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Reactions of electrophiles with $[(Bu^tN)_2Re^{VI}(\mu\text{-}NBu^t)]_2$†

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The interaction of $[(Bu^tN)_2Re^{VI}(\mu\text{-}NBu^t)]_2$ **1** with trifluoromethanesulfonic acid gave the amido complex $[(Bu^tN)(Bu^tHN)Re(\mu\text{-}NBu^t)_2Re(NBu^t)_2][CF_3SO_3]$, where the cation has a structure very similar to that of its manganese(VI) analogue. The interaction of **1** with silver triflate differs from the similar reaction with $[(Bu^tN)_2Mn^{VI}(\mu\text{-}NBu^t)]_2$ in that a silver complex $\{[(Bu^tN)Re(\mu\text{-}NBu^t)]_2(\mu\text{-}NBu^t)_2Ag(\mu\text{-}O_3SCF_3)\}_2$ that has NBu^t groups bridging both rhenium and silver atoms with the latter having $\mu\text{-}O_3SCF_3$ bridges is formed. A similar complex $[(Bu^tN)Re(\mu\text{-}NBu^t)]_2(\mu\text{-}NBu^t)_2Cu_2(O_3SCF_3)_2$ was obtained by interaction of **1** with $Cu(O_3SCF_3)\cdot 0.5C_6H_6$ but this has $Re(\mu\text{-}NBu^t)Cu(O_3SCF_3)$ groups. Interaction of **1** with $Al(O_3SCF_3)_3\cdot nCF_3SO_3H$ in CH_2Cl_2 gave a linear molecule $(Bu^tN)_2Re(\mu\text{-}NBu^t)_2Re(NBu^t)(\mu\text{-}OH)_2Al(O_3SCF_3)_3(H_2O)$. The crystal structures of four compounds have been determined. An improved synthesis of **1** involving Na/Hg reduction of $Re(NBu^t)_3I$ was elaborated.

In a previous note[1] we showed that the manganese(VI) dimer $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$ on reaction with silver trifluoromethanesulfonate (triflate) in CH_2Cl_2 gave a radical cation $[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)\}_2]^{\bullet+}$ where the electron was located on one N atom. This ion abstracted a hydrogen atom from tetrahydrofuran to give the amido cation $[(Bu^tN)(Bu^tHN)Mn(\mu\text{-}NBu^t)_2Mn(NBu^t)_2]^+$ the structure of which was determined in its $[Hg_3Cl_8]^{2-}$ salt. This cation was also shown to be obtained by direct protonation of $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$ with triflic acid. A similar study has now been made of the reactions of the rhenium(VI) analogue[2] of the manganese compound, *i.e.* $[Re(NBu^t)_2(\mu\text{-}NBu^t)]_2$ **1**, the first homoleptic imido compound to be synthesized. An improved synthesis of this rhenium compound is reported. Analytical and physical data for new compounds are given in Table 1.

Results and Discussion

The dimer **1** was first obtained on reduction of $Re(NBu^t)_3(OSiMe_3)$ in light petroleum by sodium amalgam. Conversion of this silyloxide into the iodide occurs on reaction with $SiMe_3I$ in benzene; reduction of $Re(NBu^t)_3I$ **2** gives an overall yield of **1** of *ca.* 65%.

The interaction of compound **1** with protonic acids occurs at low temperatures; use of CF_3SO_3H under carefully controlled conditions (see Experimental section) gives a crystalline product. As in the manganese case protonation occurs at a terminal NBu^t group giving the amido cation isolated as the triflate salt **3**. The ^1H NMR spectrum of **3** is very similar to that of the manganese analogue with five *tert*-butyl peaks in a 2 : 1 : 1 : 1 : 1 ratio indicating the presence of two equivalent bridging *tert*-butylimido groups. For both compounds the spectrum shows an $N\mathit{H}Bu^t$ band (Mn, δ 10.2; Re, δ 7.6).

The structure of the cation in compound **3** as determined by X-ray diffraction is shown in Fig. 1; bond lengths and angles are given in Table 2. The similarities between the structure of this dimer and the manganese complex are considerable, but this new analysis has raised one intriguing difference. In terms of similarity we note that the geometry parameters around the two Re atoms are significantly different. Thus the terminal Re≙N–Bu^t bonds at Re(2) are short, but inexplicably not equal [1.719(7) and 1.773(7) Å], and the co-ordination is linear [173.8(6) and 159.4(6)° respectively]. The bridging Re–N bonds from Re(2) are *ca.* 0.08 Å longer than those to Re(1), *i.e.* the bridges are unsymmetrical, but in a polarised fashion. An analogous situation was found for the manganese complex in the two salts studied. However, whereas in those structures the bond lengths from the second Mn atom to its terminal N atoms were very different, one short Mn≙NR and one long Mn–NHR, in the initial refinement of this rhenium structure the two Re(1)–N distances were essentially the same. Furthermore, the anisotropic 'thermal' ellipsoids for both atoms were significantly elongated, and so we ascribed this to disorder, over the two sites, of the amido and imido functions. Accordingly the two sites were each represented by two half-atoms.

