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

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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

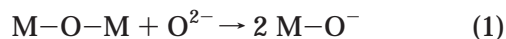
of organometallic oxides, stimulated by the remarkable properties of methylaluminum oxide (MAO) as activator for metallocene catalysts in olefin polymerization³ and the valuable catalytic properties of organorhenium oxides.⁴

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 OsO₄ and RuO₄ 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 Mn₂O₇, Tc₂O₇, tetranuclear cages (e.g., Sb₄O₆), cyclic trimers and tetramers (such as Mo₃O₉ and Mo₄O₁₂ in the vapor phase), and infinite polymeric structures, including monodimensional, single-chain oxides (e.g., HgO and CrO₃), double-chain oxides (e.g., Sb₂O₃), bidimensional layered oxides (e.g., PbO, SnO, MoO₃), and tridimensional network oxides with a broad diversity of typical structures, such as Al₂O₃ (corundum), TiO₂ (rutile), ReO₃ (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. Fischer⁷ 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:



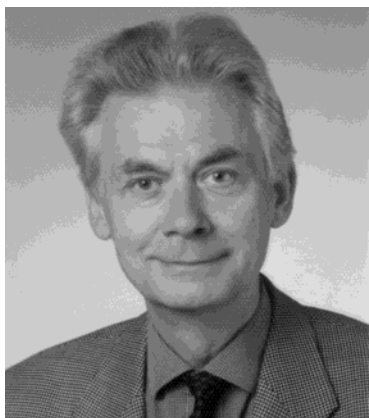
The result is the formation of polyoxometalate species, containing metal–oxygen cages of variable sizes and complexities, down to monometallic oxoanions, e.g., CrO₄^{2–} and MoO₄^{2–}.

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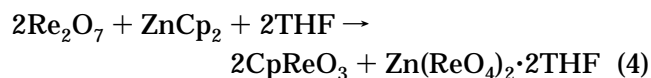
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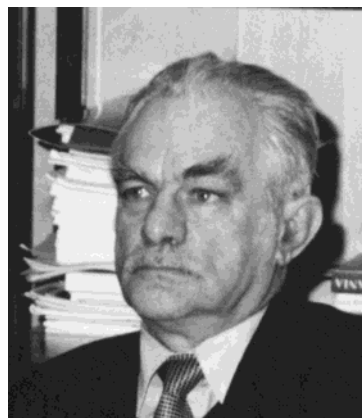
Professor Herbert W. Roesky was born in 1935 in Laukischken. He studied chemistry at the University of Göttingen, Germany, where he obtained his diploma in 1961 and doctoral degree in 1963. After one year of postdoctoral work at DuPont in Wilmington, DE, he made his habilitation at the University of 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.

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) ($\text{Cp} = \text{C}_5\text{H}_5$ or C_5Me_5), and with some organotin reagents^{4,9}



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



Ionel Haiduc is the coauthor of a recently published book, *Supramolecular Organometallic Chemistry* (with F. T. Edelman; 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 Autónoma de México (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 São 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).

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 species¹³ involving the intermediate steps of nucleation:

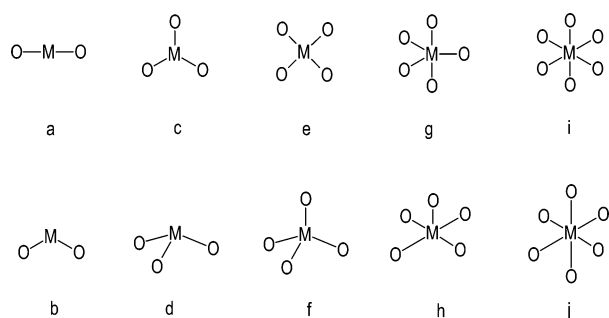


In pure inorganic systems, the process can be stopped at intermediate stages of small polyoxoanions, such as dichromate $\text{Cr}_2\text{O}_7^{2-}$ and higher polyoxochromates (with up to seven chromium atoms),¹⁴ polyoxomolybdates, $\text{Mo}_7\text{O}_{42}^{6-}$ oxoanions of intermediate size, such as $[\text{H}_{14}\text{Mo}_{37}\text{O}_{112}]$,^{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 $\text{R} = \text{C}_5\text{H}_4\text{R}'$ ($\text{R}' = \text{H, Me, Et, etc.}$), 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 $\text{M}-\text{O}-\text{M}$ arrangements and all can give rise to dinuclear organometallic oxides. The bent $\text{M}-\text{O}-\text{M}$ 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 $\text{M}-\text{O}-\text{M}$ bonds is important for the formation of cyclic molecular skeletons. In four-, six-, and eight-membered rings, the bent $\text{M}-\text{O}-\text{M}$ 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 $\text{M}-\text{O}-\text{M}$ 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 diaspor, $\text{AlO}(\text{OH})$, contains six coordinate aluminum, and Al_2O_3 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 $\text{M}-\text{O}$ bonds with $\text{M}-\text{C}$ 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.

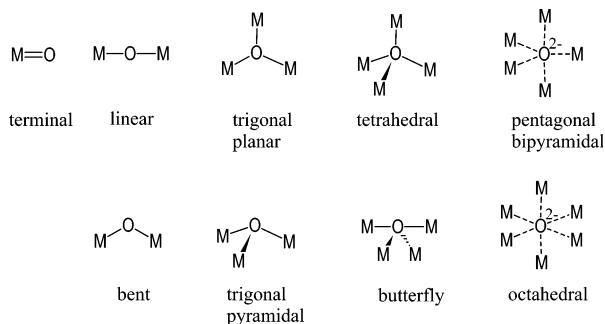
In the formation of the solid-state structures, the oxygen plays a structure-directive role.

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 $\text{M}=\text{O}$ 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).

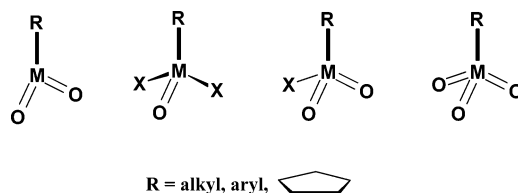
The presence of organic groups at some coordination sites reduces the metal's connectivity to lower numbers and results in a new coordination geometry. The η^5 -cyclopentadienyl ligand has been most frequently used, as it occupies three coordination sites when bound to a metal atom. Therefore this, an 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

Scheme 2



Scheme 3



functional group at the metal, such as $\text{RM}(\text{X})\text{O}_2$ moieties. The $\text{M}-\text{O}-\text{M}$ bond angles of less than 180° create curvatures and/or convexities. Thus, the RMO_x ($x = 1, 2, 3, \dots$) 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 $\text{M}-\text{O}-\text{M}$ bond angles that determine how the polyhedral units can be assembled into polynuclear structures.

