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# Two New Ditungsten Species Containing Chloride and Trimethylphosphine Ligands

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The action of PhI·Cl$_2$ on W$_2$Cl$_4$(PMe$_3$)$_4$ in 1:1 mole ratio gives brown 1,3,6-W$_2$Cl$_5$(PMe$_3$)$_3$. The EPR at 10 K in frozen CH$_2$Cl$_2$ solution has a broad signal at $g = 1.83$. The molecular structure was determined by X-ray crystallography and shows a W−W distance of 2.291(1) Å, about 0.03 Å longer than that in W$_2$Cl$_4$(PMe$_3$)$_4$. Crystal data: monoclinic space group *C*2/*c* with cell dimensions of $a = 13.423(2)$ Å, $b = 12.0768(9)$ Å, $c = 28.247(5)$ Å, $\beta = 93.360(7)°$, $V = 4571(1)$ Å$^3$, and $Z = 8$. There is a 1.8% orientational disorder. When a solution of W$_2$Cl$_6$(PMe$_3$)$_4$ in CH$_2$Cl$_2$ plus hexanes was allowed to stand at −15 °C for several months, brown crystals of [HPMe$_3$]$_2$[W$_2$Cl$_8$(PMe$_3$)]·CH$_2$Cl$_2$ were obtained. The anion is a face-sharing bioctahedron, with a W−W bond length of 2.433(1) Å. Crystal data: monoclinic space group *P*2$_1$/*m* with cell dimensions of $a = 9.398(1)$ Å, $b = 9.836(2)$ Å, $c = 16.687(5)$ Å, $\beta = 97.78(2)°$, $V = 1528.4(6)$ Å$^3$, and $Z = 2$.

## Introduction

The proximate cause of the work reported here was a purely accidental observation, namely, the formation of 1,3,6-W$_2$Cl$_5$(PMe$_3$)$_3$ when a heated solution of W$_2$Cl$_4$(NHCMe$_3$)$_2$(PMe$_3$)$_2$ containing additional PMe$_3$ was evaporated at 50 °C. Since this is the first structurally characterized compound[1] containing the W$_2^{5+}$ core, with a $\sigma^2\pi^4\delta$ bond of order 3.5, and it is fairly stable, we considered it worthwhile to seek a designed synthesis for it.

To do this, we carried out a reaction between W$_2$Cl$_4$(PMe$_3$)$_4$ and PhI·Cl$_2$. This did, in fact, provide a synthesis of 1,3,6-W$_2$Cl$_5$(PMe$_3$)$_3$, but it also afforded a second product which was shown to be the previously known[2] edge-sharing bioctahedral molecule 1,3,6,8-W$_2$Cl$_6$(PMe$_3$)$_4$.[3] In the course of handling this product, another serendipitous discovery was made, namely, that on long standing at −15 °C in a mixed solvent of isomeric hexanes and dichloromethane, 1,3,6,8-W$_2$Cl$_6$(PMe$_3$)$_4$ gives the new compound [HPMe$_3$]$_2$[W$_2$Cl$_8$(PMe$_3$)]. This type of interconversion of face- and edge-sharing bioctahedra in hydrocarbon solvents was previously observed for tungsten species.[2] We report here the structural characterization of the two new compounds noted above.

## Experimental Section

**Starting Materials.** General literature methods were used to prepare *trans*-W$_2$Cl$_4$(NHCMe$_3$)$_2$(PMe$_3$)$_2$,[4] W$_2$Cl$_4$(PMe$_3$)$_4$,[5] and PhI·Cl$_2$.[6] PMe$_3$ was purchased from Strem Chemicals. Common solvents were obtained from commercial sources and were dried and deoxygenated by refluxing over appropriate reagents before use. All manipulations were carried out under a nitrogen or an argon atmosphere by using standard vacuum-line techniques.

