Tungsten Complexes derived from *o*-Phenylenediamine: Methoxo and Dialkylhydroxylaminato Species†

Carl Redshaw,[a] Geoffrey Wilkinson,*[,a] Bilquis Hussain-Bates[b] and Michael B. Hursthouse*[,b]
[a] *Johnson Matthey Laboratory, Chemistry Department, Imperial College, London SW7 2AY, UK*
[b] *Chemistry Department, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK*

The interaction of WCl_6 and *o*-phenylenediamine (1,2-diaminobenzene, H_2pda) in Pr^iOH affords the binuclear compound $\{WCl_3[1\text{-}(HN),2\text{-}(H_2N)C_6H_4]\}_2[\mu\text{-}1,2\text{-}(N)C_6H_4]$ **1**. A similar reaction in methanol gives only a methoxide complex, $W_2Cl_3(OMe)_5(\mu\text{-}OMe)_2$ **2**. Interaction of $WCl_4(PMe_3)_3$ with H_2pda in Pr^iOH gives $WCl_2[1,2\text{-}(HN)_2C_6H_4](PMe_3)_3$ **3**. Interaction of $WOCl_4$ and H_2pda in tetrahydrofuran (thf) with a solution of $LiNMe_2$ prepared *in situ* from Me_2NH and commercial $LiBu^n$ in hexanes (which contain 2-methylpentane) gives rise to a remarkable compound **4** that has a 1,5-benzodiazepinium cation (made independently as its chloride) and an anion $[W_2Cl_4O(ONMe_2)_5]^-$ that provides the first examples of unidentate and bridging dimethylhydroxylaminate(1−) ligands (both through O). Interaction of $WOCl_4$ and $LiONR_2$ (R = Et or $PhCH_2$) in thf forms $WO_2(ONR_2)_2$ **5** and **6**. In complex **1** the metal centres, which are related by symmetry, have octahedral co-ordination with a *mer* arrangement of the three chlorides. The link to the bridging $\mu\text{-}C_6H_4(N)_2$ ligand involves a W=N double bond [1.75(2) Å]. The chelating 1-(HN),2-$(H_2N)C_6H_4$ gives W–N bond lengths of 1.92(2) (amido) and 2.29(2) Å (amino); the latter bond is *trans* to the multiply bonded imine function. In the methoxide **2** the metal centres are inequivalent: W(1) has two terminal chlorides and two terminal methoxides (mutually *trans*) whilst W(2) has one terminal chloride and three methoxides. The methoxide bridges show slight asymmetry. The metal–metal distance [2.733(3) Å] is consistent with the presumed W–W single bond. In compound **4** the dinuclear anion contains two structurally equivalent metal atoms, each with two terminal chlorides and two terminal dimethylhydroxylaminato groups. The hydroxylaminato and oxo bridges are symmetrical. The organic cation, evidently formed by reactions of $WOCl_4$ with 2-methylpentane in the solvent, has also been structurally characterised as the chloride salt. In compound **5** the W–O bonds of the η^2-diethylhydroxylaminato groups are slightly shorter than the W–N bonds: 1.97(1) (av.) *vs.* 2.14(1) Å (av.).

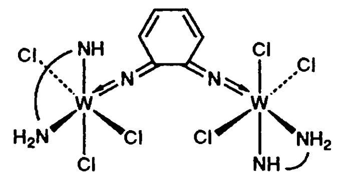
The present studies arose from attempts to synthesise the neutral tungsten(VI) compound $W[1,2\text{-}(HN)_2C_6H_4]_3$ which would be isoelectronic with the rhenium(VII) cation $[Re\{1,2\text{-}(HN)_2C_6H_4\}_3]^+$ previously characterised by X-ray diffraction.[1] Although this objective has not yet been achieved some unusual tungsten compounds have been isolated and structurally characterised. Analytical and physical data for new compounds are given in Table 1.

Results and Discussion

A number of possible routes to $W[1,2\text{-}(HN)_2C_6H_4]_3$ have been studied including the interaction of *o*-phenylenediamine (H_2pda) with hexamethyltungsten, WCl_6 and $WOCl_4$ under various conditions of solvent, presence of different bases, *etc.* A number of species have been obtained and the present paper deals with some of these; other products are not yet fully characterised.

Tungsten hexachloride and excess of H_2pda at −78 °C in Pr^iOH react to give a purple solution, but although purple crystals were obtained none was of X-ray quality due to persistent twinning. Analytical and spectroscopic data were not sufficiently diagnostic for a particular structure. However, when the reaction was carried out at room temperature blue needles were isolated. X-Ray study of the crystals obtained from toluene shows the compound to be the toluene solvate of $\{WCl_3[1\text{-}(HN),2\text{-}(H_2N)C_6H_4]\}_2\{\mu\text{-}1,2\text{-}(N)_2C_6H_4\}$ **1**.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



I

The crystal structure of the molecule is shown in Fig. 1; selected bond lengths and angles are given in Table 2. A two-fold axis of symmetry bisects the '*o*-pda' ligand and relates the two metal centres; as far as we are aware this molecule contains the first example of a bridging $1,2\text{-}(N)_2C_6H_4$ group formally derived from *o*-benzoquinonediimine. Examples of bridging $1,2\text{-}(HN)_2C_6H_4$ groups are, however, known[2a] for ruthenium, one being $[Ru_2\{\mu\text{-}1,2\text{-}(HN)_2C_6H_4\}\{\mu\text{-}(Ph_2P)_2CH_2\}(CO)_2(PPh_3)_2]$.

Each tungsten atom adopts a distorted octahedral configuration with a meridional arrangement of the three chlorine atoms. The bonding of the '*o*-pda' ligands raises some very interesting questions. The geometry of the nitrogen co-ordination from the bridging ligand is consistent with the form shown in diagram **I**. Although the W–N and N–C bond lengths and the approximate linearity at N are consistent with this form, the C–C bonds in the C_6 ring do not show the localisation of double bonds as required, although C(8)–C(9) is the shortest bond. However, Carugo *et al.*[2b] have analysed the geometries of *o*-pda type chelating ligands and found that most structures show delocalisation; in particular, no true examples of the diimine structure of the type in diagram **I** were listed. On the

Table 1 Analytical and physical data for tungsten compounds

Compound	Colour	M.p./°C	Analysis (%)[a] C	H	N
1 $\{WCl_3[1\text{-}(HN),2\text{-}(H_2N)C_6H_4]\}_2\{\mu\text{-}1,2\text{-}(N)_2C_6H_4\}$[b]	Blue	270–280 (decomp.)	33.4 (32.9)	4.1 (3.0)	7.7 (8.1)
2 $W_2Cl_3(OMe)_5(\mu\text{-}OMe)_2$	Brown-red	300	12.2 (12.2)	2.6 (3.1)	
3 $WCl_2[1,2\text{-}(HN)_2C_6H_4](PMe_3)_3$[c]	Black	—	30.3 (30.7)	5.5 (5.6)	4.5 (4.7)
4 $[C_{12}H_{17}N_2][W_2Cl_4O(ONMe_2)_5]$	Orange	179–180 (decomp.)	25.0 (26.0)	4.8 (4.6)	8.4 (9.6)
5 $WO_2(ONEt_2)_2$[d]	Colourless	143–144	24.5 (24.5)	5.3 (5.1)	7.1 (7.1)
6 $WO_2[ON(CH_2Ph)_2]_2$[e]	Colourless	202–204	55.0 (55.1)	4.6 (5.6)	4.4 (3.6)

[a] Calculated values in parentheses. [b] Toluene solvate. [c] Cl 13.0 (12.1). [d] O 16.7 (16.3). [e] 2thf Solvate.

