Tertiary Phosphine Complexes of Triply Bonded Ditungsten Bis(t-butylamide) Tetrachloride. The *X*-Ray Crystal Structures of $[W_2Cl_4(NHBu^t)_2(PMe_3)_2]$, $[W_2Cl_4(NHBu^t)_2(PEt_3)_2]$ and *cis*-$[W_2Cl_4(NHBu^t)_2(PMe_2Ph)_2]$†

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The t-butylamine ligands in $[W_2Cl_4(NHBu^t)_2(NH_2Bu^t)_2]$ (**1**) have been replaced by trialkylphosphines giving the new complexes $[W_2Cl_4(NHBu^t)_2(PMe_3)_2]$ (**2**), $[W_2Cl_4(NHBu^t)_2(PEt_3)_2]$ (**3**), and the isomeric $[W_2Cl_4(NHBu^t)_2(PMe_2Ph)_2]$ (**4a**) and (**4b**). *X*-Ray crystal structures showed that (**2**) and (**3**) have phosphines *trans* to the t-butylamides and short W–N bond lengths (1.76—1.81 Å). Compound (**4**) appears to form isomers one of which, (**4a**), was shown to have phosphines *cis* to the t-butylamides and a normal W–N bond length (1.92 Å).

Recently[1] we reported the synthesis, characterization, and *X*-ray crystal structure of tetrachlorobis(t-butylamido)bis(t-butylamine)ditungsten(III) (3*W*–*W*), $[W_2Cl_4(NHBu^t)_2(NH_2Bu^t)_2]$ (**1**). In compound (**1**) each tungsten is approximately square planar with *trans* chlorines and *trans* NBu^t groups and the two WCl_2N_2 units are eclipsed with nitrogens opposite chlorines allowing intramolecular hydrogen bonding N–H ··· Cl which is manifest in the NH_2 protons giving an AB ^1H n.m.r. spectrum. Further work has shown that the co-ordinated t-butylamines in (**1**) can be replaced by trialkylphosphines giving the new compounds $[W_2Cl_4(NHBu^t)_2(PMe_3)_2]$ (**2**), $[W_2Cl_4(NHBu^t)_2(PEt_3)_2]$ (**3**), and the isomeric mixture of *cis*- and *trans*-$[W_2Cl_4(NHBu^t)_2(PMe_2Ph)_2]$ (**4a**) and (**4b**).

Results and Discussion

The compounds were prepared by adding the appropriate phosphine to a concentrated solution of (**1**) in n-pentane or n-hexane at room temperature. In the cases of trimethylphosphine and triethylphosphine the products (**2**) and (**3**) were quantitatively precipitated in less than 5 min. With dimethylphenylphosphine the reaction was slower and the n.m.r. spectrum revealed that two compounds (**4a**) and (**4b**) had been formed in approximately 1:5 molar ratio respectively. Neither triphenylphosphine nor diphenylphosphinoethane afforded substitution products although some darkening of the solution of (**1**) was observed. The ^1H n.m.r. spectra of compounds (**2**), (**3**), (**4a**), and (**4b**) all showed that the t-butylamine in (**1**) had been completely replaced but the covalently bound t-butylamide ligands remained (δ 11.87—12.20). It was not possible to isolate both isomers (**4a**) and (**4b**) in a high state of purity and only the minor component (**4a**) was obtained as single crystals.

All of the compounds (**2**), (**3**), (**4a**), and (**4b**) were bright red solids which were moderately stable in moist air for several weeks. However, in solution they were rapidly hydrolyzed.

The *X*-ray crystal structure determinations of (**2**) and (**3**) (Figures 1 and 2) revealed a number of interesting features. The solution of both structures was complicated by the fact that the central ditungsten units were disordered between two orientations in each case. This is a relatively common phenomenon occurring in metal dimer species with eight co-ordinating atoms arranged in a cuboid.[2] The most recent report of this showed that the disorder gave rise to two chemically distinct species from the compound $[Mo_2Cl_4(dppe)_2]$, with dppe $(Ph_2PCH_2CH_2PPh_2)$ either bridging the quadruple bond or chelating each molybdenum.[3] In the current case, the disordered tungsten dimers are enantiomeric. In both species the nitrogen and phosphorus atoms on the same tungsten atom

