



$W_2Cl_4(NR_2)_2(PR'_3)_2$ molecules—9. New mixed valent W^{III}/W^{IV} face-sharing bioctahedral complexes with chelating bis(diphenylphosphino)propane and dialkylamido ligands

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Abstract—The triply-bonded ditungsten(III) species *trans,trans*- $W_2Cl_4(NBu_2^t)_2(dppp)$ (**1**) and a new mixed-valent W^{III}/W^{IV} complex $(dppp)ClW(\mu-Cl)_3WCl_2(NBu_2^t)$ (**3**) have been isolated from the reaction of $W_2Cl_4(NBu_2^t)_2(NHBu_2^t)_2$ with 1,3-bis(diphenylphosphino)propane (dppp). A complex similar to **3**, $(dppp)ClW(\mu-Cl)_3WCl_2(NEt_2)$ (**2**), has also been prepared. Both **2** and **3** are characterized by a W_2^{7+} core and they adopt face-sharing bioctahedral geometry with a chelating dppp ligand. The W—W distances in **2** and **3** are both 2.660(1) Å and each of them shows an EPR signal at $g = 1.88$. The structure of **1** contains a W_2^{6+} core with a W—W distance of 2.3055(8) Å. It has a bridging dppp ligand and a *trans,trans* stereochemistry. © 1997 Elsevier Science Ltd

Keywords: tungsten complexes; face-sharing bioctahedral complexes; bis(diphenylphosphino)propane complexes; chelating diphosphine ligand; crystal structure.

The bidentate phosphine ligands $Ph_2P(CH_2)_nPPH_2$, where $n = 1$ or 2, have been found to form triply-bonded ditungsten(III) complexes of the type $W_2Cl_4(NR_2)_2(L-L)$ ($L-L = dppm$ or $dppe$) in different isomeric forms [1,2]. The crystal structures of *cis,cis*- $W_2Cl_4(NR_2)_2(dppm)$ ($R = Et, Bu^t$) [1b] and *trans,trans*- $W_2Cl_4(NEt_2)_2(dppe)$ ² have been reported recently. In order to investigate further how the separation between the P donor atoms (i.e. the value of n) might affect the chemistry of such complexes, we have examined the chemistry that occurs with the related bidentate phosphine containing three methylene groups, namely, $Ph_2P(CH_2)_3PPH_2$ (dppp).

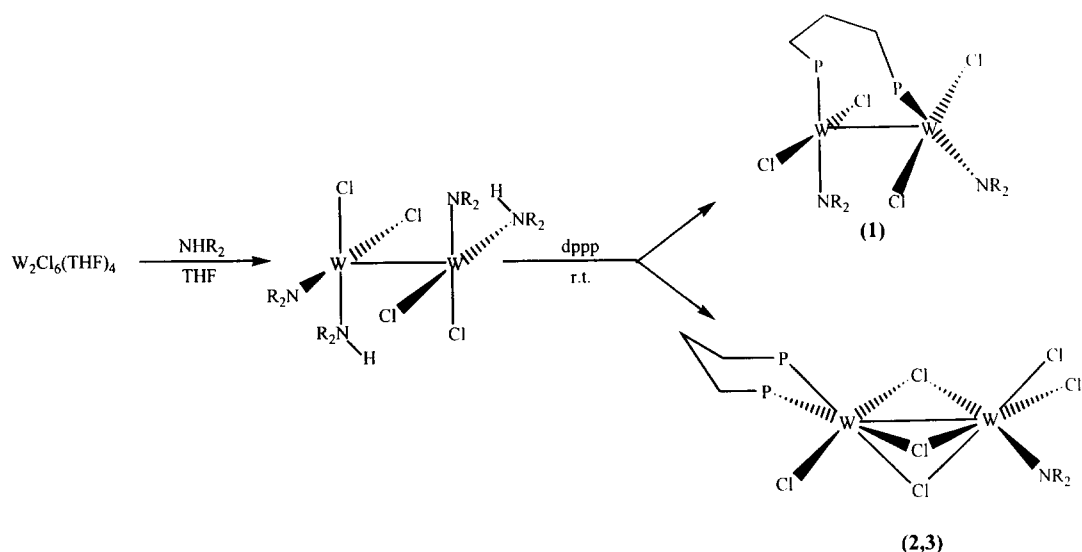
To our surprise, two interesting paramagnetic face-sharing bioctahedral complexes of tungsten (Scheme 1) of stoichiometry $(dppp)ClW(\mu-Cl)_3WCl_2(NR_2)$ [$R = Et$ (**2**), Bu^t (**3**)] have been obtained whose structures are the subject of this report. The molecular

