Synthesis and Characterisation of Binuclear and Trinuclear Organoimido Complexes of Tungsten-(VI) and -(V) and a Binuclear Tungsten(V) Oxoanion. *X*-Ray Crystal Structures of [$\{WCl_4(NEt)\}_2$], [$P(CH_2Ph)Ph_3$][$W_3Cl_7(NBu^t)_3(\mu\text{-}NPh)_3$], [$P(CH_2Ph)Ph_3$][$W_2Cl_7(NR)_2$] (R = Et or Ph), and [$P(CH_2Ph)Ph_3$][$W_2O_2Cl_7$]†

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The *X*-ray crystal structure of [$\{WCl_4(NEt)\}_2$] has been determined and shows the molecule to be binuclear with asymmetric chlorine bridges and linear ethylimido groups having a W–N distance of 1.69(1) Å. Binuclear, mixed organoimido compounds [$\{WCl_2(NBu^t)(\mu\text{-}NR)(NH_2Bu^t)\}_2$] (R = Ph or C_6H_4Me-*p*) with asymmetric NR bridges have been converted to the trinuclear anions [$W_3Cl_7(NBu^t)_3(\mu\text{-}NR)_3$]$^-$. The *X*-ray crystal structure of [$W_3Cl_7(NBu^t)_3(\mu\text{-}NPh)_3$]$^-$ shows it to contain terminal, linear NBu^t groups with an average W–N distance of 1.70 Å, almost symmetrical bridging NPh groups with an average W–N distance of 2.00 Å, and a triply bridging chlorine. Carbon-13 and ^1H n.m.r. spectra of this anion show that rotation of the phenyl rings in the μ-NPh groups is restricted. Reduction of [$WXCl_4$] with 1 equivalent of sodium amalgam in the presence of chloride ions gave the distorted confacial bioctahedral tungsten(v) anions [$W_2X_2Cl_7$]$^-$ (X = NEt, NPh, or O). *X*-Ray crystal structures of all three anions have been determined and show the π-bonding ligands to be terminal with average W–N distances of 1.69 (X = NEt) and 1.72 Å (X = NPh) and an average W–O distance of 1.67 Å. The W–W distances in the three anions are 2.839(4) (X = NEt), 2.835(4) (X = NPh), and 2.849(1) Å (X = O).

The reaction between an organic isocyanate and $WOCl_4$ [equation (1)] has been shown to be a convenient entry into

$$WOCl_4 + RNCO \longrightarrow W(NR)Cl_4 + CO_2 \quad (1)$$

organoimido-tungsten chemistry.[1] The tetrachloro compounds are useful starting materials and *X*-ray crystal structure determinations for compounds with R = C_2Cl_5, Pr^i, or C_6H_4Me-*p* have shown them to be dimeric, [$\{WCl_4(NR)\}_2$], with bridging chlorines.[2] In the presence of donor ligands (L), these compounds form adducts by cleavage of the chlorine bridges [equation (2)] and we have reported the structures of [WCl_4-

$$[\{WCl_4(NR)\}_2] + 2L \longrightarrow 2[WCl_4(NR)L] \quad (2)$$

(NC_6H_4Me-*p*)(thf)] (thf = tetrahydrofuran) and [$WCl_5(NC_6H_4Me$-*p*)]$^-$.[3]

Alkyl and alkylidene complexes of tungsten(VI) containing the phenylimido group have been prepared from [$WCl_4(NPh)$] by Pedersen and Schrock[4] who also obtained [$W(NR)(OBu^t)_4$] by metathesis using $LiOBu^t$. Nielson and co-workers[5] have shown that alcohols react with [$WCl_4(NR)$] (R = Me or Ph) in the presence of a base to give organoimidoalkoxides of tungsten(VI). Tertiary phosphines (L) reduce [$WCl_4(NR)$] to give the d^1 complexes [$WCl_3(NR)L_2$] and further reduction to the d^2 complexes [$WCl_2(NR)L_3$] can be accomplished with sodium–mercury amalgam in the presence of L.[1,3,6]

We have now determined the structure of [$WCl_4(NEt)$] by single-crystal *X*-ray diffraction and report here that this compound is dimeric with bridging chlorines. We have also reduced [$WCl_4(NR)$] in the presence of chloride ions and isolated the distorted confacial bioctahedral tungsten(V) anions [$W_2Cl_7(NR)_2$]$^-$ (R = Et or Ph). The oxo analogue [$W_2O_2Cl_7$]$^-$ was also prepared in a similar manner for comparison. As in the majority of transition-metal organoimido complexes, the tungsten compounds discussed above all contain terminal, linear NR groups which are tightly bound and fairly unreactive. Attempts have been made to increase the reactivity of co-ordinated NR groups by increasing electron density at the metal atom, thereby decreasing the extent of delocalisation of the nitrogen lone pair onto the metal. This usually involves incorporating other potential π-donor ligands to compete with the NR group for metal π orbitals, causing an increase in M–N distance and a decrease in the MNC angle.[7,8] We have prepared tungsten(VI) di-imido compounds where the extra electron density on one of the organoimido groups is donated to another metal forming binuclear, organoimido-bridged complexes.[9] In this paper we describe the conversion of the binuclear, mixed organoimido complexes [$\{WCl_2(NBu^t)(\mu\text{-}NR)(NH_2Bu^t)\}_2$] (R = Ph or C_6H_4Me-*p*) into the trinuclear anions, [$W_3Cl_7(NBu^t)_3(\mu\text{-}NR)_3$]$^-$ and report the *X*-ray crystal structure of the phenylimido derivative.

Results and Discussion

Tungsten(VI) *Compounds.*—Single crystals of [$\{WCl_4(NEt)\}_2$][1] (**1**) suitable for *X*-ray diffraction were obtained by recrystallisation from toluene and were mounted in Lindemann capillaries under nitrogen. The structure is shown in Figure 1 with relevant bond distances and angles in Table 1. The molecule has a centrosymmetric edge-shared bioctahedral structure,

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† Di-μ-chloro-bis[dichloro(ethylimido)tungsten(VI)], benzyltriphenylphosphonium μ_3-chloro-1,2;1,3;2,3-tris(μ-phenylimido)-tris[dichloro-(t-butylimido)tungstate(VI)], benzyltriphenylphosphonium tri-μ-chloro-bis[dichloro(ethylimido)tungstate(V)](*W–W*), benzyltriphenylphosphonium tri-μ-chloro-bis[dichloro(phenylimido)tungstate(V)]-(*W–W*), and benzyltriphenylphosphonium tri-μ-chloro-bis[dichloro-oxotungstate(V)](*W–W*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

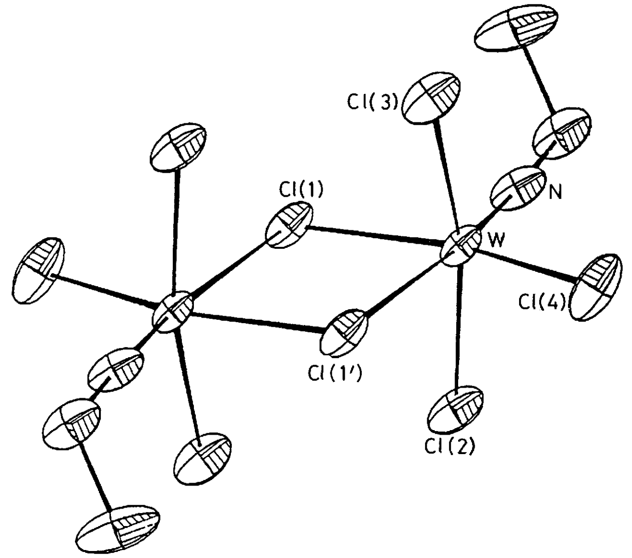

Figure 1. The structure of $[\{WCl_4(NEt)\}_2]$ (1)

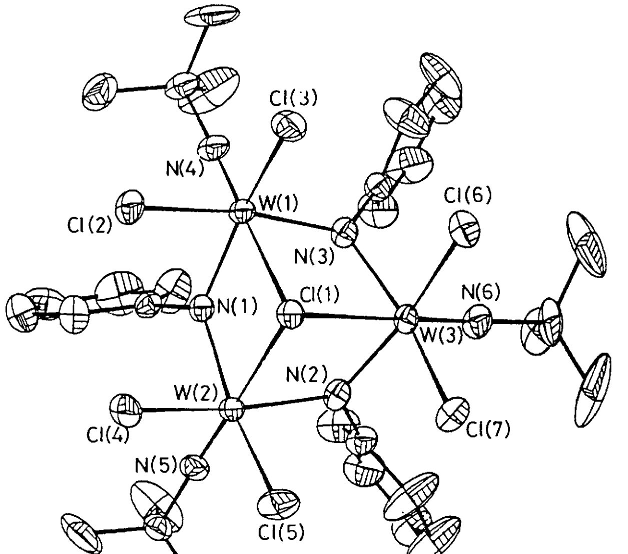

Figure 2. The structure of $[W_3Cl_7(NBu^t)_3(\mu\text{-}NPh)_3]^-$ (3)

