Organometallic Chemistry of $[W_2(OCH_2tBu)_8]$ (M=M): Substrate Uptake and Activation at a Tungsten–Tungsten Double Bond

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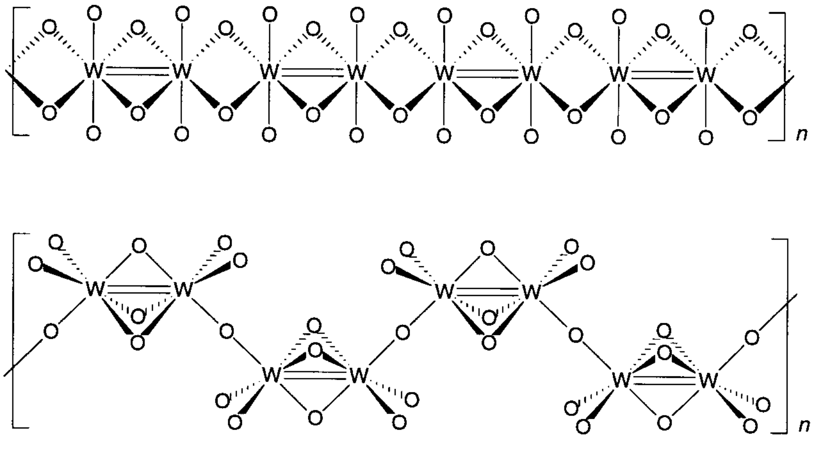
Dedicated to Lord Lewis on the occasion of his 70th birthday

Abstract: The compound $[W_2(OCH_2tBu)_8]$ reacts in hydrocarbon solvents with ethyne, ethene, allene, carbon monoxide, and benzophenone to give 1:1 adducts $[W_2(OCH_2tBu)_8(\mu\text{-}C_2H_2)]$ (**1**), $[W_2(OCH_2tBu)_8(\eta^2\text{-}C_2H_4)]$ (**2**), $[W_2(OCH_2tBu)_8(\mu,\eta^1,\eta^3\text{-}C_3H_4)]$ (**3**), $[W_2(OCH_2tBu)_8(CO)]$ (**4**), and $[W_2(OCH_2tBu)_8(\eta^2\text{-}OCPh_2)]$ (**5**), respectively. These compounds have been characterized by variable-temperature ^1H and ^{13}C NMR studies, infrared spectroscopy, elemental analysis, and for **1** and **3** by single-crystal X-ray crystallography. Compound **1** contains a nonperpendicular and nonparallel $\mu\text{-}C_2H_2$ ligand in the solid-state with W–C = 2.07(1) and 2.43(1) Å, and W–W and C–C = 2.623(1) and 1.34(1) Å, respectively. However, in solution the $\mu\text{-}C_2H_2$ ligand sees two equivalent tungsten nuclei on the NMR time-scale, even at low temperatures. In the μ,η^1,η^3-allene adduct **3**, the W–W distance of 2.917(2) Å implies a loss of M–M bonding in favor of W_2-to-allene bonding: $W1-\eta^1\text{-}C = 2.11(1)$, $W2-\eta^3\text{-}C = 2.24$ to 2.35 Å. $[W_2(OCH_2tBu)_8]$ and $Ph_2C{=}S$ react in hydrocarbon solvents to give products from the cleavage of the C=S bond, namely $[(tBuCH_2O)_4W{=}S]$ and $[(tBuCH_2O)_4W{=}CPh_2]$. A derivative of the latter, $[(Ph_2C{=})(tBuCH_2O)(EtO)_2W(\mu\text{-}OEt)]_2$ (**6**), has been characterized by a single-crystal X-ray study. The W–W distance of 3.485(1) Å is consistent with the lack of a W–W bond, while W–C = 1.967(6) Å is typical for a W–alkylidene distance. $[W_2(OCH_2tBu)_8]$ reacts with KH and [18]crown-6 in tetrahydrofuran to give $\{K^+([18]crown\text{-}6)[W_2(\mu\text{-}H)(OCH_2tBu)_8]^-\}$ (**7**), and with $Ph_3P{=}CH_2$ to give $[W_2(\mu\text{-}CH_2)(OCH_2tBu)_8]$ (**8**) and Ph_3P. These results are compared with related reactions involving $[W_2(OR)_6](M{\equiv}M)$ compounds and with the organometallic chemistry of M=M-bonded species such as $[Cp^*_2Re_2(CO)_4]$ and $[Os_2(CO)_8]$.

Keywords: alkoxides · metal–metal interactions · organometallic complexes · structure elucidation · tungsten

Introduction

The chemistry of metal–metal double bonds is much less developed than that for M–M quadruple and triple bonds.[1] Indeed, in organometallic chemistry the only two systems to have been studied extensively are $[Cp^*_2Re_2(CO)_4]$ by Casey and co-workers[2] and $[Os_2(CO)_8]$.[3] The latter, though isolable only in a matrix, acts as a template for the binding of alkynes and alkenes. Thanks to the elegant work of Norton et al.,[3b] it can be construed to exist as $[(CO)_4Os{=}Os(CO)_4]$. Our recent synthesis[4] of $[W_2(OCH_2tBu)_8]$ which, though insoluble in noncoordinating hydrocarbon solvents such as hexane and toluene, can be viewed as a d^2–d^2 W=W-bonded complex having a solid-state structure of one of the types shown in **A**.[5] This affords us the opportunity to investigate the chemistry of the $(W{=}W)^{8+}$ template supported by alkoxide ligands, which



A

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in turn allows us to compare its reactivity with the [$W_2(OR)_6$] compounds that have revealed a rich organometallic chemistry,[6] and also with the carbonyl-supported M=M bonded systems noted above. A preliminary communication of some of these results has already been published.[7]

Results and Discussions

Syntheses:

*[$W_2(OCH_2tBu)_8(\mu$-$C_2H_2)$] (**1**)*: The addition of ethyne to a toluene suspension of the purple [$W_2(OCH_2t\mathrm{Bu})_8$] gave a red solution of the 1:1 adduct, **1**, which was purified by dissolving the crude product in refluxing toluene and cooling to room temperature whereupon red crystals were formed. Compound **1** failed to show any further reactivity in the presence of a 10-fold excess of ethyne.

*[$W_2(OCH_2tBu)_8(\eta^2$-C_2H_4] (**2**)*: A toluene suspension of [$W_2(OCH_2t\mathrm{Bu})_8$] reacted with *one* equivalent of ethene to give a green solution of **2**. Concentrating the solution and cooling afforded fine microcrystals of **2** which have not thus far proved suitable for an X-ray study. Compound **2** is air-sensitive and very soluble in common organic solvents, even at low temperatures. With an excess of ethene, a mixture of numerous intractable products was formed. These have not been pursued further at this time.

*[$W_2(OCH_2tBu)_8(\mu,\eta^1,\eta^3$-$C_3H_4)$] (**3**)*: Addition of allene to a toluene suspension of [$W_2(OCH_2t\mathrm{Bu})_8$] yielded a deep green solution of the 1:1 adduct **3** which, as we show later, exists in more than one isomeric form in solution. Cooling concentrated solutions of the green solution of the 1:1 allene adduct to $-20\,^{\circ}\mathrm{C}$ yielded *orange* crystals of **3**, as shown by X-ray crystallography (see below). The 1:1 adduct did not react further with allene to form a 2:1 adduct, as did [$W_2(Ot\mathrm{Bu})_6$] in its formation of [$W_2(\mu,\eta^1,\eta^3$-$C_3H_4)(\eta^2$-$C_3H_4)(Ot\mathrm{Bu})_6$] (see below).

*[$W_2(OCH_2tBu)_8(CO)$] (**4**)*: Addition of carbon monoxide to a hydrocarbon suspension of the purple compound [$W_2(OCH_2t\mathrm{Bu})_8$] gave a red-brown solution of the 1:1 carbonyl adduct **4**. Compound **4** is air-sensitive and extremely soluble in all common organic solvents, including ethers, even at low temperatures. A red-brown microcrystalline solid of **4** has been obtained, but crystals suitable for an X-ray study were not. The 1:1 adduct **4** is inert with respect to further reaction with CO at 1 atm, room temperature in hydrocarbon solvents.

*[$W_2(OCH_2tBu)_8(\eta^2$-$OCPh_2)$] (**5**)*: Hydrocarbon suspensions of [$W_2(OCH_2t\mathrm{Bu})_8$] reacted instantaneously at room temperature with benzophenone to give the 1:1 adduct **5**, which is a deep green air-sensitive compound that may be recrystallized from concentrated toluene solutions at $-20\,^{\circ}\mathrm{C}$. Its spectroscopic properties are related to the structurally characterized compound [$W_2(Oc\mathrm{C}_5H_9)_8(\eta^2$-$OCc\mathrm{C}_5H_8)$][8] so that a single-crystal X-ray study was not undertaken.