structure of *trans,trans*- $W_2Cl_4(NBu_2^t)_2$ (dppp) (**1**) is also presented.

EXPERIMENTAL

All manipulations were carried out under a nitrogen or argon atmosphere by using standard vacuum-line techniques. Common solvents were obtained from commercial sources and were dried and deoxygenated by refluxing over appropriate reagents before use. The diphosphine dppp was purchased from Aldrich, Inc. A general literature method was used to prepare $W_2Cl_4(NR_2)_2(NHR_2)_2$ ($R = Et, Bu^t$) [3]. The IR spectrum was recorded on a Perkin-Elmer 16PC FT-IR spectrophotometer from Nujol mulls. The ¹H NMR spectrum was recorded at 200 MHz on a Varian XL-200 spectrometer, and chemical shifts were internally referenced to solvent resonances. The ³¹P{¹H} NMR spectral data (81 MHz) were obtained on a Varian XL-200 broad band spectrometer with the chemical

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shift values referenced externally and are reported relative to 85% $\text{H}_3\text{PO}_4/\text{D}_2\text{O}$. The positive FAB/DIP (DIP = direct insertion probe) mass spectra were acquired from a VG Analytical 70S high resolution, double-focusing, sector (EB) mass spectrometer using *m*-nitrobenzyl alcohol (NBA) as the matrix. X-Band EPR spectra of toluene solutions were recorded at 100 K with a frequency of 9.4 GHz on a Bruker ESP 300 spectrometer.

Preparation

trans,trans- $\text{W}_2\text{Cl}_4(\text{NBU}_2)_2(\text{dppp})$ (**1**) and $(\text{dppp})\text{ClW}(\mu\text{-Cl})_3\text{WCl}_2(\text{NBU}_2)$ (**3**). In a typical experiment, *dppp* (0.32 g, 0.77 mmol) was dissolved in toluene (8 mL) and added by cannula technique to a stirred solution of $\text{W}_2\text{Cl}_4(\text{NBU}_2)_2(\text{NHBu}_2)_2$ [**3**] prepared *in situ* from the reaction of $\text{W}_2\text{Cl}_6(\text{THF})_4$ (based on 0.50 g WCl_4 , 1.54 mmol) with dibutylamine in THF (15 mL). After stirring for 1.5 h at ambient temperature, all the volatile components of the reaction mixture were removed *in vacuo*. Toluene (20 mL) was then added to the dark residue and the resulting dark red–brown solution was filtered from the undissolved residue through Celite. The filtrate was concentrated and stored overnight at -20°C to afford first compound **1** as red crystals (0.29 g, 32%). When the supernatant liquid was allowed to stand at -20°C for a few more days, dark green crystals of **3** were obtained in 14% yield (0.12 g).

