Organometallic Hydroxides of Transition Elements

Herbert W. Roesky,*,† Sanjay Singh,† K. K. M. Yusuff,‡,§ John A. Maguire,‖ and Narayan S. Hosmane†,‡

*Institut für Anorganische Chemie, Universität Göttingen, D-37077 Göttingen, Germany, Department of Chemistry and Biochemistry,
Northern Illinois University DeKalb, Illinois 60115-2862, and Department of Chemistry, Southern Methodist University, Dallas, Texas 75275-0314*

Contents

1. Scope

The main objective of this review is to make the reader aware of the synthetic procedures and structural characterizations of environmentally friendly organometallic compounds. Since there has been a recent and extensive review on organometallic oxides,[1] this review will focus mainly on the organometallic hydroxides. Descriptions of the terminal hydroxide complexes of the late transition metals, of organometallic oxohydroxo complexes, and of the reactivity of organometallic hydroxides have appeared in a number of reviews, but these were largely devoted to other topics.[2−5] An interesting review on the structural aspects of organometallic hydroxides of the d- and f-block elements was published in 1994.[6] Since then, no review dealing exclusively with hydroxo complexes has appeared in the literature.

In general, chemists consider water a foe in organometallic reactions, and the resulting hydroxides are undesired products, which have been formed mostly by careless work. Herein we are trying to show that organometallic hydroxides can function as useful precursors. Moreover, this review will include the synthesis, structural aspects, and general properties of organometallic hydroxides of transition elements, and whenever the compound has some unique synthesis, special properties, or useful application, that will also be covered. To organize this review, we have adopted the following approach: each group of the transition metals will be discussed separately.

2. General Remarks

The following general remarks will help the reader to understand what the review emphasizes. It will be grouped into early transition metals, rare earth elements, and late transition metals. It will give a glimpse about how facile is the synthesis of an organo-hydroxide, the stability of these compounds, the nature of the hydroxide moiety (terminal, doubly bridged, or triply bridged, etc.), and the most
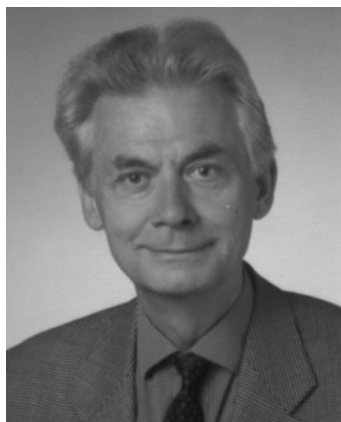
* To whom correspondence should be addressed. E-mail: hroesky@gwdg.de.
† Universität Göttingen.
‡ Northern Illinois University DeKalb.
§ On sabbatical leave from Cochin University of Science & Technology, India.
‖ Southern Methodist University.

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 his 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 he has also been a Frontier Lecturer 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, the Russian Academy of Sciences, Associé étranger de l' Académie des Sciences, 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 Leibniz award, le Grand Prix de la Maison de Chimie, ACS awards in Inorganic and Fluorine Chemistry, the Stock memorial award, and the French Alexander-von-Humboldt award. More than 1000 peer-reviewed papers, articles, patents, and books record his research activity in the areas of Inorganic Chemistry and Material Sciences.

Sanjay Singh was born at Varanasi (India), in October 1978. He attended Banaras Hindu University, where he received his B.Sc. (Hons. 2000) in Chemistry. He then joined the Indian Institute of Technology Kanpur and obtained his M.Sc. in 2002. During his masters program, he worked on organotin compounds and their application in acylation of alcohols and phenols, for which he received the best project award from the Indian Institute of Technology Kanpur for 2002. In January 2006, he received his Dr.rer.nat. degree from Georg-August University, Göttingen. During his tenure as a Ph.D. student, he worked on group 13 elements hydroxides, heterobimetallic systems, and N-heterocyclic carbene complexes of gold(I) with an emphasis on the synthesis, structural analysis, and reaction chemistry. He is the author/coauthor of more than 20 research publications in leading scientific journals.

K. K. M. Yusuff was born in Kodungallur, Kerala, India. He received his B.Sc. degree (1970), his M.Sc. degree (1972), and his Ph.D. degree with Professor C. G. Ramachandran Nair (1977) from the University of Kerala. He was awarded an UNESCO fellowship for a three-month-long advanced course in Inorganic Chemistry at University College, Dublin, Ireland, in 1977. His teaching career started in 1974 as a Junior Lecturer in the College of Engineering, Trivandrum, and from there, he moved over to the University of Calicut as a Lecturer in 1976. He became a Reader in the Cochin University of Science and Technology in 1983 and became Professor of Inorganic Chemistry in 1991. He worked as a Visiting Professor in the research group of Professor Narayan Hosmane of Northern Illinois University during the period May 2003 to October 2003. Eighteen students have obtained Ph.D. degrees under his supervision. He is the author/coauthor of over 50 publications in scientific journals. His research interests include the chemistry of zeolite encapsulated and polymer supported transition metal complexes and the use of these types of complexes in the development of catalysts for oxidation reactions.

John Maguire is Professor of Chemistry at Southern Methodist University. He was born in Alabama in 1936, received his B.S. degree in Chemistry from Birmingham Southern College in 1958, and received his Ph.D. degree in Physical Chemistry in 1963 from Northwestern University under the direction of Ralph G. Pearson. He joined the faculty of Southern Methodist University as an Assistant Professor of Chemistry and is now Professor of Chemistry. From 1976 to 1979 he was Associate Dean of University College at SMU, and from 1979 to 1981 he was Dean of University College and General Education at SMU. His research interests are in the structure and properties of intercalation compounds and in the bonding, structure, and reactivity in carborane cage compounds. He has received several awards, including the "M" Award for service to the University in 1979, the outstanding professor award for teaching in 1975 and in 1995, and the Perrine Prize for research. He has published over 120 scientific peer-reviewed papers and reviews and has been listed in the ISI's 10858 most cited chemists (1981–1997) in the world. In 2002 he was appointed University Distinguished Teaching Professor.

commonly encountered structural types, for each category. The syntheses and properties may vary for individual compounds, and this discussion is not meant to be comprehensive; nevertheless, a general overview of the basic properties of these compounds is presented below.

Narayan S. Hosmane was born in Gokarn, Southern India, and is a B.S. and M.S. graduate of Karnatak University, Karnataka State, 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 the Lambeg Research Institute in Northern Ireland, and then he moved to the U.S.A. to study carboranes and metallacarboranes. After postdoctoral work with Russell Grimes at the University of Virginia, in 1979 he joined the faculty at Virginia Polytechnic Institute and State University. In 1982 he joined the faculty at the Southern Methodist University, where he became Professor of Chemistry in 1989. In 1998, he moved to Northern Illinois University, and he is currently a Distinguished Research Professor of Chemistry and Biochemistry. He has published over 230 papers in leading scientific journals. Recently, he has served as the Jawaharlal Nehru Distinguished Chair of Chemistry at the University of Hyderabad, India, and in 2001 he received the Humboldt Research Prize for Senior U.S. Scientists from the Alexander von Humboldt-Stiftung, and also received the University's Presidential Research Professorship. He is now the recipient of the prestigious Gauss Professorship of the Göttingen Academy of Sciences for the year 2005. He has previously received a Camille and Henry Dreyfus Scholar Award, and he has been honored with the Mother India International Award and the Boron in the U.S.A. for his distinguished achievements in boron science. In 1987 he was given the Sigma Xi Outstanding Research Award. His research interests are in main-group organometallic chemistry, including the synthesis and structure of carboranes and metallacarboranes, and, most recently, in the area of boron and gadolinium neutron capture therapy in cancer treatment.

2.1. General Properties of Early Transition Metal Organo-hydroxides

Organo-hydroxides of all early transition metals have been reported. Titanium(III) hydroxide is known, but no hydroxide of Zr(III) or Hf(III) has been prepared. The OH group has the potential for utilizing its electron pairs for bonding to more than one metal, so that there are examples of organometallic hydroxides with both terminal and bridging hydroxyl groups. Doubly bridged hydroxo coordinations are most common, followed by a cubane-like arrangement with metal and hydroxide oxygen atoms occupying alternate corners of a distorted M_4O_4 cube, especially in the case of group 6 and 7 metals. In general, the clusters are electron precise, with OH^- utilizing three lone pairs to bind three metals. Moreover, a number of remarkable clusters have been encountered.

2.2. General Properties of Late Transition Metal Organo-hydroxides

A review of the pertinent literature shows that organometallic hydroxides of late transition metal ions are rare, due primarily to the intrinsic weakness of the M−OH bond. While the hydroxo ligand is a hard base, the metal ions of the late transition metals are usually in a low oxidation state,

causing the metal centers to function as soft acids. This mismatch in hard/soft interactions results in fairly weak metal−hydroxide bonding. On the other hand, one advantage of the weak M−OH bonds is that the M−OH bond is quite reactive and the OH group should be easily substituted by other ligands, leading to the synthesis of a variety of new and interesting organometallic compounds. No structurally characterized hydroxides of Cu and Ag are known. Among the structural types, the triply bridging hydroxides are the most common ones.

2.3. General Properties of Rare Earth Element Organo-hydroxides

The bonding in organolanthanide hydroxo complexes is considered to be predominantly ionic, and hard lanthanide ions have a preference for hard donor hydroxide ligands which coordinate through oxygen. This factor is responsible for the oxophilic nature of the rare earth elements. Doubly bridging coordination is relatively most frequently seen. $(Cp_2M)_2(\mu\text{-}OH)_2$-type complexes have metals in distorted tetrahedral geometry. Steric factors play a more important role in lanthanide chemistry than the electron count. Low coordination numbers (3 to 6) have been achieved by the use of sterically demanding ligands. Rare earth metals have a tendency to adopt high coordination numbers, which is far less common in the case of d-block elements.

3. Introduction

Organometallic compounds are most often prepared in moisture free, nonaqueous solvents.[7] Consequently, large quantities of such solvents are generated, resulting in significant waste disposal problems. There is a worldwide demand for "green" chemical processes and products in which reactions are carried out in environmentally friendly solvents, especially in water. The development of new and cost-effective approaches to pollution control is necessary to meet this demand.[8]

Most of the organic reactions are not compatible with aqueous conditions due to the lack of solubility of the compounds in water or, in the case of organometallic compounds, the high reactivity of the compounds with water. The presence of small quantities of water in these reaction systems often results in the formation of organometallic oxides, hydroxides, oxohydroxo compounds, and aqua complexes. Such compounds may find application as green catalysts or as environmentally friendly precursors for the synthesis of nanoparticle materials. Furthermore, as found in biological systems, water can participate in structure directing intermolecular interactions, leading to supramolecular assemblies in these systems.[9]

Hydroxo complexes of transition metals have been postulated as critical intermediates in a number of catalytic reactions involving water as a substrate.[10−17] Transition metal−hydroxide bond interactions are considered to be necessary for reactions such as the Wacker oxidation reaction;[3] the water gas shift reaction;[18,19] olefin hydrocarbonylation;[20] olefin (alkyl halide, and alcohol) carboalkoxylation;[3,21−23] carbonyl compound hydrogenation;[3] and alcohol dehydrogenation.[3] The photolytic splitting of water and the C−H bond deuteration by D_2O are known to proceed through such interactions.[24,25] In addition, hydrido hydroxo complexes are considered to be important intermediates in water splitting reactions.[26−28] Other bond cleavage reactions such as the Cp_2-
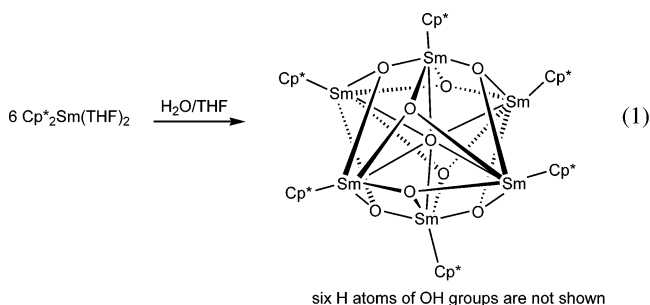
MoCl$_2$ (Cp = η^5-C$_5$H$_5$) promoted phosphoester bond cleavage are believed to proceed by an intramolecular attack of a Cp$_2$Mo-bound hydroxide on the phosphate monoester.[29-31]

Organometallic hydroxides may also find application in organometallic crystal engineering.[32] The anionic superstructures are held together by a combination of neutral and interionic O−H···O hydrogen bonds. A judicious choice of the building blocks may yield materials with attractive magnetic, conducting, superconducting,[33-37] and nonlinear optical properties.[38-41]

4. Group 3 Organo-hydroxides

Due to similar properties of Sc, Y, and lanthanides and because of similar examples of organometallic hydroxides of this group, it makes little sense to separate them in this discussion.

