Isodiazene Complexes: Synthesis and Molecular Structures of 2,2,6,6-Tetramethylpiperid-1-ylisodiazene Complexes of Tungsten(IV) and of Rhenium-(III) and -(II)†

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The interaction of 1-amino-2,2,6,6-tetramethylpiperidine, $C_9H_{18}NNH_2$, in refluxing NEt_3–$SiClMe_3$ with WO_2Cl_2(dme) (dme = 1,2-dimethoxyethane), and with $ReO_3(OSiMe_3)$ gave, respectively, $W(C_9H_{18}N_2)_2Cl_3(OSiMe_3)$ **1** and $Re(C_9H_{18}N_2)_2Cl_2(OSiMe_3)$ **3**. The interaction of **3** with HCl in Et_2O gave $Re(C_9H_{18}N_2)_2Cl_3$ **4**, which reacted with AgO_3SCF_3 in MeCN to give $[Re(\mu\text{-}O)(C_9H_{18}N_2)_2(MeCN)_2]_2[O_3SCF_3]_4$ **5**, and with excess of $C_9H_{18}N_2HLi$ in tetrahydrofuran (thf) to give $[ReO(C_9H_{18}N_2)_2]_2$ **6**. The X-ray crystal structures of five compounds, **1** and **3**–**6**, have been determined; all are formulated as having 2,2,6,6-tetramethylpiperid-1-ylnitrene ligands that formally can be regarded as isodiazenes. The tungsten complex **1** has C_s symmetry and is octahedral with *cis*-$C_9H_{18}N_2$ groups and *fac* chlorides. The rhenium complexes **3** and **4** are both trigonal bipyramidal with equatorial N and axial Cl atoms. The cation in **5** comprises two edge-sharing distorted octahedra with *cis*-N and *trans*-NCMe and a planar symmetrical $Re(\mu\text{-}O)_2Re$ bridge; the Re_2O_2 ring has a large rhombic distortion with a consequent short non-bonded transannular O···O distance. The dimeric complex **6** is C_2 symmetric with two distorted tetrahedral Re centres linked by a Re–Re single bond in a near-eclipsed conformation. In all the structures the metal–nitrogen and N–N bonds display significant multiple-bond character and the M–N–N angles are all essentially linear. In the rhenium complexes **3**–**6** there are varying small degrees of pyramidalisation at the *exo* N atoms which approximately correlate with the N–N double-bond character; the sum of the Re–N and N–N bond distances remains essentially constant.

The chemistry, both synthetic and structural, of transition-metal complexes with ligands having N–N bonds of the type NNR, NNR_2, N(H)NR, *etc.* (R = H, alkyl, aryl and other groups) has been extensively reviewed[1] and is still an active area of study.[2] There are still ambiguities in compounds with N_2R_2 ligands, particularly as to the extent of M–N and N–N multiple bonding, whether the groups are formulated as (1−) or (2−), are linear or bent, and so on. One aspect, in particular, is the question of the oxidation state of the metal; some years ago Chatt *et al.*,[3] apropos the compound $WCl_3(NNH_2)(PMe_2Ph)_2$ where X-ray data indicated very strong conjugation along the W–N–N chain, wrote: 'Structurally this ligand appears to be closer to isodiazene than hydrazido (2−) but we retain the latter name because of its common usage and the IUPAC recommendations'. Other examples of what can be properly called isodiazene complexes have been given[1b] and a particularly clear example is that of iron porphyrinato compounds, $Fe(por)(N_2C_9H_{18})$[4] (por = 5,10,15,20-tetraphenylporphyrinate and related porphyrinates, $C_9H_{18}N$ = 2,2,6,6-tetramethylpiperid-1-yl), that were made either by aerobic reaction of Fe^{III}(por)Cl with the hydrazine $C_9H_{18}NNH_2$[5] or by anaerobic interaction of Fe^{II}(por) with the free 2,2,6,6-tetramethylpiperid-1-ylnitrene,[5b] $C_9H_{18}N_2$, at −80 °C. On the basis of structural, EPR and especially Mössbauer spectra it was concluded[4] that iron was in the II oxidation state clearly implying a neutral N-bonded isodiazene ligand. The Fe–N–N group was linear with Fe–N 1.809(4) Å and N–N 1.232(5) Å indicating multiple-bond character. Bond lengths and angles for a number of $MNNR_2$ species, mainly for Mo and W, have been collected.[1b,6]

There has been further recent discussion of other such isodiazene compounds in connection with the structure of *fac*-$[W({=}NNMe_2)(CO)_3(dppe)]$[dppe = 1,2-bis(diphenylphosphino)ethane], referred to as 'a nitrene analogue to Fischer carbenes';[7] the W–N–N angle here, however, was 139(1)° and the W–N bond was 'exceptionally long 2.12(1) Å, over 0.28 Å longer than previously reported linear (1.73–1.78) or bent tungsten hydrazido complexes'. The N–N distance was 1.21(2) Å.

The present work began with the idea of obtaining compounds with more than the known (*i.e.*, one or two only) number of NNR_2 ligands since imido (NR^{2-}) compounds in high oxidation states such as $Os(NBu^t)_4$[8a] and $LiRe(NBu^t)_4$[8b] are well established.

Since no metal compounds derived from $C_9H_{18}NNH_2$ or $C_9H_{18}N_2$ other than the iron(II) porphyrinates[4] have been made, this system seemed to merit further study. We now describe, amongst others, $W(C_9H_{18}N_2)_2Cl_3(OSiMe_3)$ **1** which, if $C_9H_{18}N_2$ were taken as hydrazido(2−) would require formulation of the compound with tungsten in the impossible oxidation state of VIII, and the dimeric $[ReO(C_9H_{18}N_2)_2]_2$ **6** that has a Re–Re single bond and is similar to a $Re^{II}{}_2O_2(alkyne)_4$ complex as discussed later. A similar argument, that having three bridging hydrazido(2−) ligands in a vanadium complex would lead to too high an oxidation state for V–V single bonding to occur, has recently been used to suggest the presence of an $NNMe_2$ bridging isodiazene.[2d]

Analytical and physical data for the new compounds are given in Table 1.

Results and Discussion

The interaction of $C_9H_{18}NNH_2$ in the presence of NEt_3 or pyridine, or of molecular sieves, with Re_2O_7, WO_3 or WO_2Cl_2(dme) (dme = 1,2-dimethoxyethane) produces only

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical and physical data for the new compounds

	Compound	Colour	M.p./°C	Analysis[a] (%) C	H	N
1	$W(C_9H_{18}N_2)_2Cl_3(OSiMe_3)$	Yellow	197	35.5 (36.6)	6.2 (6.5)	8.3 (8.2)
2	$ReO_3(C_9H_{18}N_2H)\cdot(C_9H_{18}N_2H_3)^+ReO_4^-$	Yellow-green	—	26.4 (27.6)	5.0 (4.9)	6.9 (7.1)
3	$Re(C_9H_{18}N_2)_2Cl_2(OSiMe_3)$	Yellow	214–6	38.4 (38.5)	6.9 (7.2)	8.5 (8.5)
4	$Re(C_9H_{18}N_2)_2Cl_3$	Yellow	> 240	36.0 (36.1)	6.0 (6.0)	9.3 (9.3)
5	$[Re(\mu\text{-}O)(C_9H_{18}N_2)_2(MeCN)_2]_2[O_3SCF_3]_4$[b]	Orange-red	177	28.9 (30.6)	4.3 (4.5)	8.2 (8.6)
6	$[ReO(C_9H_{18}N_2)_2]_2$	Orange	> 230	41.4 (42.3)	6.8 (7.0)	10.8 (10.9)

[a] Calculated values in parentheses. [b] F analysis 13.2 (13.0)%.