1: IR (Nujol, cm^{-1}): 3052 (w), 3019 (vw), 1606 (vw), 1586 (vw), 1572 (w), 1494 (w), 1483 (m), 1434 (s), 1337 (vw), 1307 (w), 1261 (m), 1187 (w), 1158 (w), 1136 (m), 1094 (s), 1072 (m), 1028 (m), 1001 (w), 980 (vw), 952 (vw), 908 (m), 880 (vw), 846 (w), 836 (w), 802 (m), 743 (s), 729 (s), 696 (vs), 675 (vw), 651

(w), 617 (vw), 510 (ms), 504 (ms). ^1H NMR (200 MHz benzene- d_6 , 24°C): δ 0.68 (t, $J = 7.0$ Hz, 6H, distal CH_3), 0.83 (m), 1.02 (t, $J = 7.0$ Hz, 6H, proximal CH_3), 1.11–1.87 (m), 2.27 (m), 2.70 (m), 3.94 (m, 2H), 4.81 (m, 2H, proximal $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 5.96 (m, 2H, proximal $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 6.81–7.45 (m, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, benzene- d_6 , 19°C): δ -3.20 (s, $^1J_{\text{W-P}} = 75$ Hz, $J_{\text{P-P}} = 8.5$ Hz). FAB/DIP MS (NBA, C_7H_8): m/z 1178 ($[\text{M}]^+$), 1050 ($[\text{M-NBU}_2]^+$), 1014 ($[\text{M-Cl-NBU}_2]^+$).

3: FAB/DIP MS (NBA, neat): m/z 1122 ($[\text{M}]^+$).

$(\text{dppp})\text{ClW}(\mu\text{-Cl})_3\text{WCl}_2(\text{NEt}_2)$ (**2**). The synthesis of **2** followed a similar course to that of **3** using the corresponding $\text{W}_2\text{Cl}_4(\text{NEt}_2)_2(\text{NHEt}_2)_2$ complex [**3**] (from 0.50 g WCl_4). Upon the addition of a toluene solution of *dppp* (0.32 g, 0.77 mmol) to $\text{W}_2\text{Cl}_4(\text{NEt}_2)_2(\text{NHEt}_2)_2$ in THF (15 mL), *in situ* $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic studies of a portion of the reaction mixture indicated that some paramagnetic compound was present in solution. Following evaporation of the solvent and other volatile components, the residue was extracted with toluene (15 mL) and a dark brown solution was obtained after filtration. The filtrate was set aside and the solvent allowed to evaporate slowly. During the course of a week, dark-colored crystals of **2** (0.16 g, 20%) formed at the base of the Schlenk tube along with some orange crystalline materials that we have been unable to characterize so far because of their extreme sensitivity to oxygen and moisture. No attempts have been made to isolate and crystallize a compound similar to **1** in this case, though it is believed to be present in the solution mixture.

2: FAB/DIP MS (NBA, neat): m/z 1064 ($[\text{M}]^+$), 1027 ($[\text{M-Cl}]^+$), 990 ($[\text{M-2Cl}]^+$ or $[\text{M-NEt}_2]^+$), 955 ($[\text{M-3Cl}]^+$ or $[\text{M-Cl-NEt}_2]^+$), 922 ($[\text{M-4Cl}]^+$ or $[\text{M-2Cl-NEt}_2]^+$).

X-ray structure determinations

Single crystals of 1–3 were obtained as described above. In each case, a crystal of suitable size and quality was affixed on the end of a quartz fiber with grease in the cold nitrogen stream (–60 or –100°C). X-ray diffraction experiments were carried out using one of two fully automated diffractometers equipped with monochromated MoK α radiation, Enraf-Nonius CAD-4S (1) and Enraf-Nonius FAST (2 and 3). Unit cell determination and data collection followed routine procedures and practices of this laboratory [1a,3]. Oscillation photographs of principal axes were taken to confirm the Laue class and axial lengths. All data were corrected for Lorentz and polarization effects.

