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Articles

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Cyclopentoxyditungsten Compounds and Crystal and Molecular Structures and Dynamic Solution Behavior of $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$

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The reaction between $W_2(NMe_2)_6$ and cyclopentanol (≥6 equiv) in hexane solvents initially forms the dimethylamine adduct $W_2(O\text{-}c\text{-}C_5H_9)_6(HNMe_2)_2$ but with time in the presence of cyclopentanol and dimethylamine the hydrido-bridged compound $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ is formed and may be isolated as green crystals. Crystal data at −155 °C: $a = 13.057$ (3) Å, $b = 15.592$ (4) Å, $c = 10.376$ (2) Å, $\alpha = 97.72$ (1)°, $\beta = 109.55$ (1)°, $\gamma = 94.22$ (1)°, $Z = 2$, $d_{calcd} = 1.738$ g cm^{-3}, and space group $P\bar{1}$. The bridging hydride was not located crystallographically but can be inferred to occupy a position trans to the $HNMe_2$ ligand so as to complete a confacial bioctahedron. In solution, the molecule is fluxional and the dimethylamine is labile and has been replaced by PMe_3. Variable-temperature ^1H and ^{31}P NMR studies reveal that the $(RO)_3W(\mu\text{-}H)(\mu\text{-}OR)_2W(OR)_2(L)$ molecules are in a temperature dependent equilibrium with the unligated molecule $W_2(\mu\text{-}H)(OR)_7$ and the free ligand. At high temperature, rapid OR group scrambling generates two equivalent (time-averaged) W atoms, but at low temperature the NMR spectra are consistent with expectations based on the solid-state structure of $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$.

Introduction

The chemical reactivity of the hexaalkoxides of ditungsten, $W_2(OR)_6$, compounds is very sensitive to the nature of the alkoxide ligand. We have determined the structures of $W_2(O\text{-}i\text{-}Pr)_6$,[1] $W_2(O\text{-}c\text{-}C_5H_9)_6$,[2] and $W_2(OCH_2\text{-}t\text{-}Bu)_6$[2] and have shown how similar these molecules are in their $W_2(OC)_6$ cores. However, in their reactivity they are quite dissimilar. For example, whereas the addition of *i*-PrOH (excess) to $W_2(NMe_2)_6$ leads to the competitive formation of $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$,[3] $W_4(C)(NMe)(O\text{-}i\text{-}Pr)_{12}$,[4] $W_4(O\text{-}i\text{-}Pr)_{12}$ and $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$,[5] the related alcoholysis with 2,2-dimethylpropanol gives only $W_2(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)_2$.[6] We describe here the preparation and characterization of $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ formed in the reaction between $W_2(NMe_2)_6$ and cyclopentanol. This is of particular interest with respect to the formation and characterization of the $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$ molecule described previously.[5,7]

Results and Discussion

Synthesis. The reaction between $W_2(NMe_2)_6$ and cyclopentanol (≥6 equiv) in hydrocarbon solvents yields a variety of products depending upon the conditions. (1) At short reaction times, the bis(dimethylamine) adduct $W_2(O\text{-}c\text{-}C_5H_9)_6(HNMe_2)_2$ is the major product, and when the reaction is carried out in hexane at relatively high concentration, this compound crystallizes from solution. (2) When the reaction is carried out in toluene solution under similar conditions, the unligated compound $W_2(O\text{-}c\text{-}C_5H_9)_6$ (M≡M) is isolated as crystals upon cooling the solution. (3) At longer reaction times in hexane, the hydrido compound $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ is formed, and this can be prepared in separate experiments from the reactions between $W_2(O\text{-}c\text{-}C_5H_9)_6(HNMe_2)_2$ and cyclopentanol in hexane. The volume of the head space above the solution and the concentration of solution are both important in optimizing the formation of the hydride because of the equilibrium involving $W_2(O\text{-}c\text{-}C_5H_9)_6(HNMe_2)_2$ with $W_2(O\text{-}c\text{-}C_5H_9)_6$ and free amine and the relative solubilities of these species.