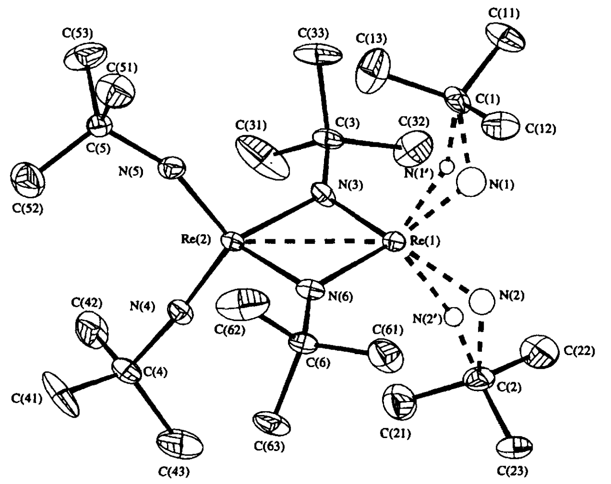

Fig. 1 Structure of $[(Bu^tN)(Bu^tHN)Re(\mu\text{-}NBu^t)_2Re(NBu^t)_2]^+$ in the triflate salt **3**

The products of reaction of compound **1** with $HBF_4\cdot OEt_2$ and HCl could not be obtained as crystals, probably due to mismatch of cation and anion sizes. The interaction with 1 equivalent of $AgOSO_2CF_3$ in CH_2Cl_2 gives a product completely different from that obtained using $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$. The structure of this compound, **4**, was determined by X-ray crystallography and is shown schematically in **I**. A diagram of the co-ordination sphere of the molecule is shown in Fig. 2; bond lengths and angles are in Table 3. The

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† *Non-SI unit employed:* mmHg ≈ 133 Pa.

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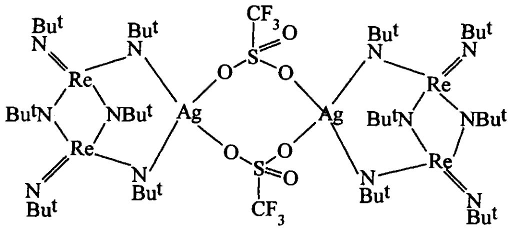
Table 1 Analytical and physical data for new compounds

Compound	Colour	M.p./°C	Analysis (%)* C	H	N
2 $Re(NBu^t)_3I$	Orange	138–140	27.5 (27.4)	5.1 (5.1)	8.1 (8.0)
3 $[Re_2(NBu^t)_3(\mu\text{-}NBu^t)_2(NHBu^t)][CF_3SO_3]$	Yellow	> 230	31.3 (31.6)	4.5 (4.8)	8.7 (8.8)
4 $\{[(Bu^tN)Re(\mu\text{-}NBu^t)]_2(\mu\text{-}NBu^t)_2Ag(\mu\text{-}O_3SCF_3)\}_2$	Pale yellow	> 240	27.8 (28.4)	4.9 (5.1)	7.8 (7.9)
5 $[(Bu^tN)Re(\mu\text{-}NBu^t)]_2(\mu\text{-}NBu^t)_2Cu_2(O_3SCF_3)_2$	Yellow	225–230	25.0 (25.5)	4.2 (4.4)	6.7 (6.8)
6 $(Bu^tN)_2Re(\mu\text{-}NBu^t)_2Re(NBu^t)(\mu\text{-}OH)_2Al(O_3SCF_3)_3(H_2O)\cdot Et_2O$	Yellow	> 240	24.3 (24.5)	4.1 (4.5)	5.2 (5.3)

* Calculated values in parentheses. Mass spectral data are given in the Experimental section.

Table 2 Selected bond lengths (Å) and angles (°) for $[(Bu^tN)(Bu^tHN)Re(\mu\text{-}NBu^t)_2Re(NBu^t)_2][CF_3SO_3]$ **3** with estimated standard deviations (e.s.d.s) in parentheses

Re(1) ••• Re(2)	2.7154(13)	Re(1)–N(6)	1.918(6)
Re(1)–N(1)	1.83(2)	Re(2)–N(3)	1.989(6)
Re(1)–N(1′)	1.790(13)	Re(2)–N(4)	1.719(7)
Re(1)–N(2)	1.88(2)	Re(2)–N(5)	1.773(7)
Re(1)–N(2′)	1.801(13)	Re(2)–N(6)	1.990(7)
Re(1)–N(3)	1.907(7)		
N(1′)–Re(1)–N(2′)	117.6(7)	N(4)–Re(2)–N(5)	113.7(3)
N(2′)–Re(1)–N(1)	102.1(8)	N(4)–Re(2)–N(6)	112.3(3)
N(1′)–Re(1)–N(2)	99.7(7)	N(5)–Re(2)–N(6)	112.7(3)
N(1′)–Re(1)–N(3)	111.3(5)	Re(1)–N(1)–C(1)	127.4(13)
N(1′)–Re(1)–N(6)	111.9(5)	Re(1)–N(1′)–C(1)	158.1(12)
N(2′)–Re(1)–N(3)	109.1(5)	Re(1)–N(2)–C(2)	126.9(11)
N(2′)–Re(1)–N(6)	110.3(5)	Re(1)–N(2′)–C(2)	163.9(12)
N(1)–Re(1)–N(2)	84.3(8)	Re(1)–N(3)–C(3)	137.8(6)
N(1)–Re(1)–N(3)	121.4(6)	Re(1)–N(6)–C(6)	137.3(6)
N(1)–Re(1)–N(6)	119.6(6)	Re(2)–N(3)–C(3)	133.5(6)
N(2)–Re(1)–N(3)	119.3(5)	Re(2)–N(6)–C(6)	134.6(5)
N(2)–Re(1)–N(6)	121.0(5)	Re(2)–N(4)–C(4)	173.8(6)
N(3)–Re(1)–N(6)	94.1(3)	Re(2)–N(5)–C(5)	159.4(6)
N(3)–Re(2)–N(4)	113.6(3)	Re(1)–N(3)–Re(2)	88.4(3)
N(3)–Re(2)–N(5)	112.8(3)	Re(1)–N(6)–Re(2)	88.0(3)
N(3)–Re(2)–N(6)	89.5(3)		