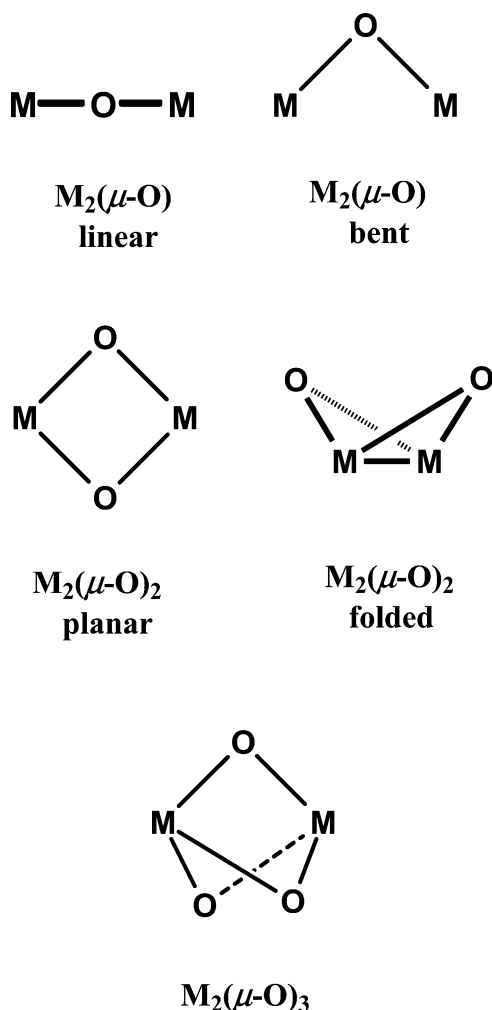
Since the $\text{M}-\text{O}-\text{M}$ bond angles are quite flexible, a great structural diversity is possible. Four-, six-, and eight-membered molecular oxide rings and cages derived from regular polyhedra (tetrahedron, trigonal bipyramid, octahedron as deltahedral polyhedra, cube, pentagonal, and 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 $\text{M}=\text{O}$ 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 $\text{O}_3\text{Re}-\text{O}-\text{ReO}_3$, and blocking the ReO_3 fragments with the methyl groups. Other examples are all well-known compounds with "piano-stool" structures as in $\text{Cp}^*\text{V}(\text{O})\text{Cl}_2$,²³ ($\text{Cp}^* = \text{C}_5\text{Me}_5$), $\text{CpMo}(\text{O})\text{Cl}_2$,²⁴ $\text{Cp}^*\text{Re}(\text{O})\text{Cl}_2$,²⁵ CpReO_3 ,²² $[\text{t-BuSiOReO}_4]_4$,²⁶ and in many other species (Scheme 3).

Breaking of $\mu\text{-O}$ 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 $\text{O} \rightarrow \text{M}$ donor acceptor bonds. Dinuclear types include linear and bent species based upon $\text{M}-\text{O}-\text{M}$ backbones, and cyclic species that result when two or three $\mu\text{-O}$ bridges connect two metal atoms (Scheme 4).

Scheme 4

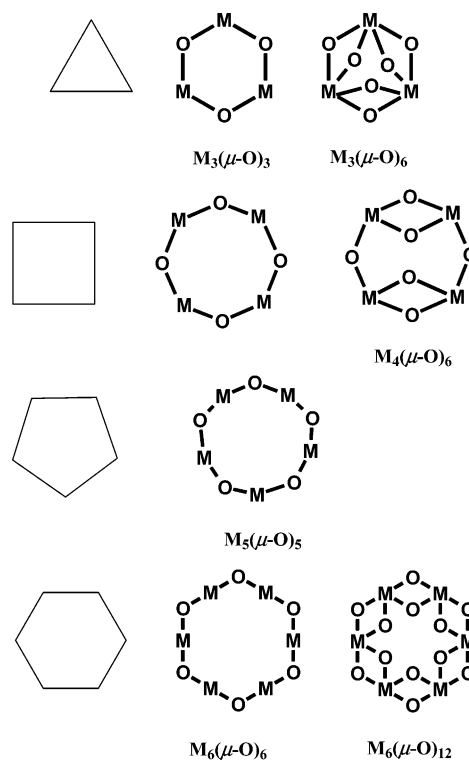


Cyclic structures can be derived from regular polygons with the corners occupied by the metal atoms of the organometallic moieties and the $\mu-O$ bridgings located on the edges (Scheme 5). These are described by the general formula, $[R_xM(\mu-O)]_n$, where R can be σ -alkyl/aryl, η^5 -cyclopentadienyl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

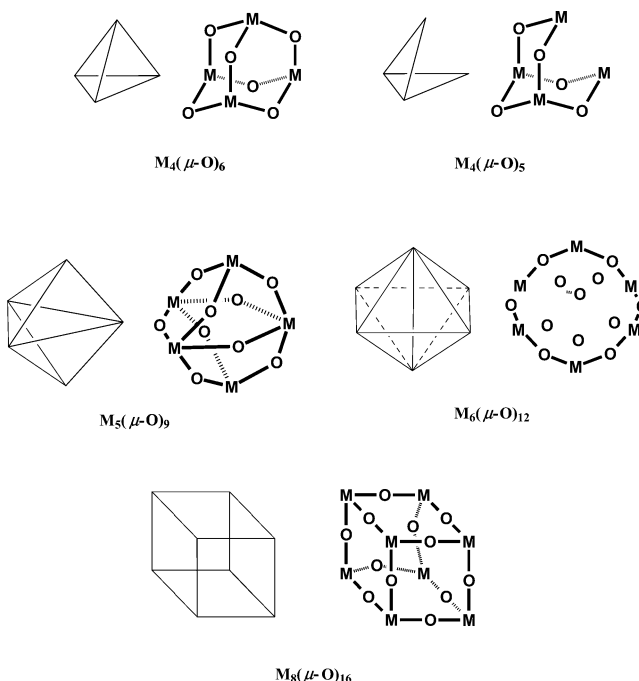
In a similar manner, polycyclic structures are derived from common regular polyhedra (tetrahedron, trigonal bipyramid, octahedron, cube, etc.) (Scheme 6). Such polymorphs require R_xMO_3 or R_xMO_4 moieties, and most of the structures illustrated in Scheme 6 have been exemplified in representative molecules 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 triconnected oxygen μ_3-O in a trigonal planar or pyramidal geometry can be found in μ_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 $Rh \cdots H \cdots Rh$ bridges is provided by the cation $[\{ Cp^*Rh(\mu-H) \}_3(\mu_3-O)]^+$. In the $Zr_3(\mu-OH)_3$ -based cyclic cation $[\{ Cp_2Zr(\mu-OH) \}_3(\mu_3-$

Scheme 5



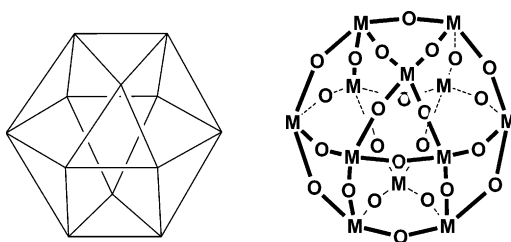
Scheme 6



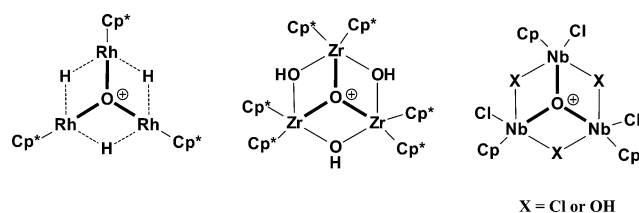
$O)]^+$, there is a trigonal planar tricoordinate oxygen,²⁷ and $[CpNbCl(\mu-X)]_3(\mu_3-O)(\mu_3-OH)$, $X = Cl, OH$, contains an Nb_3Cl_3 ring constructed around a trinuclear ONb_3 unit with a trigonal pyramidal, tricoordinate oxygen.²⁸ Related compounds are $(Cp^*ZrCl)_3(\mu-Cl)_4(\mu_3-O)$ (with trigonal pyramidal oxygen),²⁹ $(Cp^*MCl)_3(\mu_3-O)(\mu-OH)_3(\mu-Cl)$, $M = Nb, Ta$,³⁰ and $(CpMoCl)_3(\mu-Cl)_4(\mu_3-O)$.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

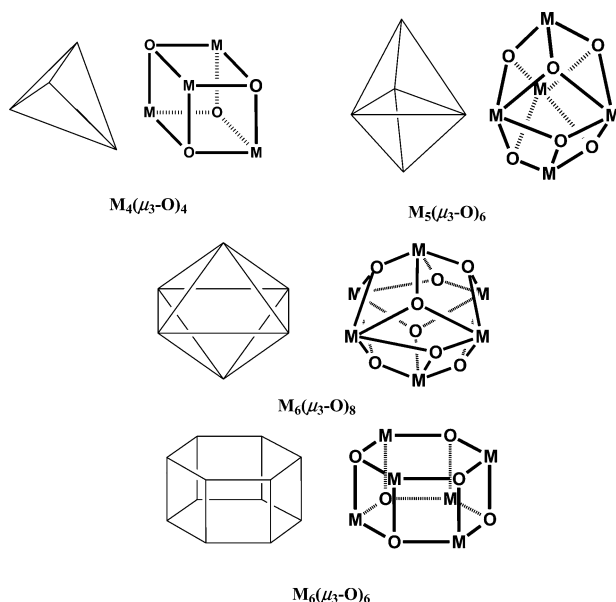
Scheme 7



Scheme 8



Scheme 9



result of a capping of the triangular faces of delta-hedral 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 $M_4(\mu_3-O)_4$ cubane structure and that of the trigonal bipyramid yield $M_5(\mu_3-O)_6$ cages, while capping of the six or eight faces of an octahedron results as $M_6(\mu_3-O)_6$ or $M_6(\mu_3-O)_8$ cage structures (Scheme 9). Like other cages, these structures require R_xMO_3 or R_xMO_4 building blocks.

