Hydrolysis of $(\eta^5\text{-}C_5Me_5)MMe_4$ (M = Mo, W) and the Formation of Organometallic Oxides with μ_3-CH Methylidyne and μ-CH_2 Methylidene Groups: Model Compounds for Catalysis on Metal Oxide Surfaces[†]

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The hydrolysis of $(\eta^5\text{-}C_5Me_5)WMe_4$ leads to the formation of the two compounds $(\eta^5\text{-}C_5Me_5)_2W_2O_2(\mu\text{-}CH_2)_2$ (**6**) and $(\eta^5\text{-}C_5Me_5)_2W_2O_2(\mu\text{-}CH_2)(\mu\text{-}O)$ (**9**), containing both methylidene and oxo moieties in one molecule. Reaction of $(\eta^5\text{-}C_5Me_5)MoMe_4$ with water leads to the trinuclear cluster $(\eta^5\text{-}C_5Me_5)_3Mo_3(\mu\text{-}O)_2(\mu\text{-}CH_2)(\mu_3\text{-}CH)$ (**10**) with oxo, methylidene, and methylidyne groups. Compounds **6**, **9**, and **10** were characterized by single-crystal X-ray structural analysis. **6**, **9**, and **10** can be considered as model compounds for catalysis on metal oxide surfaces.

Introduction

Metal oxides are used in a variety of important catalytic industrial processes.[1] One of the key steps in the discussion of the mechanisms of catalytic reactions in Fischer−Tropsch synthesis is considered to be the formation of bridging methylidene and methylidyne species on the metal oxide surface during the catalysis.[1b,c,2] On the other hand, transition-metal oxo methylidene and methylidyne compounds are thought to be intermediates in many important homogeneous catalytic processes. The presence of an oxo ligand is shown to be favorable for tungsten compounds in catalytic reactions and may be generated by the addition of an alcohol, by traces of oxygen, or by use of $WOCl_4$ instead of WCl_6 in the metathetical polymerization of olefins.[2a,3] The direct use of discrete metal oxo substituted methylidene complexes or their imido analogues as highly active metathesis catalysts demonstrates the important role of an oxo group in the formation of metallacyclic intermediates.[4] Moreover, anchoring an organometallic compound on solid surfaces such as oxides and zeolites gives the chance to obtain well-defined surface species highly active in catalysis. These are regarded as intermediates involved in homogeneous and heterogeneous catalytic processes.[2a,5] Therefore, the chemistry of organometallic oxides, containing both organic and oxo groups, is of great interest to chemists due to their model character for studying the mechanisms and the kinetics of reactions on oxide surfaces. Correlations between model systems and industrial catalysts can help to improve the catalyst performance as well as to find out new alternative catalysts for developing new processes.

The first CH_2-bridged organometallic complex, $(\eta^5\text{-}C_5H_5)_2Mn_2(CO)_4(\mu\text{-}CH_2)$, was reported by Herrmann et al. in 1975 and was prepared by treating $(\eta^5\text{-}C_5H_5)Mn(CO)_2THF$ with diazomethane.[6] The chemistry of methylidene-bridged compounds was reviewed.[7] The chemistry of μ_3-CR (R = Me, Et, Ph) tritungsten clusters, supported by alkoxide ligands, was explored by Chisholm et al., starting from $W_3(\mu_3\text{-}CMe)(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$ prepared by the reaction of $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ with 2-bu-

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[†] Dedicated to Professor Jürgen Wolfrum on the occasion of his 60th birthday.

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tyne.[8] The corresponding μ-CHR (R = *c*-C_3H_5, Ar) ditungsten compounds, bridged via alkoxide ligands, were obtained by the reductive coupling of aldehydes and ketones with ditungsten hexaalkoxides.[9]

Herein we describe the preparation and crystallographic studies of the first examples of methylidene- and methylidyne-bridged pentamethylcyclopentadienyl molybdenum and tungsten clusters, containing as bridging or terminal ligands only oxygen atoms. The compound $(\eta^5\text{-}C_5Me_5)_3Mo_3(\mu\text{-}O)_2(\mu\text{-}CH_2)(\mu_3\text{-}CH)$ is the first structurally characterized molybdenum cluster containing both μ-CH_2 and μ_3-CH moieties, whereas the compound $(\eta^5\text{-}C_5Me_5)_2W_2(O)_2(\mu\text{-}CH_2)_2$ is the first example of a dimeric oxo methylidene derivative with two μ-CH_2 groups.

Results and Discussion

In previous work we found that the reaction of $(\eta^5\text{-}C_5Me_5)TaMe_4$ with the kinetically stable silanetriol (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)Si$(OH)_3$ (**1**) leads to the formation of a compound with a $Ta_2O_6Si_2$ cage framework, which we considered to be a possible molecular model for an organometallic tantalum compound supported on a silica surface.[10] Due to our broad interest in the chemistry of transition-metal and main-group-metal siloxane complexes, we decided to explore the reactivity of group 6 metal alkyl compounds toward the silanetriol **1** in order to study the possibility of the formation of analogous cages.

Reaction of $(\eta^5\text{-}C_5Me_5)WMe_4$ with Silanetriol 1. In contrast to the previously observed reaction of the tantalum tetramethyl complex with the silanetriol **1**, no reaction was found in the case of its paramagnetic tungsten analogue under the same conditions at room temperature. However, when the temperature of the reaction mixture was increased to 120 °C, methane evolution was observed, and the solution turned from yellow to green. Analysis of the reaction products (which we were not able to separate) by NMR and mass spectroscopy indicated a mixture of diamagnetic products and the formation of $[RSi(OH)_2]_2O$ (**3**; R = (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)). Moreover, from the solution of the crude material in THF/hexane we were able to grow deep green crystals of $(\eta^5\text{-}C_5Me_5)_2W_2O_2(\mu\text{-}CH_2)_2$ (**6**) suitable for X-ray crystallographic analyses.

