Oxo 2-Adamantylidene Complexes of Mo(VI) and W(VI)

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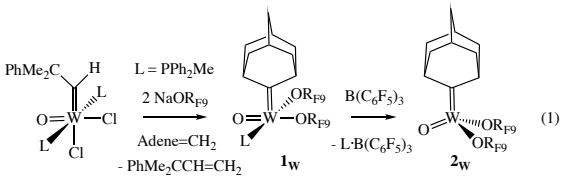
ABSTRACT: Molybdenum and tungsten oxo 2-adamantylidene (Adene) complexes have been prepared that contain two hexafluoro-*t*-butoxide (OR_{F9}) ligands through addition of 2-methylene or 2-ethylidene adamantane to neophylidene or neopentylidene complexes. The isolated oxo complexes include W(O)(Adene)(OR_{F9})$_2$(PPh_2Me) (**1**$_W$), W(O)(Adene)(OR_{F9})$_2$ (**2**$_W$), W(O)(Adene)(2,5-dimethylpyrolide)$_2$ (**3**$_W$), W(O)(Adene)(2,5-dimethylpyrolide)(2,6-dimesitylphenoxide) (**4**$_W$) Mo(O)(Adene)(OR_{F9})$_2$($PPhMe_2$) (**1**$_{Mo}$), and Mo(O)(Adene)(OR_{F9})$_2$ (**2**$_{Mo}$). Compound **2**$_W$ is a dimer that contains unsymmetrically bridging oxo ligands; it dissociates readily and reversibly into monomers especially in the presence of a donor such as THF. In contrast, **2**$_{Mo}$ is a monomer. Both **2**$_W$ and **2**$_{Mo}$ are remarkably stable thermally. The pale blue complexes, Mo(Adene)(OR_{F9})$_2$$Cl_2$ (**5**$_{Mo}$) and W(Adene)(OR_{F9})$_2$$Cl_2$ (**5**$_W$), are formed upon addition of PCl_5 to **2**$_{Mo}$ and **2**$_W$, respectively. The oxo complexes are reactive olefin metathesis initiators, while **5**$_{Mo}$ and **5**$_W$ are *relatively* inactive. We ascribe the thermal stability of **2**$_{Mo}$ and **2**$_W$ to a resistance of 2-admantylidene ligands to couple bimolecularly, and/or to the absence of an α hydrogen in the alkylidene.

Four-coordinate molybdenum(VI) and tungsten(VI) imido alkylidene complexes have been synthesized in large variety and used as initiators for olefin metathesis reactions of interest to organic,[1] polymer,[2] and surface organometallic chemists.[3] The alkylidene in these initiators is virtually always neopentylidene or neophylidene, as the alkylidene is formed through α hydrogen abstraction, although other M=CHR complexes generally can be prepared through addition of CH_2=CHR to them.[4] Oxo alkylidene complexes of W and Mo, especially the latter, are relative newcomers on the scene of well-characterized homogeneous olefin metathesis complexes.[5] Oxos are thought to be the type of catalyst present on silica surfaces in classical metathesis catalysts.[3] We have become interested in the chemistry of disubstituted alkylidenes recently, especially 2-adamantylidene complexes.[6] The 2-adamantylidene (Adene) group has characteristics that may allow new chemistry to be accessed, two being a possible greater resistance to bimolecular coupling than a neopentylidene or neophylidene and secondly, no possibility of forming alkylidyne complexes. We combined our interest in oxo and 2-adamantylidene complexes here with syntheses of oxo 2-adamantylidene (Adene) complexes of tungsten and molybdenum.

Addition of 2 equiv of $NaOR_{F9}$ (OR_{F9} = $OC(CF_3)_3$) to W(O)($CHCMe_2Ph$)Cl_2(PPh_2Me)$_2$[5b] in toluene followed by 6 equiv of 2-methyleneadamantane followed by heating to 80 °C yields five-coordinate 16e W(O)(Adene)(OR_{F9})$_2$(PPh_2Me) (**1**$_W$) as a yellow crystalline solid in 70% yield (eq 1). An X-ray study showed **1**$_W$ to be essentially a square pyramid (τ = xx) with an apical 2-adamantylidene (Adene) ligand and *cis* OR_{F9} ligands (Figure 1). Distances and angles are not unusual. The difference in the W=C-C angles in the 2-adamantylidene ligand is 14.7°, which is typical of Mo(VI) 16e Ad complexes.[6]



