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W₂(μ-H)₂Cl₄(μ-dppm)₂ : the bulk synthesis of a bridging hydride

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Abstract—The synthesis of the ditungsten species $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$ marks the first bulk preparation of a bridging hydride W(III–III) species. The compound retains the characteristic edge-sharing bioctahedral (ESBO) geometry with a W—W bond distance of 2.3918(7) Å. Although several Group VI ESBO complexes have been prepared, only two with bridging hydride groups, $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$ and $W_2(\mu\text{-H})_2(\mu\text{-O}_2CC_6H_5)_2$ $Cl_2(P(C_6H_5)_3)_2$, have been reported to date. The complex $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$ has been characterized with $^{31}P\{^1H\}$, ^1H NMR, UV–vis, and IR spectroscopic techniques. A singlet is observed in the $^{31}P\{^1H\}$ NMR spectra of $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$ at $\delta = 20.464$ ppm with $J_{P\text{-W}} = 126$ Hz and the IR spectra includes the tungsten-hydride symmetric stretch at 1602 cm⁻¹. © 1997 Elsevier Science Ltd

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Since the structural characterization of the first bridging hydride species $W_2(\mu\text{-H})_2(\mu\text{-O}_2CC_6H_5)_2Cl_2$ $(P(C_6H_5)_3)_2$ in this laboratory [1], research has focused on the development of a more general methodology for the bulk synthesis of bridging hydride species for the systematic study of the electronic and spectroscopic properties of these compounds. For edge-sharing bioctahedral (ESBO) complexes, changes in the bridging ligands result in variations in the electronic properties [1–3]. These properties have been studied on a wide variety of ESBO systems and include the bridging ligands Cl_2 [4–14], HCl [15–18], and sulfur [19,20]. Studies have also shown that the coordinated phosphine ligand may effect the electronic properties of the complexes [2]. With the development of a better synthetic route to ESBO W (III, III) species with bridging hydride groups, further studies of these complexes can now be pursued, including the reactivity of the bridging hydrides and variations of the chelating phosphine ligand.

EXPERIMENTAL

Materials and methods

Standard Schlenk and vacuum line techniques were employed using an argon atmosphere. Commercial grade THF, toluene, and hexanes were dried over potassium/sodium benzophenone ketyl and freshly distilled under argon prior to use. The starting material, WCl_4, was synthesized from WCl_6 and $W(CO)_6$ as previously reported [3]. Bis(diphenylphosphino)methane [dppm] was purchased from Strem Chemicals and evacuated overnight under dynamic vacuum to remove any residual oxygen or moisture. Tri-n-butyl phosphine $[P(n\text{-Bu})_3]$ was purchased from Johnson–Matthey and used without further purification. Sodium triethylborohydride $[NaBEt_3H]$ was purchased from Aldrich as a 1 M solution in toluene in a SureSeal bottle.

UV–vis spectra were recorded on a Hewlett Packard 8453 model diode array spectrophotometer from 190 to 1000 nm. Infrared spectra were recorded on either a MIDAC 101280-1 model FTIR or a Perkin–Elmer 293 model IR spectrophotometer. The $^{31}P\{^1H\}$ {162 MHz} and ^1H {400 MHz} NMR spectra were re-

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corded on a General Electric Omega NMR spectrometer with a variable temperature probe referenced to H_3PO_4 (0.00 ppm) and TMS (0.00 ppm), respectively. Calibration of the temperature was performed using a methanol sample and the set point did not vary from the actual temperature by more than 1 K over the temperature range 178–295.5 K [21]. When the set point for each temperature was reached in the $^{31}P\{^1H\}$ NMR experiments, the sample temperature was equilibrated for 20 min in the spectrometer before data collection.