The structures were solved and refined using the SHELXTL direct methods [4] and the SHELXL-93 programs [5] on a DEC 3000-800 AXP workstation. In each model, hydrogen atoms were included at idealized positions for the structure factor calculations but not refined. Details on data collection and structure refinement are reported in Table 1.

trans,trans-W₂Cl₄(NBu₂)₂(dppp) · 2C₇H₈, (1) · 2C₇H₈

The ω - θ scan technique was used to scan data points. C-Centering of 1 was verified by taking photographs of the *ab* face. There was no significant decay of the crystal as indicated by the intensity standards. An empirical absorption correction based on azimuthal scans of 9 reflections with their χ -angles near 90° was applied. The monoclinic space group C2/c was chosen to start the refinement of the structure and was proved to be correct through successful refinement. Anisotropic displacement parameters were assigned to all atoms of the dinuclear molecule, except for those carbon atoms associated with the disordered *n*-butyl chain. All atoms of the solvent molecules were refined isotropically. A final difference Fourier map revealed that the highest remaining peak of electron density (0.78 e/Å³) was located near W(1). Selected bond distances and angles as well as torsional angles are given in Table 2.

(dppp)ClW(μ -Cl)₃WCl₂(NEt₂) · 2C₇H₈, (2) · 2C₇H₈

Indexing based on 50 reflections resulted in a triclinic cell and the cell parameters were further refined against 250 reflections. The possible space groups were *P*1 and *P* $\bar{1}$. Direct methods solutions based on the space group *P* $\bar{1}$ readily afforded the atomic positions of the dinuclear complex and successful refinement of the structure confirmed the choice. After isotropic refinement of all atoms of the W₂ molecule, the difference Fourier map indicated several peaks that could be ascribed to solvent molecules. These peaks were modeled as C₇H₈ molecules, and the crystal contains four toluene molecules in the unit cell. The final

difference map contained several small 'ghost' peaks associated with the disordered solvent molecules, but no effort was made to correct for this problem. Important bonding parameters are collected in Table 3.

(dppp)ClW(μ -Cl)₃WCl₂(NBu₂)₂ · 2.5C₇H₈, (3) · 2.5C₇H₈. The crystal was shown to belong to the C-centered monoclinic system. Space group C2/c was chosen and proved by successful refinement. Direct methods provided the positions of the dinuclear complex. After isotropic refinement of all atoms, disorder in the butyl chains was found as well as highly disordered toluene molecules. Because of poor refinement, we will discuss some structural parameters of (3) below only for comparison purposes.

RESULTS AND DISCUSSION

trans,trans-W₂Cl₄(NBu₂)₂(dppp) (1)

While the preparation of W₂Cl₄(NR₂)₂(L–L) (L–L = bidentate phosphines) type molecules has been reported recently [1,2], there is no prior example of a structurally characterized complex containing the W₂⁶⁺ core with a dppp ligand. Compound 1 also provides the second example of a *d*³–*d*³ ditungsten complex of this type with a *trans,trans* stereochemistry, the other being W₂Cl₄(NEt₂)₂(dppe) [2]. The compound is moderately stable as a red crystalline solid and is soluble in aromatic solvents. In solution, it is quite sensitive to oxidation by oxygen and moisture.

A perspective view of the complex is illustrated in Fig. 1. The unit cell contains four ditungsten molecules and eight toluene solvent molecules. No disorder of the W₂ unit was detected. The molecule of 1 possesses a W₂⁶⁺ unit, which is spanned by a bridging dppp ligand. Each WCl₂NP fragment has a *trans* arrangement. The W–W bond distance of 2.3055(8) Å in 1 (Table 2) is ca 0.012 Å shorter than that observed in W₂Cl₄(NEt₂)₂(dppe) (2.3178(6) Å). The mean W–Cl and W–P bond lengths are 2.367(2) and 2.669(2) Å, respectively. The latter is comparable to the corresponding W–P distances observed in the *trans* WCl₂PN units of this type of molecules, and considerably longer than those for *cis* WCl₂PN units [2]. The molecule exhibits a partially staggered rotational geometry, the torsional angle P(1)–W(1)–W(1A)–P(1A) being 28.9°.