The four-coordinate oxygen, μ_4-O , is rarely found in organometallic compounds, but one such example is $\{[CpTi]_4(\mu_4-O)\}(\mu-O)(\mu_3-S_2)_4$. 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

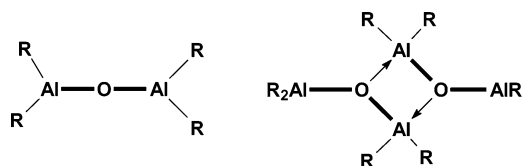
A. Open-Chain Structures

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 ^{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 $(t-Bu)_2Al-O-Al(t-Bu)_2$ that indicated a dimeric structure, with a planar Al_2O_2 ring and two $O-Al(t-Bu)_2$ 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 $(t-Bu)_2Al-O-Al(t-Bu)_2 \cdot 2Py$ 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 exocyclic), 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

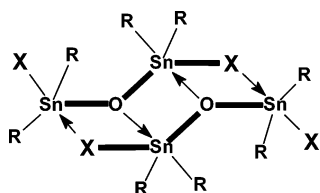
Bis(triorganotin) oxides, $R_3Sn-O-SnR_3$ ($R = \text{alkyl, aryl}$), are monomeric molecular compounds ($R = Me$, bent, $Sn-O-Sn = 140.1^\circ$, as determined by electron diffraction in the gas phase;³⁸ $R = t-Bu$,³⁹ CH_2Ph ,⁴⁰ $CH_2C_6H_4Me-2$, C_6H_4Me-2 ,⁴¹ all four are linear; $R = Ph$, bent, $Sn-O-Sn = 137.3^\circ$).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 $XR_2SnOSnR_2X$ ($X = \text{halogen, OH, OOCR, etc.}$) 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 years⁴⁴ and have been the subject of many reviews⁴⁵ and, therefore, will not be discussed further.

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

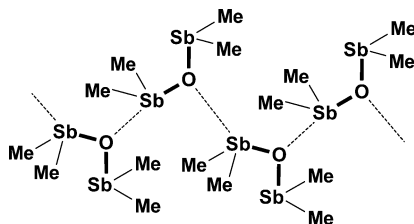
Scheme 10



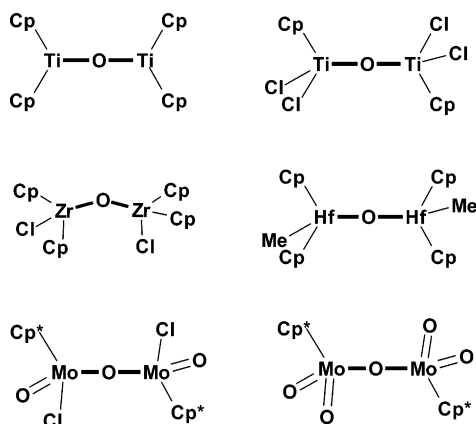
Scheme 11



Scheme 12



Scheme 13



O–SbPh₂ 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 R₂Sb–O–SbR₂, where R = Me,^{47,48} Ph, *o*-MeC₆H₄ and *p*-MeC₆H₄,⁴⁹ 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 Me₂Sb–O–SbMe₂ and valentinite, Sb₂O₃, showed that the Me₂Sb–O–SbMe₂ 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 Sb₂O₃ 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 Cp₂Ti–O–TiCp₂,⁵⁰ Cp*₂Sm–O–SmCp*₂,⁵¹ [Cp₂Lu(THF)]₂(μ-O),⁵² [(MeC₅H₄)₂NbCl]₂O,⁵³ [Cp*Me₂Ti]₂(μ-O),⁵⁴ and [Cp*TaMe₃]₂(μ-O)⁵⁵ (Scheme 13). The mixed oxide–halides of the type [Cp*TiCl₂]₂(μ-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*₂Sm–O–SmCp*₂,⁵¹ [Cp*TaMe₃]₂(μ-O) and [CpTiCl₂]₂(μ-O), while the bond angles are 170.9° in Cp₂Ti–O–TiCp₂,⁵⁰ 180° and 153.4° (two independent molecules) in [Cp*TiMe₂]₂(μ-O), 173.8° in [Cp₂TiCl]₂(μ-O),⁵⁶ 180° in [CpTiCl₂]₂(μ-O)⁵⁷ and [(PhCH₂)₃Ti]₂(μ-O),⁵⁸ 168.9° in [Cp₂ZrCl]₂(μ-O),⁵⁹ and 173.9° in [Cp₂HfMe]₂(μ-O).⁶⁰ In the crystal lattice of [Cp*₂TiCl]₂(μ-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*TiCl₂]₂(μ-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(μ-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*-Pr₄C₅H)Mo(O)₂]₂(μ-O) is linear, and the other, [(*t*-Bu₃C₅H₂)Mo(O)₂]₂(μ-O), is bent (Mo–O–Mo 162.6°).⁶³ The mixed oxide–chloride species, [Cp*Mo(O)Cl]₂(μ-O), also has a linear Mo–O–Mo backbone.⁶⁴ Interestingly, in [(neopentyl)₃WO]₂(μ-O) the entire O–W–O–W–O skeleton is linear.⁶⁵

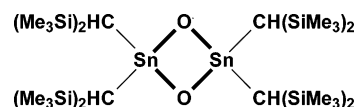
B. Cyclic Structures

The four-membered M₂O₂ rings can either be planar or folded (bent) and can also exist as cis–trans– (or syn–anti) conformers.

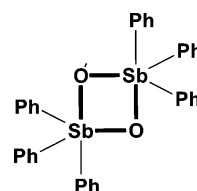
The dimer [{(SiMe₃)₂CH}₂SnO]₂ contains a Sn₂O₂ four-membered ring with Sn–O bond distance of 1.94 and 1.98 Å and Sn–O–Sn and O–Sn–O bond angles of 97.5° and 82.5°, respectively (Scheme 14). The compound is orange colored due to a small HOMO–LUMO separation.⁶⁶