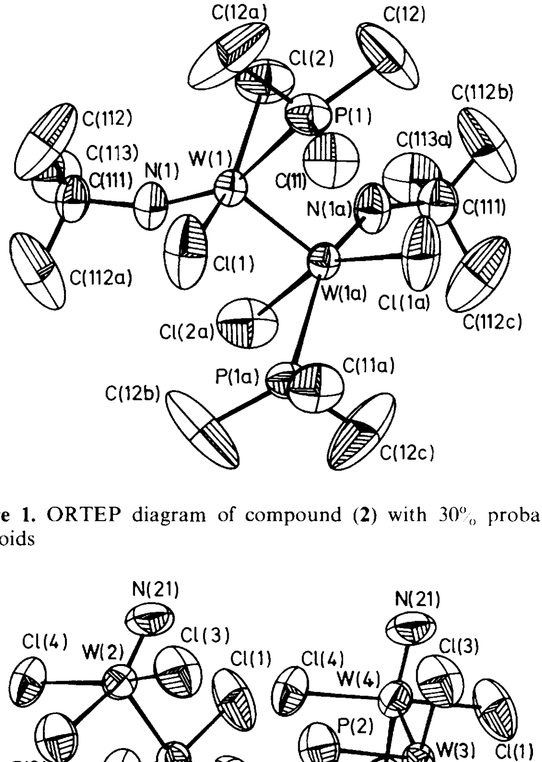

Figure 1. ORTEP diagram of compound (**2**) with 30% probability ellipsoids

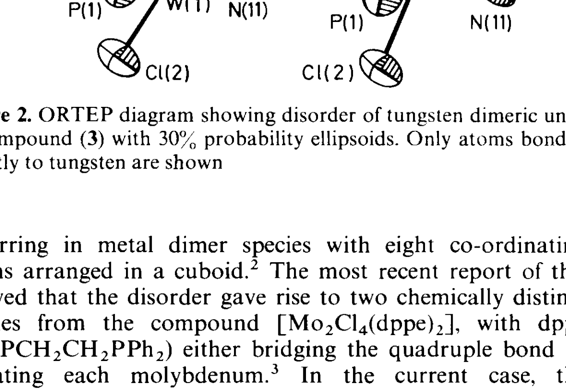

Figure 2. ORTEP diagram showing disorder of tungsten dimeric units in compound (**3**) with 30% probability ellipsoids. Only atoms bonded directly to tungsten are shown

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† 1,1,2,2-Tetrachloro-1,2-bis(t-butylamido)-1,2-bis(trimethylphosphine)-1,2-bis(triethylphosphine)- and (*cis*)-1,2-bis(dimethylphenylphosphine)-ditungsten(III) (3*W*–*W*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Crystal data, details of intensity measurements, and structure refinements for $[W_2Cl_4(NHBu^t)_2(PMe_3)_2]$ (**2**), $[W_2Cl_4(NHBu^t)_2(PEt_3)_2]$ (**3**), and *cis*-$[W_2Cl_4(NHBu^t)_2(PMe_2Ph)_2]$ (**4a**)

Complex	(**2**)	(**3**)	(**4a**)
Formula	$C_{14}H_{36}Cl_4N_2P_2W_2$	$C_{20}H_{50}Cl_4N_2P_2W_2$	$C_{22}H_{42}Cl_4N_2P_2W_2$
M	803.99	890.16	928.12
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
a/Å	13.131 5(20)	22.448 4(42)	17.690 7(51)
b/Å	11.890 5(14)	11.369 5(33)	16.640 9(90)
c/Å	8.764 0(12)	12.924 0(18)	11.318 8(76)
β/°		95.786 5(133)	
U/Å^3	1 368.41	3 281.75	3 329.14
Space group	$Pmmn$	$P2_1/a$	$Pna2_1$
D_c/g cm^{-3}	1.951	1.801	1.851
Z	2	4	4
F(000)	760	1 720	1 736
μ/cm^{-1}	90.943	75.93	74.893
$\theta_{min.,max.}$/°	1.5, 25.0	1.5, 23.0	1.5, 25.0
T/K	293	293	293
Total data	1 328	4 584	3 317
Total unique data	1 328	4 584	3 090
Total observed data [$F > 3\sigma(F)$]	809	2 676	2 446
No. of parameters	67	191	306
Parameter g in $w = 1/[\sigma^2(F_0) + gF_o^2]$	0.000 01	Unit weights	0.002
R	0.0531	0.077	0.039 2
R'	0.0456		0.037 5

