ELSEVIER

Inorganica Chimica Acta 229 (1995) 113–119

Inorganica Chimica Acta

Synthesis and structure of $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$ ☆

Judith L. Eglin [a,*], E. Marie Hines [a], Edward J. Valente [b], Jeffrey D. Zubkowski [c]

[a] *Department of Chemistry, Mississippi State University, Mississippi State, MS 39762, USA*
[b] *Department of Chemistry, Mississippi College, Clinton, MS 39058, USA*
[c] *Department of Chemistry, Jackson State University, Jackson, MS 39217, USA*

Received 10 May 1994; revised 11 July 1994

Abstract

A new ditungsten compound with a bridging ligand in a novel geometry, $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$ where dppm is bis(diphenylphosphino)methane, has been prepared from a quadruply bonded starting material. The structure of this compound is an example of a dinuclear tungsten compound with an η^2-μ-bonded acetonitrile. The use of acetonitrile as a solvent during the preparation of the known compound $W_2Cl_4(\mu\text{-dppm})_2$ results in the incorporation of an acetonitrile molecule in a bridging position with the C–N of this ligand perpendicular to the W–W axis. The bridging acetonitrile is no longer linear. The angle formed by the three-atom chain of acetonitrile, C–C–N, is 116.3(7)° with a C–N bond distance of 1.303(8) Å. The W–W bond distance is 2.4981(10) Å, significantly longer than the distance of 2.269(1) Å observed in the parent compound $W_2Cl_4(\mu\text{-dppm})_2$. Crystallographic data for this compound is as follows: $P2_1/c$ with $a = 12.577(5)$, $b = 18.644(8)$, $c = 27.024(8)$ Å, $\beta = 95.98(2)°$, $V = 6302(4)$ Å^3 and $Z = 4$.

Keywords: Crystal structures; Tungsten complexes; Acetonitrile complexes; Bridging complexes; π-bonded complexes; Dinuclear complexes

1. Introduction

The chemistry of multiply bonded transition metal compounds, including bonding, reactivity and spectroscopy, has grown significantly since the publication of the first structure of a quadruply bonded compound, $Re_2Cl_8^{2-}$ [1,2]. Dinuclear compounds or other compounds with multiple metal centers provide a reservoir of electrons that can be used in multi-electron redox reactions [3]. For example, quadruply bonded ditungsten and dimolybdenum complexes are known to undergo two-electron oxidative addition reactions and ditungsten compounds tend to be more sensitive to oxidative addition than their molybdenum analogs [4–7]. $Mo_2Cl_6(dedppe)_2$, where dedppe = 1-(diethylphosphino)-2-(diphenylphosphino) ethane, is obtained as the oxidative addition product in the reaction of $Mo_2Cl_4(dedppe)_2$ with CH_2Cl_2 [5].

In addition to oxidative addition reactions, there are a wide variety of mononuclear and dinuclear transition metal complexes that form adducts with alkynes, acetonitrile, or other multiply bonded organic molecules [8–15]. A series of triply bonded dimolybdenum compounds, $Mo_2(OR)_6$ where R = t-Bu, i-PR and CH_2CMe_3, react rapidly with the alkynes C_2H_2 and MeC_2Me in the presence of pyridine to form products of the general type $Mo_2(OR)_6(py)_2(\mu\text{-alkyne})$ [16]. Adducts of this type had not been formed from quadruply bonded ditungsten starting materials until now. The use of acetonitrile as a solvent during the preparation of the known compound $W_2Cl_4(\mu\text{-dppm})_2$ from $W_2Cl_4(P(n\text{-}Bu)_3)_4$ [17] results in the incorporation of an acetonitrile molecule in a bridging position with the C(1A)–N(1A) of the ligand perpendicular to the W(1)–W(2) axis. Both N(1A) and C(1A) of the acetonitrile are bonded equivalently to the W–W core. The synthesis and crystal structure of this new ditungsten compound are reported and the structure compared to a series of related compounds.

2. Experimental

2.1. General

Standard Schlenk and vacuum line techniques were used employing an atmosphere of argon. Commercial grade tetrahydrofuran and hexane were dried over

---

☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

*Corresponding author.

