Registry No. 1, 126295-57-6; 2, 130698-84-9; 3, 130698-85-0; 4, 126327-44-4; $[W(CO)_3(\eta^6-C_7H_8)]$, 12128-81-3; *mer*-$[W_2(CO)_6(L_2)_2(\mu-L_2)]$, 126295-42-9; *mer*-$[W(CO)_3(\eta^2-L_2)(\eta^1-L_2)]$, 126295-43-0; *cis*-$[W(CO)_4(L'_2)]$, 130698-86-1.

Supplementary Material Available: A view of the complete molecule and tables of calculated hydrogen atom positions, bond distances, interbond angles, anisotropic thermal parameters, and root-mean-square amplitudes of anisotropic displacement (13 pages); a listing of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

Preparation and Structure of $[Cl_2W(\mu-Cl)(\mu-dmpm)_2(\mu_2-PMe_2)WCl(\eta^2-CH_2PMe_2)]Cl$, a Product of an Unusual Cleavage of the dmpm Ligand

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Received April 9, 1990

Summary: The title compound $[Cl_2W(\mu-Cl)(\mu-dmpm)_2(\mu_2-PMe_2)WCl(\eta^2-CH_2PMe_2)]Cl$, **1**, is obtained when $W_2Cl_4(PBu_3)_4$ is treated with $Me_2PCH_2PMe_2$, dmpm, in a toluene–hexane mixture at reflux for 4 h. The compound has been characterized on the basis of ^1H and $^{31}P\{^1H\}$ NMR and IR spectra and electrochemical and electronic absorption properties and by analysis. A magnetic susceptibility measurement confirms that the complex contains one unpaired electron. The EPR spectrum exhibits hyperfine coupling, $g = 1.963$, $a_p = 30$ G (2.75×10^{-3} cm^{-1}). Hyperfine coupling to ^{183}W was not resolved. Red platelike crystals of composition $1 \cdot CH_2Cl_2$ grown by layering a dichloromethane solution of **1** with *n*-hexanes have been studied by X-ray crystallography: space group $P2_1/n$, $a = 8.852$ (2) Å, $b = 12.512$ (2) Å, $c = 31.341$ (6) Å, $\beta = 93.65$ (2)°, $V = 3464$ (2) Å^3, $Z = 4$. The $[Cl_2W(\mu-Cl)(\mu-dmpm)_2(\mu_2-PMe_2)WCl(\eta^2-CH_2PMe_2)]^+$ ion is an edge-sharing bioctahedron with bridging dmpm molecules above and below a central plane consisting of $Cl_2W(\mu-Cl)(\mu-PMe_2)W'Cl(CH_2PMe_2)$. The W–W' distance is 2.7331 (6) Å, and the μ-PMe_2 ligand is slightly unsymmetrical (W–P = 2.341 (3) Å; W'–P = 2.414 (3) Å). The η^2-Me_2PCH_2 ligand has W'–P = 2.448 (3) Å, W'–C = 2.28 (1) Å, P–C = 1.74 (1) Å, and P–W'–C = 43.0 (3)°.

The ligands $Ph_2PCH_2PPh_2$ (dppm) and $Me_2PCH_2PMe_2$ (dmpm) are well-known, are widely used, and display a variety of coordination modes.[1,2] In general they are preferred as bridging ligands to stabilize binuclear and cluster species, and they are assumed to be chemically inert. The work described here provides an example of where the dmpm ligand, far from being inert, undergoes P–C bond cleavage under mild conditions.

Our interest in the title compound began several years ago when we sought to prepare $W_2Cl_4(dmpm)_2$ by reaction of $W_2Cl_4(PBu_3)_4$ with dmpm.[3] Together with this green compound, we obtained some red crystals, which were not at the time characterized. In an effort to identify and characterize the red product, the mixture of green and red crystals was dissolved in CH_2Cl_2, and the solution was filtered and then layered with *n*-hexanes. At first some green crystals formed, and these were removed by filtration. The solution was then reduced to about one-third of its initial volume and again layered with *n*-hexanes. This led to the deposition of yellow and red crystalline material. The smallest crystals looked yellow, and the larger red crystals when crushed gave a yellow powder.

The red platelike crystals obtained in the way just described were shown by X-ray crystallography[4] to contain the title molecule. In addition, these crystals contain interstitial molecules of CH_2Cl_2 and possibly *n*-hexanes, and because of the difficulty of modeling these, the structure never refined as well as we desired. However, in the course of developing the improved preparative procedure reported here, we also obtained a different crystalline form in which only interstitial CH_2Cl_2 molecules were present, and this did refine to reasonable figures of merit. We thus report the latter structure in detail here together with the usual spectroscopic measurements.