Spectroscopic analysis of this compound is consistent with its solid-state structure. Its mass spectrum shows a parent ion at *m/z* = 1178, confirming the molecular formula of the dinuclear complex as W₂Cl₄P₂C₄₃H₆₂N₂. Below the molecular mass M⁺ are observed major fragment ions due to the loss of chlorine and amido groups. The ¹H NMR spectrum displays distal and proximal proton signals for the NBu₂ groups, and a set of multiplets in the aromatic region. The compound in benzene-*d*₆ solution has a central ³¹P{¹H} NMR signal at –3.20 ppm with ¹J_{W-P} = 75 Hz and J_{P-P} = 8.5 Hz, consistent with the formulation of a *trans,trans* isomer.²

Table 1. Crystallographic data for *trans,trans*-W₂Cl₄(NBU₂)₂(dppp)·2C₇H₈ (1)·2C₇H₈, (dppp)ClW(μ-Cl)₃WCl₂(NEt₂)·2C₇H₈ (2)·2C₇H₈ and (dppp)ClW(μ-Cl)₃WCl₂(NBU₂)·2.5C₇H₈ (3)·2.5C₇H₈

	1·2C ₇ H ₈	2·2C ₇ H ₈	3·2.5C ₇ H ₈
Formula	W ₂ Cl ₄ P ₂ C ₅₇ H ₇₈ N ₂	W ₂ Cl ₆ P ₂ C ₄₅ H ₅₂ N	W ₂ Cl ₆ P ₂ C _{52.5} H ₆₄ N
<i>F</i> _w	1362.65	1249.22	1351.39
Space group	C2/c (No. 15)	P $\bar{1}$ (No. 2)	C2/c (No. 15)
<i>a</i> (Å)	19.638(5)	10.6471(7)	34.356(7)
<i>b</i> (Å)	14.954(3)	17.367(2)	33.038(7)
<i>c</i> (Å)	20.572(5)	17.367(2)	33.038(7)
α (°)	90.0	89.371(7)	90.0
β (°)	105.03(2)	102.405(6)	117.58(3)
γ (°)	90.0	98.934(2)	90.0
<i>V</i> (Å ³)	5835(2)	2370.3(8)	11006(4)
<i>Z</i>	4	2	8
<i>D</i> _{calc} (g/cm ³)	1.551	1.750	1.631
Crystal size (mm)	0.50 × 0.15 × 0.15	0.30 × 0.20 × 0.15	0.28 × 0.13 × 0.08
μ (mm ⁻¹)	4.215	5.287	4.561
Data collection instrument	CAD4	FAST	FAST
Radiation (λ , Å)	Mo-K α (0.71073)	Mo-K α (0.71073)	Mo-K α (0.71073)
Orientation refl., number, range θ	25, 13.97–18.02	248, 9.05–20.80	250, 7.50–20.80
Temp. (°C)	–100	–60	–60
Scan method	ω - θ scans	frame data from ω scans	frame data from ω scans
Data collection range, θ (°)	2.05–24.97	2.32–25.08	1.98–22.50
No. unique data, total	5106	7957	7158
No. param. refined	295	478	485
Transmission factors	0.9573–0.9989	0.278–0.453	none
<i>R</i> 1 ^a , <i>wR</i> 2 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.033, 0.071	0.043, 0.103	0.072, 0.099
<i>R</i> 1 ^a , <i>wR</i> 2 ^b (all data)	0.062, 0.079	0.057, 0.109	0.151, 0.183
Goodness-of-fit ^c	1.051	1.038	1.086

^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 Goodness-of-fit = $[\sum [w(F_o^2 - F_c^2)^2] / (N_{\text{observns}} - N_{\text{params}})]^{1/2}$, based on all data.