Table I. Summary of Crystal Data for the Molecule $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$

empirical formula	$W_2C_{38}H_{66}NO_7$
color of cryst	green
cryst dimens, mm	0.25 × 0.25 × 0.25
space group	$P\bar{1}$
cell dimens	
T, °C	−155
a, Å	13.057 (3)
b, Å	15.592 (4)
c, Å	10.376 (2)
α, deg	97.72 (1)
β, deg	109.55 (1)
γ, deg	94.22 (1)
Z, molecule/cell	2
V, (Å^3)	1956.44
d_{calcd}, gm/cm^3	1.738
wavelength, Å	0.71069
mol wt	1023.68
linear abs coeff, cm^{-1}	60.476
detector-to-sample dist, cm	22.5
sample-to-source dist, cm	23.5
av ω scan width at half-height	0.25
scan speed, deg/min	6.0
scan width, deg + dispersion	1.6
individual bkgd, s	6
aperture size, mm	3.0 × 4.0
2θ range, deg	6–45
tot. no. of reflcns collcd	6200
no. of unique intens	5129
no. with $F\sigma > 0.0$	4554
no. with $F\sigma > 2.33(F)$	4081
$R(F)$	0.0912
$R_w(F)$	0.0884
goodness of fit for the last cycle	2.279
max. Δ/σ for last cycle	0.65

The unligated compound $W_2(O\text{-}c\text{-}C_5H_9)_6$ is yellow, while the hydride forms dark cubic crystals that are green. The di-

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(1) Chisholm, M. H.; Clark, D. L.; Folting, K.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 7750.

(2) Chacon, S. T.; Chisholm, M. H.; Folting, K.; Hammond, C. E.; Hampden-Smith, M. J. To be submitted for publication.

(3) Chetcuti, M. J.; Chisholm, M. H.; Huffman, J. C.; Leonelli, J. *J. Am. Chem. Soc.* **1983**, *105*, 292.

(4) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Leonelli, J.; Marchant, N. S.; Smith, C. A.; Taylor, L. E. *J. Am. Chem. Soc.* **1985**, *107*, 3722. Chisholm, M. H.; Clark, D. L.; Huffman, J. C.; Smith, C. A. *Organometallics* **1987**, *6*, 1280.

(5) Akiyama, M.; Little, D.; Chisholm, M. H.; Haitko, D. A.; Cotton, F. A.; Extine, M. W. *J. Am. Chem. Soc.* **1979**, *101*, 2504. Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Leonelli, J.; Little, D. *J. Am. Chem. Soc.* **1981**, *103*, 779.

(6) A structural analogue of $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$. See ref 3.

(7) Chisholm, M. H.; Huffman, J. C.; Smith, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 222.

