# Organometallic Oxides of Main Group and Transition Elements Downsizing Inorganic Solids to Small Molecular Fragments

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*Received July 16, 2002*

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## I. Introduction

Metal oxides are important in numerous catalytic industrial processes, and the understanding of their interactions with organic compounds is of great interest.[1] The organometallic oxides can also act as catalysts themselves and can serve as models for the catalyst-substrate interactions.[2] In this context, the study of organometallic oxides is not only an attractive subject of academic research but also relevant to the applied aspects of their chemistry. The organometallic oxides may serve as models for the surface interaction of hydrocarbons with inorganic metal oxides, that plays a considerable role in catalysis. Currently, there is considerable interest in the field of organometallic oxides, stimulated by the remarkable properties of methylaluminum oxide (MAO) as activator for metallocene catalysts in olefin polymerization[3] and the valuable catalytic properties of organorhenium oxides.[4]

The solid-state structures of metal oxides can be described as framework of architectures formed by coordinated metal-centered polyhedra, whose corners are occupied by oxygen atoms (Scheme 1).

Such polyhedra are rare, and only a few have been isolated; examples include those in tetrahedral $OsO_4$ and $RuO_4$ clusters. In almost all cases, they are assembled through shared oxygen atoms to form polynuclear aggregates.[5] The assembly of metal–oxygen polyhedra can result in low molecular oxides. Examples include dinuclear $Mn_2O_7$, $Tc_2O_7$, tetranuclear cages (e.g., $Sb_4O_6$), cyclic trimers and tetramers (such as $Mo_3O_9$ and $Mo_4O_{12}$ in the vapor phase), and infinite polymeric structures, including monodimensional, single-chain oxides (e.g., HgO and $CrO_3$), double-chain oxides (e.g., $Sb_2O_3$), bidimensional layered oxides (e.g., PbO, SnO, $MoO_3$), and tridimensional network oxides with a broad diversity of typical structures, such as $Al_2O_3$ (corundum), $TiO_2$ (rutile), $ReO_3$ (rhenium trioxide), MgO (NaCl structure), BeO (wurtzite type structure), etc.[6]

If some of the oxygen atoms in the coordination sphere of the central metal atom are replaced by organic groups, the organometallic oxides result. The first organometallic oxides have been reported by E. O. Fischer[7] and M. L. H. Green.[8] After the X-ray diffraction technique became widely available and their remarkable structures were revealed, the organometallic oxides began to receive the much deserved attention.

A number of mono- and polynuclear, water-soluble metal oxoanions are known and can be regarded as oxide fragments, in which the downsized solid-state structure generates $M-O^-$ or M–OH groups in reactions with strongly basic oxide or hydroxide:

$$M-O-M + O^{2-} \rightarrow 2\ M-O^- \qquad (1)$$

$$M-O-M + H-O^- \rightarrow M-O^- + M-OH \qquad (2)$$

The result is the formation of polyoxometalate species, containing metal–oxygen cages of variable sizes and complexities, down to monometallic oxoanions, e.g., $CrO_4^{2-}$ and $MoO_4^{2-}$.

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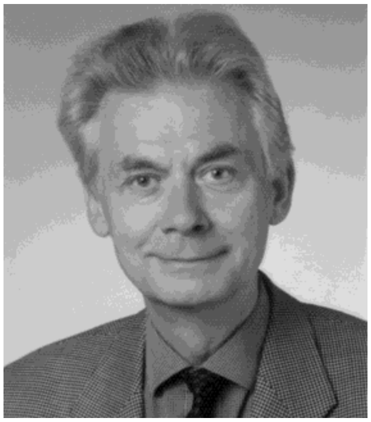
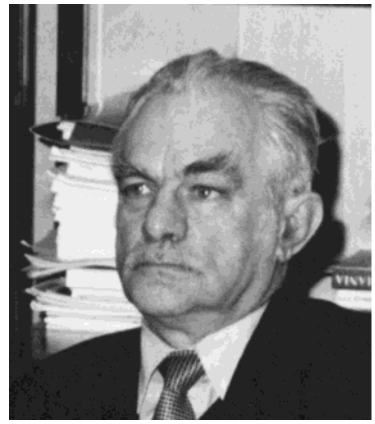
10.1021/cr020376q CCC: $44.00 
Published on Web 05/29/2003



Professor Herbert W. Roesky was born in 1935 in Laukischken. He studied chemistry at the University of Göttingen, Germany, where he obtained his diploma in 1961 and doctoral degree in 1963. After one year of postdoctoral work at DuPont in Wilmington, DE, he made his habilitation at the University of Göttingen. In 1971 he became full professor in Frankfurt/Main, and since 1980 he has been a full professor and director of the Institute of Inorganic Chemistry at the University of Göttingen. He has been a visiting professor at Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, Tokyo Institute of Technology, and Kyoto University and also frontier lecturers at Texas A&M University at College Station, University of Texas at Austin, and University of Iowa at Iowa City. He is a member of the Academy of Sciences at Göttingen, the New York Academy of Sciences, the Academy of Scientists "Leopoldina" in Halle, and the Academia Europaea in London. He served as the vice president of the German Chemical Society during 1995, and presently he is the president of the Academy of Sciences of Göttingen. He has received many awards, e.g., the Dr.rer.nat.h.c of Bielefeld and the French Alexander-von-Humboldt award. More than 900 publications, articles, patents, and books record his research activity in the areas of inorganic chemistry and material sciences.



Ionel Haiduc is the coauthor of a recently published book, *Supramolecular Organometallic Chemistry* (with F. T. Edelmann; Wiley-VCH: Weinheim, Germany, 1999), and of several other books and more than 300 journal articles. His interests include inorganic (carbon-free) ring systems, supramolecular self-assembly of organometallics, coordination, and organometallic derivatives of organophosphorus and organoarsenic ligands. He obtained his Ph.D. in 1963 with K. A. Andrianov in Moscow (USSR) and worked as a postdoc with Henry Gilman in Ames, IA (1966–1968), and R. Bruce King in Athens, GA (1971–1972). He was Visiting Professor at the University of Georgia (1992), Universidad Nacional Autonoma de Mexico (1993–1994), University of Texas at El Paso (1997, 2000–2001), Universität Magdeburg (Germany, 1997), Universidad de Santiago de Compostela (Spain, 1994, 1998), Universidade Federal de Sao Carlos (Brazil, 2000, 2001), Universität Göttingen (Germany, 2002), and National University of Singapore (2002) and Gauss Professor at Universität Göttingen (1998). He was awarded Fulbright and Humboldt research fellowships and travel grants from the NSF, the European Community, the British Council, and NATO. He is currently professor at "Babes-Bolyai" University in Cluj-Napoca, Romania, and a member of the Romanian Academy (Bucharest) and of Academia Europaea (London).

From a synthetic standpoint, the ideal route would be to start with a metal oxide and through some chemical manipulation to break into fragments (clusters) of various sizes beginning with the parent structure, and by wrapping them with blocking organic groups, to form the specific organometallic oxides. In practice this is difficult, if not impossible, due to oxides' high lattice energy. Apparently, the only known direct reactions of a metal oxide with organic group transfer reagents include the preparation of organorhenium oxides from $Re_2O_7$ with dimethylzinc or zincbis(cyclopentadienyls) ($Cp = C_5H_5$ or $C_5Me_5$), and with some organotin reagents[4,9]

$$Re_2O_7 + ZnMe_2 \rightarrow Me_4Re_2O_4 \rightarrow Me_6Re_2O_3 \quad (3)$$

$$2Re_2O_7 + ZnCp_2 + 2THF \rightarrow 2CpReO_3 + Zn(ReO_4)_2 \cdot 2THF \quad (4)$$

It is possible that these reactions could be extended to some other metals.

A similar process is less readily available for the synthesis of organometallic oxides. They have to be prepared from organometallic monomeric reagents that are the compounds in which the metal is already bonded to the organic moiety, such as organometal halides, hydrides, alkoxides, amides, etc. These species can react with water with the elimination of HX, $H_2$, HOR, $HNR_2$, or $NH_3$, followed by condensation reactions to construct the metal−oxygen backbone in a new molecule with a central inorganic $M_xO_y$ core wrapped in a lipophilic (hydrophobic) layer of organic groups. This makes the organometallic oxides soluble in organic solvents. Consequently, the organometallic oxides are usually prepared either by hydrolytic processes, starting from organometallic halides or water-sensitive metal alkyls,[10] or by oxidizing organometallic compounds with mild reagents.[11,12] Usually, these methods are using self-assembly processes, resulting in the formation of polynuclear species in most cases and, based upon metal−oxygen frameworks, rings or cages that are wrapped with organic groups. In many cases, the reaction cannot go to completion, but stable intermediate oxide−chlorides, oxide−hydroxides, and derivatives of other functional groups are isolated. These functionalized metal−oxygen molecular backbones will be discussed only in the context of the main topic.

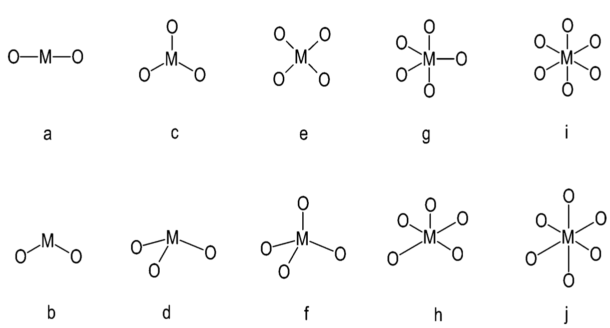
The formation of organometallic oxides may serve as a model for the preparation of metal oxides by the condensation of hydroxo intermediate species[13] involving the intermediate steps of nucleation:

$$M{-}OH + HO{-}M \rightarrow M{-}O{-}M + H_2O \quad (5)$$

In pure inorganic systems, the process can be stopped at intermediate stages of small polyoxoanions, such as dichromate $Cr_2O_7^{2-}$ and higher polyoxochromates (with up to seven chromium atoms),[14] polyoxomolybdates, $Mo_7O_{42}$,$^{6-}$ oxoanions of intermediate size, such as $[H_{14}Mo_{37}O_{112}]$,[14−15] or may form giant polyoxoanions, containing 176, 248, or even 368 molybdenum atoms,[16,17] before converting completely

Narayan S. Hosmane was born in Gokarn, Southern India, in 1948. He is a B.S. and M.S. graduate of Karnatak University, located in the state of Karnataka, India. He obtained a Ph.D. degree in Inorganic Chemistry in 1974 from the University of Edinburgh, Scotland, under the supervision of Professor Evelyn Ebsworth. After a brief postdoctoral research training in Professor Frank Glockling's laboratory at the Queen's University of Belfast, he joined Lambeg Research Institute in Northern Ireland and then moved to the USA to do research in the area of carboranes and metallacarboranes. After postdoctoral work with Professors W. E. Hill and F. A. Johnson at Auburn University and Russell Grimes at the University of Virginia, in 1979 he joined the faculty at the Virginia Polytechnic Institute and State University. In 1982, he joined the faculty at Southern Methodist University, where he rose to a rank of Professor of Chemistry in 1989. In 1998, he moved to Northern Illinois University and is currently a Presidential Research Professor of chemistry and biochemistry. In 1985, he was a Visiting Professor at the Ohio State University and worked with Professor Sheldon Shore. He was the organizer and co-founder of the first Boron in the USA (BUSA) workshop, which was hosted in Dallas in April 1988. Narayan Hosmane is an internationally recognized scientist in organometallic chemistry and has published over 190 papers in leading scientific journals. He has been highly successful in obtaining significant research grant funding during his academic career of over 23 years. In 2001, he received the Humboldt Research Prize for Senior US Scientists from the Alexander von Humboldt-Stiftung and also received the University's Presidential Research Professorship. He has previously received a Camille and Henry Dreyfus Scholar Award and has been honored with the Mother India International Award for his contribution to science education and the Boron in the USA Award for his distinguished achievements in Boron Science. The Society of Sigma Xi presented Hosmane with its 1987 Sigma Xi Outstanding Research Award. The widespread recognition of Hosmane's research efforts is apparent from his invitations to make presentations before international groups. A fellow of the Royal Society of Chemistry and the American Institute of Chemists, he has been listed in *Who's Who in the World.* His research interests are in the main group organometallic chemistry, including the synthesis and structure of carboranes, metallacarborane sandwich compounds, and organosilicon compounds, with particular emphasis on the Ziegler–Natta catalysis.