Almost all the organolanthanide complexes are extremely sensitive to moisture and air.[42] However, only a few hydroxo complexes of lanthanides have been reported despite a seemingly favorable interaction between the hard acid Ln^{3+} and the hard base OH$^-$. The hydrolysis of organometallic derivatives of electropositive metals can be viewed as the conversion of M−R (R = alkyl or aryl) to R−H and M−OH. The structure and composition of the resulting M−OH units are important in determining their subsequent reaction chemistry. Therefore, the reactions of the hydroxo complexes must be discussed in terms of their structural chemistry. Table 1 gives a list of structurally characterized organometallic hydroxo complexes. The most common method for the preparation of organometallic hydroxides of this group and also in general is the partial hydrolysis of organometallic compounds. Water for the hydrolysis reactions can be purposely introduced into organometallic systems in trace quantities by using very dilute solutions of known concentrations of H$_2$O in solvents such as THF, or in the form of water vapor. It was found that good crystallographic quality brown crystals of [Cp*Sm]$_6$O$_9$H$_6$ could be obtained in an apparatus consisting of a "H" shaped vessel in which the vapor over a water/THF solution in one side of the reaction vessel reacted with a THF solution of Cp*$_2$Sm(THF)$_2$ (Cp* = C$_5$Me$_5$) in the other side of the vessel[43] (eq 1).

$$6 \text{ Cp*}_2\text{Sm(THF)}_2 \xrightarrow{\text{H}_2\text{O/THF}} \qquad (1)$$

six H atoms of OH groups are not shown

Partial hydrolysis of the organolanthanide salt [Cp″$_2$Sm]-[BPh$_4$] (Cp″ = 1,3-(Me$_3$Si)$_2$C$_5$H$_3$) at −30 °C in toluene produced two crystalline compounds, [Cp″$_2$Sm]$_2$(μ-O)(μ-OH$_2$) and [Cp″$_2$Sm(μ-OH)]$_2$, whose crystal morphologies were sufficiently different so that they could be physically separated (Pasteur's method).[44] The structure of [Cp″$_2$Sm-(μ-OH)]$_2$ is shown in Figure 1. The complex [Cp″$_2$Lu(μ-OH)]$_2$ formed by the partial hydrolysis of [(THF)$_n$Cp″$_2$-LuRu(CO)$_2$Cp] has a similar structure.[40] The structure of the [Cp″$_2$Sm]$_2$(μ-O)(μ-OH$_2$) is similar except that, at least formally, a proton is transferred from one OH to another.

The isolation of the initial oxo-aqua complex [Cp″$_2$Sm]$_2$-(μ-O)(μ-OH$_2$)] (Cp″ = 1,3-(Me$_3$Si)$_2$C$_5$H$_3$), before the formation of the hydroxo complex [Cp″$_2$Sm(μ-OH)]$_2$, offers a hint to the mechanism of the hydrolysis reaction of organolanthanide complexes.[44] The oxo-aqua complex has been proposed as an intermediate in the transformation of [Cp″$_2$Sm-(μ-OH)]$_2$ to [Cp″$_2$Sm]$_2$(μ-O).[44] The Sm−O(H$_2$O) distances are considerably longer (2.61(1) and 2.63(1) Å) than are the Sm−O(oxo) distances (2.248(8) and 2.318(8) Å).[45] It is interesting to note that using the same procedure but starting with the [Cp″$_2$Sm][CB$_{11}$H$_6$Br$_6$] salt gave only the [Cp″$_2$Sm-(μ-OH)]$_2$, whose structure was similar, though not identical, to that derived from the [BPh$_4$]$^-$ salt.[44] The presence of both [Cp″$_2$Sm]$_2$(μ-O)(μ-OH$_2$)] and [Cp″$_2$Sm(μ-OH)]$_2$ in the same reaction mixture suggests a continuous process for the conversion of the organosamarium hydroxo [Cp″$_2$Sm(μ-OH)]$_2$ to the oxo compound [Cp″$_2$Sm]$_2$(μ-O) and also explains why one or more of these compounds can sometimes be adventitiously isolated from the same reaction mixture. The samarocene and ytterbocene hydroxides [Cp″$_2$Sm-(μ-OH)]$_2$ and [Cp′$_2$Yb(μ-OH)]$_2$ (Cp′ = η^5-C$_5$H$_4$SiMe$_3$) could be prepared from the Ln(II) complexes [Cp″$_2$Sm(THF)] and [Cp′$_2$Yb(OEt$_2$)] by treatment with water in an etheral solution.[46] The complex formation is thought to proceed via an oxidative addition of the OH radicals to the metallocene complexes. A different samarium hydroxy compound, [SmCp*]$_6$O$_9$H$_6$, was obtained from the reaction of water vapor with a solution of Cp*$_2$Sm(THF)$_2$.[43] The structure consists of six Cp*Sm groups arranged around a central oxygen atom in a roughly octahedral fashion, with triply bridging oxygens on each face. Unfortunately, the hydrogens could not be located.

The dimeric compound, [Ho(MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$(μ-OH)]$_2$, was obtained as a byproduct in the recrystallization of [Ho-(MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$(μ-H)]$_2$ from a THF/n-hexane solvent mixture. This solvent mixture evidently contained trace amounts of water.[47] Despite the serendipitous nature of its synthesis, the compound does show structural characteristics that are common to a number of bridged hydroxo-lanthanides. Dimerization occurs through bridging of the two OH ligands. Each Ho atom is also coordinated by two ether substituted cyclopentadienyl ligands and an oxygen atom from one of the substituent ethers, resulting in a distorted trigonal bipyramidal structure. This same structural motif is found in the [Y(O(CH$_2$CH$_2$C$_5$H$_4$)$_2$)(μ-OH)]$_2$ dimer[45] and in [(MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$Er(μ-OH)]$_2$ that was formed by the partial hydrolysis of (MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$ErCl[48] (eq 2).

$$[\text{Ln(MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2(\mu\text{-X})]_2 \xrightarrow{\text{H}_2\text{O}} \qquad (2)$$

Ln = Ho, X = H
Ln = Er, X = Cl

[Ln(MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$(μ-OH)]$_2$
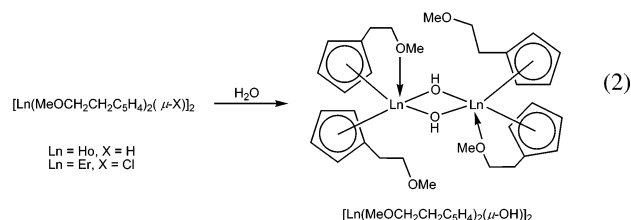
Several other hydroxo complexes have been isolated from the partial hydrolysis of tris(Cp) lanthanide complexes by trace amounts of water.[45] These are thought to be intermediates in the stepwise decomposition of these complexes, involving an initial formation of a Cp$_3$Ln(OH$_2$) complex, which then eliminates CpH to give Cp$_2$Ln(OH). This process can be repeated, resulting, ultimately, in Ln(OH)$_3$. In support of this, aqua complexes of the tris(cyclopentadienyl) lan-

Table 1. Structurally Characterized Organometallic-hydroxo Complexes

organometallic hydroxide	starting organometallic compound	spectroscopic studies done	X-ray crystal structure	ref
$[Cp''_2Sm(\mu\text{-}OH)]_2$, form A ($Cp'' = 1,3\text{-}(Me_3Si)_2C_5H_3$)	$[Cp''_2Sm][CB_{11}H_6Br_6]$	IR; MS	triclinic, $P\bar{1}$ Sm–O 2.314 Å Sm–O–Sm 107.7, 111.6, 96.1, and 88.7°	44
$[Cp''_2Sm(\mu\text{-}OH)]_2$, form B ($Cp'' = 1,3\text{-}(Me_3Si)_2C_5H_3$)	$[Cp''_2Sm][CB_{11}H_6Br_6]$	IR; MS	monoclinic, $P2_1/n$ Sm–O 2.308 Å Sm–O–Sm 107°	44
$[Y(O(CH_2CH_2C_5H_4)_2)(\mu\text{-}OH)]_2$	$[Y(O(CH_2CH_2C_5H_4)_2)(C_5H_4Me)]$	IR; NMR	monoclinic, $P2_1/n$ Y–O 2.238 Å Y–O–Y 109.1°	45
$[Cp''_2Sm(\mu\text{-}OH)]_2$ ($Cp'' = 1,3\text{-}(Me_3Si)_2C_5H_3$)	$[Cp''_2Sm(THF)]$	IR; NMR	triclinic, $P\bar{1}$ Sm–O 2.40 Å	46
$[Cp'_2Yb(\mu\text{-}OH)]_2$ ($Cp' = \eta^5\text{-}C_5H_4SiMe_3$)	$[Cp'_2Yb(OEt_2)]$	IR; NMR	monoclinic, $P2_1/c$ Yb–O 2.29 Å Yb–O–Yb 99.2, 104.1°	46
$[Ho(MeOCH_2CH_2C_5H_4)_2(\mu\text{-}OH)]_2$	$[Ho(MeOCH_2CH_2C_5H_4)_2(\mu\text{-}H)]_2$		orthorhombic, $Pbca$ Ho–O 2.256 Å	47
$[Cp'''_2Er(\mu\text{-}OH)]_2$ ($Cp'''_2 = MeOCH_2CH_2C_5H_4$)	Cp'''_2ErCl		orthorhombic, $Pbca$ Er–O 2.258, 2.216 Å Er–O–Er 108.4°	48
$[Cp_2Y(\mu\text{-}OH)]_2 \cdot (PhC{\equiv}CPh)$	$Cp_2Y(CMe_3)(THF)$ and $PhC{\equiv}CPh$		monoclinic, $P2_1/c$ Y–O 2.33, 2.36 Å Y–O–Y 100.4°	49
$[YO(CH_2CH_2C_5H_4)_2(\mu\text{-}N_2C_3H\text{-}Me_2)(\mu\text{-}OH)\text{-}YO(CH_2CH_2C_5H_4)_2]$	$[Y(O(CH_2CH_2C_5H_4)_2)Cl]$ and $NaN_2C_3HMe_2$	NMR	tetragonal, $P4_12_12$ Y–O 2.202 Å Y–O–Y 137.2°	50
$[LuO(CH_2CH_2C_5H_4)_2(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)\text{-}LuO(CH_2CH_2C_5H_4)_2]$	$[Lu(O(CH_2CH_2C_5H_4)_2)Cl]$ and $NaN_2C_3HMe_2$	NMR	tetragonal, $P4_12_12$ Lu–O 2.154 Å Lu–O–Lu 138.3°	50
$[(C_5H_4CMe\text{-}n\text{Pr}CH_2CH{:}CH_2)Nd\text{-}(OH)]Cl \cdot 2MgCl_2 \cdot 4THF$	$[C_5H_4CMePrCH_2CH{:}CH_2]LnCl_2 \cdot MgCl_2 \cdot THF$ (Ln = Nd)		triclinic, $P\bar{1}$ Nd–O 2.442 Å	51
$[(C_5H_4CMe\text{-}n\text{Pr}CH_2CH{:}CH_2)Gd\text{-}(OH)]Cl \cdot 2MgCl_2 \cdot 4THF$	(Ln = Gd)		triclinic, $P\bar{1}$ Gd–O 2.405 Å	51
$[CpTi(\mu\text{-}OH)\text{-}(\mu\text{-}C_5H_4)]_2 \cdot THF$	$[(Cp)(C_5H_4)TiH]_2$		orthorhombic, $Pna2_1$ Ti–O 2.10, 2.05 Å Ti–O–Ti 98.8°, 102.7°	65
$[Ti_3(\mu_3\text{-}O)(\mu\text{-}OH)_3(\mu\text{-}HCO_2)_3Cp_3]^+\text{-}HCO_2^- \cdot 2HCO_2H$	Cp_2TiCl_2, H_2O, and HCO_2H		triclinic, $P\bar{1}$ Ti–O 1.994–2.023 Å Ti–O–Ti 106.9–107.6°	67
$\alpha\text{-}[Cp^*_2Ti(OH)(H_2O)]CF_3SO_3 \cdot H_2O$	$[Cp^*_2Ti(H_2O)_2](CF_3SO_3)_2$		triclinic, $P\bar{1}$ Ti–O 1.88 Å	68
$\beta\text{-}[Cp^*_2Ti(OH)(H_2O)]CF_3SO_3 \cdot H_2O$	$[Cp^*_2Ti(H_2O)_2](CF_3SO_3)_2$		triclinic, $P\bar{1}$ Ti–O 1.86 Å	68
$[Cp^*_2Ti(OH)(H_2O)]CF_3SO_3 \cdot 2H_2O$	$[Cp^*_2Ti(H_2O)_2](CF_3SO_3)_2$		triclinic, $P\bar{1}$ Ti–OH 1.87 Å	68
$[Cp^*_2Ti(OH)(H_2O)]BPh_4 \cdot 2THF$	$[Cp^*_2TiMe(THF)]BPh_4$ prepared from Cp^*_2TiMe and $AgBPh_4$	IR	triclinic, $P\bar{1}$ Ti–O 1.853 Å	69
$[Cp_2Zr(NC\text{-}n\text{Pr})(\mu\text{-}OH)]_2\text{-}[BPh_4]_2 \cdot 4NC\text{-}n\text{Pr}$	$[Cp_2Zr(OH)(H_2O)_n][BPh_4] \cdot mH_2O$ and $NC\text{-}n\text{Pr}$	IR	triclinic, $P\bar{1}$ Zr–O 2.154, 2.174 Å Zr–O–Zr 113.6°	70
$[Cp^*_2Ti(OH)(HN{=}CPh_2)]\text{-}BPh_4 \cdot OEt_2$	$Cp^*_2Ti\text{-}N{=}CPh_2$ and $AgBPh_4$	IR	triclinic, $P\bar{1}$ Ti–O 1.853 Å	71
$[Cp^*Ti(OH)OSi(tBu)_2O]_2$	$Cp^*TiCl_2OSi(tBu)_2(OH)$ from Cp^*TiCl_3 and $(tBu)_2Si(OH)_2$	MS; IR; NMR	monoclinic, $C2/c$ Ti–O 1.872, 1.834 Å	72
$[Zr_3Cp_3(\mu_3\text{-}O)(\mu\text{-}OH)_3(\mu\text{-}PhCOO)_3]^+\text{-}(PhCOO)^- \cdot OEt_2$	Cp_2ZrCl_2 and $PhCOONa$	IR; NMR	triclinic, $P\bar{1}$ Zr–O 2.133 Å Zr–O–Zr 103.6°	74
$[Cp_2Zr(OCOCF_3)(\mu\text{-}OH)]_2$	Cp_2ZrCl_2 and CF_3COOH	IR	monoclinic, $P2_1/n$ Zr–O 2.152, 2.158 Å Zr–O–Zr 114.4°	75
$[CpZr(NO_3)_2(\mu\text{-}OH)]_2 \cdot 2THF$	Cp_2ZrCl_2 and HNO_3		monoclinic, $P2_1/c$ Zr–O 2.167, 2.09 Å Zr–O–Zr 110.3°	77
$[Cp^*ZrCl]_3(\mu\text{-}O)(\mu\text{-}OH)_3(\mu\text{-}Cl)$	Cp^*ZrCl_3	IR; ^{13}C, ^{1}H NMR	orthorhombic, $Pbca$ Zr–O (μ-OH) 2.134–2.159 Å Zr–O (μ_3-OH) 2.198–2.336 Å Zr–O–Zr (μ_3-OH) 88.4°, 90.9°, 91.7°	78
$[(C(NH_2)_3)_3Zr(\mu\text{-}OH)(CO_3)_3 \cdot H_2O]_2$	$(NH_4)_2CO_3$, guanidinium carbonate, and zirconyl chloride		triclinic, $P\bar{1}$ Zr–O 2.119, 2.204 Å Zr–O–Zr 110.3°	79
$Na_6[Zr(\mu\text{-}OH)(C_2O_4)_3]_2 \cdot 7H_2O$	hydrous carbonated zirconia and $H_2C_2O_4$		triclinic, $P\bar{1}$ Zr–O 2.098, 2.122, 2.236 Å Zr–O–Zr 111.6°, 112.6°	79