**Syntheses. (i) 1,3,6-W$_2$Cl$_5$(PMe$_3$)$_3$ (1).** The compound 1,3,6-W$_2$Cl$_5$(PMe$_3$)$_3$ was first obtained by passing a stream of N$_2$ through a concentrated solution of *trans*-W$_2$Cl$_4$(NHCMe$_3$)$_2$(PMe$_3$)$_2$ containing a small amount of free phosphine and heated at about 50 °C. A few brown, block-shaped crystals of **1** were found on the wall of the Schlenk tube along with black crystals of W$_2$Cl$_4$(PMe$_3$)$_4$[7] and red crystals of *cis*-W$_2$Cl$_4$(NHCMe$_3$)$_2$(PMe$_3$)$_2$.[4]

**(ii) Compound 1** was then reproduced by the type of reaction described for the Re analog.[8] W$_2$Cl$_4$(PMe$_3$)$_4$ (0.10 g., 0.12 mmol) was dissolved in 5 mL of dichloromethane. PhI·Cl$_2$ (0.034 g., 0.12 mmol) was added to the solution, which immediately turned dark brown. The mixture was stirred at room temperature for 24 h, and the solvent was then removed by vacuum distillation to leave a dark brown residue. This was dissolved in 5 mL of dichloromethane, and the solution was filtered. About 10 mL of isomeric hexanes was added, and the mixture was maintained at about −15 °C in a refrigerator. After a few days, brown powder had precipitated out of solution. Single crystals of **1** were grown by slow diffusion of isomeric hexanes into dichloromethane solutions at room temperature. Compound **1** was stable in air as a solid, but it was quickly oxidized (or disproportionated) in solutions at room temperature to leave some blue-purple products. We were able to identify one of them as the monomeric W(IV) compound WOCl$_2$(PMe$_3$)$_3$.[9]

**(iii) W$_2$Cl$_6$(PMe$_3$)$_4$ (2).** Reaction ii was carried out in the presence of PMe$_3$ (15 $\mu$L, 0.15 mmol). After the filtration to remove a white precipitate of OPMe$_3$, the brown filtrate was placed in a Schlenk tube and a stream of N$_2$ was passed through the solution. After a few days, brown crystals of W$_2$Cl$_6$(PMe$_3$)$_4$ were found on the wall of the tube.

**(iv) [HPMe$_3$]$_2$[W$_2$Cl$_8$PMe$_3$]·CH$_2$Cl$_2$ (3).** About 10 mL of isomeric hexanes was added to the concentrated dichloromethane solution of **2**, and the mixture was kept in a refrigerator at −15 °C. After 3 months, small brown crystals of **3** were observed on the bottom of a Schlenk tube. They were unstable in solution at room temperature.

**Physical Measurements.** The $^{31}$P{$^1$H} NMR spectra were recorded at 81 MHz in 10 mm NMR tubes on a Varian XL-200 spectrometer. Chemical shifts were referenced externally and are reported relative to 85% H$_3$PO$_4$. X-Band ESR spectra of dichloromethane solutions were recorded at 10, 100, and 293 K with a frequency of 9.4 GHz on a Bruker ESP 300 spectrometer.

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**Table 1.** Crystallographic Data for 1,3,6-$W_2Cl_5(PMe_3)_3$ (**1**) and $[HPMe_3]_2[W_2Cl_8(PMe_3)]\cdot CH_2Cl_2$ (**3**)

| | | |
|---|---|---|
| formula | $W_2Cl_5P_3C_9H_{27}$ | $W_2Cl_{10}P_3C_{10}H_{31}$ |
| fw | 773.17 | 966.46 |
| space group | *C*2/*c* (No.15) | *P*2$_1$/*m* (No.11) |
| *a*, Å | 13.423(2) | 9.398(1) |
| *b*, Å | 12.0768(9) | 9.836(2) |
| *c*, Å | 28.247(5) | 16.687(5) |
| $\beta$, deg | 93.360(7) | 97.78(2) |
| *V*, Å$^3$ | 4571(1) | 1528.4(6) |
| *Z* | 8 | 2 |
| $\varrho_{calc}$, g/cm$^3$ | 2.247 | 2.100 |
| $\mu$, mm$^{-1}$ | 10.840 | 8.551 |
| radiation ($\lambda$, Å) | Mo Kα (0.710 73) | Mo Kα (0.710 73) |
| temp., °C | 20 ± 2 | 20 ± 2 |
| transm. factors | 1.00−0.69 | 1.00−0.81 |
| final *R* indices [$I > 2\sigma(I)$] | R1[a] = 0.052, wR2[b] = 0.119 | R1 = 0.045, wR2 = 0.103 |
| *R* indices (all data) | R1 = 0.090, wR2 = 0.129 | R1 = 0.109, wR2 = 0.124 |
| quality-of-fit indicator[c] | 0.991 | 1.058 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] Quality-of-fit $= [\sum[w(F_o^2 - F_c^2)^2]/(N_{observns} - N_{params})]^{1/2}$; based on all data.