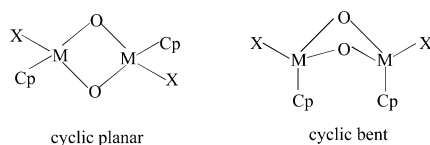
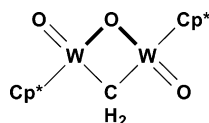
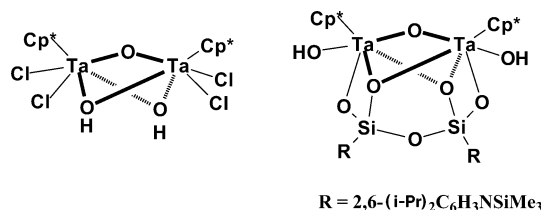
Triphenylantimony(V) oxide, [Ph₃SbO]₂, is a cyclic dimer containing a planar four-membered Sb₂O₂ ring (Scheme 15) in which the antimony is five coordinated (distorted trigonal bipyramidal geometry) with a phenyl group and an oxygen atom occupying axial positions. Two phenyl groups and an oxygen atom 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-PhOC₆H₄OC₆H₄)Ph₂Sb]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 [Ph₂BrSbO]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)(μ-O)]₂, ⁷⁰ *trans*-[Cp*Mo(O)(μ-O)]₂, ⁷¹ and *trans*-[Cp(C₃F₇)(O)W(μ-O)]₂, ⁷² whereas in *cis*-[Cp*Re(O)(μ-O)₂ReCp*(OReO₃)₂], the four-membered ring is folded along the Re=Re transannular bond (Re–O–Re 86.2°). ⁷³ The Mo₂O₂ ring in both *cis*-[CpMo(O)(μ-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)(μ-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–(μ-O) π interaction in the slightly folded geometry. The folding of the μ-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 μ-O and μ-CH₂ bridgings, are observed in Cp*₂W₂O₂(μ-O)(μ-CH₂) (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*TaCl₂]₂(μ-O)(μ-OH)₂. None of the Ta–O–Ta bonds is linear, and the bond angles in the molecule are Ta–(μ-O)–Ta = 103.0° and Ta–(μ-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(O₂RSiOSiRO₂)(μ-O) (R = 2,6-(*i*-Pr)₂C₆H₃-NSiMe₃), in which the metal atoms in the Ta₂(μ-O) unit are additionally bridged by two disiloxane fragments to form a unique Ta₂O₆Si₂ 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

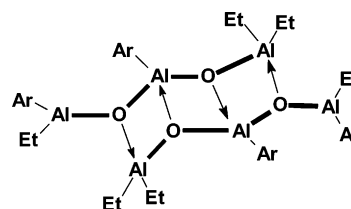
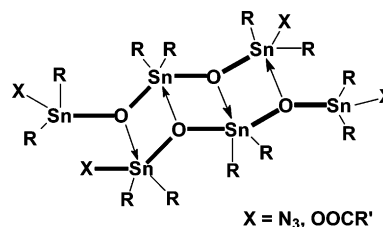
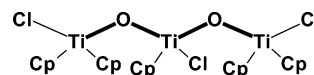
The organotin trinuclear oxides of the type R₃–SnOSnR₂OSnR₃ are not well-known. However, the α,ω-difunctional tin derivatives, XR₂SnOSnR₂OSnR₂X (X = azido ⁸¹ and carboxylato ⁸²), are known to dimerize into supramolecular ladder structures through four interchain tin–oxygen bonds (Scheme 20).

The crystal structure of a linear organometallic oxide, ClCp₂Ti–O–TiCp(Cl)–O–TiCp₂Cl (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

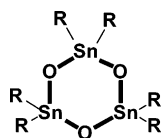
B. Cyclic Structures

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 μ-oxo bridges. These include several main group and transition metal derivatives.

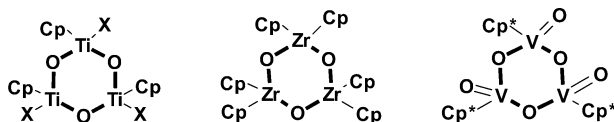
Diorganotin oxides or diorganostannoxanes, R₂–SnO, are insoluble polymeric materials containing five-coordinated tin, as confirmed by their ¹¹⁹Sn

Scheme 19**Scheme 20****Scheme 21**

Scheme 22



Scheme 23



Cp = C₅H₅, C₅Me₅,
C₅H₄Me, C₅HMe₄,
X = Cl, Br, Me, CH₂CHCHMe

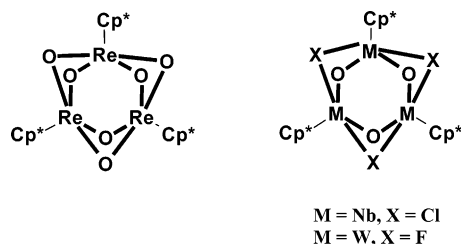
Mössbauer⁸⁴ and ¹¹⁹Sn MAS NMR⁸⁵ spectral data; but those with bulky substituents are cyclic trimers. For example, the hexaorganocyclotristannoxanes, [R₂SnO]₃, contain an almost planar Sn₃O₃ ring (Scheme 22). Several representatives of this class of organometallic oxides are known, and they have been structurally characterized. These include derivatives where R = *t*-Bu,^{86,87} CMe₂Et,⁸⁷ 2,6-Me₂C₆H₃,⁸⁸ 2,6-Et₂C₆H₃,⁸⁹ 2,4,6-*i*-Pr₃C₆H₂,^{90,91} or 2,4,6-(CF₃)₃C₆H₂,⁹² CH₂SiMe₃,⁹³ and R₂ = [C(SiMe₃)₃](Me),⁹⁴ [C(SiMe₃)₃](Cl), or [C(SiMe₃)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-Me₂C₆H₃)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 R₂SnO units.⁹⁶

Among the transition metal derivatives, titanium is best represented by organocyclotrititanoxanes, [CpTiMe(μ-O)]₃,^{97,98} and [Cp*(CH₂CH=CHMe)Ti(μ-O)]₃,⁹⁹ and its halogenated derivatives, [(C₅H₄Me)TiCl(μ-O)]₃,¹⁰⁰ and [Cp*TiX(μ-O)]₃ (X = Cl,^{56,101–104} Br¹⁰⁵). A zirconium derivative, [Cp₂Zr(μ-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)(μ-O)]₃, but no X-ray data could be obtained to confirm the formulation.¹⁰⁷ Nonetheless, the Ti₃O₃ and Zr₃O₃ rings in the corresponding organometallic oxide ring structures are planar (Scheme 23).

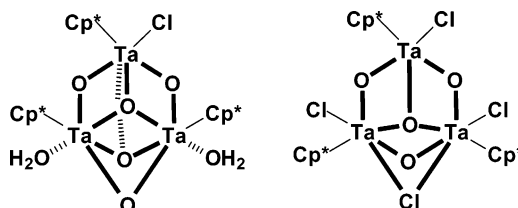
Trimeric organometallic oxides with double oxo bridges (Scheme 24) between the metal atoms are also reported. In [Cp*Re(μ-O)₂]₃¹⁰⁸ and cyclotrimetallloxanes, of the type [Cp*M(μ-O)(μ-X)]₃, additional halogen bridges can be found between the metal atoms (M = Nb, X = Cl).¹⁰⁹ In the latter species, all three oxygen atoms are on one side of the Nb₃ plane and all three chlorine atoms on the other side so that the Nb₃O₃ ring skeleton is nonplanar.

A planar Ta₃O₃ 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



Scheme 25



[{Cp*Ta(μ-O)}₃(μ₃-O)₂(Cl)(H₂O)₂]⁺Cl[−]. A related structure was observed for [Cp*TaCl(μ-O)]₃(μ-O)(μ-Cl) in which an oxygen-centered six-membered Ta₃(μ-O)₃ ring and an additional μ-chloro bridge form the Cp*₃-Ta₃O₄Cl₄ cluster core. The Ta₃O₂ fragment is essentially planar, with the other two oxygens and the bridging chlorine lying out of plane.^{53, 110}

A unique Ti₃O₃ ring framework with a μ₃-CR triple bridge between the titanium atoms has been found in the structure of [Cp*Ti(μ-O)]₃(μ₃-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*MoMe₄ leads to the trinuclear cluster, Cp*₃Mo₃(μ-O)₂(μ-CH₂)-(μ₃-CH), with oxo-methylidene and methylidyne groups, and is a rare example of compounds for use in catalysis on metal oxide surfaces.⁷⁷

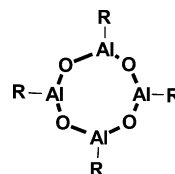
VI. Tetranuclear, Cyclic Organometallic Oxides

A. Monocyclic Structures

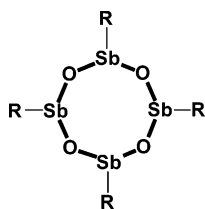
Apparently, only one cyclic monoorganoaluminum oxide is known (Scheme 26), the [RAlO]₄ tetramer with R = 2,4,6-*t*-Bu₃C₆H₂, and all other species are cage compounds (vide infra). The compound contains a planar Al₄O₄ ring with Al–O bond lengths in the range of 1.687–1.691 Å, and the pertinent bond angles 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 [(Me₃Si)₂CHSbO]₄ tetramer was confirmed by an X-ray diffraction study (Scheme 27).

