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Structures of the Bridged and Chelated Isomers of Tetrachlorobis[1,2-bis(diphenylphosphino)ethane]ditungsten(II)

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X-ray crystallographic study has shown that there are two isomeric, molecular compounds with the molecular formula $W_2Cl_4(dppe)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane). The brown isomer, **1**, contains bridging dppe ligands. It forms monoclinic crystals in space group $P2_1/n$ with $a = 23.103$ (3) Å, $b = 13.254$ (2) Å, $c = 16.781$ (3) Å, $\beta = 107.53$ (1)°, $V = 4900$ (2) Å^3, and $Z = 4$. The W–W distance is 2.314 (1) Å, and the rotational conformation is twisted 31.3° from eclipsed. Each $\overline{\text{W–W–P–C–C–P}}$ ring has a chair conformation. There is a disorder such that 7.0% of the molecules have the W–W bond oriented perpendicular to the major orientation. The green isomer, **2**, has one dppe ligand chelated to each tungsten atom and the crystal contains 0.5 H_2O per molecule of the dinuclear compound. The crystals are monoclinic and belong to space group $C2/c$ with $a = 24.702$ (5) Å, $b = 10.024$ (1) Å, $c = 22.822$ (4) Å, $\beta = 118.81$ (2)°, $V = 4951$ (3) Å^3, and $Z = 4$. The molecules reside on crystallographic inversion centers, and the refinement included all hydrogen atoms. The W–W distance is 2.281 (1) Å, and there is no net rotation away from an eclipsed rotational conformation. With the use of the present results and earlier ones, it is shown that mixed-ligand complexes of Mo_2^{4+}, W_2^{4+}, and Re_2^{6+} display structural trans influences within cis and trans MX_2Y_2 units similar to but smaller than those that occur in Pt^{II} and Pd^{II} complexes. It is also shown that the M–P bonds are unusually long compared to the M–Cl bonds.

Introduction

The quest for ditungsten analogues of the known quadruply bonded dimolybdenum(II) complexes, which began around 1964, gave no positive result until in 1977 compounds containing the $[W_2(CH_3)_8]^{4-}$ and $[W_2(CH_3)_xCl_{8-x}]^{4-}$ ions were prepared and characterized.[1-3] These compounds are extremely reactive and have only marginal thermal stability. It was only in 1978 that the first easily prepared and highly stable compound, $W_2(mhp)_4$, where mhp represents the anion of 6-methyl-2-hydroxypyridine, was described,[4] and since then several similar types of compounds have been reported.[5-9] A completely different type of ditungsten compound with a quadruple bond is represented by $W_2(C_8H_8)_3$, which was crystallographically characterized in 1977,[10] but this and its chromium and molybdenum congeners lie outside the main body of chemistry of quadruply bonded M_2 compounds.

Recently, the preparation by Sharp and Schrock[11] of a series of $W_2X_4(PR_3)_4$ and $W_2X_4(diphos)_2$ compounds constitutes a significant and important extension of the chemistry of the quadruply bonded W_2^{4+} unit. The structures of representative compounds from this group afford valuable insight into the comparative properties of the W_2^{4+} and much better established Mo_2^{4+} complexes. In a preliminary communication[12] and an earlier paper,[13] the structures of $W_2Cl_4(PMe_3)_4$, its molybdenum analogue, and $W_2Cl_4(dmpe)_2$, where dmpe represents 1,2-bis(dimethylphosphino)ethane, were fully described. We now present a complete report on the structures of the two isomeric forms of $W_2Cl_4(dppe)_2$ obtained from the substitution reaction between $W_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ and 1,2-bis(diphenylphosphino)ethane, dppe, in toluene at 80 °C.

Table I. Summary of Crystallographic Data and Data Collection Procedures

	1	2
formula	$W_2Cl_4P_4C_{52}H_{48}$	$W_2Cl_4P_4O_{0.5}C_{52}H_{49}$
space group	$P2_1/n$	$C2/c$
a, Å	23.103 (3)	24.702 (5)
b, Å	13.254 (2)	10.024 (1)
c, Å	16.781 (3)	22.822 (4)
β, deg	107.53 (1)	118.81 (2)
V, Å^3	4900 (2)	4951 (3)
d_{calcd}, g/cm^3	1.77	1.76
Z	4	4
fw	1306.37	1315.38
cryst size, mm	0.05 × 0.20 × 0.30	0.1 × 0.2 × 0.3
μ(Mo Kα), cm^{-1}	53.545	53.002
radiation	graphite-monochromated Mo Kα ($\lambda_{\bar{\alpha}} = 0.71073$ Å)	
scan type	ω–2θ	ω–2θ
scan width ($\Delta\omega$), deg	$0.90 + 0.35 \tan\theta$	$0.65 + 0.35 \tan\theta$
aperature width, mm	$1.5 + \tan\theta$	$1.5 + \tan\theta$
crystal–counter dist, mm	173	173
prescan rejection limit	2.0 (0.5σ)	2.0 (0.5σ)
prescan acceptance limit	0.02 (50σ)	0.02 (50σ)
max scan speed, deg/min	20.12	20.12
max counting time, s	30	30
data collection range	$+h, +k, \pm l$ $3° \leqslant 2\theta \leqslant 50°$	$+h, +k, \pm l$ for $h + k = 2n$ $3° \leqslant 2\theta \leqslant 50°$
no. of data collected	9004	4596
no. of data, $F_o^2 > 3\sigma(F_o^2)$	3517	3261
p	0.05	0.05
X-ray exposure time, h	65	38
no. of intens stds	3	3
time btwn measmnts, s	3600	3600
cryst decompn	negligible	negligible
no. of variables	317	357
R_1	0.054	0.023
R_2	0.061	0.029
esd	1.416	0.849
largest peak, e/Å^3 [a]	1.02	0.73
Δ/σ [b]	0.16	0.11

[a] Largest peak in final difference Fourier map. [b] Largest shift (Δ) to error (σ) ratio in final least-squares cycle.

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Experimental Section

A crystalline sample of brown $W_2Cl_4(dppe)_2$ was provided by Professor R. R. Schrock of the Massachusetts Institute of Technology. Inspection under a microscope revealed three differently colored components. By far the major part of the sample consisted of a crystalline, dark brown solid (**1**) with suitable crystals for X-ray diffraction having a rectangular platelike morphology. A smaller amount (less than 10%) of the sample was in the form of green diamond-shaped crystals (**2**) with well-developed faces, appearing yellow-green when viewed with transmitted light. The third component consisted of white powder which is most likely unreacted dppe ligand. Crystals of the brown and green compounds were mounted with epoxy cement on glass fibers for X-ray diffraction analysis.