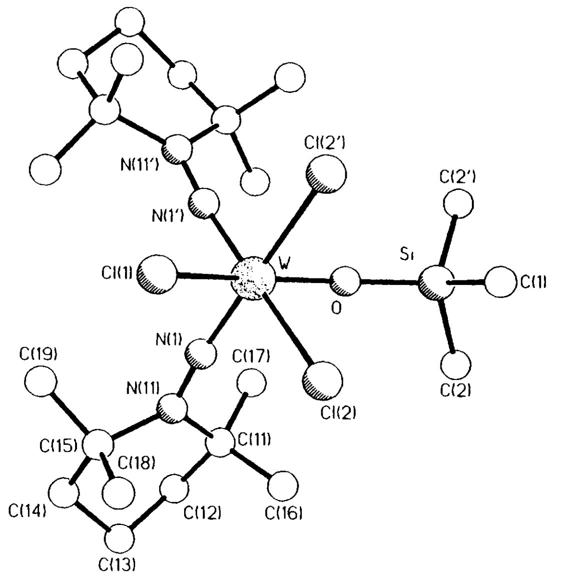

Fig. 1 The structure of $W(C_9H_{18}N_2)_2Cl_3(OSiMe_3)$ **1**

intractable products; however, $ReO_3(OSiMe_3)$ gives a complex that can be formulated on the basis of analytical and spectroscopic data as $ReO_3(C_9H_{18}N_2H)\cdot(C_9H_{18}N_2H_3)^+ReO_4^-$ **2** (see Experimental section). Thus, although the ligand metal ratio is 1 : 1, there are two Me and two broad NH peaks in the ^1H NMR spectrum indicative of two ligand types. IR data show three different N–H bands while in the oxo region there are two strong peaks and a shoulder for ReO_4^- and $ReO_3(C_9H_{18}N_2H)$. The use of pre-formed silylhydrazine, $C_9H_{18}NNH(SiMe_3)$ with oxo species, a method that is successful in the synthesis of imido compounds by reaction of metal oxides with silylamines,[6] gives incomplete conversions or difficulties in isolating clean products. We hence adopted a modification of a method used[9] for synthesis of imido compounds from aromatic amines and $(NH_4)_2Mo_2O_7$ in the presence of $SiClMe_3$ and NEt_3 in 1,2-dimethoxyethane but using neat NEt_3 as solvent. The reactions of $WO_2Cl_2(dme)$ and $ReO_3(OSiMe_3)$ with, presumably $C_9H_{18}N_2H_n(SiMe_3)_{2-n}$ (n = 0 or 1), formed *in situ*, give good yields of $W(C_9H_{18}N_2)_2Cl_3(OSiMe_3)$ **1** and $Re(C_9H_{18}N_2)_2Cl_2(OSiMe_3)$ **3**. Additional $C_9H_{18}N_2$ groups could not be introduced even after prolonged refluxing in NEt_3.

Table 2 Atomic coordinates (× 10^4) for complex **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
W	464(1)	−415(1)	2500
Cl(1)	−138(3)	−1952(2)	2500
Cl(2)	−980(2)	−258(2)	3454(1)
O	483(5)	872(4)	2500
Si	−113(3)	1860(2)	2500
C(1)	−1618(10)	1798(9)	2500
C(2)	365(7)	2493(6)	3337(4)
N(1)	1469(4)	−591(3)	3250(3)
N(11)	2073(4)	−677(3)	3805(3)
C(11)	2462(5)	198(4)	4178(4)
C(12)	3413(6)	16(5)	4701(4)
C(13)	3257(7)	−823(6)	5174(4)
C(14)	3169(7)	−1630(6)	4676(4)
C(15)	2195(6)	−1610(4)	4152(4)
C(16)	1460(6)	582(5)	4578(4)
C(17)	2832(6)	831(5)	3577(4)
C(18)	1111(6)	−1808(6)	4548(4)
C(19)	2401(8)	−2272(5)	3536(4)
C	1402(12)	−4348(11)	2500
Cl	706(3)	−4498(3)	3289(2)

Table 3 Selected bond lengths (Å) and angles(°) for complex **1** with e.s.d.s in parentheses

W–Cl(1)	2.395(4)	W–Cl(2)	2.468(3)
W–O	1.911(6)	W–N(1)	1.841(5)
W–Cl(2')	2.468(3)	W–N(1')	1.841(5)
O–Si	1.635(7)	Si–C(1)	1.824(12)
Si–C(2)	1.874(8)	Si–C(2')	1.874(8)
N(1)–N(11)	1.248(7)	N(11)–C(11)	1.538(8)
N(11)–C(15)	1.529(8)		
Cl(1)–W–Cl(2)	82.8(1)	Cl(1)–W–O	163.0(2)
Cl(2)–W–O	85.1(1)	Cl(1)–W–N(1)	93.8(2)
Cl(2)–W–N(1)	88.0(2)	O–W–N(1)	97.7(2)
Cl(1)–W–Cl(2')	82.8(1)	Cl(2)–W–Cl(2')	88.8(1)
O–W–Cl(2')	85.1(1)	N(1)–W–Cl(2')	175.6(2)
Cl(1)–W–N(1')	93.8(2)	Cl(2)–W–N(1')	175.6(2)
O–W–N(1')	97.7(2)	N(1)–W–N(1')	94.9(3)
Cl(2')–W–N(1')	88.0(2)	W–O–Si	153.1(4)
W–N(1)–N(11)	173.8(4)	N(1)–N(11)–C(11)	116.5(5)
N(1)–N(11)–C(15)	118.7(5)	C(11)–N(11)–C(15)	123.7(5)

Tungsten.—The structure of the tungsten compound **1** is shown in Fig. 1; fractional coordinates are given in Table 2, selected bond lengths and angles are given in Table 3. The complex, which has crystallographic C_s symmetry, is distorted octahedral [co-ordination angles in the ranges 82.8(1)–97.7(2)° and 163.0(2)–175.6(2)°] with *cis*-$C_9H_{18}N_2$ groups and *fac* chlorides. The WNN unit is nearly linear, with N–N–W 173.8(4)° and the *exo*-N atom is almost trigonal planar: the N atom lies 0.09 Å out of the plane of its substituents. This plane coincides with the *mer* plane defined by $OSiMe_3$, Cl(1) and one of the equatorial Cl atoms [Cl(2')]. There are two types of W–Cl distances, the ones *trans* to N atoms being longer by 0.09 Å indicating a strong *trans* influence of the N ligand. There is evidently extensive multiple bonding in the W–N–N moiety with comparatively short W–N [1.841(5) Å] and very short N–N bonds [1.248(7) Å]. The former lies towards the upper end of the observed range for tungsten–nitrogen double bonds,[10] and the latter in the middle of the range for nitrogen–nitrogen double bonds.[11] For comparison, in $WCl_3(NNH_2)(PMe_2Ph)_2$, W–N 1.752(10), N–N 1.300(17) Å and W–N–N 178.7(9)°. A similar geometry is observed for the porphyrin complex;[4] other data are available.[1b,c,6]

Various resonance forms for MN_2R_2 compounds have been proposed[1b,c]: $M \longleftarrow \overset{-}{N}{=}\overset{+}{N}R_2$, $\overset{-}{M}{-}\ddot{N}{=}\overset{+}{\dot{N}}R_2$, $M{=}\ddot{N}{-}\ddot{N}R_2$, $\overset{-}{M}{\equiv}\overset{+}{N}{-}NR_2$. It is evident that the extent of M–N and N–N multiple bonding depends on the nature of the metal and its ligands; the situation commonly lies between the extremes making the assignment of the oxidation state of the metal ambiguous. For the majority of hydrazido(2−) species, the MNN moiety is close to linear and the geometry of the *exo*-N atom usually planar within statistical significance; the MNN moiety is acting as a four-electron donor.[3,4] Another example is $[Mo(NNMe_2)_2(bipy)_2]^{2+}$ (bipy = 2,2'-bipyridine),[12a] while in $[Mo_3S_8(NNMe_2)_2]^{2-}$,[12b] the N–N separation can be considered as isodiazene-like. For **1** only the isodiazene formulation gives a realistic tungsten oxidation state of IV with two four-electron donors giving an 18-electron count. The WNN multiple bonding implies low basicity of the N atom.