*[$W(=CPh_2)(OCH_2tBu)(OEt)_2(\mu$-$OEt)]_2$ (**6**)*: The reaction between [$W_2(OCH_2t\mathrm{Bu})_8$] and thiobenzophenone gave rise to rapid cleavage of the C=S bond and products formulated as [$W(=CPh_2)(OCH_2t\mathrm{Bu})_3(\mu$-$OCH_2t\mathrm{Bu})]_2$ and [$S=W(OCH_2t\mathrm{Bu})_4]_n$. The two compounds co-crystallize from hydrocarbon solvents which has impeded their independent characterization. However, the sulfide could be prepared from the reaction between elemental sulfur and [$W_2(OCH_2t\mathrm{Bu})_8$][7] and this reaction will be described in detail elsewhere as part of a separate study of the reactivity of [$W_2(OCH_2t\mathrm{Bu})_8$] with Group 16 elements.[9] Note, the compound $S = W(Ot\mathrm{Bu})_4$ has been previously reported.[10] Evidence for the terminal alkylidene is seen from reactions which employ $Ph_2{}^{13}C=S$ to yield a readily identifiable $W={}^{13}CPh_2$ moiety having a ^{13}C chemical shift of $\delta = 263$ and $^1J(^{183}W,^{13}C) = 259$ Hz (intensity of 14%) due to coupling to ^{183}W ($I = 1/2$, 14.5% natural abundance).[11] Support for the proposed alkylidene complex was also obtained by the treatment of a hydrocarbon solution containing [$W(=CPh_2)(OCH_2t\mathrm{Bu})_4$] with ethanol which yielded the crystalline compound **6**, as determined by an X-ray study.

*{K^+([18]crown-6)[$W_2(\mu$-$H)(OCH_2tBu)_8]^-$} (**7**)*: A suspension of [$W_2(OCH_2t\mathrm{Bu})_8$] in toluene reacted rapidly with KH in the presence of [18]crown-6 to produce compound **7** as a golden-brown solid, which is soluble in all common hydrocarbon solvents. It is believed to be structurally analogous to [$NaW_2(\mu$-$H)(Oi\mathrm{Pr})_8(dme)$] and the related neopentoxide has been previously prepared from the reaction between [$W_2(OCH_2t\mathrm{Bu})_6$] and $t\mathrm{Bu}CH_2OH/NaOCH_2t\mathrm{Bu}$ in hydrocarbon solvents.[12]

*[$W_2(\mu$-$CH_2)(OCH_2tBu)_8$] (**8**)*: The reaction between a purple suspension of [$W_2(OCH_2t\mathrm{Bu})_8$] in toluene and 1:1 equiv of $Ph_3P=CH_2$ afforded a paler purple solution of **8** and Ph_3P. Compound **8** is an air-sensitive hydrocarbon-soluble compound that gives very small crystals upon recrystallization. The single crystal structure was determined from one such crystal.

Compounds **1–8** are diamagnetic. Spectroscopic data and elemental analyses are given in the Experimental Section. Selected aspects of the spectroscopic properties that are pertinent to solution-state structures and bonding will be discussed later.

Solid-state and molecular structures:

*[$W_2(OCH_2tBu)_8(\mu$-$C_2H_2)$] (**1**)*: A view of the molecular structure found in the solid-state is given in Figure 1 and selected bond lengths and angles are given in Table 1. If the μ-C_2H_2 ligand is considered as a single bridging entity, the structure may be viewed as confacial bioctahedral. Furthermore, if the μ-C_2H_2 ligand is viewed as a $C_2H_2^{2-}$ dianion, then the W–W distance of 2.623(1) Å is easily reconcilable with a $(W-W)^{10+}$ moiety which has a formal d^1-d^1 M–M single bond. Of singular note is the nonperpendicular and nonparallel mode of bonding for the μ-C_2H_2 ligand. One set of W–C distances are short [av 2.07(1) Å], while the other set are long [2.43(1) Å]. This skewed type of geometry is

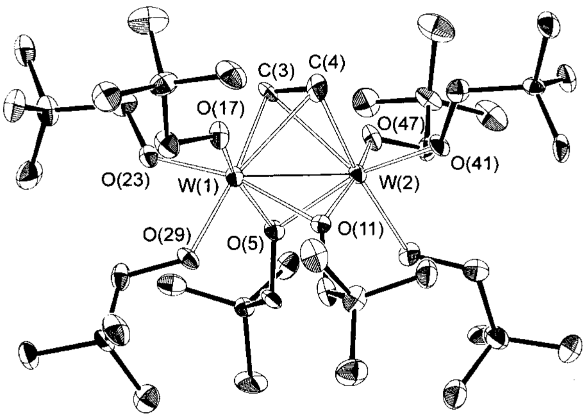

Figure 1. An ORTEP drawing of the molecular structure of **1** in the solid state, showing the atom numbering system used in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for **1.**

W1–W2 2.6228(8)	W2–O5 2.128(7)
W1–O5 2.075(7)	W2–O11 2.073(7)
W1–O11 2.118(7)	W2–O35 1.950(8)
W1–O17 1.882(7)	W2–O41 1.919(7)
W1–O23 1.933(8)	W2–O47 1.867(8)
W1–O29 1.957(7)	W2–C3 2.432(12)
W1–C3 2.08(1)	W2–C4 2.069(12)
W1–C4 2.43(1)	C3–C4 1.34(2)
W2-W1-O5 52.31(19)	W1-W2-O5 50.49(20)
W2-W1-O11 50.50(20)	W1-W2-O11 52.02(21)
W2-W1-O17 116.51(22)	W1-W2-O35 123.52(23)
W2-W1-O23 133.14(23)	W1-W2-O41 132.29(23)
W2-W1-O29 123.46(23)	W1-W2-O47 117.74(24)
W2-W1-C3 61.0(3)	W1-W2-C3 48.45(25)
W2-W1-C4 48.19(27)	W1-W2-C4 60.9(3)
O5-W1-O11 74.1(3)	O5-W2-O11 73.9(3)
O5-W1-O17 164.8(3)	O5-W2-O35 85.5(3)
O5-W1-O23 97.4(3)	O5-W2-O41 165.2(3)
O5-W1-O29 86.8(3)	O5-W2-O47 92.2(3)
O5-W1-C3 86.1(4)	O5-W2-C3 76.7(3)
O5-W1-C4 95.3(3)	O5-W2-C4 105.1(4)
O11-W1-O17 90.8(3)	O11-W2-O35 86.7(3)
O11-W1-O23 165.2(3)	O11-W2-O41 97.0(3)
O11-W1-O29 85.1(3)	O11-W2-O47 166.0(3)
O11-W1-C3 105.9(4)	O11-W2-C3 95.8(3)
O11-W1-C4 77.6(4)	O11-W2-C4 87.2(4)
O17-W1-O23 97.6(3)	O35-W2-O41 82.3(3)
O17-W1-O29 93.5(3)	O35-W2-O47 93.7(3)
O17-W1-C3 96.8(4)	O35-W2-C3 160.4(3)
O17-W1-C4 79.7(4)	O35-W2-C4 165.8(4)
O23-W1-O29 82.3(3)	O41-W2-O47 96.9(3)
O23-W1-C3 85.2(4)	O41-W2-C3 116.5(3)
O23-W1-C4 115.8(4)	O41-W2-C4 85.7(4)
O29-W1-C3 164.7(4)	O47-W2-C3 79.2(4)
O29-W1-C4 161.2(4)	O47-W2-C4 95.3(4)
C3-W1-C4 33.5(4)	C3-W2-C4 33.4(4)

relatively rare in organometallic chemistry and, as first noted by Hoffmann et al.[13] and subsequently emphasized by others,[14] this situation arises as a result of a second order Jahn–Teller distortion. The bonding in compound **1** has been the subject of a detailed theoretical study which is reported elsewhere.[15] Suffice it to note that the C–C distance is 1.34(1) Å in the μ-C_2H_2 ligand and, as such, is shorter than in $[W_2(OtBu)_6(\mu\text{-}C_2H_2)(py)]$ (C–C 1.44(1) Å).[16] This is consistent with the view that $[W_2(OtBu)_6]$ is more reducing than $[W_2(OCH_2tBu)_8]$ in its reactions with π-acid substrates. We shall return to this point.

*$[W_2(OCH_2tBu)_8(\mu,\eta^1,\eta^3\text{-}C_3H_4)]$ (**3**)*: An ORTEP drawing of the solid-state molecular structure of **3** is shown in Figure 2 and selected bond lengths and angles are given in Table 2 . The coordination geometry about W(1) may be viewed as

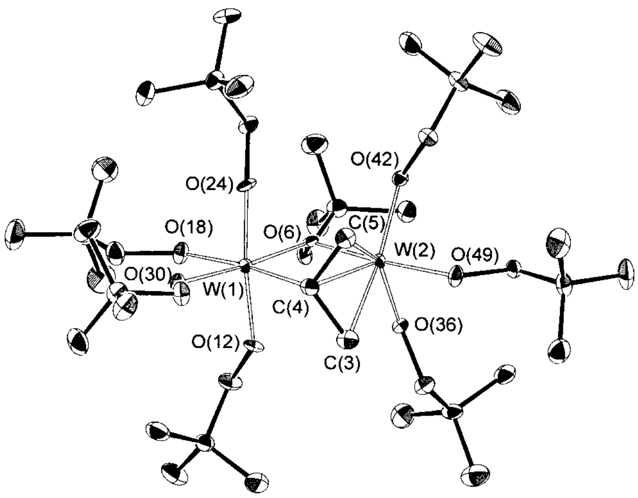

Figure 2. An ORTEP drawing of the molecular structure of **3** in the solid-state, showing the atom numbering scheme used in Table 2 .