X-ray Crystallography. Collection of Data. Preliminary examination and subsequent data collection for both **1** and **2** were performed on an Enraf-Nonius CAD-4F autodiffractometer controlled by a PDP/8A computer at 26 ± 1 °C. Crystal parameters and data collection procedures are summaried in Table I. Further details on data collection and reduction have been given previously.[14] Final cell constants for both compounds were obtained from least-squares fits to 25 reflections in the range $25° < 2\theta < 32°$. Lorentz and polarization effects were corrected for in the X-ray data for both compounds as well as the effect of absorption. Absorption corrections were based on an empirical method which uses ψ scans (ψ = 0–360° every 10°) for χ values near 90°. Nine sets of reflections for **1** ($2,\bar{3},0$; $2,\bar{2},0$; $0,\bar{8},0$; $2,\bar{6},2$; $3,\bar{5},1$; $2,\bar{4},2$; $3,\bar{4},0$; $3,\bar{4},\bar{1}$; $1,\bar{3},\bar{2}$) and **2** ($\bar{5},1,9$; $\bar{4},0,8$; $\bar{2},0,6$; $\bar{7},1,11$; $\bar{6},0,10$; $\bar{5},1,7$; $\bar{2},0,4$; $\bar{7},1,13$; $\bar{9},1,13$) were averaged to give an absorption profile for each crystal. Maximum, minimum, and average transmission factors were 1.00, 0.65, and 0,89, respectively, for **1**, while for **2** these values were, respectively, 1.00, 0.82, and 0.94.

Solution and Refinement of the Structures.[15] **Compound 1.** The unit cell parameters revealed that this compound was isomorphous to $Re_2Cl_4(dppe)_2$[16] and $Mo_2Br_4(arphos)_2$,[17] where arphos is 1-(diphenylphosphino)-2-(diphenylarsino)ethane. Refinement was immediately begun in the space group $P2_1/n$ with the use of the positional parameters for Re(1) and Re(2) which represented the major orientation in $Re_2Cl_4(dppe)_2$.[16] Three cycles of least-squares refinement of W(1) and W(2) produced residuals of

$$R_1 = \sum ||F_o| - |F_c||/\sum|F_o = 0.247$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.349$$

where the weighting factor w is given by $4F_o^2/\sigma(F_o^2)^2$. The remaining Cl, P, and C atoms from the $Re_2Cl_4(dppe)_2$ structure were then added with initial thermal parameters of 4.0 Å^2 for these atoms. After one cycle for a scale factor calculation, all 62 atoms were refined for three cycles with isotropic thermal parameters on all atoms. The two W atoms were now assigned anisotropic thermal parameters, and the entire structure was refined for three more cycles. A difference Fourier map at this point revealed the presence of two additional W atoms as peaks of 3.017 and 3.573 e/Å^3. The magnitude of these peaks showed that this W_2 unit, which formed a perpendicular bisector of the W(1)–W(2) bond, was present in relatively low abundance. Variation of occupancy factors for all four W atoms led to a distribution of 0.93 and 0.07 for the major (W(1),W(2)) and minor (W(3),W(4)) tungsten atom sites. These occupancies were held fixed in subsequent least-squares cycles. With anisotropic thermal parameters assigned to all four W atoms and the Cl and P atoms of the major orientation, the structure was refined to the final residuals shown in Table I. The lighter atoms of the major orientation were all left with occupancy factors of 1.00 while no attempt was made to locate the lighter atoms associated with the minor W_2 orientation. The final difference Fourier map showed the highest peak to be located in the vicinity of W(1). Hydrogen atom contributions were omitted from the structure.

Compound 2. Systematic absences of hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, were consistent with the space group $C2/c$ or Cc.

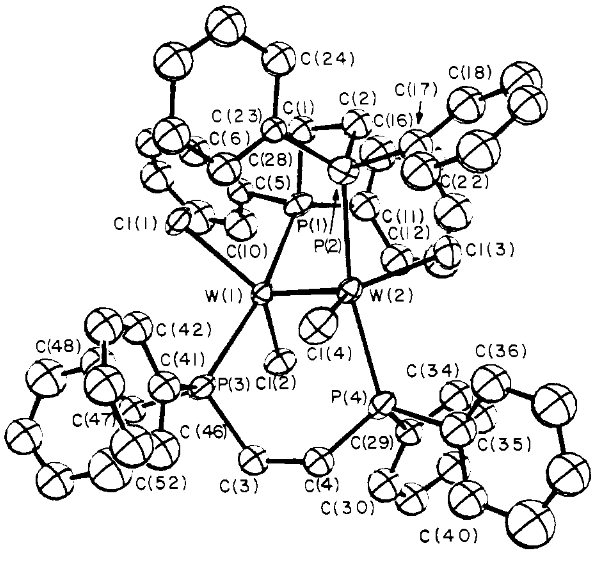

Figure 1. ORTEP drawing of the brown form of $W_2Cl_4(dppe)_2$ (**1**) with thermal ellipsoids at the 35% probability level. Unlabeled phenyl carbon atoms follow from those given.

The centric space group was initially assumed and its choice was subsequently confirmed by successful refinement of the structure. The structure solution was obtained with the aid of the direct-methods MULTAN program. An E-map produced the coordinates of W atoms located about a crystallographic center of inversion with a W–W separation appropriate for a quadruply bonded complex. Prior to this result, the compound had been assumed to be a mononuclear complex. Four cycles of least-squares refinement of the W atom position produced discrepancy indices of R_1 = 0.265 and R_2 = 0.357. Subsequent difference Fourier maps followed by least-squares refinement located the remaining 30 nonhydrogen atoms within the dinuclear molecule. Anisotropic thermal parameters were assigned to all nonhydrogen atoms, and after further least-squares refinement, a difference Fourier map revealed the positions of all 24 hydrogen atoms of the dppe ligand. Refinement continued with the hydrogen atom contributions now included with fixed isotropic thermal parameters of 5.0 Å^2. Another difference Fourier map at this point had its highest peak located away from the dinuclear $W_2Cl_4(dppe)_2$ molecules. Attempted refinement of this peak as an oxygen atom of a water molecule led to an unrealistically high thermal parameter, suggesting that the site was only partially occupied. The occupancy factor was refined to a value of 0.25 and then held fixed when the entire structure was refined to convergence. Continued refinement led to an isotropic thermal parameter of 13 Å^2 for the lattice oxygen atom, and the final residuals and largest peak in the final difference Fourier map are summarized in Table I.

Inspection of several low-angle reflections for both structures did not suggest a need for secondary extinction corrections. Tables of observed and calculated structure factor amplitudes for those reflections with $I > 3\sigma(I)$ are available.[18]

Results

The positional and thermal parameters for the atoms in **1** and **2** are presented in Tables II and III, respectively. Tables IV and V compile the bond distances and angles excluding those involving the phenyl groups in **1** and **2**, respectively. Bond distances and angles for the phenyl groups in **1** are given in Table IVA,[18] and Table VA[18] includes bond distance and angle data for both phenyl carbon atoms and hydrogen atoms in **2**. Table VI presents torsional angles about the W–W bonds in **1** and **2**, and Table VII[18] gives least-squares planes and dihedral angles within the two compounds. Each of the two structures will now be examined in detail.