The ^1H NMR spectrum of **1** shows two groups of inequivalent methyls on the $C_9H_{18}N$ ring that are invariant over the range −80 to +70 °C suggesting that the solid-state structure is retained in solution, and that this inequivalence of the Me group is due to hindered rotation about the W–N and $C_9H_{18}N$–N bonds arising from steric and/or electronic factors.

The interaction of **1** with HCl in Et_2O will be discussed separately.

Rhenium.—The compound $ReO_3(C_9H_{18}N_2H)\cdot(C_9H_{18}N_2H_3)^+ReO_4^-$ **2** has been noted earlier. Interaction of $ReO_3(OSiMe_3)$ and $C_9H_{18}NNH_2$ under the same conditions as used for the tungsten reaction above, leads to $Re(C_9H_{18}N_2)_2Cl_2(OSiMe_3)$ **3**. Interaction of this with HCl in Et_2O produces Re $(C_9H_{18}N_2)_2Cl_3$ **4** with loss of the $OSiMe_3$ group. The structures of **3** and **4** are shown in Figs. 2 and 3 respectively; fractional atomic coordinates are given in Tables 4 and 5, selected bond lengths and angles are in Tables 6 and 7. Both **3**, which crystallises with two crystallographically independent molecules in the asymmetric unit, and **4** are trigonal bipyramidal with equatorial N and axial Cl atoms. There is a high degree of consistency in the Re–N and N–N bond lengths which are in the ranges 1.732(12)–1.763(12) and 1.278(17)–1.308(17) Å, respectively. The Re–N–N angles are all close to linear [172.2(10)–178.1(8)°]. These bond distances and angles again indicate a high degree of M–N and N–N multiple bonding and as in **1** the linear MNN and near planar C_2NN groups are maintained. The N atoms are all slightly pyramidalised though the out of plane deviations are small, ranging from 0.03 Å for N(21) in **4** to 0.13 Å for N(11) in **3**. In both structures the C_2N_2 planes are almost coincident with the equatorial plane; twist angles are in the range 1–11°. The axial Re–Cl bond lengths are in the range 2.389(3) (in **4**), to 2.415(4) Å (in **3**). The equatorial Re–Cl bond in **4** is significantly shorter at 2.315(3) Å. In both structures the Cl–Re–Cl axis is non-linear and folded by *ca.* 9° away from the $C_9H_{18}N_2$ ligands. As in **1** with the ligand being a neutral donor, the rhenium oxidation state in both cases is III, d^4, and an 18-electron count; d^4 is a very stable electronic configuration for trigonal-bipyramidal geometry.[13] The ^1H NMR spectra of **3** and **4** suggest that the solid-state structures are retained in solution. However, due to the equivalence by symmetry of the ring methyl groups, no conclusions can be drawn concerning rigidity although it is likely that rotation around the Re–NN bond is still hindered as in **1**.

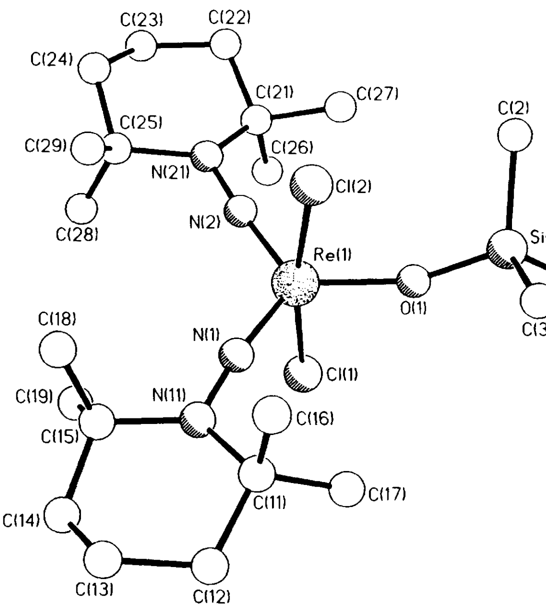

Fig. 2 The structure of one of the pair of crystallographically independent molecules of $Re(C_9H_{18}N_2)_2Cl_2(OSiMe_3)$ **3**. Both molecules have essentially identical conformations

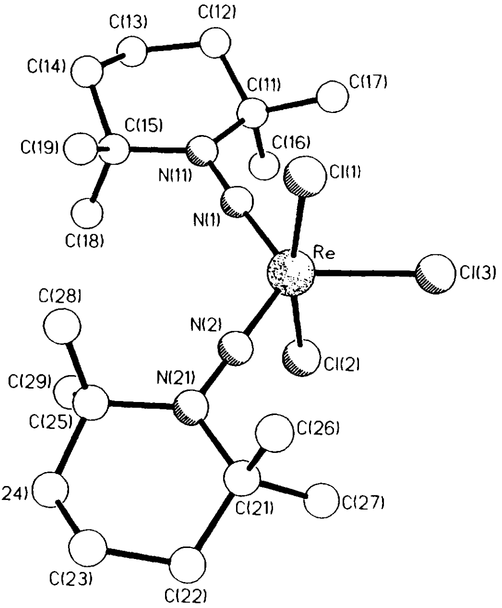

Fig. 3 The structure of $Re(C_9H_{18}N_2)_2Cl_3$ **4**

The nucleophilicity of the diazene nitrogens is low, as for **1**. Action of HCl in Et_2O preferentially attacks the Re–$OSiMe_3$ group of **3** to give **4** and use of excess does not give protonated, hydrazido(1−) species.

Interaction of **4** with AgO_3SCF_3 in MeCN leads to chloride substitution as well as the formation of μ-O groups in $[Re(\mu\text{-}O)(C_9H_{18}N_2)_2(MeCN)_2]_2[O_3SCF_3]_4$ **5**. The origin of the oxo groups is uncertain since no oxygenated solvents such as tetrahydrofuran (thf) were used, however the formation of oxo species from adventitious oxygen or water is quite common;[14] it is possible that oxygen could be abstracted from $O_3SCF_3^-$. The structure of **5** is shown in Fig. 4. Fractional atomic coordinates are given in Table 8 and bond lengths and angles are in Table 9. The cation, which is centrosymmetric, has two edge-sharing distorted octahedra with *cis*-N, *trans*-NCMe and a planar