Table 2. Selected bond lengths [Å] and angles [°] for **3**.

W1–O6 2.079(4)	W2–O6 2.068(4)
W1–O12 1.890(4)	W2–O36 1.914(4)
W1–O18 1.956(4)	W2–O42 1.886(4)
W1–O24 1.833(5)	W2–O48 1.947(4)
W1–O30 1.944(4)	W2–C3 2.347(7)
W1–C4 2.112(7)	W2–C4 2.246(6)
C3–C4 1.426(9)	W2–C5 2.271(6)
C4–C5 1.431(9)	
O6-W1-O12 86.14(17)	O6-W2-O36 84.84(16)
O6-W1-O18 89.33(17)	O6-W2-O42 85.92(18)
O6-W1-O24 85.16(19)	O6-W2-O48 167.35(17)
O6-W1-O30 173.67(17)	O6-W2-C3 110.15(21)
O6-W1-C4 95.11(20)	O6-W2-C4 91.50(20)
O12-W1-O18 87.67(19)	O6-W2-C5 109.52(20)
O12-W1-O24 171.30(20)	O18-W1-O24 92.59(19)
O12-W1-O30 95.71(19)	O18-W1-O30 84.70(18)
O12-W1-C4 88.88(21)	O18-W1-C4 174.18(23)
O24-W1-O30 92.98(19)	O24-W1-C4 91.53(21)
O30-W1-C4 90.99(20)	O36-W2-C3 84.67(20)
O36-W2-O42 127.42(18)	O36-W2-O48 88.65(18)
O36-W2-C4 114.06(21)	O36-W2-C5 144.82(22)
O42-W2-O48 89.46(20)	O42-W2-C4 117.83(21)
O42-W2-C3 146.18(20)	O42-W2-C5 86.50(22)
O48-W2-C3 79.95(22)	O48-W2-C4 101.07(22)
O48-W2-C5 81.90(21)	C3-W2-C4 36.10(22)
C3-W2-C5 60.37(23)	C4-W2-C5 36.94(23)
W1-O6-W2 89.42(16)	W1-O6-C7 124.0(4)
W1-O12-C13 138.1(4)	W2-O6-C7 131.6(3)
W1-O18-C19 131.8(4)	W2-O36-C37 134.8(4)
W1-O24-C25 144.5(4)	W2-O42-C43 132.3(4)
W1-O30-C31 127.2(4)	W2-O48-C49 122.9(4)
W1-C4-W2 83.97(22)	W2-C3-C4 68.1(4)
W1-C4-C3 120.2(5)	W2-C4-C3 75.8(4)
W1-C4-C5 117.6(4)	W2-C4-C5 72.4(4)
C3-C4-C5 108.7(6)	W2-C5-C4 70.6(4)

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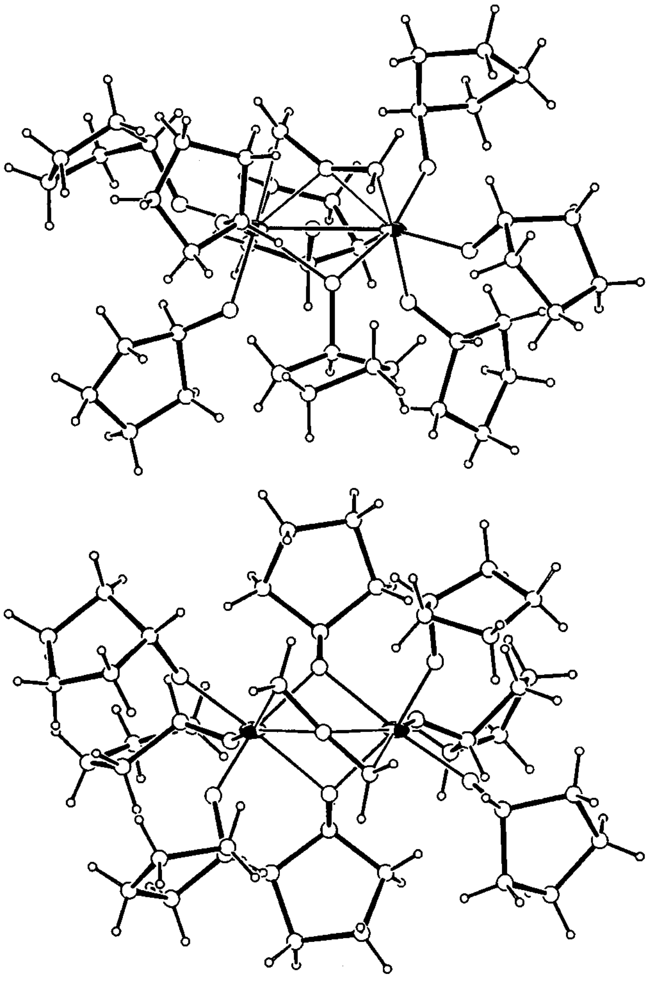
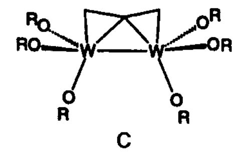
approximately octahedral, while that at W(2) is a distorted trigonal bipyramid in which the η^3-C_3 moiety occupies a single equatorial site with the methylene units lying slightly above the trigonal plane. The W–W distance of 2.917(2) Å is consistent with the absence of any significant M–M bonding interaction and suggests that the allene has effectively oxidized the W_2^{8+} center and is itself reduced by four electrons. The W(1)–C(4) distance (2.11(1) Å) is notably shorter than the W(2)–C(4) distance (2.25(1) Å), while the W(2)–C(3) and W(2)–C(5) distances are 2.35(1) and 2.27(1) Å, respectively. The C-C-C angle of 108.7(6)° is notably less than 120° and the C(3)–C(4) and C(4)–C(5) distances (1.43(1) Å) are approaching C(sp^2)–C(sp^2) single bond lengths (1.46 Å).[17] All of this is understandable in terms of maximizing metal–ligand (allene) bonding at the expense of M–M bonding, and the μ,η^1,η^3-mode of bonding has been seen previously.[18] Perhaps what is surprising is that in the closely related compound $[\mathrm{W_2(O}c\mathrm{C_5H_9)_8}(\mu\text{-allene})]$ the allene bridges are in the twisted μ,η^2,η^2-mode as shown in **B**,[8] with a W–W distance of 3.053(2) Å.



B

The latter compound was isolated from the reaction between $[\mathrm{W_2}(\mu\text{-H})(\mathrm{O}c\mathrm{C_5H_9})_7(\mathrm{HNMe_2})]$ and allene, but may be viewed as the addition product of allene and $[\mathrm{W_2(O}c\mathrm{C_5H_9)_8}]$. The point to recognize is that the mode of the allene bridge in these $[\mathrm{W_2(OR)_8}(\mu\text{-}\mathrm{C_3H_4})]$ compounds is evidently very sensitive to the nature of R. Also it is worth mentioning that in $[\mathrm{W_2(O}t\mathrm{Bu)_6}(\mu\text{-}\mathrm{C_3H_4})]$ the allene bridges have yet again a different mode in which the C-C-C moiety is aligned parallel to the W–W axis[18] as depicted by **C** (R = *t*Bu).



C

*$[\mathrm{W({=}CPh_2)(OCH_2}t\mathrm{Bu)(OEt)_2}(\mu\text{-}\mathrm{OEt})]_2$ (**6**)*: A view of the molecular structure of **6** is shown in Figure 3 and selected bond lengths and angles are given in Table 3. The edge-shared bioctahedral geometry is reminiscent of those seen in $[\mathrm{W({=}E)(OR)_3}(\mu\text{-}\mathrm{OR})]_2$ compounds, where E is oxo or imido,[19] and the W–C distance is 1.97(1) Å, which is typical of a W–C double bond.[20]

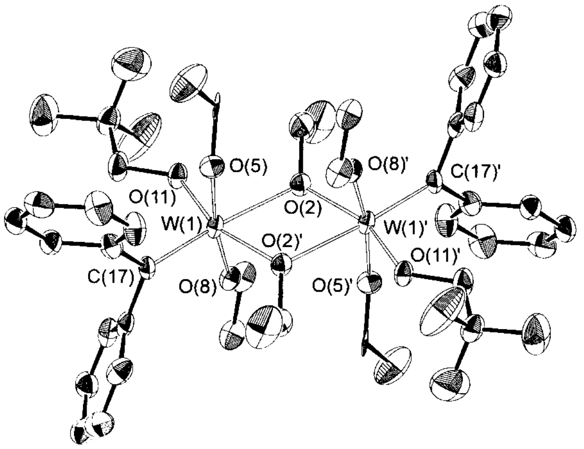


Figure 3. An ORTEP drawing of the molecular structure of **6** in the solid-state, showing the atom numbering scheme used in Table 3.