Brown $W_2Cl_4(dppe)_2$ (1). This molecule is depicted in Figure 1 with the atom labeling scheme defined. The scheme

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(18) Supplementary material.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for Brown $W_2Cl_4(dppe)_2$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	0.31142 (3)	0.29901 (6)	−0.01463 (5)	3.19 (3)	2.32 (3)	3.20 (3)	−0.19 (4)	0.84 (2)	0.04 (4)
W(2)	0.24899 (3)	0.19653 (6)	0.03524 (5)	3.01 (3)	2.57 (3)	3.39 (3)	−0.34 (4)	0.43 (3)	0.04 (4)
W(3)	0.32003 (51)	0.22795 (94)	0.06901 (74)	3.9 (5)	5.0 (7)	4.8 (5)	1.3 (5)	2.1 (4)	1.6 (5)
W(4)	0.23908 (52)	0.29282 (89)	−0.02910 (66)	6.1 (5)	2.9 (5)	3.4 (5)	2.3 (5)	1.4 (4)	0.4 (5)
Cl(1)	0.2656 (2)	0.4574 (3)	−0.0657 (3)	5.4 (2)	2.5 (2)	4.9 (2)	0.5 (2)	1.0 (2)	0.7 (2)
Cl(2)	0.4062 (2)	0.2232 (4)	0.0009 (3)	3.7 (2)	4.2 (3)	6.2 (2)	0.2 (2)	1.8 (2)	−0.2 (2)
Cl(3)	0.2856 (2)	0.1632 (4)	0.1821 (3)	5.6 (2)	5.6 (3)	4.2 (2)	0.3 (2)	1.4 (2)	1.0 (2)
Cl(4)	0.1613 (2)	0.1514 (4)	−0.0730 (3)	4.2 (2)	4.8 (2)	5.9 (3)	−0.8 (2)	−0.4 (2)	−0.5 (2)
P(1)	0.3534 (2)	0.3996 (4)	0.1174 (3)	4.1 (2)	2.6 (2)	5.0 (3)	−0.6 (2)	1.1 (2)	−0.6 (2)
P(2)	0.1951 (2)	0.3358 (4)	0.0896 (3)	3.9 (2)	4.0 (2)	4.5 (2)	−1.0 (2)	1.4 (2)	−0.8 (2)
P(3)	0.2856 (3)	0.2250 (4)	−0.1610 (3)	6.4 (3)	2.8 (2)	3.9 (2)	0.9 (2)	0.5 (2)	−0.0 (2)
P(4)	0.2931 (2)	0.0326 (4)	0.0022 (3)	4.9 (3)	2.8 (2)	4.9 (3)	0.5 (2)	0.9 (2)	0.5 (2)

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
C(1)	0.2944 (8)	0.472 (1)	0.146 (1)	4.3 (4)	C(27)	0.0826 (9)	0.487 (2)	−0.111 (1)	5.9 (5)
C(2)	0.2505 (8)	0.406 (2)	0.176 (1)	4.9 (5)	C(28)	0.1255 (8)	0.418 (2)	−0.063 (1)	5.0 (5)
C(3)	0.3092 (8)	0.089 (2)	−0.155 (1)	4.7 (5)	C(29)	0.3697 (8)	−0.009 (1)	0.051 (1)	3.9 (4)
C(4)	0.2777 (8)	0.017 (1)	−0.111 (1)	4.4 (4)	C(30)	0.4071 (9)	−0.045 (2)	0.005 (1)	6.5 (6)
C(5)	0.4033 (8)	0.498 (1)	0.100 (1)	4.0 (4)	C(31)	0.4686 (9)	−0.077 (2)	0.055 (1)	6.4 (6)
C(6)	0.3819 (9)	0.592 (2)	0.073 (1)	5.7 (5)	C(32)	0.4890 (10)	−0.074 (2)	0.136 (1)	6.6 (6)
C(7)	0.4205 (9)	0.668 (2)	0.059 (1)	5.4 (5)	C(33)	0.4521 (10)	−0.039 (2)	0.184 (1)	6.9 (6)
C(8)	0.4820 (10)	0.643 (2)	0.071 (1)	6.7 (6)	C(34)	0.3905 (9)	−0.003 (2)	0.139 (1)	5.9 (5)
C(9)	0.4989 (11)	0.549 (2)	0.087 (2)	8.5 (7)	C(35)	0.2516 (9)	−0.080 (2)	0.030 (1)	6.1 (5)
C(10)	0.4622 (10)	0.476 (2)	0.107 (1)	6.9 (6)	C(36)	0.2094 (10)	−0.063 (2)	0.070 (1)	7.1 (6)
C(11)	0.4031 (9)	0.349 (2)	0.215 (1)	5.4 (5)	C(37)	0.1791 (11)	−0.153 (2)	0.092 (2)	8.6 (7)
C(12)	0.4245 (9)	0.250 (2)	0.216 (1)	6.1 (5)	C(38)	0.2013 (11)	−0.244 (2)	0.067 (2)	8.5 (7)
C(13)	0.4683 (11)	0.218 (2)	0.289 (1)	7.7 (6)	C(39)	0.2370 (13)	−0.264 (2)	0.016 (2)	11.2 (9)
C(14)	0.4911 (12)	0.281 (2)	0.359 (2)	9.4 (8)	C(40)	0.2655 (10)	−0.172 (2)	−0.007 (1)	7.2 (6)
C(15)	0.4693 (12)	0.376 (2)	0.361 (2)	9.2 (8)	C(41)	0.2094 (8)	0.233 (1)	−0.235 (1)	4.8 (5)
C(16)	0.4219 (11)	0.417 (2)	0.286 (2)	8.2 (7)	C(42)	0.1748 (8)	0.320 (1)	−0.235 (1)	5.0 (5)
C(17)	0.1447 (9)	0.278 (2)	0.142 (1)	5.4 (5)	C(43)	0.1140 (9)	0.326 (2)	−0.294 (1)	6.1 (6)
C(18)	0.1551 (9)	0.287 (2)	0.228 (1)	6.7 (6)	C(44)	0.0927 (10)	0.246 (2)	−0.346 (1)	6.9 (6)
C(19)	0.1091 (10)	0.248 (2)	0.263 (1)	7.4 (6)	C(45)	0.1276 (11)	0.161 (2)	−0.347 (1)	7.9 (7)
C(20)	0.0606 (9)	0.196 (2)	0.215 (1)	6.4 (5)	C(46)	0.1905 (10)	0.153 (2)	−0.295 (1)	7.1 (6)
C(21)	0.0524 (10)	0.180 (2)	0.130 (1)	7.8 (7)	C(47)	0.3316 (7)	0.279 (1)	−0.223 (1)	4.0 (4)
C(22)	0.0960 (9)	0.224 (2)	0.095 (1)	6.5 (6)	C(48)	0.3455 (10)	0.378 (2)	−0.216 (1)	6.9 (6)
C(23)	0.1434 (7)	0.430 (1)	0.024 (1)	3.0 (4)	C(49)	0.3787 (11)	0.424 (2)	−0.264 (2)	8.9 (8)
C(24)	0.1176 (9)	0.502 (2)	0.065 (1)	5.5 (5)	C(50)	0.3935 (11)	0.374 (2)	−0.325 (1)	7.6 (7)
C(25)	0.0746 (10)	0.570 (2)	0.014 (1)	6.9 (6)	C(51)	0.3766 (11)	0.277 (2)	−0.336 (1)	8.0 (7)
C(26)	0.0547 (9)	0.563 (2)	−0.072 (1)	6.3 (6)	C(52)	0.3449 (13)	0.226 (2)	−0.286 (2)	10.5 (9)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

is identical with that found in the isomorphous $Re_2Cl_4(dppe)_2$ molecule[16] with the exception of the labels for minor metal atom sites which have been interchanged.

