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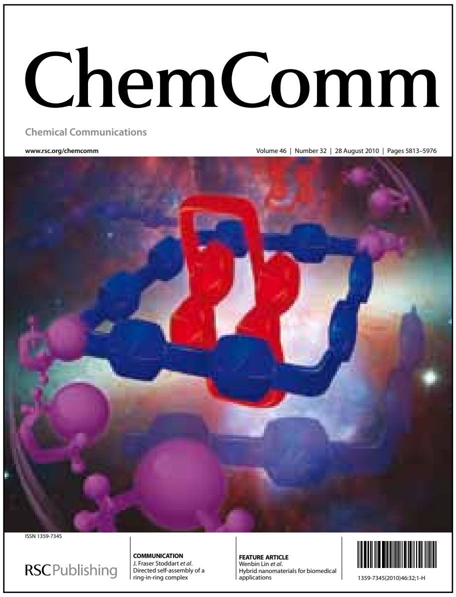

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Communication

Reactions of d^0 tungsten alkylidyne complexes with O_2 or H_2O. Formation of an oxo siloxy complex through unusual silyl migrations

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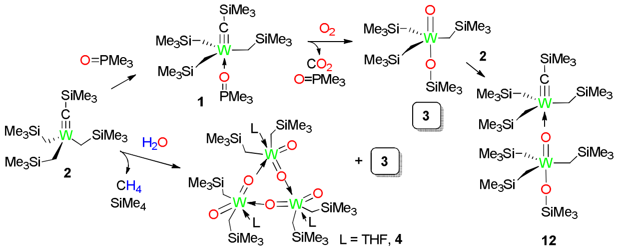
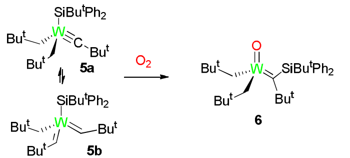
$(Me_3SiCH_2)_3(Me_3SiC\equiv)W\leftarrow O{=}PMe_3$ (1), an adduct between $(Me_3SiCH_2)_3W\equiv CSiMe_3$ (2) and $O{=}PMe_3$, reacts with O_2 to give $O{=}W(OSiMe_3)(CH_2SiMe_3)_3$ (3) and CO_2. Reaction of 2 with H_2O yields 3 and the trimer $[(\mu\text{-}O)W(CH_2SiMe_3)_2({=}O)(THF)]_3$ (4). In the reaction of D_2O with 2, 3-d_n and methane isotopologues CH_2D_2, CHD_3 and CD_4 have been observed.

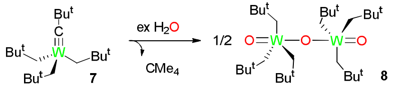
Early transition metal complexes are often sensitive to O_2 and H_2O.[1,2] Reactions of O_2 with d^0 complexes are often unique, leading to the oxidation of ligands.[1] In comparison, reactions of O_2 with d^n complexes usually involve the oxidation of metals. Earlier studies showed O insertion into the M-Si and M-C bonds of d^0 complexes in their reactions with O_2.[1c-k] The use of redox-active ligands in a Zr(IV) complex leads to the isolation of a bisperoxo complex.[1a] We have found that the reaction of O_2 with d^0 silyl alkylidyne **5a** and its bis-alkylidene tautomer **5b** leads to the formation of the oxo alkylidene compound **6** (Eq. 1).[1r] The nature of reactions between early transition metal complexes and H_2O has also been of intense interest.[2] The reaction of water with d^0 $(Bu^tCH_2)_3W\equiv CBu^t$ (**7**) was found to give CMe_4 and $O[W({=}O)(CH_2Bu^t)_3]_2$ (**8**, Eq. 2).[2f] We found earlier that $(Bu^tCH_2)_3W\equiv CSiMe_3$ (**9**) reacted with D_2O, through a rate-determination process, to give the oxo **10-d_4** which then selectively loses the CD_2SiMe_3 ligands, yielding the trimer **11** (Eq. 3). Reactions of d^0 complexes with O_2[3] or H_2O[4] have been used recently to make metal oxides as microelectronic insulating materials, leading to significant drops in leakage currents in transistors. We have found that the reaction of O_2 with d^0 **1** surprisingly yields the oxo siloxide **3** and CO_2 (Scheme 1). One $SiMe_3$ group in **1** undergoes an unusual migration to give the $OSiMe_3$ ligand in **3**.[5,6] Unexpectedly, **2**[7] reacts with H_2O to yield **3** as well. CH_4 is generated in the reaction. Another product is the trimer **4**, through O-H addition to the $W\equiv CSiMe_3$ bond and elimination of $SiMe_4$. When **2** reacts with D_2O, analysis by high-resolution mass spectrometry (HRMS) reveals the formation of the methane isotopologues CH_2D_2, CHD_3 and CD_4.



