Triple bonds between tungsten atoms with ancillary dimesitylboroalkoxide ligands. Preparations, properties and structures of $W_2(NMe_2)_4[OB(Mes)_2]_2$ and $W_2(OBu^t)_4[OB(Mes)_2]_2$

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(Received February 23, 1993)

Abstract

From the reaction between $W_2(NMe_2)_6$ and dimesitylborinic acid, $(Mes)_2BOH$ (2 equiv.), in toluene, the golden-yellow crystalline compound $W_2(NMe_2)_4[OB(Mes)_2]_2$ (**1**) has been isolated and characterized (elemental analysis, ^1H, $^{13}C\{^1H\}$, ^{11}B NMR spectroscopy, IR spectroscopy and a single crystal X-ray diffraction study). At −160 °C, $a = 39.379(7)$, $b = 13.649(2)$, $c = 21.918(4)$ Å, $\beta = 123.12(1)°$, $Z = 8$ and space group $C2/c$. The compound $W_2(OBu^t)_4[OB(Mes)_2]_2$ (**2**) has been similarly characterized as a dark red crystalline compound obtained from the reaction between $W_2(OBu^t)_6$ and $(Mes)_2BOH$ (2 equiv.) in toluene. At −159 °C, $a = 17.164(2)$, $b = 19.773(2)$, $c = 18.490(2)$ Å, $\beta = 102.91(1)°$, $Z = 4$ and space group $C2$. In both compounds there are unsupported W≡W bonds of distance 2.3068(13) and 2.3521(15) Å for compound **1** and **2**, respectively. In **1** there is a central ethane like $W_2N_4O_2$ core with the gauche conformation, W–N = 1.94(2) (av.) and W–O = 1.93(1) Å. The coordination geometry at nitrogen is trigonal planar and the NC_2 units are aligned along the W–W axis as found for related compounds. In compound **2** the $W_2O_4O'_2$ skeleton is eclipsed and most surprisingly the W–O′ distances to the $OB(Mes)_2$ ligands are shorter 1.81(1) Å than the W–O distances 1.94(1) and 1.90(1) Å to the alkoxide ligands. In both **1** and **2** the coordination geometry at boron is trigonal planar and the O–B distances fall in the range 1.37(3)–1.41(3) Å, and are statistically equivalent to that of the free borinic acid. Compound **2** has crystallographically imposed C_2 symmetry and the $OB(Mes)_2$ groups are *syn*. These are the first structurally characterized boroalkoxides coordinated to the $(W{\equiv}W)^{6+}$ moiety and comparisons of W–O π bonding are made with respect to related OR and $OSiR_3$ compounds.

Introduction

The reactivity of a metal center is greatly influenced by the steric and electronic properties of the attendant ligands. We have recently compared the reactions of $W_2(OBu^t)_6$ and $W_2(OSiBu^tMe_2)_6$ towards ethyne and nitric oxide and in both instances there were remarkable differences in the nature of the products despite the formal similarity of alkoxide and trialkyl siloxide ligands [1]. We report here our preparation and characterization of the first examples of boroalkoxide ligands attached to the $(W{\equiv}W)^{6+}$ moiety. The ligands R_2BO^- are of particular interest since there is competition for oxygen p_π bonding between boron (p) and tungsten (d) atomic orbitals.

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Results and discussion

Synthesis

Selection of the dialkylborinic acid limits one to sterically demanding R groups in order to suppress the condensation reaction shown in eqn. (1). For this reason we have worked with R = mesityl (Mes). Dimesityl borinic acid was prepared from the reaction shown in eqn. (2).

$$2R_2BOH \longrightarrow R_2B{-}O{-}BR_2 + H_2O \quad (1)$$

$$2[MesMgBr] + BF_3OEt_2 \xrightarrow[Et_2O]{22\ °C} (Mes)_2BF + 2MgBrF \quad (2a)$$

$$(Mes)_2BF + H_2O \xrightarrow[Et_2O]{22\ °C} (Mes)_2BOH + HF \quad (2b)$$

The details are given in 'Experimental'.

The mixed amido-boroalkoxide was prepared according to eqn. (3). It should be noted that even an excess of the borinic acid only leads to the substitution

0020-1693/93/$6.00

of two amido ligands—presumably, at least in part, due to steric factors that prevent further attack at the dinuclear center.

$$W_2(NMe_2)_6 + 2(Mes)_2BOH \xrightarrow[\text{toluene}]{22\ ^\circ C} W_2(NMe_2)_4[OB(Mes)_2]_2 + 2HNMe_2 \quad (3)$$

Compound **1** is a golden-yellow crystalline air-sensitive compound that is soluble in common hydrocarbon solvents (e.g. hexanes, benzene and toluene). It is thermally stable at room temperature (indefinitely) and may be heated in solution to 100 °C for short periods. Attempts to sublime the compound *in vacuo* at temperatures of *c.* 150 °C lead to thermal decomposition.

The mixed tert-butoxy-boroalkoxide, compound **2**, was similarly prepared according to eqn. (4). Again only two boroalkoxide groups were readily substituted

$$W_2(OBu^t)_6 + 2(Mes)_2BOH \xrightarrow[\text{toluene}]{22\ ^\circ C} W_2(OBu^t)_4[OB(Mes)_2]_2 + 2Bu^tOH \quad (4)$$

at the dinuclear center. The reaction shown in eqn. (4) was notably slower than that in eqn. (3). Compound **2** is a red, crystalline solid, soluble in common hydrocarbon solvents (as for compound **1**). The compound is air-sensitive and thermally stable only below 60 °C in solution.