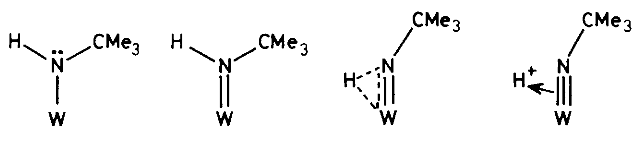

Figure 3. Possible modes of bonding of WNBu^t (*cf.* ref. 11)

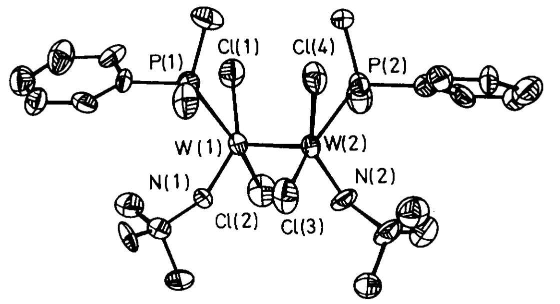

Figure 4. ORTEP diagram of compound (**4a**) with 50% probability ellipsoids

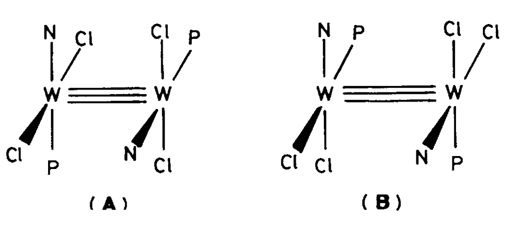

Figure 5. Co-ordination geometry of (**A**) [compounds (**2**) and (**3**)] and (**B**) [(**4a**)]

are *trans*, as are also the chlorides. As in (**1**) the two ends of the molecules are eclipsed, presumably due to the retention of hydrogen bonding between the alkylamide N-protons and the chlorides opposite: there is no metal–metal δ-bonding requirement for this conformation.[2] Support for this comes from the larger dihedral angles between the chloride and phosphorus atoms, as there can be no hydrogen bonding between these.

The W–W bond lengths are of comparable magnitude to those reported for other tungsten(III,III) dimers,[4,5] although slightly longer than in (**1**). This may be due to the π-acceptor ability of PR_3 groups allowing withdrawal of electron density from the metal–metal π-bonding orbitals.

Perhaps the most notable features of these compounds are the unexpectedly short W–N distances, which in no case are greater than 1.82 Å, only 0.04 Å longer than a W–N triple bond.[6,7] A normal W–N bond length for an alkylamido compound is *ca.* 1.92 Å, which has been found for a number of compounds.[8] In addition, the W–N–C angles in the t-butylamide ligands are unexpectedly large (143—147°) being closer to linear than expected for an sp^2-hybridized N atom. We consider this to be analogous to Schrock's alkylidene/alkylidyne systems[9–11] (Figure 3). The alkylamide N-proton is still evident in the ^1H n.m.r. spectral data and the nitrogen lone pair and the nitrogen–hydrogen bonding pair of electrons are presumably both involved in a three-centre six-electron bond, with the greatest bonding interactions between the tungsten and nitrogen atoms. In the limiting case this could be considered as a protonated tungsten–nitrogen triple bond. In either event, the reduced electron density about the proton would allow a strong interaction with the electron-rich chloride at the other end of the W–W bond. Metal alkylidene/alkylidynes which have a large degree of metal–carbon triple bonding show a large shift (*i.e.* several hundred cm^{-1}) to low frequency in the i.r. spectra of the C–H stretching mode due to semi-bridging hydrogen atoms.[9b] In the present cases only modest shifts from the N–H stretches in the parent compound (**1**) are recorded; (**1**) has three absorptions due to ν(N–H) (3 305w, 3 240w, and 3 202m cm^{-1}). This compares with (**2**) (3 200m, 3 152w), (**3**) (3 195m, 3 160m), (**4a**) (3 170w, 3 150w, 3 050w), and (**4b**) (3 195m, 3 162w, and 3 145m cm^{-1}). These significant deviations from (**1**) highlight the different environments of the N–H groups in these compounds.