0020-1669/91/1330-3122$02.50/0

Table II. Fractional Coordinates and Isotropic Thermal Parameters for $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	2875 (1)	2465 (1)	1998 (1)	32
W(2)	2376 (1)	2860 (1)	4043 (1)	27
O(3)	2652 (13)	3708 (11)	2710 (18)	37
C(4)	2949 (17)	4598 (16)	2728 (25)	29
C(5)	2117 (22)	5146 (21)	3082 (25)	43
C(6)	1204 (22)	5157 (29)	1664 (33)	72
C(7)	1823 (26)	5204 (23)	734 (33)	55
C(8)	2806 (20)	4737 (18)	1220 (28)	42
O(9)	3942 (13)	2679 (11)	4054 (17)	33 (3)
C(10)	5105 (23)	2992 (19)	4756 (30)	45 (6)
C(11)	5395 (19)	2950 (22)	6325 (27)	49
C(12)	6335 (20)	2353 (25)	6709 (30)	62
C(13)	6093 (24)	1742 (31)	5250 (39)	91
C(14)	5765 (22)	2371 (31)	4236 (32)	78
O(15)	1813 (17)	2429 (13)	207 (18)	56
C(16)	716 (29)	2391 (23)	−351 (37)	61 (8)
C(17)	430 (35)	2667 (27)	−1839 (44)	79 (10)
C(18)	−564 (50)	2604 (9)	−2115 (62)	46 (12)
C(19)	−874 (45)	1877 (36)	−1386 (57)	41 (11)
C(20)	186 (37)	1466 (31)	−610 (48)	90 (11)
O(21)	4125 (13)	3067 (11)	1596 (17)	33 (3)
C(22)	4135 (31)	2988 (25)	−112 (39)	67 (8)
C(23)	4931 (19)	3817 (17)	−116 (35)	47
C(24)	6063 (20)	3563 (16)	675 (37)	50
C(25)	6008 (29)	2774 (29)	1069 (58)	126
C(26)	4690 (29)	2413 (31)	292 (62)	117
O(27)	3230 (13)	1357 (11)	1578 (17)	31 (3)
C(28)	3355 (43)	733 (37)	2147 (55)	105 (13)
C(29)	2558 (34)	164 (21)	1665 (32)	71
C(30)	2456 (34)	−355 (29)	253 (37)	94
C(31)	3782 (55)	−411 (34)	616 (71)	133
C(32)	4139 (42)	85 (39)	2034 (49)	147
O(33)	1012 (14)	3243 (12)	3931 (16)	39
C(34)	−14 (21)	3221 (32)	2826 (28)	74
C(35)	−702 (26)	2343 (34)	2761 (45)	103
C(36)	−1163 (31)	2518 (26)	3926 (37)	68
C(37)	−1136 (21)	3530 (20)	4210 (31)	45
C(38)	−664 (24)	3872 (25)	3182 (30)	58
O(39)	2439 (12)	2061 (9)	5343 (16)	27
C(40)	2437 (21)	1126 (17)	5152 (26)	35 (5)
C(41)	1302 (45)	708 (36)	4975 (57)	129 (14)
C(42)	1648 (41)	−419 (35)	4894 (74)	135
C(43)	2123 (56)	−23 (34)	6428 (33)	158
C(44)	2985 (37)	721 (29)	6580 (46)	91 (11)
N(45)	3131 (15)	3829 (14)	6128 (18)	32
C(46)	3814 (19)	4660 (18)	6213 (24)	40
C(47)	2279 (19)	4025 (16)	6751 (24)	31
C(18)′	256 (64)	1598 (52)	−2647 (82)	73 (16)
C(19)′	391 (40)	1059 (33)	−1550 (52)	32 (9)

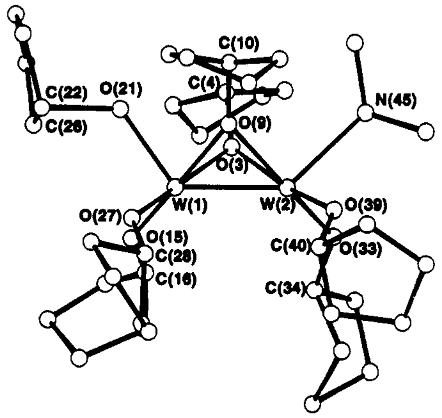

Figure 1. Ball-and-stick drawing of the $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ molecule shown perpendicular to the W–W bond axis. Note how the hydride ligand, which was not located, can complete a confacial bioctahedron by occupying the position below the W–W bond axis.

methylamine adduct $W_2(O\text{-}c\text{-}C_5H_9)_6(HNMe_2)_2$ is obtained from hexane as red-brown microcrystals. All are air and moisture sensitive, especially the hydrido complex.

Table III. Selected Bond Distances (Å) for the $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ Molecule

W(1)–W(2)	2.4380 (14)	W(2)–N(45)	2.325 (17)
W(1)–O(3)	2.056 (17)	O(3)–C(4)	1.41 (3)
W(1)–O(9)	2.087 (16)	O(9)–C(10)	1.45 (3)
W(1)–O(15)	1.901 (17)	O(15)–C(16)	1.35 (4)
W(1)–O(21)	2.013 (16)	O(21)–C(22)	1.76 (4)
W(1)–O(27)	1.855 (17)	O(21)–C(26)	1.95 (7)
W(2)–O(3)	2.132 (17)	O(27)–C(28)	1.20 (5)
W(2)–O(9)	2.081 (16)	O(33)–C(34)	1.42 (3)
W(2)–O(33)	1.892 (18)	O(39)–C(40)	1.44 (3)
W(2)–O(39)	1.943 (16)		

Table IV. Selected Bond Angles (deg) for the $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ Molecule