A description of $W_2Cl_4(dppe)_2$ is essentially the same as that given for the triply bonded $Re_2Cl_4(dppe)_2$ molecule.[16] No crystallographically imposed symmetry is present in **1** although virtual D_2 symmetry exists. The W–W bond comprises one C_2 axis; the second twofold axis bisects the C–C bond in the bridging P–C–C–P fragment of the dppe ligand, and the third C_2 axis bisects both the W–W bond and the vector between nongeminal chlorine atom pairs and is orthogonal to the other two C_2 axes. Each bridging dppe ligand forms a six-membered ring consisting of $\overline{\text{W–W–P–C–C–P}}$ atoms. Each of the two rings assumes a chair conformation with the four W and C atoms nearly coplanar and the P atoms located on opposite sides of this plane. The geometry about the W atoms is square pyramidal with Cl and P atoms trans to their own kind. However, considerable distortions from a square-pyramidal geometry can be seen in the Cl–W–Cl and P–W–P angles which average 135.0 (6) and 166.5 (6)°, respectively, instead of being equal. A contributing factor to these distortions is the discrepancy between W–Cl and W–P bond lengths which average 2.37 (1) and 2.53 (2) Å, respectively. The four basal Cl and P atoms of each square pyramid about each W atom form a plane (Table VII[18]) with deviations ranging from 0.293 to 0.325 Å. Each W atom is displaced from this plane toward the other W atom with out-of-plane displacements of 0.603 and 0.594 Å for W(1) and W(2), respectively. The eight sets of unique phenyl carbon atoms are basically planar with deviations from planarity ranging from 0.000 to 0.073 Å. Dihedral angles between these rings are summarized in Table VII.[18]

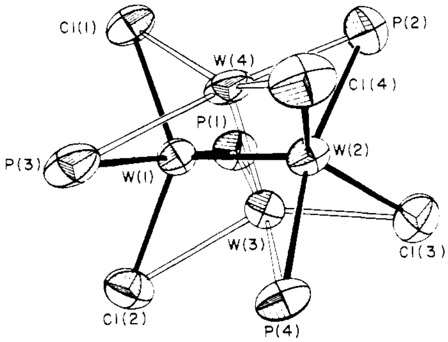

Figure 2. View of the major (shaded bonds) and minor (open bonds) orientations of the $W_2Cl_4P_4$ unit in brown $W_2Cl_4(dppe)_2$ (**1**). Vibrational ellipsoids are given at the 50% probability level.

The relationship between the major and minor W atoms sites in **1** is shown in Figure 2. The fractional occupancies among the two sites are identical with those found in $Re_2Cl_4(dppe)_2$ with 93% of the W atoms in W(1) and W(2) positions and 7% located in the W(3) and W(4) sites. Because of this low level of occupation of the minor site, no indications of the lighter atoms associated with this orientation could be found. However, it may well be that positions of the peripheral

Figure 3. Stereoview of the unit cell contents of brown $W_2Cl_4(dppe)_2$ showing only the major orientation. Thermal ellipsoids are drawn at the 20% probability level. The origin is located in the upper left front corner of the cell with the view approximately down the *b* axis with the *a* axis vertical and the *c* axis horizontal.

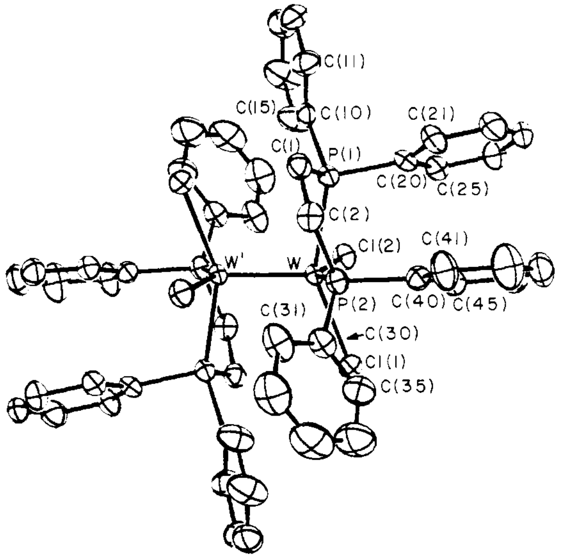

Figure 4. ORTEP drawing of the ditungsten unit in green $W_2Cl_4(dppe)_2{\cdot}0.5H_2O$ (**2**) with vibrational ellipsoids scaled so as to enclose 50% of the electron density. Unlabeled phenyl carbon atoms follow from those given.

atoms of this minor orientation coincide quite closely with those of the atoms in the major orientation. Further arguments for this description of the disorder have been presented for the isomorphous Re compound,[16] and this receives further support in the structure of $Mo_2Br_4(arphos)_2$.[17] Although this molybdenum compound is also "isomorphous", the fractional disordering of major and minor sites has shifted to a ratio of 76.5:23.5. Nevertheless, a secondary set of halide and arphos ligands could not be distinguished and was proposed to be coincident with the primary set. Figure 3 presents a stereoview of the major orientations of the four dinuclear molecules in the unit cell of **1** and clearly shows the complexities in providing an adequate description of this molecule, let alone a disordered one.

Green $W_2Cl_4(dppe)_2{\cdot}0.5H_2O$ (2). The labeling scheme for this molecule is shown in Figure 4. A crystallographic center of inversion is located at the midpoint of the W–W bond, and the molecule has overall C_{2h} symmetry. The dppe ligand forms a five-membered chelate ring with an acute P(1)–W–P(2) angle of 75.78 (5)°. The cis arrangement of Cl and P atoms leads to longer W–Cl distances (2.410 (8) Å, average) and shorter W–P distances (2.502 (3) Å), an aspect which will be examined further in the next section. The geometry about the W atom, as in **1**, is distorted square pyramidal with the trans Cl and P atoms forming average angles of 149.14 (9)° at the W atom. The four basal Cl and P atoms form a much better plane (average deviation 0.015 Å) than did the corresponding atoms in **1** with the W atom displaced 0.635 Å toward W' (see Table VII[18]). The four phenyl rings of the dppe ligand are strictly planar (Table VII[18]) with no carbon atom deviation exceeding 0.015 Å.

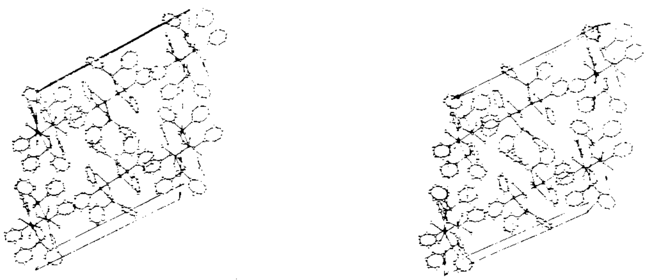

Figure 5. Stereoview of the unit cell contents of green $W_2Cl_4(dppe)_2{\cdot}0.5H_2O$ with thermal ellipsoids at the 20% probability level. Only two of the eight positions of the oxygen atom of the water molecules are occupied at any one time. The view is approximately down the *b* axis with the *a* axis vertical and the *c* axis horizontal.