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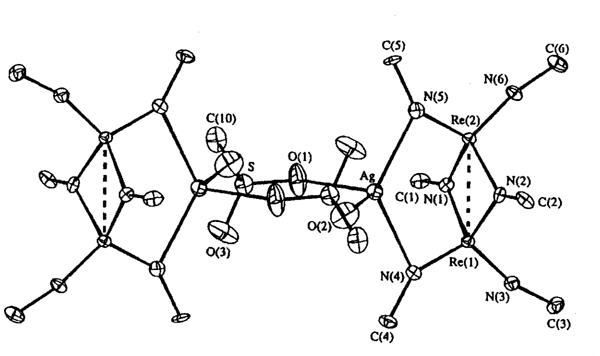


Fig. 2 Structure of $\{[(Bu^tN)Re(\mu\text{-}NBu^t)]_2(\mu\text{-}NBu^t)_2Ag(\mu\text{-}O_3SCF_3)\}_2$ **4** with *tert*-butyl carbon and triflate fluorine atoms omitted for clarity

Table 3 Selected bond lengths (Å) and angles (°) for $\{[(Bu^tN)Re(\mu\text{-}NBu^t)]_2(\mu\text{-}NBu^t)_2Ag(\mu\text{-}O_3SCF_3)\}_2$ **4** with e.s.d.s in parentheses

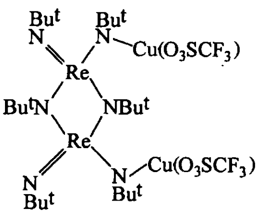
Re(1) ••• Re(2)	2.6798(14)	Re(2)–N(5)	1.751(9)
Re(1)–N(1)	1.931(8)	Re(2)–N(6)	1.728(8)
Re(1)–N(2)	1.937(7)	Ag–N(4)	2.457(8)
Re(1)–N(3)	1.743(9)	Ag–N(5)	2.410(9)
Re(1)–N(4)	1.783(8)	Ag–O(1)	2.404(8)
Re(2)–N(1)	1.929(8)	Ag–O(2′)	2.373(9)
Re(2)–N(2)	1.932(8)		
N(1)–Re(1)–N(2)	91.5(3)	N(1)–Re(2)–N(2)	91.8(3)
N(1)–Re(1)–N(3)	112.8(4)	N(1)–Re(2)–N(5)	110.7(4)
N(1)–Re(1)–N(4)	111.6(4)	N(1)–Re(2)–N(6)	114.4(4)
N(2)–Re(1)–N(3)	113.5(3)	N(2)–Re(2)–N(5)	112.1(4)
N(2)–Re(1)–N(4)	111.2(4)	N(2)–Re(2)–N(6)	113.1(3)
N(3)–Re(1)–N(4)	114.2(4)	N(5)–Re(2)–N(6)	113.1(4)
Re(1)–N(1)–Re(2)	87.9(3)	Re(1)–N(4)–Ag	93.6(3)
Re(1)–N(2)–Re(2)	87.7(3)	Re(2)–N(5)–Ag	95.0(4)
Re(1)–N(1)–C(1)	134.5(6)	N(4)–Ag–N(5)	120.0(3)
Re(2)–N(1)–C(1)	137.4(7)	N(4)–Ag–O(1)	105.7(3)
Re(1)–N(2)–C(2)	135.5(6)	N(4)–Ag–O(2′)	101.8(3)
Re(2)–N(2)–C(2)	135.1(6)	N(5)–Ag–O(1)	99.9(3)
Re(1)–N(3)–C(3)	164.9(7)	N(5)–Ag–O(2′)	123.1(3)
Re(1)–N(4)–C(4)	146.3(7)	O(1)–Ag–O(2′)	104.1(3)
Re(2)–N(5)–C(5)	145.1(7)	C(4)–N(4)–Ag	120.1(6)
Re(2)–N(6)–C(6)	169.4(8)	C(5)–N(5)–Ag	120.0(7)

Primed atoms are related by the symmetry transformation $-x$, $-y$, $-z$.

centrosymmetric dimer consists of a central, neutral $Ag(O_3SCF_3)_2Ag$ unit to which two neutral $Re_2(NBu^t)_6$ molecules co-ordinate in bidentate fashion from a bent NBu^t group on each rhenium atom. In the $Re^{VI}{}_2$ dimer the $Re(\mu\text{-}NBu^t)Re$ bridges are symmetrical, within the limits of experimental error.