Table 4 Atomic coordinates (× 10^4) for complex **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	2749(1)	4315(1)	−3218(1)	Re(1′)	2306(1)	6045(1)	−811(1)
Cl(1)	2479(3)	2341(3)	−3177(1)	Cl(1′)	2521(3)	6233(3)	−1461(1)
Cl(2)	3079(3)	6244(3)	−3357(1)	Cl(2′)	2100(3)	6182(3)	−159(1)
O(1)	2724(7)	4063(7)	−3732(2)	O(1′)	2355(7)	7629(6)	−808(2)
Si(1)	2870(3)	4568(3)	−4148(1)	Si(1′)	2314(3)	8810(3)	−592(1)
C(1)	2515(12)	3456(13)	−4470(4)	C(1′)	2526(12)	9919(11)	−949(4)
C(2)	2055(12)	5778(12)	−4246(4)	C(2′)	1081(13)	9022(15)	−381(5)
C(3)	4196(12)	4906(15)	−4216(5)	C(3′)	3303(12)	8900(13)	−230(4)
N(1)	3796(10)	4210(8)	−2938(3)	N(1′)	3374(9)	5207(9)	−759(3)
N(11)	4629(9)	4039(8)	−2756(3)	N(11′)	4193(9)	4661(10)	−704(3)
C(11)	5575(10)	4036(11)	−2989(4)	C(11′)	5120(12)	5350(13)	−760(4)
C(12)	6436(11)	3530(13)	−2764(5)	C(12′)	5999(12)	4776(15)	−564(5)
C(13)	6479(14)	3933(16)	−2364(6)	C(13′)	6043(13)	3540(17)	−639(5)
C(14)	5515(14)	3654(15)	−2175(5)	C(14′)	5095(13)	3007(13)	−507(5)
C(15)	4602(12)	4191(12)	−2345(4)	C(15′)	4135(12)	3431(12)	−692(4)
C(16)	5808(12)	5253(12)	−3100(5)	C(16′)	5324(10)	5425(14)	−1164(4)
C(17)	5393(11)	3353(12)	−3334(4)	C(17′)	4963(12)	6507(14)	−601(5)
C(18)	4535(13)	5430(13)	−2266(4)	C(18′)	3238(11)	3104(11)	−470(4)
C(19)	3682(14)	3591(14)	−2206(4)	C(19′)	4024(13)	2972(13)	−1091(4)
N(2)	1622(10)	4679(9)	−3007(3)	N(2′)	1186(9)	5305(10)	−881(3)
N(21)	791(10)	5018(10)	−2877(3)	N(21′)	336(9)	4880(9)	−960(3)
C(21)	−94(12)	4837(12)	−3113(4)	C(21′)	−538(12)	5649(14)	−926(5)
C(22)	−959(14)	5583(16)	−3011(6)	C(22′)	−1411(13)	5151(16)	−1143(6)
C(23)	−1116(13)	5623(17)	−2608(6)	C(23′)	−1588(14)	3912(16)	−1075(6)
C(24)	−228(15)	5995(17)	−2413(5)	C(24′)	−667(15)	3313(15)	−1171(6)
C(25)	764(13)	5333(14)	−2476(4)	C(25′)	263(13)	3624(12)	−966(5)
C(26)	−375(14)	3632(13)	−3117(5)	C(26′)	−774(12)	5803(13)	−527(5)
C(27)	180(12)	5103(18)	−3516(5)	C(27′)	−271(12)	6762(11)	−1101(4)
C(28)	763(19)	4324(17)	−2254(5)	C(28′)	1142(11)	3201(12)	−1171(4)
C(29)	1624(12)	6087(13)	−2406(4)	C(29′)	274(13)	3183(13)	−585(5)

Table 5 Atomic coordinates (× 10^4) for complex **4** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Re	2222(1)	7238(1)	1336(1)
Cl(1)	3295(3)	9006(3)	1037(2)
Cl(2)	1406(3)	5310(3)	1548(2)
Cl(3)	3839(3)	6236(3)	854(2)
N(1)	529(9)	7645(7)	962(4)
N(11)	−685(8)	7950(8)	664(4)
C(11)	−1075(12)	7362(12)	76(5)
C(12)	−2225(15)	8046(16)	−295(6)
C(13)	−3458(13)	8437(14)	15(6)
C(14)	−2880(14)	9209(14)	505(6)
C(15)	−1720(11)	8611(11)	970(5)
C(16)	−1575(17)	6123(13)	175(7)
C(17)	266(18)	7263(16)	−204(7)
C(18)	−2379(15)	7789(14)	1348(6)
C(19)	−893(14)	9607(12)	1296(7)
N(2)	2675(9)	7569(7)	2078(4)
N(21)	2967(10)	7798(9)	2626(4)
C(21)	4423(11)	7439(10)	2929(4)
C(22)	4485(28)	7341(17)	3593(4)
C(22′)	4958(18)	8143(30)	3485(9)
C(23)	3757(16)	8388(16)	3847(6)
C(24)	2306(20)	8421(23)	3572(6)
C(25)	1885(12)	8488(11)	2923(5)
C(26)	5440(24)	8354(16)	2729(12)
C(26′)	5596(22)	7514(22)	2539(11)
C(27)	4758(28)	6209(12)	2711(12)
C(27′)	4257(36)	6166(16)	3129(17)
C(28)	1840(14)	9690(11)	2678(7)
C(29)	485(14)	7866(12)	2786(7)

Table 6 Selected bond lengths (Å) and angles (°) for complex **3** with e.s.d.s in parentheses

Re(1)–Cl(1)	2.405(4)	Re(1)–Cl(2)	2.415(4)
Re(1)–O(1)	1.895(8)	Re(1)–N(1)	1.732(12)
Re(1)–N(2)	1.758(12)	O(1)–Si(1)	1.647(9)
N(1)–N(11)	1.308(17)	N(11)–C(11)	1.533(18)
N(11)–C(15)	1.510(17)	N(2)–N(21)	1.282(18)
N(21)–C(21)	1.476(20)	N(21)–C(25)	1.509(20)
Re(1′)–Cl(1′)	2.400(4)	Re(1′)–Cl(2′)	2.397(4)
Re(1′)–O(1′)	1.905(7)	Re(1′)–N(1′)	1.759(12)
Re(1′)–N(2′)	1.763(12)	O(1′)–Si(1′)	1.623(9)
N(1′)–N(11′)	1.294(17)	N(11′)–C(11′)	1.509(20)
N(11′)–C(15′)	1.480(18)	N(2′)–N(21′)	1.278(17)
N(21′)–C(21′)	1.499(20)	N(21′)–C(25′)	1.514(18)
Cl(1)–Re(1)–Cl(2)	171.2(1)	Cl(1)–Re(1)–O(1)	84.4(3)
Cl(2)–Re(1)–O(1)	87.0(3)	Cl(1)–Re(1)–N(1)	90.7(3)
Cl(2)–Re(1)–N(1)	92.6(3)	O(1)–Re(1)–N(1)	125.2(5)
Cl(1)–Re(1)–N(2)	95.0(4)	Cl(2)–Re(1)–N(2)	90.8(4)
O(1)–Re(1)–N(2)	117.7(5)	N(1)–Re(1)–N(2)	117.1(6)
Re(1)–O(1)–Si(1)	148.1(6)	Re(1)–N(1)–N(11)	172.8(9)
N(1)–N(11)–C(11)	115.3(10)	N(1)–N(11)–C(15)	117.0(11)
C(11)–N(11)–C(15)	125.2(11)	Re(1)–N(2)–N(21)	174.3(10)
N(2)–N(21)–C(21)	115.8(12)	N(2)–N(21)–C(25)	117.7(13)
C(21)–N(21)–C(25)	125.1(13)	Cl(1′)–Re(1′)–Cl(2′)	170.6(1)
Cl(1′)–Re(1′)–O(1′)	84.6(3)	Cl(2′)–Re(1′)–O(1′)	86.0(3)
Cl(1′)–Re(1′)–N(1′)	93.0(4)	Cl(2′)–Re(1′)–N(1′)	92.1(4)
O(1′)–Re(1′)–N(1′)	122.9(5)	Cl(1′)–Re(1′)–N(2′)	90.8(4)
Cl(2′)–Re(1′)–N(2′)	94.2(4)	O(1′)–Re(1′)–N(2′)	122.3(5)
N(1′)–Re(1′)–N(2′)	114.7(5)	Re(1′)–O(1′)–Si(1′)	151.0(5)
Re(1′)–N(1′)–N(11′)	174.9(10)	N(1′)–N(11′)–C(11′)	113.6(11)
N(1′)–N(11′)–C(15′)	117.8(12)	C(11′)–N(11′)–C(15′)	126.5(12)
Re(1′)–N(2′)–N(21′)	172.2(10)	N(2′)–N(21′)–C(21′)	115.6(11)
N(2′)–N(21′)–C(25′)	117.3(12)	C(21′)–N(21′)–C(25′)	124.5(12)

symmetrical Re(μ-O)$_2$Re bridge, an example of which is known[15] in [Re(μ-O)O(η-C$_5$H$_5$)]$_2$.