The structure of (**4a**) (Figure 4) showed that this was the isomer of $[W_2Cl_4(NHBu^t)_2(PMe_2Ph)_2]$ with chlorides mutually *cis* on the same tungsten atom. Similarly, the alkylamides and phosphines were *cis*. This implies that either the amides or the phosphines would be *cis* across the triple bond. In the recently published example of $[W_2Cl_4(NMe_2)_2(PMe_2Ph)_2]$,[5] the dimethylamides were virtually *trans* and the phosphines *cis*. However, in (**4a**) a certain degree of N–H ··· Cl hydrogen bonding is retained and the stereochemistry of the molecule dictates that the phosphines are *cis*. The phenyl rings extend away from the molecule almost parallel to the W–W triple bond, and are mutually almost coplanar. The t-butyl groups of the alkylamides are located over the edge of the rings, so a shift upfield in their ^{1}H n.m.r. resonance would be expected relative to the t-butyls in the other isomer and in (**2**) and (**3**). In fact the t-butyl resonance is shifted 0.25 upfield from the equivalent resonance for the other, presumably *trans* isomer, and nearly 0.4 upfield from (**2**) and (**3**). Similarly, as the PMe protons are subjected to anisotropic diamagnetism from the phenyl rings and the metal–metal triple bond, their chemical shift might be expected to be more downfield than for (**2**) and this is realized in practice.

The W–N bond lengths in complex (**4a**) were normal for a tungsten alkylamide at 1.92 Å (see above): this is suggestive of the strong *trans* influence of the phosphines in (**2**) and (**3**) and is believed to be the first example of a *trans* influence in metal–metal bonded dimers. The W–N–C angles are correspondingly smaller than in (**2**) or (**3**) in agreement with more sp^2 character of the nitrogen. The W–Cl bond *trans* to the alkylamide is slightly shorter than that which is *cis*, while the W–P bonds are shorter than in (**2**) or (**3**). All the dihedral angles are somewhat larger than those found in the other compounds, perhaps due to the more covalent (and hence less polar) nature of the N–H bond, giving rise to decreased hydrogen bonding.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer in Nujol mulls, n.m.r. spectra on a Bruker WP80 or WH400 spectrometer (δ relative to $SiMe_4$, referenced to incompletely deuteriated C_6D_6 solvent peak). All manipulations were carried out under dry nitrogen. Solvents were dried, degassed, and distilled before use. None of the compounds gave satisfactory elemental analyses.

Table 2. Atomic fractional co-ordinates (× 10^4) for compound (**2**)

Atom	*x*	*y*	*z*
W(1)	1 799(0.5)	1 916(0.5)	2 379(0.5)
P(1)	2 500	363(6)	587(6)
C(11)	2 500	672(22)	−1 528(19)
C(12)	3 640(16)	−508(17)	888(19)
Cl(2)	2 500	561(6)	4 162(6)
Cl(1)	805(4)	2 500	154(5)
N(1)	907(12)	2 500	3 738(16)
C(111)	−133(15)	2 500	4 290(20)
C(112)	−671(14)	1 470(17)	3 696(17)
C(113)	−64(18)	2 500	6 070(20)

The method of prepration was similar for all three complexes. A typical procedure is outlined below.

1,1,2,2-*Tetrachloro*-1,2-*bis*(*t-butylamido*)-1,2-*bis*(*triethyl phosphine*)*ditungsten*(III). The compound $[W_2Cl_4(NHBu^t)_2(NH_2Bu^t)_2]$ (**1**)[1] (0.35 g, 0.44 mmol) was dissolved in the minimum quantity of n-pentane (*ca.* 15 cm^3). Triethylphosphine [0.20 cm^3, 0.16 g, 1.3(5) mmol] was added with stirring. The colour of the solution changed rapidly from orange to red, and a pink precipitate was formed. No further change was noticed after 10 min, when the solution was almost colourless (the reaction appeared to be faster in n-pentane than in n-hexane). The solvent, liberated t-butylamine, and excess of phosphine were removed *in vacuo*. The product (0.39 g, 100%) was shown to be essentially pure (**3**) by ^{1}H n.m.r. spectroscopy: δ 0.99 [9 H, dt, $^3J_{HH}$ 8.0, $^3J_{HP}$ 14.0], 1.34 (9 H, s), 2.18 [6 H, dq, $^3J_{HH}$ 8.0, $^3J_{HP}$ 8.0 Hz], and 12.20 (1 H, s, br). I.r. spectrum: 3 195m, 3 160m, 1 362s, 1 355m, 1 332w, 1 257m, 1 202s,br, 1 090m,br, 1 035s, 1 017m,br, 958m, 915w, 815 (sh), 801m,br, 784m, 762m, 748m, 724m, 648w, 562w, 550w, 485w, 315s,br, 305 (sh), 267w, and 245w cm^{-1}.