Table 3. Selected bond lengths [Å] and angles [°] for **6**.

W1–O2′ 2.047(4)	W1–O8 1.855(4)
W1–O2 2.302(4)	W1–O11 1.950(4)
W1–O2 1.838(5)	W1–C17 1.967(6)
O2′-W1-O2 73.64(18)	O2′-W1-O5 90.70(20)
O2-W1-O5 85.16(19)	O2′-W1-O8 88.22(19)
O2-W1-O8 83.41(18)	O2′-W1-O11 158.14(17)
O2-W1-O11 84.52(17)	O2′-W1-C17 100.66(22)
O2-W1-C17 174.28(22)	O5-W1-O8 168.35(20)
O5-W1-O11 88.20(20)	O5-W1-C17 95.46(24)
O8-W1-O11 88.50(19)	O8-W1-C17 96.14(24)
O11-W1-C17 101.17(23)	W1′-O2-W1 106.36(18)
W1′-O2-C3 124.3(4)	W1-O2-C3 121.8(4)
W1-O5-C6 142.5(7)	W1-O5-C6A 138.3(8)
W1-O8-C9 138.2(4)	W1-O11-C12 130.3(4)
W1-C17-C18 123.8(5)	W1-C17-C24 124.0(4)

*$[\mathrm{W_2(OCH_2}t\mathrm{Bu)_8}(\mu\text{-}\mathrm{CH_2})]$ (**8**)*: An ORTEP drawing of the methylene-bridged compound is given in Figure 4. The structure consists of two pseudo-octahedral tungsten atoms sharing a common face formed by two μ-OR groups and one μ-CH_2 group. The W–W distance of 2.646(1) Å is consistent with a W–W single bond for a W_2^{10+} core. The W–C distance of 2.10(1) Å (average) and the other W–O distances are

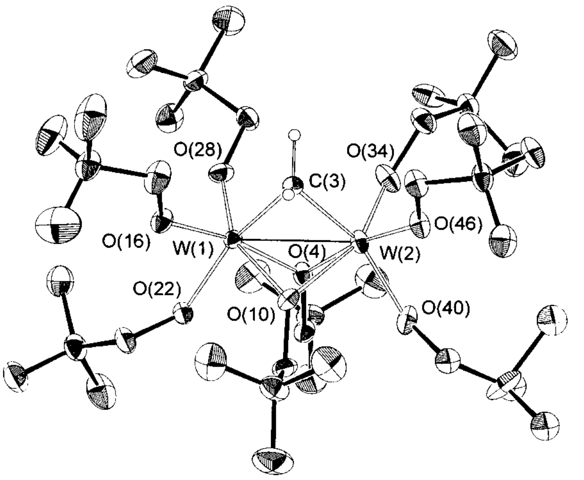


Figure 4. An ORTEP drawing of **8**, showing the atom numbering scheme.

unexceptional. This is, however, the only methylene-bridged compound of its type, in that it is exclusively supported by alkoxide ligands. Selected bond lengths and angles are given in Table 4.

Table 4. Selected bond lengths [Å] and angles [°] for **8**.

W1 - W2 2.6464(4)	W1 - O4 2.090(3)
W1 - O10 2.083(3)	W1 - O16 1.925(4)
W1 - O22 1.946(3)	W1 - O28 1.834(4)
W1 - C3 2.108(5)	W2 - O4 2.061(3)
W2 - O10 2.150(4)	W2 - O34 1.842(4)
W2 - O40 1.936(4)	W2 - O46 1.919(4)
W2 - C3 2.101(5)	
W2-W1-O4 49.90(9)	W2-W1-O10 52.43(10)
W2-W1-O16 136.13(11)	W2-W1-O22 123.00(10)
W2-W1-O28 101.51(12)	W2-W1-C3 50.94(14)
O4-W1-O10 76.30(13)	O4-W1-O16 170.32(15)
O4-W1-O22 85.69(14)	O4-W1-O28 87.78(15)
O4-W1-C3 99.00(17)	O10-W1-O16 101.82(14)
O10-W1-O22 88.01(14)	O10-W1-O28 153.89(15)
O10-W1-C3 69.98(17)	O16-W1-O22 84.76(15)
O16-W1-O28 97.16(16)	O16-W1-C3 89.11(18)
O22-W1-O28 111.62(16)	O22-W1-C3 155.43(17)
O28-W1-C3 92.73(18)	W1-W2-O4 50.88(10)
W1-W2-O10 50.18(9)	W1-W2-O34 104.94(12)
W1-W2-O40 121.28(11)	W1-W2-O46 135.45(11)
W1-W2-C3 51.16(14)	O4-W2-O10 75.47(13)
O4-W2-O34 88.71(15)	O4-W2-O40 86.05(15)
O4-W2-O46 170.84(15)	O4-W2-C3 100.15(17)
O10-W2-O34 155.12(15)	O10-W2-O40 85.69(15)
O10-W2-O46 103.78(14)	O10-W2-C3 68.84(17)
O34-W2-O40 112.68(17)	O34-W2-O46 94.83(16)
O34-W2-C3 95.89(19)	O40-W2-O46 84.79(16)
O40-W2-C3 150.97(19)	O46-W2-C3 87.90(18)
W1-C3-W2 77.91(18)	W1-O4-W2 79.22(12)
W1-O10-W2 77.38(11)	

Selected spectroscopic properties and comments on bonding: [$W_2(OCH_2tBu)_6(\mu\text{-}C_2H_2)$] (**1**): The NMR data for the $\mu\text{-}^{13}C_2H_2$ labeled isotopomer of **1** are instructive as to the nature of the bonding in solution. Even at low temperatures, −80 °C in [D$_8$]toluene, a single ^{13}C NMR signal is seen flanked by one set of tungsten satellites, ^{183}W ($I = 1/2$, 14.5 % natural abundance). The relative intensity of the satellites is 25 %, which is consistent with both carbon atoms bridging two W atoms in a time-averaged symmetric mode: $\delta = 191$ and $^1J(^{183}W,^{13}C) = 24$ Hz. The proton-coupled spectrum reveals the second-order behavior anticipated for an AA′XX′ spectrum. From a simulation of the spectrum, we obtained $^1J(^{13}C,^1H) = 181$ Hz and $J(^{13}C,^{13}C) = 28$ Hz, both of which are considerably reduced from the values for free ethyne, which are 249 and 172 Hz, respectively.[21] The magnitude of $J(^{13}C,^{13}C)$ in [$M_2(\mu\text{-}C_2H_2)$] compounds has been shown to correlate roughly with C−C distance and the degree of reduction of the C−C bond.[22] In [$W_2(OtBu)_6(\mu\text{-}C_2H_2)(py)$], for example, which exists in equilibrium with [$(tBuO)_3W{\equiv}CH$] (2 equiv) and free pyridine, $J(^{13}C,^{13}C)$ is 12 Hz, whereas in [$Co_2(CO)_6(\mu\text{-}C_2H_2)$], $J(^{13}C,^{13}C)$ is 56 Hz.[22] Within the series of [$M_2(\mu\text{-}C_2H_2)$] complexes for which $J(^{13}C,^{13}C)$ has been determined, the value in [$W_2(OCH_2tBu)_8(\mu\text{-}C_2H_2)$] most closely resembles that in [$Mo_2(OiPr)_6(\mu\text{-}C_2H_2)(py)_2$], where $J(^{13}C,^{13}C) = 24$ Hz.[22]

The ^1H NMR spectrum at 23 °C shows only one type of alkoxide ligand indicative of rapid bridge-to-terminal exchange. However, at −80 °C the expected (based on Figure 1) spectrum is observed with three *t*Bu signals in the ratio 4:2:2 and the methylene protons appear in the ratio 4:4:4:2:2:2:2. This is consistent with a time-averaged C_{2v} structure in which the two $\mu\text{-}OCH_2tBu$ groups and the terminal OCH_2tBu ligands which are *trans* to the $\mu\text{-}C_2H_2$ moiety lie on molecular mirror planes of symmetry. The remaining four OCH_2tBu ligands, which are symmetry-equivalent, have diastereotopic methylene protons. The signals for these methylene protons should be observed as two sets of doublets resulting from geminal coupling with a total intensity of four hydrogens per doublet. However, four peaks of equal intensity are seen in the methylene region presumably due to the coincidental overlap of the two diastereotopic CH_2 protons.

Finally, it should be recognized that the NMR data for the $\mu\text{-}C_2H_2$ ligand does not distinguish between a dynamic ethyne moiety which oscillates about a μ-perpendicular position and a $\mu\text{-}C_2H_2$ ligand that rapidly interconverts between a μ-perpendicular and μ-parallel mode of bonding. To our knowledge, the latter process has never been established in organometallic chemistry but, in this particular instance, the theoretical calculations reveal that μ-parallel and μ-perpendicular modes of bonding are only slightly higher in energy than the observed skewed geometry.[15]

[$W_2(OCH_2tBu)_8(\eta^2\text{-}C_2H_4)$] (2): The NMR data for **2** leaves little doubt as to its structure in solution. The molecule has C_1 symmetry, which leads to eight inequivalent OCH_2tBu groups. With no molecular mirror plane of symmetry, the methylene protons are all diastereotopic and appear as sixteen doublets, due to geminal J(H−H) coupling, of equal intensity. There is some overlap of these signals and broad multiplets at $\delta = 4.35$ and 4.05 represent two of the four inequivalent protons of the $\eta^2\text{-}C_2H_4$ ligand. The $^{13}C\{^1H\}$ NMR spectrum is more straightforward as there is less overlap of resonances. The molecule is, however, fluxional on the NMR time-scale and only at low temperatures is the confacial bioctahedral geometry frozen out; that is, at −60 °C, [D$_8$]toluene, 300 MHz for ^1H spectra.

