(5), H(8), H(10)), 6.66 (d, 2H, H(6), H(7)), 6.47 (t, 2H, H(4), H(9)), 3.82 (t, 4H, H(1), H(12)), 3.15 (br, s, 4H, 2NH<sub>2</sub>). Anal. Calc. for C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>: C 72.15, H 6.81, N 21.04. Found: C 72.10, H 6.75, N 21.15%.

#### Synthesis of [Re(tnn)(Htnn)]Br<sub>2</sub> (**1**-EtOH)

A solution of 56 mg (210 µmol) of H<sub>2</sub>ane and 100 mg (104 µmol) of *trans*-[ReOBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] in 20 mL of ethanol was refluxed for 2 h. Upon cooling, a brown precipitate formed, which was filtered and washed with diethyl ether. Recrystallization from dichloromethane/ethanol (1/1) gave brown crystals. Yield = 32%, mp >350°C.  $\nu_{max}/cm^{-1}$   $\nu$ (N-H) 3147, 3161, 3431, 3408, 3468;  $\nu$ (C=N) 1586, 1609;  $\nu$ (Re=N) 1074;  $\nu$ (Re-N) 425, 466, 494.  $\lambda_{max}$  (MeOH)/nm ( $\varepsilon$ /M<sup>-1</sup> cm<sup>-1</sup>) 369 (1890), 533

(380), 733 (210).  $\delta_{\rm H}$  (295 K) 12.95 (s, 2H, N(6)H<sub>2</sub>), 9.05 (s, 2H, H(7), H(16)), 7.68 (d, 2H, H(2), H(11)), 7.61 (t, 2H, H(4), H(13)), 7.02 (d, 2H, H(5), H(14)), 6.81 (t, 2H, H(12), H(3)), 3.38–3.50 (m, 8H, C(8)H<sub>2</sub>, C(9)H<sub>2</sub>, C(17)H<sub>2</sub>, C(18)H<sub>2</sub>)). Conductivity (MeOH, 10<sup>-3</sup> M) 173  $\Omega^{-1}$ cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calc. for C<sub>18</sub>H<sub>23</sub>N<sub>6</sub>Br<sub>2</sub>Re·C<sub>2</sub>H<sub>6</sub>O: C 33.57, H 4.09, N 11.75. Found: C 33.48, H 3.93, N 12.02%.

#### Synthesis of [ReO(dne)] (2)

A mass of 22 mg of H<sub>2</sub>ane (82 µmol) was added to a solution of 42 mg of *trans*-[ReO<sub>2</sub>(py)<sub>4</sub>]Cl (74 µmol) in 20 mL of ethanol. The solution was heated under reflux for an hour and then cooled to room temperature. The brown precipitate that formed was filtered, washed with diethyl ether, and dried under vacuum. Brown needles were obtained from the slow evaporation of the mother liquor. Yield = 69%, mp 149–152°C.  $\nu_{max}/cm^{-1}$   $\nu$ (N-H) 3397, 3280;  $\nu$ (C=N) 1609;  $\nu$ (Re=O) 909;  $\nu$ (Re-N) 466, 502.  $\lambda_{max}$  (DMF)/nm ( $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>) 355 (2410), 419 (2280).  $\delta_{\rm H}$  (295 K) 9.50 (s, 1H, CH=N), 7.70–7.98 (m, 2H, H(2), H(15)), 7.00–7.54 (m, 3H, H(4), H(5), H(13)), 6.65–6.70 (m, 3H, H(3), H(12), H(14)), 5.20 (s, 2H, H(10)), 4.32 (br s, 1H, NH), 3.75 (br s, 1H, NH), 3.15 (t, 2H, CH<sub>2</sub>), 1.04 (t, 2H, CH<sub>2</sub>). Conductivity (DMF,  $10^{-3}$  M) 21  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calc. for C<sub>16</sub>H<sub>17</sub>N<sub>4</sub>ORe: C 41.10, H 3.66, N 11.98. Found: C 40.08, H 3.54, N 12.56%.

#### Synthesis of $[ReO(ane)]PF_6$ (3)

A mixture of 100 mg of *cis*-[ReO<sub>2</sub>I(PPh<sub>3</sub>)<sub>2</sub>] (115  $\mu$ mol) and 62 mg of H<sub>2</sub>ane (233  $\mu$ mol) was heated under reflux in 20 mL of acetonitrile in an inert atmosphere for 2 h. Cooling down to room temperature produced a dark brown precipitate, which

was filtered off, washed with diethyl ether and dried under vacuum. Recrystallization from 1:2 (v/v) ethanol:dichloromethane and the addition of NH<sub>4</sub>PF<sub>6</sub> afforded dark brown crystals, suitable for X-ray analysis. Yield = 80%, mp >300°C.  $\nu_{max}/cm^{-1}$   $\nu$ (C=N) 1610;  $\nu$ (Re=O) 983;  $\nu$ (P-F) 805;  $\nu$ (Re-N) 495, 468.  $\lambda_{max}$  (MeOH)/nm ( $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>) 364 (1150), 425 (1280).  $\delta_{\rm H}$  (295 K) 13.12 (s, 2H, H(7), H(10)), 7.95 (s, 2H, 2NH), 7.71 (d, 2H, H(2), H(15)), 7.59 (t, 2H, H(4), H(13)), 7.18 (d, 2H, H(5), H(12)), 6.83 (t, 4H, H(3), H(14)), 4.35 (t, 4H, 2CH<sub>2</sub>). Conductivity (CH<sub>3</sub>CN, 10<sup>-3</sup> M) 133  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calc. for C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>ORePF<sub>6</sub>: C 32.27, H 2.71, N 9.41. Found: C 32.29, H 2.69, N 9.50%.

#### Synthesis of [ReO(dne)] (2) from $[ReO_4]^-$ and $Na_2S_2O_4$

A mass of 100 mg of NH<sub>4</sub>[ReO<sub>4</sub>] (373  $\mu$ mol) and 250 mg of H<sub>2</sub>ane (939  $\mu$ mol) were dissolved in 20 mL of a 1:1 water/ethanol mixture. Sodium dithionite (600 mg) and 2 mL of a 1.0 M NaOH solution were added, and the mixture was heated under reflux for 2 h, and then filtered while hot. The solvent was reduced in volume under vacuum, and a brown precipitate was collected by filtration. It was recrystallized from 1:2 (v/v) ethanol:dichloromethane. Yield = 38%, mp 148–151°C. Anal. Calc. for C<sub>16</sub>H<sub>17</sub>N<sub>4</sub>ORe: C 41.10, H 3.66, N 11.98. Found: C 40.86, H 3.41, N 12.31%. This product has identical spectroscopic properties to the sample prepared above from *trans*-[ReO<sub>2</sub>(py)<sub>4</sub>]Cl.

#### X-ray Diffraction

X-ray diffraction studies on crystals of 1, 2, and 3 were performed at 200(2) K using a Nonius Kappa CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71072$  Å). The structures were solved by direct methods and refined by least-squares procedures using *SHELXL-97*.<sup>[36]</sup> All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were calculated in idealized geometrical positions. Crystal and structure refinement data are given in Table 5.

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