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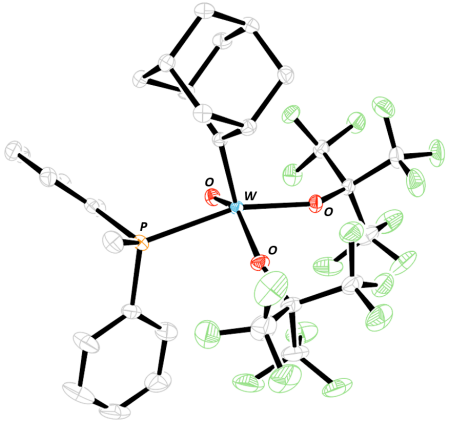


Figure 1. The structure of **1**$_W$ with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

W(O)(Adene)(OR_{F9})$_2$(PPh_2Me) was dissolved in benzene and one equivalent of $B(C_6F_5)_3$ was added. After 30 minutes W(O)(Adene)(OR_{F9})$_2$ (**2**$_W$) began to precipitate as a dark orange solid; it was isolated as an orange powder in 85% yield. Compound **2**$_W$ is poorly soluble in benzene or toluene, but dissolves readily in THF. When THF is removed all THF is ultimately lost and **2**$_W$ reforms.

A sample of $\mathbf{2_W}$ was placed in benzene that contained 1% THF in a J. Young NMR tube and the mixture was heated to 140 °C until all $\mathbf{2_W}$ dissolved; no decomposition was observed. Upon standing the solution at room temperature for two days X-ray quality orange crystals of $\mathbf{2_W}$ were harvested. A structural study showed $\mathbf{2_W}$ to be dimer with the arrangement around each metal being approximately a square pyramid (Fig 2) with an apical adamantylidene ligand. The unsymmetrically bridging oxo ligands (W-O = 1.778 and 2.168 Å) suggests that each oxo is triply bound to one W and a donor to the other in a basal position. The W-O-W angle is 103.05°. The adamantylidene ligand is slightly disordered but W=C can be measured (1.896(2) Å). The compound exhibits a *quasi* square pyramidal structure (τ = 0.03). The structure and monomer/dimer behavior of $\mathbf{2_W}$ are similar to that of (*R*,*S*)-[W(μ-O)(CHCMe$_2$Ph)(Biphenolate)]$_2$.[7]

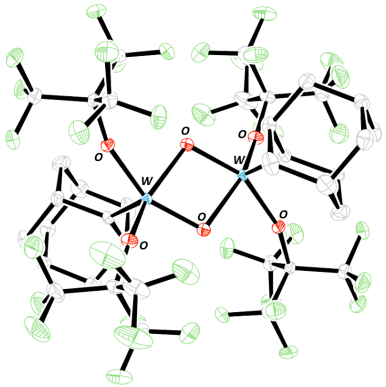


Figure 2. The structure of $\mathbf{2_W}$with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

The reaction between $\mathbf{2_W}$ and 3 equiv of LiMe$_2$Pyr (Me$_2$Pyr = 2,5-dimethylpyrrolide) in benzene at 80 °C proceeds smoothly to give a deep red solution of W(O)(Adene)(Me$_2$Pyr)$_2$ ($\mathbf{3_W}$) and a precipitate of LiOR$_{F9}$. Compound $\mathbf{3_W}$ could be isolated from the red solution in >95% yield. An X-ray structural study (Figure 3) showed it to have a pseudotetrahedral 14e structure with two η^1-Me$_2$Pyr ligands instead of one η^1-Me$_2$Pyr pyrrolide and one η^5-Me$_2$Pyr pyrrolide, which is usually observed in a complex of this type.[8] The two adamantylidene β proton resonances at x and y ppm are characteristic of an adamantylidene ligand that is not rotating about the M=C bond readily on the NMR time scale and what is found for all compounds reported here.

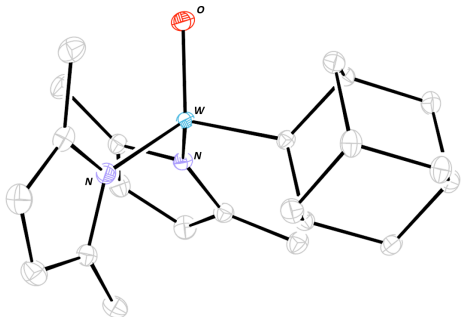


Figure 3. The structure of $\mathbf{3_W}$ with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

Addition of HMTOH (2,6-dimesitylphenol) to $\mathbf{3_W}$ gave W(O)(Adene)(Me$_2$Pyr)(OHMT) ($\mathbf{4_W}$) and 2,5-dimethylpyrrole. An X-ray study of $\mathbf{4_W}$ (Figure 4) shows that the pyrrolide is bound in an η^1 manner, as found for other tungsten 14e MAP complexes that contain a relatively bulky phenoxide ligand.[9]