Experimental Section

Reactions and manipulations were performed under dry nitrogen by using Schlenk techniques. Solvents were freshly distilled prior to use. Bis(dimethylphosphino)methane was purchased from Strem Chemicals, Inc. $W_2Cl_4(PBu_3)_4$ (Bu = *n*-C_4H_9) was prepared by a literature method.[6] The IR spectrum was recorded as a Nujol mull by using a Perkin-Elmer 783 infrared spectrophotometer. The ^1H NMR spectrum was recorded on a Varian XL200 spectrometer in acetone-d_6 and CD_2Cl_2, and a Varian EM390 spectrometer was used to do the measurement of the magnetic susceptibility with the Evans method.[5] This consisted of a 0.016 M solution of complex 1 in CD_2Cl_2 with C_6H_6 as the indicator placed inside a glass capillary, under Ar, sealed, and placed inside a 5-mm NMR tube contained CD_2Cl_2 and C_6H_6. The difference between the two proton resonances for the different C_6H_6 environments was 5.43 Hz. Attempts to record the $^{31}P\{^1H\}$ NMR spectrum were carried out on a Varian XL400 spectrometer. Electrochemical measurements were carried out with a Bioanalytical Systems Inc. Model 100 electrochemical analyzer in a dichloromethane solution that contained ca. 0.2 M tetra-*n*-butylammonium tetrafluoroborate (TBATFB) as the supporting electrolyte. A Pt-bead working electrode and a Pt-wire auxiliary electrode were utilized. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature

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(1) Puddephatt, R. *J. Chem. Soc. Rev.* **1983**, *12*, 99.

(2) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.

(3) Canich, J. A. M.; Cotton, F. A. Daniels, L. M.; Lewis, D. B. *Inorg. Chem.* **1987**, *26*, 4046.

(4) Space group $P2_1/n$ with $a = 13.476$ (3) Å, $b = 14.080$ (3) Å, $c = 21.735$ (6) Å, and $\beta = 107.25$ (2)°.

(5) Evans, D. F.; James, T. A. *J. Chem. Soc., Dalton Trans* **1979**, *723*.

(6) Schrock, R. R.; Sturgeoff, L. G.; Sharp, P. R. *Inorg. Chem.* **1983**, *22*, 2801.

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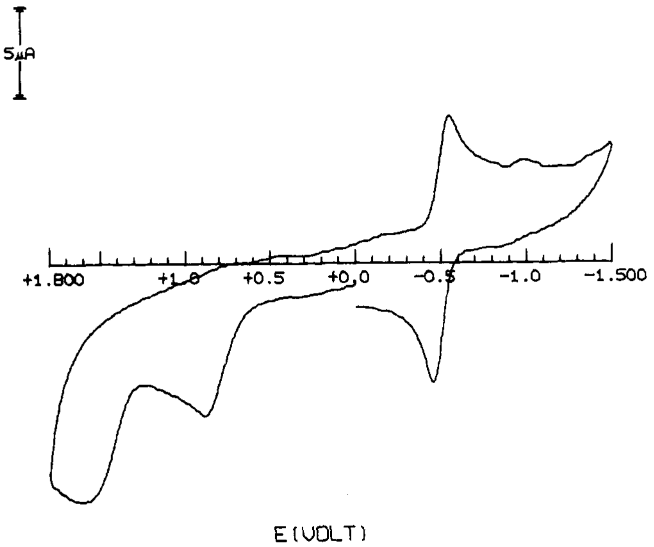

Figure 1. Cyclic voltammogram of 1 in a 0.2 M TBATBF–CH_2Cl_2 solution referenced against a Ag/AgCl electrode at 200 mV/s.

and are uncorrected for junction potentials. The ferrocenium/ferrocene couple is at $E_{1/2}$ = +0.47 V vs Ag/AgCl under these conditions. The visible absorption spectrum was recorded on a Cary 17D spectrophotometer in a CH_2Cl_2 solution. The EPR spectrum of 1 was recorded in a CH_2Cl_2/toluene, 1:1 ratio, glass at liquid nitrogen temperatures with an X-band IBM ER 200D-SRC instrument operating at 9.34 GHz. The elemental analysis was done by Galbraith Laboratories, Inc., Knoxville, TN.

