A New Tetratungstate, $[W_4O_4Cl_{10}(NBu^t)_4]^{2-}$, and its Degradation to the Mononuclear Complex $[WOCl_2(NBu^t)(bipy)]$ or $[WCl_2(NBu^t)_2(bipy)]$ (bipy = 2,2′-bipyridine)†

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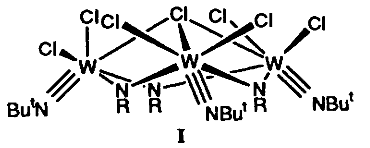
The $[NBu^n_4]^+$ and $[P(CH_2Ph)Ph_3]^+$ salts of the tetranuclear tungstate $[W_4O_4Cl_{10}(NBu^t)_4]^{2-}$ have been prepared from $WOCl_4$ and NH_2Bu^t in the presence of chloride ions. The crystal structure of the phosphonium salt has been determined and shows bridging oxo ligands [W–O 1.88 Å (av.) and WOW 159.6 ° (av.)] and terminal *tert*-butylimido groups [W–N 1.70 Å (av.) and WNC 174.9° (av.)]. Two μ-chloro ligands occupy positions *trans* to the imido groups [W–Cl 2.66 Å (av.) and WClW 115.6° (av.)] while the remaining chlorides are terminal [W–Cl 2.41 Å (av.)]. The structure is stable towards 1,2-dimethoxyethane but is degraded on addition of 2,2′-bipyridine (bipy). At lower temperatures, treatment of $[W_4O_4Cl_{10}(NBu^t)_4]^{2-}$ with bipy gives $[WOCl_2(NBu^t)(bipy)]$, whereas $[WCl_2(NBu^t)_2(bipy)]$ is crystallised from a similar reaction carried out in refluxing toluene. In the oxo complex W–N 1.741(6), W–O 1.716(5) and W–N(bipy) 2.313(5) (*trans* to O) and 2.335(5) Å (*trans* to NBu^t). In the bis(imido) complex W–N 1.754(5) and 1.747(5) and W–N(bipy) 2.373(5) and 2.370(5) Å. These results are compared with crystal structures of related complexes in an effort to understand the bond-length variations in terms of the *trans* influences and steric properties of the π-bonding imido and oxo ligands.

Competitive π bonding at metal centres can induce π-donor ligands to become bridging in associative reactions which produce oligo- or poly-nuclear complexes. The growing interest in early transition-metal polyoxometalate chemistry[1] and in the preparation of oxide materials by alkoxide hydrolysis (the 'sol-gel' technique)[2] serves to highlight the importance of these interactions. In the development of metal-organoimido catalysts for alkene metathesis,[3] sterically demanding NR groups have been used to prevent association reactions since these would effectively remove vacant co-ordination sites and prohibit access of the substrate to the metal centre. We, on the other hand, have been studying the nature of the polynuclear species formed in oligomerisation reactions when two or more strong π donors are co-ordinated to a metal centre, with particular interest in tungsten. In the mono-oxo or -organoimido alkoxides, $WO(OR)_4$ or $[W(NC_6H_4Me\text{-}4)(OR)_4]$, dimerisation occurs through bridging alkoxo ligands. The steric properties of the alkoxide groups determine the strength of the bridging interaction, and this in turn affects the nature of the solution dynamic properties of these molecules.[4] Dimerisation also occurs in the bis(organoimido) complexes $[\{WCl_2(NBu^t)(NR)(NH_2Bu^t)\}_2]$ (R = C_6H_5 or C_6H_4Me-4), where the arylimido ligands (the less sterically demanding of the imido groups) bridge the metal centres.[5] At elevated temperatures in the presence of chloride ions these bridges dissociate, allowing the fragments to reassemble and form the trinuclear anions $[W_3Cl_7(NBu^t)_3(NR)_3]^-$ **I**, again with bridging arylimido groups.[6] Several factors may determine which species can be isolated from the oligomerisation of $W(X)(Y)Cl_2$ fragments (X, Y = O or NR) in the presence of chloride (*e.g.* the nature of X and Y or the relative solubilities of the products) and we have been investigating the different structural types obtained when X and/or Y are varied.

In this paper we describe the preparation and structure of a tetranuclear *tert*-butylimido oxoanion and its reactivity towards 2,2′-bipyridine which demonstrates that ligand redistribution occurs at elevated temperatures. A preliminary account of this work has already been published.[7]



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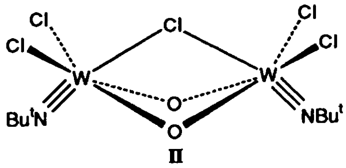

II

Results and Discussion

Investigations into the reaction between $WOCl_4$ and NH_2Bu^t have reported the production of either an intractable mixture[8] or of a material which analysed as $[WOCl_2(NBu^t)(NH_2Bu^t)]\cdot0.25C_6H_6$, but which was shown by ^{13}C NMR spectroscopy to contain *tert*-butylamido in addition to *tert*-butylimido and *tert*-butylamine ligands and was therefore also assumed to be a mixture.[9] However, in our attempts to prepare a trinuclear *tert*-butylimido oxoanion analogous to $[W_3Cl_7(NBu^t)_3(\mu\text{-}NPh)_3]^-$ **1**, we have found that when $WOCl_4$ is treated with NH_2Bu^t in the presence of Q^+Cl^- (where Q^+ is a quaternary ammonium or phosphonium cation) the products are well defined. When Q^+ = $[NBu^n_4]^+$ or $[P(CH_2Ph)Ph_3]^+$, yellow crystalline salts are obtained after extraction of the reaction products into dichloromethane. Proton NMR spectra indicated a NBu^t:Q^+ ratio of 2:1 and IR spectra contained a strong band at 845 cm^{-1} suggesting the presence of W–O–W bridges. The NMR integrals are obviously inconsistent with the target trinuclear anion but, in combination with microanalytical results, indicate instead the empirical formula $Q[W_2O_2Cl_5(NBu^t)_2]$ and we expected such a binuclear