**Table 2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 1,3,6-$W_2Cl_5(PMe_3)_3$ (**1**)

| atom | *x* | *y* | *z* | $U_{eq}$,[a] Å$^2$ |
|---|---|---|---|---|
| W(1)[b] | 0.22930(5) | −0.03417(6) | 0.61309(2) | 0.0370(2) |
| W(2)[b] | 0.35953(5) | 0.08444(6) | 0.63049(2) | 0.0351(2) |
| W(3)[c] | 0.275(3) | 0.099(3) | 0.592(1) | 0.035[d] |
| W(4)[c] | 0.316(3) | −0.042(3) | 0.644(1) | 0.037[d] |
| Cl(1) | 0.0853(4) | 0.0752(4) | 0.6094(2) | 0.065(1) |
| Cl(2) | 0.2790(4) | −0.2203(4) | 0.6049(2) | 0.055(1) |
| Cl(3) | 0.4313(3) | 0.1353(4) | 0.5602(2) | 0.054(1) |
| Cl(4) | 0.2824(4) | 0.2582(4) | 0.6355(2) | 0.061(1) |
| Cl(5) | 0.3931(3) | 0.0783(4) | 0.7128(1) | 0.052(1) |
| P(1) | 0.1745(4) | −0.0884(4) | 0.6938(2) | 0.056(1) |
| P(2) | 0.2113(4) | −0.0228(4) | 0.5240(2) | 0.046(1) |
| P(3) | 0.4996(4) | −0.0566(4) | 0.6318(2) | 0.044(1) |
| C(1) | 0.064(2) | −0.166(2) | 0.6851(9) | 0.099(8) |
| C(2) | 0.139(2) | 0.023(2) | 0.7333(7) | 0.080(7) |
| C(3) | 0.252(2) | −0.175(2) | 0.7308(7) | 0.071(6) |
| C(4) | 0.312(2) | -0.083(2) | 0.4912(6) | 0.066(6) |
| C(5) | 0.185(2) | 0.112(1) | 0.4976(7) | 0.071(6) |
| C(6) | 0.103(2) | -0.106(2) | 0.5056(8) | 0.079(7) |
| C(7) | 0.613(1) | 0.019(2) | 0.6462(7) | 0.059(5) |
| C(8) | 0.526(1) | -0.128(1) | 0.5778(6) | 0.050(5) |
| C(9) | 0.504(1) | -0.164(2) | 0.6770(6) | 0.061(5) |

[a] $U_{eq}$ is defined as one-third of the trace of the ortogonalized $\mathbf{U}_{ij}$ tensor. [b] Site modeled as 0.982(1) W. [c] Site modeled as 0.018(1) W. [d] Atoms were refined isotropically.

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for 1,3,6-$W_2Cl_5(PMe_3)_3$ (**1**)

| | | | |
|---|---|---|---|
| W(1)−W(2) | 2.291(1) | W(2)−Cl(3) | 2.340(4) |
| W(1)−Cl(1) | 2.338(5) | W(2)−Cl(5) | 2.342(4) |
| W(1)−Cl(2) | 2.360(5) | W(2)−Cl(4) | 2.347(4) |
| W(1)−P(2) | 2.518(4) | W(2)−P(3) | 2.536(5) |
| W(1)−P(1) | 2.522(5) | W(4)−W(3) | 2.29(5) |
| W(2)−W(1)−Cl(1) | 106.0(1) | W(1)−W(2)−Cl(3) | 109.2(1) |
| W(2)−W(1)−Cl(2) | 113.6(1) | W(1)−W(2)−Cl(4) | 103.8(1) |
| W(2)−W(1)−P(1) | 103.2(1) | W(1)−W(2)−Cl(5) | 107.1(1) |
| W(2)−W(1)−P(2) | 102.0(1) | W(1)−W(2)−P(3) | 98.0(1) |
| Cl(1)−W(1)−Cl(2) | 140.5(2) | Cl(3)−W(2)−Cl(4) | 91.2(2) |
| Cl(1)−W(1)−P(1) | 84.4(2) | Cl(3)−W(2)−Cl(5) | 141.8(2) |
| Cl(1)−W(1)−P(2) | 83.9(2) | Cl(3)−W(2)−P(3) | 81.2(2) |
| Cl(2)−W(1)−P(1) | 86.6(2) | Cl(4)−W(2)−Cl(5) | 91.6(2) |
| Cl(2)−W(1)−P(2) | 88.0(2) | Cl(4)−W(2)−P(3) | 158.2(2) |
| P(1)−W(1)−P(2) | 154.4(2) | Cl(5)−W(2)−P(3) | 82.2(2) |