X-ray Crystal Structure of $(\eta^5\text{-}C_5Me_5)_2W_2O_2(\mu\text{-}CH_2)_2$ (6). The crystal structure of compound **6** is shown in Figure 1; selected bond lengths and angles are listed in Table 1. To the best of our knowledge **6** represents the first example of a tungsten(V) dimeric oxo methylidene derivative. The molecular structure of **6** is centrosymmetric with a planar four-membered W_2-$(CH_2)_2$ ring and tungsten atoms in a distorted-tetrahedral environment. The two C_5Me_5 rings and the oxo ligands are arranged *trans* to each other.

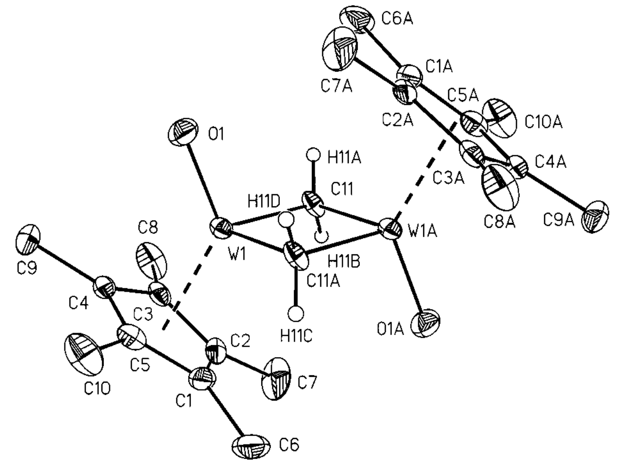

Figure 1. Molecular structure of $(\eta^5\text{-}C_5Me_5)_2W_2O_2(\mu\text{-}CH_2)_2$ (**6**) in the solid state (50% thermal ellipsoids). Hydrogen atoms of the methyl groups are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $(\eta^5\text{-}C_5Me_5)_2W_2O_2(\mu\text{-}CH_2)_2$ (6)

W1−C11	2.076(4)	W1−W1A	2.7879(5)
W1−C11A	2.078(4)	W1−O1	1.716(3)
C11−W1−C11A	95.69(14)	O1−W1−C11	103.00(17)
W1−C11−W1A	84.31(14)	O1−W1−C11A	102.69(17)
		O1−W1−W1A	109.34(11)

A comparison of the W−C(bridged) distances of **6** (average 2.07 Å) with those found for tungsten alkylidene ($[W(CO)_5]_2(\mu\text{-}CHPh)$,[11] 2.28 Å; $W_2(O)(\mu\text{-}CH\text{-}c\text{-}C_3H_5)(\mu\text{-}OCH_2CMe_3)_2(OCH_2CMe_3)_4(py)$,[9b] 2.16 Å) and alkylidyne bridging compounds ($[(\eta^5\text{-}C_5Me_5)W(\mu\text{-}CMe)Me]_2$,[12] 1.96 Å; $W_3(\mu\text{-}CMe)(O\text{-}i\text{-}Pr)_9(CO)_2$,[13] 1.97 Å) and monomeric $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$[14] (1.942(9) Å) allows us to conclude that the tungsten−carbon bond in **6** has alkylidene character. The W1−C11−W1A angle (84.31(14)°) is comparable to that found for $[(\eta^5\text{-}C_5Me_5)W(\mu\text{-}CMe)Me]_2$[12] (83.3(5)°) but larger than in $W_2(O)(\mu\text{-}CH\text{-}c\text{-}C_3H_5)(\mu\text{-}OCH_2CMe_3)_2(OCH_2CMe_3)_4(py)$[9b] (75.8(2)°).

Discussion of a Possible Mechanism for the Formation of 6. In our previous work[10] it was shown that the first step of the reaction between the tantalum tetramethyl complex and silanetriol **1** includes the dehydroxylation with the formation of the oxo-bridged compound **2** (Scheme 1). Taking into account that metal−oxygen double bond formation becomes preferable for group 6 metals rather than oxygen-bridged dimeric species, we suggest that the monomeric tungsten(V) oxo dimethyl compound **4** is formed in the first step of the reaction between $(\eta^5\text{-}C_5Me_5)WMe_4$ and silanetriol **1**.

Few examples of group 6 oxo alkyl compounds in their higher formal oxidation state were reported. However, in contrast to the reactivity of the tungsten(VI) oxo (trimethylsilyl)methyl complex $(\eta^5\text{-}C_5Me_5)W(O)(CH_2SiMe_3)_3$, which decomposes at 50 °C in 48 h to yield