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

W(1)–Cl(11)	2.414(3)	W(1)–Cl(12)	2.390(4)	W(3)–Cl(31)	2.395(2)	W(3)–Cl(32)	2.418(3)
W(1)–Cl(6)	2.689(2)	W(1)–O(1)	1.912(7)	W(3)–Cl(6)	2.672(3)	W(3)–O(2)	1.889(6)
W(1)–O(4)	1.867(6)	W(1)–N(1)	1.710(9)	W(3)–O(3)	1.879(5)	W(3)–N(3)	1.703(8)
W(2)–Cl(21)	2.406(3)	W(2)–Cl(22)	2.441(3)	W(4)–Cl(41)	2.396(3)	W(4)–Cl(42)	2.389(3)
W(2)–Cl(5)	2.619(2)	W(2)–O(1)	1.852(7)	W(4)–Cl(5)	2.648(3)	W(4)–O(3)	1.889(5)
W(2)–O(2)	1.857(5)	W(2)–N(2)	1.695(7)	W(4)–O(4)	1.887(6)	W(4)–N(4)	1.629(11)
Cl(11)–W(1)–Cl(12)	86.9(1)	Cl(11)–W(1)–Cl(6)	84.7(1)	Cl(31)–W(3)–O(3)	165.1(3)	Cl(32)–W(3)–O(3)	87.6(2)
Cl(12)–W(1)–Cl(6)	82.8(1)	Cl(11)–W(1)–O(1)	86.9(2)	Cl(6)–W(3)–O(3)	82.6(2)	O(2)–W(3)–O(3)	92.8(3)
Cl(12)–W(1)–O(1)	164.8(2)	Cl(6)–W(1)–O(1)	82.8(2)	Cl(31)–W(3)–N(3)	95.7(2)	Cl(32)–W(3)–N(3)	95.7(3)
Cl(11)–W(1)–O(4)	165.6(2)	Cl(12)–W(1)–O(4)	90.1(2)	Cl(6)–W(3)–N(3)	178.6(3)	O(2)–W(3)–N(3)	98.8(3)
Cl(6)–W(1)–O(4)	80.9(2)	O(1)–W(1)–O(4)	92.5(3)	O(3)–W(3)–N(3)	98.3(3)	Cl(41)–W(4)–Cl(42)	86.4(1)
Cl(11)–W(1)–N(1)	96.4(3)	Cl(12)–W(1)–N(1)	94.5(4)	Cl(41)–W(4)–Cl(5)	82.7(1)	Cl(42)–W(4)–Cl(5)	82.6(1)
Cl(6)–W(1)–N(1)	177.0(4)	O(1)–W(1)–N(1)	100.0(4)	Cl(41)–W(4)–O(3)	88.7(2)	Cl(42)–W(4)–O(3)	165.7(3)
O(4)–W(1)–N(1)	98.0(4)	Cl(21)–W(2)–Cl(22)	86.5(1)	Cl(5)–W(4)–O(3)	83.4(2)	Cl(41)–W(4)–O(4)	165.0(2)
Cl(21)–W(2)–Cl(5)	82.6(1)	Cl(22)–W(2)–Cl(5)	82.2(1)	Cl(42)–W(4)–O(4)	89.0(2)	Cl(5)–W(4)–O(4)	82.5(2)
Cl(21)–W(2)–O(1)	164.9(2)	Cl(22)–W(2)–O(1)	87.9(2)	O(3)–W(4)–O(4)	92.3(3)	Cl(41)–W(4)–N(4)	95.9(3)
Cl(5)–W(2)–O(1)	82.7(2)	Cl(21)–W(2)–O(2)	89.5(2)	Cl(42)–W(4)–N(4)	92.9(3)	Cl(5)–W(4)–N(4)	175.3(3)
Cl(22)–W(2)–O(2)	165.9(2)	Cl(5)–W(2)–O(2)	83.9(2)	O(3)–W(4)–N(4)	101.0(4)	O(4)–W(4)–N(4)	98.6(4)
O(1)–W(2)–O(2)	92.6(3)	Cl(21)–W(2)–N(2)	93.2(3)	W(2)–Cl(5)–W(4)	115.8(1)	W(1)–Cl(6)–W(3)	115.3(1)
Cl(22)–W(2)–N(2)	94.8(2)	Cl(5)–W(2)–N(2)	175.0(3)	W(1)–O(1)–W(2)	157.9(4)	W(2)–O(2)–W(3)	161.3(3)
O(1)–W(2)–N(2)	101.2(3)	O(2)–W(2)–N(2)	98.9(3)	W(3)–O(3)–W(4)	158.2(4)	W(1)–O(4)–W(4)	160.9(4)
Cl(31)–W(3)–Cl(32)	86.0(1)	Cl(31)–W(3)–Cl(6)	83.4(1)	W(1)–N(1)–C(1)	169.0(9)	W(2)–N(2)–C(2)	178.5(8)
Cl(32)–W(3)–Cl(6)	85.3(1)	Cl(31)–W(3)–O(2)	90.0(2)	W(3)–N(3)–C(3)	174.8(7)	W(4)–N(4)–C(4)	177.2(8)
Cl(32)–W(3)–O(2)	165.3(2)	Cl(6)–W(3)–O(2)	80.2(2)				

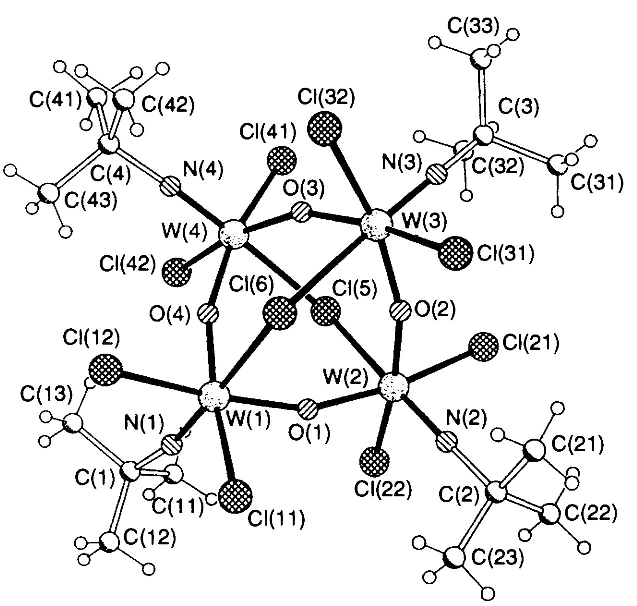


Fig. 1 A view of the structure of the anion **2**

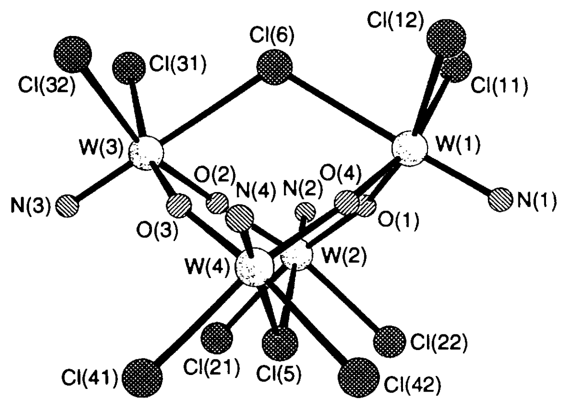


Fig. 2 A view of the anion **2** omitting the *tert*-butyl groups and showing the positions of the tungsten atoms between parallel planes of Cl, O and N, and Cl atoms

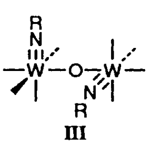
oxoimido anion to have a confacial bioctahedral geometry as in **II**. Single crystals of the phosphonium salt were obtained by diffusion of hexane into a dichloromethane solution and the structure was determined by X-ray diffraction.