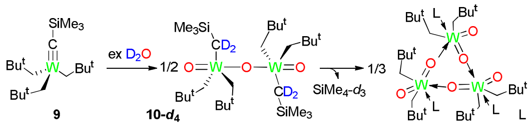
Scheme 1. Reactions of **2**. $SiMe_4$ was observed by NMR.



(Eq. 1)[1r]



(Eq. 2)[2f,g]



(Eq. 3)[2n]

L = D_2O, **11**

1 was prepared from **2** and $O{=}PMe_3$.[8] The ^{13}C NMR peak of 327.39 ppm for C≡W in the 14e **1** is up-field shifted from 343.67 ppm in 12e **2**. The W≡C bond length of 1.763(7) Å in **1** (Fig. 1) is slightly longer than 1.739(8) Å in $(Bu^tCD_2)_3W\equiv CSiMe_3$ (**9-d_6**).[9]

When **1** was exposed to O_2, it was found to convert to $O{=}W(OSiMe_3)(CH_2SiMe_3)_3$ (**3**).[8] A quantitative MS analysis of the gaseous products using $^{13}CO_2$ revealed the formation of CO_2, and the molar ratio of **3** : CO_2 is ca. 1.0 : 0.9 (Scheme 1).[8] In comparison, when **2** was exposed to O_2 in the absence of $O{=}PMe_3$, it decomposed to unknown species. Addition of **2** to the reaction mixture from **1** and O_2 and crystallization gave crystals of **12** as a 1:1 adduct between **3** and **2**.[8] The ^{29}Si NMR peak of $O\mathit{Si}Me_3$ at 10.74 ppm is downfield shifted from those of $C{\equiv}W\text{-}CH_2\mathit{Si}Me_3$ at –1.50 ppm, $O{=}W\text{-}CH_2\mathit{Si}Me_3$ at –2.97 ppm, and $\equiv C\mathit{Si}Me_3$ at –19.76 ppm in **12**.[8] The X-ray structure of **12** reveals a C_3 axis through the $C\equiv W\leftarrow O{=}W\text{-}O\text{-}Si$ bonds, giving thus a linear W(2)-O(2)-Si(4) linkage (Fig. 1). **3** and **2** are bonded through a $W{=}O\rightarrow W$ dative bond [2.578(6) Å]. The W≡C bond distance of 1.775(11) Å in **12** is longer than those in **9-d_6** [1.739(8) Å][9] and **1** [1.763(7) Å], perhaps as a result of trans influence by **2**. The W=O bond distance of 1.735(6) Å in **12** is similar to those in other W oxo complexes.[2f,5e,10]

The pathway in the formation of **3** from **1** is not clear. The alkylidyne carbon atom in **1** is the most electron-rich atom with a formal -4 charge. It is thus not surprising that the W≡C bond in **1** is attacked by O_2, an oxidant, yielding **A** in Scheme 2. Additional attack by O_2 and oxidation of the C atom give CO_2. The unusual silyl migration in **B** is perhaps driven by the oxophilicity of silicon.

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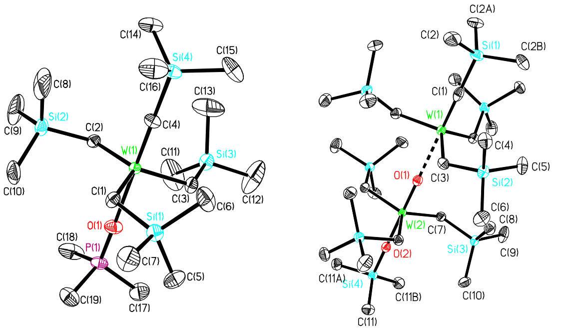
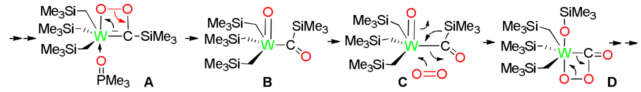


Fig. 1 Structures of **1** (Left) and **12** (Right). Bond lengths (Å) and angles (°): **1** C4-W1 1.763(7), O1-W1 2.307(7), C4-W1-O1 179.5(3), P1-O1-W1 178.5(5). **12** C1-W1 1.775(11), O1-W2 1.735(6), O2-W2 1.9246, O1→W1 2.578(6), O2-Si4 1.630(6), C1-W-C3 100.45(15), O1-W2-C7 92.33(14), O2-W2-C7 87.67(14).