Preparation. To 0.45 g (0.34 mmol) of $W_2Cl_4(PBu_3)_4$ dissolved in a mixture of 10 mL of toluene and 20 mL of *n*-hexanes was added 0.16 mL (1.02 mmol) of dmpm. The reaction mixture was stirred for $^1/_2$ h at room temperature and then refluxed for 4 h to give a dark red solid. After cooling to room temperature, the red solid was filtered, washed with *n*-hexanes (2 × 15 mL), toluene (2 × 15 mL), and ether (2 × 15 mL), and then vacuum dried. There was no sign of bluish green $W_2Cl_4(dmpm)_2$. The red solid was dissolved in dichloromethane and layered with *n*-hexanes. Red platelike crystals of the title compound were obtained (yield 0.29 g, 48%). Anal. Calcd for $W_2Cl_5P_6C_{15}H_{42}$: total Cl, 18.59; anionic $[Cl]^-$, 3.72; C, 18.90; H, 4.40. Found: total Cl, 17.88; anionic $[Cl]^-$, 6.03; C, 17.59; H, 4.02. The ^1H and $^{31}P\{^1H\}$ NMR spectra are discussed in the Results section. The cyclic voltammogram on a solution of 1 in 0.2 M TBATFB–CH_2Cl_2, Figure 1, consists of a reversible reduction at $E_{1/2}$ = −0.63 V and irreversible oxidations at $E_{p,a}$ = +0.76 V and $E_{p,a}$ = +1.47 V vs Ag/AgCl. The visible spectrum of 1 in CH_2Cl_2 consisted of a broad absorption at 800 nm and a very intense sharp absorption at 445 nm. IR (Nujol mull, cm^{-1}): 1295 w, 1280 m, 1260 w, 1150 w, 915 sh, 900 sh, 850 br, 770 br, 740 m, 720 m, 680 m, 650 br. μ_{obs} = 1.765 μ_B. The EPR spectrum is shown in Figure 2.

Crystallography. A platelike crystal of $[W_2Cl_4(dmpm)_2(PMe_2)(PMe_2CH_2)]Cl\cdot CH_2Cl_2$ was mounted at the tip of a quartz fiber with low-temperature halocarbon grease. Geometric and intensity data were gathered with an Enraf-Nonius CAD-4 diffractometer equipped with a low-temperature device by following the procedures described previously.[7] Pertinent crystallographic data are given in Table I. Lattice dimensions and Laue symmetry were verified by axial photographs. From systematic absences, the space group was uniquely determined as $P2_1/n$. Intensity data, gathered by the ω-scan method, were reduced by routine procedures.[8] Absorption corrections were applied, based on azimuthal scans of several reflections with the diffractometer angle χ near 90°.[9]

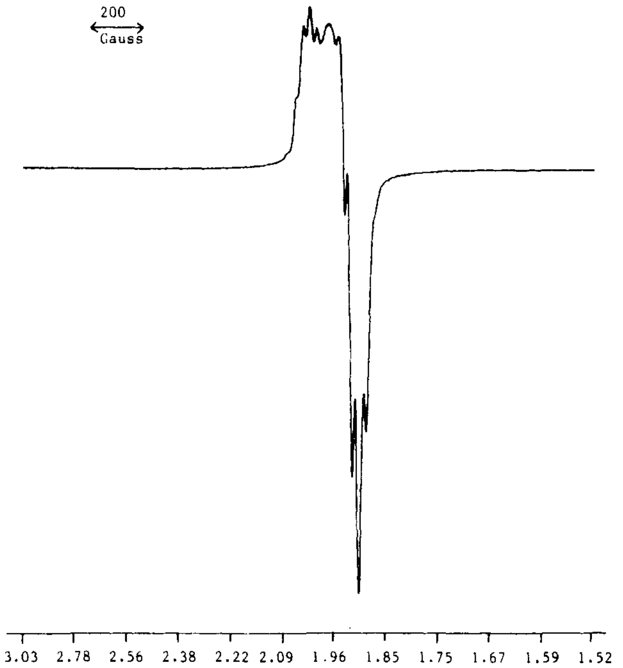

Figure 2. X-band EPR spectrum of 1 at 77 K; solvent = CH_2Cl_2/toluene, 1:1; frequency = 9.34 GHz.

Table I. Crystal Data for $[W_2Cl_4(dmpm)_2(PMe_2)(PMe_2CH_2)]Cl\bullet CH_2Cl_2$

formula	$W_2Cl_7P_6C_{16}H_{44}$
fw	1038.24
space group	$P2_1/n$
syst absences	($h0l$) $h + l = 2n + 1$; ($0k0$) $k = 2n + 1$
a, Å	8.852 (2)
b, Å	12.512 (2)
c, Å	31.341 (6)
α, deg	90
β, deg	93.65 (2)
γ, deg	90
V, Å^3	3464 (2)
Z	4
d_{calc}, g/cm^3	1.991
cryst size, mm	0.40 × 0.25 × 0.10
μ(Mo Kα), cm^{-1}	76.1
data collecn instrument	Enraf-Nonius CAD-4
radiation monochromated in incident beam (λ, Å)	Mo Kα (0.71073)
orientation reflns: no., range, deg	25, 21.4 ≤ 2θ ≤ 29.9
temp, °C	−80 ± 1
scan method	ω
data collecn range, deg	4 ≤ 2θ ≤ 50
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	5672, 4754
no. of params refined	254
transmissn factors, %: max, min	99.99, 26.96
R^a	0.044
R_w^b	0.061
quality-of-fit indicator^c	1.410
largest shift/esd, final cycle	0.005
largest peak, e/Å^3	2.095

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 0.460/[\sigma^2(|F_o|) + 0.001(|F_o|)^2]$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

The heavy atoms of the formula unit $[Cl_2W(\mu\text{-}Cl)(\mu\text{-}dmpm)_2(\mu_2\text{-}PMe_2)WCl(\eta^2\text{-}CH_2PMe_2)]Cl$ were located by the Patterson method with the XS-86 program.[8] The remainder were located in a series of least-squares refinements and difference maps. The atoms of the two solvent CH_2Cl_2 molecules, each with site occupancy of $^1/_2$, were found by an alternating sequence of

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[7] Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

[8] Calculations were done by using a Micro-Vax II (Micro VMS V4.6) with the programs SHELXS-86, SHELX-76, and the commercial package SDP/V V3.0.