In compound **4** no evidence for a one-electron electron transfer was observed as found in the manganese case. Although bridging alkyl- and aryl-imido groups are common, heterometallic imido bridges are relatively rare. Literature examples include $(\eta\text{-}C_5H_5)_2Zr(\mu\text{-}NBu^t)Ir(\eta\text{-}C_5Me_5)$ with a three-membered ring and $(\eta\text{-}C_5H_5)_2(Bu^tO)Zr(\mu\text{-}NBu^t)(\mu\text{-}X)Ir(\eta\text{-}C_5Me_5)$ (X = H or S) with four-membered rings[3] as well as compounds with the bridges $Mn(\mu\text{-}NBu^t)_2ZnMe$[4a] and $W(\mu\text{-}NBu^t)_2AlX_2$ (X = Cl or Me) and the remarkable copper cation $[W_2Cu_5(NBu^t)_2(\mu\text{-}NBu^t)_6(NHBu^t)_2]^+$ that has $W(\mu\text{-}NBu^t)Cu$ bridges.[4b] Triflate bridges such as those found in **4** are known.[5] Finally, it may be noted that the arylimido analogue of **1**, $Re_2(NC_6H_3Pr^i{}_2\text{-}2,6)_6$,[6] does not react with silver triflate in CH_2Cl_2.

The interaction of compound **1** with copper(I) triflate $CuO_3SCF_3\cdot 0.5C_6H_6$ in dichloromethane gave **5** the structure of which, determined by X-ray crystallography, is shown schematically in **II** and in Fig. 3; bond lengths and angles are in Table 4. In this complex the neutral $Re_2(NBu^t)_6$ moiety is again bidentate through terminal imido functions with co-ordination of two $Cu(O_3SCF_3)$, units to N atoms. As seen in Fig. 3 the triflate co-ordination is monodentate and the two-co-ordinate O–Cu–N geometry is close to linear [174.5(3) and 175.2(3)°]. The alignment of the two co-ordination vectors is skewed, and this allows the two-co-ordinated triflate oxygens [O(11) and O(21)] to make close bridging contacts of *ca.* 3.00 and 2.82 Å with Cu(2) and Cu(1), respectively. The $Re_2(NBu^t)_6$ unit is symmetrical at the two Re atoms and close to symmetrical in the two Re–N–Re bridges. The unsupported $Re(\mu\text{-}NBu^t)Cu$ bridge is unusual; $\mu\text{-}NBu^t$ bridges supported by metal–metal bonds have been reported for Zr–Ir[3a] and Ir–Ir.[3b]



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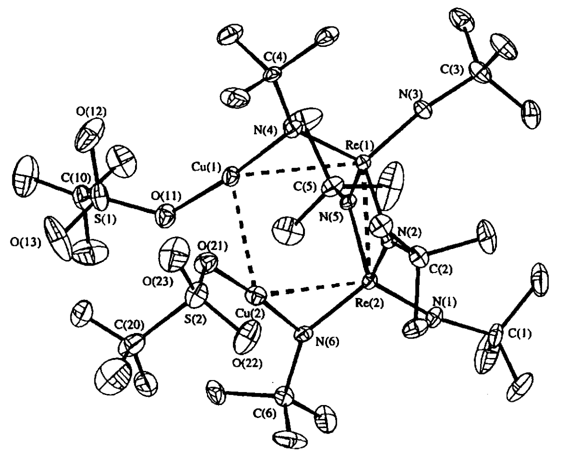


Fig. 3 Structure of $[(Bu^tN)Re(\mu\text{-}NBu^t)]_2(\mu\text{-}NBu^t)_2Cu_2(O_3SCF_3)_2$ **5**

Table 4 Selected bond lengths (Å) and angles (°) for $[(Bu^tN)Re(\mu\text{-}NBu^t)]_2(\mu\text{-}NBu^t)_2Cu_2(O_3SCF_3)_2$ **5** with e.s.d.s in parentheses

Re(1) ••• Re(2)	2.6959(6)	Re(2)–N(2)	1.903(7)
Re(1) ••• Cu(1)	2.847(2)	Re(2)–N(5)	1.952(6)
Re(2) ••• Cu(2)	2.848(1)	Re(2)–N(6)	1.823(7)
Cu(1) ••• Cu(2)	2.695(2)	Cu(1) ••• O(21)	2.820(6)
Re(1)–N(2)	1.954(6)	Cu(1)–N(4)	1.881(7)
Re(1)–N(3)	1.707(7)	Cu(1)–O(11)	1.877(7)
Re(1)–N(4)	1.831(7)	Cu(2) ••• O(11)	3.001(6)
Re(1)–N(5)	1.925(7)	Cu(2)–N(6)	1.860(7)
Re(2)–N(1)	1.726(7)	Cu(2)–O(21)	1.871(7)
N(2)–Re(1)–N(3)	112.7(3)	N(1)–Re(2)–N(5)	112.4(3)
N(2)–Re(1)–N(4)	112.6(3)	N(1)–Re(2)–N(6)	111.6(3)
N(2)–Re(1)–N(5)	91.2(3)	N(2)–Re(2)–N(5)	91.9(3)
N(3)–Re(1)–N(4)	111.5(3)	N(2)–Re(2)–N(6)	113.5(3)
N(3)–Re(1)–N(5)	113.0(3)	N(5)–Re(2)–N(6)	112.9(3)
N(4)–Re(1)–N(5)	114.6(3)	Re(1)–N(4)–Cu(1)	100.1(3)
Re(1)–N(2)–C(2)	132.7(5)	N(4)–Cu(1)–O(11)	174.5(3)
Re(1)–N(3)–C(3)	168.9(7)	Re(2)–N(6)–Cu(2)	101.3(3)
Re(1)–N(4)–C(4)	141.1(6)	N(6)–Cu(2)–O(21)	175.2(3)
Re(1)–N(5)–C(5)	140.0(5)	C(4)–N(4)–Cu(1)	116.9(5)
Re(1)–N(2)–Re(2)	88.7(3)	C(6)–N(6)–Cu(2)	118.2(6)
Re(1)–N(5)–Re(2)	88.1(3)	S(1)–O(11)–Cu(1)	126.3(5)
Re(2)–N(1)–C(1)	167.7(7)	S(2)–O(21)–Cu(2)	123.7(4)
Re(2)–N(2)–C(2)	138.3(5)	O(11)–Cu(1)–O(21)	84.1(4)
Re(2)–N(5)–C(5)	131.8(6)	O(21)–Cu(1)–N(4)	100.2(4)
Re(2)–N(6)–C(6)	139.7(6)	O(11)–Cu(2)–O(21)	79.2(5)
N(1)–Re(2)–N(2)	113.2(3)	O(11)–Cu(2)–N(6)	102.8(5)