Table 1. Bond lengths (Å) and angles (°) for $[\{WCl_4(NEt)\}_2]$ (1)

Cl(1)–W(1)	2.431(5)	Cl(2)–W(1)	2.305(5)
Cl(3)–W(1)	2.307(5)	Cl(4)–W(1)	2.279(5)
Cl(1')–W(1)	2.731(6)	N(1)–W(1)	1.685(13)
C(1)–N(1)	1.440(18)	C(2)–C(1)	1.537(24)
Cl(2)–W(1)–Cl(1)	86.8(2)	Cl(3)–W(1)–Cl(1)	86.5(2)
Cl(3)–W(1)–Cl(2)	164.7(1)	Cl(4)–W(1)–Cl(1)	163.7(1)
Cl(4)–W(1)–Cl(2)	91.0(2)	Cl(4)–W(1)–Cl(3)	91.6(2)
N(1)–W(1)–Cl(1)	94.9(4)	N(1)–W(1)–Cl(2)	97.7(4)
N(1)–W(1)–Cl(3)	96.6(5)	N(1)–W(1)–Cl(4)	101.3(5)
Cl(1)–W(1)–Cl(1')	77.8(3)	Cl(2)–W(1)–Cl(1')	82.5(2)
Cl(3)–W(1)–Cl(1')	82.6(2)	Cl(4)–W(1)–Cl(1')	85.9(2)
N(1)–W(1)–Cl(1')	172.7(1)	W(1)–Cl(1)–W(1')	102.2(3)
C(1)–N(1)–W(1)	176.3(9)	C(2)–C(1)–N(1)	111.0(14)

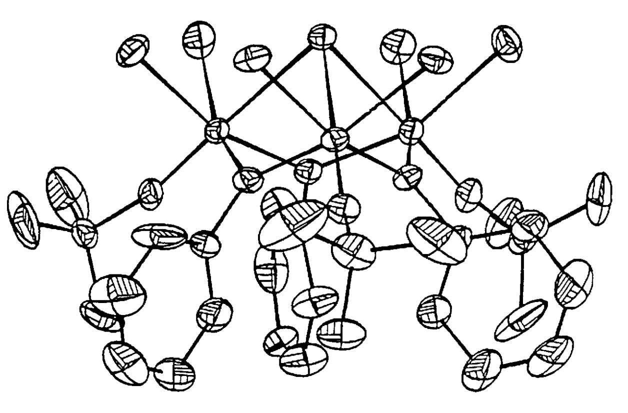

Figure 3. A view of the anion (3) showing the parallel planes of Cl, W, and N

each tungsten atom being displaced from the plane of the four chlorines, Cl(1), Cl(2), Cl(3), and Cl(4), towards the nitrogen of the ethylimido group. This distortion from ideal octahedral geometry is frequently observed in other complexes containing organoimido ligands or the related strongly π-donating nitrido and oxo ligands where relatively short M–N or M–O distances are found. The essentially linear W–N–C bonding in the ethylimido group with a WNC angle of 176.3(9)° and a W–N distance of 1.685(13) Å implies that it is a four-electron donor to tungsten, forming a W≡N triple bond. The chlorine bridges are asymmetric with the longer W–Cl distance *trans* to the ethylimido group. This is another example of the *trans*-lengthening influence of organoimido groups in sixteen-electron, d^0 tungsten(VI) compounds.[3,10–12] The bond distances in (1) are similar to those reported for other $[\{WCl_4(NR)\}_2]$ compounds (R = C_2Cl_5, Pr^i, or C_6H_4Me-*p*),[2] the W–N distances being shorter and the *trans* influence larger for the alkylimido compounds (R = Et or Pr^i) as expected.

From the reaction between $[WCl_4(NPh)]$ and 2 equivalents of $SiMe_3(NHBu^t)$, which has been shown to give the binuclear, phenylimido-bridged complex $[\{WCl_2(NBu^t)(\mu\text{-}NPh)(NH_2Bu^t)\}_2]$ (2),[9] a second compound can be crystallised after separation of (2). Samples of this second product contained varying amounts of $[NH_3Bu^t]^+$ as shown by ^1H n.m.r. spectroscopy, which also showed the presence of NBu^t and NPh organoimido groups in a 1:1 ratio. After repeated recrystallisation, however, the ratio of NBu^t to $[NH_3Bu^t]^+$ was consistently *ca.* 3:1 which suggested that this compound was a salt with formula $[NH_3Bu^t][W_3Cl_7(NBu^t)_3(NPh)_3]$. A single-crystal *X*-ray structure determination for the $[P(CH_2Ph)Ph_3]^+$ salt showed this to be correct. The anion $[W_3Cl_7(NBu^t)_3(\mu\text{-}NPh)_3]^-$ (3) adopts the *triangulo*-M_3X_{13} type of structure and is shown in Figures 2 and 3. Bond lengths and angles are given in Table 2. The terminal NBu^t groups are linear and *cis* to bridging NPh groups. The phenylimido bridges have trigonal nitrogens and are only slightly asymmetric with average W$\overset{\cdots}{-}$N distances of 1.98 Å for the shorter and 2.03 Å for the longer bonds. The overall average of the W$\overset{\cdots}{-}$NPh distances (2.00 Å) is smaller than that for the binuclear compound (2) (2.11 Å),[9] indicating a slightly higher average bond order in the bridging region of the trinuclear compound. The average W≡NBu^t distance of 1.70 Å in (3) compared with 1.729(4) Å in (2) also indicates a higher terminal bond order for the trinuclear compound. The *trans* influence of the terminal NBu^t groups is evident by the long W–(μ_3-Cl) distances (av. 2.64 Å) whereas the terminal W–Cl distances *trans* to the μ-NPh are comparable with those *trans* to Bu^{t}NH$_2$ in the binuclear compounds $[\{WCl_2(NBu^t)(\mu\text{-}NR)(NH_2Bu^t)\}_2]$ (R = Ph or C_6H_4Me-*p*).[9] The view of the anion (3) shown in Figure 3 emphasises the presence of three parallel planes consisting of consecutively seven chlorines, three

Table 2. Selected bond lengths (Å) and angles (°) for $[P(CH_2Ph)Ph_3]$-$[W_3Cl_7(\mu\text{-}NPh)_3(NBu^t)_3]$ (**3**)

W(1)–Cl(1)	2.639(5)	W(1)–Cl(2)	2.426(5)
W(1)–Cl(3)	2.384(4)	W(1)–N(1)	2.023(8)
W(1)–N(3)	1.993(9)	W(1)–N(4)	1.702(8)
W(2)–Cl(1)	2.636(5)	W(1)–Cl(4)	2.397(5)
W(2)–Cl(5)	2.396(4)	W(2)–N(1)	1.984(8)
W(2)–N(2)	2.047(9)	W(2)–N(5)	1.706(8)
W(3)–Cl(1)	2.652(5)	W(3)–Cl(6)	2.419(4)
W(3)–Cl(7)	2.382(4)	W(3)–N(2)	1.974(8)
W(3)–N(3)	2.022(8)	W(3)–N(6)	1.698(11)