[9] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

Table II. Positional Parameters, Equivalent Isotropic Thermal Parameters (Å^2), and Their Estimated Standard Deviations for $[Cl_2W(\mu\text{-}Cl)(\mu\text{-}PMe_2)(\mu\text{-}dmpm)_2WCl(CH_2PMe_2)][Cl] \cdot CH_2Cl_2$[a]

atom	x	y	z	B, Å^2
W(1)	0.39023 (4)	0.02212 (4)	0.12662 (1)	1.183 (9)
W(2)	0.48296 (4)	0.17344 (4)	0.18549 (1)	1.26 (1)
Cl(1)	0.4996 (3)	−0.1015 (3)	0.07543 (9)	2.08 (6)
Cl(2)	0.3745 (3)	0.2927 (3)	0.2371 (1)	2.52 (7)
Cl(3)	0.7220 (3)	0.2559 (3)	0.2144 (1)	2.32 (6)
Cl(4)	0.6494 (3)	0.0887 (2)	0.13892 (9)	1.64 (5)
P(1)	0.5105 (3)	−0.1215 (3)	0.1763 (1)	1.63 (5)
P(2)	0.5345 (3)	0.0430 (3)	0.2467 (1)	1.75 (6)
P(3)	0.4099 (3)	0.1542 (3)	0.06435 (9)	1.65 (6)
P(4)	0.4840 (3)	0.3261 (3)	0.1314 (1)	1.83 (6)
P(5)	0.2293 (3)	0.1272 (3)	0.16973 (9)	1.55 (6)
P(6)	0.1470 (3)	−0.0265 (3)	0.0903 (1)	1.75 (6)
C(1)	0.445 (1)	−0.259 (1)	0.1705 (4)	2.6 (3)
C(2)	0.715 (1)	−0.143 (1)	0.1747 (4)	2.4 (3)
C(3)	0.484 (1)	−0.092 (1)	0.2328 (4)	2.1 (3)
C(4)	0.729 (1)	0.033 (1)	0.2662 (4)	2.8 (3)
C(5)	0.441 (1)	0.065 (1)	0.2953 (4)	3.1 (3)
C(6)	0.276 (1)	0.141 (1)	0.0185 (4)	2.5 (3)
C(7)	0.592 (1)	0.152 (1)	0.0400 (4)	2.2 (3)
C(8)	0.387 (1)	0.293 (1)	0.0801 (4)	1.9 (2)
C(9)	0.671 (1)	0.371 (1)	0.1165 (4)	2.5 (3)
C(10)	0.400 (2)	0.448 (1)	0.1473 (5)	3.3 (3)
C(11)	0.099 (1)	0.237 (1)	0.1532 (4)	2.3 (3)
C(12)	0.119 (1)	0.069 (1)	0.2108 (4)	2.5 (3)
C(13)	0.125 (1)	−0.107 (1)	0.0417 (4)	2.7 (3)
C(14)	−0.035 (1)	0.038 (1)	0.0928 (5)	3.3 (3)
C(15)	0.207 (1)	−0.103 (1)	0.1344 (4)	2.0 (3)
Cl(5)	0.9804 (4)	0.3089 (3)	0.0466 (1)	3.20 (8)
C(32)[b]	0.5749	0.0943	0.4386	6
Cl(31)[c]	0.4220	0.1198	0.4056	3
Cl(32)[c]	0.7268	0.1589	0.4216	7
C(42)[b]	0.7731	0.0003	0.5010	7
Cl(41)[c]	0.8270	0.0944	0.4643	8
Cl(42)[d]	1.2041	0.0900	0.4571	4
Cl(43)[d]	1.0745	0.0663	0.4736	3

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3$-$[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. [b–d] Represent sites modeled as 0.5 C, 0.5 Cl, and 0.25 Cl, respectively.

least-squares refinements and difference Fourier maps. The chlorine atoms of solvent CH_2Cl_2 containing C(42) were found to be disordered over two sites. Cl(41) was refined as 0.5Cl because its two sites could not be resolved satisfactorily in the refinement. Constraints on the interatomic distances of the solvent molecules were added in the least-squares calculations. After convergence of isotropic refinement of all the non-hydrogen atoms, additional absorption corrections were applied according to the method of Walker and Stuart.[10] Then all of the hydrogen atoms (except those on the disordered CH_2Cl_2 solvent molecule) were inserted at calculated positions and their thermal parameters were all constrained to one value, which was refined.