Table 2. Selected bond distances (Å) and angles (°) and torsion angles (°) for *trans,trans*-W₂Cl₄(NBU₂)₂(dppp) (1)

W(1)—W(1A)	2.3055(8)	W(1)—P(1)	2.669(2)
W(1)—N(1)	1.924(5)	W(1)—Cl(1)	2.385(2)
W(1)—Cl(2)	2.349(2)		
P(1)—W(1)—N(1)	151.2(2)	P(1)—W(1)—Cl(1)	76.22(5)
P(1)—W(1)—Cl(2)	82.94(5)	N(1)—W(1)—Cl(1)	89.1(1)
N(1)—W(1)—Cl(2)	98.2(1)	Cl(1)—W(1)—Cl(2)	147.96(5)
W(1A)—W(1)—P(1)	104.63(4)	W(1A)—W(1)—N(1)	103.1(2)
W(1A)—W(1)—Cl(1)	105.32(4)	W(1A)—W(1)—Cl(2)	103.31(5)
P(1)—W(1)—W(1A)—P(1A)	–28.87(7)	P(1)—W(1)—W(1A)—Cl(1A)	50.54(5)
N(1)—W(1)—W(1A)—N(1A)	–44.7(3)	N(1)—W(1)—W(1A)—Cl(2A)	57.2(2)
Cl(1)—W(1)—W(1A)—P(1A)	50.54(5)	Cl(1)—W(1)—W(1A)—Cl(2A)	–35.52(6)
Cl(2)—W(1)—W(1A)—N(1A)	57.2(2)	Cl(2)—W(1)—W(1A)—Cl(1A)	–35.52(6)

(dppp)ClW(μ-Cl)₃WCl₂(NR₂) (R = Et(2), Buⁿ (3))

To our knowledge, these two complexes represent the first structurally characterized examples of a face-sharing bioctahedral (FSBO) complex with a chelating diphosphine ligand. In addition, only one example of a neutral W^{III}/W^{IV} FSBO complex,

namely, (Me₂S)Cl₂W(μ-SEt)₃WCl₂(SMe₂) [6] has been reported. The molecular structures of **2** and **3** are shown in Figs 2 and 3, respectively, and each of them contains a central W₂(μ-Cl)₃ core that is very similar to those seen in other FSBO complexes of this kind [7]. The relatively high *R* values associated with **3** are due to our inability to model the disorder of the sol-

Table 3. Selected bond distances (Å), angles (°) and torsion angles (°) for (dppp)ClW(μ-Cl)₃WCl₂(NR₂) (R = Et (2), Buⁿ (3))

	2	3
W(1)—W(2)	2.6598(4)	2.660(1)
W(1)—P(1)	2.546(2)	2.555(4)
W(1)—P(2)	2.548(2)	2.555(4)
W(2)—N(1)	1.918(6)	1.90(1)
W—Cl _i (av)	2.380(2)	2.383(4)
W—Cl _h (av)	2.458(2)	2.449(4)
P(1)—W(1)—P(2)	86.68(6)	87.7(1)
P(1)—W(1)—Cl(1)	87.51(6)	88.8(2)
P(2)—W(1)—Cl(1)	85.44(7)	85.5(1)
Cl(2)—W(1)—Cl(3)	106.86(6)	106.0(1)
Cl(2)—W(1)—Cl(4)	88.06(7)	87.9(1)
Cl(3)—W(1)—Cl(4)	84.08(6)	84.2(1)
W(1)—Cl(2)—W(2)	66.25(5)	66.6(1)
W(1)—Cl(3)—W(2)	66.22(5)	66.5(1)
W(1)—Cl(4)—W(2)	64.08(4)	64.36(9)
N(1)—W(2)—Cl(5)	95.4(2)	94.7(5)
N(1)—W(2)—Cl(6)	94.2(2)	93.6(4)
Cl(5)—W(2)—Cl(6)	87.32(8)	87.1(2)
Cl(2)—W(2)—Cl(3)	106.88(6)	106.4(2)
Cl(2)—W(2)—Cl(4)	85.49(6)	85.7(1)
Cl(3)—W(2)—Cl(4)	81.99(6)	82.7(1)

vent molecules precisely in the unit cell. Because of poor refinement of the structure of 3, only the structure of 2 will be described in detail in the following account.