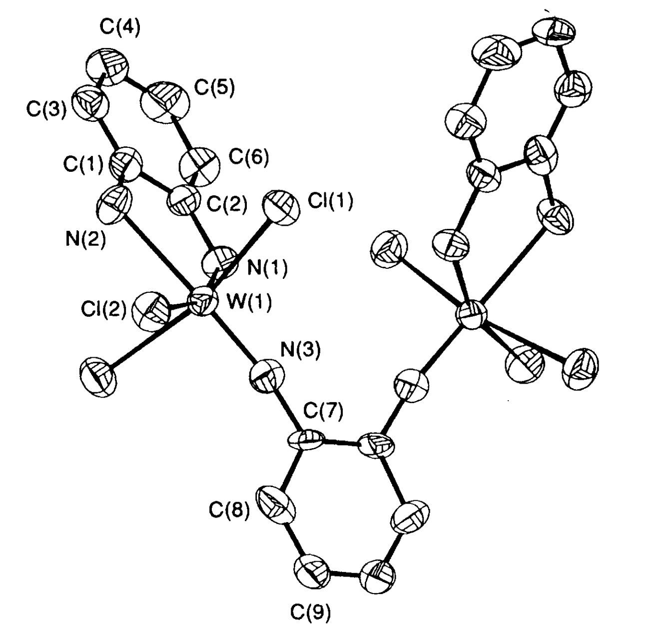
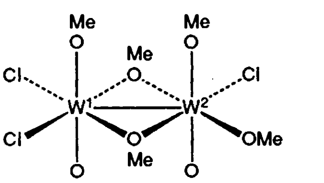
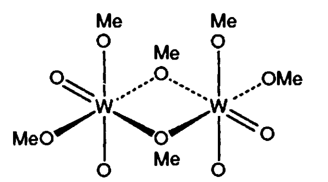


Fig. 1 The structure of $\{WCl_3[1\text{-}(HN),2\text{-}(H_2N)C_6H_4]\}_2[\mu\text{-}1,2\text{-}(N)_2C_6H_4]$



II



III

Table 2 Selected bond lengths (Å) and angles (°) for $\{WCl_3[1\text{-}(HN),2\text{-}(H_2N)C_6H_4]\}_2[\mu\text{-}1,2\text{-}(N)_2C_6H_4]\cdot 2C_6H_5Me$ **1**

Cl(1)–W(1)	2.360(6)	Cl(2)–W(1)	2.386(6)
Cl(3)–W(1)	2.388(7)	N(1)–W(1)	1.924(14)
N(2)–W(1)	2.287(17)	N(3)–W(1)	1.753(15)
C(2)–N(1)	1.355(21)	C(1)–N(2)	1.458(22)
C(3)–C(1)	1.305(25)	C(2)–C(1)	1.415(23)
C(5)–C(6)	1.375(27)	C(2)–C(6)	1.445(24)
C(4)–C(3)	1.421(27)	C(5)–C(4)	1.431(28)
C(7)–N(3)	1.316(20)	C(8)–C(7)	1.425(22)
C(7)–C(7a)	1.415(33)	C(9)–C(8)	1.350(27)
C(9)–C(9a)	1.376(51)		
Cl(2)–W(1)–Cl(1)	84.2(3)	Cl(3)–W(1)–Cl(1)	164.4(2)
Cl(3)–W(1)–Cl(2)	84.9(3)	N(1)–W(1)–Cl(1)	92.0(5)
N(1)–W(1)–Cl(2)	159.2(4)	N(1)–W(1)–Cl(3)	94.2(5)
N(2)–W(1)–Cl(1)	84.4(5)	N(2)–W(1)–Cl(2)	83.7(5)
N(2)–W(1)–Cl(3)	83.3(5)	N(2)–W(1)–N(1)	75.5(6)
N(3)–W(1)–Cl(1)	101.0(6)	N(3)–W(1)–Cl(2)	103.2(6)
N(3)–W(1)–Cl(3)	92.4(6)	N(3)–W(1)–N(1)	97.7(7)
N(3)–W(1)–N(2)	171.6(6)	C(2)–N(1)–W(1)	122.6(12)
C(1)–N(2)–W(1)	111.6(11)	C(8)–C(7)–C(7a)	117.8(16)
N(3)–C(7)–C(7a)	122.8(18)	C(8)–C(9)–C(9a)	121.8(19)
C(3)–C(1)–N(2)	128.7(19)	C(2)–C(1)–N(2)	109.5(16)
C(2)–C(1)–C(3)	121.8(18)	C(2)–C(6)–C(5)	120.3(20)
C(4)–C(3)–C(1)	124.2(19)	C(5)–C(4)–C(3)	115.4(19)
C(4)–C(5)–C(6)	121.3(22)	C(1)–C(2)–N(1)	120.4(16)
C(6)–C(2)–N(1)	122.9(17)	C(6)–C(2)–C(1)	116.7(17)
C(7)–N(3)–W(1)	171.5(14)	C(8)–C(7)–N(3)	118.2(17)
C(9)–C(8)–C(7)	119.6(20)		

Key to symmetry operations relating designated atoms to reference atoms at (x,y,z): (a) $-x, y, \frac{1}{2} - z$.

basis of the above bonding of the bridging ligand, the oxidation state of the tungsten atoms in **1** is V.

The '*o*-pda' ligand chelates very asymmetrically. Whilst the long W–N(2) bond could arise from the normal *trans* influence (*i.e.* lengthening effect) of the multiply bonded imido function from the bridge, we consider that N(2) is actually doubly protonated and therefore a donor amine (NH_2) function. Atom N(1) is from a normal amide (NH) and the W–N(1) bond length of 1.92 Å is consistent with this, particularly if we assume some additional p_π–d_π interaction. It compares with a length of 2.02 Å found for phenylamido bonding in $W_2(NHPh)_2(OCMe_2CMe_2O)_5$.[3] Confirmation of the 1-(HN),2-(H_2N)C_6H_4 bonding is provided by IR spectra where a sharp band at 3364 cm^{-1} can be assigned as the stretch of the NH group, while a broader band at 3397 cm^{-1} can be attributed to the NH_2 group. In fact we were able to locate in the X-ray study the two hydrogens of the NH_2 group but not that on the NH group. Further, the W–N–C angle (111.6°) for the amino group corresponds closely to those for the Cr–N–C angles (109.7, 109.5°) found[4] in the complex $[PPh_4][CrCl_4\{1,2\text{-}(H_2N)_2C_6H_4\}]$ whereas the W–N–C angle for the amido moiety is larger, 122.6°.

The compound shows very broad bands in the ^1H NMR spectrum suggesting paramagnetism but it is EPR silent.