Solid state and molecular structures

$W_2(NMe_2)_4[OB(Mes)_2]_2$ (1)

1 crystallizes in the space group *C*2/*c* with one unique molecule in the asymmetric unit. (There is also one half a molecule of hexane per W_2 unit.) The molecule has a virtual but not crystallographically imposed C_2 axis of symmetry and thus a gauche $W_2N_4O_2$ skeleton. An ORTEP view of the molecule is given in Fig. 1. A listing of fractional coordinates is given in Table 1 and selected bond distances and angles are given in

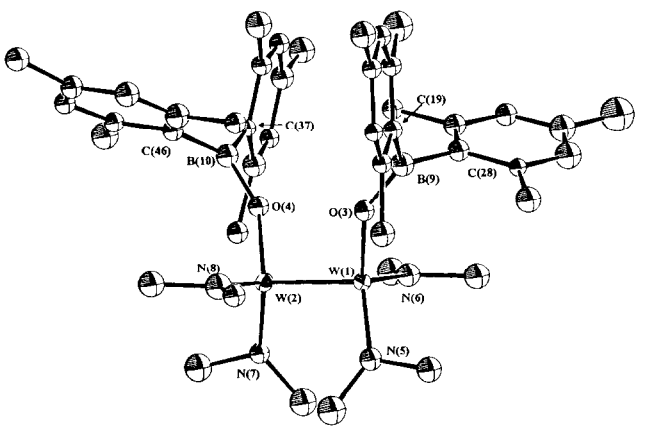

Fig. 1. ORTEP drawing with atom number scheme for $W_2(NMe_2)_4[OB(Mes)_2]_2$.

TABLE 1. Fractional coordinates and isotropic thermal parameters for $W_2(NMe_2)_4[OB(Mes)_2]_2 \cdot \frac{1}{2}$hexane

Atom	$10^4 \times x$	$10^{10} \times y$	$10^4 \times z$	$10 \times B_{iso}$
W(1)	1443.0(3)	340(1)	8833.6(5)	14
W(2)	980.3(3)	1494(1)	8705.5(5)	13
O(3)	1545(4)	−425(10)	9657(7)	17(3)
O(4)	1275(4)	2213(10)	9612(7)	16(3)
N(5)	1167(5)	−370(13)	7919(8)	17(3)
N(6)	1883(6)	1130(14)	8989(11)	28(4)
N(7)	855(5)	2262(13)	7841(9)	20(3)
N(8)	547(5)	694(14)	8584(10)	23(4)
B(9)	1789(8)	−986(19)	10272(14)	20(5)
B(10)	1213(8)	2667(20)	10102(14)	22(5)
C(11)	1420(7)	−1093(18)	7835(13)	30(5)
C(12)	759(7)	−305(18)	7246(12)	30(5)
C(13)	2254(7)	622(17)	9140(12)	28(5)
C(14)	1936(6)	2183(16)	8953(11)	21(4)
C(15)	982(7)	2202(19)	7346(13)	33(5)
C(16)	575(7)	3078(16)	7656(12)	25(4)
C(17)	485(7)	−377(20)	8553(13)	32(5)
C(18)	171(7)	1224(17)	8446(12)	27(5)
C(19)	2255(6)	−790(15)	10733(11)	18(4)
C(20)	2534(6)	−1587(16)	10901(10)	16(4)
C(21)	2948(6)	−1394(15)	11277(11)	18(4)
C(22)	3108(6)	−448(16)	11551(11)	20(4)
C(23)	2843(6)	274(17)	11398(11)	24(4)
C(24)	2429(7)	157(17)	11000(12)	24(4)
C(25)	2387(7)	−2584(17)	10656(13)	29(5)
C(26)	3568(6)	−338(17)	12037(11)	24(4)
C(27)	2169(6)	1035(15)	10853(11)	18(4)
C(28)	1576(6)	−1800(14)	10455(10)	11(3)
C(29)	1632(6)	−1873(15)	11154(11)	17(4)
C(30)	1445(6)	−2587(15)	11291(11)	17(4)
C(31)	1210(6)	−3308(16)	10799(11)	22(4)
C(32)	1148(6)	−3262(14)	10120(10)	15(4)
C(33)	1314(6)	−2521(16)	9928(11)	22(4)
C(34)	1890(7)	−1117(17)	11723(13)	28(5)
C(35)	1012(7)	−4092(18)	10989(12)	28(5)
C(36)	1250(6)	−2561(15)	9183(11)	18(4)
C(37)	815(6)	2371(15)	10085(11)	18(4)
C(38)	488(6)	3041(14)	9806(10)	12(3)
C(39)	138(7)	2815(18)	9789(12)	28(4)
C(40)	92(7)	1930(17)	10028(12)	28(5)
C(41)	390(6)	1237(15)	10266(11)	20(4)
C(42)	743(6)	1437(16)	10294(11)	20(4)
C(43)	511(7)	4053(17)	9509(12)	26(4)
C(44)	−290(8)	1661(22)	10021(15)	47(6)
C(45)	1071(6)	652(15)	10566(11)	18(4)
C(46)	1511(6)	3498(15)	10621(10)	15(3)
C(47)	1630(6)	4253(15)	10338(10)	15(4)
C(48)	1892(6)	4979(14)	10804(10)	14(4)
C(49)	2063(6)	4943(14)	11553(11)	16(4)
C(50)	1957(6)	4194(15)	11835(11)	18(4)
C(51)	1683(6)	3480(16)	11378(10)	17(4)
C(52)	1469(7)	4371(16)	9528(12)	24(4)
C(53)	2349(7)	5733(17)	12067(12)	27(4)
C(54)	1595(7)	2649(19)	11740(13)	35(5)
C(55)	9637(12)	3743(30)	3447(22)	85
C(57)	9956(13)	3508(32)	2783(21)	85
C(56)	9728(25)	4161(68)	2853(45)	85
C(56')	9746(25)	3128(65)	2966(46)	85