Scheme 2. Part of the proposed pathway in the reaction of **1** with O_2.

The alkyl alkylidyne **2** reacts with water, yielding CH_4, $SiMe_4$, and two complexes (Scheme 1). One is trimer **4** which is similar to **11**[2n] in Eq. 3. The crystal structure of **4** is given in Fig. 2. It is surprising that $O=W(OSiMe_3)(CH_2SiMe_3)_3$ (**3**) was also isolated from the reaction (Scheme 1), indicating a $SiMe_3$ migration to a W=O ligand in the reaction. When the reaction was conducted at 23 °C, the molar ratio of **3** : **4** is 0.7 : 1. The yield of **3** is higher at -25 °C or below. When **2** reacted with H_2O at -78 °C, the ratio was 29 : 1. When powders of **2** were added H_2O in THF at -25 °C, the yield of **3** was also higher with **3** : **4** = 13 : 1.

MS analyses of the gaseous products using $^{13}CH_4$ as the calibration showed the formation of 0.62 equiv of CH_4 when **1** reacts with 2 equiv of H_2O.[8] Since the yield of **3** is ca. 66%, the ratio of CH_4 and **3** in the reaction mixture is ca. 1:1. A mechanism consistent with the observations is given in Path II in Scheme 3. The ≡C- atom in **2** is basic. Addition of H_2O to the W≡C bond in **2** leads to the formation of the hydroxyl alkylidene **E** and oxo **F**. The oxophilic $SiMe_3$ group in one of the CH_2SiMe_3 ligands in **F** then undergoes a migration to the oxo ligand in Path II, yielding the $OSiMe_3$ and a methylene ligand in **C**. Addition of a second H_2O molecule gives **3** and CH_4. **F** may also be attacked by H_2O through Path I, eliminating two molecules of $SiMe_4$ to give dioxo **4** containing two alkyl ligands. In other words, rates of two competing paths here lead to two different products. Perhaps in the reaction of **10-*d*$_4$** with D_2O (Eq. 3), attack by D_2O is fast, removing the CD_2SiMe_3 ligands before they undergo a migration.

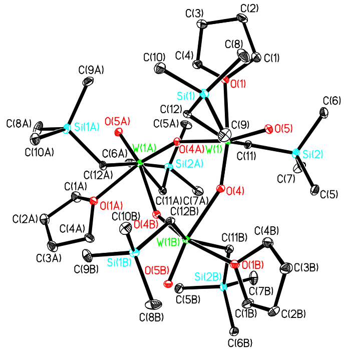
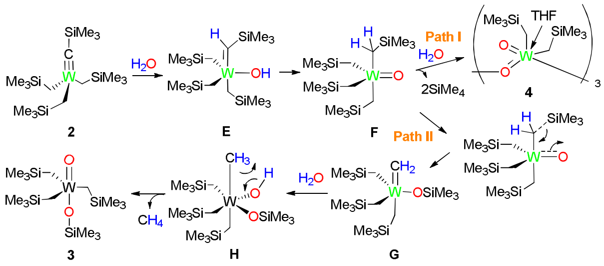


Fig. 2 Structure of **4**. Bond lengths (Å) and angles (°): W1-C11 2.167(4), W1-C12 2.159(4), W1-O1 2.363(3), W1-O4 1.758(3), W1B-O4 2.239(3), W1-O4A 2.239(3), W1-O5 1.711(3), O4-W1-O4A 89.0(2), O5-W1-O1 86.3(1), W1-O4-W1A 150.9(1), W1-C12-Si1 118.3(2).



Scheme 3

When **2** in THF-d_8 was added D_2O (99.9% D, ca. 5 equiv),[8,11] we were surprised to find that an HRMS analysis of the methane isotopologues gave the following ratios of CH_4 : CH_3D : CH_2D_2 : CHD_3 : CD_4 = 0 : 3 : 100 : 19 : 32(± 5)% (Fig. 3). CH_2D_2 and CHD_3 were unexpectedly major products in the reaction. ^2H NMR spectrum of the reaction of **2** with D_2O (Fig. S1) revealed the formation of $SiMe_{4}$-d_n and $O=W(OSiMe_3)(CH_{2-n}D_nSiMe_3)_3$ (**3-*d*$_n$**) containing partially deuterated ligands.[8] It should be noted, although the glassware was pre-dried (0.01 torr, >400 °C),[8,11] silanol groups apparently remained. They may exchange with D_2O, leading to a higher H/D ratio.[8] Thus, the above ratios of the methane isotopologues are analysed qualitatively below.