The Re$_2$O$_2$ ring displays a large rhombic distortion with the angles at Re contracted to 69.6(3)° and the transannular O···O′ distance short at 2.40 Å. The equatorial M–N and in particular the N–N bonds [1.265(12) and 1.271(16) Å] are again short indicating a significant degree of multiple bonding. The Re–N–N angles are essentially linear [179.5(10) and 178.1(7)°] and the *exo*-N atoms planar (maximum deviations from the planes of their substituents of 0.03 and 0.04 Å). In

Table 7 Selected bond lengths (Å) and angles (°) for complex **4** with e.s.d.s in parentheses

Re–Cl(1)	2.392(3)	Re–Cl(2)	2.389(3)
Re–Cl(3)	2.315(3)	Re–N(1)	1.753(8)
Re–N(2)	1.741(9)	N(1)–N(11)	1.287(11)
N(11)–C(11)	1.505(14)	N(11)–C(15)	1.490(15)
N(2)–N(21)	1.280(12)	N(21)–C(21)	1.495(13)
N(21)–C(25)	1.527(16)		
Cl(1)–Re–Cl(2)	170.8(1)	Cl(1)–Re–Cl(3)	86.2(1)
Cl(2)–Re–Cl(3)	84.6(1)	Cl(1)–Re–N(1)	91.7(3)
Cl(2)–Re–N(1)	92.6(3)	Cl(3)–Re–N(1)	120.4(3)
Cl(1)–Re–N(2)	93.1(3)	Cl(2)–Re–N(2)	91.9(3)
Cl(3)–Re–N(2)	119.9(3)	N(1)–Re–N(2)	119.6(4)
Re–N(1)–N(11)	177.1(8)	N(1)–N(11)–C(11)	115.9(8)
N(1)–N(11)–C(15)	118.2(8)	C(11)–N(11)–C(15)	124.3(8)
Re–N(2)–N(21)	178.1(8)	N(2)–N(21)–C(21)	116.7(9)
N(2)–N(21)–C(25)	119.4(8)	C(21)–N(21)–C(25)	123.7(8)

contrast to the essentially coplanar geometries observed in **3** and **4** here in **5** the C_2N_2 planes are appreciably tilted with respect to the equatorial plane, by 28 and 35° for N(11) and N(21) respectively. However, the N(1)–Re–N(2) angle is still significantly enlarged from normal octahedral at 107.9(5)° due to the steric congestion of the ligand methyl groups. The Re–NCMe distances are normal.

If **5** is again formulated with neutral ligands the oxidation state of rhenium is IV, d^3, so that the diamagnetism could arise from spin coupling across the $Re(O)_2Re$ bridge; the Re $\cdots$ Re distance of 3.45 Å is too long for a Re–Re bond as found in compound **6** discussed below.

In the hope of substituting Cl in **4** reactions with $C_9H_{18}N_2H(SiMe_3)$ and $C_9H_{18}N_2HLi$ were studied but these were very slow even on refluxing in thf for some days and only another oxo species $[ReO(C_9H_{18}N_2)_2]_2$ **6** was isolated in low yield. The structure of **6** is shown in Fig. 5; fractional coordinates are given in Table 10 with bond lengths and angles in Table 11.

Table 8 Atomic coordinates (× 10^4) for complex **5** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	7343(1)	6934(1)	532(1)	N(3)	6985(4)	5707(8)	−8(4)
O	8016(3)	7181(5)	218(3)	C(31)	6787(5)	4984(10)	−235(5)
N(1)	7843(4)	6086(7)	1068(4)	C(32)	6527(7)	4047(11)	−506(7)
N(11)	8199(5)	5494(7)	1446(4)	N(4)	7758(4)	8156(8)	1065(4)
C(12)	8679(6)	4902(10)	1321(5)	C(41)	8018(6)	8735(10)	1399(6)
C(13)	8863(9)	4021(13)	1701(7)	C(42)	8363(7)	9427(11)	1842(6)
C(14)	9042(8)	4195(13)	2355(6)	S	4578(2)	3622(3)	1127(2)
C(15)	8798(8)	5152(12)	2488(6)	O(1)	4108(3)	2994(6)	1051(4)
C(16)	8164(7)	5443(11)	2032(5)	O(2)	4664(6)	3771(9)	641(4)
C(17)	8419(8)	4642(15)	706(6)	O(3)	4559(6)	4477(6)	1399(5)
C(18)	9240(8)	5607(14)	1454(9)	C	5263(3)	2989(7)	1615(3)
C(19)	7703(8)	4692(13)	2010(7)	F(1)	5219(5)	2800(10)	2117(4)
C(20)	8022(9)	6499(12)	2173(6)	F(2)	5758(4)	3580(8)	1720(5)
N(2)	6669(4)	7103(7)	658(3)	F(3)	5341(4)	2117(8)	1386(5)
N(21)	6178(5)	7233(7)	730(4)	S′	7331(3)	1728(6)	1120(4)
C(22)	5938(7)	6401(12)	982(6)	O(1′)	7332(5)	747(9)	915(7)
C(23)	5247(7)	6512(14)	771(8)	O(2′)	7646(7)	1812(14)	1726(6)
C(24)	5008(9)	7512(16)	818(10)	O(3′)	7514(8)	2457(12)	819(10)
C(25)	5186(8)	8214(15)	426(10)	C′	6669(6)	1959(8)	983(6)
C(26)	5878(6)	8273(11)	604(6)	F(1′)	6335(10)	1855(16)	429(7)
C(27)	6092(7)	5424(10)	793(7)	F(2′)	6604(9)	2871(10)	1136(11)
C(28)	6255(8)	6483(14)	1655(7)	F(3′)	6474(13)	1328(14)	1264(10)
C(29)	6003(10)	8772(12)	159(8)	C(50)	5000	5896(18)	2500
C(30)	6187(10)	8846(14)	1160(8)	Cl(1)	5658(3)	6604(4)	2847(2)