The ^1H NMR spectrum of compound **5** shows sharp resonances for NBu^t groups bridging rhenium atoms while those bridging Re and Cu and terminal $Re(NBu^t)$ groups give a broad envelope at 25 °C in CD_2Cl_2, possibly due to fast interconversions. The silver compound **4** gave three distinct resonances in a 1:1:1 ratio. The comparable reactions of $Mn_2(NBu^t)_6$ with copper(I) triflate gave only intractable products.

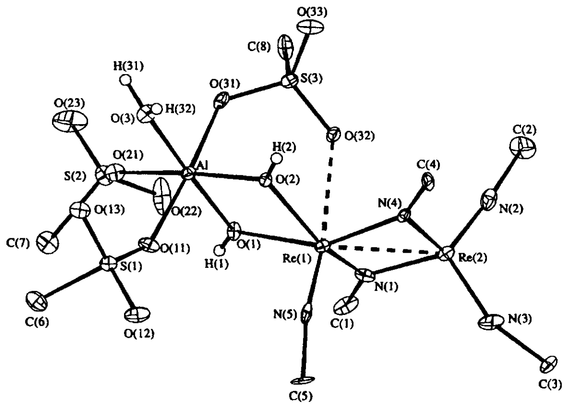
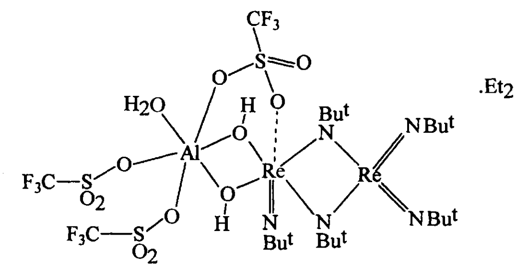


Fig. 4 Structure of $(Bu^tN)_2Re(\mu\text{-}NBu^t)_2Re(NBu^t)(\mu\text{-}OH)_2Al(O_3SCF_3)_3(H_2O)$ **6** with *tert*-butyl and triflate fluorine atoms (and the solvate Et_2O molecule) omitted for clarity



III

The interaction of **1** with 'aluminium triflate', $Al(O_3SCF_3)_3\cdot nCF_3SO_3H$, prepared by interaction of aluminium powder with anhydrous triflic acid (see Experimental section) gave a yellow crystalline product the structure of which is shown schematically in **III** and in Fig. 4; bond lengths and angles are given in Table 5. This structure shows that a different kind of reaction has occurred. One terminal $Re\equiv NBu^t$ function has been cleaved, and the imido function replaced by a bidentate, chelate (Al, O, O) function in which the bridges are hydroxo groups. A water molecule is bound to Al *trans* to one bridging OH group in a *mer*-octahedral aluminium complex, of which three co-ordination sites are filled by monodentate triflate ligands. The unsubstituted atom Re(1) has a pseudo-octahedral structure completed by a short contact with an oxygen atom from one triflate group [Re(1) ••• O(32) 2.601(7) Å]. In spite of the asymmetry between the two Re atoms the two Re–N–Re bridges are approximately symmetrical.

Experimental

Analyses were by the Imperial College microanalytical laboratory. Proton NMR data were obtained on a JEOL EX-270 spectrometer operating at 270 MHz (^1H) and Bruker Avance DRX 300 at 300 MHz and referenced to the residual hydrogen impurity in the solvent (δ 7.15, C_6D_6, δ 5.3, CD_2Cl_2). Mass spectra were obtained using VG 7070E (electron impact, EI) and Autospec spectrometers and compared with simulated spectra to good agreement.

Commercial chemicals were from Aldrich and Avocado. The light petroleum used had b.p. 40–60 °C and all solvents were purified by standard methods and degassed before use. All operations were carried out under purified Ar or N_2, in vacuum or in a Vacuum Atmospheres glove-box.