W(2)–W(1)–O(3)	55.9 (5)	O(3)–W(2)–O(39)	168.2 (6)
W(2)–W(1)–O(9)	54.1 (4)	O(3)–W(2)–N(45)	98.0 (7)
W(2)–W(1)–O(15)	119.2 (7)	O(9)–W(2)–O(33)	168.5 (7)
W(2)–W(1)–O(21)	126.0 (5)	O(9)–W(2)–O(39)	92.0 (6)
W(2)–W(1)–O(27)	120.4 (5)	O(9)–W(2)–N(45)	90.0 (6)
O(3)–W(1)–O(9)	77.9 (7)	O(33)–W(2)–O(39)	98.4 (7)
O(3)–W(1)–O(15)	93.4 (8)	O(33)–W(2)–N(45)	87.1 (7)
O(3)–W(1)–O(21)	84.5 (6)	O(39)–W(2)–N(45)	80.0 (7)
O(3)–W(1)–O(27)	172.4 (7)	W(1)–O(3)–W(2)	71.2 (6)
O(9)–W(1)–O(15)	171.1 (8)	W(1)–O(3)–C(4)	143.5 (14)
O(9)–W(1)–O(21)	85.4 (6)	W(2)–O(3)–C(4)	140.1 (15)
O(9)–W(1)–O(27)	94.5 (7)	W(1)–O(9)–W(2)	71.6 (5)
O(15)–W(1)–O(21)	95.8 (8)	W(1)–O(9)–C(10)	134.9 (15)
O(15)–W(1)–O(27)	94.2 (8)	W(2)–O(9)–C(10)	143.8 (15)
O(21)–W(1)–O(27)	93.8 (7)	W(1)–O(15)–C(16)	137.1 (22)
W(1)–W(2)–O(3)	53.0 (5)	W(1)–O(21)–C(22)	121.3 (15)
W(1)–W(2)–O(9)	54.3 (4)	W(1)–O(21)–C(26)	117.8 (13)
W(1)–W(2)–O(33)	122.4 (5)	W(1)–O(27)–C(28)	135 (3)
W(1)–W(2)–O(39)	121.2 (4)	W(2)–O(33)–C(34)	131.6 (16)
W(1)–W(2)–N(45)	135.9 (5)	W(2)–O(39)–C(40)	129.8 (14)
O(3)–W(2)–O(9)	76.4 (6)	W(2)–N(45)–C(46)	120.5 (14)
O(3)–W(2)–O(33)	93.1 (7)	W(2)–N(45)–C(47)	110.9 (13)

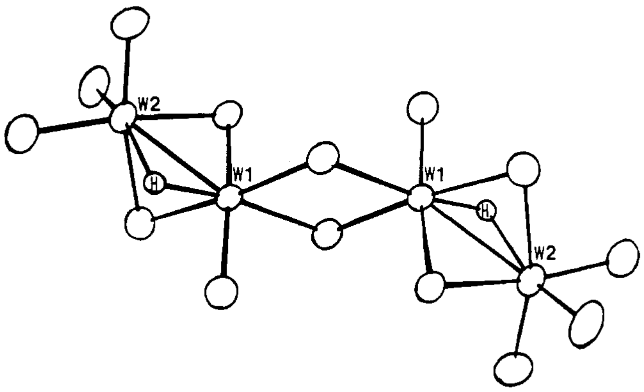

Figure 2. Ball-and-stick drawing of the inner core of the $[W_2(H)(O\text{-}i\text{-}Pr)_7]_2$ molecule showing how one half of it is analogous to the $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ molecule.

The reaction between $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ and PMe_3 (1 equiv) in either hexane or toluene yields the phosphine adduct $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(PMe_3)$ with loss of $HNMe_2$.

Crystal and Molecular Structure of $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$. A summary of crystal data is given in Table I and atomic coordinates are given in Table II.

A ball-and-stick drawing of the $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ molecule is given in Figure 1. The hydride ligand, which was not located by the X-ray data, can quite reasonably be taken to complete a confacial bioctahedral unit $NO_2W(\mu\text{-}H)(\mu\text{-}O)_2WO_3$ such that it is trans to the amine ligand. Selected bond distances and bond angles are given in Tables III and IV, respectively.