$W_2(\mu\text{-}H)_2Cl_4(\mu\text{-dppm})_2$ (**I**). A 1.0 g (3.07 mmol) suspension of WCl_4 in THF was cooled to 0°C, and 6.14 mL (6.14 mmol) of a 1 M solution of $NaBEt_3H$ in toluene was added. $P(n\text{-Bu})_3$ (1.52 mL, 6.14 mmol) was added to the blue 'WCl_2' and the solution was allowed to warm to room temperature. The solution was then transferred to a flask containing dppm (1.18 g, 3.07 mmol) and 20 mL of hexanes added. The green solution was heated at reflux overnight to yield the purple compound $W_2(\mu\text{-}H)_2Cl_4(\mu\text{-dppm})_2$ (**I**). After washing the precipitate several times with 30 mL aliquots of hexanes, the purple product **I** was dried under dynamic vacuum (1.421 g, 72%). No UV–vis absorbance peaks were observed for a THF solution of **I** in the region 350–1000 nm.

Structure determination

Deep purple X-ray quality prisms of **I** were grown from a THF solution of **I** layered with hexanes. A crystal was mounted with epoxy cement on the end of a fine glass fiber. Data were collected on a Siemens R3m/V automated diffractometer fitted with a molybdenum source and graphite monochromator. Preliminary investigations revealed that the crystal belonged to the monoclinic system with a space group of $C2/c$ or Cc. $C2/c$ was determined to be the correct group based upon reflection statistics and structure refinement. Cell constants were determined from forty reflections with higher diffraction angles. Data were collected by omega scans (1.6° wide) and 13,424 observations were made to yield a total of 10,630 independent reflections.

The structure was determined by using direct methods (SHELXS-90). The model was developed and refined with positions and anisotropic vibrational factors for all the non-hydrogen atoms. Calculated hydrogen atom positions with fixed isotropic vibrational parameters were included. In the final stages of refinement, difference Fourier calculations showed peaks with heights of approximately 2.8 Å³ in the vicinity of the tungsten atoms. An empirical absorption correction (SHELXA) was applied with the magnitude of the correction in conformity with psi-scans of reflections with χ diffraction angles near 90°. After the correction was applied, the peaks in the vicinity of the tungsten atoms were reduced by more than 50%. The two bridging hydrogen atoms were

located on the symmetry axis at 0, y, 1/4. The y coordinates of the bridging hydrogen atoms could be refined with a fixed isotropic vibrational factor assigned. Although generally hydrogen atoms cannot be located precisely in dinuclear 5d transition metal species, the hydrogen atoms locations are in chemically reasonable positions. A small extinction coefficient was also applied, and the model was refined to convergence.

Table 1 provides information on the data collection of **I**. Selected bond distances and angles for **I** are included in Table 2 and Table 3 compares key bond distances and angles of **I** to related structures [1,4].

RESULTS AND DISCUSSION

Synthesis

Upon reduction of WCl_4 at low temperatures with $NaBEt_3H$, the side products $NaCl$, BEt_3, and H_2 gas are produced. Direct addition to the reaction mixture of dppm or a monodentate phosphine results in the formation of $W_2Cl_4(\mu\text{-dppm})_2$ or $W_2Cl_4(PR_3)_4$ respectively, as the solution slowly warms to room temperature [22].

If any additional heating of the solution of $W_2Cl_4[P(n\text{-Bu}_3)]_4$ occurs in the presence of the bidentate phosphine dppm, the hydrogen gas dissolved in the THF or THF/hexanes solvent oxidatively adds to form the complex $W_2(\mu\text{-}H)_2Cl_4(\mu\text{-dppm})_2$. Removal of the dissolved H_2 gas prior to heating by precipitating $W_2Cl_4(P(n\text{-Bu}_3))_4$ from solution and washing the product with THF/hexanes solvent mixtures eliminates the formation of $W_2(\mu\text{-}H)_2Cl_4(\mu\text{-dppm})_2$ and only the quadruply bonded complex is formed.