**Scheme 1**




into a metal oxide that usually requires high temperature thermal reactions. An example is the formation of $ZrO_2$ from $ZrCl_4$; the latter undergoes hydrolysis to $ZrOCl_2$ and requires temperatures of 1200 °C to yield $ZrO_2$.

## II. Structural Motifs of Organometallic Oxides as Fragments of Solid State Oxides

In organometallic oxides the metal–oxygen framework is a finite block, containing a limited number of metal and oxygen atoms. It is of interest to explore whether these blocks can be identified as fragments of solid-state oxides or whether other structural motifs are also possible. The data presented in this review will show that, in many cases, the polynuclear backbones of molecular organometallic oxides can indeed be regarded as fragments that are cut off from a solid-state network. In certain cases, however, the backbone of a molecular oxide has no counterpart in the building blocks of inorganic oxides.

The formal replacement of oxygen in the coordination sphere of a metal atom in a metal oxide leads to organometallic building blocks, such as $R_xMO$, $R_xMO_2$, $R_xMO_3$, and $R_xMO_4$, that will form the structures of organometallic oxides by sharing oxygen atoms in a more or less complex structure. With R = alkyl or aryl, $x = 1, 2$ (mostly in Main Group metal derivatives of Al, Ga, In, Sn, and Pb); with R = $C_5H_4R'$ (R′ = H, Me, Et, etc.), usually $x = 1$ as in transition metal derivatives.

The linear dicoordinated oxygen is the simplest unit that can be regarded as a small fragment cut off from a solid-state metal oxide. In numerous oxide networks there are linear M–O–M arrangements and all can give rise to dinuclear organometallic oxides. The bent M–O–M arrangement is also observed in numerous inorganic metal oxides, but it is less likely to form bent dinuclear organometallic oxides because of the repulsion between bulky organic groups that will force a linear arrangement of the oxygen atoms.

The bending of M–O–M bonds is important for the formation of cyclic molecular skeletons. In four-, six-, and eight-membered rings, the bent M–O–M bond angles span values from less than 90° (in four-membered rings) to ca. 120° (ideally in planar six-membered rings) and larger (in nonplanar six- and eight-membered rings). Combined with tricoordinate metal sites, the bent M–O–M units can form polycyclic structural motifs (vide infra). The flexibility of the oxygen bond angles allows the formation of these rings, both in the solid-state oxides as parts of a two-dimensional layer or three-dimensional network and in organometallic oxides as molecular skeletons.

The mineral diaspore, AlO(OH), contains six coordinate aluminum, and $Al_2O_2$ and $Al_3O_3$ rings can be distinguished in its structure. In rutile $TiO_2$, in which titanium is also six-coordinated, eight-membered $Ti_4O_4$ rings are readily recognized. By replacing some of the M–O bonds with M–C bonds, smaller cyclic molecular fragments can be generated, with lower coordination numbers of the metal. If coordination number 3 is preserved, polycyclic cages (vide infra) containing the corresponding ring fragments result. The $M_8O_8$ cubane, discovered in an organotitanium oxide, can be regarded as a fragment of the structure of perovskite, $CaTiO_3$.

A unique polymeric material, formed by partial hydrolysis of $MeReO_3$, provides a spectacular illustration of the relation between the structure of an organometallic oxide and that of the parent inorganic, solid-state oxide $ReO_3$. The polymer of $MeReO_3$ has a two-dimensional layer structure that was "sliced" from the three-dimensional structure of $ReO_3$ and maintains the $Re_4O_4$ rings of the inorganic counterpart in the layer.[18] A double-layered organometallic oxide, consisting of corner-sharing $MeReO_5$ octahedra and derived from the three-dimensional $ReO_3$ structure, has also been described.[19] The structures of several cubane-type organometallic oxide clusters have been correlated to the solid-state structure of molybdenum trioxide.[20]

## III. The Structure-Directing Role of Oxygen

The metal oxygen frame work structures of both solid-state inorganic and molecular organometallic oxides are dictated by the bonding abilities of the oxygen atoms located at the corners of the metal-centered polyhedral building blocks shown in Scheme 1.

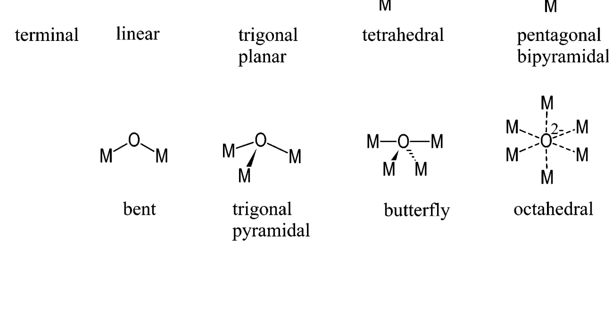
In the formation of the solid-state structures, the oxygen plays a structure-directive role.

The oxygen atom displays a remarkable variety of bonding patterns and can form one, two, three, or four covalent (polar) bonds. As an $O^{2-}$ ion, it can be encapsulated in a cage and surrounded by four, five, or six metal sites, interacting through ionic bonds. Thus, the coordination number of oxygen can vary from one to six: one in terminal M=O groups, two in linear or bent, three in trigonal planar or trigonal bipyramidal, four in tetrahedral and sometimes in butterfly-like, five in pentagonal bipyramidal and six in octahedral structures (as illustrated in Scheme 2).

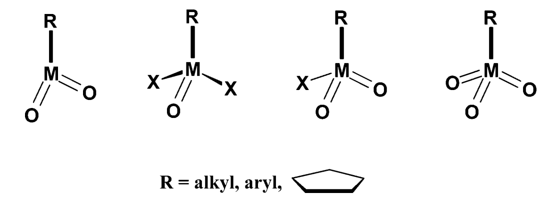
The presence of organic groups at some coordination sites reduces the metal's connectivity to lower numbers and results in a new coordination geometry. The $\eta^5$-cyclopentadienyl ligand has been most frequently used, as it occupies three coordination sites when bound to a metal atom. Therefore this, an atom which is normally six-coordinate (octahedral) in a solid state inorganic oxide will have only three coordination sites left for further bonding. Similarly, a normally seven-coordinate atom will remain with four coordinate sites unoccupied. This happens in the case of titanium, that is six-coordinated in rutile and zirconium, that is seven-coordinated in $ZrO_2$.

When some of the coordination sites are occupied by organic groups, it is more difficult for the $R_xMO_3$ and $R_xMO_4$ building units to form extended arrays (infinite) of three-dimensional structures, unless the oxygen bonds are linearly oriented. Similarly, $R_xMO_2$ units can be derived, frequently bearing an additional functional group at the metal, such as $RM(X)O_2$ moieties. The M−O−M bond angles of less than 180° create curvatures and/or convexities. Thus, the $RMO_x$ ($x$ = 1, 2, 3...) units will assemble into molecular species with ring or cage structures in which the metal occupies the corners of a polygon or polyhedron. The final outcome of the structure is dictated by the M−O−M bond angles that determine how the polyhedral units can be assembled into polynuclear structures.

**Scheme 2**




**Scheme 3**



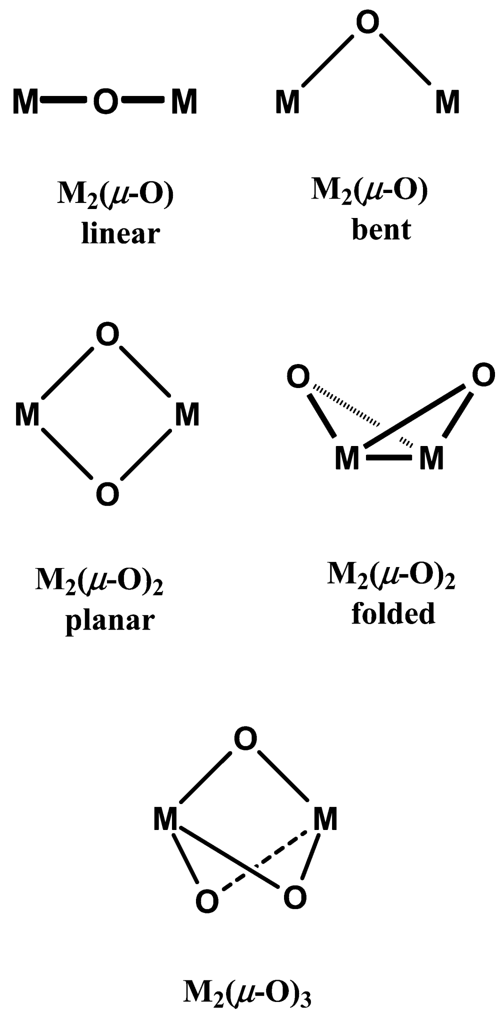

Since the M−O−M bond angles are quite flexible, a great structural diversity is possible. Four-, six-, and eight-membered molecular oxide rings and cages derived from regular polyhedra (tetrahedron, trigonal bipyramid, octahedron as deltahedral polyhedra, cube, pentagonal, and hexagonal prisms as square faced polyhedra) can be expected, and in fact, such species do exist. In principle, truncated polyhedra can also be made. Several models have been theoretically investigated by DFT methods with relevance to possible structures of methylaluminum oxide (MAO).[21]

The various connectivity patterns of oxygen, shown in Scheme 2, give rise to a series of structural motifs that can be identified in both solid state inorganic oxides and molecular organometallic oxides. Linear coordination allows only unidirectional growth, but bent coordination affords ring closure, while tricoordination results in branching, three-dimensional growth or cage formation.

The terminal M=O double bonds are observed in numerous organometallic oxides (see selected reviews[11,12]), and the detailed discussion of those will not be presented here. Methylrhenium trioxide, $MeReO_3$, which is, regarded as a fragment of molecular dirhenium heptaoxide, deserves a special comment due to its importance as a catalyst.[22] This mononuclear, molecular organometallic oxide is formally derived by breaking the metal−oxygen bridge between the rhenium atoms in the oxide $O_3Re{-}O{-}ReO_3$, and blocking the $ReO_3$ fragments with the methyl groups. Other examples are all well-known compounds with "piano-stool" structures as in $Cp^*V(O)Cl_2$,[23] ($Cp^* = C_5Me_5$), $CpMo(O)Cl_2$,[24] $Cp^*Re(O)Cl_2$,[25] $CpReO_3$,[22] $[t\text{-}BuSiOReO_4]_4$,[26] and in many other species (Scheme 3).