The final cycles of refinement were done with anisotropic thermal parameters for all non-hydrogen atoms, except for those of the disordered solvent molecule, which were refined as a fixed model, and with the H atoms represented as described above. This resulted in a data-to-parameter ratio of 18.7 and residuals of $R = 0.044$ and $R_w = 0.061$. In the final difference Fourier map, there were 16 peaks above 1 e/Å^3. The first five peaks were located near to the solvent atoms, and the remaining ones were near atoms of the main molecule. Table II lists the atomic positional parameters for the non-hydrogen atoms.

Results

Preparation and Spectroscopic Characterizations. The title molecule was first obtained as a byproduct in a reaction of $W_2Cl_4(PBu_3)_4$ with dmpm in a 1:2 mole ratio, where the intended product was $W_2Cl_4(dmpm)_2$. It was found that by employing a 1:3 mole ratio the title compound could be made the major and only isolated product. To this extent, the preparation is a rational one. However, there is still no explanation of how or why there is further oxidation, beyond that attributable to oxidative addition of $Me_2PCH_2PMe_2$ (eq 1), as represented formally by eq 2.

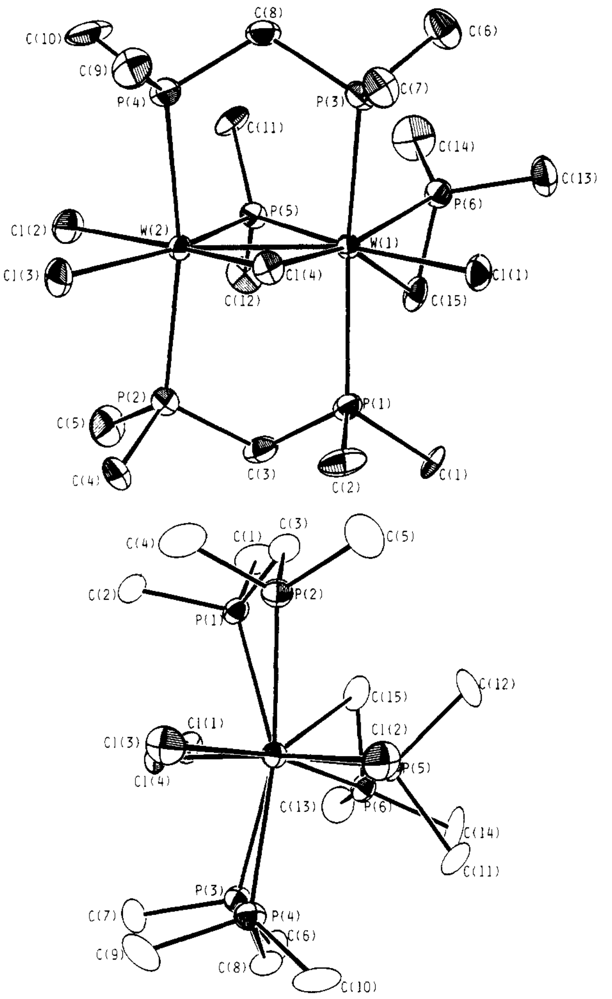

Figure 3. ORTEP diagrams of the $[W_2Cl_4(dmpm)_2(PMe_2)(PMe_2CH_2)]^+$ ion. (a, top) View showing the W–W bond. (b, bottom) View along the W–W bond showing the boat conformation. W(1) is covered by W(2).

$$W_2Cl_4(dmpm)_2 + dmpm \rightarrow W_2Cl_4(dmpm)_2(PMe_2)(Me_2PCH_2) \quad (1)$$

$$W_2Cl_4(dmpm)_2(PMe_2)(PMe_2CH_2) \rightarrow [W_2Cl_4(dmpm)_2(PMe_2)(PMe_2CH_2)]^+ \quad (2)$$

The compound was found to be slightly oxygen and moisture sensitive, and all manipulations were thus conducted under inert atmospheres. The ^1H NMR spectrum in acetone solution showed strong but broad singlets at about 2.88 and 2.90 ppm in roughly a 6:1 ratio. These were embedded in an array of weaker, broad peaks running from 2.83 to 2.91 ppm. This unusual spectrum presumably results in part from the paramagnetism of the cation and may be influenced as well by ion pairing and by some decomposition. The ^1H NMR spectrum in CD_2Cl_2, submitted as supplementary material, was equally complicated and consisted of broad signals at δ 1.60, 1.95, 2.38, and a sharp resonance at δ 1.10, and these were located on a broad bump ranging from δ 0.80 to 2.50. This complexity is not doubt due to paramagnetism in 1. There were no

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[10] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