TABLE 2. Selected bond distances (Å) and angles (°) for the $W_2(NMe_2)_4[OB(Mes)_2]_2$ molecule

W(1)–W(2)	2.3068(13)
W(1)–O(3)	1.925(13)
W(1)–N(5)	1.936(16)
W(1)–N(6)	1.908(20)
W(2)–O(4)	1.931(13)
W(2)–N(7)	1 980(17)
W(2)–N(8)	1.916(18)
O(3)–B(9)	1.39(3)
O(4)–B(10)	1.37(3)
N(5)–C(11)	1 48(3)
N(5)–C(12)	1.476(28)
N(6)–C(13)	1.48(3)
N(6)–C(14)	1.46(3)
N(7)–C(15)	1.42(3)
N(7)–C(16)	1.461(27)
N(8)–C(17)	1.48(3)
N(8)–C(18)	1.53(3)
B(9)–C(19)	1 55(3)
B(9)–C(28)	1.56(3)
B(10)–C(37)	1.60(3)
B(10)–C(46)	1.58(3)
W(2)–W(1)–O(3)	103.3(4)
W(2)–W(1)–N(5)	104.9(5)
W(2)–W(1)–N(6)	102.5(6)
O(3)–W(1)–N(5)	114.2(6)
O(3)–W(1)–N(6)	115.7(7)
N(5)–W(1)–N(6)	114.2(8)
W(1)–W(2)–O(4)	103 5(4)
W(1)–W(2)–N(7)	104.2(5)
W(1)–W(2)–N(8)	102 2(6)
O(4)–W(2)–N(7)	114.3(6)
O(4)–W(2)–N(8)	114.8(7)
N(7)–W(2)–N(8)	115.6(7)
W(1)–O(3)–B(9)	153.1(14)
W(2)–O(4)–B(10)	140.6(14)
W(1)–N(5)–C(11)	115.2(13)
W(1)–N(5)–C(12)	133.9(15)
C(11)–N(5)–C(12)	110.7(17)
W(1)–N(6)–C(13)	117.6(15)
W(1)–N(6)–C(14)	133.5(15)
C(13)–N(6)–C(14)	108.7(18)
W(2)–N(7)–C(15)	133.9(15)
W(2)–N(7)–C(16)	115 2(13)
C(15)–N(7)–C(16)	110.9(18)
W(2)–N(8)–C(17)	133.0(15)
W(2)–N(8)–C(18)	116 7(14)
C(17)–N(8)–C(18)	110.2(18)
O(3)–B(9)–C(19)	118.3(20)
O(3)–B(9)–C(28)	117.2(19)
C(19)–B(9)–C(28)	124.5(20)
O(4)–B(10)–C(37)	117.1(20)
O(4)–B(10)–C(46)	120.7(19)
C(37)–B(10)–C(46)	122 0(19)

Table 2. The NC_2 units are aligned along the M–M axis to allow for N p_π to W d_π bonding and the W–W distance of 2.307(1) Å is typical for a W–W triple bond of configuration $\sigma^2\pi^4$. The W–N distances are relatively short, 1.94(1) Å (av.), indicative of significant double bond character and the W–O distance 1.93(1) Å is notably longer than that in $W_2(OR)_6$ compounds, 1.88(1) Å. In many ways the structure of **1** resembles that of gauche-$W_2(NMe_2)_4(OSiPh_3)_2$ [2]. The coordination about boron is trigonal planar and the B–O distance, 1.38(1) Å (av.), is essentially the same as that seen in the free borinic acid [3]. The W–O–B angles differ by ≈13°. There is no other abnormal structural feature that would suggest this is caused by anything other than steric interactions or crystal packing forces. The conformation of the two mesityl rings is similar to that seen in borinic acid and in the lithio salt $[LiOB(Mes)_2 \cdot THF]_2$ [3].

It is perhaps also worth noting that in the solid state compound **1** forms infinite chains along the *b* axis through intermolecular contacts as short as 3.43 Å involving the mesityl groups. These interactions, however, would seem to have little influence on the molecular structure of **1**, nor do they influence the solution behavior of **1**.

$W_2(OBu^t)_4[OB(Mes)_2]_2$ (2)

In the space group *C*2 the unit cell contains two unique W_2 unit halves each having a crystallographically imposed C_2 axis of symmetry and half molecules of hexane. One of the $W_2(OBu^t)_4[OB(Mes)_2]_2$ molecules was disordered and the disorder involved one of the mesityl rings and one of the OBu^t groups. The other molecule was not disordered and an ORTEP drawing and a ball-and-stick drawing of this molecule is given in Fig. 2. The view looking down the M–M bond axis reveals the eclipsed nature of the W_2O_6 unit and furthermore that the W–$OB(Mes)_2$ groups are mutually *syn*.

Atomic coordinates are listed in Table 3 and selected bond distances and angles are given in Table 4.

It should be noted that the eclipsed $W_2O_4O_2'$ skeleton is also present in the disordered molecule for which structural parameters are not given in Table 4. A model for the disorder is described in 'Experimental'.