The crystal structure of 2 · 2C₇H₈ consists of discrete dinuclear molecules and interstitial toluene solvent, each residing on a general position in the triclinic unit cell. The dinuclear complex itself has a confacial bioctahedral geometry with the anti configuration of

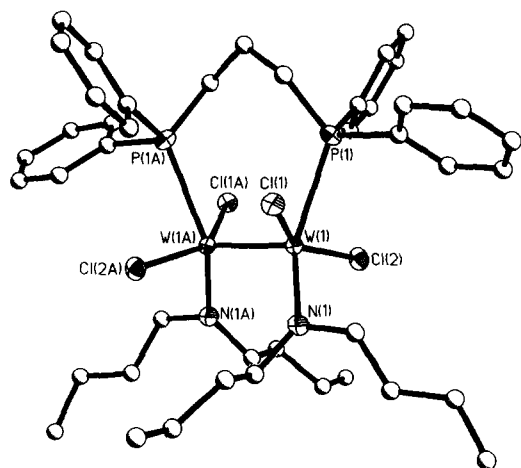


Fig. 1. Perspective drawing of *trans,trans*-W₂Cl₄(NBu₂)₂ (dppp) (1). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon atoms are shown as spheres of arbitrary radius and are not labeled for clarity.

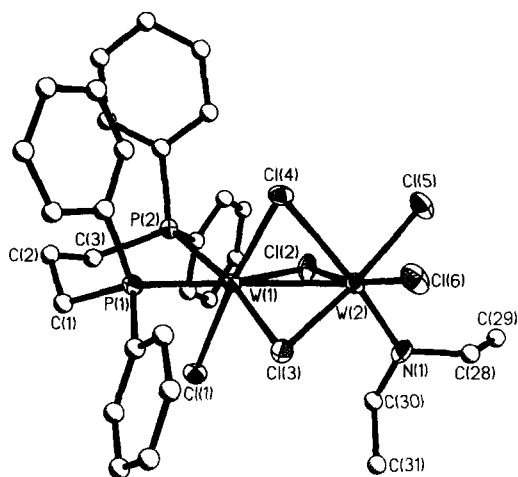


Fig. 2. Perspective drawing of (dppp)ClW(μ-Cl)₃WCl₂(NEt₂) (2). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon atoms are shown as spheres of arbitrary radius. Phenyl rings are not labeled for clarity.

the terminal ligands. The W₂Cl₆P₂N core has an effective plane of symmetry which passes through two W atoms, the terminal Cl(1) atom, the N(1) atom, and the bridging Cl(4) atom. Selected bond distances and angles for this structure are given in Table 3. For a W^{III}/W^{IV} (*d*³/*d*²) system here, a formal bond order of 2.5 is predicted [7], in spite of the relatively long W—W bond length (2.6598(4) Å) observed. In fact, this metal–metal separation is comparable to that found in [W₂Br₆]²⁻ (2.601(2) Å) [8]. The dppp ligand was shown to coordinate to the same W atom and adopts an essentially chair conformation. The average W—P bond length is 2.547(2) Å and the angle P(1)—W(1)—P(2) is 86.68(6)°. The W—N bond (1.918(6) Å) corresponds to a tungsten–alkylamide

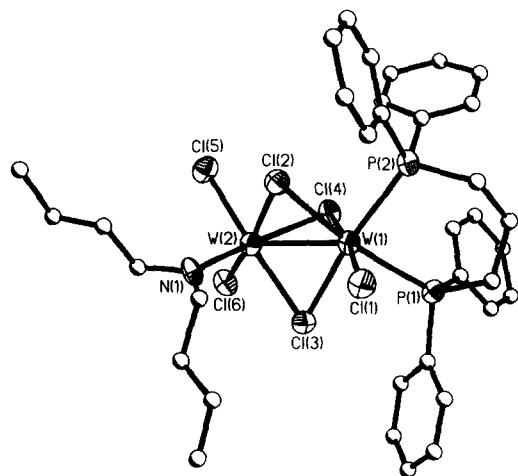


Fig. 3. Perspective drawing of (dppp)ClW(μ-Cl)₃WCl₂(NBu₂) (3). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon atoms are shown as spheres of arbitrary radius and are not labeled for clarity.