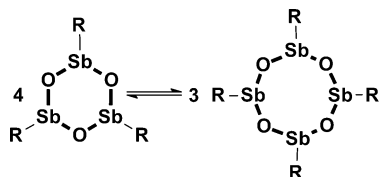
Scheme 26



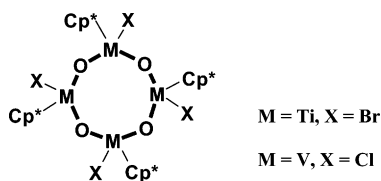
Scheme 27



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*-BuSbO] $_n$ ($n = 3$ and 4) tri- and tetramers (Scheme 28).¹¹³

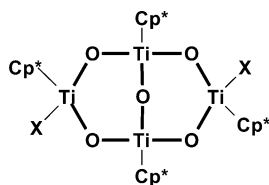
There are several transition metal organometallic oxides containing M_4O_4 rings (Scheme 29). They are mostly titanium derivatives of the types, $[\text{Cp}^*\text{TiCl}(\mu\text{-O})]_4$,¹¹⁴ $[\text{Cp}^*\text{Ti}(\text{OAr})(\mu\text{-O})]_4$,¹¹⁵ ($\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$), $[(\text{C}_5\text{H}_4\text{Me})\text{TiCl}(\mu\text{-O})]_4$,¹¹⁶ $[\text{C}_5\text{HMe}_4\text{TiCl}(\mu\text{-O})]_4$,⁵⁶ $[\text{C}_5\text{-HMe}_4\text{TiBr}(\mu\text{-O})]_4$,¹⁰⁵ $[\text{Cp}^*\text{TiBr}(\mu\text{-O})]_4 \cdot \text{CHCl}_3$,¹¹⁷ $[(\text{Me}_3\text{-SiC}_5\text{H}_4)\text{Ti}(\text{NCS})(\mu\text{-O})]_4$,¹⁰¹ $[\text{Cp}^*\text{TiEt}(\mu\text{-O})]_4$, $[\text{Cp}^*\text{Ti}(\mu\text{-O})]_4\text{F}(\mu\text{-FAlMe}_3)_3$, $[\text{Cp}^*\text{Ti}(\mu\text{-O})]_4\text{F}_3\{\mu\text{-FAl}(\text{CH}_2\text{Ph})_3\}$,¹¹⁸ and $[\text{C}_9\text{H}_7\text{TiCl}(\mu\text{-O})]_4$,¹¹⁹ ($\text{C}_9\text{H}_7 = \text{tetrahydroindenyl}$). Similarly, a vanadium compound, $[\text{Cp}^*\text{VCl}(\mu\text{-O})]_4$,¹²⁰ has also been structurally characterized.

The $\text{Cp}^*\text{Ta}[\text{Rh}(\text{COD})]_4(\mu_3\text{-O})_4$ (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

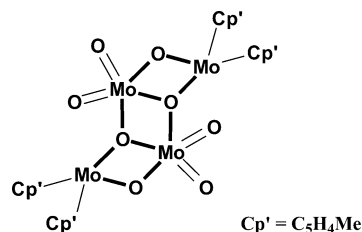
B. Bicyclic Structures

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 $(\text{Cp}^*\text{Ti})_4\text{F}_2(\mu\text{-O})_5$,¹¹⁸ $(\text{Cp}^*\text{Ti})_4\text{Cl}_2\text{-}$

Scheme 30



Scheme 31



$(\mu\text{-O})_5$,^{118,122} and $(\text{Cp}^*\text{Ti})_4\text{Me}_2(\mu\text{-O})_5$ ^{123,124} have been reported.

C. Tricyclic Structures

A ladder type tricyclic structure is found in molybdenum oxide compounds consisting of two $(\text{C}_5\text{H}_4\text{R})_2\text{-Mo}$ ($\text{R} = \text{H}, \text{Me}$) and two MoO_2 building units of composition $(\text{C}_5\text{H}_4\text{R})_4\text{Mo}_4\text{O}_8$ (Scheme 31). These compounds contain a fragment of the MoO_3 layered structure and can be formulated as $[(\text{C}_5\text{H}_4\text{R})_2\text{Mo}(\text{MoO}_2)(\mu_3\text{-O})(\mu\text{-O})]_2$. Only the methylcyclopentadienylmolybdenum compound, $(\text{C}_5\text{H}_4\text{Me})_4\text{Mo}_4\text{O}_8$, has been structurally characterized by X-ray diffraction. The tungsten analogues $(\text{C}_5\text{H}_4\text{R})_4\text{W}_4\text{O}_8$ ($\text{R} = \text{H}, \text{Me}$) are also known.¹²⁵

D. Adamantanes and Related Types

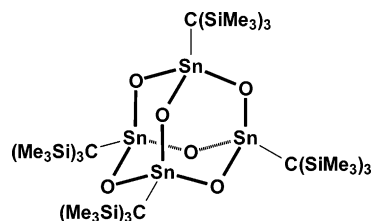
Adamantane structures are known for a large variety of inorganic and organometallic compounds.¹²⁶ Their backbone can be viewed as a fragment that is cut off from the wurtzite-type solid-state three-dimensional structures.

An organoaluminum adamantane cage is the mixed oxide–hydroxide $\text{R}_4\text{Al}_4(\mu\text{-O})_2(\mu\text{-OH})_4$ ($\text{R} = \text{C}(\text{SiMe}_3)_3$) core. A similar gallium-based oxide–hydroxide $\text{R}_4\text{-Ga}_4(\mu\text{-O})_2(\mu\text{-OH})_4$ ($\text{R} = \text{C}(\text{SiMe}_3)_3$) has been structurally characterized.¹²⁷ Monoorganotin oxides with very bulky substituents such as $(\text{RSn})_4\text{O}_6$, ($\text{R} = \text{C}(\text{SiMe}_3)_3$) 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 $(\text{R}_2\text{SnO})_3$ (vide supra).

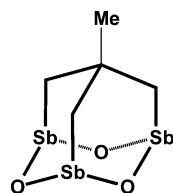
The inorganic oxide, Sb_4O_6 (senarmontit mineral) is a molecular compound displaying an adamantane-type structure. The cage compound $\text{MeC}(\text{CH}_2\text{SbO})_3$ maintains the six-membered Sb_3O_3 ring (chair-shaped) in another adamantane structure in which the rest of the core is made of carbon atoms (Scheme 33).¹²⁹

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

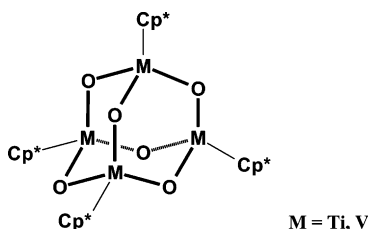
Scheme 32



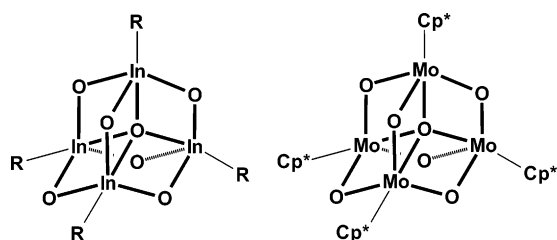
Scheme 33



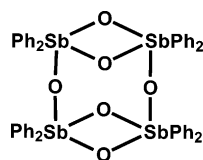
Scheme 34



Scheme 35



Scheme 36

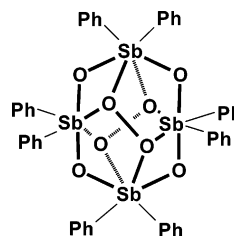


O)₆,^{122,130} and vanadium, (Cp*V)₄(μ-O)₆,^{131,132} The electronic structure of (Cp*V)₄(μ-O)₆ has been analyzed by using the extended Hückel MO calculations in order to explain its paramagnetism.¹³³

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(μ₄-O)(μ-OH)₆ (R = CH(SiMe₃)₂).¹³⁴ The organomolybdenum compound, (Cp*Mo)₄O₇, also possesses an oxygen-centered structure comprising a tetrahedral M₄O₆(μ₃-O) core that can be formulated as (Cp*Mo)₄(μ₃-O)(μ-O)₆.