Contrary to our predictions, the structure revealed a novel tetranuclear anion $[W_4O_4Cl_{10}(NBu^t)_4]^{2-}$ **2**, a view of which is shown in Fig. 1. There are no close contacts with the $[P(CH_2Ph)Ph_3]^+$ cations which have no unusual features. Relevant bond lengths and angles are given in Table 1. Tetranuclear **2** has approximately D_{2d} symmetry and the metal atoms lie at the corners of a distorted tetrahedron in which two opposite, elongated edges (W ··· W 4.462 and 4.529 Å) are bridged by chloro and the other four edges (W ··· W 3.696–3.701 Å) are bridged by oxo ligands. The *tert*-butylimido groups are in terminal positions *trans* to the two bridging chlorides and have W–N bond lengths [1.70 Å (av.)] and WNC angles [174.9° (av.)] consistent with a W–N bond order of close to three.[10] As in other organoimido complexes containing μ_3- or μ-Cl *trans* to NR groups,[6] the W–Cl bridging distances [2.66 Å (av.)] are considerably longer than the terminal W–Cl bonds [2.41 Å (av.)], which can be attributed to the combined *trans* influences of the two NBu^t groups. Fig. 2 shows that the tungsten atoms are sandwiched between three parallel planes, the outermost of which each contain five chlorines, while the central one contains the π-bonded nitrogen and oxygen atoms. This can be compared with **I** where the three tungstens occupy sites between a plane of seven chlorines and a plane of six nitrogens.

One feature of this molecule which serves to illustrate the structural and electronic flexibility of oxo ligands in polynuclear frameworks is the size of the WOW bridging angles. These average 160°, whereas in the target trinuclear anion $[W_3O_3Cl_7(NBu^t)_3]^-$ they would be expected to be about 120°, as are the analogous WNW angles in complex **1**. This is also much larger than would be possible in the binuclear structure **II**, where an angle of about 100° might be expected. In terms of co-ordination polyhedra (which traditionally have been used to describe polyoxometalate structures)[11] the octahedra in the tetranuclear complex **2** are linked by corner-sharing, while those in the trinuclear complexes **I** are edge-shared and those in **II** are face-shared. The first two bridging modes are often encountered in polyoxometalates but the latter is much less common. The tetranuclear structure adopted by complex **2** in preference to binuclear **II** or an oxo analogue of trinuclear **I** may therefore reflect an optimisation of π overlap *via* the formation of

Table 2 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*
W(1)	4 774.8(3)	−83.3(3)	2 733.8(2)
W(2)	3 276.5(2)	−1 581.6(3)	2 066.5(1)
W(3)	3 303.9(3)	−3 269.8(3)	3 303.7(1)
W(4)	6 150.5(3)	−2 740.0(3)	2 782.5(1)
Cl(11)	3 350(2)	1 255(2)	2 852(1)
Cl(12)	5 428(2)	412(3)	3 422(1)
Cl(21)	2 896(2)	−3 002(3)	1 666(1)
Cl(22)	3 970(2)	−670(2)	1 226(1)
Cl(31)	1 461(2)	−2 945(2)	3 653(1)
Cl(32)	3 589(2)	−3 841(2)	4 160(1)
Cl(41)	6 625(2)	−4 468(2)	2 574(1)
Cl(42)	7 673(2)	−2 151(3)	2 176(1)
Cl(5)	5 207(2)	−2 499(2)	1 978(1)
Cl(6)	3 523(2)	−1 316(2)	3 471(1)
O(1)	3 939(5)	−602(5)	2 318(2)
O(2)	3 061(4)	−2 477(4)	2 681(2)
O(3)	4 805(4)	−3 243(5)	3 119(3)
O(4)	5 664(4)	−1 314(5)	2 781(3)
N(1)	5 617(7)	700(9)	2 286(4)
C(1)	6 491(9)	1 261(9)	1 957(6)
C(11)	6 629(17)	895(27)	1 461(9)
C(12)	6 171(16)	2 421(13)	1 885(9)
C(13)	7 489(12)	982(19)	2 194(11)
N(2)	2 017(5)	−1 021(6)	2 075(3)
C(2)	899(7)	−549(12)	2 076(5)
C(21)	216(12)	−1 140(20)	2 531(8)
C(22)	551(12)	−761(18)	1 598(8)
C(23)	901(14)	607(14)	2 097(11)
N(3)	3 139(6)	−4 504(6)	3 190(3)
C(3)	3 052(9)	−5 537(8)	3 046(4)
C(31)	1 926(14)	−5 531(17)	2 915(8)
C(32)	3 902(13)	−5 622(12)	2 588(6)
C(33)	3 208(15)	−6 390(11)	3 477(6)
N(4)	6 824(6)	−2 881(6)	3 246(4)
C(4)	7 454(13)	−2 956(13)	3 680(5)
C(41)	8 454(30)	−3 660(34)	3 537(19)
C(42)	6 711(37)	−3 310(30)	4 165(9)
C(43)	7 778(21)	−1 822(20)	3 679(10)
P(1)	4 432(2)	2 668(2)	25(1)
C(111)	3 743(8)	2 994(9)	610(4)
C(112)	3 667(11)	2 232(12)	1 033(5)
C(113)	3 215(14)	2 564(19)	1 502(5)
C(114)	2 809(13)	3 545(21)	1 524(6)
C(115)	2 885(12)	4 312(15)	1 089(7)
C(116)	3 374(9)	4 029(13)	636(5)
C(121)	5 867(9)	2 774(10)	7(4)
C(122)	6 577(11)	2 347(14)	−359(5)
C(123)	7 680(11)	2 406(18)	−365(7)
C(124)	8 043(11)	2 898(16)	−44(7)
C(125)	7 324(12)	3 345(13)	296(6)
C(126)	6 236(10)	3 288(11)	326(5)
C(131)	3 964(9)	3 560(8)	−488(4)
C(132)	2 852(9)	3 710(10)	−474(5)
C(133)	2 482(14)	4 328(12)	−879(7)
C(134)	3 207(15)	4 739(13)	−1 286(6)
C(135)	4 245(14)	4 625(12)	−1 299(6)
C(136)	4 629(12)	4 010(10)	−891(6)
C(141)	4 203(11)	1 316(10)	−32(5)
C(142)	3 116(10)	1 173(10)	−144(5)
C(143)	2 215(12)	989(12)	234(6)
C(144)	1 199(16)	922(20)	140(9)
C(145)	1 063(15)	1 050(19)	−357(7)
C(146)	1 889(15)	1 219(17)	−735(7)
C(147)	2 929(13)	1 313(15)	−633(6)
P(2)	7 991(2)	1 561(2)	4 660(1)
C(211)	7 158(8)	2 530(9)	4 340(5)
C(212)	7 228(17)	2 684(13)	3 822(6)
C(213)	6 538(20)	3 458(18)	3 596(8)
C(214)	5 809(14)	4 041(14)	3 871(8)
C(215)	5 726(10)	3 883(11)	4 359(7)
C(216)	6 369(9)	3 090(11)	4 614(6)
C(221)	7 181(8)	449(8)	4 953(4)
C(222)	7 254(11)	−43(11)	5 443(5)
C(223)	6 663(13)	−902(13)	5 656(6)
C(224)	6 078(13)	−1 343(13)	5 365(7)
C(225)	6 016(12)	−885(13)	4 903(9)
C(226)	6 583(9)	35(11)	4 671(5)
C(231)	9 092(8)	1 113(9)	4 224(4)
C(232)	9 276(7)	51(8)	4 202(4)
C(233)	10 127(10)	−332(10)	3 886(5)
C(234)	10 838(8)	389(11)	3 586(5)
C(235)	10 658(12)	1 471(13)	3 606(6)
C(236)	9 801(11)	1 801(10)	3 926(5)
C(241)	8 506(9)	2 122(10)	5 136(5)
C(242)	9 375(9)	2 908(9)	4 907(4)
C(243)	10 441(9)	2 595(10)	4 914(5)
C(244)	11 249(11)	3 277(14)	4 715(6)
C(245)	11 004(11)	4 261(12)	4 480(6)
C(246)	9 929(13)	4 610(10)	4 460(6)
C(247)	9 130(12)	3 916(10)	4 685(6)
C(5)	502(14)	3 208(18)	965(8)
Cl(7)	415(5)	4 159(7)	456(3)
Cl(8)	−609(6)	2 469(10)	1 123(4)
C(6)	489(28)	4 459(8)	7 865(12)
Cl(9)	−172(11)	4 099(16)	8 459(10)
Cl(10)	517(13)	5 798(7)	7 695(10)