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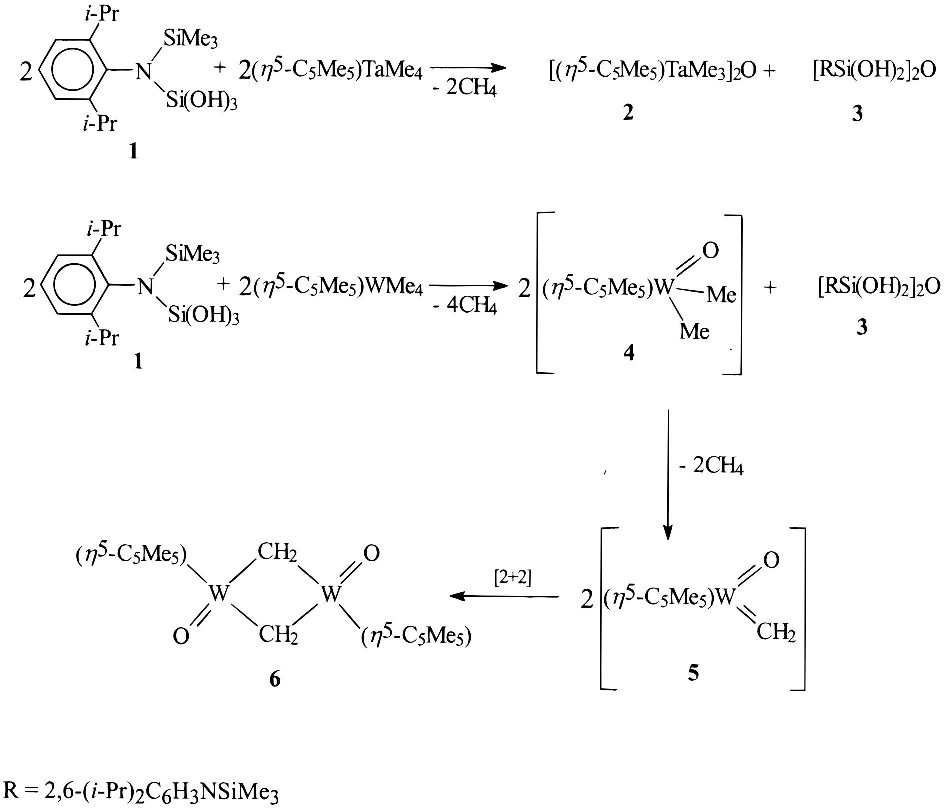
Scheme 1[a]



[a] Compounds in brackets (**4**, **5**) have not been isolated.

monomeric alkylidene species,[15] heat or radiation has no effect on the conversion of $(\eta^5\text{-}C_5Me_5)W(O)Me_3$ to $(\eta^5\text{-}C_5Me_5)W(O)({=}CH_2)Me$.[16] The only oxo alkyl compound of group 6 in the formal oxidation state (+5) is the crystallographically characterized chromium oxo dimethyl complex $(\eta^5\text{-}C_5Me_5)Cr(O)Me_2$.[17] However, no stability data for this compound were reported.

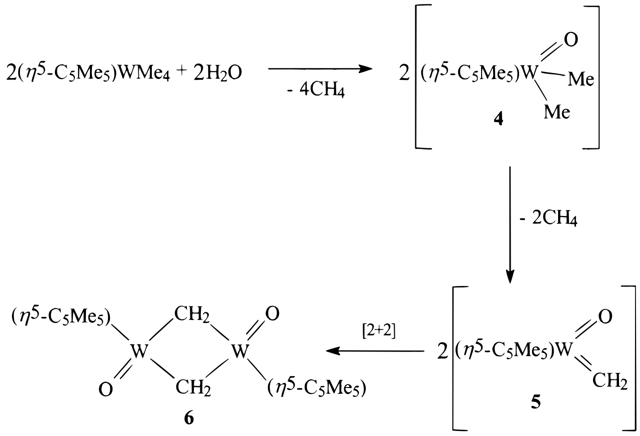
Therefore, taking into account the unexplored chemistry of group 6 metal oxo alkyl compounds, we suggest that compound **4** is an intermediate and appears to be unstable under the reaction conditions (mesitylene, 120 °C) and decomposes via α-hydrogen elimination with formation of the monomeric methylidene species **5**. Dimerization of the latter via methylidene bridges gives compound **6**.

Obviously the silanetriol functions in this reaction only as a water-transferring reagent, and therefore, we explored the hydrolysis of $(\eta^5\text{-}C_5Me_5)WMe_4$ in detail.

Studies on the Hydrolysis of $(\eta^5\text{-}C_5Me_5)WMe_4$. Surprisingly, no information was found about the reactivity of water toward the corresponding alkyl complexes of tungsten. Schrock et al. reported that $(\eta^5\text{-}C_5Me_5)WMe_4$ is thermally stable and not especially sensitive to air in the solid state.[12] Consequently, we decided to explore its reactivity toward water under various conditions.

In analogy to the phenomenon previously observed with the silanol **1**, no reaction occurred at room temperature when treating a solution of $(\eta^5\text{-}C_5Me_5)WMe_4$ with an equivalent amount of water at room temperature in toluene or 1,4-dioxane as solvent. $(\eta^5\text{-}C_5Me_5)WMe_4$ was isolated unchanged even after stirring the reaction mixture for 1 week. However, when the reaction temperature was raised (65−70 °C), methane evolution occurred, and a green solid was isolated from the reaction mixture. The signals for organometallic moieties in the ^{1}H NMR spectra of the crude product were found to be identical with those of the previous reaction with a silanetriol. X-ray crystallographic studies of **6** are in accordance with previous experiments (Scheme 2).

Scheme 2[a]



[a] Intermediates **4** and **5** have not been isolated.