SSDI 0020-1693(94)04235-N

potassium/sodium benzophenone ketyl and acetonitrile was dried over calcium hydride. All solvents were freshly distilled under an atmosphere of nitrogen prior to use. The starting material WCl_4 was synthesized from WCl_6 and $W(CO)_6$ as previously reported [18]. Tri-n-butyl phosphine was purchased from Johnson Matthey and used without any further purification. Bis(diphenylphosphino)methane (dppm) was purchased from Strem Chemicals and evacuated overnight to remove any residual oxygen or moisture. $NaBEt_3H$ was purchased as a 1 M solution in toluene from Aldrich and used without any further purification.

The UV–Vis spectra were recorded on a Hewlett Packard 8452 model diode array spectrophotometer from 190 to 820 nm. The $^{31}P\{^1H\}$ NMR spectra (121 and 162 MHz) were recorded on General Electric instruments at two different fields using QE and Omega NMR spectrometers.

2.2. Preparation of $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$

To 2.00 g (6.14 mmol) of WCl_4 in a slurry of 30 ml of THF at −60 °C, 12.28 ml (12.28 mmol) of a 1 M toluene solution of $NaBEt_3H$ were added. The reaction mixture was allowed to warm to −10 °C and 3.06 ml (12.35 mmol) of $P(n\text{-}Bu)_3$ phosphine were added. The solution was allowed to warm to room temperature slowly, filtered through Celite, and all solvent removed under vacuum to yield $W_2Cl_4(P(n\text{-}Bu)_3)_4$ as a dark green oil [19,20]. Upon addition of 28 ml of acetonitrile, a dark brownish green solution formed. Neither the addition of hexane nor more acetonitrile caused the precipitation of $W_2Cl_4(P(n\text{-}Bu)_3)_4$. Even after cooling overnight at −20 °C, no precipitate formed. All solvent was removed under vacuum and 2.33 g (6.06 mmol) of dppm dissolved in 30 ml of toluene were added directly to this oily product. After refluxing for 4 h, the solution was allowed to cool. A light brown solid product precipitated from the blue–green solution. The supernatant liquid was removed and the remaining brown solid washed with three 10 ml aliquots of hexane. A yield of 2.00 g (1.27 mmol, 41%) of product, $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)\cdot 3THF$, was recovered.

2.3. Crystallographic studies

X-ray quality crystals were grown by layering freshly-filtered THF solutions of the compound with hexane. A yellow–brown cube-like crystal was selected, coated with epoxy cement, and mounted on the end of a glass fiber. Data were collected on a Siemens R3m/V automated diffractometer fitted with a molybdenum source and a graphite monochromator. Crystallographic data for the compound are listed in Table 1. Automatic peak search and indexing procedures yielded a monoclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry.

Table 1
Crystal data for $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)\cdot 3THF$

Chemical formula	$C_{64}H_{71}Cl_4NO_3P_4W_2$
Formula weight	1535.60
Space group	$P2_1/c$ (No. 14)
a (Å)	12.577(5)
b (Å)	18.644(8)
c (Å)	27.024(8)
β (°)	95.98(2)
V (Å^3)	6302(4)
Z	4
ρ_{calc} (g cm^{-3})	1.618
Wavelength (Å)	0.71073
Final R indices ($I > 2\sigma(I)$)	
$R1$ [a]	0.0360
$wR2$ [b]	0.0778
R indices (all data)	
$R1$	0.0874
$wR2$	0.0819

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.

[b] $wR2 = \sqrt{(\Sigma[(F_o^2 - F_c^2)^2/\Sigma[wF_o^4]])}$, $w = 1/[\sigma^2(F_o^2) + (0.0600P)^2 + 0.15P]$ where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

Data were collected using omega scans ($3.5 < 2\theta < 55°$). Three standard reflections (8 0 0, 0 14 0, 0 0 16) were collected after every 100 reflections and exhibited no decomposition during the data collection. The data were corrected for absorption using SHELXA-90 with maximum and minimum transmission factors of 0.976 and 0.227 respectively, but not for extinction [21]. The structure was determined by the location of the tungsten atoms in a Patterson function map, and the remaining atoms from subsequent difference Fourier calculation maps [22,23]. Hydrogen atom positions were assigned idealized locations, and were included in structure factor calculations, but were not refined.

The solvent molecules (THF) are uncoordinated to the complex and were found to occupy three sites in the structure. Non-H atoms of the THF molecules were refined with isotropic vibrational factors and site occupancies of one. Attempts to model the THF atoms with more parameters were not warranted. In two of the THF molecules, the oxygen atoms were assigned on the basis of lower B_{eq} values and the assignments were verified during least-squares refinement. The third THF molecule could only crudely be modeled and exhibited disorder and/or partial site occupancy. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. Selected bond lengths and bond angles are listed in Table 3.