Breaking of $\mu$-O bridging leads to numerous types of open-chain and cyclic structures. Open chains are common in organosilicon chemistry (linear siloxanes, not discussed here) but are rare for true metals and tend to associate further by interchain O → M donor acceptor bonds. Dinuclear types include linear and bent species based upon M−O−M backbones, and cyclic species that result when two or three $\mu$-O bridges connect two metal atoms (Scheme 4).

**Scheme 4**



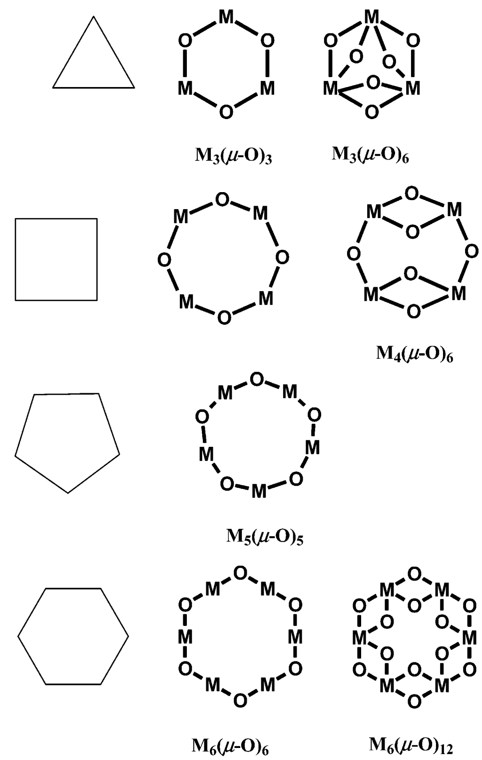

Cyclic structures can be derived from regular polygons with the corners occupied by the metal atoms of the organometallic moieties and the $\mu$-O bridgings located on the edges (Scheme 5). These are described by the general formula, $[R_xM(\mu\text{-O})]_n$, where R can be $\sigma$-alkyl/aryl, $\eta^5$-cyclopentadienyl or other organic groups. This type of structural assembly requires $R_xMO_2$ or $R_xMO_3$ building units.

In a similar manner, polycyclic structures are derived from common regular polyhedra (tetrahedron, trigonal bipyramid, octahedron, cube, etc.) (Scheme 6). Such polymorphs require $R_xMO_3$ or $R_xMO_4$ moieties, and most of the structures illustrated in Scheme 6 have been exemplified in representative molecules that make the chemistry of organometallic oxide fascinating. In principle, even larger cages can be derived in a similar fashion. One such example would be the $M_{12}O_{24}$ cluster (see Scheme 7).

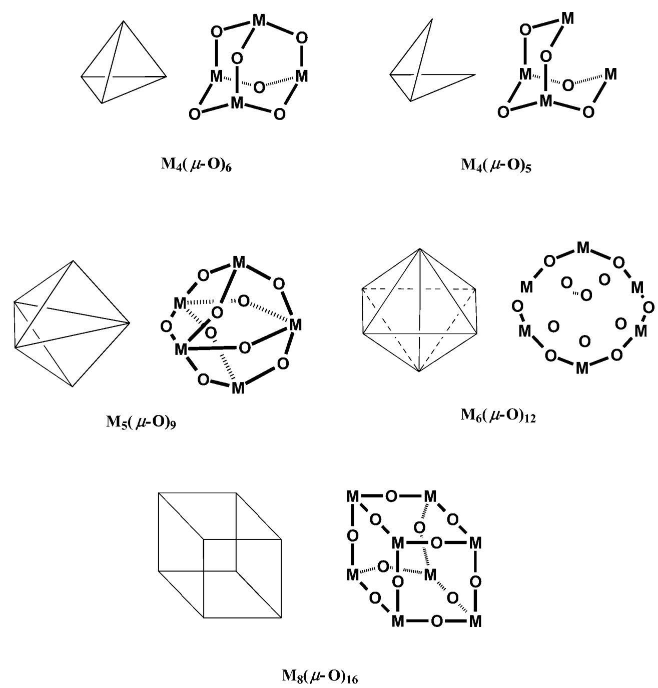
The triconnective oxygen $\mu_3$-O in a trigonal planar or pyramidal geometry can be found in $\mu_3$-oxygen centered trinuclear motifs, and there are several organometallic structures built around a tricoordinate oxygen (Scheme 8). A unique example of a trinuclear compound containing only one tricoordinated oxygen atom and three Rh···H···Rh bridges is provided by the cation $[\{Cp^*Rh(\mu\text{-H})\}_3(\mu_3\text{-O})]^+$. In the $Zr_3(\mu\text{-OH})_3$-based cyclic cation $[\{Cp_2Zr(\mu\text{-OH})\}_3(\mu_3\text{-O})]^+$, there is a trigonal planar tricoordinate oxygen,[27] and $[CpNbCl(\mu\text{-X})]_3(\mu_3\text{-O})(\mu_3\text{-OH})$, X = Cl, OH, contains an $Nb_3Cl_3$ ring constructed around a trinuclear $ONb_3$ unit with a trigonal pyramidal, tricoordinate oxygen.[28] Related compounds are $(Cp^*ZrCl)_3(\mu\text{-Cl})_4(\mu_3\text{-O})$ (with trigonal pyramidal oxygen),[29] $(Cp^*MCl)_3(\mu_3\text{-O})(\mu\text{-OH})_3(\mu\text{-Cl})$, M = Nb, Ta,[30] and $(CpMoCl)_3(\mu\text{-Cl})_4(\mu_3\text{-O})$.[31] Although these compounds are not classical organometallic oxides, they do illustrate the tricoordination of oxygen very well.

The trigonal pyramidal coordination allows the formation of polyhedral cages. These cages are the

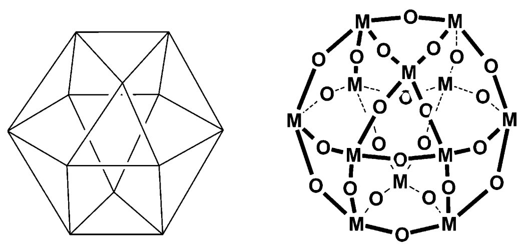
**Scheme 5**




**Scheme 6**

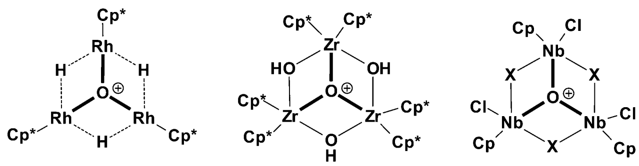


**Scheme 7**



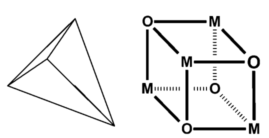
$M_{12}O_{24}$

**Scheme 8**

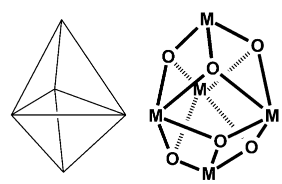



X = Cl or OH

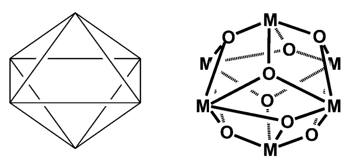
**Scheme 9**



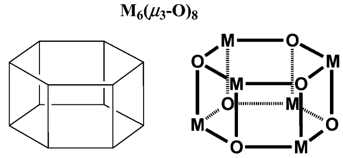
$M_4(\mu_3\text{-}O)_4$



$M_5(\mu_3\text{-}O)_6$



$M_6(\mu_3\text{-}O)_8$



$M_6(\mu_3\text{-}O)_6$

result of a capping of the triangular faces of deltahedral polyhedra (tetrahedron, trigonal bipyramid, octahedron, etc.) with the oxygen atoms. In this type of coordination, both the metal and the oxygen atoms occupy polyhedral corners. Thus, capping the tetrahedron faces produces a regular or distorted $M_4(\mu_3\text{-}O)_4$ cubane structure and that of the trigonal bipyramid yield $M_5(\mu_3\text{-}O)_6$ cages, while capping of the six or eight faces of an octahedron results as $M_6(\mu_3\text{-}O)_6$ or $M_6(\mu_3\text{-}O)_8$ cage structures (Scheme 9). Like other cages, these structures require $R_xMO_3$ or $R_xMO_4$ building blocks.

The four-coordinate oxygen, $\mu_4$-O, is rarely found in organometallic compounds, but one such example is $\{[CpTi]_4(\mu_4\text{-}O)\}(\mu\text{-}O)(\mu_3\text{-}S_2)_4$. It can be viewed as the Ti being tetrahedrally coordinated with four O−M bonds or by encapsulating an $O^{2-}$ anion in a cage structure.[32] The dinegative $O^{2-}$ anion can also be encapsulated in a cage structure that is being surrounded by six metal atoms as close neighbors (vide infra).

The main structural types of organometallic oxides are discussed below. The metals, considered in this review, exclude the semi-metals or the so-called metalloids (germanium, arsenic, tellurium), and also boron and silicon, despite the common inclusion of their organic derivatives in the organometallic chemistry in general.[33]

## *IV. Dinuclear Organometallic Oxides*

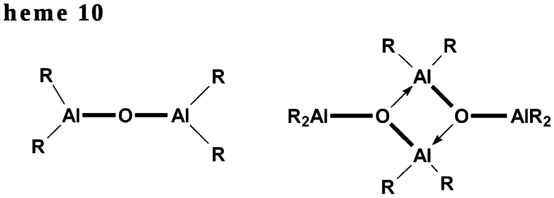
### A. Open-Chain Structures

Diorganoaluminum oxides, $R_2Al{-}O{-}AlR_2$ (R = Et), are associated in solution and their molecular weight determinations indicate a tetrameric self-assembly of the molecules. $^{27}$Al and $^{17}$O NMR measurements suggest the presence of tetracoordinate aluminum atoms and tricoordinate oxygens.[34] However, the solution geometry was speculative until the solid-state X-ray diffraction analysis of $(t\text{-Bu})_2Al{-}O{-}Al(t\text{-Bu})_2$ that indicated a dimeric structure, with a planar $Al_2O_2$ ring and two $O{-}Al(t\text{-Bu})_2$ pendant groups (Scheme 10). Only when the vacant sites of aluminum are occupied by pyridine does the dialumoxane remain monomeric. The structure of the resulting $(t\text{-Bu})_2Al{-}O{-}Al(t\text{-Bu})_2\cdot 2Py$ has a linear Al−O−Al arrangement, with the Al−O bonds being shorter (1.710 Å) than in the dimer (1.860−1.867 Å in the ring, 1.751 Å exocylic), indicating some double bond character between these atoms.[35] With very bulky organic groups, dialumoxanes can be monomeric as in $R_2Al{-}O{-}AlR_2$, (R = $CH(SiMe_3)_2$) which is also linear with Al−O distance of 1.688 Å.[36] On the other hand, the gallium and indium dinuclear oxides, $R_2M{-}O{-}MR_2$, (R = $CH(SiMe_3)_2$), are bent with large M−O−M bond angles of 142.7° for M = Ga and 138.6° for M = In.[37]

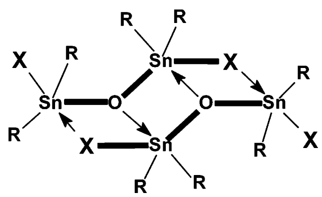
Bis(triorganotin) oxides, $R_3Sn{-}O{-}SnR_3$ (R = alkyl, aryl), are monomeric molecular compounds (R = Me, bent, Sn−O−Sn = 140.1°, as determined by electron diffraction in the gas phase;[38] R = *t*-Bu,[39] $CH_2Ph$,[40] $CH_2C_6H_4Me$-2, $C_6H_4Me$-2,[41] all four are linear; R = Ph, bent, Sn−O−Sn = 137.3°).[42] A rationalization of the skeletal bond angles of $R_3Sn{-}X{-}SnR_3$ (R = Me, Ph, $CH_2Ph$; X = O, S, NH) has been made using second-order Jahn−Teller effects.[43] The functional derivatives of $XR_2SnOSnR_2X$ (X = halogen, OH, OOCR, etc.) are basically, without exception, associated as dimers (ladder or more complex structures) involving $Sn_2O_2$ ring cores and both di- and tricoordinate oxygen atoms (Scheme 11). These and related organometallic compounds received much attention in recent years[44] and have been the subject of many reviews[45] and, therefore, will not be discussed further.