Literature procedures were used for $Re(NBu^t)_3(OSiMe_3)$[7] and $CuO_3SCF_3\cdot 0.5C_6H_6$.[8] The '$Al(O_3SCF_3)_3\cdot nCF_3SO_3H$' was obtained by dropwise addition of CF_3SO_3H (10 cm^3) to aluminium powder (*ca.* 1 g) and refluxing the mixture for *ca.* 6 h. The excess of CF_3SO_3H was removed in vacuum (100 °C, 10^{-3} mmHg) and the residual grey-white powder after washing with light petroleum and diethyl ether was heated in vacuum (150 °C 10^{-3} mmHg) for 12 h then cooled and used in the synthesis of compound **6**. The powder shows IR bands at 3550 [ν(OH)] and 1260 cm^{-1} (CF_3SO_3).[9] Extended heating (200 °C, 2 d in

Table 5 Selected bond lengths (Å) and angles (°) for $(\mathrm{Bu^tN})_2\mathrm{Re}(\mu\text{-}\mathrm{NBu^t})_2\mathrm{Re}(\mathrm{NBu^t})(\mu\text{-}\mathrm{OH})_2\mathrm{Al}(\mathrm{O_3SCF_3})_3(\mathrm{H_2O})\cdot\mathrm{Et_2O}$ **6** with e.s.d.s in parentheses

Re(1) ••• Re(2)	2.660(2)	Re(2)–N(3)	1.739(10)
Re(1)–N(1)	1.909(9)	Re(2)–N(4)	1.918(9)
Re(1)–N(4)	1.932(9)	Al–O(1)	1.838(8)
Re(1)–N(5)	1.655(10)	Al–O(2)	1.868(7)
Re(1)–O(1)	2.601(7)	Al–O(3)	1.854(9)
Re(1)–O(2)	2.113(7)	Al–O(11)	1.967(8)
Re(1) ••• O(32)	2.601(7)	Al–O(21)	1.875(8)
Re(2)–N(1)	1.894(9)	Al–O(31)	1.934(8)
Re(2)–N(2)	1.691(11)		
N(1)–Re(1)–N(4)	91.2(4)	N(1)–Re(2)–N(4)	92.1(4)
N(1)–Re(1)–N(5)	104.7(4)	N(2)–Re(2)–N(3)	114.0(5)
N(1)–Re(1)–O(1)	94.6(3)	N(2)–Re(2)–N(4)	113.3(4)
N(1)–Re(1)–O(2)	153.3(3)	N(3)–Re(2)–N(4)	111.3(4)
N(1)–Re(1)–O(32)	81.9(3)	Re(1)–O(1)–Al	107.1(3)
N(4)–Re(1)–N(5)	104.7(4)	Re(1)–O(2)–Al	103.9(3)
N(4)–Re(1)–O(1)	152.1(3)	O(1)–Al–O(2)	79.7(3)
N(4)–Re(1)–O(2)	94.1(3)	O(1)–Al–O(3)	176.9(4)
N(4)–Re(1)–O(32)	79.0(3)	O(1)–Al–O(11)	90.9(4)
N(5)–Re(1)–O(1)	100.2(4)	O(1)–Al–O(21)	94.2(3)
N(5)–Re(1)–O(2)	99.3(4)	O(1)–Al–O(31)	91.8(4)
N(5)–Re(1)–O(32)	172.2(4)	O(2)–Al–O(3)	97.3(4)
O(1)–Re(1)–O(2)	69.4(3)	O(2)–Al–O(11)	91.2(3)
O(1)–Re(1)–O(32)	74.8(3)	O(2)–Al–O(21)	173.9(4)
O(2)–Re(1)–O(32)	73.5(3)	O(2)–Al–O(31)	92.2(3)
Re(1)–N(4)–Re(2)	87.4(4)	O(3)–Al–O(11)	90.0(4)
Re(1)–N(1)–Re(2)	88.8(3)	O(3)–Al–O(21)	88.8(4)
Re(1)–N(1)–C(1)	137.8(8)	O(3)–Al–O(31)	87.5(4)
Re(1)–N(4)–C(4)	138.1(7)	O(11)–Al–O(21)	89.3(4)
Re(1)–N(5)–C(5)	167.1(8)	O(11)–Al–O(31)	176.0(4)
Re(2)–N(1)–C(1)	133.5(8)	O(21)–Al–O(31)	87.6(3)
Re(2)–N(2)–C(2)	174.8(9)	S(1)–O(11)–Al	146.9(5)
Re(2)–N(3)–C(3)	154.9(9)	S(2)–O(21)–Al	134.6(6)
Re(2)–N(4)–C(4)	134.4(7)	S(3)–O(31)–Al	128.6(4)
N(1)–Re(2)–N(2)	112.2(4)	S(3)–O(32)–Re(1)	127.4(4)
N(1)–Re(2)–N(3)	112.0(4)		

vacuum) did not remove OH bands in the IR spectra; use of this material for reaction with **1** gave only reduced yields of the triflate **3**. The substance $\mathrm{Al(O_3SCF_3)_3\cdot 3MeCN}$ made by interaction of $\mathrm{AlCl_3}$ and $\mathrm{AgO_3SCF_3}$ in MeCN[10] did not react with **1** in $\mathrm{CH_2Cl_2}$.

Preparations

Tris(*tert*-butylimido)iodorhenium(VII) 2. To a solution of $\mathrm{Re(NBu^t)_3(OSiMe_3)}$ (12 g, 24.6 mmol) in benzene (100 $\mathrm{cm^3}$) was added $\mathrm{SiMe_3I}$ (6.1 g, 30.7 mmol) and the yellow mixture stirred for 24 h at room temperature when it was orange-red. Removal of volatiles, extraction of the residue with light petroleum (3 × 50 $\mathrm{cm^3}$), concentration of the extracts to *ca.* 10 $\mathrm{cm^3}$ and cooling (−10 °C) gave orange crystals. Yield: 10.5 g, *ca.* 81%. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.31 (s, 27 H, $\mathrm{NBu^t}$). Mass spectrum (EI): *m*/*z* 527 (M^+), 512 (M^+ − Me), 456 (M^+ − $\mathrm{NBu^t}$) and 400 (M^+ − I).