Table 4. Comparison of selected structural parameters of some d^3/d^2 ditungsten FSBO complexes

Compound	W—W (Å)	W—Cl _t (Å)	W—Cl _b (Å)	W—X _b —W (av) (°)	Ref.
(dppp)ClW(μ-Cl) ₃ WCl ₂ (NEt ₂) (2)	2.6598(4)	2.380(2)	2.458(2)	65.52(5)	this work
(dppp)ClW(μ-Cl) ₃ WCl ₂ (NBu ₂) ⁺ (3)	2.660(1)	2.383(4)	2.449(4)	65.8(1)	this work
(Me ₂ S)Cl ₂ W(μ-SEt) ₃ WCl ₂ (SMe ₂)	2.505(1)	2.385(5)		62.3(2)	[6]
[Cl ₃ W(μ-Cl)(μ-SPh) ₂ WCl ₃] ²⁻	2.519(2)	2.394(6)	2.439(6)	62.3(2)	[9]
[W ₂ Cl ₆] ²⁻	2.540(1)	2.358(6)	2.453(5)	62.4(2)	[10]
[W ₂ Br ₆] ²⁻	2.601(2)			60.02(9)	[8]

bond [1a,2]. The average W—Cl terminal distance is shorter by *ca* 0.08 Å than the average W—Cl bridging distance and the average W—Cl_b—W bond angle is 65.52(5)°. It should be noted that there is no difference in W—Cl bridging distances trans to terminal Cl atoms (2.440(2) Å) and trans to P atoms (2.435(2) Å), while the corresponding distance W(2)—Cl(4) trans to N atom is significantly longer (2.559(2) Å), which clearly illustrates a high *trans* influence of amide group.

The dimensions of **2** and **3** are compared with other known d^3/d^2 mixed oxidation state species, (Me₂S)Cl₂W(μ-SEt)₃WCl₂(SMe₂) [6], [Cl₃W(μ-Cl)(μ-SPh)₂WCl₃]²⁻ [9] and [W₂X₆]²⁻ (X = Cl [10], Br [8]) in Table 4. We note that there are only four prior examples of this type of molecule and they are all W^{III}—W^{IV} complexes with an assigned metal–metal bond order of 2.5. The W—W bond distances span the range 2.505(1)–2.6598(4) Å, and the W—Cl_t and W—Cl_b distances are comparable in all cases. For **2**, the W—Cl_b—W angles subtended at the μ-Cl atoms (64.1–66.3°) are smaller than the 70.5° required for an ideal bioctahedral [11] and are suggestive of a structure in which metal–metal interaction exists. This is complemented by the obtuse angles Cl(2)—W(1)—Cl(3) (106.9°) and Cl(2)—W(2)—Cl(3) (106.9°). However, these W—Cl_b—W angles are less acute than those observed in the other four W₂⁷⁺ complexes, accompanied by the longer W—W distance in this case. Also, the angles Cl(2)—W—Cl(4) and Cl(3)—W—Cl(4) (82.0–88.1°) are lower than the expected value of 90° for the perfect bioctahedron [11].

Both compounds **2** and **3** would be expected to exhibit a doublet ground state and therefore be EPR-active. The X-band EPR spectra of **2** and **3** in frozen toluene were recorded at 100 K and confirmed the paramagnetism of these complexes. The spectra are

very similar and centered at ~3568 G showing an isotropic resonance signal at *g* = 1.88 for both complexes. We have been unable to observe any metal or ligand hyperfine structure in the spectra.

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