III

symmetric oxo bridges with larger angles. The NWWN torsion angles range from 97 to 104° [101° (av.)] and, with this geometry, increased overlap of p-type orbitals on oxygen with adjacent metal orbitals not involved in W=NBu^t π bonding (d_{xy} if the *z* axis is defined as coincident with the W–N bond) is possible, optimum overlap being achieved when WOW 180° and the NWWN torsion angle is 90° as shown in **III**.

Although there are few published structures of organoimido complexes containing bridging oxo ligands, two binuclear examples having geometries close to **III** are particularly noteworthy. One of these, the oxoanion $[\{WCl_4(NC_6H_4Me\text{-}4)\}_2(\mu\text{-}O)]^{2-}$ with a NWWN torsion angle of 83° and a bridging WOW angle of 167.0(11)°, can be hydrolysed to give the *p*-tolylimido analogue of complex **2**, $[W_4O_4Cl_{10}(NC_6H_4Me\text{-}4)_4]^{2-}$, although this tetranuclear species was not structurally characterised.[12] The other example is a diolate complex $[\{W(NPh)(OCH_2CH_2O)(OCH_2CH_2OH)\}_2(\mu\text{-}O)]$[13] where the NWWN torsion angle is 80° and WOW 157(2)°. By comparison, the distorted, confacial bioctahedral structure of $[\{W(NPh)(OBu^t)_2\}_2(\mu\text{-}O)(\mu\text{-}OBu^t)_2]$[14] contains a symmetric oxide bridge with an angle of only 104.3(2)° while the NWWN torsion angle is 107°. In all of the preceding examples, the metal centres are in the maximum formal oxidation state of VI, whereas in the mixed oxidation-state ($W^{VI}{}_2W^{V}{}_2$) tetranuclear anion $[W_4O_8Cl_8(H_2O)_4]^{2-}$ the oxide bridges are linear but the OWWO torsion angle is approximately 180° (*i.e.*, the W=O bonds are mutually *anti* with respect to the oxide bridge).[15] This configuration allows electronic exchange to occur readily between neighbouring tungsten atoms.

The general correlation between WOW bridging angles and W–O bridging bond lengths, previously noted by Jeannin *et al.*,[15] is amply demonstrated in the above structures and supports the proposition that π bonding increases with bridging angle, resulting in shorter bond lengths. Again, this is also a feature of polyoxometalate structures.

The novel geometry in complex **2** can also be adopted by metal complexes with other π-donor ligand sets, as recently

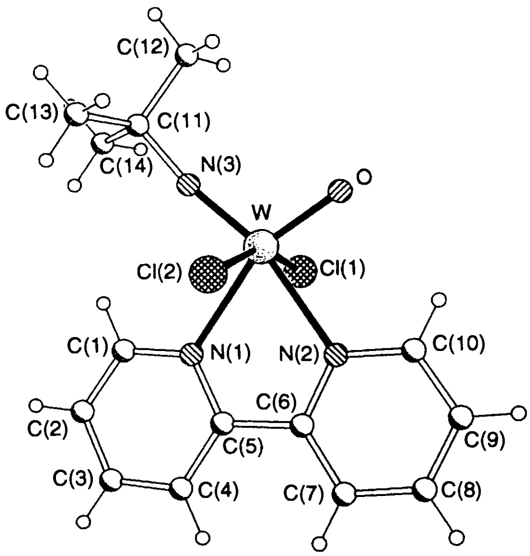


Fig. 3 A view of the molecular structure of complex **3**

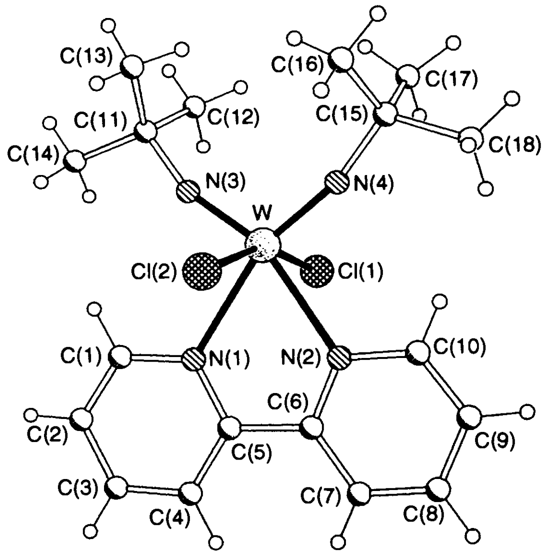


Fig. 4 A view of the molecular structure of complex **4**

Table 3 Selected bond lengths (Å) and angles (°) for complex **3**

W–Cl(1)	2.383(2)	W–Cl(2)	2.392(2)
W–N(1)	2.313(5)	W–N(2)	2.335(5)
W–N(3)	1.741(6)	W–O	1.716(5)
Cl(1)–W–Cl(2)	157.5(1)	Cl(1)–W–N(1)	79.9(1)
Cl(2)–W–N(1)	80.0(1)	Cl(1)–W–N(2)	82.3(1)
Cl(2)–W–N(2)	81.2(1)	N(1)–W–N(2)	69.1(2)
Cl(1)–W–N(3)	97.3(2)	Cl(2)–W–N(3)	95.0(2)
N(1)–W–N(3)	96.9(2)	N(2)–W–N(3)	165.9(2)
Cl(1)–W–O	96.9(2)	Cl(2)–W–O	98.0(2)
N(1)–W–O	157.9(2)	N(2)–W–O	88.8(2)
N(3)–W–O	105.2(2)	W–N(3)–C(11)	170.6(5)