An M₄O₆ molecular core is similar to that of the adamantanes but results in a different structure. Thus, Ph₈Sb₄O₆ 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-MeC₆H₄)₈Sb₄O₆.⁶⁸ An identical Sb₄O₆ nonadamantane core is also found in [(Ph₈Sb₄O₆)(AcOH)₂]·AcOH·CH₂Cl₂ (Ac = MeCOO).¹³⁶ A somewhat similar tetranuclear phenyl-substituted organoantimony oxide–peroxide, (R₂Sb)₄(μ-O)₄(μ-O₂)₂, has been structurally characterized (Scheme 37).^{49,137}

Scheme 37



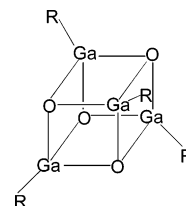
E. Cubane Structures

An organogallium cubane, [(*t*-Bu₃Si)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, [(Me₃Si)₃ClInO]₄, is also known.¹³⁹

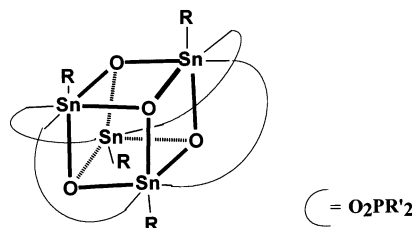
The organotin cubane clusters, based on a Sn₄O₄ core (Scheme 39), are found in tetrameric functionalized monoorganotin oxides, R(X)SnO, with X = phosphinato groups O₂PR'₂ (R' = Cy, *t*-Bu, CH₂Ph).¹⁴⁰

The M₄O₄ cubane core has been found in several organometallic oxides. Examples include the chromium compounds (Scheme 40) of the types [CpCr(μ₃-O)]₄,^{141,142} [C₅H₄MeCr(μ₃-O)]₄,¹⁴³ and [Cp*Cr(μ₃-O)]₄¹⁴⁴ and the vanadium derivatives [Cp*V(μ₃-O)]₄.¹³² Oxidation of the chromium cubane with AgBF₄ and 7,7,8,8-tetracyanoquinodimethane (TCNQ), respectively, gives [(Cp*Cr)₄(μ₃-O)]₄[BF₄] and [(Cp*Cr)₄(μ₃-O)]₄(TCNQ), both displaying antiferromagnetic properties.¹⁴⁵ Detailed spectroscopic and theoretical studies

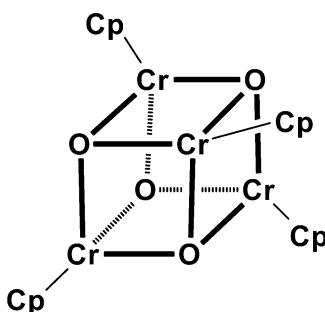
Scheme 38



Scheme 39

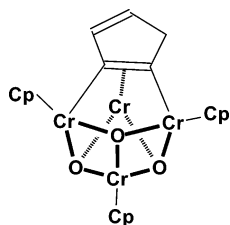


Scheme 40

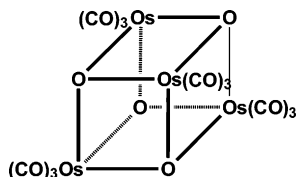


Cp = C₅H₅ or C₅Me₅

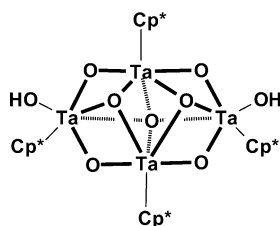
Scheme 41



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 $(\eta^2\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)_4\text{Cr}_4\text{O}_3$ cluster.¹⁴⁸ One of the Cp groups in Scheme 41 has been omitted for clarity.

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

F. Other Types

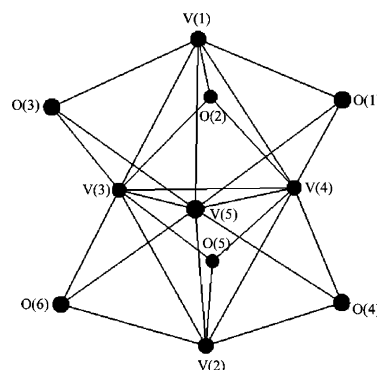
The $(\text{Cp}^*\text{Ta})_4(\mu_4\text{-O})(\mu_3\text{-O})_2(\mu\text{-O})_4(\text{OH})_2$ cluster displays a unique structure with the doubly, triply, and quadruply connected oxygen sites in an unusual butterfly geometry at the $\mu_4\text{-O}$ site (Scheme 43). There are two short Ta–O distances (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

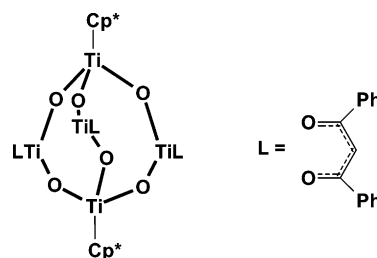
A pentanuclear vanadium species, $(\text{CpV})_5(\mu_3\text{-O})_6$, contains a cage which can be described as a trigonal bipyramid of vanadium atoms with tricoordinate oxygen atoms located above each face (Scheme 44), or better viewed as a polycyclic system made of fused four-membered V_2O_2 rings.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

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

Scheme 44



Scheme 45



atoms form a trigonal bipyramid with the Cp^*Ti units in axial positions and $(\text{Phacac})_2\text{Ti}$ 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).

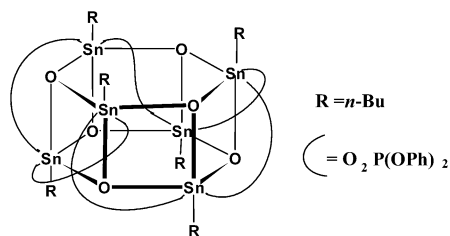
VIII. Hexanuclear Organometallic Oxides

The most common structural features of organoalumoxanes are cage-like, and these include not only hexanuclear $[\text{RAl}(\mu_3\text{-O})]_6$ core, but also larger cage $[\text{RAlO}]_n$, with $n = 7, 8$, and 9 ($\text{R} = t\text{-Bu}$) oligomers.¹⁵³ In addition to tetranuclear $\text{R}_7\text{Al}_4\text{O}_2(\text{OH})$ and pentanuclear $\text{R}_7\text{Al}_5\text{O}_3(\text{OH})_2$,¹⁵⁴ and $\text{R}_6\text{Al}_6\text{O}_4(\text{OH})_4$ ($\text{R} = t\text{-Bu}$),¹⁵⁵ several oxide–hydroxide alumoxanes, such as $\text{R}_8\text{Al}_8\text{O}_4(\text{OH})_2$ have also been structurally characterized. The reactions of $[\text{MeAl}(\mu_3\text{-O})]_n$ with AlMe_3 form larger Al cages, up to $\text{Me}_{15}\text{Al}_9\text{O}_6$ and $\text{Me}_{18}\text{Al}_{12}\text{O}_9$.¹⁵⁶ The $[t\text{-BuAlO}]_6$ hexamer reacts with AlMe_3 to form $\text{Me}_3(t\text{-Bu})_6\text{Al}_7\text{O}_6$ 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 $[\text{RAlO}]_n$ 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 $[\text{Mes}_6\text{Ga}_6(\mu\text{-O})_4(\mu_3\text{-OH})_4\cdot 4\text{THF}]\cdot 6\text{THF}$ (Mes = mesityl), are also known.¹⁵⁹