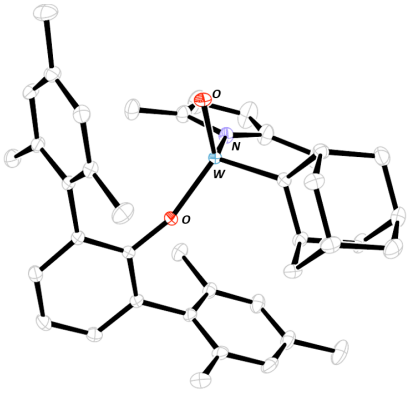
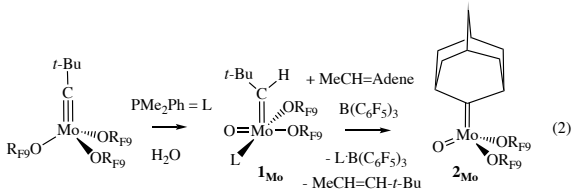


Figure 4. The structure of $\mathbf{4_W}$ with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

The only practical route to metathesis-active molybdenum oxo alkylidene complexes at this point is the addition of water to alkylidyne complexes.[8f] The rapid addition of one equivalent of water to a 1:1 mixture of Mo(C-*t*-Bu)(OR$_{F9}$)$_3$ and PMe$_2$Ph in THF yielded Mo(O)(CH-*t*-Bu)(OR$_{F9}$)$_2$(PMe$_2$Ph) ($\mathbf{1_{Mo}}$) in 61% yield (eq 2). All NMR data suggest that the structure of $\mathbf{1_{Mo}}$ is analogous to that of $\mathbf{1_W}$ (Fig 1). Addition of B(C$_6$F$_5$)$_3$ to a mixture of $\mathbf{1_{Mo}}$ and 2-ethylideneadamantane yielded Mo(O)(Adene)(OR$_{F9}$)$_2$ ($\mathbf{2_{Mo}}$) which was isolated in 50% yield through careful fractional crystallization to separate it from PMe$_2$Ph·B(C$_6$F$_5$)$_3$. Compound $\mathbf{2_{Mo}}$ is highly soluble in pentane, benzene, toluene, and dichloromethane, in sharp contrast to $\mathbf{2_W}$.



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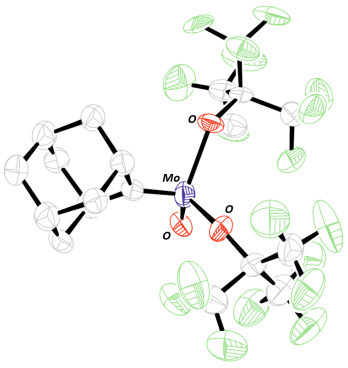
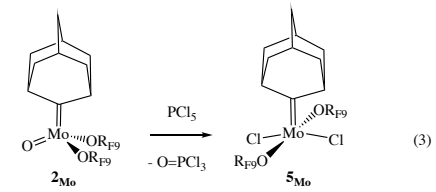


Figure 5. The structure of $\mathbf{2_{Mo}}$ with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

An X-ray study (Figure 5) shows that $\mathbf{2_{Mo}}$ is a monomer, but whole-molecule disorder (see SI) precludes a discussion of precise bond distances and angles. The alkylidene α carbon NMR resonance is found at 343.9 ppm (C_6D_6). Compound $\mathbf{2_{Mo}}$ (like $\mathbf{2_W}$) is remarkably stable thermally, with no decomposition being observed in a solution of it in C_6D_6 heated at 80 °C over a period of 24 h. We ascribe the dimeric form of $\mathbf{2_W}$, versus the monomeric form of $\mathbf{2_{Mo}}$, to the periodic stronger metal-ligand bonds for W compounds compared to Mo compounds.[10]

Addition of $B(C_6F_5)_3$ to Mo(O)(CH-*t*-Bu)$(OR_{F9})_2$(PMe_2Ph) in C_6D_6 at 22 °C gave $PMe_2Ph{\cdot}B(C_6F_5)_3$ (according to NMR spectra) and a solution that we propose contains Mo(O)(CH-*t*-Bu)$(OR_{F9})_2$, the neopentylidene analog of $\mathbf{2_{Mo}}$, on the basis of a neopentylidene α proton resonance 13.42 ppm and alkylidene α carbon resonance at 321.0 ppm. The mixture of $PMe_2Ph{\cdot}B(C_6F_5)_3$ and Mo(O)(CH-*t*-Bu)$(OR_{F9})_2$ decomposes over a period of several hours, *possibly* due to the thermal instability of Mo(O)(CH-*t*-Bu)$(OR_{F9})_2$, in contrast to the thermal stability of isolated $\mathbf{2_{Mo}}$ and $\mathbf{2_W}$.