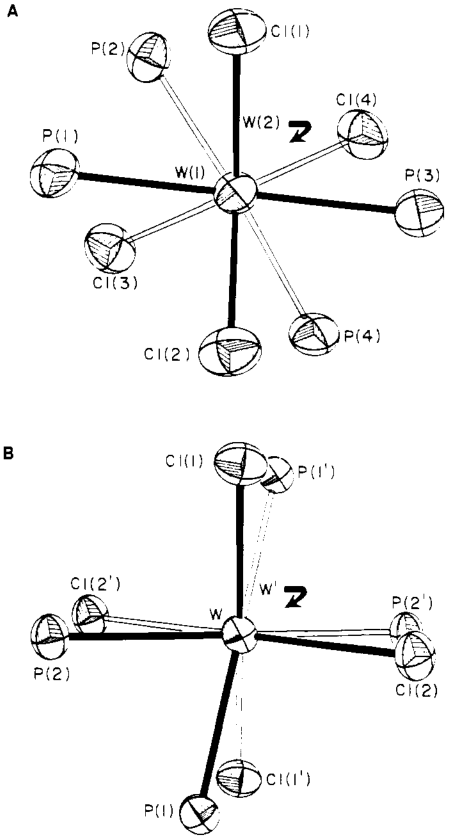

Figure 6. Views down the W–W bonds in brown $W_2Cl_4(dppe)_2$ (A) and green $W_2Cl_4(dppe)_2$ (B) showing only the coordinated chlorine and phosphorus atoms. Thermal ellipsoids are shown at the 50% probability level.

Figure 5 presents a stereoview of the unit cell in **2** with six dinuclear molecules and eight oxygen atoms of the water molecules in the lattice. Only four of the six $W_2Cl_4(dppe)_2$ molecules shown reside in the same unit cell. The 0.25 occupancy factor for the oxygen atom is interpreted as meaning that only two of the eight general positions within the unit cell at any one time are fully occupied.

The rotational conformations for both **1** and **2** are displayed in Figure 6. The view of **1** shown here would leave little doubt that this is far from an eclipsed molecule. However, the extent of the staggering, as given by the mean torsional angle of 31.3°, is considerably less than the 45° required for a completely staggered structure. The marked rotation away from the eclipsed conformation has been attributed[16] to the conformational restraints imposed by the bridging dppe ligands. In **2** the view down the W–W bond in Figure 6 shows slight

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for Green $W_2Cl_4(dppe)_2 \cdot 0.5H_2O$[a,b]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	0.74329 (1)	0.27131 (2)	0.04517 (1)	2.044 (5)	2.052 (7)	1.491 (5)	−0.283 (6)	0.919 (4)	−0.110 (6)
Cl(1)	0.70796 (6)	0.4961 (1)	0.04413 (6)	3.78 (5)	2.51 (5)	2.86 (4)	0.16 (4)	1.74 (3)	−0.10 (4)
Cl(2)	0.84048 (5)	0.3322 (1)	0.13975 (6)	2.66 (4)	3.23 (5)	2.11 (4)	−0.53 (4)	0.78 (3)	−0.44 (4)
P(1)	0.74829 (5)	0.4651 (1)	−0.08313 (6)	2.42 (4)	2.29 (5)	1.93 (4)	−0.28 (4)	1.05 (3)	−0.05 (4)
P(2)	0.86666 (5)	0.3028 (1)	0.00007 (6)	2.22 (4)	2.88 (6)	1.95 (4)	−0.40 (4)	0.91 (3)	−0.20 (4)
O	0.595 (2)	0.711 (4)	0.037 (2)	B = 13 (1) Å²					
C(1)	0.8116 (2)	0.5584 (5)	−0.0169 (2)	3.4 (2)	2.7 (2)	2.9 (2)	−0.4 (2)	1.8 (1)	−0.0 (2)
C(2)	0.8741 (2)	0.4829 (5)	0.0191 (2)	2.6 (2)	3.4 (2)	2.8 (2)	−0.7 (2)	1.2 (1)	−0.6 (2)
C(10)	0.6810 (2)	0.5758 (5)	−0.1129 (2)	2.7 (2)	2.8 (2)	1.8 (1)	0.1 (2)	1.1 (1)	−0.1 (1)
C(11)	0.6887 (2)	0.7102 (5)	−0.1183 (3)	3.9 (2)	2.8 (2)	3.8 (2)	−0.1 (2)	1.7 (1)	−0.4 (2)
C(12)	0.6378 (3)	0.7941 (6)	−0.1455 (3)	5.2 (2)	2.8 (2)	3.6 (2)	0.6 (2)	2.1 (2)	−0.3 (2)
C(13)	0.5802 (3)	0.7439 (6)	−0.1675 (3)	3.9 (2)	5.6 (3)	4.2 (2)	1.8 (2)	2.2 (1)	1.6 (2)
C(14)	0.5721 (3)	0.6078 (7)	−0.1631 (3)	3.0 (2)	6.1 (3)	6.2 (3)	0.7 (2)	2.0 (2)	2.5 (3)
C(15)	0.6232 (2)	0.5258 (6)	−0.1357 (3)	3.1 (2)	3.9 (3)	5.5 (2)	−0.0 (2)	2.0 (2)	1.6 (2)
C(20)	0.7612 (2)	0.4757 (5)	−0.1560 (2)	3.3 (2)	2.6 (2)	2.3 (2)	0.4 (2)	1.4 (1)	0.8 (2)
C(21)	0.8069 (2)	0.5511 (6)	−0.1579 (2)	4.1 (2)	3.7 (2)	3.1 (2)	−0.4 (2)	2.1 (1)	0.6 (2)
C(22)	0.8133 (2)	0.5563 (6)	−0.2148 (3)	4.6 (2)	3.9 (3)	4.4 (2)	0.3 (2)	2.9 (1)	1.0 (2)
C(23)	0.7730 (2)	0.4863 (6)	−0.2703 (2)	5.3 (2)	4.4 (3)	3.3 (2)	1.9 (2)	3.1 (1)	1.3 (2)
C(24)	0.7266 (3)	0.4116 (6)	−0.2707 (2)	4.7 (2)	4.2 (3)	2.5 (2)	0.3 (2)	1.8 (1)	−0.1 (2)
C(25)	0.7206 (2)	0.4057 (5)	−0.2133 (2)	3.5 (2)	3.1 (2)	2.5 (2)	0.2 (2)	1.4 (1)	0.3 (2)
C(30)	0.9372 (2)	0.2274 (6)	0.0682 (2)	2.4 (2)	4.2 (3)	2.6 (2)	−0.1 (2)	1.1 (1)	0.4 (2)
C(31)	0.9712 (2)	0.2870 (6)	0.1301 (3)	2.9 (2)	5.9 (3)	2.6 (2)	−1.1 (2)	0.8 (1)	0.1 (2)
C(32)	1.0267 (3)	0.2249 (8)	0.1768 (3)	3.5 (2)	7.6 (4)	3.4 (2)	−0.8 (3)	0.6 (2)	−0.4 (3)
C(33)	1.0464 (3)	0.1116 (8)	0.1608 (3)	2.6 (2)	7.7 (4)	5.1 (3)	1.0 (3)	0.7 (2)	2.2 (3)
C(34)	1.0134 (3)	0.0530 (8)	0.0997 (3)	4.5 (3)	6.6 (4)	5.4 (3)	1.6 (3)	1.5 (2)	1.5 (3)
C(35)	0.9579 (3)	0.1112 (7)	0.0535 (3)	4.3 (2)	4.8 (3)	3.8 (2)	1.1 (2)	1.6 (2)	0.8 (2)
C(40)	0.8879 (2)	0.2904 (5)	−0.0671 (2)	2.6 (2)	3.0 (2)	2.6 (2)	0.6 (2)	1.4 (1)	0.3 (2)
C(41)	0.8513 (2)	0.2235 (5)	−0.1258 (2)	3.0 (2)	3.0 (2)	2.8 (2)	0.1 (2)	1.6 (1)	0.2 (2)
C(42)	0.8669 (3)	0.2177 (6)	−0.1764 (3)	3.8 (2)	4.3 (3)	2.9 (2)	0.5 (2)	1.5 (1)	−0.0 (2)
C(43)	0.9198 (3)	0.2767 (7)	−0.1675 (3)	4.5 (2)	5.8 (3)	3.7 (2)	0.5 (2)	2.8 (1)	0.7 (2)
C(44)	0.9585 (3)	0.3394 (8)	−0.1085 (3)	3.6 (2)	7.9 (4)	4.8 (2)	−1.9 (2)	2.5 (1)	−0.7 (3)
C(45)	0.9427 (2)	0.3477 (7)	−0.0580 (2)	3.2 (2)	6.0 (3)	3.2 (2)	−1.3 (2)	1.8 (1)	−0.4 (2)