Table 1 (Continued)

| organometallic hydroxide	starting organometallic compound	spectroscopic studies done	X-ray crystal structure	ref
$[Cp^*ZrCl]_3(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu\text{-}OH)_3\cdot 2THF$	Cp^*ZrCl_3		orthorhombic, $Pbca$ Zr–O (μ-OH) 2.147 Å Zr–O (μ_3-OH) 2.276 Å	80
$[(Cp^*Zr)_6(\mu_4\text{-}O)(\mu\text{-}O)_4(\mu\text{-}OH)_8]\cdot 2(C_7H_8)$	Cp^*ZrCl_3, KOH, liq NH$_3$, and toluene	IR; NMR	monoclinic, $C2/m$ Zr–O 2.106 Å Zr–O–Zr 120.5°	81
$[\{(Cp^*Zr)_4(\mu_5\text{-}O)(\mu_3\text{-}O)_2(\mu\text{-}OH)_4\}_2\text{-}Zr(\mu\text{-}O)_4]\cdot 2(C_7H_8)$	$[(Cp^*Zr)_6(\mu_4\text{-}O)(\mu\text{-}O)_4\text{-}(\mu\text{-}OH)_8]\cdot 2(C_7H_8)$ and Cp_2ZrMe_2 or $(MeC_5H_4)_2ZrH_2$	IR; NMR	monoclinic, $P2_1/c$ Zr–O 2.121–2.333 Å Zr–O–Zr 86.1, 109.1°	83
$[Cp_2Zr_2(\mu\text{-}OH)_2(H_2O)_6]^{4+}\text{-}(CF_3SO_3^-)_4\cdot 4THF$	Cp_2ZrCl_2 and $AgCF_3SO_3$	IR; NMR	triclinic, $P\bar{1}$ Zr–O 2.16 Å Zr–O–Zr 110.8°	85
$[Cp_2Zr_2(\mu\text{-}OH)_2(H_2O)_6]^{4+}\text{-}(ClO_4^-)_4\cdot 8THF$	Cp_2ZrCl_2 and $AgClO_4$	IR; NMR	monoclinic, $P2_1/c$ Zr–O 2.163 Å Zr–O–Zr 110.3°	85
$[Cp^*ZrCl_2(H_2O)(\mu\text{-}OH)]_2$	Cp^*ZrCl_3	IR; NMR	monoclinic, $P2_1/n$ Zr–O 2.081 Å Zr–O–Zr 114°	86
$Cp^*_2Zr(OH)Cl$	$Cp^*_2Zr(nBu)Cl$		monoclinic, $P2_1/c$ Zr–O 1.95 Å Zr–O–Zr 99.7°	88
$Cp^*_2Zr(OH)_2$	$Cp^*_2ZrMe_2$		monoclinic, $P2_1/n$ Zr–O 1.978 Å Zr–O–Zr 99.7°	88
$[Cp_2V(\mu\text{-}OH)B(C_6F_5)_3]$	Cp_2V, $B(C_6F_5)_3$, and H$_2$O	IR; ^{19}F, ^{11}B, ^{1}H NMR	monoclinic, $C2/c$ V–O 2.087 Å B–O 1.518 Å	90
$\{[CpNb(\mu\text{-}OOCH)(\mu\text{-}OH)]_3(\mu_3\text{-}O)\}H$	$CpNb(CO)_3PPh_3$		monoclinic, $P2/m$ Nb–O 1.97 Å Nb–O–Nb 106°	92
$[(Cp^*NbCl)_3(\mu\text{-}Cl)(\mu\text{-}O)_2(\mu_3\text{-}OH)\text{-}(\mu_3\text{-}O)]\cdot[Zn_4Cl_{10}]^-$	$[\{Cp^*NbCl_2\}_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)]$		orthorhombic, $P2_12_12_1$ Nb–O 2.145 Å	96
$Cp'_3Nb_3Cl_3(\mu\text{-}Cl)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)$ $(Cp' = C_5H_4Me)$	$[Cp'Nb(CO)_2Cl_2]_2$	IR; ESR	monoclinic, $P2_1/n$ Nb–O 2.20, 2.209, 2.263 Å	96
$[CpNbCl(\mu\text{-}Cl)]_3(\mu_3\text{-}OH)(\mu_3\text{-}O)$	hydrolysis of CpNbCl$_4$ followed by reduction with Al powder	IR; ESR	monoclinic, $P2_1/c$ Nb–O 2.201, 2.171, 2.231 Å	97
$[Cp^*TaCl_2(\mu\text{-}OH)]_2(\mu\text{-}O)$	$[Cp^*TaCl_4]$ or $[Cp^*Ta(CO)_2Cl_2(THF)]$	IR; NMR	orthorhombic, $F2dd$ Ta–O 2.13, 2.18 Å Ta–O–Ta 89.2°, 103.4°	99, 100
$[Cp^*_4Cr_4(\mu\text{-}OH)_6](BF_4)_2$	$Cp^*_2Cr_2(CO)_4$ with a (Cr≡Cr)	IR	tetragonal $I4^-$ Cr–O 1.952 Å Cr–O–Cr ~140°	101
$[Et_4N]_4[Cr_4(CO)_{12}(\mu_3\text{-}OH)_4]$	$Cr(CO)_6$	IR	monoclinic, $I2/a$ Cr–O–Cr 103.4° Cr–O 2.121 Å	102
$[Et_4N]_4[Mo(CO)_3(\mu_3\text{-}OH)]_4$	$Mo(CO)_6$	IR	monoclinic, $C2/c$ Mo–O–Mo 105° Mo–O 2.25 Å	105
$[Et_4N]_4[W(CO)_3(\mu_3\text{-}OH)]_4$	$W(CO)_6$	IR	monoclinic, $C2/c$ W–O–W 106° W–O 2.24 Å	105
$(Cp)(NO)Cr(\mu\text{-}Se\text{-}nBu)(\mu\text{-}OH)\text{-}Cr(NO)(Cp)$	$CpCr(NO)_2Cl$	IR; NMR; MS	monoclinic, $P2_1/c$ Cr–O 1.961 Å Cr–O–Cr 93.1°	107
$[Mo(CO)_2(OH)(\eta^3\text{-}C_4H_7)(3,5\text{-}diMepzH)]_2\cdot C_6H_6$	reaction of $Mo(MeCN)_2\text{-}(\eta^3\text{-}C_4H_7)(CO)_2Cl_2$ with $[Me_2Ga(3,5\text{-diMepzH})_2]^-$	IR; NMR	monoclinic, $P2_1/c$ Mo–O 2.239, 2.235 Å Mo–O–M 102.1°, 102.4°	108
$[\{MoCp\}_2(\mu\text{-}OH)(\mu\text{-}H)\text{-}\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]\cdot 2PF_6$	$[MoHCp(\mu\text{-}(\eta^1:\eta^5\text{-}C_5H_4))]_2$	NMR	monoclinic, $P2_1$ Mo–O 2.07 Å M–O–M 94.3°	109
$K_3[Mo_2(OH)_3(CO)_6]$	$Mo(CO)_6$	IR; XPS	triclinic, $P\bar{1}$ Mo–O 2.24 Å Mo–O–Mo 104°	115
$[Cp_2Mo(\mu\text{-}OH)_2MoCp_2]^{2+}(OTs^-)_2$	Cp_2MoH_2 and $Cp_2Mo(OTs)_2$ (OTs = p-MeC$_6$H$_4$SO$_3$)	IR; NMR	orthorhombic, $Pbna$ Mo–O 2.096 Å Mo–O-M 113.8°	116
$[Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2$	Cp_2WH_2 and $Cp_2W(OTs)_2$ (OTs = p-MeC$_6$H$_4$SO$_3$)	NMR	orthorhombic, $Pbna$ W–O 2.088 Å W–O–W 114.6°	116
$(\eta^5\text{-}C_5R_5)Mo(OH)_2(dppe)$ (R = Me, Et)	$(\eta^5\text{-}C_5R_5)MoH_3(dppe)$ and CpFe$^+$	EPR; NMR	triclinic, $P\bar{1}$ Mo–O 1.984, 2.011 Å	124
$[Cp_2Mo(OH)NH_2Me]PF_6$	$[Cp_2Mo(SMe_2)Br]PF_6$ and aq MeNH$_2$	IR; NMR	monoclinic $P2_1/n$ Mo–O 2.050 Å	126, 111

Table 1 (Continued)