All attempts to isolate reaction intermediates failed. Carrying out the reaction in the presence of phosphines

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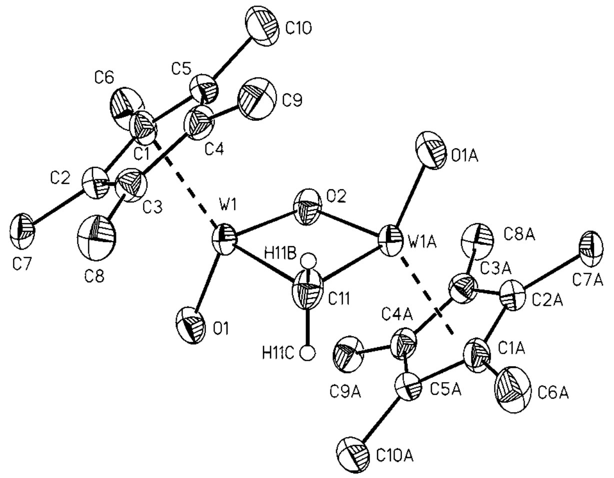


Figure 2. Molecular structure of $(\eta^5\text{-}C_5Me_5)_2W_2O_2(\mu\text{-}CH_2)(\mu\text{-}O)$ (**9**) in the solid state (50% thermal ellipsoids). Hydrogen atoms of the methyl groups are omitted for clarity.

had no influence on the reaction products. Parallel studies on the thermal stability of $(\eta^5\text{-}C_5Me_5)WMe_4$ in dry toluene showed no formation of decomposition products. This observation excludes the possible decomposition of $(\eta^5\text{-}C_5Me_5)WMe_4$ prior to the reaction with water.

Spectroscopic Studies. The ^1H NMR spectrum of the product obtained from the hydrolysis of $(\eta^5\text{-}C_5Me_5)WMe_4$ showed signals at 2.01 and 4.23 ppm (integration 15:2), which are assigned to the protons of the methyl groups of the cyclopentadienyl rings and the methylidene protons of compound **6**. Additionally, signals at 2.05 and 5.39 ppm (integration 15:1) were found. The signal at 2.05 can be clearly assigned to the protons of the C_5Me_5 ligand, while the signal at 5.39 ppm belongs to the protons of the CH_2 group. ^{13}C NMR showed two resonances for methylidene carbons (85.11 ppm, $J(WC) = 106.78$ Hz; 95.85 ppm, $J(WC) = 118.75$ Hz) with characteristic tungsten satellites. Therefore, we suggest the formation of compound **9**, isostructural to **6**, with only one bridging methylidene group between two magnetically equivalent tungsten atoms. The ^{13}C NMR DEPT experiment proved the alkylidene character of the CH_2 groups for **6** and **9**.

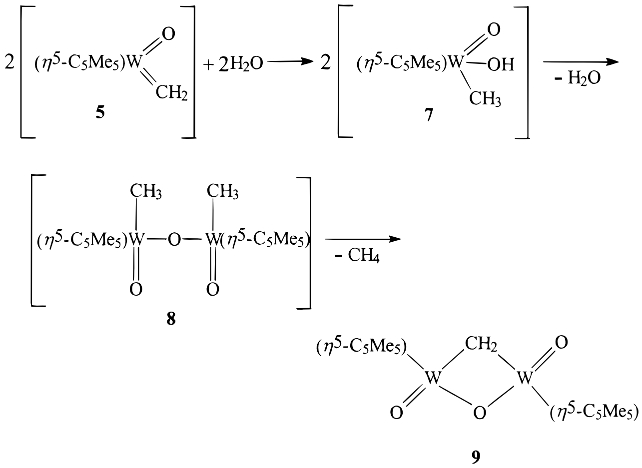
In addition, we found that the hydrolysis of $(\eta^5\text{-}C_5Me_5)WMe_4$ with an excess of water resulted in the formation of **9** in higher yields than that of **6**, respectively. Moreover, it was possible to separate the mixture of compounds by column chromatography under inert conditions using silylated silica. Recrystallization of the crude product by slow evaporation of the THF/acetonitrile solvent at room temperature yielded green crystals of **9**. Compound **9** was characterized by a single-crystal X-ray study.

X-ray Study of $(\eta^5\text{-}C_5Me_5)_2W_2O_2(\mu\text{-}CH_2)(\mu\text{-}O)$ (9). The crystal structure of compound **9** is presented in Figure 2; selected bond lengths and angles are given in Table 2. To the best of our knowledge, **9** represents the first example of a dimeric tungsten(V) oxo methylidene compound containing an O═W−O−W═O unit and a bridging alkylidene group. Molecule **9** has a planar four-membered W_2OCH_2 ring with the tungsten atoms in distorted-tetrahedral environments. The two C_5Me_5 rings and the exocyclic oxo ligands are arranged *trans* to each other.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(\eta^5\text{-}C_5Me_5)_2W_2O_2(\mu\text{-}CH_2)(\mu\text{-}O)$ (9)

W1−O1	1.723(3)	W1−C11	2.094(19)
W1−O2	1.987(11)	W1A−C11	2.089(19)
W1A−O2	1.979(11)	W1−W1A	2.7279(15)
C11−W1−O2	95.6(7)	O1−W1−O2	102.1(7)
W1−O2−W1A	86.9(4)	O1−W1−C11	100.7(14)
W1−C11−W1A	81.4(6)		

Scheme 3[a]



[a] Compounds **5**, **7**, and **8** have not been observed (brackets).