Table III. Bond Distances (Å) and Angles (deg) for $[Cl_2W(\mu\text{-}Cl)(\mu\text{-}PMe_2)(\mu\text{-dmpm})_2WCl(CH_2PMe_2)][Cl]$[a]

Distance

W(1)-W(2)	2.7331 (6)	W(2)-P(2)	2.538 (3)	P(3)-C(8)	1.82 (1)
W(1)-Cl(1)	2.470 (3)	W(2)-P(4)	2.554 (3)	P(4)-C(8)	1.82 (1)
W(1)-Cl(4)	2.448 (2)	W(2)-P(5)	2.341 (3)	P(4)-C(9)	1.83 (1)
W(1)-P(1)	2.564 (3)	P(1)-C(1)	1.82 (1)	P(4)-C(10)	1.79 (1)
W(1)-P(3)	2.572 (3)	P(1)-C(2)	1.84 (1)	P(5)-C(11)	1.84 (1)
W(1)-P(5)	2.414 (3)	P(1)-C(3)	1.84 (1)	P(5)-C(12)	1.82 (1)
W(1)-P(6)	2.448 (3)	P(2)-C(3)	1.80 (1)	P(6)-C(13)	1.83 (1)
W(1)-C(15)	2.28 (1)	P(2)-C(4)	1.80 (1)	P(6)-C(14)	1.81 (1)
W(2)-Cl(2)	2.442 (3)	P(2)-C(5)	1.80 (1)	P(6)-C(15)	1.74 (1)
W(2)-Cl(3)	2.474 (3)	P(3)-C(6)	1.81 (1)		
W(2)-Cl(4)	2.387 (3)	P(3)-C(7)	1.83 (1)		

Angle

W(2)-W(1)-Cl(1)	139.38 (6)	W(1)-W(2)-Cl(4)	56.63 (6)	C(3)-P(2)-C(5)	103.3 (6)
W(2)-W(1)-Cl(4)	54.54 (7)	W(1)-W(2)-P(2)	95.55 (7)	C(4)-P(2)-C(5)	101.9 (6)
W(2)-W(1)-P(1)	88.85 (7)	W(1)-W(2)-P(4)	94.81 (7)	W(1)-P(3)-C(6)	118.0 (4)
W(2)-W(1)-P(3)	92.02 (7)	W(1)-W(2)-P(5)	56.19 (8)	W(1)-P(3)-C(7)	114.2 (4)
W(2)-W(1)-P(5)	53.67 (7)	Cl(2)-W(2)-Cl(3)	82.3 (1)	W(1)-P(3)-C(8)	113.2 (4)
W(2)-W(1)-P(6)	134.73 (8)	Cl(2)-W(2)-Cl(4)	163.8 (1)	C(6)-P(3)-C(7)	102.5 (5)
W(2)-W(1)-C(15)	126.1 (3)	Cl(2)-W(2)-P(2)	87.2 (1)	C(6)-P(3)-C(8)	103.0 (6)
Cl(1)-W(1)-Cl(4)	85.02 (9)	Cl(2)-W(2)-P(4)	90.1 (1)	C(7)-P(3)-C(8)	104.3 (6)
Cl(1)-W(1)-P(1)	78.0 (1)	Cl(2)-W(2)-P(5)	83.0 (1)	W(2)-P(4)-C(8)	113.3 (4)
Cl(1)-W(1)-P(3)	82.0 (1)	Cl(3)-W(2)-Cl(4)	82.10 (9)	W(2)-P(4)-C(9)	116.0 (4)
Cl(1)-W(1)-P(5)	166.93 (9)	Cl(3)-W(2)-P(2)	83.3 (1)	W(2)-P(4)-C(10)	116.0 (5)
Cl(1)-W(1)-P(6)	84.9 (1)	Cl(3)-W(2)-P(4)	83.8 (1)	C(8)-P(4)-C(9)	103.0 (5)
Cl(1)-W(1)-C(15)	87.1 (3)	Cl(3)-W(2)-P(5)	165.3 (1)	C(8)-P(4)-C(10)	104.9 (6)
Cl(4)-W(1)-P(1)	78.11 (9)	Cl(4)-W(2)-P(2)	95.1 (1)	C(9)-P(4)-C(10)	102.0 (6)
Cl(4)-W(1)-P(3)	78.04 (9)	Cl(4)-W(2)-P(4)	84.2 (1)	W(1)-P(5)-W(2)	70.14 (7)
Cl(4)-W(1)-P(5)	107.89 (9)	Cl(4)-W(2)-P(5)	112.5 (1)	W(1)-P(5)-C(11)	128.9 (4)
Cl(4)-W(1)-P(6)	161.0 (1)	P(2)-W(2)-P(4)	167.02 (9)	W(1)-P(5)-C(12)	122.7 (5)
Cl(4)-W(1)-C(15)	152.0 (3)	P(2)-W(2)-P(5)	97.2 (1)	W(2)-P(5)-C(11)	116.6 (4)
P(1)-W(1)-P(3)	149.95 (9)	P(4)-W(2)-P(5)	95.1 (1)	W(2)-P(5)-C(12)	120.2 (4)
P(1)-W(1)-P(5)	106.2 (1)	W(1)-Cl(4)-W(2)	68.82 (7)	C(11)-P(5)-C(12)	98.3 (6)
P(1)-W(1)-P(6)	115.3 (1)	W(1)-P(1)-C(1)	119.0 (4)	W(1)-P(6)-C(13)	124.7 (4)
P(1)-W(1)-C(15)	74.0 (3)	W(1)-P(1)-C(2)	117.2 (4)	W(1)-P(6)-C(14)	128.9 (5)
P(3)-W(1)-P(5)	98.4 (1)	W(1)-P(1)-C(3)	111.8 (4)	W(1)-P(6)-C(15)	63.2 (4)
P(3)-W(1)-P(6)	84.6 (1)	C(1)-P(1)-C(2)	99.7 (6)	C(13)-P(6)-C(14)	103.7 (6)
P(3)-W(1)-C(15)	127.3 (3)	C(1)-P(1)-C(3)	103.0 (6)	C(13)-P(6)-C(15)	111.7 (6)
P(5)-W(1)-P(6)	82.1 (1)	C(2)-P(1)-C(3)	104.0 (5)	C(14)-P(6)-C(15)	116.2 (6)
P(5)-W(1)-C(15)	82.3 (3)	W(2)-P(2)-C(3)	113.1 (4)	P(1)-C(3)-P(2)	112.1 (6)
P(6)-W(1)-C(15)	43.0 (3)	W(2)-P(2)-C(4)	115.0 (5)	P(3)-C(8)-P(4)	113.5 (6)
W(1)-W(2)-Cl(2)	139.17 (7)	W(2)-P(2)-C(5)	118.0 (5)	W(1)-C(15)-P(6)	73.8 (4)
W(1)-W(2)-Cl(3)	138.54 (7)	C(3)-P(2)-C(4)	103.8 (6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