The ability to synthesize other compounds of the general type, $W_2(\mu\text{-}H)_2Cl_4(P\text{-}P)_2$ or $W_2(\mu\text{-}H)_2Cl_4(PR_3)_4$ where P–P is a bidentate and PR_3 is a monodentate phosphine, is currently under investigation. Preliminary studies with $Mo_2Cl_4(\mu\text{-dppm})_2$ indicate that $Mo_2(\mu\text{-}H)_2Cl_4(\mu\text{-dppm})_2$ is not formed under the same mild reaction conditions. Since tungsten is more easily oxidized with an oxidation potential of 0.6 V over molybdenum, it is not too surprising that $W_2Cl_4(\mu\text{-dppm})_2$ is more reactive towards the dissolved H_2 gas than $Mo_2Cl_4(\mu\text{-dppm})_2$ [23,24].

Molecular structure

As shown in Table 3, the W—W bond distance of 2.3918(7) Å for $W_2(\mu\text{-}H)_2Cl_4(\mu\text{-dppm})_2$ (**I**) is slightly longer, 0.042 Å, than the W—W bond distance of 2.350(1) Å observed in $W_2(\mu\text{-}H)_2Cl_2(PPh_3)_2(\mu\text{-}O_2CC_6H_5)_2$ (**II**) [1]. The difference in the W—W bond distances for the triply bonded tungsten compounds parallels the change in the W—W bond distance when comparing the quadruply bonded dppm complex, $W_2Cl_4(\mu\text{-dppm})_2$ (W—W = 2.269 Å) [25], with the

Table 1. Crystal data for $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$

Chemical Formula	$C_{50}H_{46}Cl_4P_4W_2$
Formula weight	1278.55
Space group	$C2/c$
a(Å)	17.493(5)
b(Å)	17.052(4)
c(Å)	16.223(4)
$\beta(°)$	93.86(2)
$V(\text{Å}^3)$	4828(2)
Z	4
ρ_{calcd} (g/cm^3)	1.759
Absorption coefficient	5.255 mm^{-1}
$F(000)$	2488
Crystal Size (mm)	$0.10 \times 0.08 \times 0.06$
Wavelength (Å)	0.71073
Temperature (K)	293(2)
θ range for data collection (°)	2.04–35.00
Index ranges	$0 \leqslant h \leqslant 28, 0 \leqslant k \leqslant 27, -26 \leqslant l \leqslant 26$
Reflections collected	12702
Independent reflections	10630 [$R_{(int)} = 0.0740$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10630/1/274
Goodness-of-fit on F^2	0.656
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0448$, $wR2 = 0.0823$
R indices (all data)	$R1 = 0.1119$, $wR2 = 0.0909$
Extinction coefficient	0.000090(11)
Largest diff. Peak and hole (e Å^{-3})	1.654/−1.760

Table 2. Selected bond distances (Å) and angles (°) for $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$

W—W(Oa)	2.3918(7)	W—P(2)	2.532(2)
W—H(1)	1.83(8)	W—Cl(1)	2.396(2)
W—H(2)	1.74(8)	W—Cl(2)	2.413(2)
W—P(1a)	2.570(2)		
H(1)—W—H(2)	95.8(24)	P(2)—W—P(1a)	170.05(5)
W(Oa)—W—Cl(1)	128.53(4)	W(Oa)—W—P(2)	94.84(4)
W(Oa)—W—Cl(2)	128.22(4)	W(Oa)—W—P(1a)	94.40(4)
Cl(1)—W—Cl(2)	103.11(6)		

Table 3. Comparison of selected bond distances (Å) and angles (°) for $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$, $W_2(\mu\text{-H})_2Cl_2(PPh_3)_2(\mu\text{-}O_2CC_6H_5)_2$, and $W_2(\mu\text{-Cl})_2Cl_4(\mu\text{-dppm})_2$