Refinement of the X-ray data for compound **9** shows one bridging oxygen atom and one bridging CH_2 group disordered in mutual positions. When for the refinement only bridging oxygen or only bridging CH_2 groups were used, unreasonable thermal ellipsoids were obtained. Support for the correct formulation of **9** is given by NMR, mass, and IR spectroscopic investigations and elemental analytical data.

The bond lengths and angles for **9** are comparable with those found for **6**. The W−W distance (2.7279(15) Å) is shorter than that of **6**. The W1−O(bridged)−W1A angle (86.9(4)°) is smaller than those found for the oxo-bridged $[CpWO(\mu\text{-}O)(C_3F_7)]_2$[18] (105.4(7)°) or alkoxide bridged $[(t\text{-}BuO)_3W{\equiv}CMe]_2$[19] (104.9(2)°) and comparable to those of the alkylidyne alkoxide bridged compound $W_3(\mu\text{-}CMe)(O\text{-}i\text{-}Pr)_9(CO)_2$ (83.0(6)°).[13]

Discussion of the Possible Mechanism for the Formation of 9. We assume that the possible mechanism for the formation of **7** is similar to the proposed one by Schrock et al. for the formation of the compound containing a O═W−O−W═O unit by hydrolysis of $W(CCMe_3)(CH_2CMe_3)_3$[20] (Scheme 3). Addition of a water molecule to the intermediate **5** followed by condensation of the resulting compound **7** (via oxo bridge) and decomposition by CH activation gives compound **9**.

Studying the yield of compound **9** by NMR spectroscopy shows that its amount increases with an increasing amount of water in the reaction mixture. The ^1H NMR

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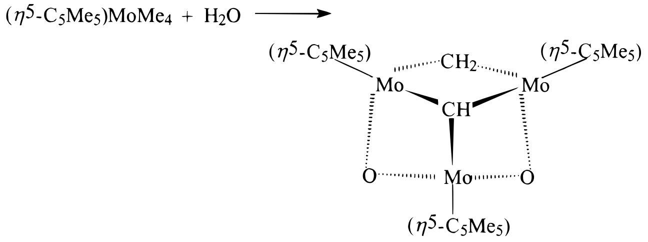
Scheme 4



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spectroscopic investigations of the crude product (after the reaction of the tetramethyl complex with water in a ratio of 1:1.5−2) show the formation of the former compound in an almost pure state. This result supports the proposed mechanism, taking into account that excess water is necessary for the formation of the intermediate **7**. Analogously to the formation of **6**, we have not observed any intermediates in this reaction. Independent studies of the hydrolysis of **6** showed a mixture of products. However, the formation of **9** was not observed. This fact excludes the possible formation of **9** as the product of hydrolysis of **6** during the reaction of $(\eta^5\text{-}C_5Me_5)WMe_4$ with water. The analogous decomposition of **9** via intermolecular CH activation was previously observed for the formation of the methylidene-bridged dinuclear cluster $[\{(\eta^5\text{-}C_5Me_5)Cr(\mu\text{-}Me)\}_2(\mu\text{-}CH_2)]$ from the methyl-bridged compound $[(\eta^5\text{-}C_5Me_5)(Me)Cr(\mu\text{-}Me)]_2$.[21]

Hydrolysis of $(\eta^5\text{-}C_5Me_5)MoMe_4$. Exploring the reaction of the homologous molybdenum tetramethyl complex with the silanetriol **1**, we found the formation of a mixture of uncharacterizable products. According to the results obtained in the hydrolysis studies of the tungsten tetramethyl complex, we decided to explore the reactivity of its molybdenum analogue with water under the same conditions. In agreement with the case for the tungsten analogue, no reaction was observed when $(\eta^5\text{-}C_5Me_5)MoMe_4$ was treated with an equivalent amount of water in toluene or 1,4-dioxane at room temperature. Increasing the reaction temperature to 50−60 °C resulted in gas evolution, and a green product was isolated from the reaction mixture. Characterization of the product **10** by spectroscopic, analytical, and X-ray measurements show that a trinuclear molybdenum oxo methylidene methylidyne cluster was formed (Scheme 4).

As the byproduct of this reaction, we isolated the previously reported[22] oxo-bridged dimer $[(\eta^5\text{-}C_5Me_5)MoO(\mu\text{-}O)]_2$.

X-ray Study of $(\eta^5\text{-}C_5Me_5)_3Mo_3(\mu\text{-}O)_2(\mu\text{-}CH_2)(\mu_3\text{-}CH)$ (10). Single crystals of **10** suitable for an X-ray investigation were grown from a THF/hexane mixture at room temperature over 3 months. The general view of a molecule of **10** and the atom-labeling scheme is shown in Figure 3; selected bond lengths and angles are listed in Table 3. Compound **10** represents the first example of an oxo cluster containing both methylidene and methylidyne moieties in one molecule.