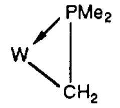
resonances observed in the $^{31}P\{^1H\}$ NMR experiment, which is a further indication of the paramagnetic property of 1.

Complex 1 can be reversibly reduced ($W_2^{7+} + e^- \Leftrightarrow W_2^{6+}$) as is shown in the cyclic voltammogram, Figure 1. No attempts were made to isolate the reduced (W_2^{6+}) species. The visible absorption spectrum of 1 in CH_2Cl_2 consisted of a broad band at 800 nm and a sharp, intense one at 445 nm. The precise assignment of the absorption at 800 nm is not possible as the nature of the HOMO is ambiguous for this complex; see below. In the solution state and at room temperature, 1 exhibits an effective magnetic moment consistent with one unpaired electron (Evans' method).[5]

In the earlier work,[4] crystals of larger unit cell volume (3938 (3) Å^3) were obtained whereas later the more compact crystals of $1\cdot CH_2Cl_2$ were formed. The question of which crystal form is obtained seems to depend on the relative amounts of *n*-hexanes (a mixture of isomers) and CH_2Cl_2 that are present in the solvent from which the crystals grow. It must be acknowledged that in each case some crystals of each type may have been present, but we looked at only one crystal from each batch.

Structural and EPR Results. The structure of the binuclear cation is depicted in Figure 3. It is a somewhat distorted edge-sharing bioctahedron. The central four-membered ring is essentially planar. The W(1)-W(2) distance of 2.7331 (6) Å and the angles (obtuse P-W-Cl angles of 107.89 (9)° and 112.5 (1)° with acute W-P-W and W-Cl-W angles of 70.14 (7)° and 68.82 (7)°) are consistent with strong W-W bonding. The principal bond distances and angles are listed in Table III.

The Me_2PCH_2 moiety is bonded to W(1) through both the P atom and the CH_2 carbon atom, C(15), and occupies one of the in-plane terminal ligand positions. The W(1)-P(6) distance, 2.448 (3) Å, is considerably shorter than those to the normal dmpm phosphorus atoms, while the W(1)-C(15) distance is roughly that expected for a W-C bond. Thus, the bonding of the Me_2PCH_2 moiety to W(1) can probably be satisfactorily described by the schematic drawing I. The W(1)-P(6)-C(15) ring plane is nearly perpendicular (93.7 (3)°) to the mean plane of the central W(1)-P(5)-W(2)-Cl(4) ring.



I

The coordination about each tungsten atom shows some notable distortions from octahedral, especially about W(1). This can best be seen in Figure 3b, which is a projection down the W-W axis with W(2) above and W(1) behind it. The central plane is, indeed, a near-perfect plane and the P(2)-W(2)-P(4) chain is nearly linear and nearly perpendicular to it. The P(1)-W(1)-P(3) chain is severely bent

(150°) so as to move the two PMe_2 groups away from the bulky Me_2PCH_2 ligand.