3. Results and discussion

3.1. Synthesis and structure

The preparation of $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)\cdot 3THF$ was the result of the incomplete removal

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$

Atom	x	y	z	U_{eq} [a]
W(1)	4740(1)	1458(1)	1576(1)	32(1)
W(2)	2799(1)	1480(1)	1264(1)	31(1)
P(1)	5370(1)	2001(1)	790(1)	36(1)
P(2)	3034(1)	1909(1)	381(1)	34(1)
P(3)	4489(1)	1078(1)	2471(1)	35(1)
P(4)	2162(1)	1245(1)	2117(1)	35(1)
Cl(1)	6163(2)	561(1)	1590(1)	60(1)
Cl(2)	6045(2)	2296(1)	1967(1)	63(1)
Cl(3)	1498(1)	588(1)	919(1)	51(1)
Cl(4)	1362(2)	2351(1)	1212(1)	59(1)
C(1A)	3943(5)	764(4)	1041(2)	40(2)
N(1A)	3713(4)	568(4)	1480(2)	58(2)
C(2A)	4264(8)	129(5)	676(3)	108(4)
C(1)	4409(5)	1786(4)	250(2)	36(2)
C(2)	6648(5)	1683(4)	618(2)	40(2)
C(3)	6757(6)	1255(4)	216(3)	57(2)
C(4)	7758(7)	1016(5)	127(3)	69(3)
C(5)	8654(6)	1205(5)	431(3)	67(3)
C(6)	8543(7)	1630(6)	828(3)	84(4)
C(7)	7550(6)	1851(5)	927(3)	69(3)
C(8)	5491(6)	2971(4)	719(3)	43(2)
C(9)	5866(7)	3239(5)	306(3)	67(3)
C(10)	5960(8)	3973(6)	232(4)	84(3)
C(11)	5614(8)	4449(6)	572(4)	86(3)
C(12)	5200(8)	4182(6)	980(4)	87(3)
C(13)	5166(7)	3453(5)	1057(3)	67(3)
C(14)	2266(5)	1412(4)	−114(2)	35(2)
C(15)	2704(6)	952(4)	−438(3)	46(2)
C(16)	2070(7)	554(4)	−790(3)	55(2)
C(17)	976(7)	628(5)	−810(3)	58(2)
C(18)	531(6)	1078(5)	−491(3)	59(3)
C(19)	1180(6)	1483(5)	−149(2)	59(2)
C(20)	2766(5)	2846(4)	199(3)	42(2)
C(21)	2726(6)	3370(4)	545(3)	55(2)
C(22)	2546(8)	4078(5)	395(4)	83(3)
C(23)	2415(8)	4238(5)	−105(4)	86(3)
C(24)	2477(8)	3728(5)	−454(4)	76(3)
C(25)	2662(6)	3030(5)	−299(3)	60(2)
C(26)	3155(5)	692(4)	2486(2)	41(2)
C(27)	4590(5)	1718(4)	2990(2)	42(2)
C(28)	4615(6)	1462(5)	3479(2)	65(2)
C(29)	4698(8)	1945(7)	3863(3)	83(3)
C(30)	4712(8)	2669(7)	3775(4)	93(4)
C(31)	4629(8)	2944(5)	3307(3)	86(3)
C(32)	4559(6)	2444(5)	2911(3)	58(2)
C(33)	5428(6)	382(4)	2721(2)	42(2)
C(34)	5217(7)	−339(5)	2706(3)	64(3)
C(35)	5971(8)	−823(5)	2890(3)	81(3)
C(36)	6929(7)	−602(6)	3099(3)	70(3)
C(37)	7186(7)	107(6)	3117(3)	80(3)
C(38)	6432(6)	594(5)	2923(3)	69(3)
C(39)	887(5)	796(4)	2117(2)	39(2)
C(40)	824(7)	65(5)	2156(3)	65(3)
C(41)	−187(7)	−243(5)	2147(3)	69(3)
C(42)	−1104(7)	135(5)	2094(3)	64(3)
C(43)	−1028(6)	867(5)	2057(3)	69(3)
C(44)	−18(6)	1183(5)	2068(3)	61(2)
C(45)	1967(6)	1984(4)	2547(3)	44(2)
C(46)	2140(7)	2689(5)	2433(3)	61(2)
C(47)	1978(8)	3220(5)	2774(4)	86(3)
C(48)	1669(8)	3036(6)	3219(4)	80(3)
C(49)	1503(8)	2364(6)	3332(3)	86(3)
C(50)	1649(6)	1820(5)	3009(3)	60(2)
C(1T)	868(20)	−1370(13)	3499(7)	245(9)
C(2T)	76(16)	−782(14)	3604(7)	232(9)
C(3T)	583(19)	−76(12)	3613(7)	225(9)
C(4T)	1836(19)	−1011(16)	3524(8)	260(10)
O(5T)	1646(12)	−220(9)	3516(5)	243(6)
C(6T)	1695(15)	−1897(11)	1525(7)	220(8)
C(7T)	1941(15)	−2088(11)	2022(7)	226(8)
C(8T)	2833(12)	−1498(9)	2209(5)	160(5)
C(9T)	2412(13)	−1261(10)	1324(6)	182(6)
O(10T)	3007(7)	−946(5)	1789(4)	167(4)
C(11T)	8390(22)	3974(15)	−605(10)	258(13)
C(12T)	8110(24)	3179(17)	−525(11)	333(14)
C(13T)	9111(25)	3519(20)	−740(11)	425(15)
C(14T)	9260(20)	3170(14)	−154(9)	264(11)
C(15T)	9271(21)	4015(16)	−107(10)	337(13)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