The $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ molecule can be viewed as a half of the $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$ molecule where the $HNMe_2$ ligand and one other terminal $O\text{-}c\text{-}C_5H_9$ ligand at W(2) substitute bridging O-*i*-Pr ligands. The $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$ structure involves two confacial bioctahedra fused along a common edge as shown in Figure 2. Of particular note is the very long W–O

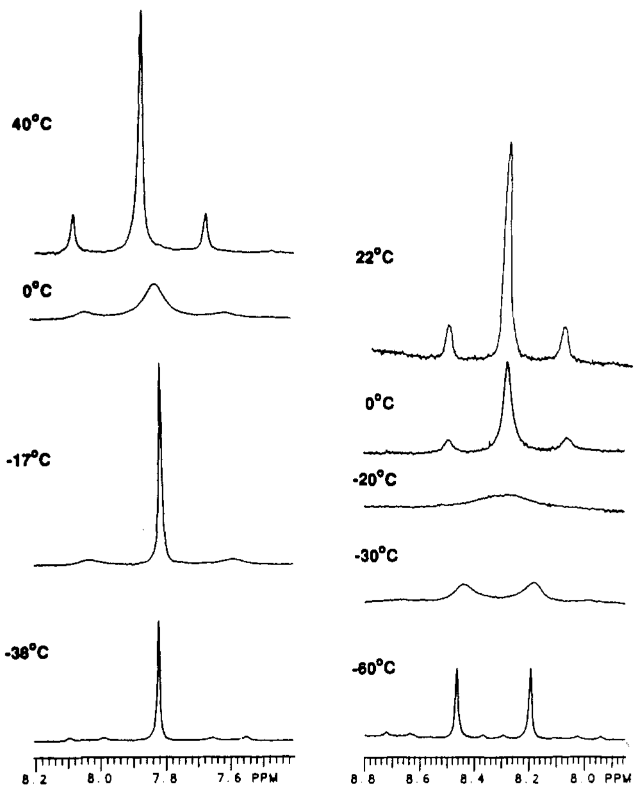

Figure 3. Variable-temperature ^{1}H NMR spectra for $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ on the left and $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(PMe_3)$ on the right, all recorded at 300 MHz showing the hydride resonance. At high temperature, coupling to two equivalent tungsten atoms is observed as well as no phosphorus coupling, indicating alkoxide scrambling and $HNMe_2$ or PMe_3 ligand dissociation. At low temperature, phosphorus coupling is observed, as well as coupling to two inequivalent tungsten atoms, consistent with the solid-state structure.

terminal distance, 2.014 (16) Å, associated with the $O\text{-}c\text{-}C_5H_9$ ligand trans to the hydride. The W–N distance of 2.325 (17) Å is also very long, suggestive of a weak dative bond. The W–W distance of 2.4380 (14) Å is essentially identical with that in $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$ and is in the range expected for a W=W double bond.[8]

Solution ^{1}H NMR Studies. The molecule $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ is fluxional on the NMR time scale at room temperature (300 MHz, toluene-d_8), showing only one time averaged type of OR ligand and a hydride resonance at ca. δ 7.8 ppm flanked by satellites due to coupling to ^{183}W ($I = 1/2$, 14.5% natural abundance), which are rather broad. When the temperature is raised to +40 °C, both the hydride signal and the satellites sharpen. The relative intensity of the satellites indicate the presence of a $W_2(\mu\text{-}H)$ moiety where both tungsten atoms are chemically equivalent, $J_{^{183}W-^{1}H} = 130$ Hz. However, at −48 °C, the hydride signal at δ ca. 7.8 is flanked by *two* sets of satellites, $J_{^{183}W-^{1}H} = 160$ and 100 Hz, each of only half the intensity of those at +40 °C. These changes with temperatures are shown on the left of Figure 3. At room temperature and above, the signals associated with the $HNMe_2$ protons are broad while at low temperature they are sharp. Thus there is little doubt that the structure found in the solid state is present in solution. The fluxionality involves reversible dissociation of $HNMe_2$ and bridge $\rightleftarrows$ terminal OR exchange.

The variable-temperature ^{1}H NMR spectra of the hydride signal of the phosphine complex $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(PMe_3)$ are shown on the right side of Figure 3 and are particularly informative because of the presence or lack of coupling between the hydride ligand and the phosphorus nuclei. At low temperatures, we observe a spectrum consistent with a bound PMe_3 ligand and two inequivalent tungsten centers. However, in the high-temperature limit we see the fluxional $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7$ molecule in which there is no evidence for a bound PMe_3 ligand and the hydride sees two equivalent tungsten nuclei. The variable-temperature ^{31}P NMR spectra are complementary to the ^{1}H NMR spectra. Namely, at low temperatures (−60 °C in toluene-d_8), the ^{31}P signal shows coupling to ^{183}W ($I = 1/2$, 14.5% natural abundance), $J_{^{183}W-^{31}P} = 260$ Hz, and coupling to the hydride ligand, $^2J_{^{31}P-^{1}H} = 90$ Hz. However, when the temperature is raised, the signal broadens and moves to higher field and loses its coupling to both ^{1}H and ^{183}W by 0 °C, consistent with rapid and reversible PMe_3 dissociation.