organometallic hydroxide	starting organometallic compound	spectroscopic studies done	X-ray crystal structure	ref
$K_3[W_2(OH)_3(CO)_6] \cdot 2H_2O$	$W(CO)_6$		monoclinic, $P2_1/c$ W$-$O 2.16 Å W$-$O$-$W 97°	129
$WCo(OH)(\mu\text{-}CC_6H_4Me\text{-}4)$- $(\mu\text{-}PPh_2)_2(CO)_2(Cp)$	$WCo(Cl)(\mu\text{-}CC_6H_4Me\text{-}4)$- $(\mu\text{-}PPh_2)(CO)_2(Cp)$	IR; NMR	monoclinic, $P2_1/c$ W$-$O 2.087 Å	131
$[\{Mn(\mu_3\text{-}OH)(CO)_3\}_4]$	$Mn_2(CO)_{10}$ and $Me_3NO \cdot 2H_2O$	IR	tetragonal, $P4_2/nnm$ Mn$-$O 2.051 Å	134
$[Mn_7(\mu_3\text{-}OH)_8(CO)_{18}]$	$Mn_2(CO)_{10}$ and benzophenone	IR	monoclinic, $I2/a$ Mn$-$O 2.055 Å (outer six Mn atoms), 2.169 Å (to central Mn atom)	134
$[Mn_4(CO)_{12}F_x(OH)_{4-x}]$	$Mn(CO)_5X$ (X = Cl, Br), with TlF (X = 1 and 2); with AgX (X = 2 and 3)	IR	cubic, $Pn3m$ Mn$-$O$-$Mn 102° Mn$-$O 2.052 Å	136
$[Tc(\mu_3\text{-}OH)(CO)_3]_4$	$[NEt_4]_2[TcCl_3(CO)_3]$ and NaOH	IR; ^{99}Tc NMR	tetragonal, $I\bar{4}$ Tc$-$O 2.181, 2.185, 2.191 Å Tc$-$O$-$Tc 102.3, 105.1°	138
$[Re(CO)_3OH]_4 \cdot 2C_6H_6$	$Re_2(CO)_{10}$	IR; NMR	cubic, $Pn3m$ Re$-$O 2.207 Å Re$-$O$-$Re 104°	135, 139
$[Re_2(CO)_6(\mu\text{-}H)(\mu\text{-}OH)](dppm)$	$Re_2(CO)_8(dppm)$	IR; ^{13}C NMR	triclinic, $P\bar{1}$ Re$-$O 2.177, 2.16 Å Re$-$O$-$Re 88.6°	141
$[Fe_2(CO)_6(\mu\text{-}OH)\{\mu\text{-}PH[CH(SiMe_3)_2]\}]$	$(Me_3Si)_2CHPCl_2$ and $[NEt_4]_2[Fe_2(CO)_8]$	NMR	triclinic, $P\bar{1}$ Fe$-$O 1.99 Å Fe$-$O$-$Fe 76.6°	145
$[Ru(\eta^6\text{-}C_6H_6)(\mu_3\text{-}OH)]_4(SO_4)_2 \cdot 12H_2O$	$[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$, aq Na_2CO_3, and excess Na_2SO_4		cubic, $Pn3m$ Ru$-$O 2.12 Å Ru$-$O$-$Ru 102.2°	147, 149
$[Ru_4(\eta^6\text{-}C_6H_6)_4(\mu\text{-}OH)_4(\mu_4\text{-}O)]$- $(BPh_4)_2 \cdot 2Me_2CO$	$[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$, excess Na_2CO_3 and Na_2BPh_4		monoclinic, $P2_1/c$ Ru$-$O 2.12, 2.09 Å Ru$-$O$-$Ru 77.2°	148
$[Os_4(\eta^6\text{-}C_6H_6)_4(\mu\text{-}OH)_4(\mu_4\text{-}O)]$- $(BPh_4)_2 \cdot 2Me_2CO$	$[Os(\eta^6\text{-}C_6H_6)Cl_2]_2$		monoclinic, $P2_1/c$ Os$-$O 2.146, 2.09 Å Os$-$O$-$Os 74.8°	148
$[Ru_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2$- $(\mu\text{-}OH)_3]Cl \cdot 3H_2O$	$[Ru(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)Cl_2]_2$		rhombohedral, $R3m$ Ru$-$O 2.087 Å Ru$-$O$-$Ru 102.2°	149
$[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl \cdot 3H_2O$	$[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OPh)_3]^+$		orthorhombic, $Pbcn$ Ru$-$O 2.079 Å Ru$-$O$-$Ru 91.5°	150
$[Ru(dmpe)_2(H)(OH)(\mu\text{-}OH_2)]_2$	$Ru(dmpe)_2(C_2H_4)$		triclinic, $P1$ Ru$-$O 2.23 Å	10
$[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu\text{-}OH)_2(\mu_4\text{-}S)]$	$[Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)]$ and $[Ru_3(CO)_{12}]$	IR; UV$-$vis; NMR	triclinic, $P\bar{1}$ Ru$-$O 2.116$-$2.134 Å Ru$-$O$-$Ru 89$-$91.8°	153
$Ru_4(COEt)_4(OH)_2(CF_3SO_3)_2(CO)_8$	$[Ru(COEt)(CO)_2(H_2O)_3][CF_3SO_3]$		monoclinic, $P2_1/n$ Ru$-$O 2.12 Å Ru$-$O$-$Ru 102.6°	154
$[Ru_4(CO)_{10}(C \equiv CH\text{-}iPr)(OH)(PPh_2)]$	$[Ru_3(CO)_{11}(Ph_2PC \equiv C\text{-}iPr)]$	IR; NMR	triclinic, $P\bar{1}$ Ru$-$O 2.14 Å	155
$OsH(OH)(CO)(P\text{-}tBu_2Me)_2$	$OsH(Ph)(CO)(P\text{-}tBu_2Me)_2$	IR; ^{1}H, ^{31}P NMR	monoclinic, $P2_1/n$ Os$-$O 2.022 Å	156
	(L = 2,6-di(p-tolyl)benzoic acid)	UV$-$vis	Co$-$O$-$Co 92.08° Co$-$O $\sim$1.865 Å	
$[(CF_3CH_2CoL)_2(\mu\text{-}OH)]ClO_4$	$[Co(L)_2]ClO_4$, $NaBH_4$, NaOH, and CF_3CH_2I		monoclinic, $C2/c$ Co$-$O 1.919, 1.922 Å	157
$[(CyCoL)_2(\mu\text{-}OH)]ClO_4$ (L = 2-(2-pyridylethyl)imino-3-butanone oximato)	$[Co(L)_2]ClO_4$, $NaBH_4$, NaOH, and CyI		monoclinic, $P2_1/n$ Co$-$O 1.907, 1.927 Å	157
$[\{MeCo(LE\text{-}py)\}_2(\mu\text{-}OH)]ClO_4 \cdot 0.5H_2O$ (LE-py = 2-(2-pyridyl)imino-3-butanone oximato)	$[Co(LE\text{-}py)_2]ClO_4$, NaOH, $NaBH_4$, H_2O, MeI, and $NaClO_4$		monoclinic, $P2_1/c$ Co$-$O 1.917, 1.911 Å Co$-$O$-$Co 105.9°	158
$(Et_4N)_2[Co\{Co\{N_2(SO_2)\}(CN)(OH)\}_2]$	$(Et_4N)_2[Co(N_2S_2)(CN)(MeCN)]$ and (O_2)	IR; NMR; UV$-$vis	monoclinic, $C2/c$ Co$-$O 1.940, 2.015 Å	159
$[\{IrCp^*\}_2(\mu\text{-}OH)_3]OAc \cdot 14H_2O$	$[\{Cp^*Ir\}(OAc)_2(H_2O)]$	IR; NMR; UV$-$vis	orthorhombic, $Pnma$ Ir$-$O 2.12 Å Ir$-$O$-$Ir 92.7, 92.8°	160
$[\{RhCp^*\}_2(\mu\text{-}OH)_3]OH$	$[(RhCp^*)_2Cl_4]$		orthorhombic, $Pnma$ Rh$-$O 2.109 Å Rh$-$O$-$Rh 89.2, 89.89°	160

Table 1 (Continued)

organometallic hydroxide	starting organometallic compound	spectroscopic studies done	X-ray crystal structure	ref
[{RhCp*}$_2$(HL)$_2$(μ-OH)$_2$][BF$_4$]$_2$ (HL = 3,5-dimethylpyrazole)	[{RhCp*}$_2$(μ-OH)$_3$[BF$_4$]	IR; NMR	monoclinic, $P2_1/n$ Rh−O 2.186, 2.172 Å Rh−O−Rh 101°	165
[{RhCp*}$_2$(μ-L)$_2$(μ-OH)][ClO$_4$] (HL = pyrazole)	[Cp*Rh(Me$_2$CO)$_3$][ClO$_4$]$_2$		monoclinic, $C2/c$ Rh−O 2.11, 2.104 Å Rh−O−Rh 11.7°	165
IrH(OH)[C$_6$H$_3$-2,6-(CH$_2$P-tBu$_2$)$_2$]	IrH$_2$[C$_6$H$_3$-2,6-(CH$_2$P-tBu$_2$)$_2$], $tert$-butylethylene, and H$_2$O	^{1}H, ^{13}C, ^{31}P NMR; IR	orthorombic, $Pbca$ Ir−O 2.00 Å	172
$trans$-[Ir(CO)(PCy$_3$)$_2$OH]	[$trans$-Ir(CO)(P(p-tolyl)$_3$)$_2$OH] and PCy$_3$	IR; NMR	triclinic, $P\bar{1}$ Ir−O 1.978 Å	173
[Ir(OH)(COD)]$_2$	[Ir(COD)(μ-Cl)]$_2$ and KOH (COD = 1,5-cyclooctadiene)	IR	orthorombic, $Cmcm$ Ir−O 2.098, 2.024 Å Ir−O−Ir 86.2, 90.2°	176
[Ni(R)(PMe$_3$)$_2$(μ-OH)]$_2$·HNC$_4$H$_2$Me$_2$	$trans$-Ni(R)Cl(PMe$_3$)$_2$ (R = CH$_2$C$_6$H$_4$-oMe)	IR; NMR	monoclinic, $C2/c$ Ni−O 1.92, 1.917 Å Ni−O−Ni 91°	180
[Ni$_3$(CH$_2$C$_6$H$_4$-o-Me)$_4$(PMe$_3$)$_2$-(μ_3-OH)$_2$]	NiCl$_2$(PMe$_3$)$_2$ and Mg(CH$_2$C$_6$H$_4$-o-Me)Cl		triclinic, $P\bar{1}$ Ni−O 1.906−2.004 Å	181
(NBu$_4$)$_2$[Ni(C$_6$F$_5$)$_2$(μ-OH)]$_2$	[Ni(C$_6$F$_5$)$_2$(PhCN)$_2$] and NBu$_4$OH	IR; NMR; UV−vis	monoclinic, $P2_1/c$ Ni−O 1.89 Å Ni−O−Ni 99.2°	182
(NBu$_4$)$_2$[(Ni(C$_6$F$_5$)$_2$)$_2$(μ-OH)(μ-pz)]	(NBu$_4$)$_2$[Ni(C$_6$F$_5$)$_2$(μ-OH)]$_2$	IR; NMR; UV−vis	monoclinic, $P2_1/c$ Ni−O 1.89 Å Ni−O−Ni 119.3°	183
[L$_2$Pd$_2$(Ph)$_2$(μ-OH)(μ-CO)$_2$-(μ_3-CO)CrCp]·MeOH	[L$_2$Pd$_2$(Ph)$_2$(μ-OH)$_2$], CpCr(CO)$_3$H (L = PPh$_3$)	IR; ^{13}C, ^{31}P NMR	monoclinic, $C2/c$ Pd−O 2.125 Å Pd−O−Pd 105.4°	190
[Pt(OH)Me$_2${(pz)$_3$BH}]	[PtMe$_2$(SEt$_2$)]$_2$, K[(pz)$_3$BH], and H$_2$O		orthorhombic, $Pnma$ Pt−O 1.984 Å	193
[Pd(OH)(C$_4$H$_8$){(pz)$_3$BH}]·2(3-MeC$_6$H$_4$OH)]	K[Pd(C$_4$H$_8$){(pz)$_3$BH}], H$_2$O, or H$_2$O$_2$	NMR	monoclinic, $P2_1/n$ Pd−O 2.011 Å	194
[Pt(OH)Me$_2${(pz)$_3$BH}]	K[PtMe$_2${(pz)$_3$BH}]	IR; ^{13}C, ^{1}H NMR	orthorombic, $Pnma$ Pt−O 1.984 Å	196
[Pt(OH)Me$_2${(pz)$_4$B}]·H$_2$O	K[PtMe$_2${(pz)$_4$B}] and H$_2$O	IR; ^{13}C NMR	monoclinic, $P2_1/c$ Pt−O 1.996 Å	196
[Pt(OH)(p-tolyl)$_2${(pz)$_3$BH}]	[Pt(p-tolyl)$_2$(SEt$_2$)]	IR; ^{13}C NMR	monoclinic, $C2/c$ Pt−O 1.974 Å	196
[{Pt(Ph)(COD)}$_2$(μ-OH)]BF$_4$	PtI(Ph)(COD), AgBF$_4$, and H$_2$O	IR; ^{13}C, ^{31}P NMR	monoclinic, $P2_1$ Pt−O 2.030, 2.096 Å Pt−O−Pt 118.6°	201
[Me$_2$Au(μ-OH)]$_4$	Me$_2$AuI, AgNO$_3$, and NaOH	IR	orthorhombic, $Pbca$ Au−O 2.15 Å	209
[(Me$_2$PhSi)$_3$CZnOH]$_2$	(Me$_2$PhSi)$_3$CZnCl and NaOH	IR	monoclinic, $C2/c$ Zn−O 1.899 Å Zn−O−Zn 102.3°	216
[(C$_6$F$_5$)CdOH]$_4$	(C$_6$F$_5$)$_2$Cd and H$_2$O	IR	triclinic, $P\bar{1}$ Cd−O 2.209−2.282 Å Cd−O−Cd 98.4, 99.8, 100.8, 101.1°	217
[K(18-crown-6)(THF)$_2$][{Cd(C$_6$F$_5$)-(STrt)}$_3$(OH)]·THF (TrtSH = triphenylmethanethiol)	[{Cd(C$_6$F$_5$)(STrt)}$_4$], KOH, and 18-crown-6	IR; ^{13}C, ^{1}H, ^{19}F NMR	monoclinic, $P2_1/c$ Cd−O 2.368, 2.395, 2.408 Å Cd−O−Cd 96.6°	218
[Pt$_4$Cd$_6$(C≡CPh)$_4$(μ-C≡CPh)$_{12}$-(μ_3-OH)$_4$]	(NBu$_4$)$_2$[Pt(C≡CPh)$_4$] and Cd(ClO$_4$)$_2$·6H$_2$O	IR	tetragonal, $P\bar{4}$–2$_1$c Cd−O 2.221, 2.285, 2.282 Å	219
[(OH)Hg$_2$(NO$_3$Hg)CCHO]NO$_3$	Hg(NO$_3$)$_2$ and MeCHO		monoclinic, $P2_1/c$ Hg−O 2.11, 2.04 Å Hg−O−Hg 121°	221
[μ-(3,4,5,6-Me$_4$C$_6$)Hg$_2$(μ-OH)]$_2$-(CF$_3$SO$_3$)$_2$·2DMF	[μ-(3,4,5,6-Me$_4$C$_6$)Hg$_2$(μ-O)]$_2$ and CF$_3$SO$_3$H	IR; ^{13}C, ^{1}H NMR	monoclinic, $P2_1/n$ Hg−O 2.08 Å Hg−O−Hg 116.5°	222
4-Me$_2$NC$_6$H$_4$HgOH	4-Me$_2$NC$_6$H$_4$HgOAc and NaOH	IR; ^{13}C, ^{1}H, and ^{199}Hg NMR	monoclinic, $P2_1/c$ Hg−O 2.039 Å	223