atom	x	y	z	atom	x	y	z
H(1)	0.796 (2)	0.581 (6)	0.008 (2)	H(24)	0.704 (2)	0.368 (6)	−0.304 (2)
H(2)	0.815 (2)	0.648 (6)	−0.035 (2)	H(25)	0.692 (2)	0.356 (6)	−0.212 (2)
H(3)	0.889 (2)	0.478 (6)	0.065 (2)	H(31)	0.960 (2)	0.377 (6)	0.143 (2)
H(4)	0.907 (2)	0.515 (6)	0.004 (2)	H(32)	1.041 (3)	0.264 (5)	0.214 (3)
H(11)	0.727 (3)	0.736 (5)	−0.109 (3)	H(33)	1.086 (2)	0.071 (6)	0.190 (2)
H(12)	0.642 (2)	0.887 (6)	−0.152 (2)	H(34)	1.025 (2)	−0.038 (6)	0.088 (2)
H(13)	0.546 (2)	0.795 (6)	−0.185 (3)	H(35)	0.936 (2)	0.077 (6)	0.014 (2)
H(14)	0.526 (2)	0.574 (6)	−0.180 (2)	H(41)	0.820 (2)	0.178 (6)	−0.135 (2)
H(15)	0.616 (2)	0.430 (6)	−0.130 (2)	H(42)	0.835 (2)	0.178 (6)	−0.215 (2)
H(21)	0.832 (2)	0.603 (6)	−0.123 (2)	H(43)	0.933 (3)	0.278 (5)	−0.202 (3)
H(22)	0.843 (2)	0.603 (6)	−0.213 (2)	H(44)	0.988 (2)	0.382 (6)	−0.100 (2)
H(23)	0.778 (2)	0.496 (6)	−0.307 (2)	H(45)	0.969 (2)	0.408 (6)	−0.020 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] All hydrogen atoms were assigned B_{iso} values of 5.0 Å².

deviations from the eclipsed conformation with individual torsion angles of 8 and 12° (Table VI). However, according to our conventional definition of net rotational conformation, which has been fully described before,[17] the presence of an inversion center in **2** requires the algebraic mean torsional angle to be zero and leads us to describe the molecule as effectively eclipsed.

Discussion

The structures of the brown and green forms of $W_2Cl_4(dppe)_2$ present us with the first crystallographically characterized pair of compounds in which the same bidentate ligand is found in both bridging and chelating arrangements. The partly staggered conformation of Cl and P atoms found in **1** also represents the first instance of a W_2^{4+} compound in other than an eclipsed conformation. While these are new aspects to ditungsten structures, very similar results have been obtained with Mo_2^{4+} and Re_2^{4+} compounds. Walton et al.[19] reported that two forms of $Mo_2Cl_4(dppe)_2$ can be isolated. The structures were inferred primarily by comparison of infrared and electronic absorption spectra to known Mo_2^{4+} structures and led to the proposal that the gray (β) isomer had bridging dppe ligands as in **1** and the light green (α) isomer possessed chelating dppe ligands as in **2**. The results reported here on the tungsten analogues leave no doubt that Walton's structural proposals are correct.

The analogous triply bonded Re^{II} compound, $Re_2Cl_4(dppe)_2$, has been prepared[20] in only a single form with the structure[16] isomorphous to **1**. The mean torsional angle in this compound is 39° although here no inherent rotational barrier exists with the $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration showing complete cancellation of the δ-bonding component. The question of how much the strength of the δ bond must be decreased as a consequence of the internal rotation has been directly addressed in discussing the structure of the quadruply bonded $Mo_2Br_4(arphos)_2$.[17] In this compound the average twist angle, χ, is 30° and a simple analysis reveals that the δ-bond overlap varies as $\cos 2\chi$.[17] Consequently, the δ-bond strength is only reduced by a factor of 0.50 from its maximum value. The same analysis for **1** (χ = 31.3°) reveals that the δ bond is only

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(19) Best, S. A.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 99.

(20) Ebner, J. R.; Tyler, D. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 833.

Table IV. Bond Distances (Å) and Angles (Deg) for Brown $W_2Cl_4(dppe)_2$, Excluding the Atoms of the Phenyl Groups

Distances			
W(1)-W(2)	2.314 (1)	P(2)-C(2)	1.87 (2)
W(1)-Cl(1)	2.391 (4)	P(2)-C(17)	1.83 (2)
W(1)-Cl(2)	2.351 (4)	P(2)-C(23)	1.84 (2)
W(1)-P(1)	2.517 (4)	P(3)-C(3)	1.87 (2)
W(1)-P(2)	2.543 (5)	P(3)-C(41)	1.83 (2)
W(2)-Cl(3)	2.393 (4)	P(3)-C(47)	1.85 (2)
W(2)-Cl(4)	2.354 (4)	P(4)-C(4)	1.83 (2)
W(2)-P(3)	2.544 (5)	P(4)-C(29)	1.80 (2)
W(2)-P(4)	2.531 (5)	P(4)-C(35)	1.91 (2)
P(1)-C(1)	1.85 (2)	C(1)-C(2)	1.53 (2)
P(1)-C(5)	1.82 (2)	C(3)-C(4)	1.53 (2)
P(1)-C(11)	1.82 (2)		