Bis[μ-*tert*-butylimidodi-*tert*-butylimidorhenium(VI)] 1. To a solution of $\mathrm{Re(NBu^t)_3I}$ (10 g, 19.0 mmol) in $\mathrm{Et_2O}$ (*ca.* 100 $\mathrm{cm^3}$) at 0 °C was added Na/Hg (19.0 $\mathrm{cm^3}$ of 0.42% w/w, 47.5 mmol) and after allowing to warm over 12 h with stirring, removal of mercury, evaporation of the green-yellow solution to dryness and crystallisation of the residue from light petroleum (twice at −20 °C) gave yellow crystals spectroscopically identical with those obtained previously.[2] Yield: 6 g, *ca.* 80%.

[(*tert*-Butylamido)bis(μ-*tert*-butylimido)tris(*tert*-butylimido)-dirhenium(VI)]trifluoromethanesulfonate 3. To a solution of compound **1** in light petroleum (0.2 g, 0.25 mmol in 30 $\mathrm{cm^3}$) at −78 °C was added dropwise with rapid stirring a solution of $\mathrm{CF_3SO_3H}$ in $\mathrm{Et_2O}$ (0.35 mmol in 10 $\mathrm{cm^3}$). A yellow precipitate should be obtained but if acid addition is too rapid an oil may result. After slow warming (0.5 h) to room temperature the volatiles were removed and the residue was washed with light petroleum (3 × 20 $\mathrm{cm^3}$); extraction into tetrahydrofuran (thf) (20 $\mathrm{cm^3}$) and layering with light petroleum gave crystals. Yield: 0.12 g, *ca.* 51%. X-Ray-quality crystals were obtained by layering a dichloromethane solution with $\mathrm{Et_2O}$. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 7.6 (s, br, 1 H, $\mathrm{Me_3CN}H$), 1.76 (s, 18 H, μ-$\mathrm{Me_3CN}$), 1.33, 1.31 and 1.26 (s, 9 H each, terminal $\mathrm{Me_3CN}$), 0.85 (s, 9 H, Me_3CNH).

$\{[(\mathrm{Bu^tN})\mathrm{Re}(\mu\text{-}\mathrm{NBu^t})]_2(\mu\text{-}\mathrm{NBu^t})_2\mathrm{Ag}(\mu\text{-}\mathrm{O_3SCF_3})\}_2$ 4. A solution of compound **1** (0.3 g, 0.36 mmol) and $\mathrm{AgO_3SCF_3}$ (0.1 g, *ca.* 0.36 mmol) in $\mathrm{CH_2Cl_2}$ (50 $\mathrm{cm^3}$) was stirred in the dark at room temperature for 3 d. After removal of solvent, washing the residue with light petroleum (2 × 20 $\mathrm{cm^3}$), extraction into $\mathrm{Et_2O}$ (3 × 30 $\mathrm{cm^3}$), filtration, concentration of the filtrate until crystallisation started and cooling (−20 °C) gave pale yellow plate-like crystals. Yield: 0.28 g, *ca.* 75%. X-Ray-quality crystals were obtained by slowly cooling dilute $\mathrm{Et_2O}$ solutions. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.65 (s, 36 H, μ-$\mathrm{NCMe_3}$), 1.46 (s, 36 H, μ-$\mathrm{NCMe_3}$) and 1.19 (s, 36 H, $\mathrm{NCMe_3}$).

$[(\mathrm{Bu^tN})\mathrm{Re}(\mu\text{-}\mathrm{NBu^t})]_2(\mu\text{-}\mathrm{NBu^t})_2\mathrm{Cu_2(O_3SCF_3)_2}$ 5. A solution of compound **1** (0.3 g, 0.36 mmol) and $\mathrm{CuO_3SCF_3\cdot 0.5C_6H_6}$ (0.31 g, 0.8 mmol) in $\mathrm{CH_2Cl_2}$ (50 $\mathrm{cm^3}$) was stirred in the dark at room temperature (4 d). After removal of volatiles, washing the residue with light petroleum (2 × 20 $\mathrm{cm^3}$), extraction into $\mathrm{Et_2O}$ (3 × 20 $\mathrm{cm^3}$), filtration, concentration and cooling of the extracts gave yellow crystals. Yield: 0.24 g, 55%. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.8 (s, 18 H, μ-$\mathrm{NCMe_3}$), 1.6–1.4 (br, s, 36 H, μ-$\mathrm{NCMe_3}$ + $\mathrm{NCMe_3}$).