Table 4 Atomic coordinates (× 10^4) for complex **3**

Atom	*x*	*y*	*z*
W	1330.2(3)	1121.3(1)	2192.9(2)
Cl(1)	413(2)	175(1)	3397(2)
Cl(2)	3259(2)	1868(1)	1289(2)
N(1)	3609(6)	1048(3)	3522(4)
N(2)	3132(6)	174(3)	1736(4)
C(1)	3735(9)	1475(4)	4442(6)
C(2)	5070(10)	1449(4)	5256(7)
C(3)	6331(9)	964(4)	5106(7)
C(4)	6244(8)	516(4)	4165(6)
C(5)	4844(7)	565(4)	3361(5)
C(6)	4605(7)	92(4)	2362(6)
C(7)	5763(9)	−429(5)	2059(7)
C(8)	5372(11)	−864(5)	1118(8)
C(9)	3882(10)	−789(5)	501(7)
C(10)	2779(9)	−260(4)	824(6)
N(3)	379(6)	1877(3)	2789(5)
C(11)	−619(9)	2498(4)	3128(6)
C(12)	−2336(11)	2426(7)	2479(9)
C(13)	222(17)	3205(5)	2787(12)
C(14)	−756(12)	2459(6)	4370(7)
O	39(6)	890(3)	1014(5)

Table 5 Selected bond lengths (Å) and angles (°) for complex **4**

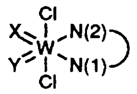
W–Cl(1)	2.413(2)	W–Cl(2)	2.411(2)
W–N(1)	2.370(5)	W–N(2)	2.373(5)
W–N(3)	1.754(4)	W–N(4)	1.747(5)
Cl(1)–W–Cl(2)	158.1(1)	Cl(1)–W–N(1)	82.9(1)
Cl(2)–W–N(1)	79.0(1)	Cl(1)–W–N(2)	78.3(1)
Cl(2)–W–N(2)	83.3(1)	N(1)–W–N(2)	67.3(2)
Cl(1)–W–N(3)	94.4(2)	Cl(2)–W–N(3)	98.6(2)
N(1)–W–N(3)	92.3(2)	N(2)–W–N(3)	158.8(2)
Cl(1)–W–N(4)	98.0(2)	Cl(2)–W–N(4)	94.8(2)
N(1)–W–N(4)	159.9(2)	N(2)–W–N(4)	93.2(2)
N(3)–W–N(4)	107.6(2)	W–N(3)–C(11)	162.7(4)
W–N(4)–C(15)	166.4(5)		

Table 6 Atomic coordinates (× 10^4) for complex **4**

Atom	*x*	*y*	*z*
W	7 659.4(1)	53.6(2)	3 830.2(1)
Cl(1)	7 756(1)	−1 841(1)	3 558(1)
Cl(2)	8 073(1)	1 682(1)	4 311(1)
N(1)	8 087(3)	−748(3)	4 603(2)
N(2)	9 403(3)	−314(4)	3 960(2)
C(1)	7 398(5)	−859(5)	4 932(2)
C(2)	7 604(5)	−1 361(5)	5 376(2)
C(3)	8 556(5)	−1 721(5)	5 496(2)
C(4)	9 282(4)	−1 578(5)	5 172(2)
C(5)	9 036(4)	−1 084(4)	4 724(2)
C(6)	9 760(4)	−882(4)	4 355(2)
C(7)	10 747(5)	−1 244(5)	4 406(2)
C(8)	11 377(5)	−1 015(5)	4 047(3)
C(9)	11 015(5)	−447(6)	3 643(3)
C(10)	10 038(4)	−98(6)	3 610(2)
N(3)	6 371(3)	−7(5)	3 917(2)
C(11)	5 288(4)	29(6)	3 835(2)
C(12)	5 025(8)	−809(13)	3 422(6)
C(13)	4 947(8)	1 154(8)	3 692(6)
C(14)	4 812(7)	−425(14)	4 279(6)
N(4)	7 799(4)	700(4)	3 270(2)
C(15)	7 666(5)	1 299(5)	2 815(2)
C(16)	7 153(18)	2 346(13)	2 890(6)
C(17)	7 139(18)	568(12)	2 450(4)
C(18)	8 689(10)	1 498(16)	2 600(5)

demonstrated by the structural characterisation[16] of the oxo–nitrido complex $[Mo_4N_4O_2(OSiMe_3)_8(py)_4]$ (py = pyridine) in which two opposite edges of the tetrahedral array of molybdenum atoms are bridged symmetrically by oxides [MoOMo 146.5(5)°], while asymmetric nitrido bridges [MoNMo 144.1(4)°] span the other four edges. The shorter Mo=N bonds at each end of an oxo bridge are oriented such that the NMoMoN torsion angle is 82°, so similar arguments to those given above are applicable to the π bonding within the oxo bridges.

Table 7 Comparison of selected bond lengths (Å) and angles (°) in [$WCl_2(X)(Y)(bipy)$] complexes



X	Y	W–X	W–Y	W–N(1)	W–N(2)	XWY	N(1)WN(2)	XWN(2)	YWN(1)	Ref.
O	O	1.745(3)	1.792(2)	2.288(2)	2.263(4)	106.7(2)	70.0(1)	90.5(2)	92.8(1)	19
NBu^t	O	1.741(6)	1.716(5)	2.335(5)	2.313(5)	105.2(2)	69.1(2)	96.9(2)	88.8(2)	This work
NBu^t	NBu^t	1.747(5)	1.754(4)	2.370(5)	2.373(5)	107.6(2)	67.3(2)	93.2(2)	92.3(2)	This work
NBu^t	NPh	1.754(10)	1.774(8)	2.312(10)	2.333(9)	104.2(5)	69.3(3)	93.2(4)	92.9(4)	9
NPh	NPh	1.781(11)	1.787(14)	2.309(12)	2.319(13)	103.6(6)	69.8(4)	95.2(5)	91.4(5)	18(*b*)
		1.783(14)	1.762(12)	2.328(11)	2.311(11)	105.0(6)	69.8(4)	92.8(5)	92.4(5)	

Bridging modes similar to that shown in **III** are not possible for a bridging organoimido group, and therefore during oligomerisation of $WCl_2(NBu^t)(NR)$ fragments in the presence of a limited amount of chloride ions, M–N π overlap is optimised by formation of the trinuclear structure **I** containing sp^2-hybridised bridging nitrogens.[6] It remains to be seen whether WO_2Cl_2 fragments, generated under appropriate conditions in the presence of the requisite amount of chloride ions, associate to form $[W_4O_8Cl_{10}]^{2-}$ with a structure analogous to that of **2**. This possibility is being investigated in our laboratory and will be the subject of a future publication.