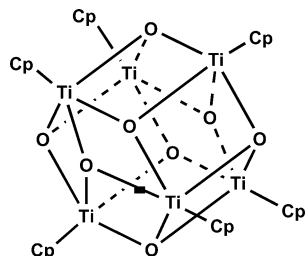
Some functionalized monorganotin oxides, RXSnO , with $\text{X} = \text{carboxylato}$ or organophosphato groups have also been characterized.^{82,160} These contain hexagonal prismatic Sn_6O_6 cages, as molecular cores, with functional groups bridging the tin atoms across the Sn_2O_2 four-membered ring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

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

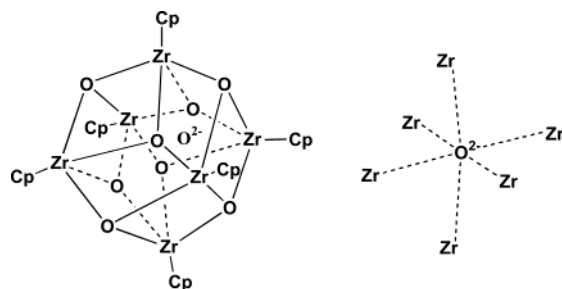
Scheme 46



Scheme 47



Scheme 48



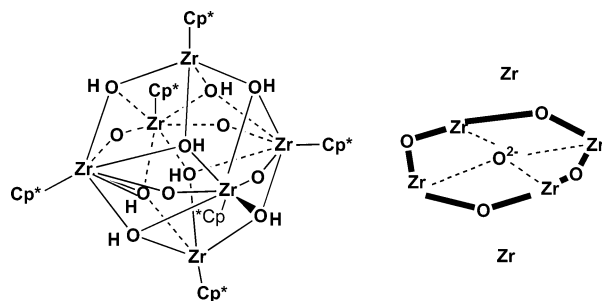
oxide, $(\text{CpTi})_6(\mu_3\text{-O})_8$, is of a Ti_6 pseudo-octahedral arrangement (Scheme 47) with eight μ_3 -oxygen atoms capping the triangular faces of the octahedron.¹⁶¹

Substituted cyclopentadienyl derivatives have also been reported. In these compounds, oxygen can be partly replaced by chlorine atoms as in $(\text{C}_5\text{H}_4\text{MeTi})_6\text{O}_4\text{Cl}_4$ and $(\text{CpTi})_6\text{O}_6\text{Cl}_2$.¹⁶² Apparently, the Ti_6O_8 cage in $(\text{CpTi})_6(\mu_3\text{-O})_8$ 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, $(\text{CpTi})_6(\mu_3\text{-O})_4(\mu_3\text{-S})_4$, is an analogue of the former Ti compound, in which four μ_3 -oxygen atoms were replaced by μ_3 -sulfur atoms in alternative triangular faces of the octahedron.¹⁶⁴

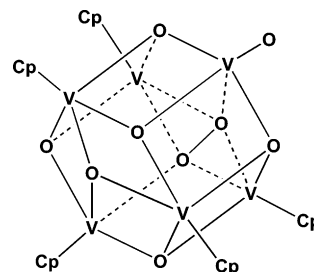
In the hexanuclear toluene and mesitylene solvated, compounds $(\text{C}_5\text{Me}_4\text{Et})_6\text{Zr}_6(\mu_6\text{-O})(\mu_3\text{-O})_8$, the metal atoms form an octahedron capping the triangular faces by triply bridging oxygen atoms ($\mu_3\text{-O}$). In addition, a central $\mu_6\text{-O}^{2-}$ ion is encapsulated within the cage (Scheme 48). The structure can be described as an assembly of 12 fused Zr_2O_2 rings. The $\text{Zr}-(\mu_6\text{-O})$ distances (2.231–2.247 Å, average 2.241 Å) are longer than $\text{Zr}-(\mu_3\text{-O})$ distances (2.136–2.169 Å, average 2.156 Å) in the toluene solvate. The bond angles in the four-membered rings are $\text{O}=\text{Zr}=\text{O} = 81.34^\circ$ and $\text{Zr}=\text{O}=\text{Zr} = 94.65^\circ$. Similar parameters were found for the core structure of the mesitylene solvate of the hexanuclear zirconium cluster.¹⁶⁵

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

Scheme 49



Scheme 50



with statistically distributed $\mu\text{-O}$ or $\mu\text{-OH}$ 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

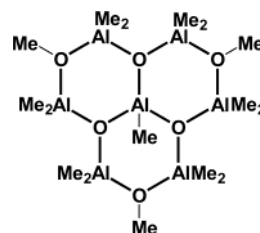
In $(\text{CpV})_5(\text{VO})(\mu_3\text{-O})_8$, five vanadium atoms bear a cyclopentadienyl ligand, while the sixth has a terminal $\text{V}=\text{O}$ bond (Scheme 50). The core of this compound is a polyhedral cage made of fused four-membered V_2O_2 rings. Two such cages can be connected through a $\mu\text{-O}$ bridge to form a dodecanuclear complex $[(\text{Cp}_5\text{V}_6(\mu_3\text{-O})_8)_2(\mu\text{-O})]$.¹⁶⁷

The hexanuclear compound $\text{Cp}^*_2\text{W}_6\text{O}_{17}$ is a neutral analogue of the $\text{W}_6\text{O}_{19}^{2-}$ anion in which two oxygen sites (O^{2-}) have been replaced by two pentamethylcyclopentadienyl (Cp^*) groups. The compound contains a central $\mu_6\text{-O}$ atom with all other 16 being $\mu\text{-O}$ bridging oxygens. The $\text{W}-(\mu_6\text{-O})$ distances display three different magnitudes: 2.204 (to WCp^*), 2.355, and 2.502 Å.¹⁶⁸

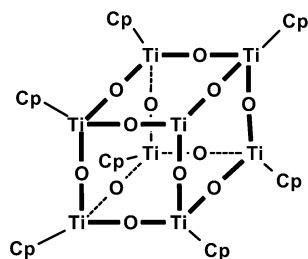
IX. Larger Cage Organometallic Oxides

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 $[\text{Me}_{16}\text{-Al}_7\text{O}_6]^-$ anion, was one of the first structurally characterized methylalumoxane compounds¹⁶⁹ and

Scheme 51



Scheme 52



has the formula $[(\text{Me}_2\text{Al})_6(\text{MeAl})(\mu_3\text{-O})_3(\mu\text{-OMe})_3]^-$. This illustrates the dramatic structural changes produced when R_2Al groups are incorporated.

An octanuclear compound, $(\text{CpTi})_8(\mu\text{-O})_{12}$, contains a Ti_8O_{12} cubane skeleton (Scheme 52). In the acetonitrile solvate, $(\text{CpTi})_8(\mu\text{-O})_{12} \cdot 6\text{MeCN}$, the Ti–O distances average 1.805 Å (range 1.795–1.818 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 $(\text{CpTi})_8(\mu\text{-O})_{12} \cdot \text{NEt}_3 \cdot \text{THF} \cdot (\text{CpTi})_4(\mu\text{-Se})_3(\mu_3\text{-Se})_3$.¹⁷⁰

The octanuclear compound $\text{Cp}^*_6\text{Mo}_8\text{O}_{16}$ contains two Mo_3O_6 units (three Mo–Mo bonds, 2.74 Å; three $\mu\text{-O}$ and three $\mu_3\text{-O}$ atoms) connected by a $\text{Mo}^{\text{V}}(\text{O})(\mu\text{-O})_2\text{Mo}^{\text{V}}(\text{O})$ 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 $\text{Mo}^{\text{V}}\text{-O-Mo}^{\text{V}}$ bridge); 1.940(2)–1.958(2) Å (to $\mu_3\text{-O}$ in the Mo_3O_6 units); 2.021(2)–2.041(2) Å (to $\mu\text{-O}$ in the Mo_3O_6 units); 2.137(2)–2.260(2) Å (from bridge Mo atoms to $\mu_3\text{-O}$ of the Mo_3O_6 units).¹⁶⁸