The use of methanol as a solvent for the interaction of WCl_6 with excess of H_2pda produced a diamagnetic red-brown crystalline tungsten(V) complex, $WCl_2(OMe)_2(\mu\text{-}OMe)_2WCl(OMe)_3$ **2**, diagram **II**. The structure is shown in Fig. 2; bond lengths and angles are given in Table 3. The binuclear compound has asymmetric methoxo bridges and a metal–metal single bond of 2.733(3) Å which may be compared with values close to 2.71 Å for M–M bonds in other structurally characterised diamagnetic d^1–d^1 compounds of Mo^V and W^V of formula $M_2Cl_4(OR)_6$[5a] and $W_2(OMe)_{10}$.[5b] The other co-ordination sites on W(1) are

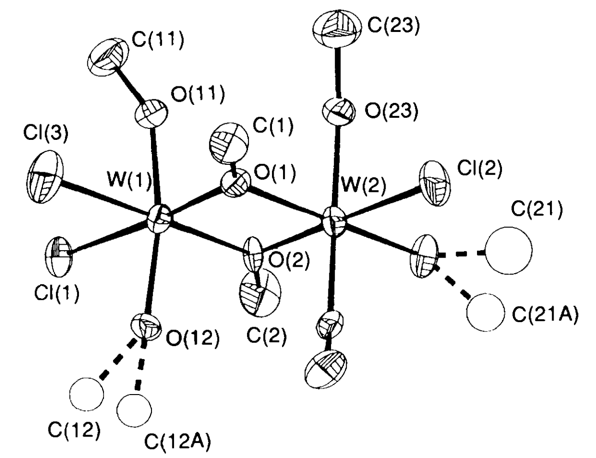


Fig. 2 The structure of $W_2Cl_3(OMe)_5(\mu\text{-}OMe)_2$, showing the disorder of two terminal methoxy methyls

Table 3 Selected bond lengths (Å) and angles (°) for $W_2Cl_3(OMe)_5(\mu\text{-}OMe)_2$ **2**

Cl(1)–W(1)	2.406(4)	Cl(3)–W(1)	2.309(5)
O(1)–W(1)	1.986(6)	O(2)–W(1)	2.055(7)
O(11)–W(1)	1.810(7)	O(12)–W(1)	1.833(6)
Cl(2)–W(2)	2.404(4)	O(1)–W(2)	2.044(7)
O(2)–W(2)	2.010(6)	O(21)–W(2)	1.978(7)
O(22)–W(2)	1.836(6)	O(23)–W(2)	1.804(7)
W(2)–W(1)	2.733(3)		
Cl(3)–W(1)–Cl(1)	89.7(2)	O(1)–W(1)–Cl(1)	178.2(2)
O(1)–W(1)–Cl(3)	88.5(3)	O(2)–W(1)–Cl(1)	86.5(2)
O(2)–W(1)–Cl(3)	176.1(1)	O(2)–W(1)–O(1)	95.3(3)
O(11)–W(1)–Cl(1)	85.0(3)	O(11)–W(1)–Cl(3)	86.8(3)
O(11)–W(1)–O(1)	94.4(3)	O(11)–W(1)–O(2)	91.9(3)
O(12)–W(1)–Cl(1)	86.2(3)	O(12)–W(1)–Cl(3)	89.2(3)
O(12)–W(1)–O(1)	94.2(3)	O(12)–W(1)–O(2)	91.6(3)
O(12)–W(1)–O(11)	170.4(2)	O(1)–W(2)–Cl(2)	87.5(2)
O(2)–W(2)–Cl(2)	177.5(1)	O(2)–W(2)–O(1)	94.9(3)
O(21)–W(2)–Cl(2)	93.3(3)	O(21)–W(2)–O(1)	178.4(2)
O(21)–W(2)–O(2)	84.2(3)	O(22)–W(2)–Cl(2)	85.6(3)
O(22)–W(2)–O(1)	86.1(3)	O(22)–W(2)–O(2)	95.0(3)
O(22)–W(2)–O(21)	95.3(3)	O(23)–W(2)–Cl(2)	85.0(3)
O(23)–W(2)–O(1)	86.6(3)	O(23)–W(2)–O(2)	94.7(3)
O(23)–W(2)–O(21)	92.1(3)	O(23)–W(2)–O(22)	168.3(2)
W(2)–O(1)–W(1)	85.4(3)	C(1)–O(1)–W(1)	136.2(5)
C(1)–O(1)–W(2)	138.1(5)	W(2)–O(2)–W(1)	84.5(3)
C(2)–O(2)–W(1)	139.6(5)	C(2)–O(2)–W(2)	135.8(5)
C(11)–O(11)–W(1)	146.1(5)	C(12)–O(12)–W(1)	143.3(6)
C(12A)–O(12)–W(1)	147.6(10)	C(12A)–O(12)–C(12)	41.5(10)
C(21)–O(21)–W(2)	136.5(7)	C(21A)–O(21)–W(2)	111.8(13)
C(22)–O(22)–W(2)	148.7(5)		
C(23)–O(23)–W(2)	144.2(5)		

occupied by two Cl and two MeO ligands whereas W(2) has one Cl and three MeO ligands, the methoxide occupying axial positions. The consequence is that the ligand atoms *trans* to the MeO bridges are not the same for the two tungsten centres. As in other cases some p_π–d_π bonding is involved in the terminal WOMe groups [W–O(av.) 1.82(1) Å] whereas the bridged W–O distances of 1.99(1)–2.06 Å are consistent with sp^2 hybridisation of oxygen and W–O–W single bonds.

The ^1H NMR spectrum, which is temperature independent, can be readily interpreted on the basis of the structure **II** and on NMR data for $W_2O_2(OMe)_4(\mu\text{-}OMe)_2$,[6] structure **III**, and $W_2(OMe)_{10}$.[5b] For the compound of structure **III** there were three bands: axial, 12 H, δ 4.7; equatorial 6 H, δ 4.6; and bridging, 6 H, δ 4.5. The spectrum for compound **2** can hence be reasonably assigned as: axial W^2, 3 H, δ 5.29; axial W^2, 3 H, δ 4.85; equatorial W^2, 3 H, δ 4.7; axial W^1, 6 H, δ 4.0; and bridging 6 H, δ 3.5. The small differences in shifts, *e.g.* for axial W, are due to different π-bonding requirements when axial O and MeO in structure **III** are replaced by Cl in **II**.

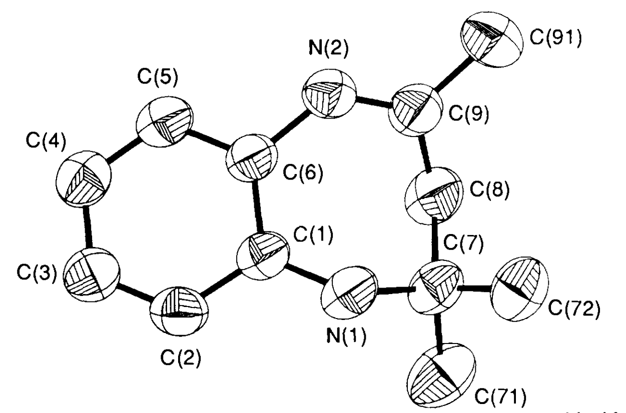
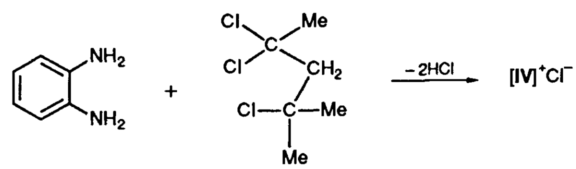
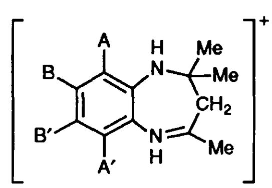


Fig. 3 The structure of the 1,5-benzodiazepinium cation in its chloride salt. This is identical with that found in the tungsten complex **4**

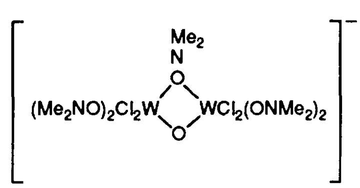
Interaction of the complex $WCl_4(PMe_3)_3$ in Pr^iOH with H_2pda produces a lustrous black crystalline compound that, on the basis of analyses and spectra, can be formulated as the seven-co-ordinate $WCl_2[1,2\text{-}(HN)_2C_6H_4](PMe_3)_3$ **3**, which can be compared with $CrCl_2[(HN)_2C_6H_4](PMe_2Ph)_2$.[7] Crystals suitable for X-ray study could not be obtained due to persistent twinning. The only related seven-co-ordinate phosphine tungsten(IV) complexes structurally characterised are $WCl_4(PMe_3)_3$[8] and $WCl_4(PMe_2Ph)_3$.[4]

The product obtained from the interaction of $LiNMe_2$ (prepared *in situ* from Me_2NH and Aldrich 1.6 mol dm^{-3} $LiBu^n$ in hexanes), which we were expecting to act as a base, with $WOCl_4$ and H_2pda in methanol–tetrahydrofuran was an orange crystalline solid **4** shown by X-ray study, as discussed below, to have a structure with the 1,5-benzodiazepinium cation **IV** and the anion **V**. The formation of the 1,5-benzodiazepinium[9] cation seemed curious until it was realised that the hexanes* contained 2-methylpentane that can be chlorinated by $WOCl_4$ or WCl_4 (or by chlorine) to give $Me_2C(Cl)CH_2C(Cl)_2Me$ which can then react in the presence of base as in equation (1).