In general, all the distances that can be compared with those in $W_2Cl_6(dmpm)_2$[3] are very similar except for the W–W distance, which is only 2.666 Å in the latter case as compared to 2.733 Å here. One obvious reason for this is the higher mean oxidation state of the metal atoms here, although the replacement of two Cl ligands by μ-Me_2P and Me_2PCH_2 may have an influence that is not known.

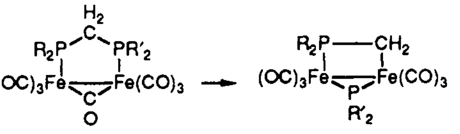
The Cl^- ions, Cl(5) in Table II, are surrounded by CH_3 and CH_2 groups and by CH_2Cl_2 molecules in an irregular but global way.

The EPR spectrum, displayed as Figure 2, exhibits hyperfine coupling with $g = 1.963$ and $a_p = 30$ G (2.75×10^{-3} cm^{-1}). Coupling to ^{183}W ($I = {}^1/_2$, 14%) was not resolved under the experimental conditions. This complex, as is evident from the solid-state structure, has no symmetry, and thus, the coupling to the ^{31}P ($I = {}^1/_2$, 100%), ^{35}Cl ($I = {}^3/_2$, 75.4%) and ^{37}Cl ($I = {}^3/_2$, 24.6%) nuclei will be very difficult to interpret. The EPR spectrum of **1** displays at least a nine-line pattern, and this pattern is not symmetrical. It is likely that, for reasons discussed above, the electron is located in a δ or δ^* orbital and thus delocalized over both W atoms, and the spectrum can thus be considered to be a complex composite of overlapping patterns due to coupling with all the spin-active nuclei.

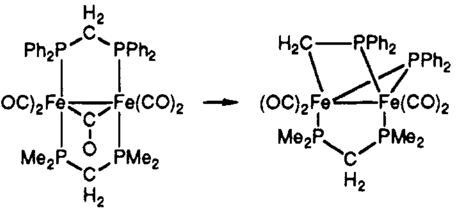
Discussion

There are three features of particular interest about the chemistry and structure of the compound described here: (1) the scission of the dmpm molecule into two fragments that are retained separately as ligands; (2) the occurrence of one fragment, Me_2P, as a bridge; (3) the occurrence of the other fragment, H_2CPMe_2, as a η^2 ligand. While none of these features is itself unprecedented, this particular combination is unique.

The closest parallels to our observations were reported in 1986, where the following reactions[11] are described:



R = R′ = CH_3
R = R′ = Ph
R = Ph; R′ = CH_3



Both of these reactions were said to proceed smoothly in boiling tetrahydrofuran or boiling toluene in good yields. It was suggested that CO loss is actually the rate-determining step, so that the P–C bond cleavage may be even more facile than these reaction conditions would imply. The most obvious difference between the products of these reactions and ours is that the R_2PCH_2 ligand is μ_2-η^2 in the diiron compounds and simply η^2 in our case.

Other cleavages of the dppm ligand under aqueous basic conditions to generate Ph_2PCH_3 and Ph_2POH as monodentate ligands[12] or in liquid ammonia to generate Ph_2PMe and Ph_2PO as monodentate ligands[13] have very little to do with the present case but are mentioned for the sake of completeness.

As for features (2) and (3) cited above, the occurrence of μ_2-R_2P ligands is, of course, so common as to require no comment. The R_2PCH_2 type of ligand, while not extremely common, is well-known in both η^2 and μ_2-η^2 forms.[14]

The formal oxidation state of the tungsten atoms is W_2^{7+}, leaving five electrons to be involved in the W–W bonding scheme. This is consistent with the short W–W distance since we may envision double bonding based on a $\sigma^2\pi^2$ configuration together with a slight strengthening or weakening depending on whether the fifth electron resides in a δ or a δ^* orbital.

The formation of the title compound in good yield under relatively mild conditions, together with the previous observations of Doherty et al.,[11] clearly shows that, whenever there are metal centers susceptible to oxidation addition, the $R_2PCH_2PR_2$-type ligand cannot be regarded as simply an inert bidentate ligand but must be considered as a potential oxidative addition reagent, by virtue of the formal process in eq 3. A more general message may be that P–C

$$R_2PCH_2PR_2 \rightarrow R_2P^\bullet + R_2PCH_2^\bullet \qquad (3)$$

bond cleavage may well occur in other phosphine ligands and that there may be reactions of this type in the literature which have not been recognized as such.

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Supplementary Material Available: Figures depicting the ^1H NMR spectrum of **1** in CD_2Cl_2 and a stereoview of the unit cell packing and tables of calculated H atom positions, bond distances, bond angles, and anisotropic displacement parameters (10 pages); a table listing observed and calculated structure factors for **1** (26 pages). Ordering information is given on any current masthead page.

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