Three different possible structures have been suggested for the octanuclear compound $\text{Cp}^*_6\text{V}_8\text{O}_{17}$, but no X-ray structural data are available for this compound.^{133a} In $\text{Cp}_{10}\text{V}_{12}\text{O}_{17}$ cluster, two $\text{V}_6(\mu_3\text{-O})_8$ cuboctahedra are linked by an oxygen bridge.¹⁶⁷

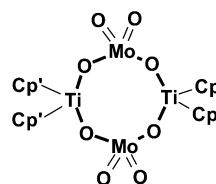
Organogallium oxides tend to form large clusters, such as the $[\text{MesGaO}]_9$ (Mes = mesityl) nonamer.¹⁷¹ Dodecanuclear clusters have been reported for gallium oxide–hydroxides, an example of such cluster is found in $(t\text{-BuGa})_{12}(\mu_3\text{-O})_8(\mu\text{-OH})_4$.¹⁵⁵ Large tin–oxygen clusters with quasi-spherical cage structures form due to incomplete hydrolysis and condensation of monoorganotin halides and they have been structurally characterized. Examples include $(i\text{-PrSn})_9(\mu_3\text{-O})_8(\mu\text{-OH})_6\text{Cl}_5 \cdot 6\text{DMSO}$,¹⁷² $(i\text{-PrSn})_{12}(\mu_3\text{-O})_{14}(\mu\text{-OH})_6\text{Cl}_2 \cdot \text{L}$ (L = $3\text{H}_2\text{O}$, $4\text{H}_2\text{O}$ or 2DMF), $(n\text{-BuSn})_{12}(\mu_3\text{-O})_{14}(\mu\text{-OH})_6\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, and $[(n\text{-BuSn})_{12}(\mu\text{-O})_{14}(\mu\text{-OH})_6](\text{OH})_2$.¹⁷³

X. Heterobimetallic Oxides

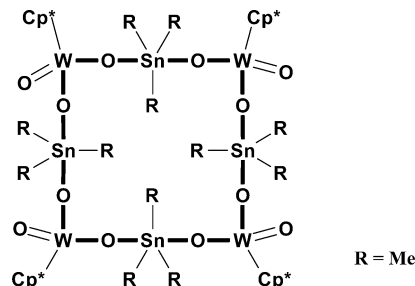
Few organometallic oxides containing two different metals have been reported, but the known examples suggest that a vast area of research on this subject could be explored.

Several organometallic oxides, including dinuclear $\text{Cp}^*(\text{O})_2\text{W-O-MCp}_2$ (M = Ti, Zr), and trinuclear $\{\text{Cp}^*(\text{O})_2\text{W-O}\}_2\text{MCp}_2$ (M = Ti, Zr) have been prepared, but only $\{\text{Cp}^*(\text{O})_2\text{W-O}\}_2\text{ZrCp}_2$ has been characterized by X-ray diffraction. Cyclic tetranuclear

Scheme 53



Scheme 54



$[\text{Cp}_2\text{Ti-O-WCp}^*(\text{O})\text{-O}]_2$ and $[(\text{C}_5\text{H}_4\text{Me})_2\text{Ti}(\mu\text{-MoO}_4)]_2$ (Scheme 53) are also known. The eight-membered monocyclic compound $[(\text{C}_5\text{H}_4\text{Me})_2\text{Ti}(\mu\text{-MoO}_4)]_2$ 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 $\text{Mo}_2\text{Ti}_2\text{O}_4$ ring is nearly planar. In the crystal lattice, the $[(\text{C}_5\text{H}_4\text{Me})_2\text{Ti}(\mu\text{-MoO}_4)]_2$ molecules are self-assembled into supramolecular chains through Mo=O...Mo intermolecular contacts (Mo...O 3.307 Å).¹⁷⁴

A macrocyclic, 16-membered ring compound, $[\text{Me}_3\text{-Sn-O-W}(\text{O})\text{Cp}^*\text{-O}]_4$, 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 $\text{Cp}(\text{CO})_3\text{W-O-ZrCp}_2\text{Cl}$ (W–O–Zr 175.7°; W–O 2.065 Å, Zr–O 1.871 Å) has also been reported.¹⁷⁶ The $[(\text{Me})\text{Cp}_2\text{ZrOAlMe}_2]_2$ dimer contains a $[\text{Me}_2\text{AlO}]_2$ ring with Cp_2ZrMe groups coordinated to the oxygens.¹⁷⁷

Other heterobimetallic compounds of complex structures include the triple cubane-type compound, $[\text{Cp}^*\text{RhMoO}_4]_4$,¹⁷⁸ the trishomocubane oxide–methoxide cluster derivative, $(\text{Cp}^*\text{Rh})_2\text{Mo}_3\text{O}_9(\text{OMe})_4\text{MeOH}$, a linear quadruple cubane derivative, $(\text{Cp}^*\text{Rh})_4\text{Mo}_6\text{O}_{22} \cdot 4\text{CH}_2\text{Cl}_2$,¹⁷⁹ a quadruple-cubane type structure of $(\text{Cp}^*\text{M})_4\text{V}_6\text{O}_{19}$, (M = Rh, Ir),¹⁸⁰ and the complex salt $[\text{N}(n\text{-Bu})_4]_2[\{\text{Cp}^*\text{Rh}\}_2\text{Mo}_6\text{O}_{20}(\text{OMe})_2]$.¹⁸¹ All these structures suggest a possible continuous transition from organometallic oxides to traditional polyoxo species.¹⁸²

Organometallic oxide with η^6 -arene moieties are extremely rare. The two known examples, $\{(\eta^6\text{-}p\text{-}i\text{-PrC}_6\text{H}_4\text{Me})\text{Ru}\}_4\text{Mo}_4\text{O}_{16}$ ¹⁸³ and $\{(\eta^6\text{-}p\text{-}i\text{-PrC}_6\text{H}_4\text{Me})\text{-Ru}\}_4\text{W}_2\text{O}_{10}$, contain a core of two fused cubane units.¹⁸⁴

Organotin vanadates (mixed oxides), $[\text{Me}_3\text{SnVO}_3]_x$ and $[(\text{Me}_2\text{Sn})_4\text{V}_2\text{O}_9]_x$, are three-dimensional polymers whose building blocks are related to the molecular organotin oxide species discussed above.¹⁸⁵ A polymeric, chainlike bimetallic oxide, $[\text{Me}_3\text{Sn}-\text{O}-\text{ReO}_2-(\mu\text{-O})]_x$, contains linear O-Sn-O fragments with the chains bent at rhenium and oxygen.¹⁸⁶ Other mixed organotin metal oxides include $[(\text{ReO}_4)\text{Ph}_2\text{SnOSnPh}_2\text{-OH}]_2$ (ladder tricyclic supermolecule),¹⁸⁷ $[\text{Me}_3\text{SnTcO}_4]_x$ (1D chain polymer),¹⁸⁸ $[(\text{Me}_3\text{Sn})_3\text{CrO}_4(\text{OH})]_x$ (3D polymer),¹⁸⁹ $[\text{Me}_2\text{SnMoO}_4]_x$ (3D polymer),¹⁹⁰ $[(\text{Me}_3\text{-Sn})_2\text{MoO}_4]_x$, $[(\text{Me}_3\text{Pb})_2\text{MoO}_4]_x$, and $[(\text{Me}_3\text{Sn})_2\text{WO}_4]_x$.¹⁹¹ A five-coordinated tin derivative, $\text{Cp}_2\text{Nb}(\text{Cl})(\mu\text{-O})\text{-SnPh}_2\text{Cl}_2$, that seems to contain a Nb=O double bond can be regarded as an adduct of $\text{Cp}_2\text{Nb}(\text{Cl})(=\text{O})$ 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 $\mu\text{-O}$ (on the edges) and $\mu_3\text{-O}$ (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 $\mu\text{-O}$ and $\mu_3\text{-O}$ 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

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