of acetonitrile during the synthesis of the reaction intermediate, $W_2Cl_4(P(n\text{-}Bu)_3)_4$. The general synthetic route is shown in Eq. (1).

$$WCl_4(P(n\text{-}But)_3)_4 \xrightarrow[\text{refluxing toluene/hexane}]{\text{dppm, acetonitrile}} W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN) \quad (1)$$

The range of reaction conditions required to form this acetonitrile adduct are under investigation. For example, the reaction was repeated on a smaller scale (200 mg of WCl_4) and after the removal of acetonitrile, evacuated overnight. Under these conditions a mixture of $W_2Cl_4(\mu\text{-dppm})_2$ and $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$ is formed. If excess acetonitrile is used, neither of these compounds are formed. The unknown products of this reaction are currently under investigation. From these preliminary studies, the acetonitrile concentration has been determined to be an important factor in the product distribution.

There is no disorder of the acetonitrile ligand in $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$ as shown in Fig. 1. If the acetonitrile is considered as a single bridging atom, the geometry is an edge-sharing bioctahedron with an open coordination site. Table 4 compares selected bond distances in $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$ with the parent compound $W_2Cl_4(\mu\text{-dppm})_2$ and two edge-sharing bioctahedral compounds with HCl and Cl_2 as bridging ligands: $W_2(\mu\text{-H})(\mu\text{-Cl})Cl_4(\mu\text{-dppm})_2$ and $W_2(\mu\text{-Cl})_2Cl_4(\mu\text{-dppm})_2$ [17,24,25]. The $W_2P_4Cl_4XY$ core is shown in Fig. 2 where X = H and Y = Cl for $W_2(\mu\text{-H})(\mu\text{-Cl})Cl_4(\mu\text{-dppm})_2$, X = Y = Cl for $W_2(\mu\text{-Cl})_2Cl_4(\mu\text{-dppm})_2$ and X is an empty coordination site and Y = C–N for $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$. The W–W bond

Table 3
Selected bond distances (Å) and angles (°) for $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$