Several diorganoantimony oxides, $R_2Sb{-}O{-}SbR_2$, are known. Of these, the phenyl derivative $Ph_2Sb{-}$

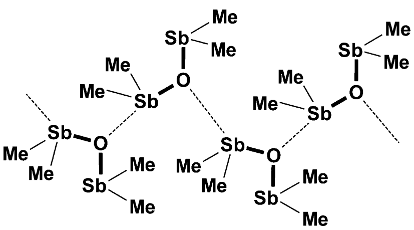
**Scheme 10**



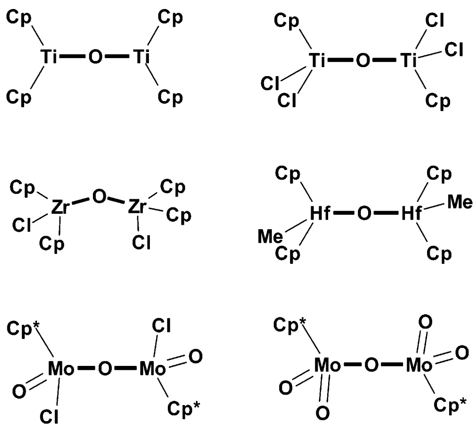
**Scheme 11**




**Scheme 12**




**Scheme 13**




O−SbPh$_2$ has long been structurally characterized by X-ray diffraction. The compound is monomeric with a bent Sb−O−Sb core (122.1°).[46] Recently, detailed structural investigations of R$_2$Sb−O−SbR$_2$, where R = Me,[47,48] Ph, *o*-MeC$_6$H$_4$ and *p*-MeC$_6$H$_4$,[49] using gas-phase electron diffraction (for the methyl derivative), X-ray diffraction analyses and DFT calculations have been reported. These studies confirmed that the compounds are not identical species despite their similar compositions. A comparison between the structures of Me$_2$Sb−O−SbMe$_2$ and valentinite, Sb$_2$O$_3$, showed that the Me$_2$Sb−O−SbMe$_2$ molecules adopt a syn−anti conformation in the solid state and they are associated into supramolecular arrays through Sb···O secondary bonds. They have Sb−O bond length of 1.988 Å and 2.099 Å, Sb···O bond length of 2.585 Å and O···Sb−O bond angle of 173.5° and Sb−O···Sb bond angle of 117.8° (Scheme 12). Such weak intermolecular contacts were also found in the structure of Sb$_2$O$_3$ in which the Sb−O double chains are interconnected through Sb···O secondary bonds (2.518 Å).[48]

Numerous dinuclear transition metal organometallic oxides are known, and they are the derivatives of cyclopentadienylmetal species, including Cp$_2$Ti−O−TiCp$_2$,[50] Cp*$_2$Sm−O−SmCp*$_2$,[51] [Cp$_2$Lu(THF)]$_2$($\mu$-O),[52] [(MeC$_5$H$_4$)$_2$NbCl]$_2$O,[53] [Cp*Me$_2$Ti]$_2$($\mu$-O),[54] and [Cp*TaMe$_3$]$_2$($\mu$-O)[55] (Scheme 13). The mixed oxide−halides of the type [Cp*TiCl$_2$]$_2$($\mu$-O)[56] (as products of partial substitution) are also important class of functionalized organometallic oxides.

The M−O−M fragment is linear or nearly linear in most dimetal oxides. For example, the M−O−M bond angle of 180° is found in Cp*$_2$Sm−O−SmCp*$_2$,[51] [Cp*TaMe$_3$]$_2$($\mu$-O) and [CpTiCl$_2$]$_2$($\mu$-O), while the bond angles are 170.9° in Cp$_2$Ti−O−TiCp$_2$,[50] 180° and 153.4° (two independent molecules) in [Cp* TiMe$_2$]$_2$($\mu$-O), 173.8° in [Cp$_2$TiCl]$_2$($\mu$-O),[56] 180° in [CpTiCl$_2$]$_2$($\mu$-O)[57] and [(PhCH$_2$)$_3$Ti]$_2$($\mu$-O),[58] 168.9° in [Cp$_2$ZrCl]$_2$($\mu$-O),[59] and 173.9° in [Cp$_2$HfMe]$_2$($\mu$-O).[60] In the crystal lattice of [Cp*$_2$TiCl]$_2$($\mu$-O), there were two independent molecules with Ti−O−Ti angles of 153° and 180°. On the other hand, the solid-state structure of [Cp*TiCl$_2$]$_2$($\mu$-O) contains three independent molecules with rather bent Ti−O−Ti bond angles of 159.1°, 154.4°, and 157.7°. It is of interest to note that [Cp*Mo(O)$_2$]$_2$($\mu$-O) contains six independent molecules in its unit cell. These are two centrosymmetric molecules with a linear Mo−O−Mo bond (180°) and four noncentrosymmetric molecules with almost linear Mo−O−Mo bond with an angle of 177.9°.[61,62] Of the two compounds, the one with bulky substituents, [(*i*-Pr$_4$C$_5$H)Mo(O)$_2$]$_2$($\mu$-O) is linear, and the other, [(*t*-Bu$_3$C$_5$H$_2$)Mo(O)$_2$]$_2$($\mu$-O), is bent (Mo−O−Mo 162.6°).[63] The mixed oxide−chloride species, [Cp*Mo(O)Cl]$_2$($\mu$−O), also has a linear Mo−O−Mo backbone.[64] Interestingly, in [(neopentyl)$_3$WO]$_2$($\mu$-O) the entire O−W−O−W−O skeleton is linear.[65]

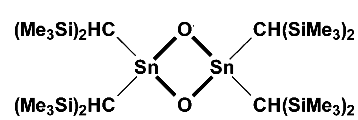
## B. Cyclic Structures

The four-membered M$_2$O$_2$ rings can either be planar or folded (bent) and can also exist as cis−trans- (or syn−anti) conformers.

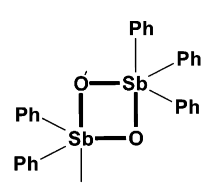
The dimer [{(SiMe$_3$)$_2$CH}$_2$SnO]$_2$ contains a Sn$_2$O$_2$ four-membered ring with Sn−O bond distance of 1.94 and 1.98 Å and Sn−O−Sn and O−Sn−O bond angles of 97.5° and 82.5°, respectively (Scheme 14). The compound is orange colored due to a small HOMO−LUMO separation.[66]

Triphenylantimony(V) oxide, [Ph$_3$SbO]$_2$, is a cyclic dimer containing a planar four-membered Sb$_2$O$_2$ ring (Scheme 15) in which the antimony is five coordinated (distorted trigonal bipyramidal geometry) with a phenyl group and an oxygen atom occupying axial positions. Two phenyl groups and an oxygen atom are in equatorial positions. The parameters are as follows: axial Sb−O = 2.071 Å, equatorial Sb−O = 1.928 Å; axial O−Sb−C = 167.5°; equatorial O−Sb−C = 121.0° and 124.9°, C−Sb−C = 111.7°; axial−

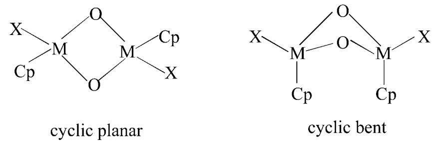
**Scheme 14**



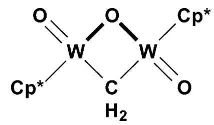

**Scheme 15**



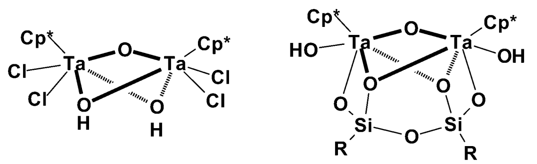
**Scheme 16**




**Scheme 17**



**Scheme 18**




equatorial O−Sb−C = 87.9° and 90.4°; endocyclic O−Sb−O = 77.1° and Sb−O−Sb 102.9°.[67] A recently characterized related compound, $[(2\text{-}PhOC_6H_4OC_6H_4)Ph_2Sb]_2O$, shows the same pattern with axial Sb−O = 2.060 Å, equatorial Sb−O = 1.943 Å, O−Sb−O = 78.2°, and Sb−O−Sb 101.8°.[68] The structure of $[Ph_2BrSbO]_2$ exhibits the bromine and oxygen occupying the axial positions of the distorted trigonal-bipyramid with the Sb−O (axial) and Sb−O (equatorial) distances of 2.04 and 1.93 Å, respectively.[69]

Organo transition metal oxides display both the planar and folded four-membered rings (Scheme 16). Planar rings have been found in *trans*-$[Cp^*Cr(O)(\mu\text{-}O)]_2$,[70] *trans*-$[Cp^*Mo(O)(\mu\text{-}O)]_2$,[71] and *trans*-$[Cp(C_3F_7)(O)W(\mu\text{-}O)]_2$,[72] whereas in *cis*-$[Cp^*Re(O)(\mu\text{-}O)_2ReCp^*(OReO_3)_2]$, the four-membered ring is folded along the Re=Re transannular bond (Re−O−Re 86.2°).[73] The $Mo_2O_2$ ring in both *cis*-$[CpMo(O)(\mu\text{-}O)]_2$ (in the ring: Mo−O = 1.932 and 1.948 Å; Mo−O−Mo = 84.2°, O−Mo−O = 92.2° and 93.1°; exocyclic Mo=O = 1.695 Å)[74] and *cis*-$[Cp^*Mo(O)(\mu\text{-}O)]_2$ (in the ring Mo−O = 1.946 Å, exocyclic Mo=O = 1.692 Å)[75] is bent and is explained on the basis of more favorable Mo−($\mu$-O) $\pi$ interaction in the slightly folded geometry. The folding of the $\mu$-oxo ligands toward the cis cyclopentadienyl substituents, rather than away from them, in a sterically less congested environment was found to be the electronically preferred geometry.[76]

The mixed organometallic oxide rings, containing both $\mu$-O and $\mu$-$CH_2$ bridgings, are observed in $Cp^*_2W_2O_2(\mu\text{-}O)(\mu\text{-}CH_2)$ (Scheme 17). They bear direct relevance for modeling the catalysis on metal oxide surfaces.[77]

The triple M−O−M bridged dinuclear compounds are rare (Scheme 18). A bicyclic structure based on a Ta−O−Ta bridge and two additional hydroxo bridges is found in $[Cp^*TaCl_2]_2(\mu\text{-}O)(\mu\text{-}OH)_2$. None of the Ta−O−Ta bonds is linear, and the bond angles in the molecule are Ta−($\mu$-O)−Ta = 103.0° and Ta−($\mu$-OH)−Ta = 89.6 and 103.4°. The short Ta···Ta distance of 3.028 Å suggests a metal−metal bond.[78] Another example of a tantalum compound is $\{Cp^*Ta(OH)\}_2(O_2RSiOSiRO_2)(\mu\text{-}O)$ (R = 2,6-($i$-Pr)$_2C_6H_3$-$NSiMe_3$), in which the metal atoms in the $Ta_2(\mu\text{-}O)$ unit are additionally bridged by two disiloxane fragments to form a unique $Ta_2O_6Si_2$ core.[79]

## V. Trinuclear Organometallic Oxides

### A. Open-Chain Structures

A trinuclear aluminum−oxygen chain is present in Mes*(Et)Al−O−Al(Mes*)−O−Al(Et)$_2$, but the compound dimerizes to a ladder-like hexanuclear structure (Scheme 19) that is induced by the O → Al donor−acceptor bonds with Al−O distances of 1.762−1.901 Å.[80]

The organotin trinuclear oxides of the type $R_3SnOSnR_2OSnR_3$ are not well-known. However, the $\alpha,\omega$-difunctional tin derivatives, $XR_2SnOSnR_2OSnR_2X$ ($X$ = azido[81] and carboxylato[82]), are known to dimerize into supramolecular ladder structures through four interchain tin−oxygen bonds (Scheme 20).