Compound	W—W bond distance (Å)	W-bridge bond distance	W-Bridge-W bond angle (°)	W—W—Cl bond angles (°)
$W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$	2.3918(7)	1.83(8) Å 1.74(8) Å	84.4^a	128.53(4) 128.22(4)
$W_2(\mu\text{-H})_2Cl_2(PPh_3)_2(O_2CC_6H_5)_2$ [1]	2.350(1)	1.67(8) Å 1.90(8) Å	82(3)	131.26(8)
$W_2(\mu\text{-Cl})_2Cl_4(\mu\text{-dppm})_2$ [4]	2.691(1)	2.405(3) Å 2.393(3) Å	68.23(9)	137.65^a

^{a} Calculated value.

quadruply bonded benzoate complex, $W_2(\mu\text{-}O_2CC_6H_5)_4$ (W—W = 2.196 Å) [24].

The W—W bond distance for $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$ (**I**) is 0.089 Å shorter than the asymmetrically bridging ESBO complex $W_2(\mu\text{-H})(\mu\text{-Cl})Cl_4(\mu\text{-dppm})_2$ (**III**) and 0.30 Å shorter than the bridging dichloride ESBO complex $W_2(\mu\text{-Cl})_2Cl_4(\mu\text{-dppm})_2$ (**IV**) due to the progressive decrease in size of the bridging ligands [1,4]. The W—W bond distances for both $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$ and $W_2(\mu\text{-H})_2Cl_2(PPh_3)_2(\mu\text{-O}_2CC_6H_5)_2$ with the $\sigma^2\pi^2\delta^2$ electron configuration are slightly longer than the W—W bond distances observed in Chisholm type triply-bonded compounds with the $\sigma^2\pi^4$ electron configuration [26,27].

Of note in the structure of **I** is the average W—W—Cl_t bond angle of 128.38°. The W—W—Cl_t bond angle is 3° more acute than the W—W—Cl_t bond angle observed in **II** (131.26°). However, **II** contains terminal PPh_3 ligands and a more acute P_t—W—Cl_t bond angle of 101.63(9)° versus the Cl_t—W—Cl_t bond angle of 103.11(6)° observed for **I** [1]. In **IV**, an 8° more obtuse W—W—Cl_t bond angle of 137.65° is observed in comparison to **I**, but a more acute Cl_t—W—Cl_t of 84.1(1)° is observed when two bridging chlorides are present [4]. All of the W—W—Cl_t bond angles observed are similar to the theoretical value of 135° predicted based on the d_{xy} orbital symmetry with small differences observed due to changes in the size of either the bridging or terminal ligands.

The W—H_b—W bond angle of 84.4° (calculated value) observed in **I** similar to the W—H_b—W bond angle in **II** of 82(3)° [1]. The X_t—W—X_t angles are dependent upon the X_b—W—X_b angles due to the reverse scissoring effect [2]. This effect is reflected in
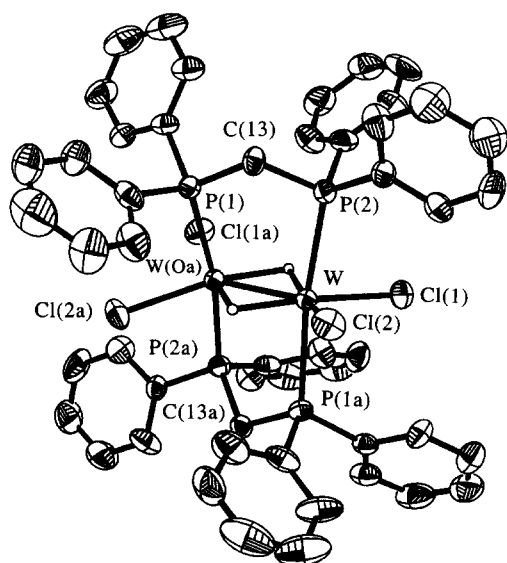
the 111.77(9)° Cl_b—W—Cl_b angle for $W_2(\mu\text{-Cl})_2Cl_4(\mu\text{-dppm})_2$ and 95.82(4)° H_b—W—H_b angle for $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$ with Cl_t—W—Cl_t angles of 84.1(1)° and 103.11(6)°, respectively [1,2,4].