thanides, Cp$_3$Ln(OH$_2$) (Ln = Y, Ho and Cp = C$_5$H$_5$; Ln = Ho and Cp = C$_5$H$_4$Me), were isolated from saturated toluene solutions of the respective Cp$_3$Ln compounds that had been stored under refrigeration for several days.[45] In much the same way, X-ray quality crystals of a mixed [Cp$_2$Y(μ-OH)]$_2$/PhC≡CPh solid were obtained by the partial hydrolysis of a mixture of Cp$_2$Y(CMe$_3$)(THF) and PhC≡CPh in toluene.[49] The molecular structure consists of two Cp$_2$Y moieties

bridged by two OH ligands, similar to what is seen in [Ho-(MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$(μ-OH)]$_2$, with the PhC≡CPh molecules and the [Cp$_2$Y(μ-OH)]$_2$ units forming alternate layers in the solid.[49] The reaction of Cp$_3$Y(THF) and NaOH in THF produced a mixture of Cp$_2$Y(OH)(THF) and NaCp that was very difficult to separate. However, commercially available (NPCl$_2$)$_x$ (80:20 mixture of (NPCl$_2$)$_3$ and (NPCl$_2$)$_4$) was found to react preferentially with NaCp to give the pure Cp$_2$Y-
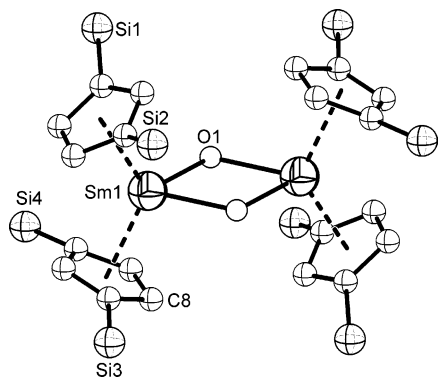
Figure 1. ORTEP drawing of [Cp″$_2$Sm(μ-OH)]$_2$ (Cp″ = 1,3-(Me$_3$Si)$_2$C$_5$H$_3$). Methyl groups on Si atoms and hydrogen atoms are omitted for clarity.

(OH)(THF).[49] On this basis it was suggested that (NPCl$_2$)$_x$ should be used as a general chemical scavenger for NaCp. This procedure can be useful in many instances where the physical separation of metal hydroxides from other reaction products may present difficulties.

The reaction of [Ln(O(CH$_2$CH$_2$C$_5$H$_4$)$_2$)Cl] (Ln = Y or Lu) with NaN$_2$C$_3$HMe$_2$ (N$_2$C$_3$H$_4$ = pyrazole) in THF at room temperature generates the complexes [Ln(O(CH$_2$CH$_2$C$_5$H$_4$)$_2$)-(μ-N$_2$C$_3$HMe$_2$)].[50] These compounds are highly moisture sensitive and are partially hydrolyzed to form the hydroxo complexes, [LnO(CH$_2$CH$_2$C$_5$H$_4$)$_2$(μ-N$_2$C$_3$HMe$_2$)(μ-OH)LnO-(CH$_2$CH$_2$C$_5$H$_4$)$_2$]. The complexes are dinuclear with a bridging OH and a dimethylpryazole group. Figure 2 shows
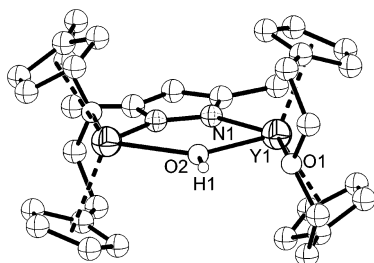
Figure 2. ORTEP drawing of [O(CH$_2$CH$_2$C$_5$H$_4$)$_2$Y(μ-N$_2$C$_3$HMe$_2$)-(μ-OH)YO(CH$_2$CH$_2$C$_5$H$_4$)$_2$]. Hydrogen atoms are deleted for clarity.

the structure of the complex where Ln = Y; the structure of the lutetium compound is quite similar.[50]

The mixed-metal hydroxo complexes [C$_5$H$_4$C(Me)−nPrCH$_2$CH=CH$_2$]Ln(OH)Cl·2MgCl$_2$·4THF (Ln = Nd or Gd) resulted from the storage of their respective dichloro complexes, [C$_5$H$_4$CMe−nPrCH$_2$CH=CH$_2$]LnCl$_2$·MgCl$_2$·THF, in a THF/n-hexane solution for several days at 0 °C.[51] The structure of the neodymium compound is shown in Figure 3. As can be seen, the Nd is coordinated to four chlorines, one oxygen, and a Cp ring in a very distorted octahedral geometry; the effect of the distortion is that the neighboring Nd−ligand bonds are bent away from the Nd−Cp bond, presumably due to the large steric bulk of the C$_5$H$_4$CMe−nPrCH$_2$CH=CH$_2$ ligand. It is of interest that the OH seems to be bridging the Nd and both of the Mg atoms.

As pointed out above, most of the hydroxo-lanthanide compounds arose by arresting the decomposition process of water sensitive lanthanide compounds at an early stage. This process also occurs in the 5f series. For example, the uranium(IV) hydroxo complexes, [U(C$_5$H$_4$R)$_3$(OH)] (R = SiMe$_3$ or CMe$_3$), were found to be precursors in the
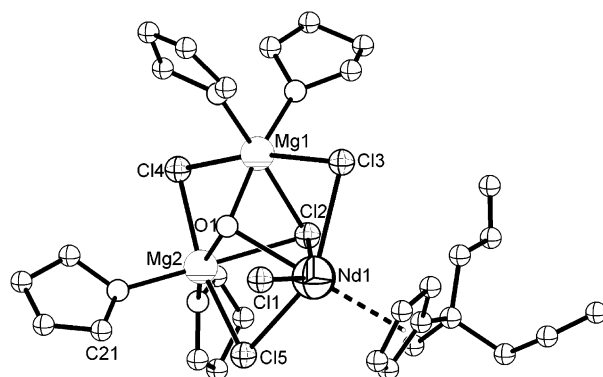
Figure 3. ORTEP drawing of [C$_5$H$_4$C(Me)−nPrCH$_2$CH=CH$_2$]-Nd(OH)Cl·2MgCl$_2$·4THF. Hydrogen atoms are omitted for clarity.

formation of the oxo derivatives, [{U(C$_5$H$_4$R)$_3$}$_2$(μ-O)] and [{U(C$_5$H$_4$R)$_2$(μ-O)}$_3$].[52] The hydroxo complexes could be obtained from the partial hydrolysis of the corresponding hydrides, [U(C$_5$H$_4$R)$_3$H], or, more reliably, from the reaction of [U(C$_5$H$_4$R)$_3$][BPh$_4$] with 1 mol equiv of powdered sodium hydroxide in THF.[52]

Apart from the diverse and interesting aspect of the structural chemistry of lanthanide hydroxides, their subsequent reaction chemistry, which could lead to the formation of hetero-bimetallic compounds containing metal atoms from other groups of the periodic table, is an interesting area and has a wide range of applications.

In a quest to prepare hetero-bimetallic compounds of lanthanides and main group metals, an obvious route is the reaction of lanthanide hydroxides with main group hydrides, alkyls, aryls, or amides, and another route is reaction of main group organometallic hydroxides with lanthanide compounds. In view of the availability of useful synthons, both the routes seem to be equally favorable. However, the former are aggregated structures of lanthanide hydroxides, as they often have bridging −OH groups and show unforeseen reaction patterns. While working toward the synthesis and application of organometallic hydroxides, we have successfully assembled a variety of main group monomeric hydroxides such as LGeOH,[53] LAl(OH)$_2$,[54] LAl(OH)Me,[55] LGa(OH)$_2$,[56] and so forth [L = HC{(Me)CN(2,6-iPr$_2$C$_6$H$_3$)}$_2$]. These molecules, on the contrary to lanthanide hydroxides, are mononuclear and have terminal −OH groups; therefore, they can be utilized as starting materials to synthesize the desired lanthanide−main group hetero-bimetallic systems containing a Ln-O−Al arrangement in a controlled manner (Ln = Yb, Er, Dy).[57] These compounds exhibit very good catalytic activity for the polymerization of ϵ-caprolactone.[57]

5. Group 4 Organo-hydroxides

The group 4 metals in their +4 oxidation state exhibit tendencies to form strong bonds to hard ligands, particularly with oxygen-containing ligands. As a result, many complexes of these metals are sensitive to water and, consequently, a large number of investigations of the reaction between water and Ti(IV) or Zr(IV) complexes have been reported.[58−64] A common characteristic of these reactions is the facile formation of robust μ-oxo complexes containing multiple metal centers.[1] The widespread interest in organotitanium and, to a lesser extent, in organozirconium chemistry has been due to their activity as catalysts in the polymerization of olefins and in the chemical fixation of nitrogen.

The syntheses of group 4 organometallic hydroxides have been accomplished by various routes, and the most diversified hydrolysis methods have been employed for this group compared to any other group of transition elements. These different ways of preparing hydroxides incorporate hydrolyis in the presence of salts and acids, base assisted hydrolysis, use of moist silver oxide or silver salts, hydrolysis of hydrides or alkyl derivatives, and reactions under UV irradiation. Each synthetic method will be discussed in this section with known examples.

5.1. Titanium

The reaction of the titanocene $[CpTi(\mu\text{-}H)]_2C_{10}H_8$ with water leads to the hydrogen evolution and formation of the hydroxo derivative $[CpTi(\mu\text{-}OH)]_2C_{10}H_8$, shown in Figure 4. The titanium atoms are bridged by two OH ligands and
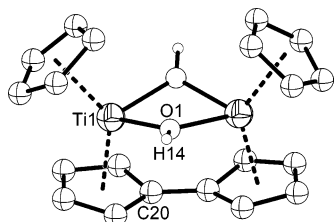
Figure 4. ORTEP drawing of $[(C_5H_5)Ti(OH)]_2C_{10}H_8$. Hydrogen atoms only on oxygen atoms are shown.

the fulvalene ligand, which is η^5-bonded to both titanium atoms.[65] The Ti–Ti separation in this complex is 3.195 Å. All titanium–cyclopentadienyl interactions are essentially the same, with an average Ti–C$_5$ ring plane distance of 2.080 Å. The fulvalene ligand is folded with 15.1° between C$_5$ rings, which are separated by 1.43(3) Å.

Proton and ^{13}C NMR spectra, as well as IR spectra, showed that in aqueous solution Cp_2TiX_2 (X = Cl, Br, I, NO$_3$) exists in pH-dependent equilibria involving $[Cp_2Ti(OH_2)_2]^{2+}$, $[Cp_2Ti(OH)(OH_2)]^+$, $[Cp_2(OH_2)Ti–O–Ti(OH_2)Cp_2]^{2+}$, and $Cp_2TiX–O–TiXCp_2$.[66] Hydrolysis of dicyclopentadienyltitanium dichloride in water at pH > 5 resulted in the loss of one cyclopentadienyl group.[67] The hydrolysis product was found to react with formic acid to give the ionic crystalline trinuclear complex $[Ti_3(\mu_3\text{-}O)(\mu\text{-}OH)_3(\mu\text{-}HCO_2)_2Cp_3]^+HCO_2^-\cdot 2HCO_2H$.[67] Each titanium is coordinated to two bridging hydroxides, two bridging formates, a central oxygen, and a Cp ligand in a distorted octahedral arrangement, with the oxygens of the bridging groups oriented away from the Cp ligand. While three titaniums are arranged around the central oxide ion, the Ti–O–Ti angles are close to the tetrahedral, being 107.6°, 107.4°, and 106.9°, respectively, which is consistent with a stereochemically active lone pair on the central oxygen.[67]

The reaction of $Cp^*_2TiCl_2$ with $AgCF_3SO_3$ in wet THF produced the diaqua complex $[Cp^*_2Ti(H_2O)_2](CF_3SO_3)_2$, whose aqueous solution afforded the hydroxo complex $[Cp^*_2Ti(OH)(H_2O)]CF_3SO_3\cdot xH_2O$ (x = 1 or 2).[68] The crystal structures of the three compounds were all quite similar in that they showed the titanium to be essentially tetrahedrally surrounded by the four ligands.[68] The $[Cp^*_2Ti(OH)(H_2O)]^+$ cation could also be obtained by the oxidation of Cp^*_2TiMe by $AgBPh_4$, followed by reaction with traces of water[69] (eq 3). The crystal structure of the resulting $[Cp^*_2Ti(OH)(H_2O)]$-$BPh_4\cdot 2THF$ is the same as that of the former three complexes, except for the THF's of solvation.
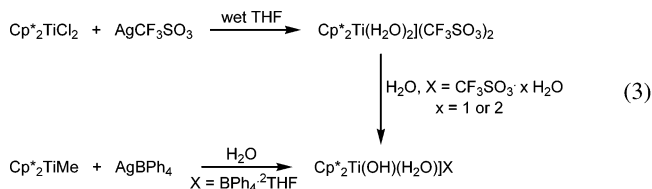
In a similar fashion, the reactions of Cp_2TiCl_2 with water in the presence of $NaBPh_4$ produced the complexes $[\{Cp_2Ti(H_2O)\}_2O][BPh_4]_2\cdot mH_2O$ and $[Cp_2Ti(OH)(H_2O)_n]$-$[BPh_4]\cdot mH_2O$, which could easily be dehydrated or converted into anhydrous nitrile and isocyanide derivatives.[70] A Ti–OH cationic complex could also be obtained from the oxidation of $Cp^*_2Ti–N=CPh_2$ with $AgBPh_4$ in the presence of traces of moisture. The crystal structure of the resulting $[Cp^*_2Ti(OH)(HN=CPh_2)]BPh_4\cdot OEt_2$ again shows a tetrahedral arrangement of the four ligands around the Ti atom.[71] In all the titanium hydroxo complexes, the Ti–OH distances are short [1.85–1.87 Å], indicating Ti–O double-bond character via polar interactions.