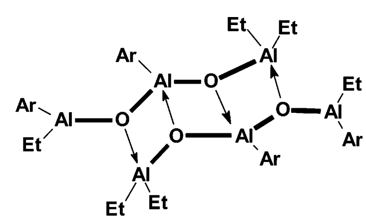
The crystal structure of a linear organometallic oxide, $ClCp_2Ti$−O−TiCp(Cl)−O−$TiCp_2Cl$ (Scheme 21), displays two sets of Ti−O bonds with the distances of 1.869 and 1.880 Å to terminal Ti atoms and 1.759 and 1.769 Å to the central Ti atom. Two different Ti−O−Ti bond angles of 162.0° and 176.1° and a rather small O−Ti−O bond angle of 107.0° in the center of the chain were also observed in the structure.[83]

### B. Cyclic Structures

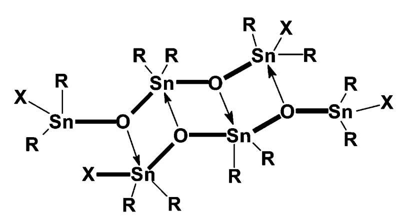
Several six-membered organometallic oxide rings with some variations in the structural details have been well established. The simplest ones are monocyclic species with three metal atoms and three $\mu$-oxo bridges. These include several main group and transition metal derivatives.

Diorganotin oxides or diorganostannoxanes, $R_2SnO$, are insoluble polymeric materials containing five-coordinated tin, as confirmed by their $^{119}$Sn

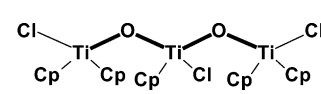
**Scheme 19**



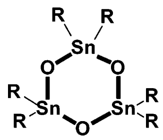
**Scheme 20**



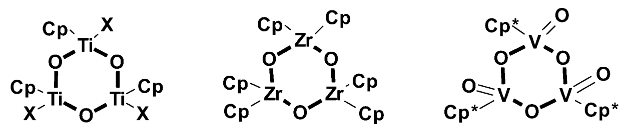

**Scheme 21**



**Scheme 22**



**Scheme 23**



**Cp = $C_5H_5$, $C_5Me_5$, $C_5H_4Me$, $C_5HMe_4$, X = Cl, Br, Me, $CH_2CHCHMe$**

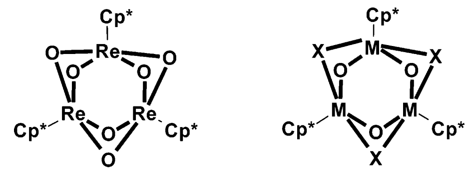
Mössbauer[84] and $^{119}$Sn MAS NMR[85] spectral data; but those with bulky substituents are cyclic trimers. For example, the hexaorganocyclotristannoxanes, $[R_2SnO]_3$, contain an almost planar $Sn_3O_3$ ring (Scheme 22). Several representatives of this class of organometallic oxides are known, and they have been structurally characterized. These include derivatives where R = *t*-Bu,[86,87] $CMe_2Et$,[87] 2,6-$Me_2C_6H_3$,[88] 2,6-$Et_2C_6H_3$,[89] 2,4,6-*i*-$Pr_3C_6H_2$,[90,91] or 2,4,6-$(CF_3)_3C_6H_2$,[92] $CH_2SiMe_3$[93] and $R_2$ = $[C(SiMe_3)_3](Me)$,[94] $[C(SiMe_3)_3](Cl)$, or $[C(SiMe_3)_3](OH)$.[95] The Sn−O distances in these species are short (1.96 Å), and the O−Sn−O bond angles are smaller (103−107°) for the tetrahedral arrangement. The Sn−O−Sn bond angles are close to 120° in one derivative, namely, $[(2,6\text{-}Me_2C_6H_3)_2SnO]_3$, but significantly vary from this value (133−136°) in the other species. The cyclotristannoxanes are reactive compounds and their chemistry is mostly of various redistribution reaction, leading to fascinating structures comprising $R_2SnO$ units.[96]

Among the transition metal derivatives, titanium is best represented by organocyclotrititanoxanes, $[CpTiMe(\mu\text{-}O)]_3$[97,98] and $[Cp^*(CH_2CH{=}CHMe)Ti(\mu\text{-}O)]_3$,[99] and its halogenated derivatives, $[(C_5H_4Me)TiCl(\mu\text{-}O)]_3$[100] and $[Cp^*TiX(\mu\text{-}O)]_3$ (X = Cl,[56,101−104] Br[105]). A zirconium derivative, $[Cp_2Zr(\mu\text{-}O)]_3$, is also known.[106] A similar cyclic structure with a trans conformation has been proposed for a vanadium compound. On the basis of osmometric molecular weight measurements and mass, NMR, and IR spectroscopic data, the organocyclotrivandoxane was formulated to be $[Cp^*V(O)(\mu\text{-}O)]_3$, but no X-ray data could be obtained to confirm the formulation.[107] Nonetheless, the $Ti_3O_3$ and $Zr_3O_3$ rings in the corresponding organometallic oxide ring structures are planar (Scheme 23).

Trimeric organometallic oxides with double oxo bridges (Scheme 24) between the metal atoms are also reported. In $[Cp^*Re(\mu\text{-}O)_2]_3$[108] and cyclotrimetalloxanes, of the type $[Cp^*M(\mu\text{-}O)(\mu\text{-}X)]_3$, additional halogen bridges can be found between the metal atoms (M = Nb, X = Cl).[109] In the latter species, all three oxygen atoms are on one side of the $Nb_3$ plane and all three chlorine atoms on the other side so that the $Nb_3O_3$ ring skeleton is nonplanar.

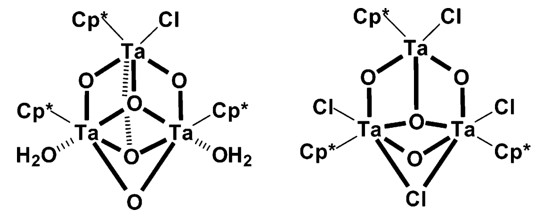
A planar $Ta_3O_3$ ring, capped above and below by the two additional tricoordinated oxygen atoms (Scheme 25) has been found in the cation of a salt,

**Scheme 24**



**M = Nb, X = Cl**
**M = W, X = F**

**Scheme 25**



$[\{Cp^*Ta(\mu\text{-}O)\}_3(\mu_3\text{-}O)_2(Cl)(H_2O)_2]^+Cl^-$. A related structure was observed for $[Cp^*TaCl(\mu\text{-}O)]_3(\mu\text{-}O)(\mu\text{-}Cl)$ in which an oxygen-centered six-membered $Ta_3(\mu\text{-}O)_3$ ring and an additional $\mu$-chloro bridge form the $Cp^*_3Ta_3O_4Cl_4$ cluster core. The $Ta_3O_2$ fragment is essentially planar, with the other two oxygens and the bridging chlorine lying out of plane.[53, 110]

A unique $Ti_3O_3$ ring framework with a $\mu_3$-CR triple bridge between the titanium atoms has been found in the structure of $[Cp^*Ti(\mu\text{-}O)]_3(\mu_3\text{-}CR)$ (R = H, Me). The formation of such compounds is of interest with respect to understanding of the interaction between metal oxide surfaces and hydrocarbon compounds during catalysis.[111] The hydrolysis of $Cp^*MoMe_4$ leads to the trinuclear cluster, $Cp^*_3Mo_3(\mu\text{-}O)_2(\mu\text{-}CH_2)(\mu_3\text{-}CH)$, with ox*o*-methylidene and methylidyne groups, and is a rare example of compounds for use in catalysis on metal oxide surfaces.[77]

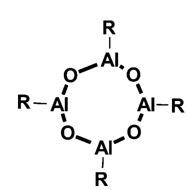
## VI. Tetranuclear, Cyclic Organometallic Oxides

### A. Monocyclic Structures

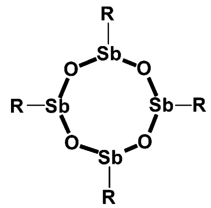
Apparently, only one cyclic monoorganoaluminum oxide is known (Scheme 26), the $[RAlO]_4$ tetramer with R = 2,4,6-*t*-$Bu_3C_6H_2$, and all other species are cage compounds (vide infra). The compound contains a planar $Al_4O_4$ ring with Al−O bond lengths in the range of 1.687−1.691 Å, and the pertinent bond angles are O−Al−O = 117.92° and 119.85° and Al−O−Al = 150.51° and 151.32°. However, the planarity of eight-membered rings is a rare structural feature.[80]

The monoorganoantimony oxides, RSbO, are believed to be polymeric materials (amorphous and insoluble), but with bulky organic groups distinct molecular species can be obtained. Thus, a cyclic $[(Me_3Si)_2CHSbO]_4$ tetramer was confirmed by an X-ray diffraction study (Scheme 27).