The variable-temperature $^{13}C\{^1H\}$ NMR spectra of the $\eta^2\text{-}^{13}C_2H_4$ ligand in the labeled isotopomer of **2** are shown in Figure 5. At 100 °C in [D$_8$]toluene there is a sharp signal due

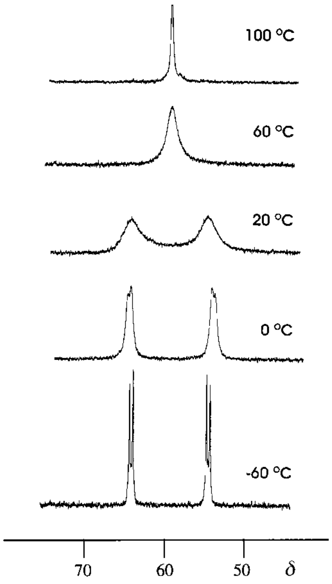
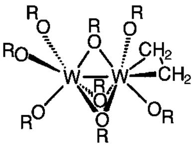


Figure 5. Variable-temperature $^{13}C\{^1H\}$ NMR spectra for the ethene carbon signals in **2**, recorded in [D$_8$]toluene at 75 MHz in the temperature range between −60 and +100 °C.

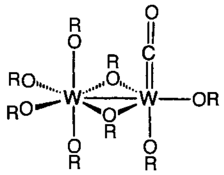
to two equivalent ^{13}C nuclei. However, on lowering the temperature, this resonance broadens and splits into two signals of equal intensity separated by roughly 10 ppm and at −60 °C a $^1J(^{13}C,^{13}C)$ coupling of 31 Hz is clearly evident. Coupling to ^{183}W ($I = 1/2$) is not seen (or is not resolved). The proposed structure of **2** is shown in **D** ($R = CH_2tBu$) below. The magnitude of $^1J(^{13}C,^{13}C)$ is significantly reduced from 67 Hz[21] in free ethylene and this, together with the restricted rotation about the W–η^2-C_2 axis, leads us to propose that there is extensive W(d$_\pi$)-to-C_2 π^*-back bonding. In as much as the structure shown in **D** represents a confacial bioctahedron, the restricted rotation about the W–η^2-C_2 axis can be understood as a result of the mutual competition of the olefin and the metal atoms for t_{2g} electrons in order to allow for both a M–M bond and M(d$_\pi$)-to-C_2 π^*-bonding. Although at 100 °C the two ethene carbon atoms are equivalent, which can be described by rapid-rotation about the W-η^2-C_2 axis, the whole molecule is fluxional with rapid bridge–terminal alkoxide exchange. So it is more likely that the η^2-C_2H_4 ligand passes through a molecular plane of symmetry as it moves from one side of a confacial bioctahedron to the other. An estimation of the activation energy, $\Delta G^{\neq}$ for this process can be obtained from the ^{13}C spectra (Figure 5) and is 15 kcal mol^{-1}.[23]



D

*$[W_2(OCH_2tBu)_8(\mu,\eta^1,\eta^3\text{-}C_3H_4]$ (**3**)*: The allene adduct **3**, which is orange in the solid state, is green in solution. (Red crystals yield green solutions and from these green solutions red crystals form.) The molecule is fluxional on the NMR timescale in solution at 23 °C as only one type of OCH_2tBu is observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra. If the the temperatuure is cooled to −65 °C, several resonances are frozen out in the ^1H and $^{13}C\{^1H\}$ NMR spectra (see Experimental Section) but it is evident that the spectra cannot be reconciled to the observed solid-state structure shown in Figure 2. Indeed, we observe five allene methylene carbon signals in the $^{13}C\{^1H\}$ spectrum between $\delta = 60$ and 90. Thus, it is possible that, in addition to an isomer having the structure found in the solid-state, other isomers are also present, such as those shown in **B**, or **C**, and even an ethene-like structure, $[W_2(OCH_2tBu)_8(\eta^2\text{-}CH_2CCH_2)]$, akin to that shown in **D**. Further speculation is pointless, but it is worth emphasizing how flexible the $[W_2(OR)_8]$ template is for coordination of allene.

*$[W_2(OCH_2tBu)_8(CO)]$ (**4**)*: The most striking feature of **4** is that the carbonyl ligand does not bridge two metal atoms. It is bound to one W atom with an anomolously low ^{13}C chemical shift[24] $\delta = 323$ with $^1J(^{183}W,^{13}C) = 220$ Hz, $I = 14\,\%$.[24a] Also the values of $\tilde{\nu}(C{=}O) = 1854$ cm^{-1} and of $\tilde{\nu}(^{13}C{=}O) = 1817$ cm^{-1} imply extensive back-bonding and the ketene-like nature of the W=C=O moiety.[24b] The ^1H NMR spectrum is consistent with the structure shown in **E** ($R = CH_2tBu$) in which one W atom is in an octahedral environment and the other is trigonal bipyramidal. The carbonyl ligand is proposed to occupy an axial site which allows for a mixing of M–M and M–CO π bonding.



E

As shown in Figure 6, the pseudotrigonal bipyramidal metal may be viewed as d^4, $(d_{xz},d_{yz})^4$. In this way all four electrons from the W_2 center can be involved in W(d$_\pi$)–CO π^* bonding. However, some residual bonding to the hexacoordinate tungsten is possible since it has formally vacant t_{2g} orbitals which match the symmetry of the filled $(d_{xz},d_{yz})^4$ orbitals on the other W atom.

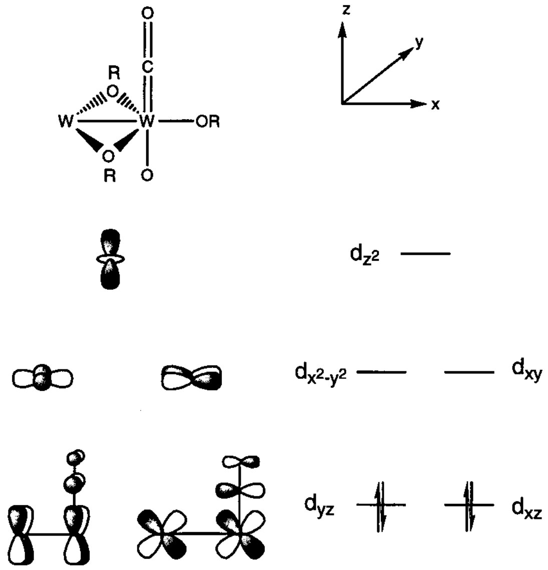


Figure 6. An orbital interaction diagram showing the M(dπ)–CO π^*-orbital and M–M d–d interaction for **4**, which has the proposed structure shown in **E** in the text.

*$[W_2(OCH_2tBu)_8(\eta^2\text{-}OCPh_2)]$ (**6**)*: The 1:1 benzophenone adduct is deep green in solution and the NMR data are

consistent with a C_1 structure akin to that shown for the ethene adduct **D** and as seen in the crystal and molecular structure of $[W_2(OcC_5H_9)_8(\eta^2\text{-}(OCcC_5H_8))]$.[8] The carbonyl carbon of the η^2-$O^{13}CPh_2$ ligand shows coupling to ^{183}W with $^1J(^{183}W,^{13}C) = 47$ Hz ($I = 14\%$), which implies a strong interaction with the tungsten atom to which it is bonded.

*$\{K^+([18]crown\text{-}6)[W_2(\mu\text{-}H)(OCH_2tBu)_8]^-\}$ (**7**)*: The spectral data for the μ-hydrido anion are consistent with a confacial bioctahedral geometry, as seen for $[W_2(\mu\text{-}H)(OcC_5H_9)_7(HNMe_2)]$[25] and $[NaW_2(\mu\text{-}H)(OiPr)_8(dme)]$,[12] and the hydride signal in the ^1H NMR spectrum is downfield at $\delta = 9.8$ with $J(^{183}W,^1H) = 119$ Hz ($I = 24\%$).