For (**2**), ^{1}H n.m.r.: δ 1.27 (9 H, s), 1.37 [9 H, d, $^2J_{HP}$ 8.0 Hz], and 11.87 (1 H, s, br). I.r. spectrum: 3 200m, 3 152w, 1 722w, 1 410m, 1 328m, 1 292m, 1 200s, 950s, 855m, 795vs, 395m, 385m, 370m, 355w, 348w, 340w, 330w, 312m, and 299m cm^{-1}.

Dimethylphenylphosphine reacted more slowly than the trialkylphospines, reaching completion after *ca.* 15 min in hexane with the formation of compounds (**4a**) and (**4b**) in the ratio of 1:5 respectively. For (**4a**), ^{1}H n.m.r.: δ 0.89 (9 H, s), 2.28 [3 H, d, $^2J_{HP}$ 9.5], 2.40 [3 H, d, $^2J_{HP}$ 10.7 Hz], 6.90 (5 H, m), and 12.20 (1 H, s, br). I.r. spectrum: 3 170w, 3 150w, 3 050w, 1 622w,vbr, 1 430m, 1 355m, 1 335w, 1 330w, 1 290m, 1 270w, 1 256m, 1 212m, 1 200m, 1 100m,vbr, 1 015s,br, 956w, 940m, 923m, 915s, 837w, 800m,vbr, 742s, 708w, 693m, 666w, 525w,br, 486m, 461w, 449w, 422w, 418w, 405w, 396w, 374w, and 302s cm^{-1}. For (**4b**), ^{1}H n.m.r.: δ 1.14 (9 H, s), 1.97 [3 H, d, $^2J_{HP}$ 9.4], 2.00 [3 H, d, $^2J_{HP}$ 8.6 Hz], and 11.93 (1 H, s, br). I.r. spectrum: 3 195m, 3 162w, 3 145m, 2 700w, 2 590w, 2 490w, 1 602w,br, 1 580vw, 1 505w, 1 502w, 1 480 (sh), 1 462m, 1 445 (sh), 1 427s, 1 410m, 1 398w, 1 360s, 1 352s, 1 330m, 1 287s, 1 270s, 958s, 912vs, 867m,br, 797(vs,br), 738s, 725 (sh), 715w, 703w, 692s, 670w, 485s, 460w, 446w, and 400s,br cm^{-1}.

Crystallography.—*X*-Ray quality crystals of compounds (**2**), (**3**), and (**4a**) were grown readily from hot hexane and mounted

Table 3. Atomic fractional co-ordinates (× 10^4) for compound (**3**)

Atom	*x*	*y*	*z*
W(1)	8 750(0.5)	1 921(0.5)	3 190(0.5)
W(2)	9 110(0.5)	3 504(0.5)	2 324(0.5)
W(3)	8 452(0.5)	2 843(0.5)	2 787(0.5)
W(4)	9 459(0.5)	2 546(0.5)	2 681(0.5)
Cl(1)	9 626(5)	1 825(9)	4 487(7)
Cl(2)	7 969(4)	1 078(8)	2 010(6)
Cl(3)	8 533(5)	4 948(7)	3 158(7)
Cl(4)	9 575(4)	2 618(9)	867(6)
P(1)	9 432(4)	241(7)	2 508(6)
P(2)	8 178(4)	3 826(8)	931(7)
N(11)	8 300(10)	2 519(23)	4 102(16)
N(21)	9 826(11)	3 900(21)	3 006(21)
C(111)	7 862(12)	2 228(26)	4 792(23)
C(211)	10 394(18)	4 601(39)	2 958(35)
C(112)	7 834(27)	901(61)	5 023(50)
C(113)	7 227(11)	2 617(21)	4 203(18)
C(114)	8 026(12)	2 873(25)	5 814(21)
C(212)	10 860(20)	3 633(41)	2 721(33)
C(213)	10 294(19)	5 475(39)	2 100(34)
C(214)	10 548(21)	5 127(44)	4 044(39)
C(11)	9 143(15)	−277(31)	1 147(26)
C(12)	9 439(24)	−1 351(52)	839(41)
C(13)	10 319(40)	365(76)	2 643(63)
C(14)	10 678(42)	−355(83)	2 649(69)
C(15)	9 339(31)	−949(63)	3 392(51)
C(16)	8 830(21)	−1 647(43)	3 388(35)
C(21)	8 076(14)	2 745(28)	−138(25)
C(22)	7 810(20)	3 099(41)	−1 210(35)
C(23)	7 449(33)	4 566(66)	984(55)
C(24)	7 083(26)	3 914(54)	1 410(44)
C(25)	8 328(44)	5 496(87)	182(72)
C(26)	8 752(40)	5 441(78)	180(65)