**Table 4.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[HPMe_3]_2[W_2Cl_8(PMe_3)]\cdot CH_2Cl_2$ (**3**)

| atom | *x* | *y* | *z* | $U_{eq}$,[a] Å$^2$ | occ |
|---|---|---|---|---|---|
| W(1) | 0.29510(7) | 0.25 | 0.17328(4) | 0.0538(2) | 1.00 |
| W(2) | 0.19867(7) | 0.25 | 0.30145(4) | 0.0568(3) | 1.00 |
| Cl(1) | 0.0303(5) | 0.25 | 0.1737(3) | 0.086(2) | 1.00 |
| Cl(2) | 0.3570(4) | 0.0621(4) | 0.2692(2) | 0.091(1) | 1.00 |
| Cl(3) | 0.0478(4) | 0.0736(5) | 0.3414(2) | 0.097(1) | 1.00 |
| Cl(4) | 0.2569(5) | 0.0771(6) | 0.0728(3) | 0.120(2) | 1.00 |
| Cl(5) | 0.3424(7) | 0.25 | 0.4301(3) | 0.126(3) | 1.00 |
| P(1) | 0.5588(5) | 0.25 | 0.1638(3) | 0.067(1) | 1.00 |
| C(1) | 0.668(6) | 0.25 | 0.261(2) | 0.09(2)[b] | 0.49(8) |
| C(2) | 0.619(4) | 0.103(2) | 0.111(2) | 0.09(2)[b] | 0.49(8) |
| C(1a) | 0.667(6) | 0.164(6) | 0.254(2) | 0.07(2)[b] | 0.26(4) |
| C(2a) | 0.655(6) | 0.293(4) | 0.157(4) | 0.08(2)[b] | 0.26(4) |
| C(2b) | 0.607(6) | 0.146(6) | 0.080(3) | 0.08(2)[b] | 0.26(4) |
| P(2) | 0.7821(8) | 0.25 | 0.5152(4) | 0.099(2) | 1.00 |
| C(3) | 0.975(3) | 0.25 | 0.545(2) | 0.088(9) | 0.75 |
| C(4) | 0.735(2) | 0.098(2) | 0.460(1) | 0.087(6) | 0.75 |
| C(5) | 0.692(4) | 0.25 | 0.601(2) | 0.10(1) | 0.75 |
| P(3) | 0.973(1) | 0.25 | 0.8799(5) | 0.129(3) | 1.00 |
| C(6) | 0.907(4) | 0.25 | 0.964(2) | 0.11(1) | 0.75 |
| C(7) | 1.056(3) | 0.107(3) | 0.864(2) | 0.15(1) | 0.75 |
| C(8) | 0.864(8) | 0.25 | 0.799(5) | 0.8(2) | 0.75 |
| Cl(6) | 0.431(2) | 0.25 | 0.878(2) | 0.30(1) | 1.00 |
| Cl(7) | 0.336(3) | 0.25 | 0.709(1) | 0.34(1) | 1.00 |
| C(9) | 0.487(7) | 0.25 | 0.782(2) | 0.30(4)[b] | 1.00 |

[a] $U_{eq}$ is defined as one-third of the trace of the ortogonalized $\mathbf{U}_{ij}$ tensor. [b] Atoms were refined isotropically.

**X-ray Crystallographic Procedures.** Crystallographic data for 1,3,6-$W_2Cl_5(PMe_3)_3$ (**1**), $W_2Cl_6(PMe_3)_4$ (**2**), and $[HPMe_3]_2[W_2Cl_8\text{-}PMe_3]\cdot CH_2Cl_2$ (**3**) were obtained using general procedures that have been fully described elsewhere.[10] All calculations were performed on a DEC 3000-800 AXP workstation. Data were corrected for Lorentz and polarization effects. The coordinates of W atoms were obtained by Patterson and direct methods in SHELXS-86.[11] Final least-squares refinement for each structure was performed using the SHELXL-93 structure refinement program.[12] Crystallographic parameters and basic information pertaining to data collection and structure refinement are summarized in Table 1. A listing of positional and isotropic parameters for compounds **1** and **3** will be found in Tables 2 and 4. Selected bond distances and angles are listed in Tables 3 and 5. Tables of anisotropic displacement parameters as well as complete tables of bond distances and angles and coordinates of hydrogen atoms are available as supporting information.