*$[W_2(OCH_2tBu)_8(\mu\text{-}CH_2)]$ (**8**)*: The proton-coupled ^{13}C NMR spectrum of the ^{13}C-labeled ligand in $[W_2(OCH_2tBu)_8(\mu\text{-}^{13}CH_2)]$ is shown in Figure 7. The resonance at $\delta = 147.5$ appears as a 1:2:1 triplet due to coupling to two protons. Each resonance is flanked by satellites due to coupling to ^{183}W, with integral intensity 24%: $^1J(^{13}C,H) = 135$ Hz and $^1J(^{183}W,^{13}C) = 77$ Hz. Evidently, at 23 °C the two W nuclei are chemically equivalent and there is rapid scrambling of the alkoxide ligands. At −80 °C the ^1H NMR spectrum shows five tBu resonances in the ratio 2:2:2:1:1, while the methylene region exhibits twelve peaks. The low-temperature spectrum can best be explained by the adoption of the structure shown in **F** (R = CH_2tBu), given that there is accidental magnetic degeneracy associated with some of the diastereotopic methylene protons. It is not consistent with the confacial bioctahedral structure seen in the solid state (Figure 4). The data do, however, clearly indicate that reaction with the phosphorus ylide has led to a transfer of the methylene group and formation of the bridging methylene complex $[W_2(OCH_2tBu)_8(\mu\text{-}CH_2)]$ (**8**).

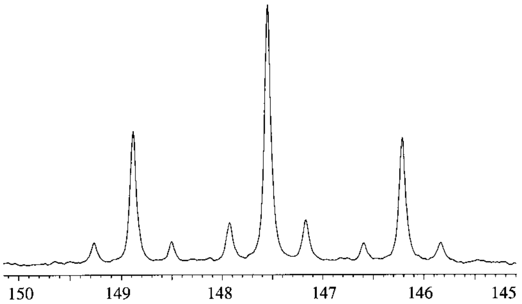
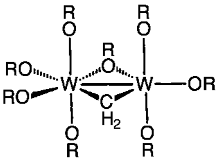


Figure 7. The proton-coupled spectrum of the μ-$^{13}CH_2$ ligand in the labeled compound **8**, recorded in [D$_8$]toluene at 75 MHz, 23 °C.



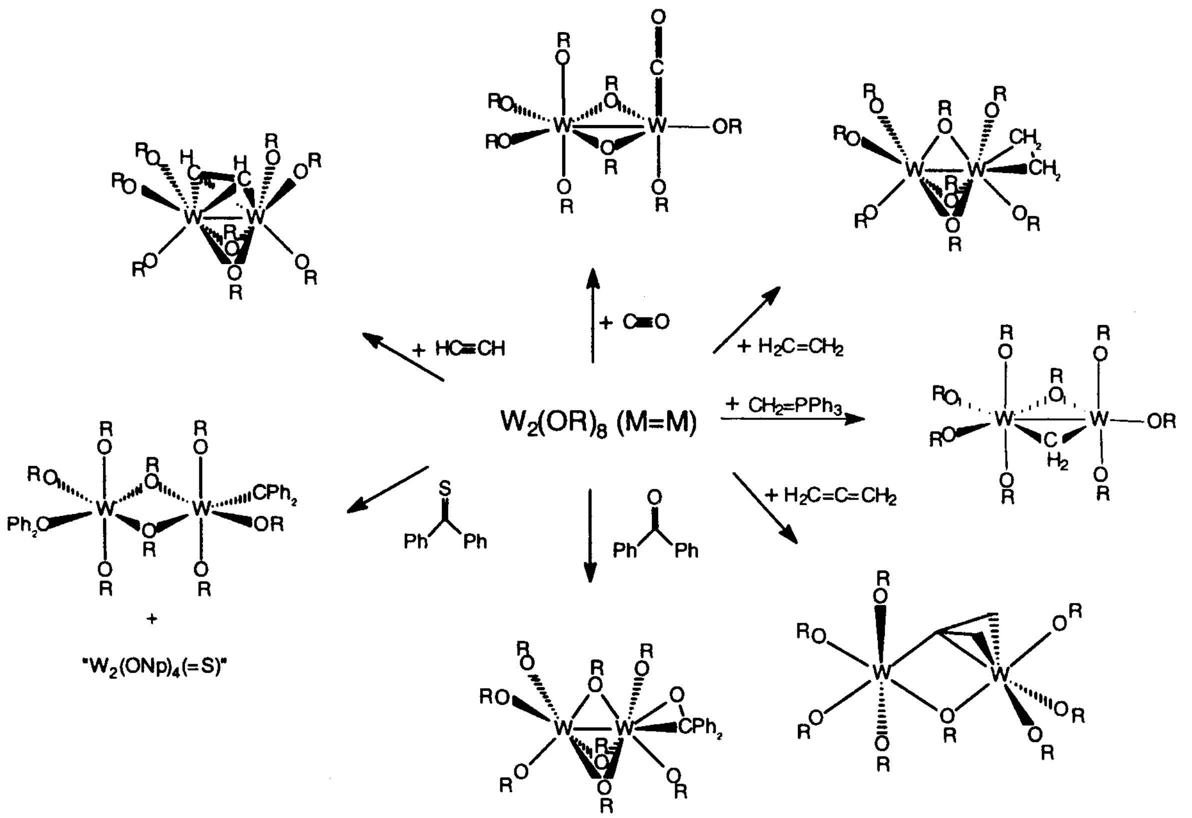
F

Comparisons with related systems: There are many interesting comparisons to be made with the chemical reactions of $[M_2(OR)_6]$ (M≡M) compounds. The W≡W bond supported by alkoxides appears more reactive and more reducing, as evidenced by its ability to reductively cleave alkynes and ketones and take up more than one equivalent of ethene or allene.[6] In some respects the reducing power of the $[W_2(OCH_2tBu)_8]$ moiety is comparable to $[Mo_2(OR)_6]$ compounds which bind alkynes and reductively cleave the C−S double bond of thiobenzophenone, but not an aldehyde or ketone.[26] Of course, the comparison in reactivity between a M−M double and a M−M triple bond is expected to reveal significant differences, just as observed for C−C and C−N double and triple bonds.

One of the most influential concepts in linking structures and products of reactions focuses on the frontier molecular orbitals of fragments. Two fragments are said to be isolobal if their frontier orbitals have the same symmetry and electronic configuration. By developing the isolobal analogy, Hoffmann forged an understanding of basic building blocks in organometallic chemistry and foresaw the beautiful analogies that exist between organic and inorganic systems.[26] We have tried to further this analogy to understand the nature of metal alkoxide clusters of molybdenum and tungsten in relationship to carbonyl clusters of the later transition elements. For example, a d^3-$W(OR)_3$ fragment can be viewed to be isolobal with CR, $[Co(CO)_3]$, $[CpMo(CO)_2]$, and P. Thus, the compounds $[(RO)_3W{\equiv}W(OR)_3]$, $R'C{\equiv}CR'$, and $[(RO)_3W{\equiv}CR']$ are simply related dimers while compounds such as $[Co_3(CO)_9(\mu_3\text{-}CR)]$, $[W_3(OR)_9(\mu\text{-}CR')]$, and $[W_3(OR)_9(\mu_3\text{-}P)]$ are merely tetrahedrane analogues.[28] Within this context it is interesting to note that the d^2-$W(OR)_4$ fragment may be compared to a carbene, CR_2, or an organometallic equivalent, such as $[M(CO)_4]$, where M = Fe, Ru, and Os, or $[Cp^*Re(CO)_2]$.[27] This leads us to speculate that it may be possible to isolate a triangular $[W_3(OR)_{12}]$ complex which has three M−M single bonds, a trimetallacyclopropane, and an analogue of the well-known trinuclear $[M_3(CO)_{12}]$ compounds, where M = Fe, Ru, and Os. The compound $[W_2(\mu\text{-}CH_2)(OCH_2tBu)_8]$ can, indeed, be viewed as a dimetallacyclopropane. However, many of the reactions of $[W_2(OCH_2tBu)_8]$ are very different from those of $[Cp^*_2Re_2(CO)_4]$ and $[Os_2(CO)_8]$. The Os=Os moiety adds alkynes and alkenes to form 1,2-dimetallacyclobutenes and -cyclobutanes, that is, the substrates add in a parallel fashion across the M=M bond.[3] In contrast, we observe rather unsymmetrical structures in the ethyne, ethene, allene, and benzophenone adducts. This may well reflect the more electron-rich nature of the W=W bond, supported by alkoxide π-donor ligands as compared to the later d^8-metals with attendant π-acceptor carbonyl ligands. In addition, in $[W_2(OR)_8]$ the 1:1 adducts maximize metal−ligand bonding by means of alkoxide bridges. Given the relative sparsity of inorganic and organometallic complexes with M−M double bonds and an even less well-established data base for reactions, further speculation is not warranted.

Conclusions

The hydrocarbon-insoluble compound $[W_2(OCH_2tBu)_8]_n$ behaves as a source of $[W_2(OCH_2tBu)_8]$ (M=M) in its reactions with small unsaturated molecules, as summarized in Scheme 1. The substrates must be small, presumably for steric reasons, as we have observed no reactions with either MeC≡CMe or MeCH=CH$_2$ under similar conditions. However, it would seem likely that it should be possible to prepare



Scheme 1. The reactions of $[W_2(OCH_2tBu)_8]$ (M=M) with unsaturated molecules.

further complexes from $[W_2(OR)_8L]$, where R = Me or Et and L = a neutral donor ligand that can bind reversibly in solution. If this should prove to be the case, the chemistry of the W=W bond could become quite extensive. It is also probably true to state that the structures of compounds **1–7** could not have been predicted, though all may be understood with hindsight. The reaction between a phosphorus ylide and the W=W bond to give a μ-methylene dimetal complex is, to our knowledge, without precedent[29] and suggests a potential new route to μ-alkylidene complexes in this field of metal alkoxide chemistry.