 (1)



IV



V

The diazepinium salt could alternatively arise from the diazepine since the interaction of *o*-phenylenediamine with butyllithium in hexanes is extremely oxygen sensitive, the colour rapidly changing from yellow-brown to the blue of the diazepine (see Experimental section).

The structure of the cation is the same in both **4** and in the red chloride salt, also structurally characterised and made independently using 2-methylpentane (see Experimental section).

* We thank Aldrich Chemical Co. for confirming the composition of the solvent as 60–85% *n*-hexane with the remainder 2,3-dimethylbutane, 2-methyl- and 3-methyl pentane.

Table 4 Bond lengths (Å) and angles (°) for 1,5-benzodiazepinium cation as its chloride (*a*) and in the $[W_2Cl_4O(ONMe_2)_5]^-$ salt (*b*)

	(*a*)	(*b*)
C(7)–N(1)	1.450(8)	1.470(39)
C(1)–N(1)	1.348(7)	1.389(35)
C(6)–N(2)	1.417(7)	1.405(32)
C(9)–N(2)	1.243(8)	1.356(32)
C(8)–C(7)	1.518(9)	1.496(41)
C(71)–C(7)	1.513(11)	1.569(43)
C(72)–C(7)	1.483(9)	1.524(43)
C(1)–C(6)	1.389(7)	1.430(38)
C(5)–C(6)	1.358(7)	1.470(38)
C(2)–C(1)	1.404(8)	1.434(42)
C(91)–C(9)	1.493(12)	1.487(38)
C(8)–C(9)	1.470(9)	1.465(37)
C(5)–C(4)	1.373(8)	1.368(39)
C(3)–C(4)	1.359(8)	1.462(44)
C(3)–C(2)	1.336(8)	1.400(44)
C(1)–N(1)–C(7)	124.6(5)	126.8(27)
C(9)–N(2)–C(6)	124.9(6)	126.2(24)
C(8)–C(7)–N(1)	109.3(5)	109.0(27)
C(71)–C(7)–N(1)	109.6(7)	110.7(27)
C(71)–C(7)–C(8)	108.1(6)	111.7(29)
C(72)–C(7)–N(1)	108.2(6)	103.8(29)
C(72)–C(7)–C(8)	111.0(6)	111.8(28)
C(72)–C(7)–C(71)	110.6(6)	109.5(28)
C(1)–C(6)–N(2)	120.4(5)	131.0(26)
C(5)–C(6)–N(2)	118.3(5)	111.1(24)
C(5)–C(6)–C(1)	121.0(6)	117.9(27)
C(6)–C(1)–N(1)	121.3(6)	125.5(30)
C(2)–C(1)–N(1)	122.3(5)	115.3(29)
C(2)–C(1)–C(6)	115.9(5)	119.2(29)
C(91)–C(9)–N(2)	118.8(8)	114.8(23)
C(8)–C(9)–N(2)	119.6(7)	122.0(27)
C(8)–C(9)–C(91)	121.5(7)	123.1(27)
C(9)–C(8)–C(7)	112.7(6)	117.4(26)
C(3)–C(4)–C(5)	119.0(6)	118.3(32)
C(4)–C(5)–C(6)	121.0(6)	122.9(31)
C(3)–C(2)–C(1)	122.4(6)	121.3(30)
C(2)–C(3)–C(4)	120.6(6)	120.4(31)

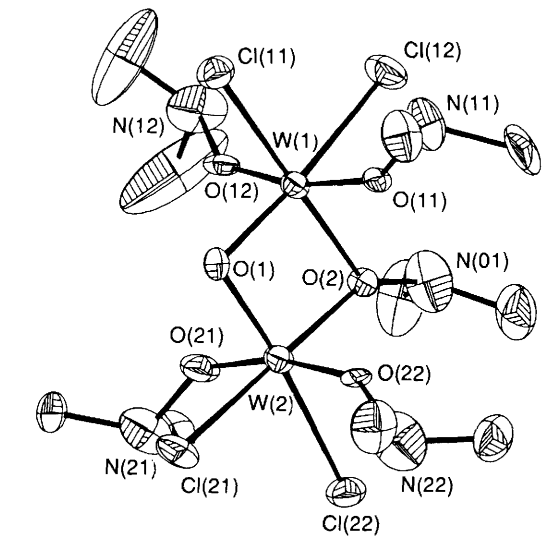


Fig. 4 The structure of the anion $[W_2Cl_4O(ONMe_2)_5]^-$ in its 1,5-benzodiazepinium salt

This is shown in Fig. 3 with bond lengths and angles for both structures in Table 4. No hydrogens on the cation were located in the complex salt, but all were experimentally located and refined in the chloride. This confirmed protonation at the imine nitrogen.

The structure of the anion is shown in Fig. 4 with bond lengths and angles in Table 5. As far as we are aware no

Table 5 Selected bond lengths (Å) and angles (°) for the anion in $[C_{12}H_{17}N_2][W_2Cl_4O(ONMe_2)_5]$ **4**

W(2)–W(1)	2.643(4)	Cl(12)–W(1)	2.460(9)
Cl(11)–W(1)	2.417(9)	O(11)–W(1)	1.810(20)
O(1)–W(1)	1.912(16)	O(2)–W(1)	2.002(18)
O(12)–W(1)	1.789(21)	Cl(21)–W(2)	2.405(9)
Cl(22)–W(2)	2.455(9)	O(21)–W(2)	1.828(17)
O(1)–W(2)	1.925(17)	O(2)–W(2)	2.054(16)
O(22)–W(2)	1.829(19)		
Cl(11)–W(1)–Cl(12)	88.4(4)	O(1)–W(1)–Cl(12)	172.3(5)
O(11)–W(1)–Cl(12)	85.2(7)	O(11)–W(1)–Cl(11)	85.2(7)
O(1)–W(1)–Cl(11)	83.9(6)	O(1)–W(1)–O(11)	94.6(8)
O(2)–W(1)–Cl(12)	90.8(5)	O(2)–W(1)–O(1)	96.9(7)
O(2)–W(1)–Cl(11)	179.2(5)	O(2)–W(1)–O(11)	95.1(8)
O(12)–W(1)–Cl(12)	83.7(7)	O(12)–W(1)–Cl(11)	87.2(7)
O(12)–W(1)–O(11)	166.6(7)	O(12)–W(1)–O(1)	95.5(8)
O(12)–W(1)–O(2)	92.4(8)	Cl(22)–W(2)–Cl(21)	89.3(4)
O(21)–W(2)–Cl(21)	87.0(6)	O(21)–W(2)–Cl(22)	83.7(6)
O(1)–W(2)–Cl(21)	84.8(6)	O(1)–W(2)–Cl(22)	174.1(5)
O(1)–W(2)–O(21)	96.1(8)	O(22)–W(2)–Cl(21)	88.3(6)
O(2)–W(2)–Cl(21)	178.9(5)	O(2)–W(2)–Cl(22)	91.1(6)
O(2)–W(2)–O(21)	92.0(8)	O(2)–W(2)–O(1)	94.8(7)
O(22)–W(2)–Cl(22)	84.0(6)	O(22)–W(2)–O(21)	166.9(7)
O(22)–W(2)–O(1)	95.6(7)	O(22)–W(2)–O(2)	92.8(8)
N(21)–O(21)–W(2)	144.4(16)	N(11)–O(11)–W(1)	142.8(16)
W(2)–O(1)–W(1)	87.0(7)	W(2)–O(2)–W(1)	81.3(6)
N(01)–O(2)–W(1)	145.2(17)	N(01)–O(2)–W(2)	133.2(17)
N(22)–O(22)–W(2)	148.3(17)	N(12)–O(12)–W(1)	145.2(19)