Table 4. Atomic fractional co-ordinates (× 10^4) for compound (**4a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	1 267(0.5)	2 198(0.5)	1 610(0.5)	C(18)	2 267(12)	211(12)	1 961(21)
W(2)	1 307(0.5)	2 358(0.5)	3 654(1)	C(11)	2 646(8)	1 122(10)	−64(13)
Cl(3)	2 388(2)	3 208(4)	3 877(5)	C(12)	2 155(10)	670(11)	−812(16)
Cl(2)	124(3)	2 888(3)	1 109(5)	C(13)	2 341(12)	603(15)	−2 056(17)
Cl(1)	612(3)	1 002(3)	975(5)	C(14)	3 000(13)	987(14)	−2 537(21)
Cl(4)	2 072(3)	1 343(4)	4 613(5)	C(15)	3 490(12)	1 381(13)	−1 734(19)
P(2)	253(2)	1 362(3)	4 098(4)	C(16)	3 335(11)	1 467(11)	−527(18)
C(27)	−609(9)	1 495(13)	3 267(17)	N(2)	565(7)	3 208(8)	3 780(16)
C(28)	470(10)	295(10)	3 974(17)	C(41)	402(10)	3 777(11)	4 776(19)
C(21)	−35(9)	1 457(11)	5 661(16)	C(42)	−477(11)	3 767(13)	4 951(20)
C(22)	532(9)	1 408(11)	6 568(21)	C(43)	809(13)	3 538(14)	5 887(21)
C(23)	334(11)	1 510(12)	7 740(20)	C(44)	636(14)	4 630(13)	4 336(23)
C(24)	−418(12)	1 678(13)	8 071(19)	N(1)	1 914(7)	3 075(8)	1 194(12)
C(25)	−971(12)	1 724(12)	7 196(20)	C(31)	2 053(11)	3 500(11)	69(17)
C(26)	−770(9)	1 629(11)	5 965(19)	C(32)	2 912(11)	3 667(13)	32(18)
P(1)	2 384(2)	1 242(3)	1 452(4)	C(33)	1 790(13)	3 057(13)	−938(20)
C(17)	3 246(9)	1 594(14)	2 129(17)	C(34)	1 660(14)	4 317(12)	169(22)

Table 5. Selected comparative bond distances (Å) for (*a*) W(1)–W(2) dimer of compound (**3**), (*b*) W(3)–W(4) dimer of compound (**3**), (*c*) compound (**2**), and (*d*) compound (**4a**)

(*a*)		(*b*)		(*c*)		(*d*)	
W(1)–W(2)	2.309(5)	W(3)–W(4)	2.305(5)	W(1)–W(1a)	2.306(5)	W(1)–W(2)	2.330(3)
W(1)–Cl(1)	2.456(10)	W(3)–Cl(2)	2.448(9)	W(1)–Cl(2)	2.426(7)	W(1)–Cl(2)	2.391(7)
W(1)–Cl(2)	2.404(9)	W(3)–Cl(3)	2.444(10)	W(1)–Cl(1)	2.447(6)	W(1)–Cl(1)	2.411(7)
W(1)–P(1)	2.645(10)	W(3)–P(2)	2.662(11)	W(1)–P(1)	2.593(8)	W(1)–P(1)	2.544(8)
W(1)–N(11)	1.764(24)	W(3)–N(11)	1.804(23)	W(1)–N(1)	1.809(15)	W(1)–N(1)	1.912(16)
W(2)–Cl(3)	2.412(10)	W(4)–Cl(1)	2.466(10)			W(2)–Cl(3)	2.392(7)
W(2)–Cl(4)	2.459(10)	W(4)–Cl(4)	2.387(9)			W(2)–Cl(4)	2.420(7)
W(2)–P(2)	2.645(11)	W(4)–P(1)	2.631(11)			W(2)–P(2)	2.544(8)
W(2)–N(21)	1.810(26)	W(4)–N(21)	1.775(26)			W(2)–N(2)	1.935(17)

Table 6. Selected comparative bond angles (°) for (*a*) W(1)–W(2) dimer of compound (**3**), (*b*) W(3)–W(4) dimer of compound (**3**), (*c*) compound (**2**), and (*d*) compound (**4a**)