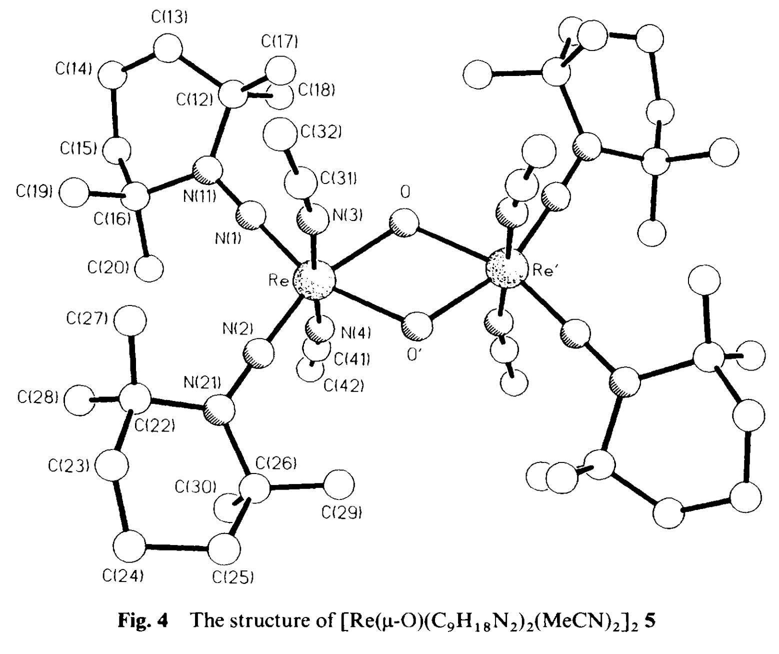

Fig. 4 The structure of $[Re(\mu\text{-}O)(C_9H_{18}N_2)_2(MeCN)_2]_2$ **5**

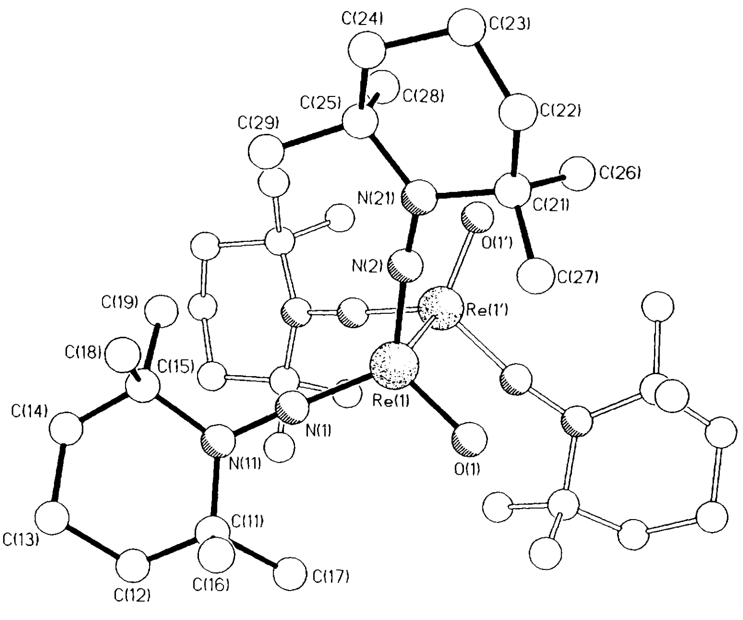

Fig. 5 The structure of $[ReO(C_9H_{18}N_2)_2]_2$ **6**

Table 9 Selected bond lengths (Å) and angles (°) for complex **5** with e.s.d.s in parentheses

Re–O	2.095(9)	Re–N(1)	1.795(8)
Re–N(2)	1.779(11)	Re–N(3)	2.084(10)
Re–N(4)	2.094(10)	Re–O′	2.106(7)
N(11)–C(12)	1.530(20)	N(1)–N(11)	1.265(12)
C(12)–C(13)	1.472(21)	N(11)–C(16)	1.530(19)
N(2)–N(21)	1.271(16)	C(16)–C(20)	1.531(23)
N(21)–C(26)	1.537(17)	N(21)–C(22)	1.511(21)
N(4)–C(41)	1.127(16)	N(3)–C(31)	1.126(16)
O–Re–N(1)	91.0(4)	O–Re–N(2)	160.3(3)
N(1)–Re–N(2)	107.9(5)	O–Re–N(3)	92.4(4)
N(1)–Re–N(3)	88.0(4)	N(2)–Re–N(3)	93.7(4)
O–Re–N(4)	83.9(4)	N(1)–Re–N(4)	90.9(4)
N(2)–Re–N(4)	90.2(4)	N(3)–Re–N(4)	176.1(5)
O–Re–O′	69.6(3)	N(1)–Re–O′	159.7(4)
N(2)–Re–O′	92.0(3)	N(3)–Re–O′	86.7(3)
N(4)–Re–O′	93.1(3)	Re–O–Re′	110.4(3)
Re–N(1)–N(11)	179.5(10)	N(1)–N(11)–C(12)	119.4(11)
N(1)–N(11)–C(16)	118.6(12)	C(12)–N(11)–C(16)	121.9(9)
Re–N(2)–N(21)	178.1(7)	N(2)–N(21)–C(22)	119.6(10)
N(2)–N(21)–C(26)	118.1(11)	C(22)–N(21)–C(26)	122.2(12)
Re–N(3)–C(31)	170.5(12)	N(3)–C(31)–C(32)	177.5(17)
Re–N(4)–C(41)	172.1(10)	N(4)–C(41)–C(42)	177.0(15)

The complex has crystallographic C_2 symmetry about an axis perpendicular to and bisecting the Re–Re bond. The geometry about each rhenium can be described as distorted tetrahedral, the distortion being towards trigonal pyramidal; this is most marked in the N(2)–Re(1)–Re(1′) angle of 93.0(3)°. The dimer is an ethane-like molecule in a near-eclipsed conformation [the N(2)–Re(1)–Re(1′)–O(1′) and N(1)–Re(1)–Re(1′)–N(1′) torsion angles are 10 and 12°, respectively]. The Re–Re separation is 2.696(2) Å and in the range for Re–Re single bonds.[16]

The Re–N and N–N distances are again short and the Re–N–N angles close to linear. The Re–O distance is normal. There is a noticeable increase in the pyramidalisation at the *exo*-N atoms which deviate from the planes of their substituents by 0.22 and 0.16 Å for N(11) and N(21) respectively. Indeed for the Re complexes **3**–**6** there appears to be an approximate correlation between the degree of pyramidalisation and the

Table 10 Atomic coordinates (× 10^4) for complex **6** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Re(1)	419(1)	1201(1)	2107(1)
O(1)	1255(3)	408(5)	2533(3)
N(1)	634(4)	2600(5)	2071(3)
N(11)	844(4)	3585(5)	2003(3)
C(11)	1732(4)	3757(8)	2278(5)
C(12)	1892(5)	4971(8)	2347(6)
C(13)	1388(7)	5596(9)	1667(8)
C(14)	501(6)	5420(8)	1482(6)
C(15)	255(5)	4231(7)	1400(5)
C(16)	2076(6)	3204(9)	1824(6)
C(17)	2150(5)	3247(9)	3033(5)
C(18)	162(6)	3784(8)	676(4)
C(19)	−562(5)	4159(8)	1421(5)
N(2)	−367(4)	554(5)	1371(3)
N(21)	−838(4)	−11(5)	822(3)
C(21)	−684(5)	−1198(7)	880(5)
C(22)	−1127(8)	−1737(9)	151(7)
C(23)	−1968(7)	−1350(9)	−282(6)
C(24)	−1982(7)	−146(9)	−383(6)
C(25)	−1633(5)	486(7)	327(5)
C(26)	−947(8)	−1693(9)	1407(7)
C(27)	208(7)	−1375(9)	1113(8)
C(28)	−2196(6)	517(12)	666(6)
C(29)	−1477(7)	1607(9)	161(6)

Table 11 Selected bond lengths (Å) and angles (°) for complex **6** with e.s.d.s in parentheses

Re(1)–O(1)	1.714(5)	Re(1)–N(1)	1.782(6)
Re(1)–N(2)	1.778(6)	Re(1)–Re(1′)	2.696(2)
N(1)–N(11)	1.304(9)	N(11)–C(11)	1.499(10)
N(11)–C(15)	1.487(9)	N(2)–N(21)	1.297(8)
N(21)–C(21)	1.489(11)	N(21)–C(25)	1.510(9)
O(1)–Re(1)–N(1)	114.1(3)	O(1)–Re(1)–N(2)	113.8(3)
N(1)–Re(1)–N(2)	120.9(3)	O(1)–Re(1)–Re(1′)	108.1(2)
N(1)–Re(1)–Re(1′)	102.8(3)	N(2)–Re(1)–Re(1′)	93.0(3)
Re(1)–N(1)–N(11)	172.8(7)	N(1)–N(11)–C(11)	114.8(6)
N(1)–N(11)–C(15)	116.6(5)	C(11)–N(11)–C(15)	121.6(7)
Re(1)–N(2)–N(21)	169.7(6)	N(2)–N(21)–C(21)	115.3(6)
N(2)–N(21)–C(25)	117.6(6)	C(21)–N(21)–C(25)	123.4(6)

amount of N–N double bond character, *i.e.*, the longer the bond the greater the pyramidalisation. The statistical significance of this may however be questionable as the standard deviations in the bond lengths are large. The compound can be compared with the rhenium(II) dimer, $[ReO(MeC{\equiv}CMe)_2]_2$, whose structure was determined by X-ray diffraction.[16a] Thus **6** can be similarly formulated as a rhenium(II) compound taking $C_9H_{18}N_2$ as a neutral ligand as in the compounds discussed earlier.