Bond distances	
W(1)–W(2)	2.4981(10)
W(1)–N(1A)	2.103(7)
W(1)–C(1A)	2.114(7)
W(2)–N(1A)	2.101(7)
W(2)–C(1A)	2.096(8)
C(1A)–N(1A)	1.303(8)
C(1A)–C(2A)	1.617(11)
W(1)–Cl(1)	2.447(2)
W(1)–Cl(2)	2.427(2)
W(2)–Cl(3)	2.448(2)
W(2)–Cl(4)	2.423(2)
W(1)–P(1)	2.552(2)
W(2)–P(2)	2.562(2)
W(1)–P(3)	2.573(2)
W(2)–P(4)	2.556(2)
Bond angles	
N(1A)–C(1A)–C(2A)	116.3(7)
W(2)–N(1A)–W(1)	72.9(2)
W(2)–C(1A)–W(1)	72.8(2)
N(1A)–C(1A)–W(1)	71.5(4)
N(1A)–C(1A)–W(2)	72.1(4)
N(1A)–W(1)–C(1A)	36.0(2)
N(1A)–W(2)–C(1A)	36.2(2)
C(1A)–W(1)–Cl(1)	83.4(2)
C(1A)–W(1)–Cl(2)	160.6(2)
C(1A)–W(2)–Cl(3)	84.9(2)
C(1A)–W(2)–Cl(4)	160.1(2)
N(1A)–W(1)–Cl(1)	84.3(2)
N(1A)–W(1)–Cl(2)	160.1(2)
N(1A)–W(2)–Cl(3)	83.2(2)
N(1A)–W(2)–Cl(4)	160.3(2)
N(1A)–W(1)–W(2)	53.5(2)
C(1A)–W(1)–W(2)	53.3(2)
Cl(1)–W(1)–W(2)	134.70(6)
Cl(2)–W(1)–W(2)	136.82(6)
Cl(3)–W(2)–W(1)	135.15(5)
Cl(4)–W(2)–W(1)	136.62(6)
Cl(2)–W(1)–Cl(1)	88.46(8)
Cl(4)–W(2)–Cl(3)	88.14(8)
W(2)–W(1)–P(1)	95.16(5)
W(1)–W(2)–P(2)	96.67(4)
W(2)–W(1)–P(3)	96.35(4)
W(1)–W(2)–P(4)	94.61(5)
P(1)–W(1)–P(3)	166.25(6)
P(4)–W(2)–P(2)	166.02(6)
Cl(1)–W(1)–P(1)	89.67(7)
Cl(4)–W(2)–P(4)	82.19(6)

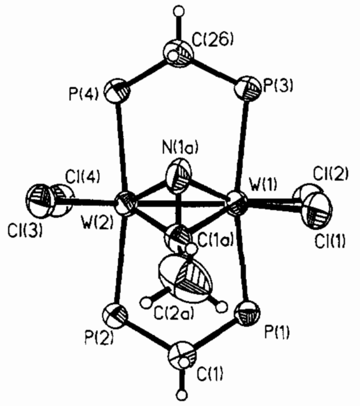

Fig. 1. An ORTEP drawing of the core atoms in $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$. Thermal ellipsoids for W, Cl, P, N and C are shown at 50% probability. The hydrogen atoms are shown as arbitrarily sized uniform circles.

distance in $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$ is closest to that observed in the edge-sharing HCl adduct, but the W–W–Cl bond angles of the edge-sharing compound $W_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_4(\mu\text{-dppm})_2$ vary by over 25° when comparing the side of the molecule with the bridging H to the side with the bridging Cl, reflecting the asymmetry of the bridging atoms. The variation is considerably smaller, on the order of 2° at the extreme, in $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$. This negligible variation in bond angles plus the diamagnetism of the molecule, indicate that the presence of a bridging hydride is unlikely.

The bonding scheme within the molecule and W–W bond order is still in question. The low symmetry of this molecule increases the difficulties in performing theoretical calculations to determine an accurate bonding picture. The key to any bonding explanation is the diamagnetism of the molecule and the bond distances and angles related to the acetonitrile ligand, N(1A)–C(1A)–C(2A). The angle formed by N(1A)–C(1A)–C(2A) is 116.3(7)° close to the value for an sp^2 hybrid and is shown in Fig. 3 in a view down the W–W axis. The N(1A)–C(1A) bond distance is 1.303(8) Å which is in the order of a shortened partial double bond, 1.322 ± 0.003 Å, and considerably longer than the expected value of the triple bond in RCN compounds of 1.158 ± 0.002 Å [26]. In a series of trinuclear iron compounds of the general formula $Fe_3(X)(CO)_9$ where X is butyronitrile or benzonitrile [27,28], C–N distances of 1.260(3) and 1.28(3) Å and N–C–C angles of 135.1(2) and 139(2)°, respectively, have been observed. The bonding of the nitrile in these molecules is described as a σ bond to one of the iron centers in the cluster and two π bonds to the other iron centers. Therefore, the bonding of the acetonitrile to the ditungsten core may consist of a combination of σ and π bonds.