NMR spectroscopy

Only a singlet at $\delta = 20.464$ ppm with $J_{P\text{-}W} = 126$ Hz was observed in the $^{31}P\{^1H\}$ NMR spectra of $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$, verifying the bulk purity of the compound. A pentet for the bridging hydrides at $\delta = 4.516$ ppm was observed in the ^1H NMR spectra due to the coupling of the hydrogens to the four equivalent phosphorus atoms with $J_{H\text{-}P} = 5.54$ Hz. Tungsten–hydrogen sidebands were observed with $J_{H\text{-}W} = 108$ Hz. As discussed in previous studies, the ordering of energy levels of $W^{III}\text{-}W^{III}$ systems with ESBO geometries is $\sigma \ll \pi < \delta < \delta^* < \pi^* < \sigma^*$ based on W—W overlap alone. However, as the bridging ligands are altered the orbital ordering changes [1,4,19,28]. Based on Fenske–Hall calculations, the bridging hydride compound $W_2(\mu\text{-H})_2Cl_2(PPh_3)_2$ $(\mu\text{-O}_2CC_6H_5)_2$ (**II**) was predicted to be diamagnetic with a large $-2J$ value due to the δ bond's increased stability and energy level ordering of $\sigma < \pi < \delta \ll \sigma^* < \delta^* < \pi^*$ in the bridging hydride species [1]. Extrapolating from the calculations for **II**, the new species synthesized, $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$, should have a similar molecular orbital diagram.

The molecule is diamagnetic as predicted and verified by the singlet observed in the $^{31}P\{^1H\}$ NMR spectra of $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$. Variable temperature $^{31}P\{^1H\}$ NMR experiments were performed on mixtures of **I** and the compound $W_2Cl_4(\mu\text{-dppm})_2$ to determine if a thermally accessible triplet state is present. The sample was warmed to 50°C from 20.1°C and the peak for compound **I** shifted $\Delta = 0.548$ ppm upfield, smaller than the shift observed for $W_2Cl_4(\mu\text{-dppm})_2$ ($\Delta = 0.731$ ppm upfield) indicating that the singlet–triplet gap for $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$ is larger the 12,568 cm^{-1} [29].

IR spectroscopy

IR measurements were made and the tungsten–hydride symmetric stretch, v (WH$_{symm}$), was identified at 1601 cm^{-1}. In related $(\mu\text{-Cl})(\mu\text{-H})$ ESBO compounds with a single bridging hydride, the tungsten–hydride symmetric stretch has been identified at 1585 cm^{-1} for $MoWCl_4(\mu\text{-Cl})(\mu\text{-H})(\mu\text{-dppm})_2$ [16] and 1538–1580 cm^{-1} for a series of M_2X_8H (M = Mo and/or W and X = Cl or Br) complexes [30]. The tungsten–hydride asymmetric stretch for **I** could not be identified. However, this is not uncommon for the tungsten–hydride asymmetric stretch as the related peaks in the IR spectrum tend to be weak and broad in the 1300–800 cm^{-1} region [16,30–33]. Several ditungsten structures are known which contain both terminal and bridging hydride ligands [32–35]. IR

Fig. 1. A thermal ellipsoid plot of $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$. Thermal ellipsoids for W, Cl, P, and C are shown at 50% probability. The hydrogen atoms are shown as arbitrarily sized uniform circles.

measurements made on complexes with only terminal hydride ligands allowed the identification of the tungsten-hydride stretch, v (WH) 1875–1931 cm^{-1}. When these compounds were reacted further to form bridging hydride species, the tungsten–hydride stretch could not be identified [32,33].

Supplementary material— Listing of observed and calculated structure factors (6 pages) and complete tables of crystal data, positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, bond distances, and bond angles for molecule I (24 pages) are available from author J.L.E. upon request.

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