The W–W–O angles span the range 100–111°, typical of so called ethane-like dimers, with the largest angle involving the W–$OB(Mes)_2$ group. Most interestingly the W–O distance to the boroalkoxide ligand is much shorter, 1.81(1) Å relative to the W–OBu^t distances, 1.90(1) and 1.94(1) Å. Again the coordination about the boron atom is trigonal planar and the B–O distance is 1.41(3) Å which is within 3σ of the distance seen in compound **1**. The conformation of the mesityl groups in **2** is similar to that in **1**.

NMR solution behavior

The dimethylamido compound **1** which crystallizes in the gauche rotamer was also found to exist in exclusively the gauche rotamer in solution. Specifically, on dissolving crystals of **1** in toluene-d_8 at −60 °C,

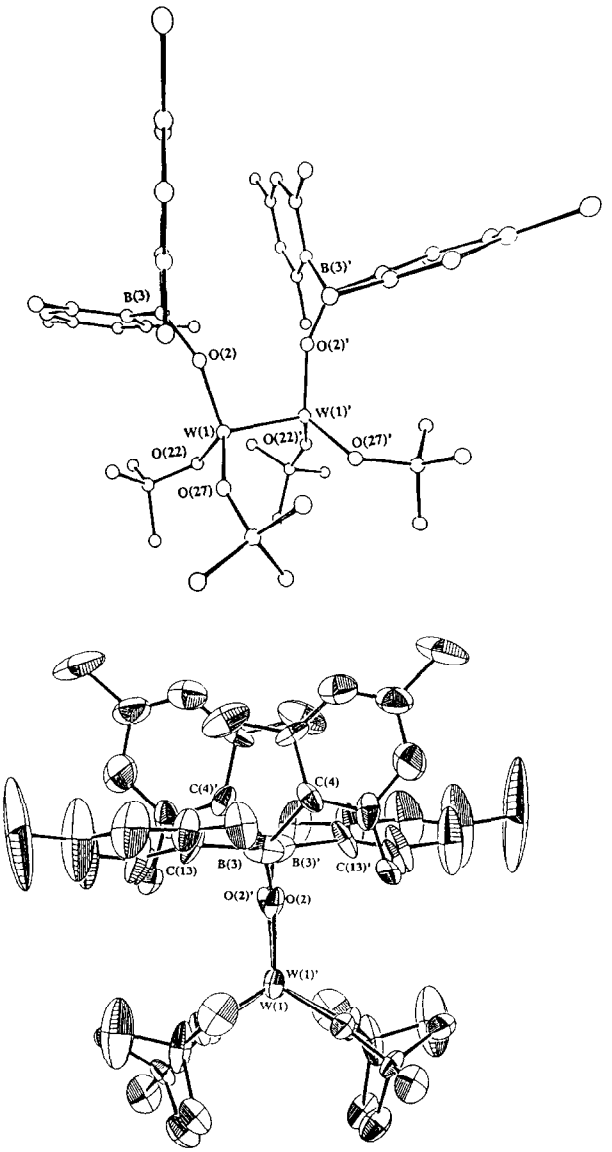

Fig. 2. Two views of the $W_2(OBu^t)_4[OB(Mes)_2]_2$ molecule showing the number scheme and the eclipsed W_2O_6 skeleton.

there were two sets of proximal and distal NMe_2 groups in the integral ratio 1:1. At -60 °C there is only one type of mesityl group present but the *ortho* Me groups show a broad resonance relative to the *para* Me singlet presumably because of hindered rotations about the B–C(aryl) bond. These rotations, as well as other conjugative and steric interactions have been shown to play significant roles in the stereochemistry of alkoxydiarylboranes [4]. The *meta* protons on the ring also are broad at low temperatures but are not frozen out.

Upon raising the temperature to −20 °C the *ortho* methyl protons sharpen as do the *meta* protons on the aryl ring. One of the sets of NMe_2 groups starts to broaden at −8 °C and is lost into the baseline at c. 25 °C. The other NMe_2 group remains relatively sharp

TABLE 3 Fractional coordinates and isotropic thermal parameters for $W_2(OBu^t)_4[OB(Mes)_2]_2 \cdot \frac{1}{2}$hexane