Although our attempts to prepare a trinuclear oxoimido complex were unsuccessful, a trinuclear trimethylphosphine adduct $[W_3O_3Me_6(NPh)_3(PMe_3)_3]$ has been structurally characterised.[17] However, this molecule contains a planar W_3O_3 ring with asymmetric oxo bridges [W–O 1.79 and 2.11 Å (av.)] wherein W–O π bonding occurs only when the oxo is *cis* to the imido ligand, the longer W–O bonds being *trans* to the imido groups. The preference of the methyl groups to occupy *trans* co-ordination sites presumably prevents the $W(O)Me_2(NPh)(PMe_3)$ fragments from adopting a geometry which would enable extended π bonding, such as that observed in $[W_4O_8Cl_8(H_2O)_4]^{2-}$ which contains *cis* chlorides and a planar W_4O_4 ring.[15]

Having determined the true nature of complex **2**, we were interested in its stability with respect to disproportionation. An attempt to prepare the mononuclear 1,2-dimethoxyethane (dme) adduct [$WOCl_2(NBu^t)(dme)$] by heating **2** in dme proved unsuccessful, the starting material being recovered unchanged. Reaction does occur, however, with the stronger donor ligand 2,2′-bipyridine (bipy). Treatment of **2** with one equivalent of bipy per W in dichloromethane at ambient temperatures gave the expected oxoimido degradation product [$WOCl_2(NBu^t)(bipy)$] **3** as green, air-stable needles after recrystallisation from dichloromethane–hexane. In the IR spectrum of this compound, bands are observed for ν(W=O) and ν(W–Cl) at 913 and 320 cm^{-1} respectively, and the ^1H and ^{13}C NMR spectra reflect the asymmetric nature of the bipy ligand. In contrast, when this reaction was carried out in toluene under reflux the bis(imido) complex [$WCl_2(NBu^t)_2(bipy)$] **4** could be crystallised after filtration of some insoluble material. Nielson and co-workers[9] previously obtained this compound by treatment of the initial product from the reaction between $WOCl_4$ and NH_2Bu^t (the mixture mentioned earlier) with bipy. Since these two mononuclear complexes offered an opportunity to assess the comparative *trans* influences of the oxo and *tert*-butylimido ligands, the crystal structures of both complexes were obtained and views of the molecules are shown in Figs. 3 and 4. Relevant bond lengths and angles and the atomic coordinates for complexes **3** and **4** are given in Tables 3–6. A range of bis(imido) bipy complexes of the type [$WCl_2(NR)(NR')(bipy)$] and an oxo-*p*-tolylimido derivative [$WOCl_2(NC_6H_4Me\text{-}4)(bipy)$] have previously been described,[9,18] of which the symmetric [$WCl_2(NPh)_2(bipy)$][18b] and the unsymmetric [$WCl_2(NBu^t)(NPh)(bipy)$][9] have been structurally characterised. The structure of the dioxo complex [$WO_2Cl_2(bipy)$] has also been determined.[19]

The metal–ligand bonding parameters in the plane of the π-donor ligands for [$WCl_2(X)(Y)(bipy)$] (where X, Y = O, NPh or NBu^t) are shown in Table 7. The general features of all of these molecules are similar but some variations in the bonding parameters occur due to the different steric and electronic properties of the ligand sets. Looking first at the symmetric compounds, it can be seen that the bonds to bipy are longest in [$WCl_2(NBu^t)_2(bipy)$], shortest in [$WO_2Cl_2(bipy)$] and intermediate in [$WCl_2(NPh)_2(bipy)$], suggesting that the order of *trans* influence is NBu^t > NPh > O. This is contrary to that which is normally observed, where an oxo ligand exerts a larger *trans* influence than an NR ligand,[10] and could mean that other factors need to be considered when comparing these structures. It was noted that hydrogen bonding in the dioxo compound results in different W=O bond lengths and this may be responsible for a reduction in the *trans* influence of these oxo ligands. It may therefore be significant that in complex **3**, where the NBu^t ligand has the larger *trans* influence, the close intermolecular contact between the oxo ligand and C(10) in the bipy of a symmetry-related molecule is suggestive of a similar hydrogen-bonding interaction (O $\cdots$ H 2.419 Å) which may be associated with the lower than expected *trans* influence for the oxo ligand. Nielson and co-workers[9] proposed that a steric interaction between NBu^t and the nearby *ortho* hydrogen of bipy causes a lengthening of the W–N(bipy) *cis* to NBu^t (*i.e.*, *trans* to NPh) in [$WCl_2(NBu^t)(NPh)(bipy)$] although the standard deviations were quite high for these bond lengths and the difference may not be significant. Steric compression of this type should be evident from the angles given in Table 7 and indeed in complex **3**, where the steric requirements of X and Y are more disparate, N(3)WN(2) is larger than OWN(1). However, in the other organoimido compounds XWN(2) and YWN(1) do not differ significantly except for one of the two independent molecules present in the structure of [$WCl_2(NPh)_2(bipy)$]. This suggests that the NBu^t and NPh ligands have similar steric effects in these complexes and therefore their apparently higher *trans* influences compared with the oxo ligands in complex **3** and [$WO_2Cl_2(bipy)$] might also be due partly to steric compression.

The production of complex **4** in the reaction between complex **2** and bipy at elevated temperatures indicates that under these conditions ligand exchange occurs in addition to degradation of the tetranuclear structure. This implies a transition state or intermediate containing *tert*-butylimido and oxo bridges which then dissociates with concomitant ligand transfer. Similar oxo–imido ligand exchange was observed on treatment of the initial product from the reaction between $WOCl_4$ and NH_2Bu^t with bipy to produce complex **4** and insoluble oxo compounds.[9] Gibson and co-workers[20] have studied this type of exchange in more detail for the co-ordinatively unsaturated, four-coordinate complexes $MoX_2(OBu^t)_2$ (X = O or NR) and showed that the reaction between $\mathrm{MoO_2(OBu^t)_2}$ and $[\mathrm{Mo(NC_6H_3Pr^i{}_2\text{-}2,6)_2(OBu^t)_2}]$ occurs readily at room temperature. It is interesting that the association reactions to produce **2** (from what are presumably oxoimido precursors in solution) occur in refluxing toluene without ligand redistribution, presumably because of the limited solubility of **2** in this solvent. We also observed[18b] oxo–imido exchange during a reaction between the binuclear tungsten(v) anion $[\mathrm{W_2O_2Cl_7}]^-$ and *p*-tolyl azide, where the product obtained was dependent upon the cation present. With $[\mathrm{P(CH_2Ph)Ph_3}]^+$, the mononuclear anion $[\mathrm{WCl_5(NC_6H_4Me\text{-}4)}]^-$ crystallised, whereas with $[\mathrm{NBu^n{}_4}]^+$ a novel hexanuclear oxoanion $[\mathrm{W_6O_{14}Cl_{10}}]^{2-}$ was obtained.[7] Solubility obviously plays an important role in the formation and isolation of these polynuclear oxo or oxoimido anions. We have now developed more rational routes to some tungsten oxoanions including $[\mathrm{W_6O_{14}Cl_{10}}]^{2-}$ and this work will be described in a forthcoming paper.