Reaction of compound 1 with $\mathrm{Al(O_3SCF_3)_3}\cdot n\mathrm{CF_3SO_3H}$ to give 6. To a solution of compound **1** (0.2 g, 0.25 mmol) in $\mathrm{CH_2Cl_2}$ (30 $\mathrm{cm^3}$) was added a suspension of '$\mathrm{Al(O_3SCF_3)_3}\cdot n\mathrm{CF_3SO_3H}$' (0.3 g) in the same solvent. The yellow reaction mixture was stirred at room temperature (2 d). After removal of volatiles under reduced pressure, washing the residue with light petroleum (2 × 20 $\mathrm{cm^3}$), extraction into $\mathrm{Et_2O}$ (3 × 30 $\mathrm{cm^3}$), filtration, concentration of the filtrate to *ca.* 30 $\mathrm{cm^3}$ and cooling (−20 °C) gave yellow crystals. Yield: 0.22 g; 73% based on rhenium. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): 3.4 [q, 4 H, $(\mathrm{CH_3C}H_2)_2\mathrm{O}$], 1.9 (s, 18 H, μ-$\mathrm{NCMe_3}$), 1.5, 1.4 and 1.3 (s, 9 H each, terminal $\mathrm{NCMe_3}$) and 1.2 [t, 6 H, $(\mathrm{C}H_3\mathrm{CH_2})_2\mathrm{O}$]; broad peaks at δ 6.8 and 8.6 are due to μ-OH and $\mathrm{H_2O}$ although no assignment was made. IR (Nujol mull): 3350 and 3250 $\mathrm{cm^{-1}}$ (br, OH).

X-Ray crystallography

X-Ray data for compounds **3**–**6** were collected at low temperature; details are listed in Table 6. A FAST TV area detector diffractometer with Mo-Kα radiation (λ = 0.710 69 Å) was employed, as previously described.[11] Compounds **3** and **4** were solved using the PATT instruction of SHELXS 86,[12] whilst **5** and **6** were solved *via* direct methods procedures of the same program. The structures were refined by full-matrix least squares on F_o^2, using the program SHELXL 93.[13] All data used were corrected for Lorentz-polarisation factors, and subsequently for absorption using the program DIFABS[14] with maximum and minimum correction factors listed in Table 6. The non-hydrogen atoms were refined with anisotropic thermal parameters. However, for compound **3** nitrogens N(1) and N(2) showed 'cigar-shaped' ellipsoids and we interpreted this in terms of disorder of one linear imido and one bent amido function at each site. Accordingly, these atoms were replaced by two separated half-atoms, which were refined isotropically. All hydrogen atoms in the four compounds were included in idealised positions, except the two water hydrogen atoms in **6**

Table 6 Crystal data and structure refinement details for compounds **3**–**6** *

Compound	**3**	**4**	**5**	**6**
Formula	$[C_{24}H_{55}N_6Re_2][CF_3O_3S]$	$C_{50}H_{108}Ag_2F_6N_{12}O_6Re_4S_2$	$C_{26}H_{54}Cu_2F_6N_6O_6Re_2S_2$	$C_{23}H_{49}AlF_9N_5O_{12}Re_2S_3{\cdot}C_4H_{10}O$
M_r	949.22	2112.17	1224.38	1328.37
a/Å	13.385(6)	17.069(9)	10.659(2)	14.43(1)
b/Å	14.770(5)	11.226(6)	19.382(9)	10.110(4)
c/Å	19.673(1)	19.882(6)	20.739(2)	33.366(7)
β/°	101.93(4)	99.24(9)	94.973(9)	93.70(2)
U/Å^3	3805(2)	3760(3)	4268(2)	4858(4)
Z	4	2	4	4
D_c/Mg m^{-3}	1.657	1.865	1.905	1.816
F(000)	1856	2040	2376	2608
Crystal colour	Yellow	Yellow	Deep yellow	Yellow
Crystal size/mm	0.40 × 0.21 × 0.10	0.48 × 0.30 × 0.18	0.30 × 0.27 × 0.27	0.11 × 0.09 × 0.06
μ(Mo-Kα)/mm^{-1}	6.206	6.749	6.554	5.021
Collection temperature/K	170	200	150	120
Reflections collected	13 648	14 957	17 597	14 489
Independent reflections (R_{int})	5662(0.0747)	5643(0.0876)	6454 (0.0566)	7269 (0.1278)
Maximum, minimum correction factors	1.273, 0.829	1.477, 0.718	1.167, 0.870	1.082, 0.751
Data, restraints, parameters	5661, 0, 406	5640, 0, 388	6451, 0, 469	7264, 0, 566
Goodness of fit S on F^2	1.018	1.003	1.032	0.962
Final $R1$, $wR2$				
$[I > 2\sigma(I)]$	0.0459, 0.1053	0.0552, 0.1286	0.0517, 0.1209	0.0523, 0.1173
(all data)	0.0540, 0.1082	0.0684, 0.1328	0.0575, 0.1245	0.0868, 0.1391
Largest difference peak and hole/e Å^{-3}	4.419, −1.801	6.052, −2.578	6.416, −1.195	1.796, −1.308

* Details in common: monoclinic, space group $P2_1/c$; $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{\frac{1}{2}}$; $R1 = \Sigma[(F_o - F_c)]/\Sigma F_o$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + gP]$, $P = [\max(F_o^2) + 2F_c^2]/3$; n = number of reflections and p = total number of parameters; x = 0.0545, 0.0761, 0.0851 and 0.0424 for compounds **3**, **4**, **5** and **6** respectively; g = 0.

which were experimentally located from the difference map, and the hydrogens on N(1) and N(2) in **3**, which were not included. The two components of the CF_3SO_3 ion also showed disorder in this complex, with two oxygens and two fluorines being represented by split sites. The equations used in the refinement, the weighting scheme and parameters employed for each compound are included in Table 6.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/109.

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