(*a*)		(*b*)		(*c*)		(*d*)	
Cl(1)–W(1)–W(2)	94.0(4)	Cl(2)–W(3)–W(4)	104.6(3)			Cl(2)–W(1)–W(2)	101.9(2)
Cl(2)–W(1)–W(2)	105.8(3)	Cl(3)–W(3)–W(4)	95.8(3)			Cl(3)–W(2)–W(1)	101.3(3)
Cl(2)–W(1)–Cl(1)	154.0(3)	Cl(3)–W(3)–Cl(2)	154.7(3)	Cl(1)–W(1)–Cl(2)	154.7(1)	Cl(1)–W(1)–Cl(2)	85.4(3)
P(1)–W(1)–W(2)	99.1(3)	P(2)–W(3)–W(4)	98.4(3)			P(1)–W(1)–W(2)	96.7(2)
P(1)–W(1)–Cl(1)	75.3(4)	P(2)–W(3)–Cl(2)	85.5(4)	Cl(2)–W(1)–P(1)	77.4(3)	P(1)–W(1)–Cl(1)	80.6(3)
P(1)–W(1)–Cl(2)	84.9(4)	P(2)–W(3)–Cl(3)	76.8(4)	Cl(1)–W(1)–P(1)	84.8(2)	P(1)–W(1)–Cl(2)	160.0(2)
N(11)–W(1)–W(2)	106.0(9)	N(11)–W(3)–W(4)	107.8			N(1)–W(1)–W(2)	98.0(6)
N(11)–W(1)–Cl(1)	92.0(8)	N(11)–W(3)–Cl(2)	95.8(7)	N(1)–W(1)–Cl(2)	94.4(5)	N(1)–W(1)–Cl(1)	147.5(5)
N(11)–W(1)–Cl(2)	98.5(7)	N(11)–W(3)–Cl(3)	91.9(9)	N(1)–W(1)–Cl(1)	94.0(5)	N(1)–W(1)–Cl(2)	94.7(6)
N(11)–W(1)–P(1)	152.6(9)	N(11)–W(3)–P(2)	152.4(9)	N(1)–W(1)–P(1)	154.4(3)	N(1)–W(1)–P(1)	89.7(6)
Cl(3)–W(2)–W(1)	94.8(3)	Cl(1)–W(4)–W(3)	92.8(4)			Cl(4)–W(2)–W(1)	112.5(2)
Cl(4)–W(2)–W(1)	104.4(3)	Cl(4)–W(4)–W(3)	104.9(3)			Cl(1)–W(1)–W(2)	113.8(2)
Cl(4)–W(2)–Cl(3)	155.5(3)	Cl(4)–W(4)–Cl(4)	87.4(4)			Cl(4)–W(2)–Cl(3)	85.4(3)
P(2)–W(2)–W(1)	98.4(3)	P(1)–W(4)–W(3)	97.8(3)			P(2)–W(2)–W(1)	95.7(2)
P(2)–W(2)–Cl(3)	77.7(4)	P(1)–W(4)–Cl(1)	75.5(4)			P(2)–W(2)–Cl(3)	161.8(2)
P(2)–W(2)–Cl(4)	84.4(4)	P(1)–W(4)–Cl(4)	87.4(4)			P(2)–W(2)–Cl(4)	82.5(3)
N(21)–W(2)–W(1)	107.2(10)	N(21)–W(4)–W(3)	107.0(9)			N(2)–W(2)–W(1)	97.8(7)
N(21)–W(2)–Cl(3)	95.9(9)	N(21)–W(4)–Cl(1)	92.4(10)			N(2)–W(2)–Cl(3)	95.8(5)
N(21)–W(2)–Cl(4)	92.9(9)	N(21)–W(4)–Cl(4)	96.3(10)			N(2)–W(2)–Cl(4)	148.9(5)
N(21)–W(2)–P(2)	154.2(9)	N(21)–W(4)–P(1)	152.9(9)			N(2)–W(2)–P(2)	88.0(5)
C(11)–P(1)–W(1)	112.0(12)	C(11)–P(1)–W(4)	112.9(12)	C(11)–P(1)–W(1)	117.1(9)	C(11)–P(1)–W(1)	109.7(7)
C(13)–P(1)–W(1)	121.8(25)	C(13)–P(1)–W(4)	84.6(26)	C(12)–P(1)–W(1)	127.1(8)	C(17)–P(1)–W(1)	115.1(9)
C(15)–P(1)–W(1)	102.9(22)	C(15)–P(1)–W(4)	134.4(21)			C(18)–P(1)–W(1)	118.6(9)
C(111)–N(11)–W(1)	143.4(20)	C(111)–N(11)–W(3)	147.3(20)	C(111)–N(1)–W(1)	146.1(9)	C(31)–N(1)–W(1)	132.6(14)
C(211)–N(21)–W(2)	145.4(25)	C(211)–N(21)–W(4)	145.1(24)			C(41)–N(2)–W(2)	130.3(15)
C(21)–P(2)–W(2)	116.6(11)	C(21)–P(2)–W(3)	113.3			C(21)–P(2)–W(2)	109.6(7)
C(23)–P(2)–W(2)	132.9(21)	C(23)–P(2)–W(3)	106.4(23)			C(27)–P(2)–W(2)	115.9(9)
C(25)–P(2)–W(2)	106.1(26)	C(25)–P(2)–W(3)	137.4(24)			C(28)–P(2)–W(2)	117.8(7)