The ^1H NMR spectrum of **6** indicates that the solid-state structure is maintained in solution and the CH_2 and four CH_3 resonances [*cf.* the compound $Re_2O_2(MeC_2Me)_4$ above] are unchanged over the temperature range −80 to +80 °C. Having in mind that there is restricted rotation about the Re–Re bond due to steric congestion and restricted rotation around the Re–N–N vector in agreement with previous structures **1**–**4**, it appears that **6** is static in solution (excluding conformational changes in the ring that are probably fast on the NMR timescale). It does not react further with $C_9H_{18}N_2HLi$ and decomposes in the presence of reducing agents such as Na/Hg which, in addition to deoxygenation might also attack the N–N bond.

Conclusion

Several important features have emerged from the above structural studies. For all the rhenium complexes both the Re–N and N–N bonds are short and the Re–N–N angle essentially linear. Furthermore, regardless of whether the complex is tetrahedral, trigonal bipyramidal or octahedral, neutral or cationic, the ligand geometry does not vary appreciably. The Re–N bonds are in the range 1.732(12) Å (in **3**) to 1.795(8) Å (in **5**), the N–N bonds in the range 1.265(12) Å (in **5**) to 1.308(17) Å (in **3**) and the angles in the range 169.7(6)° (in **6**) to 179.5(10) (in **5**). Small increases in the Re–N distance are often accompanied by a reduction in the N–N distance, the sum of the Re–N and N–N distances remaining fairly constant with a mean value for structures **3**–**6** of 3.05 Å. Conclusions regarding bond order have to be approached with caution. Many literature assignments of canonical forms seem somewhat arbitrary and take little account of the observed bond lengths. In the case of heavy-metal hydrazido species both the metal–nitrogen and in particular the nitrogen–nitrogen distances frequently have very large error margins which render the assignment of anything other than an approximate bond order meaningless. All that can be said with certainty for compounds **3**–**6** is that both the Re–N and N–N bonds display a significant amount of multiple-bond character, the former being consistent with strong π bonding to the metal.

The tungsten complex **1** is slightly anomalous in that the W–N distance, 1.841(5) Å, is significantly longer than the mean value (1.752 Å) reported for tungsten hydrazido compounds and the N–N distance [1.248(7) Å] very much shorter. This geometry is much closer to that observed, for example, in the diazenido species $W(\eta^5\text{-}C_5H_5)(CO)_2(N_2Me)$ where the W–N and N–N distances are 1.856(3) and 1.215(5) Å respectively,[17] and even closer to that in the related complex $(\eta^5\text{-}C_5H_5)(CO_2)W(NNMe)Cr(CO)_5$ [W–N 1.830(3), N–N 1.247(4) Å], where the increase in the N–N distance and reduction in W–N distance is attributed to the chromium atom removing electron density on the tungsten through the organodiazo linkage.[18]

Experimental

Microanalyses were by Medac Ltd., Brunel University, Pascher, Germany and Imperial College Laboratories. General techniques are as described.[19] NMR data were obtained on a JEOL-EX-270 spectrometer at 270 MHz and referenced internally on residual H impurity in the solvent (δ 7.15 C_6D_6, 7.26 $CDCl_3$, 2.0 CD_3CN). Electron impact (EI) mass spectra on a VG7070E with isotopic envelopes calculated for $^{181}Re(62.5)$, $^{185}Re(37.5)$, $^{182}W(26.4)$, $^{183}W(14.4)$ and $^{186}W(28.4\%)$.

Commercial chemicals were from Aldrich. Literature syntheses were used for $C_9H_{18}N_2H_2$,[5a] $ReO_3(OSiMe_3)$[20] and $WO_2Cl_2(dme)$.[21]

Syntheses.—Trichlorobis(2,2,6,6-*tetramethylpiperid*-1-*ylnitrene*)*trimethylsilyloxotungsten*(IV) **1**. To a suspension of $WO_2Cl_2(dme)$ (0.6 g, 1.6 mmol) in $SiClMe_3$ and NEt_3 (10 cm^3, 1 : 1) was added $C_9H_{18}N_2H_2$ (0.55 g, 3.52 mmol) and the mixture refluxed (12 h) to give a brown suspended solid. After removal of solvents the residue was washed with hexane (3 × 30 cm^3) and extracted with toluene (3 × 10 cm^3). Concentration of the extracts to *ca.* 5 cm^3 and cooling (−20 °C) gave orange crystals of **1**. Yield: 0.65 g, *ca.* 60%. X-Ray quality crystals were obtained by layering CH_2Cl_2 solutions with Et_2O. ^1H NMR ($CDCl_3$): δ 1.53 (s, 12 H) and 1.30 (s,12 H) ($NCMe_2CH_2CH_2CH_2CMe_2$), 1.2–1.0 (m, 12 H, CH_2) and 0.62 (s, 9 H, $OSiMe_3$).

Trioxo-2,2,6,6-*tetramethylpiperid*-1-*ylamidorhenium*(VII) 2,-2,6,6-*tetramethylpiperid*-1-*ylammonium perrhenate* **2**. To a solution of $ReO_3(OSiMe_3)$ (0.3 g, 0.95 mmol) in thf containing dried activated 4 A molecular sieves, was added $C_9H_{18}N_2H_2$ (0.47 g, 3 mmol) and the mixture stirred at room temperature for 12 h. The resulting red-brown suspension was evaporated, the residue washed with hexane and Et_2O (2 × 20 cm^3) and then extracted with CH_2Cl_2 (3 × 20 cm^3). The organic phases were filtered, reduced to *ca.* 10 cm^3 and layered with Et_2O. After 2–3 d, light yellow-green crystals were collected. ^1H NMR ($CDCl_3$): δ 1.40, 1.56 (s, 2 × 12 H, $NCMe_2CH_2CH_2CH_2CMe_2$), 1.60–1.95 (m, 12 H, $NCMe_2CH_2CH_2CH_2CMe_2$), 4.2 (s, 3 H, NH_3) and 9.2 (s, 1 H, NH). $\tilde{\nu}_{max}/cm^{-1}$: 3346, 3250, 3180 (NH, NH_3); 904, 911 (Re=O).

Dichlorobis(2,2,6,6-*tetramethylpiperid*-1-*ylnitrene*)(*trimethylsilyloxo*)*rhenium*(III) **3**. To $ReO_3(OSiMe_3)$ (0.7 g, 2.16 mmol) suspended in NEt_3 (5 cm^3) was added $C_9H_{18}N_2H_2$ (1.12 g, 7.15 mmol), followed by $SiClMe_3$ (5 cm^3). After refluxing the reaction mixture overnight (yellow colouration), the volatiles were removed under vacuum, the solid residue transferred in the dry-box to a Soxhlet apparatus and extracted with hexane (50 cm^3), until the organic extracts were colourless. The yellow-orange organic phase was concentrated and cooled (−20 °C) to give yellow crystals. Yield: 0.92 g, *ca.* 65%. NMR (C_6D_6): ^1H, δ 1.40 (s, 24 H, $NCMe_2CH_2CH_2CH_2CMe_2$), 1.10 (m, 12 H, CH_2) and 0.60 (s, 9 H, $OSiMe_3$); $^{13}C\text{-}\{^1H\}$, δ 63.9 ($NCMe_2CH_2CH_2CH_2CMe_2$), 39.9 ($NCMe_2CH_2CH_2CH_2CMe_2$), 31.5 ($NCMe_2CH_2CH_2CH_2CMe_2$), 16.3 ($NCMe_2CH_2CH_2CH_2CMe_2$) and 3.8 $[OSi(CH_3)_3]$.