The crystal structure of **2** obtained at room temperature was found to be essentially identical to that reported[2] at −152 °C and does not need to be described here.

**1,3,6-$W_2Cl_5(PMe_3)_3$ (1).** A block-shaped single crystal with approximate dimensions 0.25 × 0.12 × 0.05 mm$^3$ was covered with a thin layer of epoxy resin and placed on the tip of a glass fiber. Least-squares refinement of 25 carefully centered reflections in the range $26 < 2\theta < 38°$ resulted in cell parameters consistent with a *C*-centered monoclinic lattice. Analysis of systematic absences, which were consistent with space group *Cc* or *C*2/*c*, and axial photographs confirmed the lattice symmetry. Intensity data were collected at ambient temperature on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromated MoKα ($\lambda\alpha$ = 0.710 73 Å) radiation. A total of 3163 data in the range $4 \leq \theta \leq 46°$ were measured using an $\omega - 2\theta$ scan technique. Periodic monitoring of three representative reflections revealed no loss in crystal integrity throughout data collection. An absorption correction based on azimuthal scans of five reflections with Eulerian angle $\chi$ near 90° was applied to the data. With eight formula units in the unit cell, the space group was initially assumed to be *C*2/*c*, and this was confirmed by the refinement.

The positions of two W atoms (W(1) and W(2)) were located using the direct-methods program in SHELXS-86. The chlorine, phosphorus,

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**Table 5.** Selected Bond Lengths (Å) and Angles (deg) for $[HPMe_3]_2[W_2Cl_8(PMe_3)]\cdot CH_2Cl_2$ (**3**)[a]

| | | | |
|---|---|---|---|
| W(1)−W(2) | 2.433(1) | W(2)−Cl(2) | 2.477(4) |
| W(1)−Cl(1) | 2.490(4) | W(2)−Cl(3) | 2.392(4) |
| W(1)−Cl(2) | 2.462(4) | W(2)−Cl(5) | 2.377(5) |
| W(1)−Cl(4) | 2.381(4) | P(1)−C(1) | 1.80(4) |
| W(1)−P(1) | 2.505(5) | P(1)−C(2) | 1.82(3) |
| W(2)−Cl(1) | 2.477(5) | | |
| Cl(1)−W(1)−Cl(2) | 98.4(1) | Cl(2)−W(2)−Cl(2′) | 96.5(2) |
| Cl(1)−W(1)−Cl(4) | 86.9(1) | Cl(2)−W(2)−Cl(3) | 85.2(1) |
| Cl(1)−W(1)−P(1) | 176.6(2) | Cl(2)−W(2)−Cl(3′) | 176.3(1) |
| Cl(2)−W(1)−Cl(2′) | 97.3(2) | Cl(2)−W(2)−Cl(5) | 84.9(2) |
| Cl(2)−W(1)−Cl(4) | 85.5(2) | Cl(3)−W(2)−Cl(3′) | 93.0(2) |
| Cl(2)−W(1)−Cl(4′) | 173.5(1) | Cl(3)−W(2)−Cl(5) | 91.9(2) |
| Cl(2)−W(1)−P(1) | 83.8(1) | W(1)−W(2)−Cl(1) | 60.9(1) |
| Cl(4)−W(1)−Cl(4′) | 91.2(3) | W(1)−W(2)−Cl(2) | 60.17(8) |
| Cl(4)−W(1)−P(1) | 90.7(1) | W(1)−W(2)−Cl(3) | 123.4(1) |
| W(2)−W(1)−Cl(1) | 60.4(1) | W(1)−W(2)−Cl(5) | 124.1(2) |
| W(2)−W(1)−Cl(2) | 60.80(8) | W(1)−Cl(1)−W(2) | 58.7(1) |
| W(2)−W(1)−Cl(4) | 125.5(1) | W(1)−Cl(2)−W(2) | 59.03(9) |
| W(2)−W(1)−P(1) | 123.0(1) | C(1)−P(1)−C(2) | 105(1) |
| Cl(1)−W(2)−Cl(2) | 98.4(1) | C(2)−P(1)−C(2′) | 105(2) |
| Cl(1)−W(2)−Cl(3) | 84.6(1) | W(1)−P(1)−C(1) | 113(2) |
| Cl(1)−W(2)−Cl(5) | 175.0(2) | W(1)−P(1)−C(2) | 114(1) |

[a] Symmetry transformation used to generate equivalent atoms: (′) $x, -y + {}^1/_2, z$.