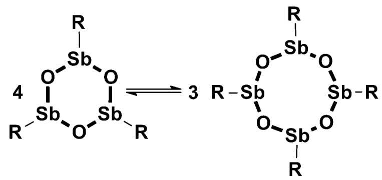
**Scheme 26**



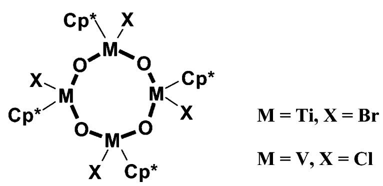
**Scheme 27**




**Scheme 28**




**Scheme 29**




The eight-membered $Sb_4O_4$ ring core is also a part of the structure of valentinite mineral, $Sb_2O_3$, which is a double-chain (tape-like) polymer. The $Sb_4O_4$ ring is boat-shaped and the substituents are in trans positions.[112] The *tert*-butyl derivative, *t*-BuSbO, could be obtained only as an equilibrium mixture of cyclic $[t\text{-BuSbO}]_n$ ($n = 3$ and 4) tri- and tetramers (Scheme 28).[113]

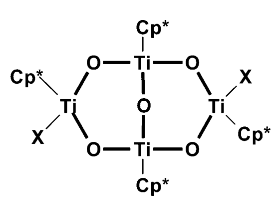
There are several transition metal organometallic oxides containig $M_4O_4$ rings (Scheme 29). They are mostly titanium derivatives of the types, $[CpTiCl(\mu\text{-}O)]_4$,[114] $[CpTi(OAr)(\mu\text{-}O)]_4$,[115] (Ar = 2,4,6-$Me_3C_6H_2$), $[(C_5H_4Me)TiCl(\mu\text{-}O)]_4$,[116] $[C_5HMe_4TiCl(\mu\text{-}O)]_4$,[56] $[C_5HMe_4TiBr(\mu\text{-}O)]_4$,[105] $[Cp^*TiBr(\mu\text{-}O)]_4\cdot CHCl_3$,[117] $[(Me_3SiC_5H_4)Ti(NCS)(\mu\text{-}O)]_4$,[101] $[Cp^*TiEt(\mu\text{-}O)]_4$, $[Cp^*Ti(\mu\text{-}O)]_4F(\mu\text{-}FAlMe_3)_3$, $[Cp^*Ti(\mu\text{-}O)]_4F_3\{\mu\text{-}FAl(CH_2Ph)_3\}$,[118] and $[C_9H_7TiCl(\mu\text{-}O)]_4$,[119] ($C_9H_7$ = tetrahydroindenyl). Similarly, a vanadium compound, $[Cp^*VCl(\mu\text{-}O)]_4$,[120] has also been structurally characterized.

The $Cp^*Ta[Rh(COD)]_4(\mu_3\text{-}O)_4$ (COD = 1,5-cyclooctadiene) has a unique structure, in which a $Rh_4O_4$ ring is capped by a Cp*Ta moiety, that is similar to a crown-ether complexation.[121]

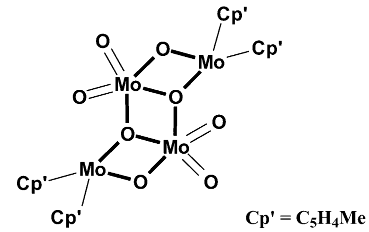
## B. Bicyclic Structures

Bicyclic tetranuclear metal oxides containing two fused six-membered $Ti_3O_3$ rings (Scheme 30) and a sharing Ti−O−Ti fragment are known for titanium metal. Structures of $(Cp^*Ti)_4F_2(\mu\text{-}O)_5$,[118] $(Cp^*Ti)_4Cl_2(\mu\text{-}O)_5$,[118,122] and $(Cp^*Ti)_4Me_2(\mu\text{-}O)_5$[123,124] have been reported.

**Scheme 30**




**Scheme 31**




## C. Tricyclic Structures

A ladder type tricyclic structure is found in molybdenum oxide compounds consisting of two $(C_5H_4R)_2$-Mo (R = H, Me) and two $MoO_2$ building units of composition $(C_5H_4R)_4Mo_4O_8$ (Scheme 31). These compounds contain a fragment of the $MoO_3$ layered structure and can be formulated as $[(C_5H_4R)_2Mo(MoO_2)(\mu_3\text{-}O)(\mu\text{-}O)]_2$. Only the methylcyclopentadienylmolybdenum compound, $(C_5H_4Me)_4Mo_4O_8$, has been structurally characterized by X-ray diffraction. The tungsten analogues $(C_5H_4R)_4W_4O_8$ (R = H, Me) are also known.[125]

## D. Adamantanes and Related Types

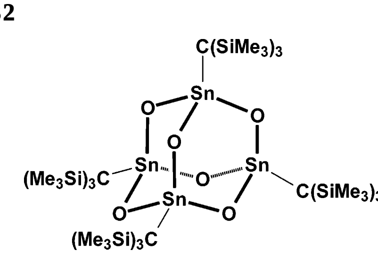
Adamantane structures are known for a large variety of inorganic and organometallic compounds.[126] Their backbone can be viewed as a fragment that is cut off from the wurtzite-type solid-state three-dimensional structures.

An organoaluminum adamantane cage is the mixed oxide−hydroxide $R_4Al_4(\mu\text{-}O)_2(\mu\text{-}OH)_4$ (R = $C(SiMe_3)_3$) core. A similar gallium-based oxide−hydroxide $R_4Ga_4(\mu\text{-}O)_2(\mu\text{-}OH)_4$ (R = $C(SiMe_3)_3$) has been structurally characterized.[127] Monoorganotin oxides with very bulky substituents such as $(RSn)_4O_6$, (R = $C(SiMe_3)_3$) can also adopt adamantane structures (Scheme 32).[128] The Sn−O bonds in these oxides are rather short (1.968 Å). The bond angles are Sn−O−Sn = 120.0° and O−Sn−O = 103.8°, and these are similar to the values found in some monocyclic tristannoxanes $(R_2SnO)_3$ (vide supra).

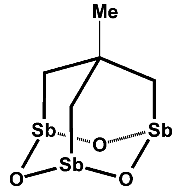
The inorganic oxide, $Sb_4O_6$ (senarmontit mineral) is a molecular compound displaying an adamantane-type structure. The cage compound $MeC(CH_2SbO)_3$ maintains the six-membered $Sb_3O_3$ ring (chair-shaped) in another adamantane structure in which the rest of the core is made of carbon atoms (Scheme 33).[129]

Some of the known transition metal organometallic oxides of an adamantane structure backbone (Scheme 34) include the derivatives of titanium, $(Cp^*Ti)_4(\mu\text{-}$

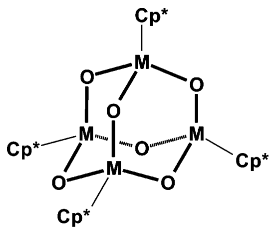
**Scheme 32**



**Scheme 33**

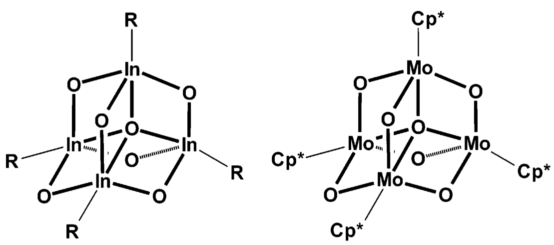



**Scheme 34**

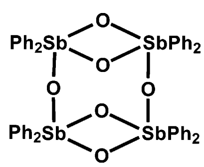



M = Ti, V

**Scheme 35**




**Scheme 36**

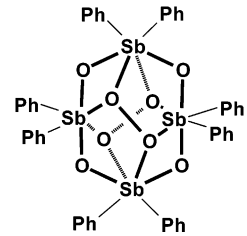



$O)_6$,[122,130] and vanadium, $(Cp^*V)_4(\mu\text{-}O)_6$.[131,132] The electronic structure of $(Cp^*V)_4(\mu\text{-}O)_6$ has been analyzed by using the extended Hückel MO calculations in order to explain its paramagnetism.[133]

Oxygen-centered organometallic adamantanes are also known (Scheme 35). They are formed around a four-coordinate oxygen atom in a tetrahedron with each vertex occupied by metal atoms. This type of geometry was found in organoindium hydroxo complex $(RIn)_4(\mu_4\text{-}O)(\mu\text{-}OH)_6$ ($R = CH(SiMe_3)_2$).[134] The organomolybdenum compound, $(Cp^*Mo)_4O_7$, also possesses an oxygen-centered structure comprising a tetrahedral $M_4O_6(\mu_3\text{-}O)$ core that can be formulated as $(Cp^*Mo)_4(\mu_3\text{-}O)(\mu\text{-}O)_6$.

An $M_4O_6$ molecular core is similar to that of the adamantanes but results in a different structure. Thus, $Ph_8Sb_4O_6$ is a polycyclic molecule, on the basis of five-coordinated, antimony coordination centers in a distorted trigonal bipyramid (Scheme 36). The phenyl groups are in equatorial positions; the Sb−O interatomic distances cover a broad range, from 1.881(12) to 2.273(11) Å, with longer bonds to the atoms at the axial positions.[67] A similar structure was recently observed for $(o\text{-}MeC_6H_4)_8Sb_4O_6$.[68] An identical $Sb_4O_6$ nonadamantane core is also found in $[(Ph_8Sb_4O_6)(AcOH)_2]\cdot AcOH\cdot CH_2Cl_2$ (Ac = MeCOO).[136] A somewhat similar tetranuclear phenyl-substituted organoantimony oxide−peroxide, $(R_2Sb)_4(\mu\text{-}O)_4(\mu\text{-}O_2)_2$, has been structurally characterized (Scheme 37).[49,137]

**Scheme 37**



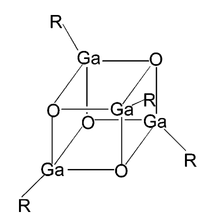

## E. Cubane Structures

An organogallium cubane, $[(t\text{-}Bu_3Si)GaO]_4$ (with Ga−Si bonds), has been reported (Scheme 38). The core is an essentially perfect cube with the O−Ga−O bond angles in the range of 89.5−90.2° and Ga−O−Ga bond angles of 89.7−90.5°. The Ga−O bond distances range from 1.902 to 1.928 Å.[138] A related indium cubane, $[(Me_3Si)_3CInO]_4$, is also known.[139]

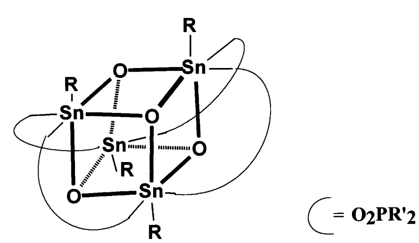
The organotin cubane clusters, based on a $Sn_4O_4$ core (Scheme 39), are found in tetrameric functionalized monoorganotin oxides, R(X)SnO, with X = phosphinato groups $O_2PR'_2$ (R′ = Cy, *t*-Bu, $CH_2Ph$).[140]

The $M_4O_4$ cubane core has been found in several organometallic oxides. Examples include the chromium compounds (Scheme 40) of the types $[CpCr(\mu_3\text{-}O)]_4$,[141,142] $[C_5H_4MeCr(\mu_3\text{-}O)]_4$,[143] and $[Cp^*Cr(\mu_3\text{-}O)]_4$[144] and the vanadium derivatives $[Cp^*V(\mu_3\text{-}O)]_4$.[132] Oxidation of the chromium cubane with $AgBF_4$ and 7,7,8,8-tetracyanoquinodimethane (TCNQ), respectively, gives $[(Cp^*Cr)_4(\mu_3\text{-}O)_4][BF_4]$ and $[(Cp^*Cr)_4(\mu_3\text{-}O)_4](TCNQ)$, both displaying antiferromagnetic properties.[145] Detailed spectroscopic and theoretical studies

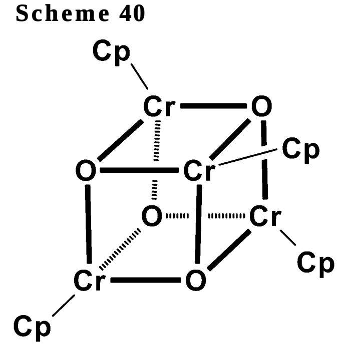
**Scheme 38**




**Scheme 39**

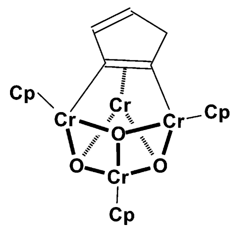



**Scheme 40**

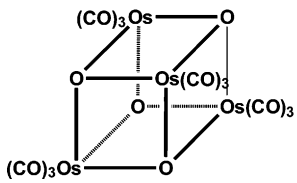



Cp = $C_5H_5$ or $C_5Me_5$

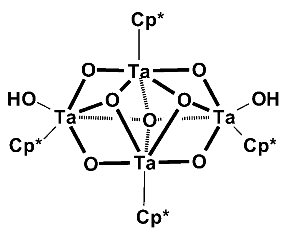
**Scheme 41**




**Scheme 42**




**Scheme 43**




were performed in order to investigate the magnetic and other physical properties of these compounds.[146,147]

Formal replacement of an oxygen in the corner of the $Cr_4O_4$ cube by a cyclopentadienyl group results in an unprecedented, bowl-shaped $Cr_4O_3$ core (Scheme 41), containing three $Cr_2O_2$ fused rings to form the $(\eta^2\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)_4Cr_4O_3$ cluster.[148] One of the Cp groups in Scheme 41 has been omitted for clarity.