compounds with *O*-bonded unidentate or bridging dialkylhydroxylaminato(1–) ligands have been described; dialkylhydroxylaminato species are either chelate, or *N,O*-bridged.[10] Dialkylhydroxylaminato compounds of tungsten have not been previously reported. The source of the oxygen atoms required to convert NMe_2^- into $ONMe_2^-$ is uncertain; they could arise in part from $WOCl_4$, part from the solvent and possibly some adventitious oxygen.

The overall structure is similar to that of the neutral methoxide chloride described above but with the oxo function replacing one bridging methoxide and one terminal methoxide replaced by chloride. The tungsten(VI) centres have distorted octahedral environments. The bulkier Me_2NO group imposes greater steric constraints than the O atom, which is reflected in the longer W–O bond length (2.00, 2.054 *vs.* 1.93, 1.91 Å for WOW). The W–Cl bonds *trans* to the oxo bridge are longer compared to the others (2.455 *vs.* 2.405 Å) suggesting a greater *trans* influence of the oxo compared to the Me_2NO group. The W–O bond lengths for the unidentate *O*-Me_2NO ligands are relatively short [1.79–1.83 Å (*cf.* bonds to the methoxide above)] and are close to the value[11] of 1.79 Å for the W–O bonds in WO_4^{2-} suggesting significant multiple-bond character. This is also confirmed by the relatively large (142–148°) W–O–N angles; the axial positions of these unidentate $ONMe_2$ ligands and the position *cis* to μ-O thus allows the tungsten atoms to maximise the π-electron density. Since ligands of the RO type (here R = NMe_2) are better π donors than is Cl, this is reflected in the W–Cl bond lengths (2.405–2.460 Å) which suggest minimal W–Cl π bonding [*cf.* WCl_6,[12] W–Cl(av.) 2.24 Å]. Regarding the Cl and Me_2NO ligands, formally as 1e donors, each W atom has a σ-electron count of 12. π Donations from any three of the four oxygen functions attached to each tungsten will increase this to 18e.

Neutral 1,5-benzodiazepines related to the present cation are known.[13a] It is of interest that interaction of acetylacetone with $[Cr\{1,2-(HN)_2C_6H_4\}_6]Cl_2$ has also been found to give a purple black 2,4-dimethyl-1,5-benzodiazepinium chloride.[13b] A complex containing N(5) co-ordinated 7,8-dichloro-2,3-dihydro-2,2,4-trimethyl-1*H*-1,5-benzodiazepine (L), $PdCl_2L(PPr^n_3)_3$,[13c] whilst very recently some platinum(II) complexes with benzodiazepines have been prepared.[13d]

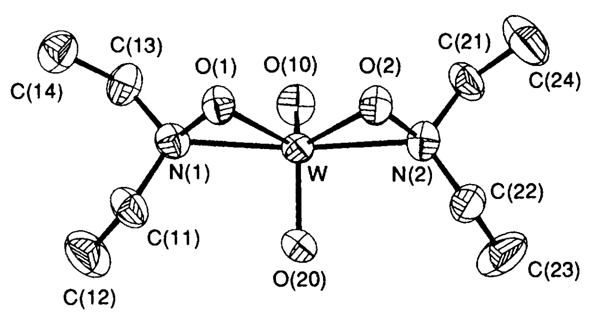


Fig. 5 The structure of $WO_2(ONEt_2)_2$

In an attempt to make σ-dialkylhydroxylaminato(1 −) derivatives directly, $WOCl_4$ and $LiONR_2$ (from R_2NOH and $LiBu^n$ in hexanes) were allowed to react in tetrahydrofuran (thf) or Et_2O. The isolated colourless crystals, however, were of the dioxo complex $WO_2(\eta^2\text{-}ONR_2)_2$ (R = Et **5** or $PhCH_2$ **6**). The oxygen doubtless comes from the solvent. The molybdenum analogue of the diethyl and some similar molybdenum oxo [14a–c] and sulfido [14d] compounds have been made in other ways, *e.g.* interaction of Na_2MoO_4 in 30% H_2O_2 with the dialkylhydroxylamine, and some structures have been determined.

A diagram of the molecule of **5**, which is isostructural with its molybdenum analogue,[14a] is given in Fig. 5; bond lengths and angles are in Table 6. The molecule has non-crystallographic mirror symmetry within the limits of experimental error. The W=O distances are also equal within error. The η^2-diethylhydroxylaminato ligand has W–O slightly shorter [1.966(9) and 1.973(9) Å] than W–N bonds [2.134(10) and 2.152(10) Å]. The N–O bonds [1.447(11) and 1.463(12) Å] are single.

The ^1H NMR spectrum of compound **5** is also similar to that of the molybdenum analogue;[4b] owing to hindered inversion at the nitrogen centre, the CH_2 hydrogen atoms are diastereotopic and give rise to two six-line multiplets while the CH_3 group gives a triplet. The IR stretches at 898 and 932 cm^{-1} are assignable to the *cis* dioxotungsten group.

Table 6 Selected bond lengths (Å) and angles (°) for $WO_2(ONEt_2)_2$ **5**

O(10)–W	1.721(9)	O(1)–W	1.973(9)
O(2)–W	1.966(9)	N(1)–W	2.134(10)
N(2)–W	2.152(10)	O(20)–W	1.721(9)
N(1)–O(1)	1.447(11)	N(2)–O(2)	1.463(12)
O(1)–W–O(10)	112.3(4)	O(2)–W–O(10)	113.6(4)
O(2)–W–O(1)	85.1(4)	N(1)–W–O(10)	92.7(4)
N(1)–W–O(1)	41.0(3)	N(1)–W–O(2)	126.1(4)
N(2)–W–O(10)	94.7(4)	N(2)–W–O(1)	126.4(4)
N(2)–W–O(2)	41.3(3)	N(2)–W–N(1)	167.4(3)
O(20)–W–O(10)	116.3(5)	O(20)–W–O(1)	112.8(4)
O(20)–W–O(2)	112.8(5)	O(20)–W–N(1)	93.2(4)
O(20)–W–N(2)	92.8(5)	N(2)–O(1)–W	75.5(6)
N(2)–O(2)–W	76.2(5)	O(1)–N(1)–W	63.5(5)
C(11)–N(1)–W	119.5(8)	C(11)–N(1)–O(1)	107.6(8)
C(13)–N(1)–W	122.9(8)	C(13)–N(1)–O(1)	109.3(9)
C(13)–N(1)–C(11)	116.4(10)	O(2)–N(2)–W	62.5(5)
C(21)–N(2)–W	119.8(8)	C(21)–N(2)–O(2)	109.2(9)
C(22)–N(2)–W	121.8(8)	C(22)–N(2)–O(2)	109.6(9)
C(22)–N(2)–C(21)	116.9(10)		

Experimental

General procedures and instrumentation have been described.[1] Microanalyses were by Imperial College, University College London and Pascher Laboratories.