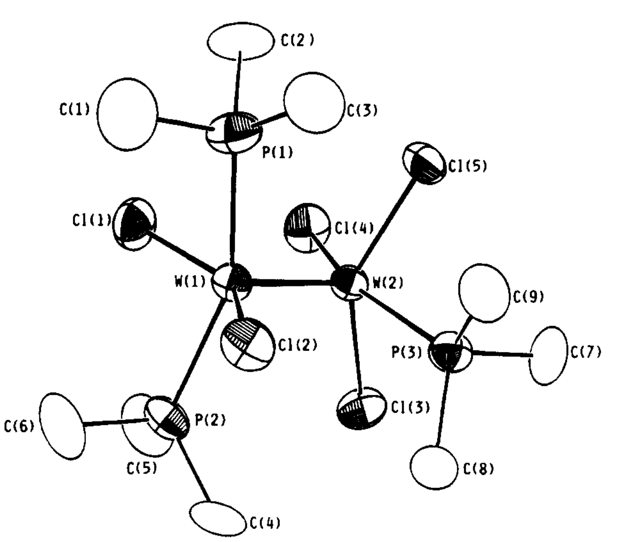

**Figure 1.** ORTEP drawing of the 1,3,6-$W_2Cl_5(PMe_3)_3$ molecule. Atoms are represented by thermal ellipsoids at the 50% probability level.

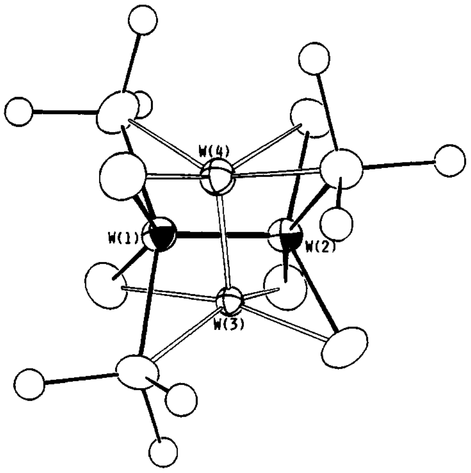

**Figure 2.** A drawing showing how the two orientations of the $W_2$ unit in 1,3,6-$W_2Cl_5(PMe_3)_3$ both conform to the same arrangement of ligands.

and carbon atoms were found from a subsequent least-squares refinement and a difference Fourier map. After anisotropic refinement, a second pair of W atoms (W(3) and W(4)), i.e., the second orientation of the W−W unit, was located. These atoms were included in the refinement, and their site occupancy factors (sof's) were allowed to vary against those of W(1) and W(2) but were constrained so that the sum of W atoms in the molecule equaled 2. The sof's converged to final values of 0.982 for W(1), W(2) and 0.018 for W(3), W(4). A total of 180 parameters were varied in the final anisotropic refinement for all atoms except W(3), W(4), and hydrogen atoms of the methyl groups, to give $R = 0.052$ (for 2295 reflections with $I > 2\sigma(I)$) and $R = 0.090$ (for all 3163 data). The highest peak in the final difference map was 2.3 e/Å$^3$, lying 1.03 Å from the W atom.

**$[HPMe_3]_2[W_2Cl_8PMe_3]\cdot CH_2Cl_2$ (3).** A block-shaped crystal having dimensions 0.18 × 0.10 × 0.10 mm$^3$ was selected and glued to the tip of glass fiber with epoxy cement. The data collection procedure at room temperature on the CAD-4 diffractometer was essentially the same as that for the crystal of **1**. A total of 2866 reflections in the range $4 \le \theta \le 50°$ were collected using an $\omega-2\theta$ scan technique. The centric space group $P2_1/m$ (rather than $P2_1$) was chosen and proved to be correct by successful refinement.

The positions of the two W atoms were determined from the Patterson map. Following least-squares refinements on the metal atom parameters, a difference Fourier map revealed the atoms of the coordination sphere of the $W_2$ unit and also the P atoms of trimethylphosphonium cations and the Cl atoms of the dichloromethane molecule. Subsequent least-squares refinement and a difference Fourier map then showed disorder in the $PMe_3$ ligand and also in the $(HPMe_3)^+$ cations. The occupancies of four carbon atoms in each of the trimethylphosphonium cations were set at 75%. Three sets of $Me_3$ groups were refined for the $PMe_3$ ligand. The two C−Cl distances in the $CH_2Cl_2$ molecule were constrained to be equal. All non-hydrogen atoms except the carbon atoms of the $PMe_3$ ligand and the dichloromethane molecule were refined with anisotropic thermal parameters. Final least-squares refinement of 148 parameters with 29 restraints resulted in $R = 0.045$ (for 1847 reflections with $I > 2\sigma(I)$) and $R = 0.109$ (for all 2866 data). The highest peak in the final difference map was 1.3 e/Å$^3$, lying 0.95 Å from the W atom.