Atom	$10^4 \times x$	$10^4 \times y$	$10^4 \times z$	$10 \times B_{iso}$
W(1)	4298.2(4)	2301	9817.4(5)	23
O(2)	4082(9)	1404(9)	9724(7)	27
B(3)	3648(13)	800(15)	9714(18)	34
C(4)	3642(13)	242(13)	9133(13)	30
C(5)	3488(15)	416(15)	8401(14)	40
C(6)	3480(22)	−105(17)	7866(19)	60
C(7)	3647(20)	−772(14)	8071(20)	54
C(8)	3814(16)	−916(15)	8792(18)	47
C(9)	3820(11)	−453(11)	9365(14)	26
C(10)	3313(15)	1108(12)	8133(12)	30
C(11)	3613(30)	−1288(17)	7449(30)	102
C(12)	4031(17)	−628(17)	10200(22)	57
C(13)	3254(17)	718(18)	10454(15)	44
C(14)	2424(14)	552(18)	10309(15)	45
C(15)	2040(20)	518(29)	10874(22)	80
C(16)	2458(20)	613(41)	11625(20)	122
C(17)	3243(19)	783(31)	11738(16)	89
C(18)	3651(15)	848(18)	11221(14)	51
C(19)	1919(13)	524(19)	9517(15)	49
C(20)	2048(42)	523(60)	12241(28)	254
C(21)	4513(12)	938(14)	11378(12)	30
O(22)	4039(8)	2777(9)	10649(8)	28
C(23)	3180(14)	2970(19)	10668(14)	49
C(24)	3124(12)	3731(13)	10513(14)	32
C(25)	3067(20)	2782(30)	11395(20)	98
C(26)	2592(13)	2619(17)	10052(18)	50
O(27)	3938(9)	2800(8)	8926(8)	27
C(28)	4059(13)	3244(12)	8377(12)	27
C(29)	3195(17)	3469(16)	7920(16)	48
C(30)	4521(15)	3885(15)	8723(15)	41
C(31)	4519(17)	2847(13)	7877(15)	38
W(32)	9343(1)	606(1)	4658(1)	54
O(33)	9115(12)	1588(11)	4597(11)	46(4)
B(34)	8644(31)	2169(32)	4601(29)	83(12)
C(35)	8078(14)	2199(15)	5056(14)	41(5)
C(36)	8437(19)	2171(19)	5743(18)	58(7)
C(37)	7964(25)	2316(30)	6199(23)	90(10)
C(38)	6967(24)	2319(32)	6016(23)	91(10)
C(39)	6721(17)	2386(20)	5205(17)	58(6)
C(40)	7249(15)	2302(18)	4777(14)	47(5)
C(41)	9264(38)	2101(36)	6109(35)	136(16)
C(42)	6353(34)	2260(39)	6589(33)	133(14)
C(43)	6916(20)	2454(21)	3943(20)	70(8)
C(44)	8735(28)	2781(26)	4271(28)	31(9)
C(45)	8439(27)	2086(20)	2990(22)	38(8)
C(46)	8846(21)	3466(19)	3069(20)	56(7)
C(47)	9085(31)	3917(30)	3336(30)	38(10)
C(48)	9171(16)	4030(15)	4280(16)	0(5)
C(49)	9025(19)	3492(18)	4577(19)	52(7)
C(50)	8766(21)	2149(20)	2980(21)	18(9)
C(51)	9267(39)	4552(34)	2861(36)	72(15)
C(52)	9108(37)	3561(35)	5316(35)	53(12)
C(53)	8830(33)	2579(29)	2390(32)	46(11)
C(54)	8894(27)	3287(24)	2446(26)	29(8)
C(55)	8781(23)	1416(20)	2895(23)	17(7)
C(56)	9004(35)	3695(31)	1759(34)	48(11)
C(57)	8720(24)	2551(24)	3594(24)	80(10)
C(58)	8799(32)	3136(31)	3792(32)	107(13)
O(59)	8763(18)	157(16)	5263(17)	87(7)

(*continued*)

TABLE 3. (*continued*)

Atom	$10^4 \times x$	$10^4 \times y$	$10^4 \times z$	$10 \times B_{iso}$
C(60)	7814(23)	78(21)	4827(23)	73(9)
C(61)	7402(34)	506(32)	4227(33)	117(14)
C(62)	7681(30)	−714(26)	4535(29)	96(12)
C(63)	7598(31)	92(29)	5674(30)	102(12)
O(64)	9092(17)	403(15)	3572(17)	25(6)
O(65)	9455(18)	19(16)	4006(17)	30(6)
C(66)	9345(31)	9(29)	3040(28)	36(10)
C(67)	9244(41)	−698(38)	3055(39)	144(17)
C(68)	8630(38)	−17(34)	2374(37)	54(12)
C(69)	10054(31)	470(28)	2787(31)	42(10)
C(70)	9734(24)	−560(21)	3468(24)	20(7)
C(71)	10118(35)	−1070(33)	4113(34)	49(11)
C(72)	10421(30)	−168(27)	3213(29)	38(10)
C(73)	5213(14)	811(13)	4686(14)	35(5)
C(74)	4844(36)	422(31)	3963(35)	48(12)
C(75)	5290(42)	338(36)	3387(40)	61(14)
C(76)	5175(45)	1243(40)	3519(43)	68(14)
C(77)	4768(36)	1215(32)	4127(34)	49(11)

TABLE 4. Selected bond distances (Å) and angles (°) for the non-disordered $W_2(OBu^t)_4[OB(Mes)_2]_2$ molecule

W(1)–W(1)′	2.3521(15)
W(1)–O(2)	1.812(18)
W(1)–O(22)	1.937(14)
W(1)–O(27)	1.901(15)
O(2)–B(3)	1.41(3)
O(22)–C(23)	1.533(26)
O(27)–C(28)	1.393(26)
W(1)′–W(1)–O(2)	101.7(4)
W(1)′–W(1)–O(22)	100.0(4)
W(1)′–W(1)–O(27)	111.3(4)
O(2)–W(1)–O(22)	118.2(7)
O(2)–W(1)–O(27)	113.9(6)
O(22)–W(1)–O(27)	110.3(7)
W(1)–O(2)–B(3)	158.4(15)
W(1)–O(22)–C(23)	122.2(14)
W(1)–O(27)–C(28)	152.4(13)
O(2)–B(3)–C(4)	122.6(24)
O(2)–B(3)–C(13)	112.6(23)
C(4)–B(3)–C(13)	124.4(25)

until *c.* 30 °C and at 60 °C is lost in the baseline. At *c.* 70 °C neither of the NMe_2 groups have appeared from the baseline which implies significant rotational barriers for the M–NC_2 units (as was seen for $W_2(NMe_2)_4(OSiPh_3)_2$) [2].