Further studies of the reactivity of $[W_2(OR)_8]$ complexes are underway and a variety of atom-transfer reactions will be described elsewhere.[9]

Experimental Section

All synthesis and handling of samples were carried out under purified inert atmospheres (N_2, Ar, or He) with standard Schlenk, vacuum manifold, and drybox techniques.

Acetylene, allene, carbon monoxide (Air Products), and ^{13}C-labeled ethene, ethyne, and carbon monoxide (Cambridge Isotopes) were subjected to three freeze-thaw-degas cycles before use. Benzophenone (Aldrich) was recrystallized from hexane (60 to 23 °C) and stored in a N_2 glove box. KH (Aldrich) was washed with hexanes and stored in the glove box. [18]crown-6 (Aldrich) was used as received. $Ph_2{}^{13}CO$ was prepared from the reaction between $^{13}CO_2$ (Cambridge Isotopes) and 2 equiv of PhLi according to the procedure of Gilman.[30] The thiobenzophenones ($^{12}C{=}S$ and $^{13}C{=}S$) were prepared from the corresponding ketone and Lawesson's reagent[31] and were purified by sublimation (100 °C, 10^{-2} Torr). $[W_2(OCH_2tBu)_8]$ was prepared as previously described.[4]

Elemental analyses were performed on a Perkin–Elmer 2400 Series II analyzer (CHNO and S), or were sent to Analytic Microlab, Inc., Nocross, GA. Infrared spectra were obtained on a Perkin–Elmer 283 spectrophotometer as Nujol mulls between NaCl plates or as pressed KBr pellets. ^1H NMR spectra were recorded on Varian GEM-300, Varian I-400, or Bruker AM-500 NMR spectrometers in dry degassed $[D_8]$toluene or $[D_6]$benzene. ^1H chemical shifts are in ppm relative to the residual protio impurity in $[D_6]$benzene set at $\delta = 7.15$, or to the CHD_2 quintet of $[D_8]$toluene set at $\delta = 2.09$. ^{13}C NMR spectra were recorded on Varian GEM 300, Varian I 400, or Brucker AM 500 spectrometers at 75, 100, and 125 MHz, respectively. ^{13}C NMR chemical shifts are reported in ppm relative to the triplet of $[D_6]$benzene set at $\delta = 128.0$ or the downfield singlet of $[D_8]$toluene at $\delta = 137.5$. The ^{13}C data simulation for $[W_2(OCH_2tBu)_8(\mu\text{-}^{13}C_2H_2)]$ was performed with the computer program GNMR.[32]

$[W_2(OCH_2tBu)_8(\mu\text{-}C_2H_2)]$ (1): Ethyne (0.225 mmol) was added through a calibrated gas manifold to a suspension of $[W_2(OCH_2tBu)_8]_n$ (120 mg, 0.113 mmol) in dry, degassed hexanes (10 mL) at −196 °C. The solution/suspension was allowed to warm to 23 °C and stirred for 1 h. The solvent was removed under dynamic vacuum. Recrystallization in a minimal volume of dry, degassed toluene at −20 °C afforded X-ray quality, dark red crystals in 86 % yield. ^1H NMR (300 MHz, $[D_8]$toluene, −65 °C): $\delta = 11.65$ (singlet, 2H), 4.82 (4H), 4.72 (4H), 4.58 (doublet, $^2J(H,H) = 4.2$ Hz, 8H), 1.21 (18H), 1.03 (18H), 0.96 (36H); $^{13}C\{^1H\}$ NMR (75 MHz, $[D_8]$toluene, −65 °C): $\delta = 191$ [$^1J(^{183}W,^{13}C) = 24$ Hz (25 %)], 86.8, 81.4, 74.6 (2:1:1 ratio for $C(CH_3)_3$), 34.9, 34.2, 33.7 (2:1:1 ratio for CH_2), 27.81, 27.77, 26.77 (1:1:2 ratio for $C(CH_3)_3$); IR (Nujol): $\tilde{\nu}(C{=}C) = 1650\ cm^{-1}$; anal. calcd for $C_{42}H_{90}O_8W_2$: C 46.24, H 8.32; found: C 46.56, H 8.50.

$[W_2(OCH_2tBu)_8(\eta^2\text{-}C_2H_4)]$ (2): Ethene (0.103 mmol) was added to a suspension of $[W_2(OCH_2tBu)_8]_n$ (100 mg, 9.39×10^{-2} mmol) in dry, degassed hexanes (10 mL) at −196 °C through a calibrated gas manifold. The solution/suspension was allowed to warm to 23 °C. The reaction mixture turned dark green upon stirring. After 2 h, the solvent was removed in vacuo. Recrystallization in a minimal volume of dry, degassed toluene at −20 °C afforded dark green crystals in 78 % yield. ^1H NMR (500 MHz, $[D_8]$toluene, −65 °C): $\delta = 5.3–3.3$ 16 doublets (1H per doublet). 1.48 (9H), 1.30 (9H), 1.20 (9H), 1.26 (9H), 1.09 (18H), 0.90 (9H), 0.88 (9H); $^{13}C\{^1H\}$

NMR (125 MHz, $[D_8]$toluene, −65 °C): $\delta = 64.3$, 55.1 ($CH_2{=}CH_2$, $^1J(^{13}C,^{13}C) = 31$ Hz), 36.1, 35.3, 35.0, 34.7, 35.5, 34.4, 33.5, 33.3 (CH_2), 28.5, 27.9, 27.7, 27.6, 27.5, 27.3, 26.7 ($C(CH_3)_3$; anal. calcd for $C_{42}H_{92}O_8W_2$: C 46.16, H 8.49; found: C 46.54, H 8.70.

$[W_2(OCH_2tBu)_8(\mu,\eta^1,\eta^3\text{-}C_3H_4)]$ (3): Allene (0.129 mmol) was added to a suspension of $[W_2(OCH_2tBu)_8]_n$ (125 mg, 0.117 mmol) in dry, degassed hexanes (10 mL) at −196 °C through a calibrated gas manifold. Upon warming to 23 °C, a deep green solution formed. After stirring for 3 h, the solvent was removed under dynamic vacuum. Crystallization from a concentrated hexanes solution at −20 °C yielded X-ray quality, pale orange crystals in 82 % yield. ^1H NMR (500 MHz, $[D_8]$toluene, −65 °C): $\delta = 6.05$, 5.59, 5.18, 3.99, 3.68,. 3.49 (doublets, 2H per doublet), 5.34, 5.31, 4.88 4.86 (singlets, 2H per singlet) for (CH_2); 1.27 (18H), 1.17 (18H), 0.90 (18H), 0.75 (18H) ($C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $[D_8]$toluene, −65 °C): $\delta =$ 35.6, 34.7, 33.9, 33.8 (1:1:1:1 ratio for CH_2), 27.9, 27.8, 27.7, 26.6 (1:1:1:1 ratio for $C(CH_3)_3$), 90.5, 87.1, 81.2, 74.1, 67.8 (1:1:1:1 for CH_2-C-CH_2); anal. calcd for $C_{43}H_{92}O_8W_2$: C 46.74, H 8.39; found: C 47.02, H 8.63.

$[W_2(OCH_2tBu)_8(CO)]$ (4): Carbon monoxide (0.103 mmol) was added to a suspension of $[W_2(OCH_2tBu)_8]_n$ (100 mg, 9.39×10^{-2} mmol) in dry, degassed hexanes (10 mL) at −196 °C through a calibrated gas manifold. The solution was allowed to warm to 28 °C and stirred for 3 h. The solvent was removed under dynamic vacuum. Recrystallization in dry, degassed Et_2O at −20 °C afforded dark red crystals in 81 % yield. ^1H NMR (500 MHz, $[D_8]$toluene, −65 °C): $\delta = 5.14$, 4.78, 4.70, 4.68 (singlets, 2H), 4.61, 4.43, 4.31, 3.84 (doublets, 2H per doublet); 1.42 (18H), 1.14 (9H), 1.13 (9H), 1.09 (18H), 1.03 (9H), 0.98 (9H); $^{13}C\{^1H\}$ NMR (125 MHz, $[D_8]$toluene, −65 °C): $\delta = 323$ (CO, $^1J(^{183}W,^{13}C) = 227$ Hz (14 %)), 35.4, 35.1, 35.0, 34.8, 34.5, 34.1 (CH_2, in relative ratios of 1:2:1:1:1:2), 28.0, 27.4, 27.2, 27.0, 26.8 ($C(CH_3)_3$, in a 1:1:2:2:2 ratio); IR: $\tilde{\nu} = 1854$ (CO), 1817 (^{13}CO), 1770 ($^{13}C^{18}O$) cm^{-1}; anal. calcd for $C_{41}H_{88}O_9W_2$: C 45.06, H 8.12; found: C 45.50, H 8.33.