This exchange between metal centres of what are normally regarded as strongly π-bonded ligands is relevant to various aspects of our work with oxotungsten compounds. During $^{17}\mathrm{O}$ NMR studies of alkoxide hydrolysis, we have observed enrichment of the terminal oxide during the first stages of the hydrolysis of $\mathrm{WO(OR)_4}$ with $^{17}\mathrm{O}$-enriched $\mathrm{H_2O}$.[21] This is presumably due to a ready oxo exchange between $\mathrm{WO(OR)_4}$ and small amounts of enriched species such as $[\mathrm{WO^{17}O(OR)_2}]$ formed in the reaction. We have also structurally characterised an oxoalkoxoanion $[\mathrm{W_2O_5(OMe)_4}]^{2-}$ in which each tungsten is bonded to two *cis*, terminal oxides.[22] Since this anion was prepared from $\mathrm{WO_4}^{2-}$ and $\mathrm{WO(OMe)_4}$ at room temperature, ligand redistribution by oxo and methoxo exchange clearly occurs readily under these conditions. An understanding of such hydrolysis and redistribution reactions is important if control over the aggregation processes involved in transition-metal polyoxometalate and 'sol-gel' chemistry is to be achieved.

Experimental

All manipulations were carried out under dry, oxygen-free conditions using standard Schlenk techniques, or in a dry-box fitted with a nitrogen recirculation system. Solvents were dried over and distilled from appropriate drying agents [sodium for toluene; sodium–benzophenone, with the addition of a small amount of tetraglyme (tetraethylene glycol dimethyl ether), for hexane; calcium hydride for dichloromethane]. *tert*-Butylamine was dried over and distilled from calcium hydride, $\mathrm{NBu^n{}_4Cl}$ was dried at 80 °C *in vacuo* for 16 h and stored under nitrogen and $\mathrm{WOCl_4}$ was prepared from $\mathrm{WO_3{\cdot}H_2O}$ and $\mathrm{SOCl_2}$ and purified by sublimation *in vacuo*. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin Elmer 598 spectrometer and NMR spectra were recorded on Bruker WP 200 or WM 300 spectrometers. Elemental analyses were performed by the microanalytical service, the Department of Chemistry, University of Newcastle upon Tyne (C, H and N), or at the University of Durham (W and Cl).

Preparations.—$[\mathrm{NBu^n{}_4}]_2[\mathrm{W_4O_4Cl_{10}(NBu^t)_4}]$. *tert*-Butylamine (4.16 $\mathrm{cm^3}$, 39.6 mmol) was added to $\mathrm{WOCl_4}$ (4.50 g, 13.2 mmol) and $\mathrm{NBu^n{}_4Cl}$ (1.22 g, 4.39 mmol) in toluene (50 $\mathrm{cm^3}$) and the mixture was heated under reflux for 6 h. The volatiles were removed under reduced pressure and the residue was extracted with $\mathrm{CH_2Cl_2}$ (40 $\mathrm{cm^3}$) and filtered. Diffusion of hexane into the solution gave the product as yellow prisms (5.24 g, 40% based on $\mathrm{NBu^n{}_4Cl}$) (Found: C, 29.9; H, 5.8; Cl, 20.2; N, 4.4; W, 37.7. $\mathrm{C_{48}H_{108}Cl_{10}N_6O_4W_4}$ requires C, 30.0; H, 5.7; Cl, 18.5; N, 4.4; W, 38.2%). IR: 1278s, 1220m, 1165w, 1110w, 1065w, 1032w, 978w, 903m, 847s, 808m, 742m, 569s, 460w, 398m, 308s and 289s $\mathrm{cm^{-1}}$. NMR ($\mathrm{CDCl_3}$): $^1\mathrm{H}$ (200.13 MHz), δ 3.23 (16 H, m, $\mathrm{NCH_2}$), 1.56 (16 H, br m, $\mathrm{NCH_2}CH_2$), 1.45 (36 H, s, $\mathrm{NC_4H_9}$), 1.43 [16 H, m, $\mathrm{N(CH_2)_2}CH_2$] and 0.92 [24 H, t, $\mathrm{N(CH_2)_3}CH_3$]; $^{13}\mathrm{C}$ (50.32 MHz), δ 71.9 ($\mathrm{N}C\mathrm{Me_3}$), 59.3 ($\mathrm{NCH_2}$), 32.1 ($\mathrm{NC}Me_3$), 24.5 ($\mathrm{NCH_2}C\mathrm{H_2}$), 20.0 [$\mathrm{N(CH_2)_2}C\mathrm{H_2}$] and 13.9 [$\mathrm{N(CH_2)_3}C\mathrm{H_3}$].

$[\mathrm{P(CH_2Ph)Ph_3}]_2[\mathrm{W_4O_4Cl_{10}(NBu^t)_4}]$. This was prepared using the same method as for the tetrabutylammonium salt above, from $\mathrm{WOCl_4}$ (1.42 g, 4.17 mmol), $\mathrm{NH_2Bu^t}$ (1.31 $\mathrm{cm^3}$, 12.5 mmol) and $[\mathrm{P(CH_2Ph)Ph_3}]\mathrm{Cl}$ (0.81 g, 2.08 mmol). Yield 2.17 g, 97% (Found: C, 36.8; H, 3.7; Cl, 16.8; N, 2.5; W, 28.8. $\mathrm{C_{66}H_{80}Cl_{10}N_4O_4P_2W_4}$ requires C, 36.9; H, 3.8; Cl, 16.5; N, 2.6; W, 34.2%). IR: 3060w, 2730w, 1585m, 1278s, 1218m, 1186w, 1169w, 1160w, 1113s, 1070w, 1046w, 1039w, 999m, 978w, 900m, 865m, 840s, 808m, 787w, 759w, 751m, 726m, 708w, 692m, 588m, 570m, 520m, 510w, 504m, 394m, 308s, 300s and 288s $\mathrm{cm^{-1}}$. NMR ($\mathrm{CD_2Cl_2}$): $^1\mathrm{H}$ (200.13 MHz), δ 7.9–6.9 (40 H, several multiplets, $\mathrm{C_6H_5}$), 4.80 [4 H, d, *J*(PH), 13.7, $\mathrm{PCH_2}$] and 1.35 (36 H, $\mathrm{NC_4H_9}$); $^{13}\mathrm{C}$ (50.32 MHz), δ 134.7 [d, *J*(PC) 3], 134.5 [d, *J*(PC) 10], 131.9 [d, *J*(PC) 6], 130.4 [d, *J*(PC) 12], 128.8, 128.7, 128.0 (aromatics), 118.2 [d, *J*(PC) 85 Hz, $\mathrm{PCH_2}$], 71.9 ($\mathrm{N}C\mathrm{Me_3}$) and 32.0 ($\mathrm{NC}Me_3$).