Cl(2)–W(1)–Cl(1)	86.3(2)	Cl(3)–W(1)–Cl(1)	83.9(2)
Cl(3)–W(1)–Cl(2)	84.1(2)	Cl(1)–W(1)–N(1)	77.3(3)
Cl(2)–W(1)–N(1)	86.6(3)	Cl(3)–W(1)–N(1)	159.5(2)
Cl(1)–W(1)–N(3)	78.0(3)	Cl(2)–W(1)–N(3)	164.0(2)
Cl(3)–W(1)–N(3)	91.5(3)	N(1)–W(1)–N(3)	92.5(4)
Cl(1)–W(1)–N(4)	177.8(3)	Cl(2)–W(1)–N(4)	95.9(4)
Cl(3)–W(1)–N(4)	96.8(4)	N(1)–W(1)–N(4)	102.3(4)
N(3)–W(1)–N(4)	99.8(4)	Cl(4)–W(2)–Cl(1)	85.3(2)
Cl(5)–W(2)–Cl(1)	85.0(2)	Cl(5)–W(2)–Cl(4)	84.6(2)
Cl(1)–W(2)–N(1)	78.0(3)	Cl(4)–W(2)–N(1)	90.8(3)
Cl(5)–W(2)–N(1)	162.7(2)	Cl(1)–W(2)–N(2)	77.8(3)
Cl(4)–W(2)–N(2)	162.2(2)	Cl(5)–W(2)–N(2)	88.5(3)
N(2)–W(2)–N(1)	91.0(4)	Cl(1)–W(2)–N(5)	178.4(3)
Cl(4)–W(2)–N(5)	96.0(4)	Cl(5)–W(2)–N(5)	96.0(3)
N(5)–W(2)–N(1)	101.0(4)	N(5)–W(2)–N(2)	101.0(4)
Cl(6)–W(3)–Cl(1)	85.9(2)	Cl(7)–W(3)–Cl(1)	85.1(2)
Cl(7)–W(3)–Cl(6)	86.1(29)	Cl(1)–W(3)–N(2)	78.6(3)
Cl(6)–W(3)–N(2)	164.3(2)	Cl(7)–W(3)–N(2)	90.0(3)
Cl(1)–W(3)–N(3)	77.2(3)	Cl(6)–W(3)–N(3)	87.4(3)
Cl(7)–W(3)–N(3)	161.5(2)	N(3)–W(3)–N(2)	91.7(3)
Cl(1)–W(3)–N(6)	177.6(2)	Cl(6)–W(3)–N(6)	95.6(3)
Cl(7)–W(3)–N(6)	96.8(3)	N(6)–W(3)–N(2)	100.0(4)
N(6)–W(3)–N(3)	101.0(4)	W(2)–Cl(1)–W(1)	82.8(2)
W(3)–Cl(1)–W(1)	82.7(2)	W(3)–Cl(1)–W(2)	82.6(2)
W(2)–N(1)–W(1)	121.0(4)	C(11)–N(1)–W(1)	119.2(6)
C(11)–N(1)–W(2)	119.8(6)	W(3)–N(2)–W(2)	120.4(4)
C(21)–N(2)–W(2)	118.6(6)	C(21)–N(2)–W(3)	120.9(6)
W(3)–N(3)–W(1)	121.1(5)	C(31)–N(3)–W(1)	121.0(6)
C(31)–N(3)–W(3)	117.9(6)	C(41)–N(4)–W(1)	169.8(7)
C(51)–N(5)–W(2)	167.7(7)	C(61)–N(6)–W(3)	165.9(6)

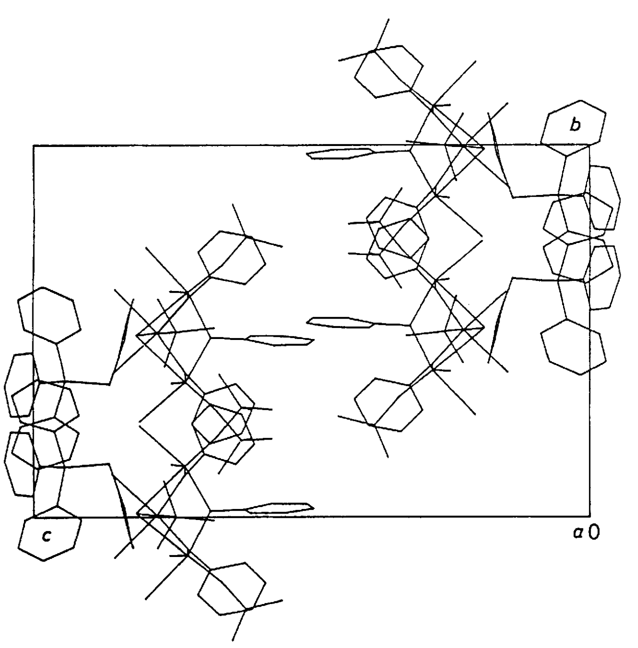

Figure 4. Packing diagram for $[P(CH_2Ph)Ph_3][W_3Cl_7(NBu^t)_3(\mu\text{-}NPh)_3]$

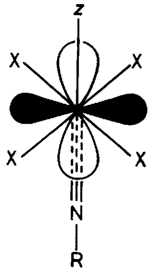

Figure 5. Diagram showing the empty d_{xy} orbital in the fragment $W(NR)X_4$

tungstens, and six nitrogens in the molecule. It also shows that the anion contains an 'inorganic side' consisting of the plane of seven chlorines and an 'organic side' consisting of the t-butyl and phenyl groups of the organoimido ligands. The packing of the ions in the crystal is shown in Figure 4 where the cations sit between the planes of chlorines and the anions pack with their organic faces together. Another feature of (**3**) is that the 'organic side' of the molecule is sterically congested. This is reflected in the ^1H and ^{13}C n.m.r. spectra of (**3**). There are six separate resonances for the carbon atoms of the μ-NPh phenyl groups in the ^{13}C n.m.r. spectrum at ambient temperature, indicating that rotation about the C–N bond is restricted by the bulky NBu^t groups. This in turn causes each t-butyl group to be shielded by the diamagnetic anisotropy of two aromatic rings and consequently the NBu^t resonance in the ^1H n.m.r. spectrum occurs at δ 0.58, about 0.8 p.p.m. upfield from the NBu^t groups in the binuclear compound (**2**).

Proton n.m.r. studies showed trinuclear (**3**) to be present in solution together with binuclear (**2**) after mixtures of $[WCl_4(NPh)]$ and $SiMe_3(NHBu^t)$ had been heated in toluene. Prolonged heating increased the amount of the trinuclear anion (**3**). It seems, then, that at higher temperatures the $W \leftarrow NH_2Bu^t$ and $W \leftarrow NPh$ bonds in $[\{WCl_2(NBu^t)(\mu\text{-}NPh)(NH_2Bu^t)\}_2]$ are broken and, in the presence of chloride ions, $[W_3Cl_7(NBu^t)_3(\mu\text{-}NPh)_3]^-$ (**3**) is formed with optimisation of π bonding [equation (3)]. Indeed, trinuclear (**3**) was produced in higher yield by treating binuclear (**2**) with the stoicheiometric amount of $[P(CH_2Ph)Ph_3]Cl$ in toluene under reflux. When a similar

$$\underset{(\mathbf{2})}{3[\{WCl_2(NBu^t)(\mu\text{-}NPh)(NH_2Bu^t)\}_2]} \xrightarrow{2Cl^-} \underset{(\mathbf{3})}{2[W_3Cl_7(NBu^t)_3(\mu\text{-}NPh)_3]^-} + 6NH_2Bu^t \quad (3)$$

reaction with $[\{WCl_2(NBu^t)(\mu\text{-}NC_6H_4Me\text{-}p)(NH_2Bu^t)\}_2]$ was monitored by ^1H n.m.r. spectroscopy, a high-field NBu^t resonance appeared in a similar position to that seen in the ^1H n.m.r. spectrum of (**3**), but a longer reaction time was required for all of the binuclear compound to react. Other uncharacterised products were also formed and pure $[W_3Cl_7(NBu^t)_3(\mu\text{-}NC_6H_4Me\text{-}p)_3]^-$ could not be isolated from the reaction mixture. This suggests that the bonding in the bridging region of the binuclear compounds $[\{WCl_2(NBu^t)(\mu\text{-}NR)(NH_2Bu^t)\}_2]$ is stronger when R = C_6H_4Me-*p* and this is consistent with the shorter average W–N bond lengths for the *p*-tolylimido bridges.[9]

The $[M_3(\mu_3\text{-}X)(\mu\text{-}Y)_3L_9]$ structure is one of the triangular types which play an important part in the chemistry of molybdenum and tungsten.[13] As a metal–metal bonded unit, this is found in polymeric compounds as well as in discrete trinuclear molecules and the bonding involved has been examined.[13b] The trinuclear structure of $[W_3Cl_7(NBu^t)_3(\mu\text{-}NPh)_3]^-$ (**3**) reported here does not contain any metal–metal bonds, however, and is therefore more closely related to the M_3O_{13} structural elements which occur in many polyoxometalates.[14] In these trinuclear

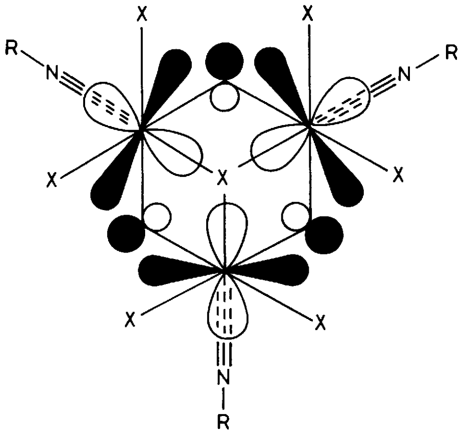

Figure 6. Diagram showing π overlap in the bridging region of $[W_3Cl_7(NBu^t)_3(\mu\text{-}NPh)_3]^-$