The compounds $LiONR_2$ (R = Et or $PhCH_2$) were obtained by interaction of the dialkylhydroxylamine in hexane with a stoichiometric quantity of $LiBu^n$ in hexane at 0 °C; $LiNMe_2$ was prepared similarly in hexane from $LiBu^n$ and $NHMe_2$ at −78 °C. All operations were carried out under N_2 or Ar. Proton NMR spectra (250 MHz) in ppm referenced to $SiMe_4$, IR spectra in Nujol mulls and mass spectra by electron impact. Commercial chemicals were from Aldrich.

μ-(1,2-*Phenylenediimido*)-*bis*[(1-*amido*-2-*aminobenzene*)-*trichlorotungsten*(V)] **1**.—To a solution of WCl_6 (5 g, 12.6 mmol) in Pr^iOH (50 cm^3) at 25 °C was added dropwise *via* a cannula a solution of $o\text{-}C_6H_4(NH_2)_2$ (4.1 g, 37.9 mmol) in Pr^iOH (30 cm^3). After stirring for 12 h the resulting blue mixture was filtered and the filtrate concentrated (60 cm^3) and cooled at 0 °C to give blue needles. Yield: 1.3 g, 23%. The mother-liquor provided further crops of product. IR: 3397,

Table 7 Crystal data, details of intensity measurements and structure refinement

	1	2	4		5
Formula	$C_{18}H_{22}Cl_6N_6W_2{\cdot}2C_7H_8$	$C_7H_{21}Cl_3O_7W_2$	$[C_{12}H_{17}N_2][C_{10}H_{30}Cl_4N_5O_6W_2]$	$[C_{12}H_{17}N_2]Cl$	$C_8H_{20}N_2O_4W$
M	1 087.116	691.298	1 016.181	225.741	392.108
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	*Pbcn*	$P2_1/a$	$P2_1/n$	$P2_1/n$	*Pbca*
a/Å	9.657(2)	11.113(10)	10.212(2)	8.981(1)	22.988(4)
b/Å	18.152(2)	13.081(4)	24.549(1)	13.488(1)	11.132(1)
c/Å	20.807(2)	12.818(7)	15.044(2)	10.039(1)	10.203(2)
α/°	90	90	90	90	90
β/°	90	106.83(4)	91.71(1)	99.71(1)	90
γ/°	90	90	90	90	90
U/Å^3	3 647.24	1 783.53	3 769.76	1 198.66	2 610.97
Z	4	4	4	4	8
D_c/g cm^{-3}	1.972	1.287	1.759	1.299	1.9950
F(000)	2 072	1 272	1 900	484	1 504
μ/cm^{-1}	69.164	136.44	65.56	2.98	90.38
Total no. of reflections	16 439	4 832	15 773	8 471	15 498
No. of unique reflections	3 447	2 445	7 528	2 906	3 256
No. of observed reflections [$F_o > 3\sigma(F_o)$]	2 068	1 845	2 238	1 207	2 324
No. of refined parameters	224	172	410	204	157
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0	0	Unit weights	Unit weights	0
Final R	0.0568	0.0504	0.0404	0.0562	0.0485
Final R'	0.0569	0.0538	0.0404	0.0562	0.0482

Table 8 Fractional atomic coordinates (× 10^4) for compound **1**

Atom	x	y	z
W(1)	1240.2(4)	619(1)	1931.2(3)
Cl(1)	1273(3)	−873(4)	2829(2)
Cl(2)	2470(2)	1178(5)	2243(3)
Cl(3)	1528(3)	1854(5)	969(2)
N(1)	438(7)	−392(13)	1551(7)
N(2)	1794(8)	−1182(16)	1406(8)
C(1)	1254(10)	−2144(16)	1142(6)
C(6)	−69(10)	−2446(22)	1009(9)
C(3)	1365(10)	−3333(19)	860(9)
C(4)	794(12)	−4213(22)	633(11)
C(5)	61(13)	−3730(22)	747(11)
C(2)	536(9)	−1610(17)	1239(8)
N(3)	725(7)	2005(14)	2238(7)
C(7)	370(9)	3146(17)	2393(9)
C(8)	733(11)	4439(20)	2299(9)
C(9)	364(15)	5630(18)	2408(12)
C(12)	1784(10)	659(14)	4547(8)
C(13)	1018(10)	682(14)	4604(8)
C(14)	610(10)	1710(14)	4295(8)
C(15)	968(10)	2715(14)	3929(8)
C(16)	1734(10)	2693(14)	3871(8)
C(11)	2141(10)	1664(14)	4180(8)
C(10)	2952(12)	1475(25)	4141(15)

3364w (NH): 1618w, 1586m, 1535s, 1500m, 1312m, 1191w, 1152m, 984m, 760s, 725s, 623w, 592w, 537m and 455m cm^{-1}.

*Trichloro bis(μ-methoxo)pentamethoxoditungsten(*V*)* **2**.—To WCl_6 (3.0 g, 7.56 mmol) in MeOH (*ca.* 40 cm^3) was added a solution of 1,2-$C_6H_4(NH_2)_2$ (2.5 g, 23.1 mmol) in MeOH (40 cm^3) at −78 °C and the orange mixture stirred for 12 h during warming to room temperature. The filtered solution on cooling at −20 °C gave red-brown X-ray-quality crystals of the methanol solvate in *ca.* 20% yield. Further crops can be obtained from the mother-liquor. IR: 3168m, 2605m, 2568m, 1630w, 1615w, 1528m, 1495m, 1318w, 1277w, 1247w, 1186w, 1160w, 1107w, 1021s, 938w, 878w, 829w, 804w, 758m, 748s, 732m, 604w, 585w, 533m and 446s cm^{-1}. ^1H NMR (C_6D_6): δ 3.5 (s, 6 H), 4.0 (s, 6 H), 4.7 (s, 3 H), 4.85 (s, 3 H) and 5.29 (s, 3 H); for assignments see text.

*Dichloro(1,2-phenylenediamido)tris(trimethylphosphine)-tungsten(*IV*)* **3**.—To $WCl_4(PMe_3)_3$[8] (1.0 g, 1.8 mmol) in Pr^{i}OH at −78 °C was added a solution of 1,2-$C_6H_4(NH_2)_2$ (0.6 g, 5.5 mmol) in Pr^{i}OH, and the red-black solution stirred for 12 h while warming to room temperature. Removal of volatiles under vacuum and extraction of the residue with toluene, followed by concentration and cooling (−20 °C) of the filtered extract, gave black, lustrous crystals. Yield: 0.41 g, 39%. Further crops can be obtained from the mother-liquor; overall yield *ca.* 90%. IR: 3418w, 3312w, 3187w, 1713w, 1605m, 1340m, 1322m, 1300m, 1280m, 1262m, 1158m, 1094m, 1033w, 945s, 808m, 804m, 751s, 723s, 668m, 595w, 494w, 421w and 344w cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.5 (m, PMe_3) and 6.3–7.6 (aromatic bands).