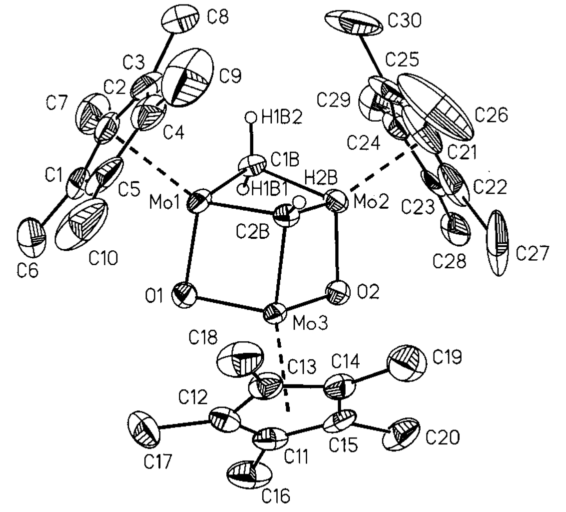

Figure 3. Molecular structure of $(\eta^5\text{-}C_5Me_5)_3Mo_3(\mu\text{-}O)_2(\mu\text{-}CH_2)(\mu_3\text{-}CH)$ (**10**) in the solid state (50% thermal ellipsoids). Hydrogen atoms of the methyl groups are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $(\eta^5\text{-}C_5Me_5)_3Mo_3(\mu\text{-}O)_2(\mu\text{-}CH_2)(\mu_3\text{-}CH)$ (10)

Mo1−Mo2	2.7454(9)	Mo2−C2B	2.060(4)
Mo1−Mo3	2.6006(5)	Mo3−C2B	2.120(4)
Mo2−Mo3	2.5951(6)	Mo1−O1	1.926(3)
Mo1−C1B	2.093(4)	Mo3−O1	1.935(3)
Mo2−C1B	2.084(4)	Mo3−O2	1.934(2)
Mo1−C2B	2.043(4)	Mo2−O2	1.918(3)
Mo2−Mo1−Mo3	58.006(13)	Mo1−C2B−Mo3	77.31(12)
Mo1−Mo3−Mo2	63.80(2)	Mo2−C2B−Mo3	76.75(12)
Mo1−C1B−Mo2	82.20(13)	Mo1−O1−Mo3	84.67(10)
Mo1−C2B−Mo2	84.00(14)	Mo2−O2−Mo3	84.72(10)

Two molybdenum atoms (Mo1 and Mo2) of **10** are each surrounded by pentamethylcylopentadienyl ligands, one bridging oxygen atom, methylidene, and methylidyne carbon atoms. One molybdenum atom (Mo3) is coordinated to a $\eta^5\text{-}C_5Me_5$ ligand, two oxo atoms, and the methylidyne bridging group. The metal−bridging oxygen bond lengths were found to be in the same range (1.918(3) Å for Mo2−O2 to 1.935(3) Å for Mo3−O1) and are comparable with the distances between molybdenum atoms and bridging oxygens in $[(\eta^5\text{-}C_5Me_5)MoO(\mu\text{-}O)]_2$ (1.94(1) Å).[22]

An interesting feature was found in the comparison of distances between the molybdenum atoms and the methylidene and methylidyne carbons, respectively. The bond lengths between molybdenum atoms connected to the methylidene carbon, bridging oxygen, and methylidyne carbon (Mo1−C2B and Mo2−C2B), falling in the "normal" range (2.043(4) and 2.060(4) Å, respectively), are shorter than those between molybdenum and methylidene carbons (Mo1−C1B = 2.093(4) Å and Mo2−C1B = 2.084(4) Å). The bond length between the molybdenum atom, connected with bridging oxygens, and the methylidyne carbon appears to be significantly longer (Mo3−C2B = 2.120(4) Å). This is obviously the "weakest" bond in the molecule of **10**. This result demonstrates that the bonds between methylidyne carbons and the metal atoms in oxide catalysts are in general weaker and easier to break with increasing Lewis acidity of the metal center (Mo3).

Analysis[23] of the bonding situation for the compounds **2**−**4** shows for all metal−metal bonds a bond order of

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(21) Noh, S. K.; Heintz, R. A.; Janiak, C.; Sendlinger, S. C.; Theopold, K. H. *Angew. Chem.* **1990**, *102*, 805; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 775.

(22) de Jesús, E.; de Miguel, A. V.; Royo, P.; Lanfredi, A. M. M.; Tiripicchio, A. *J. Chem Soc., Dalton Trans.* **1990**, 2779.

approximately 0.3. At the same time, the analysis of electron density[24] cannot detect the so-called (3, −1) critical point (characteristics of direct bonding). Instead, a critical point of (3, +1) type was found: i.e., a feature of a cyclic moiety.

Among the different contributions to the gain of energy in the bonding, only the electron−nuclear potential causes the density accumulation. However, in our case, it happens that the exchange terms are the most important ones, as compared to the potential part.

In summary, there are partial metal−metal bonds particularly due to the exchange interactions and not to the electron density accommodation. This situation is rather a specific one, outside the considerations developed in the semiempirical calculation on related compounds.[25]

Spectroscopic and analytical investigations of compound **10** are consistent with the structure in the solid state. The signal for the methylidyne proton in the ^{1}H NMR spectrum is shifted downfield (14.85 ppm). The signal for the methylidene protons appears in the same range as for compound **6** (4.10 ppm). Unfortunately, the low solubility of compound **10** in common organic solvents did not allow ^{13}C NMR investigations.

The mechanism of the formation of compound **10** remains unclear. However, the CH activation process and the condensation reaction are different from those observed in the corresponding tungsten system, since reduction from Mo(V) to Mo(IV) is observed.

Conclusions

In contrast to the reaction of group 4 and group 13 metal alkyls with the silanetriol, the corresponding reactions of tantalum, molybdenum, and tungsten compounds lead to dehydroxylation and formation of metal oxo species. In the previous work[10] on a tantalum compound we have shown that the initial step is the formation of the oxo dimer $[(\eta^5\text{-C}_5\text{Me}_5)\text{TaMe}_3]_2\text{O}$ (**2**), which reacts further, forming a cage compound.