$[W_2(OCH_2tBu)_8(\eta^2\text{-}OCPh_2)]$ (5): $[W_2(OCH_2tBu)_8]_n$ (100 mg, 9.39×10^{-2} mmol) and benzophenone (34 mg, 0.19 mmol) were dissolved in dry, degassed hexanes (10 mL) at 24 °C to give a forest green solution. After stirring the mixture for 2 h, the solvent was removed in vacuo. Et_2O was added to dissolve the remaining solid. The solution was concentrated in vacuo and cooled to −20 °C. Isolation of crystals in this manner resulted in a 79 % yield. ^1H NMR (400 MHz, $[D_8]$toluene, −65 °C): $\delta = 5.9 - 3.5$ 23 peaks (seven distinct doublets in a 2:1:1:1:1:1:1 ratio, two multiplets of equal intensity and twice the integration of the largest doublet), 1.55 (9H), 1.25 (9H), 1.09 (9H), 0.95 (9H), 0.88 (18H), 0.74 (9H), 0.66 (9H); $^{13}C\{^1H\}$ NMR (100 MHz, $[D_8]$toluene, −65 °C): $\delta = 100$ [Ph-C(O)-Ph, $^1J(^{183}W,^{13}C) = 47$ Hz (14 %)], 36.1, 36.0, 35.3, 35.1, 34.4, 33.8, 33.6, 33.3 (CH_2), 28.4, 27.9, 27.7, 27.6, 27.5, 26.1 ($C(CH_3)_3$) (in a 1:2:2:1:1:1 relative ratio); anal. calcd for $C_{53}H_{98}O_9W_2$: C 51.05, H 7.92; found: C 49.84, H 7.78.

$[W({=}CPh_2)(OCH_2tBu)_4]_2$, $[WS(OCH_2tBu)_4]_n$, and $[W({=}CPh_2)(OEt)_3(OCH_2tBu)]_2$: Addition of thiobenzophenone (56 mg, 0.28 mmol) to a suspension of $[W_2(OCH_2tBu)_8]_n$ (150 mg, 0.141 mmol) in dry, degassed hexanes (10 mL) at 24 °C gave a brown solution. The solution was stirred for 3 h followed by removal of the solvent under a dynamic vacuum. Attempts to recrystallize a single compound from hydrocarbon solutions always led to mixtures of $[W({=}CPh_2)(OCH_2tBu)_4]_2$ and $[W(S)(OCH_2tBu)_4]_n$. The latter compound can be prepared independently[7, 9] and was characterized spectroscopically, and the former was characterized by the ^{13}C signal assignable to a terminal $W{=}^{13}CPh_2$ moiety: $\delta = {}^1J(^{183}W,^{13}C) =$ 259 Hz, $I = 14$ %. Addition of ethanol to a hydrocarbon solution of the mixture gave, upon crystallization, the mixed alkoxide complex $[W({=}CPh_2)(OEt)_3(OCH_2tBu)]_2$ (**6**), which was characterized crystallographically.

$\{K^+([18]crown\text{-}6)[W_2(\mu\text{-}H)(OCH_2tBu)_8]^-\}$ (7): KH (5.2 mg, 0.129 mmol) and [18]crown-6 (34.1 mg, 0.129 mmol) were dissolved in THF (10 mL). This solution was transferred by means of a cannula to a Schlenk flask (30 mL) containing $[W_2(OCH_2tBu)_8]_n$ (125 mg, 0.117 mmol) in dry, degassed hexanes (10 mL). The reaction mixture became brown-gold upon mixing. The reaction was stirred for 6 h at 23 °C followed by removal of the solvent under dynamic vacuum. Hexanes were added to dissolve the remaining solid. The solution was Schlenk-filtered over Celite followed by reduction of the solvent volume in vacuo. Crystallization at −20 °C gave golden-brown crystals of **7**. Yield: 48 %; ^1H NMR (400 MHz, $[D_8]$toluene, 23 °C): $\delta = 9.8$ [$^1J(^{183}W,H) = 119$ Hz (24 %)], 4.9–4.4 (16H, multiplets), 3.26 (24H, singlet), 1.4–1.1 (72H, overlapping singlets).

$[W_2(OCH_2tBu)_8(\mu\text{-}CH_2)]$ (8): Either KO*t*Bu (11.6 mg, 0.103 mmol, 1.1 equiv relative to metal complex) or *n*BuLi (52 µL, 2.0 M solution in hexanes, 0.103 mmol, 1.1 equiv) was added to $[Ph_3PMe][I]$ (42 mg, 0.103 mmol) at 0 °C and allowed to warm to 23 °C for 2 h. (NOTE: The phosphonium salt must be dry; check Aldrich samples if problems are experienced. Drying with P_2O_5 as a desiccant will remove any excess water. The ylide hexane solution was Schlenk-filtered to remove alkali metal salts (LiI or KI) prior to addition to the $[W_2(OCH_2tBu)_8]$ suspension.) The solution became bright yellow upon formation of the ylide. The phosphorus ylide solution was then added by means of a cannula to a suspension of $[W_2(OCH_2tBu)_8]_n$ (100 mg, 9.39×10^{-2} mmol) in dry, degassed hexanes (10 mL) at 0 °C. The reaction was stirred at 0 °C for 3 h, then allowed to warm to 23 °C, and stirred at this temperature for a further 3 h. The solvent was then removed under dynamic vacuum. Recrystallization in dry, degassed diethyl ether at −20 °C gave dark purple crystals in 68 % yield. Crystallization from a concentrated toluene solution at −20 °C yielded X-ray quality crystals. ^1H NMR (300 MHz, $[D_8]$toluene, −80 °C): $\delta = 5.69$, 5.49, 4.03 doublets (2H per doublet); 5.11 (3H), 5.06 (1H), 3.16 (2H), 3.64 (AB quartet); 1.36 (9H), 1.22 (18H), 1.18 (18H), 0.71 (18H), 0.60 (9H); $^{13}C\{^1H\}$ NMR (75 MHz, $[D_8]$toluene, −80 °C): $\delta = 147.5$ [$^1J(^{183}W-^{13}C) =$ 77 Hz (25 %)], 35.5, 35.2, 35.1, 34.8, 33.9, 33.7 (2:2:1:2:1 for CH_2), 28.0, 27.3, 27.2, 26.4, 26.0 (1:2:2:1:2 for $C(CH_3)_3$); ^{13}C NMR (75 MHz, $[D_8]$toluene, −80 °C): $\delta = 147.5$ [triplet, $^1J(C-H) = 135$ Hz, $^1J(^{183}W-^{13}C) = 77$ Hz (25 %)]; anal. calcd for $C_{41}H_{90}O_8W_2$: C 45.65, H 8.41; found: C 45.87, H 8.80.

Crystallographic studies: A summary of the crystallographic data is given in Table 5. Listings of programs and the description of the equipment and handling procedures have been given previously.[31] Crystallographic data (excluding the structure factors) for $[W_2(OCH_2tBu)_8(\mu\text{-}C_2H_2)]$, $[W_2(OCH_2tBu)_8(\mu\text{-}C_3H_4)]$, $[W({=}CPh_2)(OEt)_3(OCH_2tBu)]_2$, and $W_2(OCH_2tBu)_8(\mu\text{-}CH_2)$ have been deposited with the Cambridge Crystallographic Data Base as supplementary publication no. CSD-59380 and CCDC-101191. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+ 44) 1223-336-033; e-mail: deposit§ccdc.cam.ac.uk). Full crystallographic data are also available from the Reciprocal Data Base at the Internet url http://www.iumsc.indiana.edu. Please request data files 95224 for $[W_2(OCH_2tBu)_8(\mu\text{-}C_2H_2)]$, 96022 for $[W_2(OCH_2tBu)_8(\mu\text{-}C_3H_4)]$, 95215 for $[W({=}CPh_2)(OEt)_3(OCH_2tBu)]_2$, and 97405 for $[W_2(OCH_2tBu)_8(\mu\text{-}CH_2)]$.

Table 5. Summary of crystal data

Compound	**1**	**3**	**6·2toluene**	**8**
empirical formula	$C_{42}H_{90}O_8W_2$	$C_{43}H_{92}O_8W_2$	$C_{48}H_{72}O_8W_2$; $2C_6H_5CH_3$	$C_{41}H_{90}O_8W_2$
color of crystal	dark red	amber	dark red	dark purple
space group	$P2_1/a$	$C2$	$P\bar{1}$	$\mathrm{P2_1/a}$
temperature [°C]	−172	−170	−172	−172
Z	4	4	1	4
molecular weight	1090.85	1104.88	1329.06	1078.84
$R(F)$	0.0651	0.0256	0.0408	0.0308
$Rw(F)$	0.0564	0.0248	0.0380	0.0331
a [Å]	18.836(4)	19.620(3)	12.408(4)	19.156(2)
b [Å]	11.518(2)	18.252(3)	13.295(4)	13.804(1)
c [Å]	23.620(5)	15.179(3)	9.453(3)	20.759(2)
α [°]			93.86(2)	
β [°]	99.87(1)	111.19(1)	94.34(2)	112.31(1)
γ [°]			69.91(1)	

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