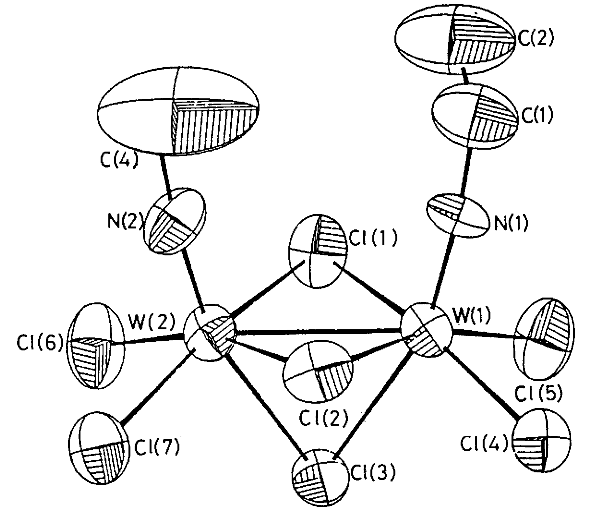

Figure 7. The structure of $[W_2Cl_7(NEt)_2]^-$ **(4)**

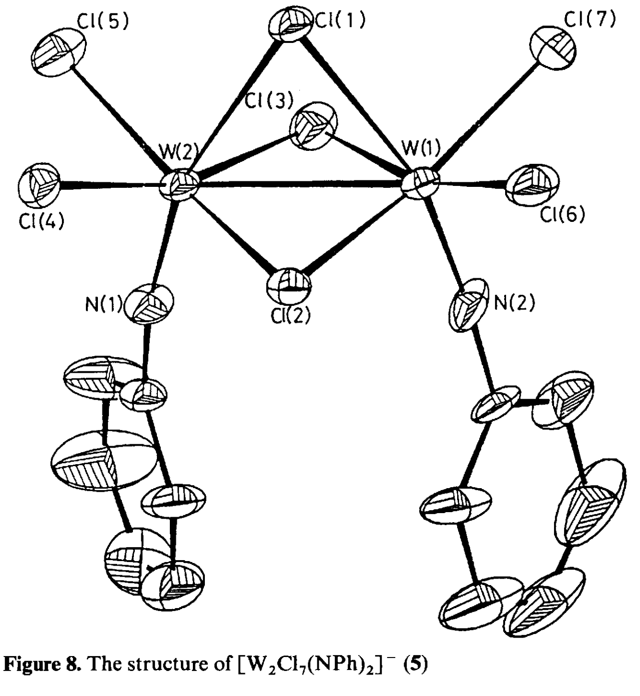

Figure 8. The structure of $[W_2Cl_7(NPh)_2]^-$ **(5)**

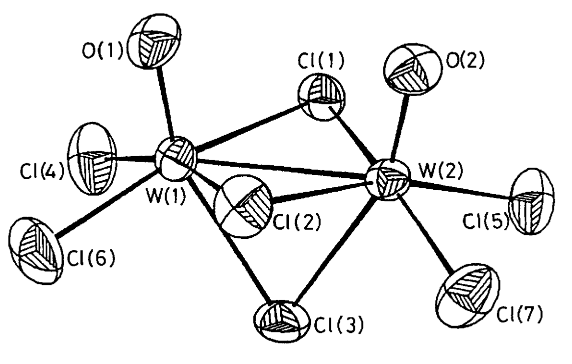

Figure 9. The structure of $[W_2O_2Cl_7]^-$ **(6)**

species containing metals in high oxidation states, metal orbitals involved in metal–metal bonding interactions in the cluster species mentioned above are used to accept π-electron density from the terminal oxo or organoimido ligands. In a simple bonding picture for the $[WX_4(NR)]$ fragment the d_{z^2} and $d_{x^2-y^2}$ metal orbitals are involved in σ bonding and the d_{xz} and d_{yz} orbitals can participate in π bonding with the nitrogen. This leaves the d_{xy} orbital available to accept π-electron density from a potential π donor in the plane perpendicular to the W≡NR bond (Figure 5). In the trinuclear complex **(3)**, π overlap (simply represented in Figure 6) gives symmetrical bridges. In the binuclear compounds $[\{WCl_4(NR)\}_2]$ and $[\{WCl_2(NBu^t)(\mu\text{-}NR)(NH_2Bu^t)\}_2]$ (R = Ph or $C_6H_4Me\text{-}p$) this type of overlap is not possible and asymmetric bridges are formed. The oxo bridges in trinuclear $[\{W(NPh)(\mu\text{-}O)Me_2(PMe_3)\}_3]$[12] are probably asymmetric for similar reasons. It is interesting that a trinuclear vanadium(V) unit '$V_3(NBu^t)_3(\mu\text{-}NPh)_3$' similar to '$W_3(NBu^t)_3(\mu\text{-}NPh)_3$' in ion **(3)** has been structurally characterised in $[V_3Cl_3(NBu^t)_3(\mu\text{-}NPh)_3\{\eta^3\text{-}PhNC(O)NHBu^t\}]$.[15]

Tungsten(V) *Compounds.*—Reduction of $WXCl_4$ (X = NEt, NPh, or O) with 1 equivalent of sodium amalgam in dichloromethane in the presence of $[P(CH_2Ph)Ph_3]Cl$ [equation (4)]

$$2WXCl_4 + 2Na + [P(CH_2Ph)Ph_3]Cl \longrightarrow [P(CH_2Ph)Ph_3][W_2X_2Cl_7] + 2NaCl \quad (4)$$

gave the binuclear tungsten(V) anions $[W_2X_2Cl_7]^-$; [X = NEt **(4)**, NPh **(5)**, or O **(6)**]. The benzyltriphenylphosphonium salts of $[W_2Cl_7(NEt)_2]^-$ **(4)**, $[W_2Cl_7(NPh)_2]^-$ **(5)**, and $[W_2O_2Cl_7]^-$ **(6)** were recrystallised from dichloromethane–hexane and their structures determined by *X*-ray diffraction. All three anions have distorted confacial bioctahedral geometries with three bridging chlorines and terminal organoimido or oxo groups. The structures are shown in Figures 7, 8, and 9 respectively and bond lengths and angles are given in Tables 3, 4, and 5. The anions **(4)** and **(5)** are among the first structurally characterised organoimido compounds with this geometry[16] and the first to contain W^V. The organoimido groups are linear, the ethylimido anion **(4)** having the shortest W–N distances, the average (1.69 Å) being the same as that in $[\{WCl_4(NEt)\}_2]$ **(1)**. From the W–Cl distances *trans* to the π donor in **(4)**—**(6)**, the order of increasing *trans* influence is NPh < NEt < O. The ^1H n.m.r. spectrum of **(4)**, which shows $^3J(WH)$ of 10 Hz for the CH_2 protons, indicates that this anion is diamagnetic. This raises the question as to whether these compounds contain metal–metal bonds. The W–W distances in **(4)**—**(6)** are slightly longer than in other W^V–W^V singly bonded compounds.[17] Confacial bioctahedral oxo compounds containing sulphur donor ligands have been structurally characterised[18] and the anion $[W_2O_2Cl_5(SBu^i)_2]^-$ has a W–W distance of 2.854 Å,[18b] which is close to

Table 3. Selected bond lengths (Å) and angles (°) for $[P(CH_2Ph)Ph_3][W_2Cl_7(NEt)_2]$ (**4**)

W(2)–W(1)	2.839(4)	Cl(1)–W(1)	2.432(6)
Cl(2)–W(1)	2.416(4)	Cl(3)–W(1)	2.585(7)
Cl(4)–W(1)	2.390(6)	Cl(5)–W(1)	2.384(6)
N(1)–W(1)	1.700(12)	Cl(1)–W(2)	2.420(6)
Cl(2)–W(2)	2.428(6)	Cl(3)–W(2)	2.548(6)
Cl(6)–W(2)	2.366(6)	Cl(7)–W(2)	2.378(6)
N(2)–W(2)	1.684(14)		
Cl(2)–W(1)–Cl(1)	106.7(2)	Cl(3)–W(1)–Cl(1)	76.7(2)
Cl(3)–W(1)–Cl(2)	77.4(2)	Cl(4)–W(1)–Cl(1)	162.5(1)
Cl(4)–W(1)–Cl(2)	82.9(2)	Cl(4)–W(1)–Cl(3)	91.6(2)
Cl(5)–W(1)–Cl(1)	83.3(2)	Cl(5)–W(1)–Cl(2)	163.3(1)
Cl(5)–W(1)–Cl(3)	92.4(3)	Cl(5)–W(1)–Cl(4)	84.3(2)
N(1)–W(1)–Cl(1)	91.9(5)	N(1)–W(1)–Cl(2)	92.7(5)
N(1)–W(1)–Cl(3)	161.8(4)	N(1)–W(1)–Cl(4)	102.4(5)
N(1)–W(1)–Cl(5)	100.4(6)	Cl(2)–W(2)–Cl(1)	106.7(2)
Cl(3)–W(2)–Cl(1)	77.0(2)	Cl(3)–W(2)–Cl(2)	77.2(2)
Cl(6)–W(2)–Cl(1)	83.2(3)	Cl(6)–W(2)–Cl(2)	163.2(2)
Cl(6)–W(2)–Cl(3)	92.3(2)	Cl(7)–W(2)–Cl(1)	161.8(2)
Cl(7)–W(2)–Cl(2)	82.8(3)	Cl(7)–W(2)–Cl(3)	90.5(2)
Cl(7)–W(2)–Cl(6)	84.2(3)	N(2)–W(2)–Cl(1)	92.3(6)
N(2)–W(2)–Cl(2)	92.5(5)	N(2)–W(2)–Cl(3)	162.0(5)
N(2)–W(2)–Cl(6)	100.8(5)	N(2)–W(2)–Cl(7)	102.9(6)
W(2)–Cl(1)–W(1)	71.6(2)	W(2)–Cl(2)–W(1)	71.8(2)
W(2)–Cl(3)–W(1)	66.6(2)	C(1)–N(1)–W(1)	173.7(12)
		C(3)–N(2)–W(2)	174.2(14)