The reaction of Cp^*TiCl_3 with $(tBu)_2Si(OH)_2$ gives $Cp^*TiCl_2OSi(tBu)_2(OH)$, which, on hydrolysis in the presence of Et_3N, produces the dimeric hydroxo complex $[Cp^*Ti-(OH)OSi(tBu)_2O]_2$.[72] The structure of the compound, shown in Figure 5, consists of an eight-membered Ti$_2$Si$_2$O$_4$ ring in
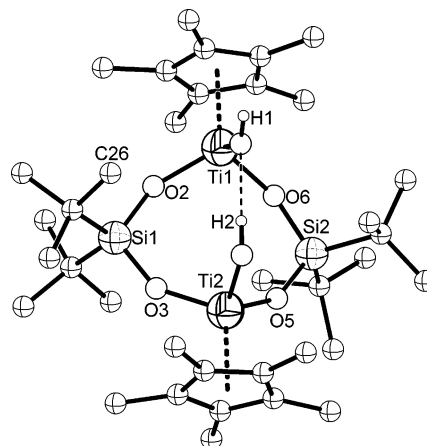
Figure 5. ORTEP drawing of $[(\eta^5\text{-}C_5Me_5)Ti(OH)OSi(tBu)_2O]_2$. Hydrogen atoms except those on terminal oxygen atoms are omitted for clarity.

a boat configuration. Each titanium is also bonded to a hydroxide and a cyclopentadienyl ring, in a tetrahedral arrangement. The two OH groups are not equivalent in that the hydrogen atom of one OH group (H(2) in Figure 5) is involved in a transannular bridge to O(1), the hydroxide O on the other Ti. The latter OH hydrogen (H(1)) is end-on bonded. The hydrogen bridge gives an increase in the coordination number at O(1), resulting in an increase of the Ti(1)–O(1) bond length. In such cases, it would be expected that a molecule of water would be eliminated, giving rise to the oxo compound $[Cp^*TiOSi(tBu)_2O]_2O$. However, there seems to be very little tendency for this to occur. It was argued that steric factors prevent further reaction. However, the dimeric oxide could be obtained from the reaction of Cp^*Li, $TiCl_3\cdot 3THF$, $(tBu)_2Si(OH)_2$, and oxygen.[72]

In addition to moisture introduced into a system, either deliberately or inadvertently, water formed as a product of the reaction can bring about hydrolysis to form the hydroxo complexes and, ultimately, the oxo complexes. This was

found to be the case in the homogeneous hydrogenation reaction of CO in the presence of $Cp_2Ti(CO)_2$. A 3:1 hydrogen to carbon monoxide molar ratio at 150 °C, or at 25 °C under UV irradiation, in the presence of $Cp_2Ti(CO)_2$ both produced CH_4 and converted the titanocene to the diamagnetic cluster, $Cp_6Ti_6O_8$.[73] It was suggested that the water formed from the reaction of CO and hydrogen was responsible for the hydrolysis reaction and the consequent formation of the oxide cluster.[73]

5.2. Zirconium

The reaction of the dicyclopentadienylzirconium dichloride, Cp_2ZrCl_2, with sodium benzoate in aqueous solution produced the trinuclear complex $[Zr_3(\mu_3-O)(\mu-OH)_3(\mu-PhCOO)_3Cp_3]^+PhCOO^-\cdot O(C_2H_5)_2$, whose structure is similar to that of $[Ti_3(\mu_3-O)(\mu-OH)_3(\mu-HCO_2)_3Cp_3]^+HCO_2^-\cdot 2HCO_2H$ except that $PhCO_2$ groups replace the HCO_2 as bridging groups.[74] Similar to the case of titanocene chloride, the reaction of Cp_2ZrCl_2 with $NaBPh_4$ and water afforded the complexes $[\{Cp_2Zr(H_2O)\}_2O][BPh_4]_2\cdot mH_2O$ and $[Cp_2Zr-(OH)(H_2O)_n][BPh_4]\cdot mH_2O$, which have been shown to be dehydrated or converted into anhydrous nitrile and isocyanide derivatives.[70] The reaction of Cp_2ZrCl_2 with CF_3COOH in a two-phase $CHCl_3/H_2O$ system produced the dinuclear complex $[Cp_2Zr(OCOCF_3)(\mu-OH)]_2$.[75] The structure is typical for a $[Cp_2M(OH)]_2$ dimer (Figures 1 and 4) with the addition of CF_3COO^- coordinated to each Zr to give a five coordinate metal. $Cp^*_2Zr(OH)Ph$ was prepared by the reaction of $Cp^*Zr(Ph)(\eta^1:\eta^5-CH_2C_5Me_4)$ with water ($Cp^* = \eta^5-C_5Me_5$).[76]

In some cases, the presence of acid seems to be important in the formation of hydroxo complexes, as was found in the preparation of the dinuclear, doubly OH-bridged complex $[CpZr(NO_3)_2(\mu-OH)]_2\cdot 2THF$ from the reaction of Cp_2ZrCl_2 with nitric acid in $CHCl_3$.[77] The complex can be recrystallized from THF to give the crystalline $[CpZr(NO_3)_2(\mu-OH)]_2\cdot 2THF$.[77] The structure of this complex (see Figure 6) shows
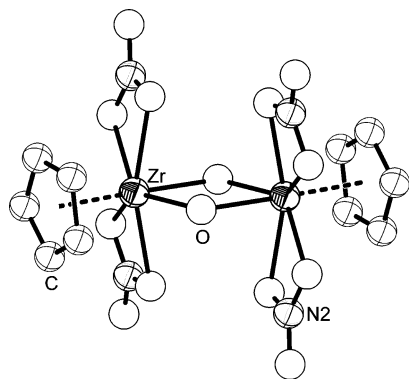
**Figure 6.** ORTEP drawing of $[(\eta^5-C_5H_5)Zr(NO_3)_2(\mu-OH)]_2$. Hydrogen atoms are deleted for clarity.

a centrosymmetric dimer of two $CpZr(NO_3)_2$ units bridged by two OH ligands. The structure is of interest in that each Zr atom is seven coordinated, being surrounded by an η^5-bonding Cp, two OH groups, and two nitrates acting as bidentate ligands. The geometry was described as being that of a distorted pentagonal bipyramid with the Cp and one of the OH ligands occupying axial positions and the two chelating NO_3 ligands and the remaining OH bridging group constituting the equatorial plane (see Figure 6). The distortions are such that the equatorial groups are oriented away from the Cp ligand by $\sim 10°$. The $O(11/21)-Zr-O(12/22)$

angles are $55.7 \pm 0.2°$ instead of the $72°$ in an ideal pentagonal bipyramid.

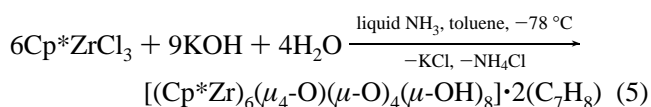The complexes $[Cp^*ZrCl]_3(\mu-O)(\mu-OH)_3(\mu-Cl)$ and $[Cp^*ZrCl]_3O(OH)_4\cdot 2THF$ have been prepared by the hydrolysis of Cp^*ZrCl_3 in THF.[78] The former compound was prepared by using a deficit of water in the reaction, while the latter one was obtained with an excess of water. Moreover, the monochloro monooxo trihydroxo metal complexes can be converted into the monooxo tetrahydroxo compounds by using stoichiometric amounts of water. These compounds display three types of Cp* and OH ligands in their ^{13}C and ^1H NMR spectra.

Treatment of zirconyl chloride with saturated aqueous ammonium carbonate and guanidinium carbonate affords the complex $[(C(NH_2)_3)_3Zr(\mu-OH)(CO_3)_3\cdot H_2O]_2$. This compound consists of cationic $[C(NH_2)_3]^+$ and the dimeric anion $[\{ZrOH(CO_3)_3\}_2]$.[6-] The anion is centrosymmetric, with each metal atom bonded to two bridging OH groups and three chelating CO_3^{2-} ions. Another closely related complex $Na_6[Zr(\mu-OH)(C_2O_4)_3]_2\cdot 7H_2O$ was isolated during the attempted preparation of a mixed carbonate/oxalate of zirconium.[79] The complexes $[CpZr(NO_3)_2(\mu-OH)]_2\cdot 2THF$, $[(C(NH_2)_3)_3Zr(\mu-OH)(CO_3)_3\cdot H_2O]_2$, and $Na_6[Zr(\mu-OH)-(C_2O_4)_3]_2\cdot 7H_2O$ have a similar structure of the core of the dimeric molecule and the same metalated oxygen environment. However, compared to the case of the nitrate complex, the Cp groups are replaced by chelating CO_3^{2-} or $C_2O_4^{2-}$ ligands in the second and third compound, respectively, giving rise to eight coordinate Zr atoms in carbonate and oxalate complexes as opposed to seven coordinate Zr in the nitrate compound.

Base hydrolysis of Cp^*ZrCl_3 in THF gives $[Cp^*ZrCl]_3-(\mu_3-O)(\mu_3-OH)(\mu-OH)_3\cdot 2THF$.[80] The X-ray structure reveals the presence of a cluster containing a nearly equilateral triangular core of three Zr atoms, capped above and below by μ_3-O and μ_3-OH groups. Three bridging OH groups span the sides of the triangular core; two of the three OH groups are associated with THF molecules via hydrogen bonds (eq 4).

$$3Cp^*ZrCl_3 \ + \ 5\,H_2O \ + \ 6\,Et_3N \ \xrightarrow{\text{THF}} \quad (4)$$
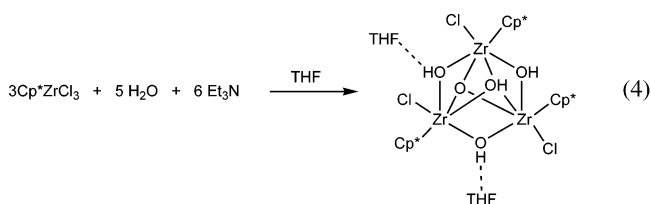
A larger aggregate of zirconiumoxide hydroxide $[(Cp^*Zr)_6-(\mu_4-O)(\mu-O)_4(\mu-OH)_8]\cdot 2(C_7H_8)$ was prepared by the hydrolysis of Cp^*ZrCl_3 in the two phase ammonia/toluene system in the presence of the reagents KOH and water.[81] The methodology was similar to that adapted for the synthesis of the polyoxometallic zirconium clusters $[\{(EtMe_4C_5)Zr\}_6-(\mu_6-O)(\mu_3-O)_8]\cdot(C_7H_8)$ and $[\{(EtMe_4C_5)Zr\}_6(\mu_6-O)(\mu_3-O)_8]\cdot(C_9H_{12})$,[82] which mimic soluble analogues of solid ZrO_2 where all the oxygen and zirconium atoms are coordinatively saturated. Thus, the hydrolysis of Cp^*ZrCl_3 in the presence of KOH and H_2O in a liquid NH_3/toluene two phase system affords the chlorine free $[(Cp^*Zr)_6(\mu_4-O)(\mu-O)_4(\mu-OH)_8]\cdot 2(C_7H_8)$[81] (eq 5).

$$6Cp^*ZrCl_3 + 9KOH + 4H_2O \xrightarrow[-KCl, -NH_4Cl]{\text{liquid } NH_3, \text{ toluene}, -78\,°C}$$

$$[(Cp^*Zr)_6(\mu_4-O)(\mu-O)_4(\mu-OH)_8]\cdot 2(C_7H_8) \quad (5)$$

The IR spectrum of this compound shows a broad absorption at 3689 cm^{-1} attributed to the O−H stretching frequency, and the ^{1}H NMR spectrum exhibits a single resonance (δ 2.05 ppm) for the Cp* protons, indicating six equivalent Cp* groups in the solution state. The solid-state structure consists of an octahedron with Cp*Zr fragments arranged around an interstitial oxygen atom that occupies two positions, 0.933-(13) Å apart from each other. Twelve edges of the octahedron are bridged by oxygen atoms forming eight six-membered Zr$_3$O$_3$ rings with chair conformation. The angles between adjacent zirconium atoms are either 60° or 89°. The Zr−(μ-O) or Zr−(μ-OH) bond lengths (2.072(2)−2.171(2) Å, average 2.106 Å) are similar to those mentioned above for zirconiumoxide hydroxide.[81] Moreover, reaction of [(Cp*Zr)$_6$(μ_4-O)(μ-O)$_4$(μ-OH)$_8$]·2(C$_7$H$_8$) with Cp$_2$ZrMe$_2$ or (MeC$_5$H$_4$)$_2$ZrH$_2$ in toluene at room temperature results in the formation of the dumb-bell-like polyoxozirconium hydroxide [{(Cp*Zr)$_4$(μ_5-O)(μ_3-O)$_2$(μ-OH)$_4$}$_2$Zr-(μ-O)$_4$]·2(C$_7$H$_8$).[83] The OH protons on the periphery of the former react with the Me or H group of Cp$_2$ZrMe$_2$ or (MeC$_5$H$_4$)$_2$ZrH$_2$ and lead to the new Zr−O bonds. Furthermore, these intermediates react under the elimination of CpH or MeC$_5$H$_5$ with the concomitant formation of [{(Cp*Zr)$_4$-(μ_5-O)(μ_3-O)$_2$(μ-OH)$_4$}$_2$Zr(μ-O)$_4$]·2(C$_7$H$_8$)[83] (eq 6).