In addition to the similarities of $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$ to edge-sharing bioctahedral compounds, the structure of this new compound can be compared to adducts formed with triply bonded ditungsten and dimolybdenum compounds. A similar compound is the product of the reaction of dimethylcyanamide with the hexaalkoxides of dimolybdenum [29,30]. However, $W_2(OR)_6$, where R = t-Bu, forms the polymer $[(t\text{-}BuO)_3WN]_x$ and $(t\text{-}BuO)_3WCNMe_2$. The triple bond between the terminal nitrogen and the adjacent carbon in the dimethylcyanamide is completely destroyed to

Table 4
Comparison of selected bond distances (Å) and angles (°) of $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$ and related compounds

Compound	W–W bond distance	W-bridge bond distance	W–bridge–W bond angle	W–W–Cl bond angle
$W_2Cl_4(dppm)_2$ [17]	2.269(1)			106.48(6) 109.28(7)
$W_2Cl_4(dppm)_2 \cdot CH_3CN$	2.4981(10)	2.103(7) [N] 2.101(7) [N] 2.114(7) 2.096(8)	72.9(2) [N] 72.8(2)	134.70(6) [a] 136.82(6) 135.15(5) [a] 136.62(6)
$W_2HCl_5(dppm)_2$ [24]	2.4830(9)	2.470(4) 2.486(5)	60.1(1)	144.9(1) 145.9(1) 119.7(1) [b] 119.8(1) [b]
$W_2Cl_6(dppm)_2$ [25]	2.691(1)	2.405(3) 2.393(3)	68.23(9)	138 [c]

[a] Angle on the side of the molecule with the bridging acetonitrile.

[b] Angle on the side of the molecule with the bridging hydride.

[c] Calculated value.

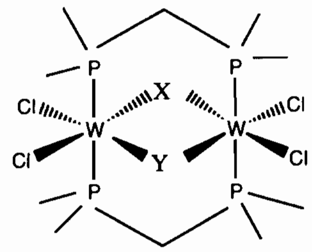

Fig. 2. Representative geometry of edge-sharing bioctahedral molecules.

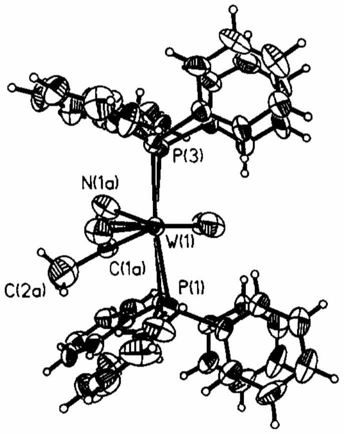

Fig. 3. An ORTEP drawing of $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$ viewed down the W–W axis. Thermal ellipsoids for W, Cl, P, N and C are shown at 50% probability. The hydrogen atoms are shown as arbitrarily sized uniform circles.

form two mononuclear tungsten compounds. $Mo_2(OCH_2\text{-t-Bu})_6$ reacts with dimethylcyanamide and retains the dinuclear transition metal core to form $Mo_2(OCH_2\text{-t-Bu})_6(\mu\text{-NCNMe}_2)$. The terminal C–N bond of the dimethylcyanamide ligand in $Mo_2(OCH_2\text{-t-Bu})_6(\mu\text{-NCNMe}_2)$ is slightly longer than the one observed in $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$, 1.333(4) Å. The N–C–N angle of the bridging ligand $NCNMe_2$ is also slightly larger than the one observed in the acetonitrile adduct, 127 versus 116.3(7)°. However, the bonding in this molecule is more asymmetric than that observed in $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$. The terminal nitrogen of $NCNMe_2$ is bonded to both of the metal centers at distances of 1.908(3) and 2.134(2) Å, respectively, but the dimethylcyanamide is parallel to the Mo–Mo bond and only one metal center is bonded to the central carbon of the $N\text{–}C\text{–}NMe_2$ ligand at a distance of 2.014(4) Å.

In $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$, the distances from the metal centers to the nitrogen are equivalent within experimental error (see Table 3) and the W–C distances are 2.114(7) and 2.096(8) Å. In this respect, the acetonitrile adduct of $W_2Cl_4(\mu\text{-dppm})_2$ more closely resembles the alkyne adduct of ditungsten hexaneopentoxide where the geometry of the W_2C_2 core of $W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$ is similar to the W_2NC core of $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$ [9]. The W–C distances of $W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$ are as follows: W(1)–W(2) = 2.5719(12), C(5)–C(6) = 1.402(22), W(1)–C(5) = 2.296(14), W(1)–C(6) = 2.107(11), W(2)–C(5) = 2.012(14), W(2)–C(6) = 2.112(12) Å, with W(1)–C(5)–W(2) = 73.0(5)°. The bonding in these compounds has been described as a dimetallatetrahedrane with a bond order of one for the M–M, M–C and C–C bonds. The W(1)–N(1A)–W(2) bond angle in $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$ is 72.9(2)°, similar to the angle observed in $W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$. In contrast, the angles observed in ditungsten edge-sharing bioctahedral compounds are typically below 70° [31,32].