Table 4. Selected bond lengths (Å) and angles (°) for $[P(CH_2Ph)Ph_3][W_2Cl_7(NPh)_2]$ (**5**)

W(2)–W(1)	2.835(4)	Cl(1)–W(1)	2.573(5)
Cl(2)–W(1)	2.417(4)	Cl(3)–W(1)	2.436(5)
Cl(6)–W(1)	2.378(5)	Cl(7)–W(1)	2.365(4)
N(2)–W(1)	1.731(9)	Cl(1)–W(2)	2.577(6)
Cl(2)–W(2)	2.430(4)	Cl(3)–W(2)	2.443(4)
Cl(4)–W(2)	2.356(4)	Cl(5)–W(2)	2.368(5)
N(1)–W(2)	1.713(10)		
Cl(2)–W(1)–Cl(1)	78.3(2)	Cl(3)–W(1)–Cl(1)	77.2(2)
Cl(3)–W(1)–Cl(2)	107.0(2)	Cl(6)–W(1)–Cl(1)	92.6(2)
Cl(6)–W(1)–Cl(2)	82.2(2)	Cl(6)–W(1)–Cl(3)	164.2(1)
Cl(7)–W(1)–Cl(1)	90.4(2)	Cl(7)–W(1)–Cl(2)	162.2(1)
Cl(7)–W(1)–Cl(3)	83.4(2)	Cl(7)–W(1)–Cl(6)	84.7(2)
N(2)–W(1)–Cl(1)	162.9(3)	N(2)–W(1)–Cl(2)	92.9(3)
N(2)–W(1)–Cl(3)	91.8(4)	N(2)–W(1)–Cl(6)	100.7(4)
N(2)–W(1)–Cl(7)	101.3(3)	Cl(2)–W(2)–Cl(1)	78.0(2)
Cl(3)–W(2)–Cl(1)	77.0(2)	Cl(3)–W(2)–Cl(2)	106.4(2)
Cl(4)–W(2)–Cl(1)	92.3(2)	Cl(4)–W(2)–Cl(2)	83.1(2)
Cl(4)–W(2)–Cl(3)	163.6(1)	Cl(5)–W(2)–Cl(1)	91.1(2)
Cl(5)–W(2)–Cl(2)	163.1(1)	Cl(5)–W(2)–Cl(3)	83.3(2)
Cl(5)–W(2)–Cl(4)	84.5(2)	N(1)–W(2)–Cl(1)	161.6(3)
N(1)–W(2)–Cl(2)	94.0(3)	N(1)–W(2)–Cl(3)	89.7(3)
N(1)–W(2)–Cl(4)	103.2(3)	N(1)–W(2)–Cl(5)	100.0(4)
W(2)–Cl(1)–W(1)	66.8(2)	W(2)–Cl(2)–W(1)	71.6(2)
W(2)–Cl(3)–W(1)	71.0(2)	C(11)–N(1)–W(2)	168.7(6)
C(12)–C(11)–N(1)	119.1(10)	C(16)–C(11)–N(1)	121.9(10)
C(16)–C(11)–C(12)	118.9(11)	C(13)–C(12)–C(11)	120.2(13)
C(14)–C(13)–C(12)	121.9(15)	C(15)–C(14)–C(13)	119.0(17)
C(16)–C(15)–C(14)	122.0(14)	C(15)–C(16)–C(11)	117.9(12)
C(21)–N(2)–W(1)	174.8(7)	C(22)–C(21)–N(2)	120.4(10)
C(26)–C(21)–N(2)	120.9(9)	C(26)–C(21)–C(22)	118.7(12)
C(23)–C(22)–C(21)	119.6(14)	C(24)–C(23)–C(22)	119.6(16)
C(25)–C(24)–C(23)	120.5(21)	C(26)–C(25)–C(24)	120.9(17)
C(25)–C(26)–C(21)	120.5(13)		

Table 5. Selected bond lengths (Å) and angles (°) for $[P(CH_2Ph)Ph_3][W_2O_2Cl_7]$ (**6**)

W(2)–W(1)	2.849(1)	Cl(1)–W(1)	2.438(4)
Cl(2)–W(1)	2.417(4)	Cl(3)–W(1)	2.598(5)
Cl(4)–W(1)	2.327(4)	Cl(6)–W(1)	2.317(4)
O(1)–W(1)	1.677(7)	Cl(1)–W(2)	2.429(4)
Cl(2)–W(2)	2.422(4)	Cl(3)–W(2)	2.614(5)
Cl(6)–W(2)	2.335(4)	Cl(7)–W(2)	2.323(4)
O(2)–W(2)	1.669(7)		
Cl(1)–W(1)–W(2)	54.0(1)	Cl(2)–W(1)–W(2)	54.0(1)
Cl(2)–W(1)–Cl(1)	106.7(2)	Cl(3)–W(1)–W(2)	57.1(1)
Cl(3)–W(1)–Cl(1)	76.1(2)	Cl(3)–W(1)–Cl(2)	77.2(2)
Cl(4)–W(1)–W(2)	131.7(1)	Cl(4)–W(1)–Cl(1)	83.8(2)
Cl(4)–W(1)–Cl(2)	163.7(1)	Cl(4)–W(1)–Cl(3)	93.9(2)
Cl(6)–W(1)–W(2)	129.6(2)	Cl(6)–W(1)–Cl(1)	163.5(1)
Cl(6)–W(1)–Cl(2)	82.2(2)	Cl(6)–W(1)–Cl(3)	93.0(2)
Cl(6)–W(1)–Cl(4)	84.8(2)	O(1)–W(1)–W(2)	100.2(3)
O(1)–W(1)–Cl(1)	90.0(3)	O(1)–W(1)–Cl(2)	90.2(3)
O(1)–W(1)–Cl(3)	157.3(2)	O(1)–W(1)–Cl(4)	102.4(3)
O(1)–W(1)–Cl(6)	104.0(3)	Cl(1)–W(2)–W(1)	54.3(1)
Cl(2)–W(2)–W(1)	53.9(1)	Cl(2)–W(2)–Cl(1)	106.9(2)
Cl(3)–W(2)–W(1)	56.6(1)	Cl(3)–W(2)–Cl(1)	75.9(2)
Cl(3)–W(2)–Cl(2)	76.8(2)	Cl(5)–W(2)–W(1)	130.3(1)
Cl(5)–W(2)–Cl(1)	82.2(2)	Cl(5)–W(2)–Cl(2)	164.2(1)
Cl(5)–W(2)–Cl(3)	93.5(2)	Cl(7)–W(2)–W(1)	129.6(2)
Cl(7)–W(2)–Cl(1)	162.6(1)	Cl(7)–W(2)–Cl(2)	82.8(2)
Cl(7)–W(2)–Cl(3)	92.7(2)	Cl(7)–W(2)–Cl(5)	85.4(2)
O(2)–W(2)–W(1)	102.0(3)	O(2)–W(2)–Cl(1)	91.8(3)
O(2)–W(2)–Cl(2)	90.5(3)	O(2)–W(2)–Cl(3)	158.6(2)
O(2)–W(2)–Cl(5)	102.2(3)	O(2)–W(2)–Cl(7)	102.8(3)
W(2)–Cl(1)–W(1)	71.7(1)	W(2)–Cl(2)–W(1)	72.1(2)
W(2)–Cl(3)–W(1)	66.3(1)		

that in (**6**). A theoretical study of the bonding in M_2L_9 complexes has been published[19] and supports a delocalised bonding scheme involving the bridging atoms in this type of compound. The two metal electrons in the confacial bioctahedral complexes (**4**)—(**6**) therefore probably reside in a molecular orbital derived from the tungsten and bridging chlorine atomic orbitals.

We used the same type of reduction reaction as used for the preparation of (**4**)—(**6**) in an attempt to synthesise a M_3X_{13}-type trinuclear tungsten(V) anion $[W_3Cl_{10}(NPh)_3]^-$ but could only isolate the binuclear anion (**5**) from the product.