Angles			
W(2)-W(1)-Cl(1)	112.8 (1)	C(1)-P(1)-C(11)	105.9 (8)
W(2)-W(1)-Cl(2)	111.7 (1)	C(5)-P(1)-C(11)	98.6 (8)
W(2)-W(1)-P(1)	96.3 (1)	W(2)-P(2)-C(2)	110.2 (6)
W(2)-W(1)-P(3)	97.6 (1)	W(2)-P(2)-C(17)	108.7 (6)
Cl(1)-W(1)-Cl(2)	135.4 (1)	W(2)-P(2)-C(23)	124.9 (5)
Cl(1)-W(1)-P(1)	82.1 (1)	C(2)-P(2)-C(17)	102.9 (8)
Cl(1)-W(1)-P(3)	92.5 (1)	C(2)-P(2)-C(23)	107.2 (7)
Cl(2)-W(1)-P(3)	92.5 (1)	C(17)-P(2)-C(23)	100.5 (8)
Cl(2)-W(1)-P(1)	91.7 (1)	W(1)-P(3)-C(3)	109.9 (6)
Cl(2)-W(1)-P(3)	83.2 (2)	W(1)-P(3)-C(41)	122.3 (6)
P(1)-W(1)-P(3)	166.1 (2)	W(1)-P(3)-C(47)	112.9 (6)
W(1)-W(2)-Cl(3)	114.5 (1)	C(3)-P(3)-C(41)	107.1 (8)
W(1)-W(2)-Cl(4)	110.8 (1)	C(3)-P(3)-C(47)	101.3 (8)
W(1)-W(2)-P(2)	97.4 (1)	C(41)-P(3)-C(47)	101.0 (7)
W(1)-W(2)-P(4)	95.1 (1)	W(2)-P(4)-C(4)	111.1 (5)
Cl(3)-W(2)-Cl(4)	134.6 (2)	W(2)-P(4)-C(29)	124.5 (6)
Cl(3)-W(2)-P(2)	79.9 (2)	W(2)-P(4)-C(35)	110.7 (7)
Cl(3)-W(2)-P(4)	91.5 (2)	C(4)-P(4)-C(29)	107.2 (8)
Cl(4)-W(2)-P(2)	93.5 (2)	C(4)-P(4)-C(35)	102.1 (8)
Cl(4)-W(2)-P(4)	85.5 (2)	C(29)-P(4)-C(35)	98.4 (8)
P(2)-W(2)-P(4)	166.9 (2)	P(1)-C(1)-C(2)	114 (1)
W(1)-P(1)-C(1)	112.7 (5)	P(2)-C(2)-C(1)	114 (1)
W(1)-P(1)-C(5)	109.5 (5)	P(3)-C(3)-C(4)	117 (1)
W(1)-P(1)-C(11)	124.7 (7)	P(4)-C(4)-C(3)	117 (1)
C(1)-P(1)-C(5)	102.6 (8)		

Table V. Bond Distances (Å) and Angles (Deg) for Green $W_2Cl_4(dppe)_2 \cdot 0.5H_2O$, Excluding the Atoms of the Phenyl Groups and Hydrogen Atoms

Distances			
W-W′	2.281 (1)	P(1)-C(10)	1.835 (6)
W-Cl(1)	2.412 (1)	P(1)-C(20)	1.840 (6)
W-Cl(2)	2.408 (1)	P(2)-C(2)	1.845 (6)
W-P(1)	2.497 (1)	P(2)-C(30)	1.847 (6)
W-P(2)	2.508 (1)	P(2)-C(40)	1.848 (6)
P(1)-C(1)	1.825 (6)	C(1)-C(2)	1.553 (9)

Angles			
W′-W-Cl(1)	112.06 (4)	P(1)-W-P(2)	75.78 (5)
W′-W-Cl(2)	109.96 (4)	C(1)-P(1)-C(10)	105.0 (3)
W′-W-P(1)	96.42 (4)	C(1)-P(1)-C(20)	105.4 (3)
W′-W-P(2)	99.95 (4)	C(10)-P(1)-C(20)	98.6 (2)
Cl(1)-W-Cl(2)	88.38 (5)	C(2)-P(2)-C(30)	104.8 (3)
Cl(1)-W-P(1)	149.21 (5)	C(2)-P(2)-C(40)	103.0 (3)
Cl(1)-W-P(2)	87.58 (5)	C(30)-P(2)-C(40)	98.1 (3)
Cl(2)-W-P(1)	92.82 (5)	P(1)-C(1)-C(2)	115.1 (4)
Cl(2)-W-P(2)	149.08 (5)	P(2)-C(2)-C(1)	113.0 (4)

Table VI. Torsional Angles (Deg) in Brown $W_2Cl_4(dppe)_2$ (1) and Green $W_2Cl_4(dppe)_2 \cdot 0.5H_2O$ (2)

planes defining the angle		angle	
atoms in plane 1	atoms in plane 2	1	2
Cl(1), W(1), W(2)	W(1), W(2), P(2)	−32.5	
Cl(2), W(1), W(2)	W(1), W(2), P(4)	−30.4	
P(1), W(1), W(2)	W(1), W(2), Cl(3)	−30.7	
P(3), W(1), W(2)	W(1), W(2), Cl(4)	−31.8	
Cl(1), W, W′	W, W′, P(1′)		12.0
P(2), W, W′	W, W′, Cl(2′)		8.0
	mean angle	−31.3	10.0

Table VIII. Comparison of W–W Bond Lengths in Quadruply Bonded W_2^{4+} Compounds[a]

compd	W–W, Å	ref
$W_2(dmhp)_4 \cdot 0.5(diglyme)$	2.155 (2)	6
$W_2(mhp)_4 \cdot CH_2Cl_2$	2.161 (1)	4
$W_2(dmhp)_4 \cdot (diglyme)$	2.163 (1)	6
$W_2(map)_4 \cdot 2THF$	2.164 (1)	5
$W_2(dmhp)_2[(PhN)_2N]_2 \cdot 2THF$	2.169 (1)	8
$W_2(dmhp)_2[(PhN)_2CCH_3]_2 \cdot 2THF$	2.174 (1)	7
$W_2(chp)_4$	2.177 (1)	9
$W_2(O_2CCF_3)_4 \cdot {}^2/_3(diglyme)$	2.209 (2)[b]	22
$W_2Cl_4(PMe_3)_4$	2.262 (1)	13
$Li_4W_2Me_xCl_{8-x} \cdot 4THF$	2.263 (2)	3
$Li_4W_2Me_8 \cdot 4Et_2O$	2.264 (1)	3
$W_2Cl_4(dppe)_2 \cdot 0.5H_2O$ (green form)	2.281 (1)	this work
$W_2Cl_4(dmpe)_2 \cdot (toluene)$	2.287 (1)	13
$W_2Cl_4(dppe)_2$ (brown form)	2.314 (1)	this work
$W_2(C_8H_8)_3$	2.375 (1)	10

[a] Abbreviations used: Hdmhp, 2,4-dimethyl-6-hydroxypyrimidine; Hmhp, 2-hydroxy-6-methylpyridine; Hmap, 2-amino-6-methylpyridine; THF, tetrahydrofuran; Ph, phenyl; Me, methyl; Et, ethyl; dppe, 1,2-bis(diphenylphosphino)ethane; dmpe = 1,2-bis(dimethylphosphino)ethane. [b] Average of two crystallographically unique dinuclear molecules. Axial W–O distances to the diglyme oxygen atoms range from 2.48 (1) to 2.70 (1) Å.

0.46 times its strength in the eclipsed conformation. This loss of δ bonding is consistent with the 0.33 Å increase in the W–W bond lengths from **2** to **1**. Both **1** and **2** can be described, however, in light of the above analysis, as quadruply bonded W_2^{4+} species.

As noted in the introduction, examples of quadruply bonded W_2^{4+} complexes until only recently were exceedingly rare. The latest review articles[21] contain only a fraction of the W_2^{4+} compounds currently known. In the following sections we will examine the structures of quadruply bonded W_2^{4+} molecules and review some trends which emerge in chloro–phosphine mixed-ligand complexes.