If the W(1)–W(2) bond in $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$ is only a single bond then variation of the chelating phosphine ligand from dppm to dppe (1,2-bis(diphenylphosphino)ethane) with an additional $-CH_2-$bridge would significantly alter the W(1)–W(2) bond distance. In addition, the bidentate phosphine ligand dppe is known to both chelate and bridge the ditungsten core in $W_2Cl_4(dppe)_2$ [33]. This could lead to the formation of a chelated analog of $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$. Therefore, future studies of this reaction include the use of other chelating phosphine ligands, variation of the bridging ligand and the study of the reactivity of $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$.

3.2. *UV–Vis spectroscopy*

Solutions of the compound appear brown in color, but within the range of the UV–Vis spectrometer available (190–820 nm) no absorption band was observed. Future studies of this compound will include near-IR spectroscopy.

3.3. *$^{31}P\{^1H\}$ NMR spectroscopy*

The sharp lines observed in the $^{31}P\{^1H\}$ NMR spectrum are an indication that the compound is diamagnetic, minimizing the possibility of the presence of a bridging hydride. An AA′BB′ pattern is observed in the NMR spectrum at room temperature as shown in Fig. 4. Since the phosphines *trans* to one another are inequivalent, the acetonitrile ligand displays no fluxional behavior at room temperature. The multiplets are centered at 4 and 15 ppm, upfield to the chemical shift of the parent compound $W_2Cl_4(\mu\text{-dppm})_2$ (18.14 ppm) [20]. Spectra were recorded at 121 and 162 MHz with no change in the chemical shift difference of these multiplets. The *trans* coupling of the different phosphorus environments is expected to be on the order of 150 Hz, but 2D NMR spectroscopy will be used to investigate the coupling in this complex pattern [34,35].

One of the multiplets is due to the dppm molecule (P(3) and P(4)) bound to the W–W core closest to the nitrogen and the other multiplet is due to the dppm molecule (P(1) and P(2)) bound to the same core but closest to the carbon of the acetonitrile. Future studies that vary the bridging ligand will be used to assign the chemical shifts. The shift of the phosphorus atoms P(1) and P(2) should vary more than the phosphorus atoms P(3) and P(4) if acetonitrile is replaced with diphenylacetonitrile or phenylacetonitrile. Neither coupling of the phosphorus atoms to the tungsten nor to the nitrogen was observed.

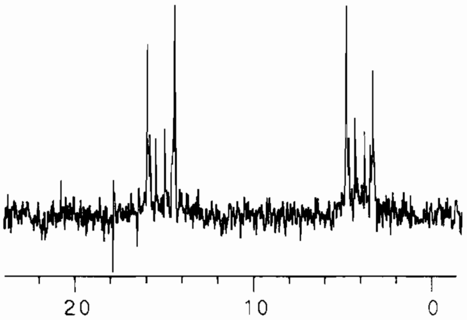

Fig. 4. $^{31}P\{^1H\}$ NMR spectrum of $W_2Cl_4(\mu\text{-dppm})_2(\eta^2\text{-}\mu\text{-}CH_3CN)$ recorded at 121 MHz.

4. Supplementary material

Listing of observed and calculated structure factors (33 pages) and complete tables of crystal data, positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, bond distances, and bond angles for the molecule (7 pages) are available from author J.L.E. upon request.

Acknowledgements

Authors J. Eglin and E. Hines acknowledge the support of the National Science Foundation EPSCoR program (Grant No. EHR 9108767), ARI Program (Grant No. CHE-92-14521), and the Anna McLean Award Program. Authors E. Valente and J. Zubkowski acknowledge the support of the Office of Naval Research.