Trichlorobis(2,2,6,6-*tetramethylpiperid*-1-*ylnitrene*)*rhenium*(III) **4**. To a solution of **3** (0.75 g, 1.15 mmol) in Et_2O (30 cm^3) at −78 °C, was added dropwise a solution of HCl in Et_2O (1.2 cm^3 of 1 mol dm^{-3} solution). The reaction mixture was allowed to reach room temperature and stirred for 2 h. Removal of volatiles under vacuum, washing of the yellow residue with hexane (3 × 20 cm^3) and crystallisation from toluene at −20 °C affords yellow prisms of **4**. Yield: 0.55 g, *ca.* 80%. NMR ($CDCl_3$): ^1H, δ 1.74 (m, 12 H, $NCMe_2CH_2CH_2CH_2CMe_2$) and 1.58 (s, 24 H, $NCMe_2CH_2CH_2CH_2CMe_2$); $^{13}C\text{-}\{^1H\}$, δ 66.4 ($NCMe_2CH_2CH_2CH_2CMe_2$), 39.8 ($NCMe_2CH_2CH_2CH_2CMe_2$), 31.8 ($NCMe_2CH_2CH_2CH_2CMe_2$) and 22.1 ($NCMe_2CH_2CH_2CH_2CMe_2$).

Bis[*bis*(*acetonitrile*)(μ-*oxo*)*bis*(2,2,6,6-*tetramethylpiperid*-1-*ylnitrene*)*rhenium*(IV)] *tetrakis*(*trifluoromethanesulfonate*) **5**. To **4** (0.3 g, 0.5 mmol) in acetonitrile (10 cm^3) was added silver trifluoromethanesulfonate (0.38 g, 1.5 mmol) when a grey precipitate (AgCl) is formed immediately. The mixture was stirred for 8 h and filtered. After removal of acetonitrile under vacuum, the residue was washed with Et_2O (2 × 20 cm^3) and extracted into CH_2Cl_2 (20 cm^3). Filtration, concentration

Table 12 Details of the data collections and refinements for compounds **1** and **3**–**6**[a]

Compound	**1**	**3**	**4**	**5**	**6**
Empirical formula	$C_{21}H_{45}Cl_3N_4OSiW{\cdot}CH_2Cl_2$	$C_{21}H_{45}Cl_2N_4OReSi$	$C_{18}H_{36}Cl_3N_4Re$	$C_{49}H_{86}Cl_2F_{12}N_{12}O_{14}Re_2S_4$	$C_{36}H_{72}N_8O_2Re_2$
M	772.8	654.8	601.1	1866.8	1021.4
Colour, habit	Yellow plates	Yellow plates	Yellow needles	Orange prisms	Orange needles
Crystal size/mm	0.056 × 0.37 × 0.62	0.094 × 0.266 × 0.30	0.096 × 0.158 × 0.50	0.13 × 0.20 × 0.50	0.134 × 0.134 × 1.00
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pnam*	$P2_1/c$	$P2_1/c$	$C2/c$	$C2/c$
a/Å	12.101(7)	13.411(2)	9.409(2)	23.842(5)	18.469(7)
b/Å	14.847(11)	12.018(2)	11.323(2)	13.386(3)	12.353(6)
c/Å	18.095(14)	36.411(5)	23.088(4)	25.475(6)	20.796(7)
β/°		90.57(2)	98.84(2)	114.51(2)	115.73(2)
U/Å^3	3261(4)	5868(2)	2434(1)	7398(3)	4274(3)
Z	4[b]	8[c]	4	4[d]	4[e]
D_c/g cm^{-3}	1.574	1.482	1.643	1.676	1.587
μ/mm^{-1}	4.01	4.38	5.34	3.55	5.70
F(000)	1552	2640	1192	3728	2040
2θ range/°	3–50	3–50	3–50	3–50	4–55
Independent reflections (R_{int})	2965 (0.00)	10 329 (0.027)	4285 (0.056)	6521 (0.043)	4904 (0.033)
Observed reflections	2135 [$F > 4.0\sigma(F)$]	4894 [$F > 5.0\sigma(F)$]	2791 [$F > 4.0\sigma(F)$]	4265 [$F > 4.0\sigma(F)$]	3356 [$F > 4.0\sigma(F)$]
Minimum, maximum, transmission	0.251, 0.798	0.343, 0.660	0.418, 0.619	0.398, 0.569	0.418, 0.542
No. of parameters refined	163	541	232	434	218
g In weighting scheme	0.0006	0.0006	0.0006	0.0005	0.0006
Final *R* (*R'*)	0.0383 (0.0365)	0.0499 (0.0449)	0.0432 (0.0401)	0.0578 (0.0537)	0.0372 (0.0369)
Largest and mean Δ/σ	0.002 and 0.000	0.001 and 0.000	0.033 and 0.002	0.797 and 0.038	0.043 and 0.008
Data/parameter ratio	13.1	9.0	12.0	9.8	15.4
Largest difference peak, hole/e Å^{-3}	1.08, −0.86	1.10, −0.68	0.90, −0.97	1.31, −1.03	0.99, −0.83

[a] Details in common: Siemens P4/PC diffractometer; graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å); room temperature; numerical absorption corrections (face-indexed crystals); weighting scheme, $w^{-1} = \sigma^2(F) + gF^2$. [b] The complex has crystallographic C_s symmetry. [c] Two crystallographically independent molecules. [d] The complex has crystallographic C_i symmetry. [e] The complex has crystallographic C_2 symmetry.

and layering with Et_2O gave orange-red prisms. Yield: 0.2 g, 40%. NMR (CD_3CN): ^{1}H, δ 2.15 (s, 6 H, CH_3CN), 1.80 (s, 24 H, $\overline{\mathrm{NC}Me_2\mathrm{CH_2CH_2CH_2C}Me_2}$) and 1.70–1.75 (m, 12 H, CH_2); ^{19}F, δ −194.

Bis[*oxobis*(2,2,6,6-*tetramethylpiperid*-1-*ylnitrene*)*rhenium*-(II)] **6**. To a solution of **3** (0.3 g, 0.5 mmol) in thf (20 cm^3) at −78 °C was added a solution of $C_9H_{18}N_2HLi$ in thf [prepared from $C_9H_{18}N_2H_2$ (0.25 g, 1.58 mmol) and an equivalent amount of $LiBu^n$ in hexanes]. The mixture was allowed to warm to room temperature then refluxed overnight. After removal of thf under vacuum, the orange residue was extracted with boiling hexane (3 × 50 cm^3) which was again removed under vacuum. The residue was dissolved in Et_2O, filtered, concentrated and crystallised at −20 °C. Yield: 0.05 g, *ca.* 20%. NMR (C_6D_6): ^{1}H, δ 1.72, 1.54, 1.34, 1.30 (s, 4 × 12 H, methyls, no assignment proved possible), 1.14–1.55 (br, 24 H, CH_2); ^{13}C-{^{1}H}, δ 55.0, 53.4 ($\overline{\mathrm{N}C\mathrm{Me_2CH_2CH_2CH_2}C\mathrm{Me_2}}$), 33.5, 33.2 ($\overline{\mathrm{NCMe_2}C\mathrm{H_2CH_2}C\mathrm{H_2CMe_2}}$), 23.8, 23.7 ($\overline{\mathrm{NCMe_2CH_2}C\mathrm{H_2CH_2CMe_2}}$), 17.2, 15.9 ($\overline{\mathrm{NC}Me_2\mathrm{CH_2CH_2CH_2C}Me_2}$).

X-Ray Crystallography.—Single crystals of compounds **1** and **3**–**6** suitable for X-ray analysis were either coated with epoxy resin or sealed under Ar in capillary tubes to prevent decomposition. Details of the data collections and refinements are given in Table 12. In compound **1** a Δ*F* map revealed the presence of an included molecule of CH_2Cl_2 positioned about a mirror plane. In compound **4** one of the piperidine rings is partially disordered. Two different conformations for this ring of estimated occupancies 0.4 and 0.6 were identified. In compound **5** there is severe disorder in one of the O_3SCF_3 anions. However, reasonable partial occupancy alternative orientations for this group could not be identified. The full-occupancy non-hydrogen atoms in all five structures were refined anisotropically, the partial occupancy atoms isotropically. All of the hydrogen atoms were placed in idealised positions, assigned isotropic thermal parameters $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ and allowed to ride on their parent carbon atoms. Refinements were by full-matrix least squares using the SHELXTL PC system.[22]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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