W_2^{4+} Compounds. Table VIII lists the known ditungsten(II) compounds containing quadrupule bonds. The W–W distances span a rather large range (0.220 Å, from 2.155 (2) to 2.375 (1) Å). As mentioned earlier, $W_2(C_8H_8)_3$[10] differs from the other 14 ditungsten compounds present in that it has an 18-electron configuration about each tungsten atom, while all others have only a 16-electron configuration. These 14 compounds can be divided into three groups. The first group contains seven compounds bounded by $W_2(dmhp)_4 \cdot 0.5$(diglyme) and $W_2(chp)_4$, and all have four three-atom bridging ligands. The second group has only recently been established[22] and consists of $W_2(O_2CCF_3)_4 \cdot {}^2/_3$(diglyme) with an average W–W bond length of 2.209 (1) Å as the sole member. Weak (2.48–2.70 Å) axial interactions are found in this compound with the diglyme oxygen atoms. The third group, with the exception of brown $W_2Cl_4(dppe)_2$, contains no bridging ligands and encompasses a range of W–W distances longer than those of the first group. Ligands which offer the least steric hindrance comprise the shorter (2.262–2.264 Å) W–W bond lengths in this group while the bulkier diphosphine ligands lead to somewhat longer (2.281–2.314 Å) distances. None of the compounds in either the first or third groups contains axial ligands.

The range of W–W distances established by the third group of W_2^{4+} complexes in Table VIII corresponds almost identically with the range of known W–W triply bonded compounds.[23-25] Triply bonded W–W distances range from 2.255

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(21) (a) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225. (b) Templeton, J. L. *Prog. Inorg. Chem.* **1979**, *26*, 211. (c) Dori, Z. *Ibid.* **1981**, *28*, 239.

(22) Sattelberger, A. P.; McLaughlin, K. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2880.

(23) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356.

Table IX. Comparison of M–P and M–Cl Bond Lengths

	bond lengths, Å[a]				bond length differences, Å[b]			
	$M{-}P_P$	$M{-}P_{Cl}$	$M{-}Cl_P$	$M{-}Cl_{Cl}$	$\Delta_{1,2}$	$\Delta_{3,4}$	$\Delta_{1,3}$	$\Delta_{2,4}$
Mo_2	2.56 (5)			2.40 (2)				
W_2	2.52 (3)	2.48 (1)	2.42 (1)	2.38 (1)	0.04 (3)	0.04 (2)	0.10 (3)	0.10 (2)
Re_2	2.48 (4)	2.45 (1)	2.35 (1)	2.35 (3)	0.03 (4)	0.00 (4)	0.13 (4)	0.10 (2)
Pd	2.37 (1)	2.25 (1)	2.37 (1)	2.28 (1)	0.12 (1)	0.09 (1)	0.00 (1)	−0.03 (1)
Pt	2.35 (1)	2.24 (1)	2.38 (1)	2.30 (1)	0.11 (1)	0.08 (1)	−0.03 (1)	−0.06 (1)

[a] Subscripts indicate the trans ligand; e.g., $M{-}P_P$ denotes an M–P bond which is trans to another M–P bond. [b] $\Delta_{m,n}$ = the distance in column *m* minus that in column *n*.

(2) Å in $W_2(CH_2SiMe_3)_6$ to 2.332 (1) Å in $W_2(OCHMe_2)_6(py)_2$. The overlap of the metal–metal bond lengths for quadruple and triple bonds has been encountered previously for rhenium[16] and suggests that for the metals in the third transition series the M–M quadruple bonds owe little of their shortness to the δ component of the metal–metal bond.

Metal–Ligand Bond Lengths. A comparison of the W–Cl and W–P distances in the two structures reveals two significant patterns, namely: (1) that there may be structural trans influences in these compounds and (2) that the M–P bonds are unexpectedly long relative to the M–Cl bonds. This prompted us to look at all of the available structural data for all $M_2X_4L_4$- and $M_2X_6L_2$-type complexes (M = Mo, W, Re)[26] and compare the results with those for some representative square complexes[27] of Pt^{II} and Pd^{II}. Average values and pertinent differences are presented in Table IX. The available data for the Mo, W, and Re complexes are sparse, and the uncertainties in the average values are therefore relatively large. For the Pd^{II} and Pt^{II} complexes, there are also surprisingly few data of useful accuracy. However, despite these limitation, the following important conclusions concerning the above two points seem clear.

Trans Influence. If we examine the $\Delta_{1,2}$ and $\Delta_{3,4}$ values, it appears that the phosphine ligands exert a detectable trans influence (ca. 0.03 Å) in the binuclear compounds, but it is a considerably smaller one than that found in the Pd^{II} and Pt^{II} complexes (0.08–0.12 Å). There are two possible reasons for this. One is that the MX_2L_2 halves of the $M_2X_4L_4$ molecules are not planar; the trans bonds instead of being collinear make angles at the metal atom of about 150–155°. A second is that the metal d orbitals and d electrons that must play a role in the trans interactions are tied up in the M–M multiple bonding in the dinuclear complexes whereas they are probably much more available in the square complexes of Pd^{II} and Pt^{II}.

Relative M–P and M–Cl Bond Lengths. An examination of the $\Delta_{1,3}$ and $\Delta_{2,4}$ values, which are the differences between M–P and M–Cl bonds when the trans ligands are the same, shows a dramatic difference between the mononuclear and the dinuclear complexes. In the former, the M–P bond lengths are equal to or slightly less than the M–Cl bond lengths. In the dinuclear compounds they are $\geq$0.10 Å longer. This relatively greater length of the M–P bonds surely means that they are relatively weaker and that the M–P bonding electrons are in less stable molecular orbitals than are the M–Cl bonding electrons. As will be shown elsewhere in a report on photoelectron spectra and SCF–Xα–SW calculations on the $M_2X_4(PR_3)_4$ molecules, this is indeed the case.

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Registry No. **1**, 73470-13-0; **2**, 73470-12-9.

Supplementary Material Available: Tables of bond distances and angles for the phenyl groups in **1** (Table IVA), bond distances and angles for the phenyl groups and hydrogen atoms in **2** (Table VA), least-squares planes and dihedral angles in **1** and **2** (Table VII), and observed and calculated structure factor amplitudes for **1** and **2** (37 pages). Ordering information is given on any current masthead page.

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(26) Bond lengths for the following compounds were used. Brown and green isomers of $W_2Cl_4(dppe)_2$ were reported in this work. $W_2Cl_4(dmpe)_2$, $W_2Cl_4(PMe_3)_4$, and $Mo_2Cl_4(PMe_3)_4$ were taken from ref 13. $Mo_2Cl_4(dppm)_2$ was taken from: Abbott, E. H.; Bose, K. H.; Cotton, F. A.; Hall, W. T.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3240. $Re_2Cl_6(PEt_3)_2$ was taken from: Cotton, F. A.; Foxman, B. M. *Ibid.* **1968**, *7*, 2135. $Re_2Cl_4(PEt_3)_4$ was taken from: Cotton, F. A.; Frenz, B. A.; Ebner, J. R.; Walton, R. A. *Ibid.* **1976**, *15*, 1630. $Re_2Cl_4(dppe)_2$ was taken from ref 16. $Re_2Cl_5(dppm)_2$ was taken from: Cotton, F. A.; Shive, L. W.; Stults, B. R. *Ibid.* **1976**, *15*, 2239.

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