The ^1H NMR spectrum of **2** in toluene-d_8 at 22 °C and above shows one sharp OBu^t resonance and 2:1 methyl resonances of the mesityl groups as well as a singlet for the *meta* aromatic protons. At low temperatures, −40 °C and below, the *ortho* methyl groups broaden as does the *meta* proton signal of the mesityl group and at −60 °C the OBu^t signal is also quite broad. There are two possible interpretations of this behavior. (i) At room temperature and above there is rapid rotation about the W–W triple bond as well as about the B–C(aryl) bonds but at lower temperatures these rotations are slowed but never frozen out. (ii) The molecule exists in solution in the eclipsed form as found in the solid state and at low temperatures restricted rotations about B–C(aryl) bonds lead to a broadening of the mesityl *ortho* methyl and *meta* protons and as these interconversions become slow the four otherwise equivalent OBu^t ligands also become inequivalent [4]. There really is at present no way to distinguish between these two possibilities. However, it is worth noting that in sterically demanding gauche molecules such as 1,2-$Mo_2(CH_2Bu^t)_2(OCH_2Bu^t)_4$ rotations about the M–M triple bond are frozen out below −40 °C [5]. Thus the likelihood that the eclipsed conformation is maintained in solution seems most plausible.

Conclusions

We have described the preparation and characterization of two new $(W{\equiv}W)^{6+}$ containing compounds supported, in part, by boroalkoxide ligands. The gauche confirmation of the dimethylamido compound **1** was perhaps as to be expected based on earlier work. On the other hand compound **2**, $W_2(OBu^t)_4[OB(Mes)_2]_2$, provided us with two most unexpected findings.

(i) It provides the first example of an eclipsed non-bridged ethane-like dimer. (We have examined the unit cell packing diagram and find no evidence for intermolecular forces favoring this structure). The matter of eclipsed versus staggered ethane-like dimers has been a matter of some theoretical and experimental interest in the past [6]. The present finding could be taken to support the original hypothesis of Hoffmann and Albright [7] that the eclipsed geometry would be favored on electronic grounds. However, the M–M distance in **2** is within the normal range for $W_2(OR)_6$ compounds and we are inclined to the view that favorable interligand interactions across the M–M bond cause the eclipsed geometry.

(ii) The planarity at the boron atoms in compounds **1** and **2** together with the relatively short B–O distances (comparable to those in the free borinic acid) suggest that there is significant O p_π to B p_π bonding. Such bonding would be expected to reduce the extent of O p_π to W d_π bonding relative to a normal alkoxide. In the complex $Co[OB(Mes)_2]_2 \cdot Li(THF)_2Cl_2Li(THF)_2$ where there is an Li–O–Co bridge involving the boroalkoxide ligand, Power *et al.* [3] noted that the Co–O bond was longer than in related alkoxide derivatives and suggested that this might be due to the poorer donating properties of the $OB(Mes)_2$ ligand. It is, therefore, quite a surprise to find that the W–$OB(Mes)_2$

distance of 1.81(1) Å is more than 0.1 Å shorter than the W–OBu^t distances in **2**. The hybridization at oxygen which is indicated by the W–O–B (158°) and W–O–C (122 and 152°) angles cannot account for such a large difference in W–O distances.

Therefore the present work presents two unresolved issues: (i) the origin of the eclipsed geometry of **2** and (ii) the unprecedentedly short W–O boroalkoxide bonds. These matters together with the reactivity of the $(W{\equiv}W)^{6+}$ center supported by boroalkoxide ligands will be investigated in future studies.

Experimental

General operating procedures and the preparation of $W_2(NMe_2)_6$ and $W_2(OBu^t)_6$ have been described previously [8]. Elemental analyses were obtained by Oneida Research Services, New York. ^{1}H NMR spectra were recorded on a Varian-300 NMR spectrometer at 299.9 MHz and chemical shifts (δ) were referenced to the protio impurities in the solvent. ^{13}C{H} NMR spectra were obtained on a Varian-300 at 75.4 MHz and ^{11}B NMR spectra were recorded on a Nicolet-360 at 115.8 MHz. IR spectra were recorded on a Perkin-Elmer 283 spectrometer and were obtained from KBr pellets. The 2-mesityl magnesium bromide Grignard and $BF_3 \cdot OEt_2$ were purchased from Aldrich and used as received.

Preparation of dimesitylborinic acid (Mes_2BOH)

Slight modifications were made to the literature procedures for the synthesis of Mes_2BF [3a] and Mes_2BOH [9] which is based on the preparation of the xylyl analogues [3b].

A 500 ml flask was charged with BF_3/OEt_2 (10.4 g, 73.1 mmol). 2.5 g of MesMgBr (183.1 mmol, 1.0 M in Et_2O) were added over a period of 1.5 h. The reaction solution was then refluxed for 3 h. The solvent was then removed *in vacuo*. Mes_2BF was isolated by sublimation at 100 °C and 10^{-4} Torr as a white crystalline solid, collected on a water-cooled cold finger (16.1 g, 82%). Mes_2BF (16.1 g, 60.1 mmol) was dissolved in 100 ml of Et_2O. 100 ml of distilled water were then added and the mixture was stirred vigorously for 2 h. The Et_2O layer was then separated and collected and the solvent removed *in vacuo*. By sublimation at 110 °C and 10^{-4} Torr onto a water-cooled cold finger Mes_2BOH was isolated as a white crystalline solid (13.6 g, 85%). ^{1}H NMR (benzene-d_6, 22 °C, 300 MHz): 6.73 (s, *m*-H, 4H); 5.35 (s, OH, 1H); 2.60 (s, *o*-Me, 12H); 2.14 (s, *p*-Me, 6H). ^{11}B NMR (benzene-d_6, 22 °C, 116 MHz): 49.9 (br s).