$[\mathrm{WOCl_2(NBu^t)(bipy)}]$ **3**. 2,2′-Bipyridine (0.25 g, 1.6 mmol) was added to a solution of $[\mathrm{P(CH_2Ph)Ph_3}]_2[\mathrm{W_4O_4Cl_{10}(NBu^t)_4}]$ (0.86 g, 0.4 mmol) in $\mathrm{CH_2Cl_2}$ (15 $\mathrm{cm^3}$) with stirring. After 6 h a layer of hexane was diffused into the solution to give the product as green needles (0.37 g, 46%) (Found: C, 33.6; H, 3.3; N, 8.0. $\mathrm{C_{14}H_{17}Cl_2N_3OW}$ requires C, 33.8; H, 3.4; N, 8.4%). IR: 1608w, 1600m, 1575w, 1490w, 1445m, 1357w, 1312m, 1285m, 1275m, 1267m, 1218w, 1171w, 1155w, 1120w, 1102w, 1073w, 1063w, 1048w, 1030m, 1020w, 913s, 906m, 895w, 776s, 738m, 658w, 655w, 639w, 590w, 530w, 422w and 320s $\mathrm{cm^{-1}}$. NMR ($\mathrm{CDCl_3}$): $^1\mathrm{H}$ (200.13 MHz), δ 9.92 (1 H, d, α-H, bipy), 9.37 (1 H, d, α-H, bipy), 8.3–8.1 (4 H, m, β-H, bipy), 7.8–7.6 (2 H, m, γ-H, bipy) and 1.55 (9 H, $\mathrm{NCMe_3}$); $^{13}\mathrm{C}$ (75.47 MHz), δ 153.9, 152.4 (α-CH, bipy), 151.4, 151.1 (α-C, bipy), 140.6, 140.4 (γ-CH, bipy), 126.8, 123.1, 122.9 (β-CH, bipy), 69.3 ($\mathrm{N}C\mathrm{Me_3}$) and 30.6 ($\mathrm{NC}Me_3$).

$[\mathrm{WCl_2(NBu^t)_2(bipy)}]$ **4**. A mixture of 2,2′-bipyridine (0.41 g, 2.63 mmol) and $[\mathrm{P(CH_2Ph)Ph_3}]_2[\mathrm{W_4O_4Cl_{10}(NBu^t)_4}]$ (1.41 g, 0.66 mmol) in toluene (45 $\mathrm{cm^3}$) was heated under reflux for 2 h and filtered while still hot. The volume was reduced to 20 $\mathrm{cm^3}$ and yellow crystals of the product were deposited on cooling to room temperature. Yield 0.6 g, 82% (Found: C, 39.1; H, 4.6; N, 10.1. $\mathrm{C_{18}H_{26}Cl_2N_4W}$ requires C, 39.1; H, 4.7; N, 10.1%). IR: 1599m, 1568w, 1357m, 1310m, 1284m, 1277m, 1240s, 1215m, 1175w, 1157w, 1139w, 1104w, 1059w, 1044w, 1023s, 1013w, 904w, 894w, 803w, 770s, 735s, 725w, 652m, 632m, 601w, 577w, 478w, 420w, 360w and 310s $\mathrm{cm^{-1}}$. NMR ($\mathrm{CDCl_3}$): $^1\mathrm{H}$ (200.13 MHz), δ 9.68 (2 H, d, α-H, bipy), 8.15–7.96 (4 H, m, β-H, bipy), 7.64–7.52 (2 H, m, γ-H, bipy) and 1.61 (18 H, s, $\mathrm{NCMe_3}$); $^{13}\mathrm{C}$ (75.47 MHz), δ 154.1 (α-CH, bipy), 151.2 (α-C, bipy), 139.4 (γ-CH, bipy), 126.2, 122.0 (β-CH, bipy), 68.1 ($\mathrm{N}C\mathrm{Me_3}$) and 32.3 ($\mathrm{NC}Me_3$).

X-Ray Crystallography.—Crystals of complexes **2**, **3** and **4**, sealed in Lindemann glass capillaries, were examined at room temperature on a Stoe-Siemens diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Crystal data are listed in Table 8, together with other information on the structure determinations. Cell parameters were refined from 2θ values (20–25°) of 32 reflections measured at ±ω in each case. Intensities were measured with ω–θ scans and on-line profile fitting.[23] Semi-empirical absorption corrections were applied,[24] together with standard Lorentz polarisation and intensity-decay factors. Each data set consisted of a complete unique set of reflections together with some equivalent reflections. Unique reflections with $F > 4\sigma(F)$ were used in structure determination.

Atoms were located from Patterson and difference syntheses and refined[24] by blocked-cascade methods to minimise $\Sigma w\Delta^2$, with $\Delta = |F_o| - |F_c|$ and $w = 1/\sigma^2(F)$; $\sigma^2(F)$ included contributions from the counting statistics and from an empirical analysis of the variance of observed and calculated data.[25] Atomic scattering factors were taken from ref. 26. Extinction

Table 8 Crystallographic data

Compound	**2**	**3**	**4**
Formula	$C_{68}H_{84}Cl_{14}N_4O_4P_2W_4$	$C_{14}H_{17}Cl_2N_3OW$	$C_{18}H_{26}Cl_2N_4W$
M	4460.4	474.0	553.2
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$
a/Å	12.639(2)	8.103(3)	13.3517(7)
b/Å	12.839(2)	17.865(6)	12.0723(6)
c/Å	27.463(4)	11.907(4)	27.4968(12)
α/°	79.79(1)	90	
β/°	79.97(1)	95.73(4)	93.857(7)
γ/°	90	85.67(1)	90
U/Å^3	4314.3	1715.1	4422.0
Z	2	4	8
D_c/g cm^{-3}	1.717	1.836	1.662
μ/mm^{-1}	5.89	7.19	5.59
F(000)	2232	904	2160
Crystal size/mm	0.39 × 0.39 × 0.16	0.35 × 0.31 × 0.23	0.31 × 0.27 × 0.19
Maximum indices hkl	13, 13, 29	9, 21, 14	15, 14, 32
Transmission factors	0.077–0.226	0.061–0.097	0.124–0.191
Reflections measured	17 456	3352	5766
Unique reflections	11 298	3026	3901
Observed reflections	9714	2149	2790
R_{int}	0.020	0.030	0.023
No. of refined parameters	866	261	222
R^a	0.0577	0.0286	0.0313
R'^b	0.0447	0.0275	0.0279
Goodness of fit	1.20	1.04	1.12
Maximum shift/e.s.d.	0.034	0.025	0.007
Maximum, minimum electron density/e Å^{-3}	2.46, −2.68	1.27, −0.66	0.79, −0.61

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

effects were negligible. Isotropic H atoms were constrained to give C–H 0.96 Å, H–C–H 109.5°, aromatic H atoms on ring-angle external bisectors, and U(H) = 1.2U(C), and all other atoms were refined anisotropically. In the case of complex **2**, geometry restraints were applied to the CH_2Cl_2 solvent molecules, which show high thermal motion and are possibly somewhat disordered. The largest peaks in the final difference syntheses were close to the heavy atoms.

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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