(6)
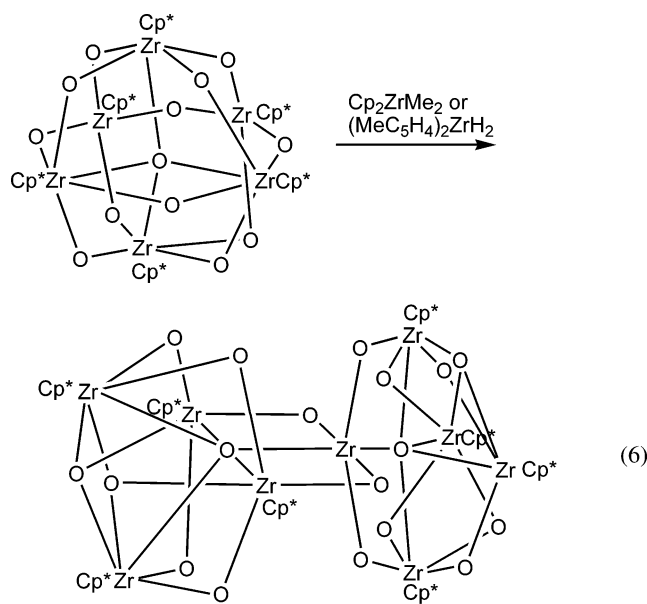
Moist silver oxide is considered a good reagent for the formation of the hydroxo complexes in that it can act as both a source of hydroxide and a halogen abstracting agent (especially for iodine).[84] Other silver salts can also be used for the preparation of hydroxo complexes. For example, salts of the novel dinuclear dihydroxy-bridged cation [Cp$_2$Zr$_2$(μ-OH)$_2$(H$_2$O)$_6$]$^{4+}$ have been obtained in the reaction of Cp$_2$ZrCl$_2$ with AgX salts (X = CF$_3$SO$_3^-$ and ClO$_4^-$), followed by subsequent treatment of the reaction solutions with H$_2$O.[85] X-ray structure determinations of [Cp$_2$Zr$_2$(μ-OH)$_2$(H$_2$O)$_6$](CF$_3$SO$_3$)$_4$·4THF and [Cp$_2$Zr$_2$(μ-OH)$_2$(H$_2$O)$_6$]-(ClO$_4$)$_4$·8THF show that the Zr atoms have a distorted octahedral coordination geometry with the Cp group oriented *trans* to one of the bridging OH groups. This structure is very similar to that of the complex [Cp*ZrCl$_2$(H$_2$O)(μ-OH)]$_2$, which was obtained by the reaction of [Cp*ZrCl$_3$] with wet lithium hydroxide in THF.[86]

Water reacts with Cp*$_2$ZrH$_2$ in a clean, stepwise manner to yield Cp*$_2$Zr(H)(OH), (Cp*$_2$ZrH)$_2$O, Cp*$_2$Zr(OH)$_2$, and finally Cp*$_2$Zr(OH)$_2$·H$_2$O.[26] In much the same manner, Cp*$_2$ZrHCl yielded Cp*$_2$Zr(OH)Cl. Cp*$_2$ZrH$_2$ reacted with Cp*$_2$Zr(OH)X (X = Cl, OH, H) to form Cp*$_2$(X)Zr−O−Zr(H)Cp*$_2$. In all cases, conversion of a Zr−H bond to an Zr−O bond takes place with hydrogen evolution. Free water undergoes a rapid H exchange and a slower O exchange with the hydroxy derivatives. [Cp*$_2$Zr(N$_2$)]$_2$(μ-N$_2$) reacts rapidly and cleanly with 1 equiv of H$_2$O to produce N$_2$ (3 equiv) and (Cp*$_2$MH)$_2$O. In these and other studies, ^{17}O NMR spectroscopy was used in elucidating the structures of the transition metal oxo complexes.[87] Chemical shift and $^1J_{OH}$ coupling data can show the presence of different types of oxygen containing ligands. Oxo groups exhibit resonances around 500 ppm (relative to water) with no proton coupling. On the other hand, hydroxo groups exhibit resonances between 140 and 250 ppm with proton coupling; the $^1J_{17OH}$ values are approximately 80 Hz. Line widths for the OH resonances are in the range 50−60 Hz, while the μ-oxo resonances are somewhat sharper (20−30 Hz). Further, ^{17}O NMR provides a convenient means for observing the dynamic water exchange process for the hydroxo complexes. The monomeric complexes Cp*$_2$Zr(OH)Cl and Cp*$_2$Zr(OH)$_2$ were prepared by the treatment of Cp*$_2$Zr(nBu)Cl and Cp*$_2$Zr(Me)$_2$ with 1 and 2 equiv of water, respectively, in hexane.[88] In both molecules, two Cp* groups and the two ancillary ligands surround the Zr in a very distorted tetrahedral arrangement. Figure 7 shows the structure of the Cp*$_2$Zr(OH)Cl; the
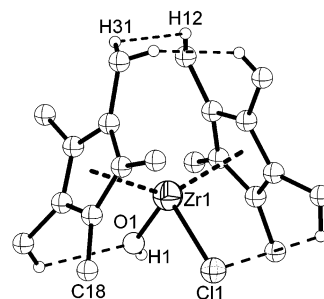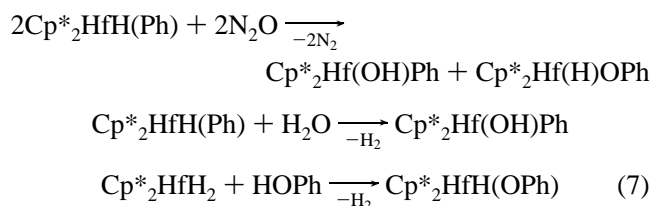

Figure 7. ORTEP drawing of (η^5-C$_5$Me$_5$)$_2$Zr(OH)Cl. Hydrogen atoms except those involved in short intramolecular interactions are omitted for clarity.

dihydroxo complex is similar. As can be seen from Figure 7, there are several very short H- - -H interactions, especially the H(31)−H(12) distance of 2.08 Å, which is well within twice the van der Waals radius of H (1.20 Å).

5.3. Hafnium

Treatment of Cp*$_2$HfH(Ph) with N$_2$O results in the formation of Cp*$_2$Hf(OH)Ph and Cp*$_2$HfH(OPh), accompanied by N$_2$ evolution. This involves competitive oxidation of the hydride and phenyl ligands of Cp*$_2$Hf(H)Ph. Interestingly, Cp*$_2$Hf(OH)Ph and Cp*$_2$HfH(OPh) can be prepared independently; reaction of Cp*$_2$HfH(Ph) with H$_2$O affords Cp*$_2$Hf(OH)Ph, whereas the reaction of Cp*$_2$HfH$_2$ with HOPh results in the formation of Cp*$_2$HfH(OPh)[89] (eq 7).

$$2\text{Cp*}_2\text{HfH(Ph)} + 2\text{N}_2\text{O} \xrightarrow{-2\text{N}_2}$$
$$\text{Cp*}_2\text{Hf(OH)Ph} + \text{Cp*}_2\text{Hf(H)OPh}$$

$$\text{Cp*}_2\text{HfH(Ph)} + \text{H}_2\text{O} \xrightarrow{-\text{H}_2} \text{Cp*}_2\text{Hf(OH)Ph}$$

$$\text{Cp*}_2\text{HfH}_2 + \text{HOPh} \xrightarrow{-\text{H}_2} \text{Cp*}_2\text{HfH(OPh)} \quad (7)$$

Analogous to the zirconium complexes, the complexes, [Cp*HfCl]$_3$(μ-O)(μ-OH)$_3$(μ-Cl) and [Cp*HfCl]$_3$O(OH)$_4$·2THF have been obtained by the hydrolysis of Cp*HfCl$_3$ in THF[78] by using a deficit of water in the reaction and with an excess of water, respectively. Addition of a stoichiometric amount of water to the monochloro monooxo trihydroxo metal complex leads to the formation of the monooxo tetrahydroxo complex. Water reacts with Cp*$_2$HfH$_2$ to yield Cp*$_2$Hf(H)(OH), (Cp*$_2$HfH)$_2$O, Cp*$_2$Hf(OH)$_2$, and finally Cp*$_2$Hf(OH)$_2$·H$_2$O.[26] Similarly, Cp*$_2$HfHCl yielded Cp*$_2$Hf(OH)Cl. Cp*$_2$HfH$_2$ reacted with Cp*$_2$Hf(OH)X (X = Cl, OH, H) to form Cp*$_2$(X)Hf−O−Hf(H)Cp*$_2$. In all cases, conversion of a Hf−H bond to an Hf−O bond involves hydrogen evolution.

It has been reported that certain metallocene dihalides and bis(pseudo-halides) of the type Cp$_2$MX$_2$ (M = Ti, V, Nb, Mo; X = F, Cl, Br, I, SCN, N$_3$) resulted in rapid Cl⁻ dissociation after the addition of H$_2$O to Cp$_2$MCl$_2$ (M = Ti, V, Zr). These molecules have structures analogous to *cis*-platin and *cis*-Pt(NH$_3$)$_2$Cl$_2$ and exhibit antitumor activity; the aqueous solution behavior of Cp$_2$MCl$_2$ (M = Ti, V, Zr) has been studied and compared to that of *cis*-platin.[61] The hydrolysis studies showed that only Cp$_2$VCl$_2$ had a stable M−Cp bond at physiological pH's, with the order of decreasing hydrolytic stability of the M−Cp bond being V > Ti ≫ Zr in unbuffered aqueous KNO$_3$ (0.32 M).

6. Group 5 Organo-hydroxides

Most of the structurally characterized organometallic hydroxides in this group are those of niobium; in fact, to our knowledge, one organometallic hydroxide of vanadium has recently been reported.

6.1. Vanadium

The reaction of vanadocene with B(C$_6$F$_5$)$_3$ in the presence of water yields the yellow-orange complex [Cp$_2$V(μ-H)B-(C$_6$F$_5$)$_3$] and the blue [Cp$_2$V(μ-OH)B(C$_6$F$_5$)$_3$]. Their crystals can be physically separated due to their different morphologies. The overall process has been proposed to occur by the two electron reduction of H$_2$O by Cp$_2$V, this involves the intermediate V(IV) species [Cp$_2$VH]$^+$[HOB(C$_6$F$_5$)$_3$]$^-$, which further evolves through disproportionation of Cp$_2$V into the vanadium(III) complexes [Cp$_2$V(μ-H)B(C$_6$F$_5$)$_3$] and [Cp$_2$V(μ-OH)B(C$_6$F$_5$)$_3$].[90]
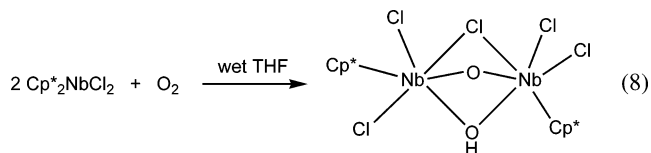
6.2. Niobium