Experimental

All manipulations were carried out under dry, oxygen-free nitrogen using standard Schlenk techniques. Hydrocarbon solvents were distilled from sodium–benzophenone. Chlorinated solvents were dried over and distilled from P_4O_{10}. The preparations of $[\{WCl_4(NEt)\}_2]$[1] and $[\{WCl_2(NBu^t)(\mu\text{-NR})(NH_2Bu^t)\}_2]$ (R = NPh or C_6H_4Me-*p*)[9] have been described previously. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer PE577 spectrometer, n.m.r. spectra on Bruker WP-80 and WH-400 spectrometers. Elemental analyses were carried out by the University College Microanalytical Department.

t-Butylammonium μ_3-*Chloro-hexachloro-tris*(μ-*phenylimido*)-*tris*(*t-butylimido*)*tritungstate*(VI) (**3**).—A stirred suspension of $[WCl_4(NPh)]$ (6.5 mg, 15.6 mmol) in toluene (40 cm^3) was treated with a solution of $SiMe_3(NHBu^t)$ (4.8 g, 31.2 mmol) in toluene (20 cm^3). After 17 h a yellow precipitate was present in a red-orange solution. The mixture was heated until all the solid had dissolved and then allowed to cool to yield a yellow crystalline precipitate, $[\{W_2Cl_4(NBu^t)_2(\mu\text{-NPh})_2(NH_2Bu^t)_2\}]$, which was filtered off. The filtrate was evaporated to dryness under reduced pressure and the residue recrystallised from chloroform–hexane to yield orange crystalline $[NH_3Bu^t][W_3Cl_7(NBu^t)_3(\mu\text{-NPh})_3]\cdot xNH_3Bu^tCl$ ($x \approx 3$). I.r.: 3 315br m,

Table 6. Crystal data and details of structure analysis for compounds (**1**) and (**3**)—(**6**)

Compound	(1)	(3)	(4)	(5)	(6)
Crystal data					
M	737.46	1 638.80	1 055.43	1 151.52	1 001.29
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
a/Å	7.803(4)	20.203(6)	8.737(2)	9.865(10)	12.020(2)
b/Å	7.912(1)	14.349(3)	14.980(3)	16.370(3)	17.141(4)
c/Å	8.000(2)	23.106(4)	15.552(3)	13.658(2)	15.419(3)
α/°	83.32(2)	90.00	73.59(2)	111.63(1)	90.00
β/°	109.17(3)	110.88(2)	80.65(2)	93.90(5)	104.88(2)
γ/°	67.68(3)	90.00	84.61(1)	99.56(5)	90.00
U/Å^3	414.8	6 258.6	1 924.2	2 001.7	3 070.4
Space group	$P\bar{1}$	$P2_1/a$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Z	1	4	2	2	4
D_c/g cm^{-3}	2.953	1.739	1.821	1.910	2.166
μ/cm^{-1}	144.87	56.03	62.35	59.98	78.14
F(000)	332	3 168	1 004	1 100	1 880
Data collection					
$\theta_{min.}$, $\theta_{max.}$/°	1.5, 25	1.5, 25	1.5, 22	1.5, 22	1.5, 25
Total data	1 459	11 766	4 701	4 909	5 805
Total unique	1 459	10 994	4 701	4 909	5 394
Total observed [$F_o > 3\sigma(F_o)$]	1 375	7 987	3 857	4 452	4 210
Refinement					
No. of parameters	82	723	433	559	403
Weighting scheme coefficient g	0.000 05	0.005	—	0.0003	0.0005
Final R	0.0407	0.0374	0.0412	0.0409	0.0313
Final R'	0.0399	0.0376	0.0412	0.0436	0.0298

$R = \Sigma||F_o - F_c||/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$.

Table 7. Fractional atomic co-ordinates (× 10^4) for complex (**1**)

Atom	x	y	z
W(1)	2 393(1)	978(1)	2 756(1)
Cl(1)	3 484(5)	795(4)	6 017(4)
Cl(2)	2 832(5)	−2 097(4)	3 571(5)
Cl(3)	2 876(5)	3 678(5)	2 398(4)
Cl(4)	2 334(6)	725(6)	−69(4)
N(1)	−102(16)	2 095(14)	2 273(14)
C(1)	−2 206(21)	3 127(21)	1 933(21)
C(2)	−2 587(27)	4 924(24)	2 606(26)

2 811w, 2 713w, 2 604m, 2 506w, 2 082w, 1 607w, 1 584m, 1 579 (sh), 1 510m, 1484m, 1 405m, 1 363m, 1 302w, 1 260s, 1 219m, 1 200m, 1 168w, 1 070w, 1 024w, 910w, 861w, 788s, 716w, 693m, 587w, 558w, 517w, 489m, 452m, 348w, 333m, 304m, and 280w cm^{-1}. δ_H(400 MHz, $CDCl_3$) 8.06 (13 H, s br, $Bu^tNH_3^+$), 7.63, 7.41, 6.94 (5 H, m, NC_6H_5), 1.54 (38 H, s, $Bu^tNH_3^+$), and 0.58 (9 H, s, Bu^tN). δ_C(100 MHz, $CDCl_3$) 171.18 (*ipso*-C_6H_5N), 127.70, 127.50 (*o*- or *m*-C_6H_5N), 124.93 (*p*-C_6H_5N), 121.94, 119.37 (*o*- or *m*-C_6H_5N), 73.26 [$NC(CH_3)_3$], 53.45 [$H_3NC(CH_3)_3$], 28.16 and 27.89 p.p.m. [$C(CH_3)_3$].

A sample was treated with a slight excess of $[NEt_4]Cl$ and recrystallised from toluene to give $[NEt_4][W_3Cl_7(NBu^t)_3(\mu\text{-}NPh)_3]\cdot C_7H_8$ {Found: C, 35.2; H, 4.5; Cl, 16.5; N, 6.5. $[NEt_4][W_3Cl_7(NBu^t)_3(NPh)_3]\cdot C_7H_8$ requires C, 35.8; H, 4.7; Cl, 16.45; N, 6.5%}. I.r.: 1 582m, 1 577w, 1 365m, 1 302w, 1 258s, 1 216w, 1 198m, 1 168w, 1 067w, 1 025w, 998w, 973w, 907w, 865w, 859w, 789w, 735w, 728w, 712w, 695m, 586w, 555w, 576w, 489m, 331m, 304m, and 281w cm^{-1}.

Benzyltriphenylphosphonium μ_3-*Chloro-hexachlorotris*(μ-*phenylimido*)*tris*(*t-butylimido*)*tritungstate*(VI) (**3**).—A mixture of $[\{WCl_2(NBu^t)(\mu\text{-}NPh)(NH_2Bu^t)\}_2]$ (0.51 g, 0.52 mmol) and $[P(CH_2Ph)Ph_3]Cl$ (0.13 g, 0.35 mmol) in toluene (7 cm^3) was heated under reflux for 1 h and allowed to cool. The orange solution was filtered and solvent removed under reduced pressure. The residue was recrystallised from dichloromethane–hexane to give crystals suitable for an *X*-ray crystal structure determination.

Benzyltriphenylphosphonium Tri-μ-*chloro-tetrachlorobis*(*ethylimido*)*ditungstate*(V) (**4**).—$[\{WCl_4(NEt)\}_2]$ (1.56 g, 2.12 mmol) was added to sodium amalgam (0.3%, 4.13 mmol) and $[P(CH_2Ph)Ph_3]Cl$ (0.8 g, 2.05 mmol) in CH_2Cl_2 (40 cm^3) with vigorous stirring. After 15 h the green suspension was filtered and the residue washed with CH_2Cl_2 (15 cm^3). The solvent was removed from the green solution under reduced pressure to give a green, glassy residue. This was dissolved in CH_2Cl_2 (10 cm^3) and hexane added gradually with swirling. After addition of hexane (20 cm^3), the solvent was removed to give a green crystalline product. Yield 1.67 g, 75% {Found: C, 31.9; H, 3.1; Cl, 25.5; N, 2.5. $[P(CH_2Ph)Ph_3][W_2Cl_7(NEt)_2]$ requires C, 33.0; H, 3.1; Cl, 23.5; N, 2.7%}. I.r.: 1 601w, 1 589w, 1 402w, 1 341w, 1 322w, 1 295s, 1 267w, 1 244w, 1 190w, 1 165w, 1 145w, 1 110s, 1 072w, 1 030w, 998m, 972w, 926w, 837m, 792m, 759m, 752s, 747s, 725s, 707m, 620w br, 609s, 585m, 515s, 509s, 498s, 452w, 440w, 390w, 344s, 327s, 296w, 270w, and 255w cm^{-1}. δ_H(400 MHz, CD_2Cl_2) 7.77 (3 H, t), 7.62 (6 H, br s), 7.41 (6 H, dd), 7.26 (1 H, t), 7.15 (2 H, t), 6.85 (2 H, d) (C_6H_5), 4.42 [2 H, d, ^2J(PH) 14 Hz, CH_2Ph], 4.18 [2 H, q, ^3J(HH) 7 Hz, ^3J(WH) 10 Hz, NCH_2Me], and 1.23 [3 H, t, ^3J(HH) 7 Hz, NCH_2CH_3].