2,2,4-*Trimethyl*-1,5-*benzodiazepinium Dichloro(μ-dimethylhydroxylaminato)tetrakis(dimethylhydroxylaminato)-μ-oxo-di-tungstate(*VI*)* **4**.—To a solution of $WOCl_4$[15] (0.45 g, 1.32 mmol) in thf (*ca.* 40 cm^3) containing MeOH (0.05 cm^3, 1.23 mmol) at −78 °C was added *via* a cannula a solution of $LiNMe_2$ (5.28 mmol) in hexane. The mixture was stirred for 3 h at room temperature, after which 1,2-$C_6H_4(NH_2)_2$ (0.43 g, 3.98 mmol) in thf (*ca.* 20 cm^3) was added. Stirring for 12 h, removal of volatiles and extraction of the residue with hot toluene (*ca.* 35 cm^3) gave, on cooling (−20 °C), a bright orange microcrystalline solid which was recrystallised from toluene as the toluene solvate. Yield: 0.37 g, 55%. IR: 3392w, 3208s, 2729s, 2608s, 1713w,

Table 9 Fractional atomic coordinates (× 10^4) for compound **2**

Atom	x	y	z
W(1)	1690(1)	393(1)	2858(1)
W(2)	3742(1)	−246(1)	2267(1)
Cl(1)	1423(7)	1469(5)	4298(5)
Cl(2)	4024(7)	−1326(5)	839(6)
Cl(3)	−457(8)	140(7)	2256(7)
O(1)	1855(15)	−511(9)	1662(12)
C(1)	999(25)	−1151(18)	812(20)
O(2)	3586(13)	657(10)	3491(11)
C(2)	4415(26)	1229(18)	4317(20)
O(11)	1739(16)	−647(10)	3801(13)
C(11)	1475(28)	−960(20)	4763(20)
O(12)	1491(14)	1560(9)	2033(11)
C(12)	819(32)	2522(22)	1822(26)
O(21)	5566(15)	−4(12)	2892(12)
C(21)	6604(41)	−329(28)	2708(32)
O(22)	3498(14)	790(9)	1259(11)
C(22)	2920(27)	1133(19)	220(19)
O(23)	3816(16)	−1419(10)	3022(12)
C(23)	3365(28)	−2418(18)	2966(24)
C(12A)	1780(68)	2685(54)	1981(58)
C(21A)	6222(90)	272(73)	1975(82)

Partial occupancies: C(12) 0.7194, C(12A) 0.2806, C(21) 0.8117, C(21A) 0.1883.

Table 10 Fractional atomic coordinates (× 10^4) for $[C_{10}H_{17}N_2]Cl$

Atom	x	y	z
Cl	1682(2)	491(1)	2250(2)
C(6)	5304(6)	9097(4)	2114(5)
C(5)	5639(7)	9395(4)	3446(6)
C(4)	7068(7)	9723(5)	3986(6)
C(3)	8141(7)	9778(4)	3153(6)
C(2)	7833(6)	9469(4)	1847(6)
C(1)	6406(6)	9093(4)	1265(5)
N(2)	3773(5)	8877(4)	1573(5)
N(1)	6062(6)	8854(4)	−78(5)
C(9)	3351(7)	8191(5)	742(6)
C(8)	4466(8)	7464(5)	387(7)
C(7)	5447(7)	7895(4)	−597(6)
C(91)	1698(11)	8085(10)	201(13)
C(71)	6730(11)	7165(7)	−678(10)
C(72)	4546(10)	8061(6)	−1979(7)

1652w, 1608m, 1581m, 1557m, 1528s, 1486s, 1309s, 1261m, 1231w, 1197w, 1142m, 1127m, 1097s, 1044m, 954m, 884m, 865m, 805m, 775s, 755s, 722s, 530w, 504w, 466w, 462w, 407w, 351w, 330w, 317w, 308w and 292w cm^{-1}. ^1H NMR [$(CD_3)_2CO$]: δ 6.9–8.0 (aromatic bands), 2.3 (s, 2 H, CH_2), 1.3 (s, 24 H, $ONMe_2$), 0.9 (s, 9 H, CH_3), and 0.1 (s, 6 H, μ-$ONMe_2$). Conductivity (MeCN, 20 °C); Λ_M = 27.3 ohm^{-1} cm^2 mol^{-1}.

The 1,5-benzodiazepinium chloride was obtained as follows. (*a*) Butyllithium in hexanes (6.47 mmol) was added to a solution of 1,2-$C_6H_4(NH_2)_2$ (0.7 g, 6.47 mmol) in thf (25 cm^3) at −40 °C. After stirring for 4 h at 25 °C the solution was added to WCl_4 (1 g, 3.07 mmol) in thf (25 cm^3) at −40 °C. After stirring for *ca.* 1 d the mixture was warmed to room temperature, filtered and the solution allowed to stand at room temperature when red crystals of the chloride were formed; these were separated manually in *ca.* 20% yield, m.p. 167–169 °C, mass spectrum identical to that given by Hunter and Webb.[13a]

(*b*) 2-Methylpentane (20 cm^3) was treated with excess chlorine at 25 °C for *ca.* 3 h. No attempt was made to separate the mixture but the presence of the trichlorinated product was confirmed by mass spectrometry. Addition of excess of 1,2-$C_6H_4(NH_2)_2$ in thf and work-up as above gave a similar red product in *ca.* 10% yield. ^1H NMR ($CDCl_3$), see diagram **IV** for labels: δ 1.39 (s, 6 H, Me_2), 2.62 (s, 2 H, CH_2) 2.95 (s, 3 H, Me),

Table 11 Fractional atomic coordinates (× 10^4) for the anion in compound **4**

Atom	x	y	z
W(1)	1233(1)	1288(1)	2015(1)
W(2)	3493(1)	1807(1)	2191(1)
Cl(21)	5170(6)	1774(3)	3347(5)
Cl(12)	−646(6)	1182(3)	968(5)
Cl(22)	4832(7)	2458(3)	1377(5)
Cl(11)	205(7)	641(3)	2985(5)
O(21)	4450(14)	1298(7)	1604(10)
O(11)	228(15)	1790(8)	2552(12)
O(1)	2583(14)	1296(6)	2923(9)
O(2)	2070(14)	1819(7)	1197(10)
O(22)	2848(14)	2417(6)	2719(11)
O(12)	1869(17)	716(7)	1431(12)
N(21)	5712(26)	1152(11)	1358(18)
N(11)	−1104(26)	1895(10)	2838(21)
N(22)	2982(32)	3001(10)	2902(27)
N(12)	1553(32)	219(14)	1002(24)
C(211)	6073(33)	636(13)	1774(22)
C(111)	−1679(29)	2401(14)	2354(22)
C(112)	−1119(31)	1938(13)	3807(19)
C(212)	5652(31)	1086(17)	344(20)
N(01)	1899(32)	2129(12)	409(21)
C(101)	2092(38)	1777(17)	−402(21)
C(122)	1883(34)	223(15)	74(24)
C(121)	2294(36)	−239(14)	1497(25)
C(101)	1018(43)	2550(15)	459(25)
C(221)	1602(62)	3217(20)	2838(45)
C(222)	3484(67)	3118(25)	3726(41)
N(1)	2122(24)	208(10)	6281(16)
N(2)	2726(17)	934(8)	4609(14)
C(7)	1573(32)	748(14)	6464(20)
C(6)	2939(25)	375(11)	4750(18)
C(1)	2649(26)	33(13)	5488(19)
C(9)	2553(21)	1316(12)	5247(15)
C(91)	2316(27)	1876(12)	4905(18)
C(8)	2528(32)	1175(12)	6192(20)
C(4)	3810(34)	−423(12)	3931(22)
C(5)	3524(26)	120(12)	3972(22)
C(71)	206(30)	821(14)	5976(23)
C(2)	2922(34)	−539(12)	5438(23)
C(3)	3503(31)	−765(15)	4693(24)
C(72)	1396(36)	745(15)	7467(23)

Table 12 Fractional atomic coordinates (× 10^4) for compound **5**

Atom	x	y	z
W	1233(1)	349.4(1)	1969(1)
O(10)	652(3)	147(7)	3011(7)
O(1)	984(3)	667(6)	152(7)
O(2)	1548(3)	−1159(6)	1262(7)
N(1)	792(4)	1709(7)	880(8)
N(2)	1700(4)	−1205(8)	2653(8)
C(11)	1127(5)	2774(9)	382(12)
C(12)	1009(7)	3870(11)	1266(15)
C(13)	157(5)	1792(10)	813(11)
C(14)	−92(6)	2101(11)	−494(12)
C(21)	1378(5)	−2212(9)	3288(12)
C(22)	2329(5)	−1200(10)	2798(12)
C(23)	2507(7)	−957(15)	4193(14)
C(24)	1555(9)	−3433(11)	2790(17)
O(20)	1767(4)	1320(6)	2493(8)

4.7 (br s, 2 H, NH); aromatic regions, δ_A = 7.95 (dd, 1 H) (J_{AB} = 7.55, $J_{AB'}$ = 0.96), δ_B = 7.25 (t*, 1 H) (J = 8.14, $J_{BA'}$ = 1.32 Hz), $\delta_{B'}$ = 7.00 (t*, 1 H) (J = 7.69, $J_{B'A}$ = 1.14), $\delta_{A'}$ = 6.9 (dd, 1 H) ($J_{A'B'}$ = 8.24) (t* signifies singlet between two doublets; $J_{A'B}$ not seen).