Concluding Remarks. Perhaps not surprisingly the chemistry reported here for the cyclopentoxide compounds resembles that of the isopropoxy analogues since they are sterically very similar in terms of their demands at the metal center. However, the isolation of the Lewis base adducts of formula $W_2(\mu\text{-}H)(OR)_7(L)$ where R = c-pentyl and their dynamic behavior throw further light on the chemistry of $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$. (1) Though the latter is known to be tetranuclear in benzene by cryoscopy, a substitutionally labile dimethylamine adduct of the type reported now is presumably its precursor. (2) The fact that $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$ is fluxional down to −80 °C in toluene-d_8 is consistent with the view that the bridging alkoxide ligand is a weaker Lewis base in $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$ than $HNMe_2$ or PMe_3 is in the cyclopentoxide–hydride derivatives. This work therefore supports the original suggestion concerning bridge breaking as the rate-determining step in the fluxionality of $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$. (3) The reversible dissociation of L from $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7L$ where L = $HNMe_2$ and PMe_3 allows ready substrate uptake at the W_2 center. The reactivity of this hydride ligand is under investigation.

Experimental Section

General procedures including the preparation of $W_2(NMe_2)_6$ have been described.[9]

Preparation of $W_2(O\text{-}c\text{-}C_5H_9)_6(HNMe_2)_2$. $W_2(NMe_2)_6$ (1.469 g, 2.324 mmol) was placed in a 30 mL Schlenk flask equipped with a Teflon-coated stir bar and 5 mL of hexanes was added. Cyclopentanol (1.7 mL, 19 mmol, 8 equivalents) was added, and the solution was stirred at room temperature overnight. The flask was cooled to −20 °C after which time $W_2(O\text{-}c\text{-}C_5H_9)_6(HNMe_2)_2$ (1.906 g, 1.968 mmol) was isolated in two batches as red/brown crystals in 85% yield. It is important to stir the mixture overnight in a closed system or the yellow solid $W_2(O\text{-}c\text{-}C_5H_9)_6$ will result.

^{1}H NMR (benzene-d_6, 25 °C, 500 MHz, δ): 5.96, broad multiplet, 6 H, $HN(CH_3)_2$; 2.43, s, 12 H, $HN(CH_3)_2$; 2.02, s, 12 H, methylene, CH_2; 1.91, s, 24 H, methine, CH: 1.64, s, 12 H, methylene, CH_2.

^{1}H NMR (toluene-d_8, −30 °C, 360 MHz, δ): 6.01, m, 6 H, $HN(CH_3)_2$; 4.74, 2 H, methine, CH; 4.09, 4 H, methylene, CH_2; 2.57, d, $^3J_{H-H} = 2$ Hz, 12 H, $HN(CH_3)_2$; 2.1–1.7, overlapping multiplets, 48 H, methylene, CH_2.

IR (KBr disk, cm^{-1}): 2930 s, 2848 m, 1458 w, 1440 w, 1425 w, 1330 w, 1159 m, 1060 m, 1027 sh, 996 s, 928 w, 886 w, 853 w.

Anal. Calcd for $C_{34}H_{68}N_2O_6W_2$: C, 42.15; H, 7.07; N, 2.89. Found: C, 42.09; H, 7.04; N, 2.81.

Preparation of $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$. $W_2(O\text{-}c\text{-}C_5H_9)_6(HNMe_2)_2$ (1.785 g, 1.843 mmol) was placed in a 30-mL Schlenk flask equipped with a Teflon-coated stir bar, and 25 mL of hexanes and 0.3 mL of cyclopentanol (3 mmol) were added. The solution was stirred at room temperature for 4 days after which time the solution was reduced to 5 mL and cooled to −20 °C for 2 days. $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ (1.076 mg, 1.066 mmol) was isolated as green crystals in 58% yield.