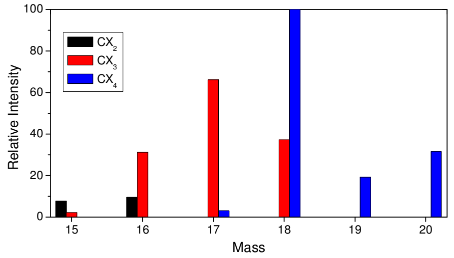
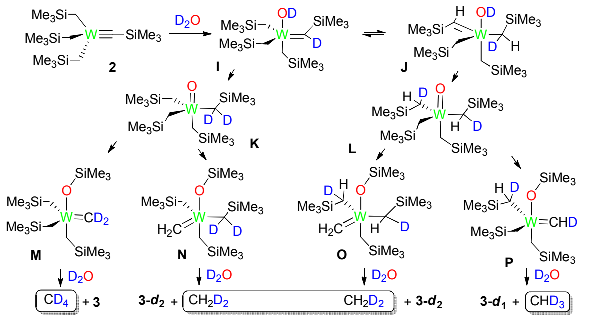


Fig. 3 The HRMS for the methane isotopologues in the 15-20 Dalton region. Isotopologues of methylene (CX_2), methyl (CX_3) and methane. (CX_4) are given in black, red, and blue colours, respectively.[8]



Scheme 4

The formation of CH_2D_2 and CHD_3 and observation of $O=W(OSiMe_3)(CH_{2-n}D_nSiMe_3)_3$ (**3-*d*$_n$**) are consistent with exchanges of the α-H atoms between $=CDSiMe_3$ and $–CH_2SiMe_3$ in **I** in Scheme 4 to yield **J** containing a W=CH– bond, after the D–OD addition to the W≡C– bond in **2**. Similar α-H migrations have been reported.[9,12] In addition to the α-H exchange, the migration of the second D atom in W-OD to the $W=CDSiMe_3$

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ligand affords the tetraalkyl W oxo intermediate **K**. In **J**, subsequent D migration from W-OD to W=CH- yields **L**. The $SiMe_3$ group in *one* of these alkyl ligands in **K** and **L** undergoes the C–Si bond cleavage and $SiMe_3$ migration to the oxo ligand to give **M/N** and **G/P**, respectively, containing a methylene ligand (W=CD_2– in **M**, W=CH_2– in **N/O**, or W=CHD– in **P**), which subsequently reacts with D_2O to yield the methane isotopologues. The presence of HOD in the D_2O-THF-d_8 may lead to the formation of 3(± 5)% CH_3D.[9,11]

It is interesting to note that the reactions of H_2O with $(Bu^tCH_2)_3W{\equiv}CBu^t$ (**7**, an analog of **2**, Eq. 2), and $(Bu^tCH_2)_2Mo(=CHBu^t)(=NBu^t)$ give **8**[2f] and $[\{Mo(=NBu^t)(CH_2Bu^t)_3\}_2(MoO_4)]$,[2g] respectively. The alkylidene intermediate $(Bu^tCH_2)_3W(=CDBu^t)(OD)$ in the reaction of **7** with D_2O does not undergo α-H migration.[2f] Reactions of H_2O/O_2 with d^4 $Cp^*M(NO)(CH_2SiMe_3)_2$ (M = Mo, W) afford $Cp^*M(=O)_2$-(CH_2SiMe_3),[2h] with no $SiMe_3$ migration to the oxo ligands.

The formation of the novel siloxide **3** demonstrates rich chemistry in the reactions of d^0 complexes with O_2 or H_2O. The reactions of **1** with O_2 and **2** with H_2O are of different nature: The former a redox reaction and the latter an acid-base reaction. Both, however, involve the alkylidyne carbon atoms and yield the same complex **3**. At the oxidation state of -4, the ≡C- atoms in **1** and **2** are electron rich. Two molecules of O_2, an oxidant, obtain a total of 8 electrons from the ≡C atom in **1**, oxidizing it to CO_2 and yielding **3**. When **2** is exposed to H_2O, the ≡C- atom in **2** acts as a base, abstracting a total of four H^+ ions from two H_2O molecules, yielding **3** and converting itself to CH_4. Oxophilicity of silicon and tungsten plays a critical role here, obtaining oxygen atoms and driving the formation of CO_2 and CH_4 in the reactions.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental section, aditional HDMS analysis, and cif files of X-ray crystal structures. See DOI: 10.1039/b000000x/

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