Benzyltriphenylphosphonium Tri-μ-*chloro-tetrachlorobis*(*phenylimido*)*ditungstate*(V) (**5**).—The complex $[WCl_4(NPh)(OEt_2)]$ (1.83 g, 3.73 mmol) was added to CH_2Cl_2 (35 cm^3) over sodium amalgam (0.4%, 3.91 mmol) with stirring; $[P(CH_2Ph)Ph_3]Cl$ (0.5 g, 1.29 mmol) was added and the mixture stirred vigorously for 1.5 h. The yellow-brown solution

Table 8. Fractional atomic co-ordinates (× 10^4) for complex (**3**)

Atom	x	y	z	Atom	x	y	z
W(1)	−556(0.5)	1 370(0.5)	7 238(0.5)	N(5)	−994(3)	−1 794(4)	6 577(3)
W(2)	−648(0.5)	−1 058(0.5)	7 190(0.5)	C(51)	−1 336(4)	−2 536(6)	6 146(4)
W(3)	998(0.5)	47(0.5)	7 745(0.5)	C(52)	−2 085(6)	−2 591(9)	6 139(7)
Cl(1)	−97(1)	106(1)	8 121(1)	C(53)	−1 345(7)	−2 284(10)	5 505(5)
Cl(2)	−1 625(1)	1 421(2)	7 486(1)	C(54)	−911(8)	−3 410(8)	6 396(7)
Cl(3)	−115(1)	2 448(2)	8 073(1)	N(6)	1 676(4)	18(5)	7 473(3)
Cl(4)	−1 658(1)	−1 077(2)	7 505(1)	C(61)	2 365(5)	0(8)	7 401(5)
Cl(5)	−201(1)	−2 252(2)	7 955(1)	C(62)	2 708(6)	962(12)	7 618(6)
Cl(6)	1 548(1)	1 161(2)	8 561(1)	C(63)	2 251(5)	−102(8)	6 717(5)
Cl(7)	1 448(1)	−1 120(2)	8 520(1)	C(64)	2 757(7)	−858(12)	7 740(7)
N(1)	−939(3)	170(4)	6 783(3)	P	3 089(1)	3 656(2)	9 422(1)
C(11)	−1 450(4)	212(5)	6 166(3)	C(71)	3 609(4)	4 687(2)	9 573(4)
C(12)	−2 140(5)	104(7)	6 059(5)	C(72)	3 831(5)	5 084(6)	10 167(4)
C(13)	−2 628(6)	129(7)	5 416(7)	C(73)	4 268(5)	5 853(6)	10 282(4)
C(14)	−2 403(9)	227(8)	4 933(5)	C(74)	4 503(5)	6 198(6)	9 837(5)
C(15)	−1 718(7)	357(10)	5 048(5)	C(75)	4 296(5)	5 826(7)	9 260(5)
C(16)	−1 235(6)	368(9)	5 673(5)	C(76)	3 853(5)	5 062(7)	9 127(4)
N(2)	358(3)	−881(5)	7 192(3)	C(81)	3 677(4)	2 682(6)	9 608(4)
C(21)	591(4)	−1 457(6)	6 786(4)	C(82)	3 999(5)	2 421(7)	10 234(5)
C(22)	1 039(7)	−2 143(9)	7 009(5)	C(83)	4 504(6)	1 722(7)	10 398(6)
C(23)	1 259(9)	−2 704(13)	6 627(7)	C(84)	4 682(6)	1 293(7)	9 937(7)
C(24)	1 079(7)	−2 531(10)	6 037(7)	C(85)	4 392(6)	1 563(8)	9 330(6)
C(25)	631(6)	−1 810(8)	5 793(5)	C(86)	3 872(5)	2 251(7)	9 161(5)
C(26)	387(7)	−1 270(7)	6 164(5)	C(91)	2 537(4)	3 606(7)	9 888(4)
N(3)	418(3)	1 116(4)	7 248(3)	C(92)	2 248(5)	4 428(9)	10 015(5)
C(31)	727(4)	1 684(6)	6 895(4)	C(93)	1 794(6)	4 369(12)	10 349(5)
C(32)	729(6)	1 411(7)	6 335(5)	C(94)	1 653(6)	3 503(15)	10 536(6)
C(33)	1 021(7)	1 964(9)	5 999(6)	C(95)	1 936(6)	2 710(10)	10 414(5)
C(34)	1 317(6)	2 767(10)	6 222(6)	C(96)	2 370(5)	2 747(8)	10 074(5)
C(35)	1 327(9)	3 036(12)	6 786(7)	C(100)	2 513(5)	3 569(8)	8 620(5)
C(36)	1 014(7)	2 520(9)	7 110(5)	C(101)	1 947(5)	4 297(7)	8 447(4)
N(4)	−826(3)	2 174(4)	6 659(3)	C(102)	2 065(7)	5 212(10)	8 307(6)
C(41)	−1 124(5)	2 941(6)	6 227(4)	C(103)	1 531(10)	5 861(11)	8 183(9)
C(42)	−1 920(5)	2 884(8)	6 046(6)	C(104)	901(12)	5 636(16)	8 220(9)
C(43)	−875(8)	2 887(9)	5 683(6)	C(105)	767(6)	4 746(11)	8 340(6)
C(44)	−844(6)	3 836(7)	6 635(6)	C(106)	1 300(5)	4 091(7)	8 488(4)

Table 9. Fractional atomic co-ordinates (× 10^4) for complex (**4**)

Atom	x	y	z	Atom	x	y	z
W(1)	5 520(1)	2 466(0.5)	2 444(0.5)	C(14)	6 884(19)	4 294(11)	5 026(12)
W(2)	3 918(1)	4 241(0.5)	2 068(0.5)	C(15)	6 378(16)	3 501(10)	5 682(10)
Cl(1)	4 822(5)	3 360(3)	981(2)	C(20)	4 762(17)	1 220(10)	6 411(11)
Cl(2)	5 189(5)	3 520(3)	3 391(2)	C(21)	3 412(17)	1 938(10)	6 427(10)
Cl(3)	2 533(4)	2 697(2)	2 767(3)	C(22)	3 053(18)	2 527(11)	5 615(12)
Cl(4)	5 583(4)	1 308(3)	3 858(3)	C(23)	1 852(27)	3 171(16)	5 615(22)
Cl(5)	5 348(6)	1 170(3)	1 866(3)	C(24)	978(25)	3 244(16)	6 410(30)
Cl(6)	2 023(6)	4 858(3)	1 100(3)	C(25)	1 326(24)	2 697(19)	7 188(21)
Cl(7)	2 264(6)	4 946(3)	3 092(3)	C(26)	2 526(19)	2 036(14)	7 219(13)
N(1)	7 428(12)	2 685(9)	2 098(8)	C(30)	8 013(15)	690(9)	6 464(9)
C(1)	8 971(22)	2 966(16)	1 749(14)	C(31)	7 806(18)	8(10)	6 073(10)
C(2)	9 255(28)	3 194(21)	760(18)	C(32)	8 951(19)	−676(10)	6 001(11)
N(2)	5 309(16)	5 013(8)	1 619(9)	C(33)	10 306(21)	−696(12)	6 377(12)
C(3)	6 596(24)	5 593(15)	1 220(13)	C(34)	10 552(19)	−9(13)	6 718(13)
C(4)	7 485(40)	5 654(27)	1 793(23)	C(35)	9 419(19)	695(12)	6 796(13)
P	6 581(4)	1 597(2)	6 543(2)	C(40)	6 508(15)	1 797(9)	7 627(9)
C(10)	7 130(15)	2 623(9)	5 679(9)	C(41)	7 048(19)	2 577(11)	7 741(11)
C(11)	8 349(17)	2 545(11)	4 989(10)	C(42)	7 072(21)	2 685(11)	8 607(11)
C(12)	8 814(19)	3 340(12)	4 320(11)	C(43)	6 506(22)	2 000(13)	9 360(12)
C(13)	8 104(21)	4 211(12)	4 332(11)	C(44)	5 941(25)	1 229(14)	9 267(12)
				C(45)	5 950(21)	1 101(11)	8 399(11)

was filtered and evaporated under reduced pressure to give a crystalline solid. Recrystallisation from dichloromethane–hexane gave green needles (1.20 g, 56%) {Found: C, 38.5; H, 2.8; Cl, 19.8; N, 2.25. $[P(CH_2Ph)Ph_3][W_2Cl_7(NPh)_2]$ requires C, 38.6; H, 2.8; Cl, 21.6; N, 2.4%. I.r.: 1 600w, 1 588w, 1 357w, 1 315w, 1 288w, 1 265w, 1 190w, 1 162w, 1 111s, 1 068w, 1 029m, 1 015w, 997m, 975w br, 925w, 911w, 850w, 839m, 787mm, 763s, 755s, 748 (sh), 725m, 720m, 703m, 686s, 620w, 581m, 552w, 537w, 515s, 499m, 475w, 452w, 391w, 388w, 345s, 337s, 301w, 265w, and 254w cm^{-1}.