## Results and Discussion

**1,3,6-$W_2Cl_5(PMe_3)_3$.** While the preparation of $[W_2Cl_4(PBu_3)_4]PF_6$ has been reported,[1b] there is no prior example of a structurally characterized complex containing the $W_2^{5+}$ core with a $\sigma^2\pi^4\delta$ configuration. In fact, there are relatively few known for $Mo_2^{5+}$ and there is no reported Mo analog of the present compound.

The compound shows a strong ESR signal when examined in the form of a solution in $CH_2Cl_2$ frozen to 10 K. The quasi-isotropic signal was centered at $g = 1.83$ but showed shoulders at $g \approx 1.78$ and $g \approx 1.90$, and the overall width at half-height was *ca.* 120 G. These results are consistent with the presence of one unpaired electron in a molecule with a rhombic **g** tensor, but no more detailed interpretation is possible. At higher temperatures, in fluid solution very complex hyperfine and superhyperfine structure was observed, but due to its complexity it has not been interpreted.

The structure of the molecule is depicted in Figure 1, and the important dimensions are presented in Table 3. A little reflection will show that it is possible to orient a 1,3,6-$M_2X_5(PR_3)_3$ molecule in each of three mutually perpendicular directions on a given site. In this case, such a disorder is observed but (a) with only two such orientations and (b) with one of them having only a very low occupancy, namely, 1.8%. This is shown in Figure 2.

The 1,3,6-$W_2Cl_5(PMe_3)_3$ molecule can be compared with other compounds in two ways. First, we note that there are three prior examples of this type of molecule. One is an exact analog, 1,3,6-$Re_2Cl_5(PMe_3)_3$, which is, in fact, crystallographi-

**Table 6.** Distances (Å) and Angles (deg) in 1,3,6-$M_2Cl_5(PR_3)_3$ (M = W, Re, Tc; $R_3$ = $Me_3$, $Et_3$, $Me_2Ph$) Compounds

| | 1,3,6- $W_2Cl_5(PMe_3)_3$ | 1,3,6-$Re_2Cl_5(PMe_3)_3$[8] | 1,3,6- $Re_2Cl_5(PEt_3)_3$[8] | 1,3,6-$Tc_2Cl_5(PMe_2Ph)_3$[13] |
|---|---|---|---|---|
| M−M′ | 2.291(1) | 2.218(1) | 2.221(2) | 2.1092(4) |
| M−Cl(av) | 2.349(5) | 2.348(4) | 2.392(8) | 2.349(1) |
| M−P (av) | 2.520(5) | 2.433(4) | 2.459(8) | 2.474(1) |
| M′−Cl(av) | 2.343(4) | 2.344(3) | 2.343(8) | 2.341(1) |
| M′−P | 2.536(5) | 2.444(3) | 2.430(6) | 2.465(1) |
| ∠P−M−P | 154.4(2) | 154.7(1) | 153.2(2) | 150.84(3) |
| M−M in $M_2X_4(PR_3)$ analog | 2.262(1)[7] | 2.247(1)[14] | 2.232(6)[15] | 2.127(1)[16] |
| Δ(M−M)[a] | 0.029(1) | −0.029(1) | −0.011(4) | −0.018(1) |

[a] Δ(M−M) = M−M distance in $M_2Cl_5(PR_3)_3$ minus that in $M_2Cl_4(PR_3)_4$

**Table 7.** Distances (Å) in FSBO Complexes of $[M_2Cl_{9-x}(PR_3)_x]^{(3-x)-}$ (M = W, Mo; *R* = Me, Et; *x* = 0, 1−3)

| | $[W_2Cl_8(PMe_3)]^{2-}$ | $[Mo_2Cl_8(PEt_3)]^{2-}$ [17] | $[W_2Cl_9]^{3-}$ [18] | $[W_2Cl_7(PEt_3)_2]^{-}$ [2] | $W_2Cl_6(PEt_3)_3$[2] |
|---|---|---|---|---|---|
| M−M | 2.433(1) | 2.767(2) | 2.4329(6) | 2.438(2) | 2.4705(7) |
| M−P | 2.505(5) | 2.557(3) | | 2.522(9) | 2.547(3) |
| $M-Cl_b$ | 2.474(4) | 2.469(3) | 2.490(3) | 2.494(9) | 2.492(3) |
| $M-Cl_t$ | 2.385(4) | 2.416(3) | 2.414(3) | 2.391(9) | 2.383(3) |