Formation of intermediate **2** was also observed when the starting tetramethyl compound was treated with water in THF at room temperature.[26] However, the hydrolysis of its tungsten or molybdenum analogue is followed by CH activation processes and unexpectedly leads to the formation of a new class of compounds containing bridging methylidene and methylidyne groups and oxo ligands in one molecule.

Herein, we have shown the ability of the methylidene and methylidyne groups to act as μ and μ_3 bridging groups in organometallic oxo compounds. Compounds of this type may function as "realistic" models for the binding of CH and CH_2 species on metal oxide surfaces during the catalytic process. The X-ray structure investigations clearly demonstrate that the (formal) higher oxidation states at the metal centers weaken the metal−carbon bonds due to the higher Lewis acidity of the metals. Consequently, studies aimed at exploring the chemistry of oxo alkylidene and alkylidyne compounds of group 6 in medium oxidation states are in progress.

Experimental Section

General Methods and Materials. All reactions were performed under a deoxygenated argon or dinitrogen atmosphere using glovebox and high-vacuum techniques. The starting materials were prepared according to literature methods[13,27,28] and were sublimed or recrystallized prior to use. Aromatic, hydrocarbon, and ether solvents were dried over Na/K alloy and vacuum-transferred to the reaction flasks prior to use. Acetonitrile was dried over CaH_2. NMR spectra were recorded on Bruker AM 200 and Bruker AM 250 instruments. Chemical shifts are reported in δ units with reference to external SiMe_4 for ^{1}H and ^{13}C NMR. Mass spectra were obtained on a Finnigan MAT System 8230 and a Varian MAT CH5 mass spectrometer. FT-IR spectra were measured on a Bio-Rad FTS-7 instrument as Nujol mulls between KBr plates. Melting points were obtained on a HWS-SG 3000 apparatus. Elemental analyses were performed by the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Göttingen, Göttingen, Germany.

Reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{WMe}_4$ with Silanetriol 1. A solution of RSi(OH)_3 (1.04 g, 3.17 mmol) in ether (30 mL) was added dropwise to a solution of $(\eta^5\text{-C}_5\text{Me}_5)\text{WMe}_4$ (1.20 g, 3.17 mmol) in ether (30 mL). After complete addition, the reaction mixture was stirred for 8 h at room temperature. All volatiles were removed in vacuo, and the residue was dissolved in mesitylene (50 mL). The solution was slowly warmed to 110−120 °C and stirred for 2 h at this temperature until gas evolution had ceased. After the mixture was cooled, all volatiles were removed in vacuo and the residue was treated with *n*-hexane (15 mL). The precipitate was filtered off and dried in vacuo. Yield: 0.23 g. ^{1}H NMR (CDCl_3) of crude product: δ 0.47 (s, $\text{C}H_3$ ($\text{Si(CH}_3)_3$)), 1.16 (d, $\text{C}H_3$ (*i*-Pr)), 2.01 (s, $\text{C}H_3$ (C_5Me_5)), 2.05 (s, $\text{C}H_3$ (C_5Me_5)), 3.50 (sept, C*H* (*i*-Pr)), 4.23 (s, $\text{C}H_2$), 5.39 (s, $\text{C}H_2$), 7.10 (m, arom *H*). IR (cm^{-1}): ν(Si−OH) 3340 br, 3580 m. EI MS for **3** (70 eV): *m/e* [M$^+$] 636. EI MS for **6** (70 eV): *m/e* [M$^+$] 698. EI MS for **9** (70 eV): *m/e* [M$^+$] 700.

Preparation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{W}_2\text{O}_2(\mu\text{-CH}_2)_2$ (6). To a solution of $(\eta^5\text{-C}_5\text{Me}_5)\text{WMe}_4$ (5.32 g, 14 mmol) in toluene (60 mL) was added degassed H_2O (253 μL, 14 mmol) via syringe at room temperature. The reaction mixture was warmed to 70−80 °C and stirred for 2 h at this temperature until gas evolution had ceased. After the mixture was cooled, all volatiles were removed in vacuo and the residue was treated with pentane (10 mL). After filtration the crude product (2.84 g) containing a mixture of **6** and **9** was finally recrystallized twice from hot acetonitrile (15 mL) as green crystals. Yield: 1.32 g (27%). ^{1}H NMR (CDCl_3): δ 2.01 (s, 30H, $\text{C}H_3$ (C_5Me_5)), 4.23 (s, 4H, $\text{C}H_2$). ^{13}C NMR (CDCl_3): δ 11.22 (s, CH_3 (C_5Me_5)), 85.11 (s, CH_2, $J(\text{WC}) = 106.78$ Hz). IR (cm^{-1}): ν 1635 w, 1603 w, 1583 m, 1308 w, 1261 m, 1094 m, 1028 m, 943 vs, 904 w, 845 w, 803 m, 494 w. EI MS (70 eV): *m/e* (%) [M$^+$] 698 (100). Anal. Calcd for $\text{C}_{22}\text{H}_{34}\text{O}_2\text{W}_2$: C, 37.86; H, 4.87. Found: C, 37.49; H, 4.77.

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(23) The calculations were carried out with the GAMESS package at the ab initio level; see: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, *14*, 1347. For the molybdenum complexes the STO-3G basis was used, while the tungsten complexes were treated within the MINI basis. Given the experimentally detected diamagnetism of the compounds, they were determined in the RHF limit.