References

[1] F.A. Cotton and C.B. Harris, *Inorg. Chem., 4* (1965) 330.
[2] F.A. Cotton and R.A. Walton, *Multiple Bonds between Metal Atoms,* Oxford University Press, Oxford, 2nd edn., 1993.
[3] J.P. Fackler, *Metal–Metal Bonds and Clusters in Chemistry and Catalysis,* Plenum, New York, 1990.
[4] J.M. Canich, F.A. Cotton, K.R. Dunbar and L.R. Falvello, *Inorg. Chem., 27* (1988) 804.
[5] P.A. Agaskar, F.A. Cotton, K.R. Dunbar, L.R. Falvello and C.J. O'Connor, *Inorg. Chem., 26* (1987) 4051.
[6] F.A. Cotton and G.N. Mott, *J. Am. Chem. Soc., 104* (1982) 5978.
[7] F.A. Cotton and R.L. Luck, *Inorg. Chem., 28* (1989) 182.
[8] J.L. Caldarelli, L.E. Wagner, P.S. White and J.L. Templeton, *J. Am. Chem. Soc., 116* (1994) 2878.
[9] M.H. Chisholm, B.K. Conroy, K. Folting, D.M. Hoffman and J.C. Huffman, *Organometallics, 5* (1986) 2457.
[10] M. Chisholm, B.K. Conroy, D.L. Clark and J.C. Huffman, *Polyhedron, 7* (1988) 903.
[11] M. Chisholm, D.M. Hoffman and J.C. Huffman, *J. Am. Chem. Soc., 106* (1984) 6806.
[12] J.L. Kiplinger, M.A. King, A.M. Arif and T.G. Richmond, *Organometallics, 12* (1993) 3382.
[13] F.A. Cotton and W.T. Hall, *Inorg. Chem., 19* (1980) 2354.
[14] F.A. Cotton, W. Schwotzer and E.S. Shamshoum, *Organometallics, 2* (1983) 1167.

[15] R. Asselt, C.J. Elsevier, W.J.J. Smeets and A.L. Spek, *Inorg. Chem.*, *33* (1994) 1521.

[16] M.H. Chisholm, K. Folting, J.C. Huffman and I.P. Rothwell, *J. Am. Chem. Soc.*, *104* (1982) 4389.

[17] J.M. Canich and F.A. Cotton, *Inorg. Chim. Acta*, *142* (1988) 69.

[18] M.A.S. King and R.E. McCarley, *Inorg. Chem.*, *12* (1973) 1972.

[19] R.R. Schrock, L.G. Sturgeoff and P.R. Sharp, *Inorg. Chem.*, *22* (1983) 2801.

[20] F.A. Cotton, J.L. Eglin and C.A. James, *Inorg. Chem.*, *32* (1993) 681.

[21] *SHELXA-90*, Siemens Analytical X-ray, Madison, WI, USA, 1990.

[22] *International Tables for X-Ray Crystallography*, Vol. IV, Reidel, Dordrecht, Netherlands, 1985.

[23] G.M. Sheldrick, *Acta Crystallogr., Sect. A*, *46* (1990) 467; *J. Appl. Crystallogr.*, (1994) to be published.

[24] P. Fanwick, W.S. Harwood and R.A. Walton, *Inorg. Chem.*, *26* (1987) 242.

[25] J.M. Canich, F.A. Cotton, L.M. Daniels and D.B. Lewis, *Inorg. Chem.*, *26* (1987) 4046.

[26] R. Weast and M. Astle (eds.), *CRC Handbook*, CRC, Boca Raton, FL, 63rd edn., 1982–1983, p. F-180.

[27] M.A. Andrews, C.B. Knobler and H.D. Kaesz, *J. Am. Chem. Soc.*, *101* (1979) 7260.

[28] E. Keller and D. Wolters, *Chem. Ber.*, *117* (1984) 1572.

[29] M.H. Chisholm, J.C. Huffman and N.S. Marchant, *J. Am. Chem. Soc.*, *105* (1983) 6162.

[30] M.H. Chisholm, J.C. Huffman and N.S. Marchant, *Organometallics*, *6* (1987) 1073.

[31] F.A. Cotton and S.K. Mandal, *Inorg. Chem.*, *31* (1992) 1267.

[32] J.L. Templeton, R.A. Jacobson and R.E. McCarley, *Inorg. Chem.*, *16* (1977) 3320.

[33] F.A. Cotton and T.R. Felthouse, *Inorg. Chem.*, *20* (1981) 3880.

[34] G.S. Girolami, V.V. Mainz, R.A. Andersen, S.H. Vollmer and V.W. Day, *J. Am. Chem. Soc.*, *103* (1983) 3953.

[35] F.A. Cotton, L.R. Falvello, C.A. James and R.L. Luck, *Inorg. Chem.*, *29* (1990) 4759.