The apparent robust nature of the 2-adamantylidene ligand raised the question as to whether the oxo ligand could be replaced by two chlorides, a type of reaction that was observed almost 40 years ago by Osborn in an exploration of W and Mo oxo neopentyl complexes in the presence of $AlCl_3$.[11] The reaction between $\mathbf{2_{Mo}}$ and PCl_5 in DCM (10 mL) after 30 minutes at room temperature gave a pale blue solution from which Mo(Adene)$(OR_{F9})_2Cl_2$ ($\mathbf{5_{Mo}}$) was isolated as a pale blue solid in 89% yield.



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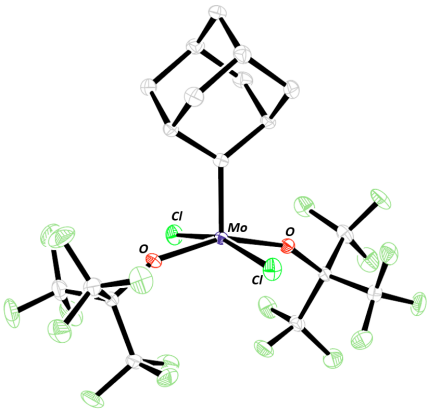

Figure 6. The structure of Mo(Adene)$(OR_{F9})_2Cl_2$ ($\mathbf{5_{Mo}}$) with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

An X-ray study (Figure 6) revealed that the structure of $\mathbf{5_{Mo}}$ is close to a square pyramid ($\tau^{12} = 0.12$) with the adamantylidene ligand in the apical position. The dihedral angle (C2–C1–Mo1–O1) is 4.0°, *i.e.*, the C6-C1-C2 plane is close to being oriented along the O2-Mo2-O1 axis. The carbene carbon NMR resonance appears at 355.5 ppm (CD_2Cl_2). The two Mo-C_α-C_β angles are essentially identical (123.82(7) and 122.68(7)), which precludes any significant agostic C-H_β interaction similar to that found in imido adamantylidene complexes that contain <18e. The pale blue tungsten analog ($\mathbf{5_W}$) is prepared in a similar reaction between $\mathbf{2_W}$ and PCl_5 and in a similar yield; $\mathbf{5_W}$ is essentially isostructural with $\mathbf{5_{Mo}}$ (see SI). Compound $\mathbf{5_W}$ is analogous to W(cyclopentylidene)$Br_2(OCH_2CMe_3)_2$ prepared by Osborn[13] and rare analogous tungsten complexes prepared through addition of HCl to alkylidynes.[14] As far as we know $\mathbf{5_{Mo}}$ is the first Mo alkylidene complex of this general type. W(cyclopentylidene)$Br_2(OCH_2CMe_3)_2$ was found by Osborn[11,13] to be relatively inactive as a metathesis initiator in the absence of a Lewis acid.

Preliminary studies of the polymerization of 5,6-dicarbomethoxynorbornadiene by $\mathbf{4_W}$ (2% in $CDCl_3$) shows that polymerization is complete in 10 minutes to give >99% *cis,syn-diotactic*-polyDCMNBD, as found for other MAP initiators,[2] and characteristic of polymerization by the monomeric form of $\mathbf{4_W}$. The homocoupling of neat 1-decene catalyzed by 1% $\mathbf{4_W}$ was 99% complete in 24 h (89% in 5 h) to give 99% *Z*-octadecene. In contrast, polymerization of DCMNBD by $\mathbf{5_W}$ in $CDCl_3$ was only 13% complete in 24 h, while polymerization of DCMNBD by $\mathbf{5_{Mo}}$ was 90% complete in 24 h to give a mixture of *cis* and *trans*-polyDCMNBD.

We conclude that 14e Mo and W oxo 2-adamantylidene complexes are thermally relatively robust, yet reactive, as initiators in olefin metathesis reactions. Lack of an α hydrogen along with a resistance of the 2-adamantylidene to intermolecular homocoupling, are plausible explanations for the apparent robustness of 2-adamantylidene complexes compared to M=CHR complexes. The oxo ligand can be removed to yield otherwise not readily accessible "oxo-free" adamantylidene complexes. We look forward to further exploration of these and other issues surrounding disubstituted high oxidation state alkylidene complexes.

ASSOCIATED CONTENT

Syntheses of compounds, NMR spectra and chemical shift data, and details of X-ray studies.

Accession Codes

CCDC 2055615-2055621 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

MB and FZ contributed equally to the synthetic studies. MB performed all W work, FZ performed all Mo work, and CT performed all X-ray studies.

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Notes

The authors declare no competing financial interest.

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