The neutral benzodiazepine was obtained in *ca.* 10% yield by addition of $LiBu^n$ in hexanes to H_2pda in Et_2O or thf and treatment with oxygen; the mass, IR and NMR spectra of the product were as reported.[13a]

Bis(η^2-*diethylhydroxylaminato*)*dioxotungsten*(VI) **5**.—To $WOCl_4$ (1.0 g, 2.94 mmol) in either diethyl ether of thf (20 cm^3) was added a suspension of Et_2NOLi (11.8 mmol) in Et_2O or thf (*ca.* 30 cm^3) with stirring at −78 °C. After stirring at 25 °C (12 h) volatiles were removed in vacuum and the solid residue extracted with hot toluene. Filtration, reduction (to 30 cm^3) and cooling (−20 °C) gave large colourless crystals in 50–60% yield. Further crops can be obtained after reduction in volume and cooling, the overall yield being *ca.* 90%. Mass spectrum: *m/z* 392 (M^+). IR: 2728w, 2468w, 1823w, 1311s, 1294s, 1262w, 1178s, 1127s, 1087s, 1046s, 1012s, 932s, 898s, 829s, 799s, 756s, 634s, 621s, 579s, 490s, 466s, 444s and 286s cm^{-1}. ^1H NMR ([$^2H_8$]toluene): δ 0.83 (t, 12 H, CH_3), 2.93 (4 H) and 3.2 (4 H) were six-line multiplets due to the stereotopic CH_2 groups. Cyclic voltammetry in MeCN with 0.1 mol dm^{-3} (NBu^n_4)PF_6 as supporting electrolyte, scan range −2.0 to +2.0 V, and referenced to Ag–Ag^+ in MeCN showed irreversible reductions at −1.0 and −1.38 V.

Bis(η^2-*dibenzylhydroxylaminato*)*dioxotungsten*(VI) **6**.—As above but using $WOCl_4$ (1.2 g, 3.52 mmol) and $(PhCH_2)_2NOLi$ (14.1 mmol) in thf (40 cm^3). Concentration of the toluene extract and cooling gave colourless crystals of the solvate with two thf molecules. Yield: 70–75%. ^1H NMR [$(CD_3)_2CO$]: δ 3.86 (8 H, CH_2Ph) and 7.19–7.40 (aromatic bands, 20 H).

X-Ray Crystallography.—All crystals used for the X-ray studies were sealed under argon in glass capillaries. Unit-cell and intensity data were recorded with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) using a FAST TV area diffractometer following procedures previously described.[16] The structures were solved *via* the heavy-atom method and refined by full-matrix least squares. Non-hydrogen atoms were refined anisotropically except for two disordered methyl carbons in the methoxide complex which were represented by partial atoms and refined isotropically. Hydrogen atoms were included in idealised positions in all except compound **1**. Crystal data and details of data collection and refinement are given in Table 7, final atomic positional parameters in Tables 8–12.

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

Acknowledgements

We thank the SERC for support and provision of X-ray facilities.

References

1 A. A. Danopoulos, A. C. C. Wong, G. Wilkinson, B. Hussain and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1990, 315.
2 (*a*) A. Anillo, R. Obeso-Rosete, M. A. Pellinghelli and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1991, 2019; (*b*) O. Carugo, K. Djinovic, M. Rizzi and C. B. Castellani, *J. Chem. Soc., Dalton Trans.*, 1991, 1551.
3 P. A. Bates, A. J. Nielson and J. M. Waters, *Polyhedron*, 1985, **4**, 999.
4 C. Redshaw, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, unpublished work.
5 (*a*) F. A. Cotton, D. DeMarco, B. S. W. Kolthammer and R. A. Walton, *Inorg. Chem.*, 1981, **20**, 3048; (*b*) J. C. Bryan, D. R. Wheeler, D. L. Clark, J. C. Huffman and A. P. Sattelberger, *J. Am. Chem. Soc.*, 1991, **113**, 3184.
6 C. Redshaw, Ph.D. Thesis, University of Newcastle-upon Tyne, 1989.
7 W.-H. Leung, A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1991, 2051.
8 R. D. Rogers, E. Carmona, A. Galindo, J. L. Atwood and L. G. Canada, *J. Organomet. Chem.*, 1984, **277**, 403.
9 D. Lloyd and H. P. Cleghorn, *Adv. Heterocycl. Chem.*, 1974, **17**, 27.

10 J. A. McCleverty, *Transition Met. Chem.*, 1987, **12**, 282; R. S. Vagg, *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, p. 798.
11 W. H. Zachariasen and H. A. Mettinger, *Acta Crystallogr.*, 1961, **14**, 229.
12 J. A. A. Katelaar and G. W. Oosterhout, *Recl. Trav. Chim. Pays-Bas*, 1943, **62**, 197.
13 (*a*) M. C. Aversa, A. Ferlazzo, P. Giannetto and F. H. Kohnke, *Synthesis*, 1986, 230; P. W. W. Hunter and G. A. Webb, *Tetrahedron*, 1972, **28**, 5573; 1973, **29**, 147; R. M. Acheson and W. R. Tully, *J. Chem. Soc. C*, 1970, 1117; (*b*) J. Jubb, L. F. Larkworthy, L. F. Oliver, D. C. Povey and G. W. Smith, *J. Chem. Soc., Dalton Trans.*, 1991, 2045; (*c*) M. C. Aversa, P. Giannetto, G. Bruno, M. Cusumano, A. Giannetto and S. Geremia, *J. Chem. Soc., Dalton Trans.*, 1990, 2433; M. Cusumano, A. Giannetto, P. Ficarra, R. Ficarra and S. Tommasini, *J. Chem. Soc., Dalton Trans.*, 1991, 1581; (*d*) M. C. Aversa, P. Bonaccorsi, M. Cusumano, P. Giannetto and D. Minniti, *J. Chem. Soc., Dalton Trans.*, 1991, 3431.
14 (*a*) L. Saussine, H. Mimoun, A. Mitschler and J. Fisher, *Nouv. J. Chim.*, 1980, **21**, 235; (*b*) K. Wieghardt, E. Hofer, W. Holzbach, B. Nuber and J. Weiss, *Inorg. Chem.*, 1980, **19**, 2927; (*c*) W. Holzbach, K. Wieghardt and J. Weiss, *Z. Naturforsch., Teil B*, 1981, **36**, 289; (*d*) S. F. Gheller, T. W. Hambley, P. R. Trail, R. T. C. Brownlee, M. J. O'Connor, M. R. Snow and A. G. Wedd, *Aust. J. Chem.*, 1982, **35**, 2183.
15 R. Colton and I. B. Tomkins, *Aust. J. Chem.*, 1965, **18**, 447.
16 A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1991, 1855.

Received 13*th September* 1991; *Paper* 1/04751E