^{1}H NMR (benzene-d_6, 22 °C, 300 MHz, δ): 7.91, s, 1 H, μ-H, $J_{W-H} = 130$ Hz, 22%; 5.81 br s, 1 H, $HN(CH_3)_2$; 5.27, br m, 7 H, methine, CH; 2.32, br s, 6 H, $HN(CH_3)_2$; 1.87, br m, 44 H, methylene, CH_2; 1.58, br m, 12 H, methylene, CH_2.

$^{13}C\{^1H\}$ NMR (toluene-d_8, 22 °C, 126 MHz, δ): 88.7 m, methine, CH; 65.7, s, $HN(CH_3)_2$; 40.9, s, methylene; 37.6, s, methylene; 37.1, s, methylene; 24.2 s, methylene.

IR (KBr disk, cm^{-1}): 2952 br, s, 2861 m, 1470 w, 1460 w, 1448 w, 1441 w, 1429 w, 1341 m, 1333 m, 1167 m, 1070 m, 1038 s, 1010 s, 1002 s, 992 s, 937 w, 902 w, 897 w, 890 w, 870 w, 864 w, 859 w, 660 br, w, 550 br, w.

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(8) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

(9) Chisholm, M. H.; Martin, J. D. *Inorg. Synth.*, in press.

Anal. Calcd for $W_2O_7C_{37}H_{71}N$: C, 44.00; H, 7.09; N, 1.39. Found: C, 43.83; H, 6.95; N, 1.45.

Variable-Temperature ^{1}H NMR Data for $W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7(HNMe_2)$. ^{1}H NMR (benzene-$d_6$, 40 °C, 300 MHz, δ): 7.93, s, 1 H, μ-*H*, J_{W-H} = 120 Hz, 20%; 5.45, m, 7 H, methine CH; 2.28, br s, 6 H, $HN(CH_3)_2$; 1.91, br s, 42 H, methylene, CH_2; 1.58, m, 14 H, methylene, CH_2.

^{1}H NMR (toluene-d_8, 0 °C, 360 MHz, δ): 7.84, br s, 1 H, μ-*H*; 5.33, br s, 7 H, methine, CH; 2.75, br s, 6 H, $HN(CH_3)_2$; 2.24 s, 7 H, methylene, CH_2; 1.88, br m, 44 H, methylene, CH_2; 1.61, s, 12 H, methylene, CH_2.

^{1}H NMR (toluene-d_8, −17 °C, 360 MHz, δ): 7.80, 1 H, μ-*H*; 5.34, br s, 7 H, methine, CH; 2.81, br s, 6 H, $HN(CH_3)_2$; 2.19, s, 6 H, methylene, CH_2; 1.90, br m, 38 H, methylene, CH_2; 1.63, s, 12 H, methylene, CH_2.

^{1}H NMR (toluene-d_8, −38 °C, 360 MHz, δ): 7.80, s, 1 H, μ-H, J_{W-H} = 160 Hz, 10%, J_{W-H} = 100 Hz, 10%; 5.50, br m, 3 H, methine, CH; 5.19, br m, 4 H, methine, CH; 2.80, br m, 6 H, $HN(CH_3)_2$; 1.99, s, 6 H, methylene, CH_2; 1.89, s, 38 H, methylene, CH_2; 1.64, 12 H, methylene, CH_2.

^{1}H NMR (toluene-d_8, −48 °C, 360 MHz, δ): 7.81, s, μ-H, J_{W-H} = 160 Hz, 10%, J_{W-H} = 100 Hz, 10%; 5.8, br m, 1 H, $HN(CH_3)_2$; 5.58, br m, 3 H, methine, CH; 5.13, br m, 4 H, methine, CH; 2.80, br m, 6 H, $HN(CH_3)_2$; 2.02–1.63, br m, 50 H, methylene, CH_2.

Preparation of $W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7(PMe_3)$. $W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7(HNMe_2)$ (851 mg, 0.843 mmol) was placed in a 30-mL Schlenk flask equipped with a Teflon-coated stir bar, and 2 mL of hexanes was added. The solution was frozen in N_2(l), the flask was evacuated, and PMe_3 (0.93 mmol) was condensed into the flask by using a calibrated vacuum manifold. The solution was stirred overnight at room temperature and then cooled to −20 °C for 2 days. $W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7(PMe_3)$ (682 mg, 0.655 mmol) was isolated as a red solid in 78% yield.