Table 7. Torsion angles (°) about the W–W axis for (*a*) W(1)–W(2) dimer of compound (**3**), (*b*) W(3)–W(4) dimer of compound (**3**), (*c*) compound (**2**), and (*d*) compound (**4a**)

(*a*)		(*b*)	
Cl(1)–W(1)–W(2)–Cl(4)	96.7	Cl(2)–W(3)–W(4)–Cl(4)	67.9
Cl(1)–W(1)–W(2)–N(21)	−2.1	Cl(2)–W(3)–W(4)–P(1)	−21.2
Cl(1)–W(1)–W(2)–Cl(4)	−66.1	Cl(3)–W(3)–W(4)–Cl(1)	98.2
Cl(1)–W(1)–W(2)–P(2)	20.5	Cl(3)–W(3)–W(4)–N(21)	6.3
P(1)–W(1)–W(2)–Cl(4)	20.7	P(2)–W(3)–W(4)–Cl(4)	−19.7
P(1)–W(1)–W(2)–N(21)	−78.2	P(2)–W(3)–W(4)–N(21)	83.4
N(11)–W(1)–W(2)–Cl(3)	−5.1	N(11)–W(3)–W(4)–Cl(1)	4.1
N(11)–W(1)–W(2)–N(21)	91.6	N(11)–W(3)–W(4)–N(21)	87.9
(*c*)		(*d*)	
Cl(1)–W(1)–W(1a)–Cl(12a)	−69.0	Cl(1)–W(1)–W(2)–Cl(4)	67.1
Cl(2)–W(1)–W(1a)–N(1a)	−3.0	Cl(1)–W(1)–W(2)–P(2)	−17.0
Cl(2)–W(1)–W(1a)–Cl(2a)	95.8	Cl(2)–W(1)–W(2)–P(2)	73.2
Cl(1)–W(1)–W(1a)–P(1a)	17.7	Cl(2)–W(1)–W(2)–N(2)	−15.4
P(1)–W(1)–W(1a)–Cl(12a)	17.7	P(1)–W(1)–W(2)–Cl(4)	−15.6
P(1)–W(1)–W(1a)–N(1a)	−81.1	P(1)–W(1)–W(2)–Cl(3)	74.1
N(1)–W(1)–W(1a)–Cl(1a)	−3.0	N(1)–W(1)–W(2)–Cl(3)	−16.4
N(1)–W(1)–W(1a)–N(1a)	93.3	N(1)–W(1)–W(2)–N(2)	81.4

under argon in glass capillaries. Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[12] using a CAD4 diffractometer operating in the ω–2θ scan mode with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). Semi-empirical absorption corrections use azimuthal scan data for three reflections in each case. Further experimental data are given in Table 1.

The structures were solved *via* routine heavy-atom procedures and refined by full-matrix least-squares methods. Initial difficulties in solving the structures of (**2**) and (**3**) were overcome when the tungsten dimers were included as disordered pairs of dimers, each with occupancy 0.5. This disorder gave rise to rather large thermal motion parameters for the non-tungsten atoms. All atoms were refined anisotropically except the terminal carbons in the phosphine ethyl groups in compound (**2**). No hydrogens were located or included in any of the structures.

Details of the refinements are given in Table 1, final atomic coordinates in Tables 2—4, and selected bond lengths and angles in Tables 5—7.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Acknowledgements

H. R. P. would like to thank the S.E.R.C. for financial support and the provision of a Research Studentship. Also we are grateful to Mr. P. Haycock for obtaining the 400-MHz n.m.r. spectra under the ULIRS scheme, and Mr. G. Coumbarides for the 80-MHz n.m.r. spectra.

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Received 25th May 1988; *Paper* 8/02089B