The formation of a unique osmium carbonyl oxide, $[Os(CO)_3(\mu_3\text{-}O)]_4$,[149] (Scheme 42) suggests that the cubane structures are not limited to early transition metalcyclopentadienyls and, therefore, further developments can be expected in this area.

## F. Other Types

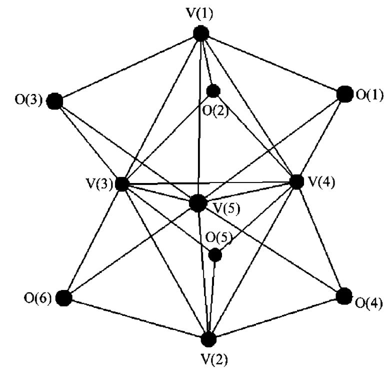
The $(Cp^*Ta)_4(\mu_4\text{-}O)(\mu_3\text{-}O)_2(\mu\text{-}O)_4(OH)_2$ cluster displays a unique structure with the doubly, triply, and quadruply connected oxygen sites in an unusual butterfly geometry at the $\mu_4$-O site (Scheme 43). There are two short Ta−O distances (equatorial 2.103 Å and 2.128 Å) and two long Ta−O distances (axial 2.358 Å) in an apparent distorted trigonal bipyramidal geometry of the metal atoms.[150]

## VII. Pentanuclear Organometallic Oxides

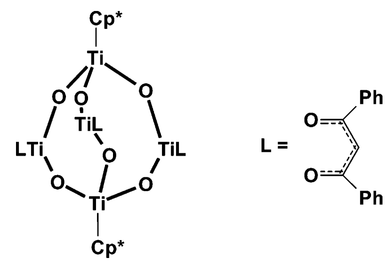
A pentanuclear vanadium species, $(CpV)_5(\mu_3\text{-}O)_6$, contains a cage which can be described as a trigonal bipyramid of vanadium atoms with tricoordinate oxgen atoms located above each face (Scheme 44), or better viewed as a polycyclic system made of fused four-membered $V_2O_2$ rings. There are two sets of V−O bonds: six $V_{ax}$−O = average 1.861 Å and 12 $V_{eq}$−O bonds of each average 1.992 Å.[148,151]

A totally different structure is found in the pentanuclear complex, $(Cp^*Ti)_2\{(Phacac)_2Ti\}_3(\mu\text{-}O)_6$ (Phacac = 1,3-diphenyl-1,3-diketonato).[152] The five titanium

**Scheme 44**




**Scheme 45**




atoms form a trigonal bipyramid with the Cp*Ti units in axial positions and $(Phacac)_2Ti$ units in equatorial positions, and the entire cluster can be described as a bicyclic (Scheme 45) ring. The Ti−O bonds are shorter in the $Ti_5O_6$ cage (1.806−1.829 Å) than the exohedral Ti−O bonds in the $TiO_2C_3$ chelate rings (1.98−2.10 Å).

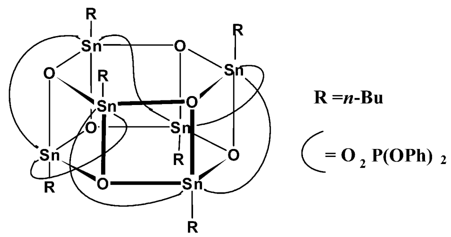
## VIII. Hexanuclear Organometallic Oxides

The most common structural features of organoalumoxanes are cage-like, and these include not only hexanuclear $[RAl(\mu_3\text{-}O)]_6$ core, but also larger cage $[RAlO]_n$, with $n$ = 7, 8, and 9 (R = *t*-Bu) oligomers.[153] In addition to tetranuclear $R_7Al_4O_2(OH)$ and pentanuclear $R_7Al_5O_3(OH)_2$,[154] and $R_6Al_6O_4(OH)_4$ (R = *t*-Bu),[155] several oxide−hydroxide alumoxanes, such as $R_8Al_6O_4(OH)_2$ have also been structurally characterized. The reactions of $[MeAl(\mu_3\text{-}O)]_n$ with $AlMe_3$ form larger Al cages, up to $Me_{15}Al_9O_6$ and $Me_{18}Al_{12}O_9$.[156] The $[t\text{-}BuAlO]_6$ hexamer reacts with $AlMe_3$ to form $Me_3(t\text{-}Bu)_6Al_7O_6$ by breaking one of the Al−O bonds and then coordinating to $AlMe_3$ at the newly created vacant site.[157] It has been suggested that the interaction of $[RAlO]_n$ with $Cp_2ZrMe_2$, in MAO-activated catalytic processes of olefin polymerization, involves the coordination of a methyl group to the alumoxane cage.[158] Organogallium compounds, similar to those of aluminum, such as $[Mes_6Ga_6(\mu\text{-}O)_4(\mu_3\text{-}OH)_4\cdot 4THF]\cdot 6THF$ (Mes = mesityl), are also known.[159]

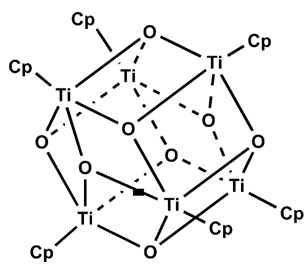
Some functionalized monorganotin oxides, RXSnO, with X = carboxylato or organophosphato groups have also been characterized.[82,160] These contain hexagonal prismatic $Sn_6O_6$ cages, as molecular cores, with functional groups bridging the tin atoms across the $Sn_2O_2$ four-membered ring subunits (Scheme 46).

The organometallic oxides of transition metals are, as a rule, cage-like molecules. A hexanuclear mixed

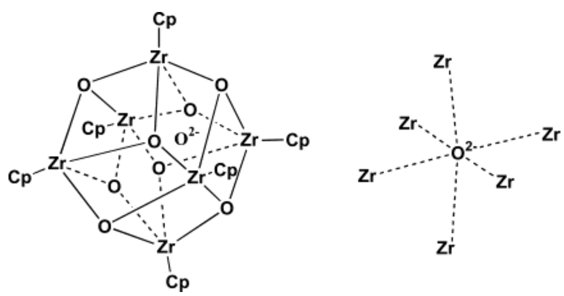
**Scheme 46**




**Scheme 47**



**Scheme 48**



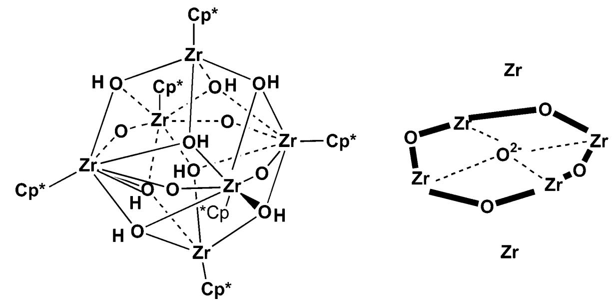
oxide, $(CpTi)_6(\mu_3\text{-}O)_8$, is of a $Ti_6$ pseudo-octahedral arrangement (Scheme 47) with eight $\mu_3$-oxygen atoms capping the triangular faces of the octahedron.[161]

Substituted cyclopentadienyl derivatives have also been reported. In these compounds, oxygen can be partly replaced by chlorine atoms as in $(C_5H_4MeTi)_6O_4Cl_4$ and $(CpTi)_6O_6Cl_2$.[162] Apparently, the $Ti_6O_8$ cage in $(CpTi)_6(\mu_3\text{-}O)_8$ contains Ti−Ti bonds, since the interatomic Ti−Ti distance of average 2.891 Å is comparable with that in metallic α-titanium (2.951 Å). Titanium clusters can be used for epoxidation reactions.[163] The hexanuclear mixed oxide−sulfide, $(CpTi)_6(\mu_3\text{-}O)_4(\mu_3\text{-}S)_4$, is an analogue of the former Ti compound, in which four $\mu_3$-oxygens were replaced by $\mu_3$-sulfur atoms in alternative triangular faces of the octahedron.[164]

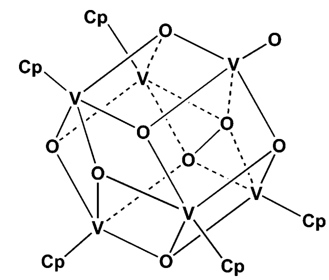
In the hexanuclear toluene and mesitylene solvated, compounds $(C_5Me_4Et)_6Zr_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8$, the metal atoms form an octahedron capping the triangular faces by triply bridging oxygen atoms ($\mu_3$-O). In addition, a central $\mu_6{-}O^{2-}$ ion is encapsulated within the cage (Scheme 48). The structure can be described as an assembly of 12 fused $Zr_2O_2$ rings. The Zr−($\mu_6$-O) distances (2.231−2.247 Å, average 2.241 Å) are longer than Zr−($\mu_3$-O) distances (2.136−2.169 Å, average 2.156 Å) in the toluene solvate. The bond angles in the four-membered rings are O−Zr−O = 81.34° and Zr−O−Zr = 94.65°. Similar parameters were found for the core structure of the mesitylene solvate of the hexanuclear zirconium cluster.[165]

Another example of a hexanuclear cluster, $(Cp^*Zr)_6(\mu_4\text{-}O)(\mu\text{-}O)_4(\mu\text{-}OH)_8$, also contains a $Zr_6$ octahedron,

**Scheme 49**



**Scheme 50**



with statistically distributed $\mu$-O or $\mu$-OH bridges on the edges, resulting in an assembly of 8 $Zr_3O_3$ rings on the edges. A planar $Zr_4O_4$ ring in the equatorial plane of this cluster can also be visualized in Scheme 49.[166]

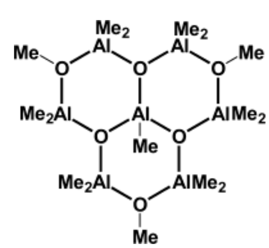
In $(CpV)_5(VO)(\mu_3\text{-}O)_8$, five vanadium atoms bear a cyclopentadienyl ligand, while the sixth has a terminal V═O bond (Scheme 50). The core of this compound is a polyhedral cage made of fused four-membered $V_2O_2$ rings. Two such cages can be connected through a $\mu$-O bridge to form a dodecanuclear complex $[(Cp_5V_6(\mu_3\text{-}O)_8]_2(\mu\text{-}O)$.[167]

The hexanuclear compound $Cp^*_2W_6O_{17}$ is a neutral analogue of the $W_6O_{19}^{2-}$ anion in which two oxygen sites ($O^{2-}$) have been replaced by two pentamethylcyclopentadienyl (Cp*) groups. The compound contains a central $\mu_6$-O atom with all other 16 being $\mu$-O bridging oxygens. The W−($\mu_6$−O) distances display three different magnitudes: 2.204 (to WCp*), 2.355, and 2.502 Å.[168]

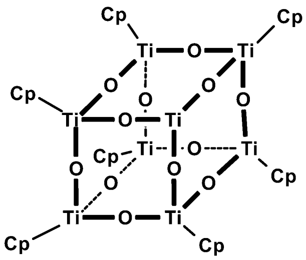
## IX. Larger Cage Organometallic Oxides

Some larger aluminum−oxygen cages have been described above. The X-ray crystal structure of $[t\text{-}BuAlO]_9$ has been determined, but suitable crystals of $[t\text{-}BuAlO]_8$ for X-ray analysis could not be obtained.[35] A tricyclic, noncage cluster of a seven metal atom alumoxane (Scheme 51), namely, the $[Me_{16}Al_7O_6]^-$ anion, was one of the first structurally characterized methylalumoxane compounds[169] and

**Scheme 51**



**Scheme 52**



has the formula $[(Me_2Al)_6(MeAl)(\mu_3\text{-}O)_3(\mu\text{-}OMe)_3]^-$. This illustrates the dramatic structural changes produced when $R_2Al$ groups are incorporated.