^{1}H NMR (toluene-d_8, 22 °C, 300 MHz, δ): 8.23, s, 1 H, μ-*H*, J_{W-H} = 120 Hz, 22%; 5.31, s, 7 H, methine, CH; 1.85, br m, 44 H, methylene, CH_2; 1.59, s, 12 H, methylene, CH_2; 1.12, d, J_{P-H} = 8 Hz, 9 H, $P(CH_3)_3$.

^{1}H NMR (toluene-d_8, 0 °C, 360 MHz, δ): 8.25, s, 1 H, μ-H, J_{W-H} = 120 Hz, 22%; 5.31, s, 7 H, methine, CH; 1.86, s, 40 H, methylene CH_2; 1.60, s, 16 H, methylene, CH_2; 1.09, d, J_{P-H} = 8 Hz, 9 H, $P(CH_3)_3$.

^{1}H NMR (toluene-d_8, −20 °C, 360 MHz, δ): 8.27, br s, 1 H, μ-H; 5.4, br s, 7 H, methine, CH; 1.86, s, 40 H, methylene, CH_2; 1.61, s, 16 H, methylene, CH_2; 1.06, d, J_{P-H} = 8 Hz, 9 H, $P(CH_3)_3$.

^{1}H NMR (toluene-d_8, −30 °C, 360 MHz, δ): 8.33, br d, J_{P-H} = 60 Hz, 1 H, μ-H; 5.55, br s, 7 H, methine, CH; 1.84, s, 40 H, methylene CH_2; 1.63, s, 16 H, methylene, CH_2; 1.05, d, J_{P-H} = 8 Hz, 9 H, $P(CH_3)_3$.

^{1}H NMR (toluene-d_8, −60 °C, 360 MHz, δ): 8.33, d, J_{P-H} = 80 Hz, J_{W-H} = 100, 10%, J_{W-H} = 150, 10%, 1 H, μ-H; 5.60, s, 3 H, methine, CH; 5.51, s, 2 H, methine, CH; 4.74, s, 2 H, methine, CH; overlapping singlets at 2.01, 1.81, 1.68, 56 H, methylene, CH_2; 1.01, d, J_{P-H} = 8 Hz, 9 H, $P(CH_3)_3$.

$^{31}P\{^1H\}$ NMR (relative to 85% H_3PO_4) (toluene-d_8, 146 MHz, δ): 0 °C, −37.3, br; −20 °C, −35.7, br; −60 °C, −34.1, s, J_{W-P} = 260 Hz, 13%.

^{31}P NMR (δ): −40 °C, −34.8, d, J_{H-P} = 90 Hz; −60 °C, −34.1, d, J_{H-P} = 90 Hz.

IR (KBr disk, cm^{-1}): 2940 s, 2888 sh, 2852 m, 1425 w, 1540 m, 1160 m, 1060 m, 990 m, 950 m, 850 w, 665 w, 530 w.

Anal. Calcd for $C_{38}H_{73}O_7PW_2$: C, 43.86; H, 7.07. Found: C, 43.83; H, 7.04.

Single-Crystal X-ray Determination: $W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7(HNMe_2)$. General operating procedures and a listing of programs have been reported.[10] A summary of crystal data is given in Table I.

A suitable crystal was located, transferred to the goniostat, and cooled to −155 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, corresponding to one of the triclinic space groups. Subsequent solution and refinement of the structure confirmed the centrosymmetric space group $P\bar{1}$.

Data were collected using a continuous θ–2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ's in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques.

During the Fourier synthesis it became apparent that disorder was present with several of the –OR ligands. Several different models were introduced with varying degrees of success. In the final model, two partial occupancy atoms (C(18)′ and C(19)′) were introduced, and the remaining atoms were refined anisotropically. In all, over 24 cycles were required to properly converge.

While the structure is certainly correct, in all of its gross features, the distances and angles are less trustworthy.

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Supplementary Material Available: Crystallographic data for $W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7(HNMe_2)$, including listings of anisotropic thermal parameters, bond distances, and bond angles and an ORTEP diagram (6 pages); a listing of F_o and F_c values (11 pages). Ordering information is given on any current masthead page.

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(10) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.