Preparation of $W_2(NMe_2)_4[OB(Mes)_2]_2$ (1)

$W_2(NMe_2)_6$ (0.60 g, 0.95 mmol) was dissolved in 10 ml toluene. $HOB(Mes)_2$ (0.51 g, 1.90 mmol) was dissolved in 2 ml toluene. The $HOB(Mes)_2$ solution was added to the bright yellow $W_2(NMe_2)_6$ solution. The reaction solution immediately went golden-yellow. The solution was allowed to stir for 6 h where upon the solvent was removed *in vacuo* leaving an orange–yellow powder. X-ray quality and analytically pure crystals of **1** (0.92 g, 90%) were formed as orange cubes from concentrated hexane solutions at −20 °C. *Anal.* Calc. for $C_{44}H_{68}B_2N_4O_2W_2$: C, 49.45; H, 6.29; N, 4.91. Found: C, 49.18; H, 6.39; N, 5.21%. ^{1}H NMR (benzene-d_6, 22 °C, 300 MHz): 6.73 (s, *m*-H, 8H); 4.19 (s, NMe_2-distal, 12H); 2.50 (s, *o*-Me, 24H); 2.38 (s, NMe_2-proximal, 12H); 2.16 (s, *p*-Me, 12H). ^{13}C NMR (CD_2Cl_2, 22 °C, 75 MHz): 141.4 (B–C[Mes]); 140.7 (*o*-*C*Me); 137.3 (*p*-*C*Me); 128.1 (*m*-*C*H); 59.8 (NMe-distal); 39.2 (NMe_2-proximal); 22.7 (*o*-Me); 21.2 (*p*-Me). ^{11}B NMR (benzene, 22 °C, 116 MHz): 53.9 (br s). VT NMR in $C_6D_5CD_3$: T_c-gauche, 55 °C, $\Delta = 984$ Hz, $\Delta G^{\neq} = 61.8$ kJ/mol; T_c-gauche, 100 °C, $\Delta = 530$ Hz, $\Delta G^{\neq} = 71.2$ kJ/mol. Estimated from the T_c. IR (cm^{-1}, KBr): 2921m, 2863m, 2820w, 2776w, 1607m, 1559vw, 1447m, 1426m, 13352, 1300s, 1283s, 1215w, 1177w, 1150w, 1086w, 1022w, 955s, 939s, 835s, 806m, 750w, 671w.

Preparation of $W_2(OBu^t)_4[OB(Mes)_2]_2$ (2)

$W_2(OBu^t)_6$ (0.50 g, 0.62 mmol) as dissolved in 10 ml toluene. $HOB(Mes)_2$ (0.23 g, 1.24 mmol) was dissolved in 2 ml toluene. The $HOB(Mes)_2$ solution was added to the dark red $W_2(OBu^t)_6$ solution. There was no apparent color change. The solution must stir for 5 days in order to insure complete reaction. After 5 days the solvent was removed *in vacuo* leaving a dark red powder. X-ray quality and analytically pure crystals of **2** (0.59 g, 80%) were formed as dark red cubes from concentrated hexane solutions at −20 °C. *Anal.* Calc. for $C_{52}H_{80}B_2O_6W_2$: C, 52.80; H, 7.15; N, 0.00. Found: C, 52.45; H, 6.80; N, 0.03%. ^{1}H NMR (benzene-d_6, 22 °C, 300 MHz): 6.79 (s, *m*-H, 8H); 2.41 (s, *o*-Me, 24H); 2.17 (s, *p*-Me, 12H); 1.39 (s, t-Bu, 36H). ^{13}C NMR (CD_2Cl_2, 22 °C, 75 MHz): 141.2 (*o*-*C*Me); 140.2 (B-C[Mes]); 137.8 (*p*-*C*Me); 128.1 (*m*-*C*H); 81.5 (*C*Me$_3$); 33.1 (C*Me*$_3$); 23.5 (*o*-Me); 21.3 (*p*-Me). ^{11}B NMR (benzene, 22 °C, 116 MHz): 49.9 (br s). VT NMR completed in $C_6D_6CD_3$. IR (cm^{-1}, KBr): 2967s, 2923s, 1609m, 1559w, 1425w, 1362w, 1296s, 1277s, 1240m, 1167s, 1090m, 1026m, 976s, 912w, 885m, 839m, 801w.

Crystallographic studies

General operating procedures and listings of programs have already been described [10]. A summary of crystal data for the two compounds studied in this work is given in Table 5.

TABLE 5. Summary of crystallographic data

	I	II
Empirical formula	$C_{44}H_{68}B_2N_4O_2W_2{:}C_3H_7$	$C_{52}H_{80}B_2O_6W_2{\cdot}\frac{1}{2}C_6H_{14}$
Color of crystal	yellow	red–orange
Crystal dimensions (mm)	0.09×0.12×0.20	0.10×0.12×0.12
Space group	*C*2/*c*	*C*2
Cell dimensions		
Temperature (°C)	−160	−159
a (Å)	39.379(7)	17.164(2)
b (Å)	13.649(2)	18.773(2)
c (Å)	21.918(4)	18.490(2)
β (°)	123.12(1)	102.91(0)
Z (molecules/cell)	8	4
Volume (Å^3)	9867.01	6116.42
Calculated density (g/cm^3)	1.504	1.339
Wavelength (Å)	0.71069	0.71069
Molecular weight	1117.46	1233.61
Linear absorption coefficient (cm^{-1})	47.970	38.785
Detector to sample distance (cm)	22.5	22.5
Sample to source distance (cm)	23.5	23.5
Average *ω* scan width at half height	2.0	2.0
Scan speed (°/min)	6.0	6.0
Scan width (° + dispersion)	2.0	1.8
Individual background (s)	6	6
Aperture size (mm)	3.0×4.0	3.0×4.0
2*θ* Range (°)	6–45	6–45
Total no. reflections collected	7561	4959
No. unique intensities	6487	4144
No. with $F\sigma$ 0.0	5506	4011
No. with $F\sigma$3.0(F)	3527	3894
$R(F)$	0.0541	0.0664
$R_w(F)$	0.0520	0.0670
Goodness of fit for the last cycle	0.953	1.824
Maximum Δ/σ for last cycle	0.57	0.35

$W_2(NMe_2)_4[OB(Mes)_2]_2\cdot 1/2$hexane

A single crystal (0.09×0.12×0.2 mm) was selected and affixed to a glass fiber with silicon grease. The sample was then transferred to the goniostat where it was cooled to −160 °C. Inert atmosphere techniques were employed for all operations.