cally isostructural with the present tungsten compound.[8] The others are 1,3,6-$Re_2Cl_5(PEt_3)_3$[8] and 1,3,6-$Tc_2Cl_5(PMe_2Ph)_3$, which was only recently prepared in this laboratory.[13] Table 6 compares dimensions for these four molecules and also shows, for each one, how the M−M distance compares to that for each corresponding $M_2Cl_4(PR_3)_4$ compound. In all four $M_2Cl_5(PMe_3)_3$ compounds the M−M bond order is 3.5, but this is achieved in two ways. For the tungsten compound one $\delta$ electron is absent whereas in the other three compounds there is one $\delta^*$ electron in addition to two $\delta$ electrons. This is clearly why the W−W bond length increases (i.e., Δ(W−W) is about +0.03 Å) while the Re−Re bond length decreases (i.e., Δ(Re−Re) values are about −0.03 and −0.01 Å) on going from the $M_2Cl_4(PR_3)_4$ to the $M_2Cl_5(PR_3)_3$ compound. The Tc compound, as expected, behaves similarly to its Re analogs.

It is also interesting that, in all four compounds, the corresponding metal−ligand distances are not significantly different in the halves of the molecule, thus suggesting that the odd electron, be it a $\delta$ or a $\delta^*$ electron, is substantially delocalized over both metal atoms.

**$[HPMe_3]_2[W_2Cl_8(PMe_3)]\cdot CH_2Cl_2$.** This compound provides only the second example of a face-sharing bioctahedral complex of the type $[M_2X_8L]^{n-}$, the other being a molybdenum analog of this one, $[Mo_2Cl_8(PEt_3)]^{2-}$ recently reported.[17] The compound in $CH_2Cl_2$ solution has $^{31}P$ NMR signals at 34.1 ppm (with $J_{W-P}$ = 172 MHz) and 16.5 ppm, due respectively to the $PMe_3$ in the anion and the $HPMe_3^+$ ion. The dimensions of the $[W_2Cl_8(PMe_3)]^{2-}$ anion are compared with those of the molybdenum species as well as with related ditungsten species, $[W_2Cl_9]^{3-}$,[18] $[W_2Cl_7(PEt_3)_2]^-$,[2] and $[W_2Cl_6(PEt_3)_3]^2$ in Table 7.

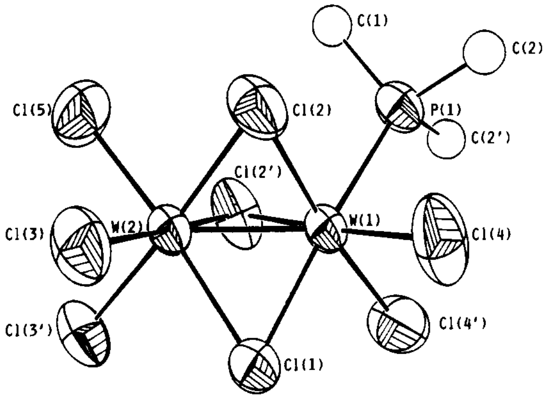

**Figure 3.** ORTEP drawing of the $[W_2Cl_8(PMe_3)]^{2-}$ anion in compound **3**. Atoms are represented by thermal ellipsoids at the 50% probability level.

The relationships are entirely as expected. The W−W distance is more than 0.3 Å shorter than the Mo−Mo distance, in accord with the usual tendency of tungsten to form stronger metal−metal bonds in bioctahedral complexes. Moreover, the W−W distances in the three species $[W_2Cl_9]^{3-}$, $[W_2Cl_8(PMe_3)]^{2-}$, and $[W_2Cl_7(PEt_3)_2]^-$ are not significantly different (2.4329(6), 2.433(1), and 2.438(2) Å, respectively) although in $W_2Cl_9(PEt_3)_3$ there is a slight increase to 2.4705(7) Å.

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**Supporting Information Available:** Tables of crystal data and structure refinement parameters, complete bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters (17 pages). Ordering information is given on any current masthead page.

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