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Table 4. Crystallographic Data for Compounds 6, 9, and 10

	6	**9**	**10**
empirical formula	$C_{22}H_{34}O_2W_2$	$C_{21}H_{32}O_3W_2$	$C_{32}H_{48}Mo_3O_2$
fw	698.18	700.47	752.52
color of cryst	green	green	green
temp (K)	133(2)	133(2)	133(2)
cryst size (mm)	0.6 × 0.6 × 0.2	0.3 × 0.3 × 0.2	0.2 × 0.2 × 0.2
cryst syst	tetragonal	triclinic	monoclinic
space group	$P4_2/n$	$P\bar{1}$	$P2_1/n$
a (Å)	16.080(2)	8.262(2)	11.887(2)
b (Å)	16.080(2)	8.589(2)	11.934(2)
c (Å)	8.350(2)	9.429(3)	21.943(4)
α (deg)	90	109.03(3)	90
β (deg)	90	97.24(2)	99.20(3)
γ (deg)	90	117.37(3)	90
cell vol (Å^3)	2159.0(6)	530.5(2)	3072.8(9)
Z	4	1	4
ρ_c (g mm^{-3})	2.148	2.192	1.627
μ (mm^{-1})	10.660	10.850	1.232
F(000)	1320	330	1528
2θ range (deg)	2.53−27.61	2.42−27.61	1.88−24.99
no. of data measd, unique	42 713, 2512	8625, 2455	74 419, 5387
R_{int}	0.0670	0.0319	0.0501
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0255, 0.0627	0.0218, 0.0465	0.0302, 0.0762
R1, wR2 (all data)	0.0280, 0.0640	0.0253, 0.0471	0.0412, 0.0799
goodness of fit, S[c]	1.210	1.117	1.040
no. of refined params	124	130	445
largest diff peak/hole (e Å^{-3})	1.336/−1.293	0.940/−0.919	1.518/−0.498

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$. [c] $S = [\sum w(F_o^2 - F_c^2)^2]/[\sum(n - p)]^{1/2}$.

Preparation of (η^5-C_5Me_5)$_2W_2O_2$(μ-CH_2)(μ-O) (9). To a solution of (η^5-C_5Me_5)WMe_4 (2.00 g, 5.30 mmol) in toluene (40 mL) was added degassed H_2O (200 μL, 11.10 mmol) via syringe at room temperature. The reaction mixture was warmed to 70−80 °C and stirred for 2 h at this temperature until gas evolution had ceased. After the mixture was cooled, all volatiles were removed in vacuo and the residue was treated with pentane (10 mL). After filtration the crude product was finally dried in vacuo. Further purification was achieved by recrystallization from a acetonitrile/THF (3:1) mixture at room temperature. Compound **9** can be also separated from the crude product by column chromatography on silylated silica using ether/trichloromethane (1:1) as an eluent. Yield: 0.60 g (33%) of green crystals. ^{1}H NMR ($CDCl_3$): δ 2.05 (s, 30H, CH_3 (C_5Me_5)), 5.39 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 10.80 (s, CH$_3$ (C_5Me_5)), 95.85 (s, CH$_2$, J(WC) = 118.75 Hz). IR (cm^{-1}): ν 1507 w, 1160 w, 1027 s, 929 vs, 863 s, 723 w, 680 s, 635 w, 426 w, 418 w, 352 w. EI MS (70 eV): m/e (%) [M$^+$] 700 (100). Anal. Calcd for $C_{21}H_{32}O_3W_2$: C, 36.04; H, 4.57. Found: C, 35.82; H, 4.74.

Hydrolysis Reaction of (η^5-C_5Me_5)$MoMe_4$. To a solution of (η^5-C_5Me_5)$MoMe_4$ (1.40 g, 4.80 mmol) in 1,4-dioxane (40 mL) was added degassed H_2O (87 μL, 4.80 mmol) via syringe. The reaction mixture was warmed to 50−60 °C and was stirred for 2 h at this temperature. After the mixture was cooled, the volume of the solvent was reduced to 5 mL and the residue was treated with n-hexane (15 mL). The precipitate was filtered off and dried in vacuo to yield 0.27 g (25%) of **10** as green crystals. Storing the filtrate at −26 °C led to precipitation of [(η^5-C_5Me_5)MoO(μ-O)]$_2$ (0.30 g, 23% yield). ^{1}H NMR ($CDCl_3$) of **10**: δ 1.80−1.90 (m, 45H, CH_3 (C_5Me_5)), 4.10 (s, 2H, CH_2), 14.85 (s, 1H, CH). IR (cm^{-1}): ν 1646 w, 1571 w, 1306 w, 1261 w, 1168 w, 1157 w, 1120 w, 1082 w, 1024 s, 888 w, 874 w, 802 m, 720 vs, 695 w, 613 w, 574 w, 523 w. EI MS (70 eV): m/e (%) [M$^+$] 752 (100). Anal. Calcd for $C_{32}H_{48}Mo_3O_2$: C, 51.10; H, 6.38. Found: C, 50.81; H, 5.98.

Crystal Structure Solution and Refinement for 6, 9, and 10 (Table 4). Data for structures **6**, **9**, and **10** were collected on a Stoe-Siemens-Huber four-circle diffractometer with a Siemens CCD area detector by use of φ and ω scans. A semiempirical absorption correction was applied. All structures were solved by direct methods (SHELXS-97)[29] and refined against F^2 using SHELXL-97.[30] All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was employed.

Acknowledgment. We are thankful to the Deutsche Forschungsgemeinschaft for support of this work.

Supporting Information Available: Tables of crystal data, non-hydrogen atom fractional coordinates and U values, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and U values for **6**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000062Y

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