A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited monoclinic symmetry. The systematic absences of the hkl, $h+k=2n+1$ and $h0l$, $h=2n+1$ and $l=2n+1$ and subsequent refinement confirmed the choice of the space group *C*2/*c*. The 8 0 0, 0 0 4, −3 −3 3 and 1 −3 −1 reflections were used as standards which were collected every 300 reflections.

Following normal data reduction averaging and an absorption correction, a unique set of 6487 reflections was obtained with the R for averaging of 0.012 for 586 redundant data. However, with the overall weak intensity from the crystal, only the 3527 reflections with $I>2.33\sigma$ were used for the refinement of 244 variables.

The structure was solved using SHELX-86 and standard Fourier techniques. The two tungsten atoms were located in the original E-map and all other non-hydrogens were located by successive difference Fouriers. One third of the hydrogens were located and the remainder placed in calculated positions and fixed in the final least-squares cycle. In addition a disordered hexane solvent molecule was located across an axis of symmetry. B was fixed for the disordered solvent molecule in the final least-squares cycle. The shortest contact between the tungsten dimer and the solvent is 3.3 Å between the methyl hydrogens of the mesityl ligand and the solvent C(55).

Furthermore, it should be noted that intermolecular contacts as short as 3.43 Å are found between mesityl rings forming chains along the b axis.

The final difference map was essentially featureless with the largest peaks of 0.9 e/Å^3 in the immediate vicinity of the tungsten atoms and the disordered solvent. The maximum Δ/σ of 0.57 in the final least-squares cycle was from C(56) of the solvent molecule.

$W_2(OBu^t)_4[OB(Mes)_2]_2\cdot 1/2$hexane

A suitable small crystal was selected from the bulk sample. The crystal was affixed to a glass fiber with

silicone grease and was transferred to the goniostat where it was cooled to −159 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited monoclinic (2/*m*) Laue symmetry. The systematic extinction of *hkl* for $h+k=2n+1$ led to the choice of space groups *C*2 (No. 5), *Cm* (No. 8) or *C*2/*m* (No. 12). The non-centrosymmetric space group *C*2 was confirmed by the subsequent solution and refinement of the structure. Unit cell dimensions were determined by a least-squares fit of the setting angles of 68 carefully centered reflections, having 2θ values between 19 and 28°. A total of 4959 reflections (including standards) was collected in the given range. Following the usual data reduction, correction for absorption and averaging of redundant data, a unique set of 4144 reflections was obtained. 3894 reflections were considered observed by the criterion $F > 3.0\sigma(F)$. The *R* for the averaging of 747 redundant data was 0.065. Plots of the four standard reflections (−6 0 0, 0 0 4, 0 6 0 and −2 4 3) measured every 300 reflections showed no significant variations.

The structure was solved by the usual combination of direct methods and Fourier techniques. The two unique W atoms were located after some initial difficulty. The problems in locating the heavy atoms were caused by the fact that the asymmetric unit contains two W_2 complex halves. Each dimer is located at a two-fold axis, molecule 1 is located at $\frac{1}{2}$, *y*, 0 and molecule 2 is located at the two-fold axis at 0, *y*, $\frac{1}{2}$. Once the two W atoms were located the non-hydrogen atoms were located without difficulty. Molecule 2 (W(32) through C(72)) is disordered. The disorder involves one of the mesityl groups at B(34) (C(44) through C(58)) and one of the −OR groups (O(64) through C(72)). The asymmetric unit was also found to contain one half molecule of disordered n-hexane (C(73) through C(77)) again located at a two-fold axis. The full-matrix least-squares refinement was completed using anisotropic thermal parameters and fixed idealized hydrogen atoms on the atoms of molecule 1, while the atoms in molecule 2 and the solvent molecule were refined using isotropic thermal parameters (except for W(32)). Due to the disorder problems the refinement did not converge as well as we would have liked. The final $R(F)$ was 0.066 and $R_w(F)$ was 0.067. The shifts remained large in the disordered molecules as could be expected. During the refinement reflections having $F < 3.0\sigma(F)$ were given zero weight (marked with * in the listing of F_o and F_c values, see 'Supplementary material'.

The final difference Fourier contained several peaks of 1.5 to 2.0 e/Å^3 in the area of molecule 2, indicating that the disorder is not completely resolved (see the VERSORT plots, 'Supplementary material').

An attempt at establishing the absolute structure in this non-centrosymmetric space group was made, however, the difference between the two refinements was not significant, possibly due to the disorder problems.

Supplementary material

Listings of anisotropic thermal parameters, complete listings of bond distances and angles, VERSORT drawings showing the disorder of molecule **2** and the complete atom number scheme and listings of F_o and F_c values are available from the authors on request.

Acknowledgements

We thank the National Science Foundation for financial support and Professor Philip P. Power for helpful discussions on the synthesis of the dimesitylborinic acid.

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