Table 10. Fractional atomic co-ordinates (× 10^4) for complex (**5**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	3 015(0.5)	2 804(0.5)	1 660(0.5)	P	2 291(2)	6 900(1)	2 539(2)
W(2)	2 910(0.5)	2 632(0.5)	3 645(0.5)	C(31)	1 585(8)	7 895(5)	2 839(6)
Cl(1)	1 257(2)	3 402(2)	2 911(2)	C(32)	1 668(12)	8 480(7)	3 895(8)
Cl(2)	4 526(2)	3 751(1)	3 295(2)	C(33)	1 205(13)	9 265(7)	4 126(9)
Cl(3)	1 873(2)	1 472(2)	1 912(2)	C(34)	731(10)	9 506(7)	3 339(10)
Cl(4)	3 241(2)	3 764(2)	5 367(2)	C(35)	689(11)	8 950(7)	2 290(9)
Cl(5)	1 061(2)	1 917(2)	4 254(2)	C(36)	1 119(10)	8 148(6)	2 037(8)
Cl(6)	3 488(3)	4 131(2)	1 301(2)	C(41)	4 102(8)	7 198(5)	2 451(6)
Cl(7)	1 266(3)	2 288(2)	172(2)	C(42)	4 557(11)	7 069(8)	1 485(8)
N(1)	4 132(7)	2 020(4)	3 726(5)	C(43)	5 965(11)	7 353(8)	1 460(10)
C(11)	5 048(9)	1 440(6)	3 577(7)	C(44)	6 891(11)	7 739(8)	2 347(10)
C(12)	4 557(13)	567(8)	3 469(12)	C(45)	6 432(10)	7 887(6)	3 318(9)
C(13)	5 417(18)	−30(9)	3 262(14)	C(46)	5 050(9)	7 622(7)	3 374(8)
C(14)	6 769(17)	210(10)	3 177(12)	C(51)	2 083(8)	6 488(5)	3 570(6)
C(15)	7 280(13)	1 059(12)	3 319(11)	C(52)	3 051(9)	6 033(5)	3 816(7)
C(16)	6 444(10)	1 712(8)	3 539(10)	C(53)	2 871(9)	5 674(6)	4 555(7)
N(2)	4 321(7)	2 280(5)	1 101(5)	C(54)	1 695(11)	5 748(7)	5 070(8)
C(21)	5 408(9)	1 863(6)	744(7)	C(55)	707(11)	6 168(6)	4 805(8)
C(22)	5 184(16)	1 108(9)	−166(10)	C(56)	908(10)	6 531(7)	4 067(8)
C(23)	6 297(21)	703(12)	−524(14)	C(61)	1 425(9)	6 035(6)	1 265(7)
C(24)	7 545(22)	1 018(14)	75(18)	C(62)	5(8)	5 564(5)	1 366(6)
C(25)	7 752(14)	1 746(14)	986(18)	C(63)	−1 171(9)	5 858(6)	1 200(8)
C(26)	6 710(12)	2 176(9)	1 319(12)	C(64)	−2 446(11)	5 399(8)	1 310(10)
				C(65)	−2 515(11)	4 685(8)	1 612(10)
				C(66)	−1 319(11)	4 392(8)	1 765(10)
				C(67)	−72(11)	4 819(7)	1 631(9)

Table 11. Fractional atomic co-ordinates (× 10^4) for complex (**6**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	2 061(0.5)	1 713(0.5)	4 498(0.5)	C(7)	3 152(7)	1 491(4)	1 763(6)
W(2)	4 418(0.5)	1 948(0.5)	5 409(0.5)	C(8)	2 703(6)	750(4)	1 273(5)
Cl(1)	3 463(1)	2 447(1)	3 931(1)	C(9)	1 841(7)	765(5)	501(6)
Cl(2)	2 923(2)	1 482(1)	6 074(1)	C(10)	1 478(9)	83(6)	23(7)
Cl(3)	3 657(2)	698(1)	4 473(1)	C(11)	2 010(10)	−621(5)	338(7)
Cl(4)	1 146(2)	1 557(1)	2 984(1)	C(12)	2 837(10)	−632(5)	1 119(7)
Cl(5)	6 040(2)	2 056(1)	4 846(2)	C(13)	3 194(8)	35(4)	1 595(7)
Cl(6)	787(2)	767(1)	4 723(2)	C(14)	6 606(9)	1 294(5)	1 677(6)
Cl(7)	5 598(2)	1 231(2)	6 564(2)	C(15)	7 588(8)	917(5)	2 118(7)
O(1)	1 493(5)	2 551(3)	4 749(4)	C(16)	7 667(8)	568(5)	2 925(6)
O(2)	4 384(5)	2 822(3)	5 877(4)	C(17)	6 762(9)	608(5)	3 305(6)
P	4 416(2)	1 880(1)	1 502(1)	C(18)	5 763(8)	987(4)	2 878(5)
C(1)	4 593(6)	2 869(4)	1 914(4)	C(19)	5 672(6)	1 324(4)	2 039(5)
C(2)	5 631(7)	3 113(4)	2 426(6)	C(20)	4 227(6)	1 842(4)	316(5)
C(3)	5 751(8)	3 877(5)	2 748(7)	C(21)	4 314(7)	1 126(5)	−92(5)
C(4)	4 834(8)	4 367(5)	2 548(7)	C(22)	4 165(9)	1 068(7)	−996(7)
C(5)	3 799(7)	4 128(4)	2 028(7)	C(23)	3 923(9)	1 733(8)	−1 508(7)
C(6)	3 667(6)	3 375(4)	1 717(6)	C(24)	3 807(8)	2 450(6)	−1 145(7)
				C(25)	3 956(7)	2 502(5)	−200(6)

Benzyltriphenylphosphonium Tri-µ-chloro-tetrachlorodioxoditungstate(V) (**6**).—The compound $WOCl_4$ (1.47 g, 4.30 mmol) was added to a solution of $[P(CH_2Ph)Ph_3]Cl$ (0.84 g, 2.16 mmol) in CH_2Cl_2 (40 cm^3) over sodium amalgam (0.3%, 4.35 mmol) with vigorous stirring. The solution turned from orange to green and after 17 h the reaction mixture was filtered and the solvent removed under reduced pressure. Trituration of the greenish yellow oily residue with hexane gave a green solid, which was filtered off and pumped dry (1.52 g, 70%). Recrystallisation by slow diffusion of a hexane layer into a dichloromethane solution gave large, dark brown-green crystals {Found: C, 28.7; H, 2.1; Cl, 23.7. $[P(CH_2Ph)Ph_3][W_2O_2Cl_7]$ requires C, 30.0; H, 2.2; Cl, 24.7%}. I.r.: 1 603w, 1 589w, 1 397w, 1 340w, 1 188w, 1 165w, 1 112s, 1 071w, 1 029w, 998s, 993s, 972w, 924w, 855w, 830m, 787m, 756m, 748s, 731 (sh), 724m, 719 (sh), 701s, 687s, 603w, 583m, 517s, 506s, 494m, 471w, 450w, 444w, 370w, 356s, 350 (sh), 321w, 270w, and 255w br cm^{-1}.

X-Ray Crystallography.—Crystals of all complexes studied were sealed under argon in thin-walled glass capillaries. All *X*-ray measurements were made at room temperature using a Nonius CAD4 diffractometer and graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) following previously detailed procedures.[20] Intensity data were corrected for absorption on the basis of psi-scan data[21] and subsequently using the DIFABS program.[22] Crystal data and collection details are given in Table 6. The structures were solved *via* standard heavy-atom procedures and refined by full-matrix least squares, with non-hydrogen atoms anisotropic and idealised hydrogen (AFIX in SHELX[23]) isotropic. The weighting scheme $w = 1/[\sigma^2(F_o) + g(F_o)^2]$ was introduced into the final stages of the refinements, with the parameter g being adjusted so as to give reasonably flat agreement analyses. However, for the $[W_2Cl_7(NEt)]^-$ complex unit weights were used. Refinement details are given in Table 6. Lists of atomic fractional co-ordinates are given in Tables 7—11. All calculations were made on a DEC VAX 11/750 computer. Atomic scattering factor data were taken from ref. 24.

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

Acknowledgements

We thank the S.E.R.C. for support. We are also grateful to the University of London Intercollegiate Research Service high-field n.m.r. service at Queen Mary College (Dr. G. E. Hawkes) and Mr. G. Coumbarides for recording n.m.r. spectra.

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Received 1*st September* 1989; *Paper* 9/03739J