An octanuclear compound, $(CpTi)_8(\mu\text{-}O)_{12}$, contains a $Ti_8O_{12}$ cubane skeleton (Scheme 52). In the acetonitrile solvate, $(CpTi)_8(\mu\text{-}O)_{12}\cdot 6MeCN$, the Ti−O distances average 1.805 Å (range 1.795−1.81.8 Å) and two pairs of the bridging Ti−O−Ti bond angles (147.9° and 148.6°) differ from the other eight Ti−O−Ti bridge angles, which are larger (range 162.9° to 163.9°). A similar structural feature was found for $(CpTi)_8(\mu\text{-}O)_{12}\cdot NEt_3\cdot THF\cdot(CpTi)_4(\mu\text{-}Se)_3(\mu_3\text{-}Se)_3$.[170]

The octanuclear compound $Cp^*_6Mo_8O_{16}$ contains two $Mo_3O_6$ units (three Mo−Mo bonds, 2.74 Å; three $\mu$-O and three $\mu_3$-O atoms) connected by a $Mo^V(O)(\mu\text{-}O)_2Mo^V(O)$ unit. The Mo−O bonds cover a broad range of interatomic distances and can be grouped into several sets: 1.691(3) Å (exohedral, terminal Mo═O bonds); 1.949(2) Å (in the $Mo^V$-O−$Mo^V$ bridge); 1.940(2)−1.958(2) Å (to $\mu_3$-O in the $Mo_3O_6$ units); 2.021(2)−2.041(2) Å (to $\mu$-O in the $Mo_3O_6$ units); 2.137(2)−2.260(2) Å (from bridge Mo atoms to $\mu_3$-O of the $Mo_3O_6$ units).[168]

Three different possible structures have been suggested for the octanuclear compound $Cp^*_6V_8O_{17}$, but no X-ray structural data are available for this compound.[133a] In $Cp_{10}V_{12}O_{17}$ cluster, two $V_6(\mu_3\text{-}O)_8$ cuboctahedra are linked by an oxygen bridge.[167]

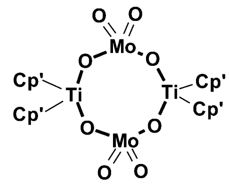
Organogallium oxides tend to form large clusters, such as the $[MesGaO]_9$ (Mes = mesityl) nonamer.[171] Dodecanuclear clusters have been reported for gallium oxide−hydroxides, an example of such cluster is found in $(t\text{-}BuGa)_{12}(\mu_3\text{-}O)_8(\mu\text{-}OH)_4$.[155] Large tin−oxygen clusters with quasi-spherical cage structures form due to incomplete hydrolysis and condensation of monoorganotin halides and they have been structurally characterized. Examples include $(i\text{-}PrSn)_9(\mu_3\text{-}O)_8(\mu\text{-}OH)_6Cl_5\cdot 6DMSO$,[172] $(i\text{-}PrSn)_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}OH)_6Cl_2\cdot L$ (L = $3H_2O$, $4H_2O$ or 2DMF), $(n\text{-}BuSn)_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}OH)_6Cl_2\cdot 2H_2O$, and $[(n\text{-}BuSn)_{12}(\mu\text{-}O)_{14}(\mu\text{-}OH)_6](OH)_2$.[173]

## X. Heterobimetallic Oxides

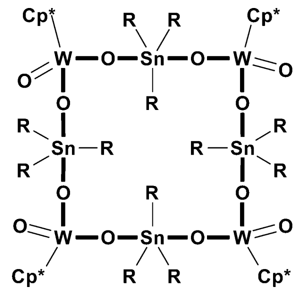
Few organometallic oxides containing two different metals have been reported, but the known examples suggest that a vast area of research on this subject could be explored.

Several organometallic oxides, including dinuclear $Cp^*(O)_2W{-}O{-}MCp_2$ (M = Ti, Zr), and trinuclear $\{Cp^*(O)_2W{-}O\}_2MCp_2$ (M = Ti, Zr) have been prepared, but only $\{Cp^*(O)_2W{-}O\}_2ZrCp_2$ has been characterized by X-ray diffraction. Cyclic tetranuclear

**Scheme 53**



**Scheme 54**



R = Me

$[Cp_2Ti{-}O{-}WCp^*(O)\text{-}O]_2$ and $[(C_5H_4Me)_2Ti(\mu\text{-}MoO_4)]_2$ (Scheme 53) are also known. The eight-membered monocyclic compound $[(C_5H_4Me)_2Ti(\mu\text{-}MoO_4)]_2$ contains four coplanar metal atoms, with the connecting oxygens located above and below the plane. The Mo−O bonds in the ring are relatively short (1.805, 1.803 Å), suggesting that some double bond character exists in the molecule, while the Ti−O bonds are longer than usual, i.e., 1.933 and 1.936 Å. The terminal Mo═O bonds are still shorter, with the distances of 1.711 and 1.702 Å. The bond angles in the ring are rather irregular, smaller at the metal and very large at oxygen, as O−Mo−O = 114.5°, O−Ti−O = 95.9°, and Ti−O−Mo = 155.7°; the exocyclic O═Mo═O angle is 106.2°. The $Mo_2Ti_2O_4$ ring is nearly planar. In the crystal lattice, the $[(C_5H_4Me)_2Ti(\mu\text{-}MoO_4)]_2$ molecules are self-assembled into supramolecular chains through Mo═O···Mo intermolecular contacts (Mo···O 3.307 Å).[174]

A macrocylic, 16-membered ring compound, $[Me_3Sn{-}O{-}W(O)Cp^*\text{-}O]_4$, has been reported and its structure determined by X-ray diffraction (Scheme 54). The bond angles in this macrocycle are nearly linear about the tin (axial bonds in a trigonal bipyramidal geometry, average 178.0°), slightly smaller than tetrahedral geometry of tungsten (average 105.3°) and also large and irregular around the oxygen atom (Sn−O−W angle range 139.7−155.4°).[175] An almost linear dinuclear compound $Cp(CO)_3W{-}O{-}ZrCp_2Cl$ (W−O−Zr 175.7°; W−O 2.065 Å, Zr−O 1.871 Å) has also been reported.[176] The $[(Me)Cp_2ZrOAlMe_2]_2$ dimer contains a $[Me_2AlO]_2$ ring with $Cp_2ZrMe$ groups coordinated to the oxygens.[177]

Other heterobimetallic compounds of complex structures include the triple cubane-type compound, $[Cp^*RhMoO_4]_4$,[178] the trishomocubane oxide−methoxide cluster derivative, $(Cp^*Rh)_2Mo_3O_9(OMe)_4\cdot MeOH$, a linear quadruple cubane derivative, $(Cp^*Rh)_4Mo_6O_{22}\cdot 4CH_2Cl_2$,[179] a quadruple-cubane type structure of $(Cp^*M)_4V_6O_{19}$, (M = Rh, Ir),[180] and the complex salt $[N(n\text{-}Bu)_4]_2[\{Cp^*Rh)_2Mo_6O_{20}(OMe)_2]$.[181] All these structures suggest a possible continuous transition from organometallic oxides to traditional polyoxo species.[182]

Organometallic oxide with $\eta^6$-arene moieties are extremely rare. The two known examples, $\{(\eta^6\text{-}p\text{-}i\text{-}PrC_6H_4Me)Ru\}_4Mo_4O_{16}$[183] and $\{(\eta^6\text{-}p\text{-}i\text{-}PrC_6H_4Me)Ru\}_4W_2O_{10}$, contain a core of two fused cubane units.[184]

Organotin vanadates (mixed oxides), $[Me_3SnVO_3]_x$ and $[(Me_2Sn)_4V_2O_9]_x$, are three-dimensional polymers whose building blocks are related to the molecular organotin oxide species discussed above.[185] A polymeric, chainlike bimetallic oxide, $[Me_3Sn{-}O{-}ReO_2(\mu\text{-}O)]_x$, contains linear O−Sn−O fragments with the chains bent at rhenium and oxygen.[186] Other mixed organotin metal oxides include $[(ReO_4)Ph_2SnOSnPh_2OH]_2$ (ladder tricyclic supermolecule),[187] $[Me_3SnTcO_4]_x$ (1D chain polymer),[188] $[(Me_3Sn)_3CrO_4(OH)]_x$ (3D polymer),[189] $[Me_2SnMoO_4]_x$ (3D polymer),[190] $[(Me_3Sn)_2MoO_4]_x$, $[(Me_3Pb)_2MoO_4]_x$, and $[(Me_3Sn)_2WO_4]_x$.[191] A five-coordinated tin derivative, $Cp_2Nb(Cl)(\mu\text{-}O)SnPh_2Cl_2$, that seems to contain a Nb═O double bond can be regarded as an adduct of $Cp_2Nb(Cl)({=}O)$ with dichlorodiphenyltin through O→Sn dative bond.[192]

## XI. Conclusions

Molecular organometallic oxides of great diverse compositions and structures are known, but the field is far from being overwhelmed. The structures of the metal−oxygen cores can be rationalized in geometric terms and can be deduced from regular polygons and polyhedra, in which the corners are occupied by metal atoms. Oxygen plays a structure directing role, as $\mu$-O (on the edges) and $\mu_3$-O (capping triangular faces) of polygons and polyhedra and thus produce open-chain (rarely), ring, and cage structures. An infinite number of novel species can be anticipated through simultaneous constructions of mixed species with $\mu$-O and $\mu_3$-O units. As a result, one can expect discoveries of new types of metal−oxygen cores in organometallic oxides. These systems have the potential to be important catalysts or cocatalysts for many chemical transformations as did the metallocenes and MAO during the past several decades. Finally, it should be noted some similarity between the fluorines and oxygens in their structure directing roles, in the construction of molecular and supramolecular architectures of organometallic fluorides and oxides.[193]

## XII. Acknowledgments

H.W.R. thanks the Deutsche Forschungsgemeinschaft and the Göttinger Akademie der Wissenschaften for financial support. I.H. and N.S.H. gratefully acknowledge the Research Awards for Senior Scientists by the Alexander von Humboldt Foundation.

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CR020376Q