The compounds are normally formed by the reaction of metal halides with an organometallic transfer agent, followed by the exposure to moisture. For example, treatment of NbCl$_5$ with [nBu$_3$Sn(C$_5$H$_4$$n$Bu)] results in [Nb($\eta^5$-C$_5H_4$$n$Bu)Cl$_4$]$_n$, which on reaction with moist HCl gave [Nb(η^5-C$_5$H$_4$$n$Bu)-Cl$_3$(OH)]·CH$_2Cl_2$.[91] The X-ray crystal structure of the trinuclear niobium(IV) complex {[(η^5-C$_5$H$_5$)Nb(μ-O$_2$CH)(μ-OH)]$_3$(μ_3-O)}H[92] was found to be similar to that of the corresponding titanium complex [Ti$_3$(μ_3-O)(μ-OH)$_3$(μ-HCO$_2$)$_3$-(η^5-C$_5$H$_5$)$_3$]$^+$. The three Nb atoms were located at vertices of an almost equilateral triangle surrounding a central O, with formate and hydroxyl bridges along the edges of the triangle. The Nb−Nb distances are too large (≥3.14. Å) to be consistent with metal−metal bonding.[92]
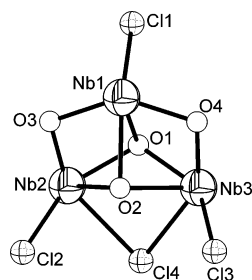
In many cases, the organometallic hydroxides are difficult to isolate due to rapid conversion to oxo compounds; this was found to be especially true for the late transition metal complexes.[93] Bottomley and Karslioglu took the Nb(IV)

complex [Cp*$_2$NbCl$_2$] through several oxidation/reduction cycles in the presence of trace amounts of moisture and structurally characterized many of the products.[94,95] The oxidation of [Cp*$_2$NbCl$_2$] with (O$_2$) in damp THF gave [{Cp*NbCl$_2$}$_2$(μ-Cl)(μ-OH)(μ-O)] and polymeric [Nb$_2$Cl$_2$O$_4$-(THF)$_3$]$_n$.[94]

The hydroxo complex consists of two Nb atoms bridged by one Cl ligand and two oxygens, one from the OH and the other from an oxide ion (eq 8). Each Nb is also bonded
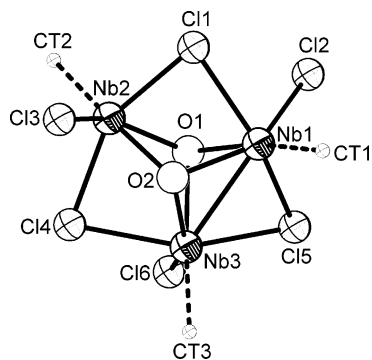
$$2\ \text{Cp*}_2\text{NbCl}_2\ +\ \text{O}_2\ \xrightarrow{\text{wet THF}}\ \text{(structure)} \qquad (8)$$

to a Cp* and two Cl's to give a roughly octahedral arrangement around each Nb atom. Reduction of the hydroxo complex, [{Cp*NbCl$_2$}$_2$(μ-Cl)(μ-OH)(μ-O)] with Zn powder gave the Nb(IV) cationic trimeric complex, [(Cp*Nb(μ-Cl)-(μ-O))$_3$]$^+$.[94] Reoxidation of this cation by oxygen (O$_2$) in CH$_2$Cl$_2$ produced [(Cp*NbCl)$_3$(μ-Cl)(μ-O)$_2$(μ_3-OH)(μ_3-O)]$^+$; the (NbCl)$_3$(μ-Cl)(μ-O)$_2$(μ_3-OH)(μ_3-O) core is shown in Figure 8. As can be seen, the cluster contains an isosceles

Figure 8. ORTEP view of the [NbCl]$_3$(μ-Cl)(μ-O)$_2$(μ_3-OH)(μ_3-O) core of [{(η^5-C$_5$Me$_5$)NbCl}$_3$(μ-Cl)(μ-O)$_2$(μ_3-OH)(μ_3-O)]$^+$.

triangle of Nb atoms (Nb−Nb 3.028 (2) Å and 3.318 (2) Å) bridged by either chlorine or oxygen atoms, with the long Nb−Nb edge being bridged by the Cl. The Nb$_3$ triangle is capped on one side by a μ_3-O ligand and on the other by a μ_3-OH ligand. The OH is symmetrically bonded to the three Nb atoms (2.207 Å), while the μ_3-O has substantially shorter bond distances to the two Nb atoms forming the long edge (2.046 Å) than to the third Nb (2.228 Å).

The Nb(III) complex [Cp'Nb(CO)$_2$Cl$_2$]$_2$ (Cp' = C$_5$H$_4$Me) was found to undergo decarbonylation on refluxing in THF to give a dark brown paramagnetic compound Cp'$_3$Nb$_3$Cl$_6$-(μ_3-O), which reacted with atmospheric oxygen to produce Cp'$_3$Nb$_3$Cl$_3$(μ-Cl)$_3$(μ_3-O)(μ_3-OH).[96] As expected, this Nb(IV) hydroxo complex was found to be paramagnetic but exhibited a 10-line ESR spectrum characteristic of a spin-$1/2$ system with the odd electron coupled to only one Nb nucleus. This is consistent with the X-ray structure which showed a Nb$_3$ triangular core having one short Nb−Nb distance of approximately 2.92 Å, corresponding to a Nb−Nb bond, and two long Nb···Nb distances (3.28 Å). Figure 9 shows the inner coordination of the cluster. As can be seen, the Nb$_3$ triangle is bridged by Cl atoms along each edge and is capped by a μ_3-oxo ligand and a μ_3-hydroxo on opposite sides of the Nb$_3$ plane, with terminal Cp and Cl ligands completing the coordination sphere about each Nb atom. This same isosceles triangular Nb$_3$ core was found in the [CpNbCl(μ-Cl)]$_3$(μ_3-OH)(μ_3-O) cluster, formed by the reduction of the hydrolysis product of CpNbCl$_4$ with aluminum powder.[97]

Figure 9. ORTEP view of the inner coordination sphere of $Cp'_3Nb_3Cl_3(\mu\text{-}Cl)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)$ ($Cp' = C_5H_4Me$). Hydrogen atoms are omitted for clarity, and only the centroid of each Cp' ring is shown.

Again, the Nb–Nb distances indicate two of the three Nb atoms are singly bonded, with no bonding to the third Nb atom. This is consistent with both its magnetic moment and ESR spectrum, which showed a single unpaired electron.[97] The compound $[Cp'NbCl(\mu\text{-}Cl)]_3(\mu_3\text{-}OH)(\mu_3\text{-}O)$ was found to decompose slowly in THF solution to give $Cp'_4Nb_5Cl_5$-$(OH)_9O(THF)_2$ which was thought to have an adamantane-like $Nb_4(OH)_6$ core, with a Nb attached through an O bridge.[97] Use of reducing agents other than aluminum powder gave different products; for example, zinc powder produced $[CpNbCl(\mu\text{-}OH)]_3(\mu_3\text{-}OH)(\mu_3\text{-}O)$, as did sodium amalgam.
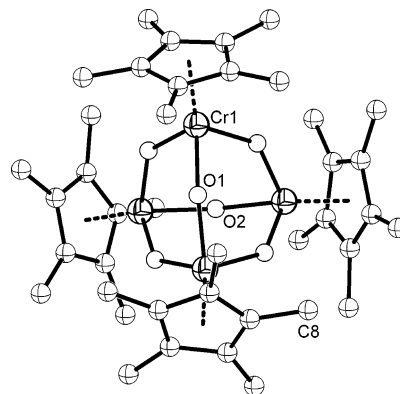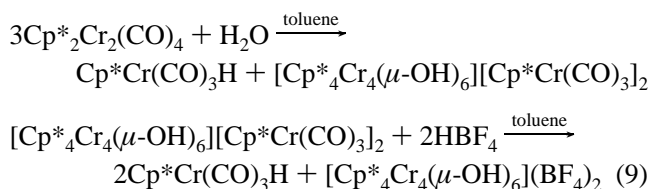
6.3. Tantalum

A tantalum hydroxo complex, $[Cp^*TaCl_2(OH)]_2(\mu\text{-}O)$, has been prepared and structurally characterized.[98–100] The compound could be obtained either by the controlled hydrolysis of $[Cp^*TaCl_4]$ or by air oxidation of $[Cp^*Ta\text{-}(CO)_2Cl_2(THF)]$.[100] The structure of the $[Cp^*TaCl_2(\mu\text{-}OH)]_2$-$(\mu\text{-}O)$ shows that the two Ta atoms are bridged by three oxygens and are terminally bonded to two Cl and one Cp^* ligand to give a distorted octahedral arrangement. Although the dihydroxo complex is stable in the solid state under ambient conditions, it quantitatively transforms on heating with the elimination of HCl and H_2O to give the trinuclear oxide cluster $Cp^*_3Ta_3(\mu\text{-}O)_3(\mu_3\text{-}O)(\mu\text{-}Cl)Cl_3$.

7. Group 6 Organo-hydroxides

A large number of organometallic hydroxides are known for metals in this group. However, only a few terminal hydroxo complexes are known, while complexes having doubly or triply bridged hydroxo ligands are more common.

7.1. Chromium

Reaction of the metal–metal triply bonded complex $Cp^*_2Cr_2(CO)_4$ with H_2O in refluxing toluene gave $Cp^*Cr\text{-}(CO)_3H$ along with the salt $[Cp^*_4Cr_4(\mu\text{-}OH)_6][Cp^*Cr\text{-}(CO)_3]_2$.[101] Metathesis of this salt with $HBF_4 \cdot OMe_2$ gave $Cp^*Cr(CO)_3H$ and $[Cp^*_4Cr_4(\mu\text{-}OH)_6](BF_4)_2$, which was structurally characterized[101] (eq 9).

$$3Cp^*_2Cr_2(CO)_4 + H_2O \xrightarrow{\text{toluene}}$$
$$Cp^*Cr(CO)_3H + [Cp^*_4Cr_4(\mu\text{-}OH)_6][Cp^*Cr(CO)_3]_2$$

$$[Cp^*_4Cr_4(\mu\text{-}OH)_6][Cp^*Cr(CO)_3]_2 + 2HBF_4 \xrightarrow{\text{toluene}}$$
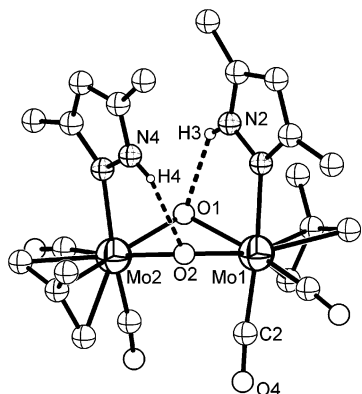$$2Cp^*Cr(CO)_3H + [Cp^*_4Cr_4(\mu\text{-}OH)_6](BF_4)_2 \quad (9)$$

Figure 10. ORTEP drawing of the cation $[(\eta^5\text{-}C_5Me_5)_4Cr_4(\mu\text{-}OH)_6]$-$(BF_4)_2$. Hydrogen atoms have been deleted for clarity.

The cation has an unusual adamantane-like cage structure formed by four Cr atoms and six $\mu\text{-}OH$ groups (Figure 10).[101] Unlike the case of adamantane, the O–Cr–O bond angles are $\sim90°$ ($90.7 \pm 0.3°$), which forces the Cr–O–Cr angles to open to $\sim140°$. A different type of Cr_4 core is found in the $[Cr_4(CO)_{12}(\mu_3\text{-}OH)_4]^{4-}$ anion.[102] The structure of this complex consists of a cubane-like Cr_4O_4 arrangement with triply bridging $\mu_3\text{-}OH$ groups linking $Cr(CO)_3$ units. This structure seems to be a general one found for a number of group 6 hydroxocarbonyl complexes of the type $[M_4(CO)_{12}$-$(\mu_3\text{-}OR)_4]^{4-}$ (M = Cr and R = Me, Ph;[102,103] M = Mo, W and R = H[104,105]) as well as in the nitrosyl-substituted complex $[Mo(OH)(CO)_2(NO)]_4 \cdot 4Ph_3PO$.[106]

The direct oxidation of the neutral complexes $[Cr(\eta^6\text{-}C_6H_6)_2]$ and $[Cp_2Co]$ by O_2 in THF produced the interesting solid organometallic hydroxides $[Cr(\eta^6\text{-}C_6H_6)_2][OH]$ and $[Cp_2Co][OH]$.[32] The compounds have a laminar structure consisting of layers of $[\{M(\eta^6\text{-}C_6H_6)_2\}^+]_n$ (M = Cr, Co) cations intercalated with $([OH]^- \cdot 3H_2O)_x$ layers, stabilized by hydrogen bonded water molecules and OH^- groups. The hydroxides are just one example of a series of solids consisting of one-, two-, and three-dimensional superanion framework structures encapsulating organometallic cations, such as $[Cr(\eta^6\text{-}C_6H_6)_2]^+$ and $[Cp_2Co]^+$.[32] A four-membered Cr_2X_2 core is found in the complexes $Cp(NO)Cr(\mu\text{-}Se\text{-}nBu)$-$(\mu\text{-}OH)Cr(NO)Cp$ and $Cp(NO)Cr(\mu\text{-}SePh)_2Cr(NO)Cp$; in the latter complex the two bridging groups are SePh, while in the former they are OH and Se–nBu ligands.[107]

7.2. Molybdenum

The di-μ-hydroxo-dimolybdenum complex $[Mo(CO)_2$-$(OH)(\eta^3\text{-}C_4H_7)(3,5\text{-}diMepzH)]_2 \cdot C_6H_6$ (C_4H_7 = methylallyl, 3,5-diMepzH = 3,5-dimethylpyrazole) was the unexpected product of the reaction of $Mo(MeCN)_2(\eta^3\text{-}C_4H_7)(CO)_2Cl_2$ with the organogallate ligand, $[Me_2Ga(3,5\text{-}diMepz)_2]^-$, in acetonitrile.[108] Although the source of water is not known, it was speculated that the acetonitrile solvent, although dried, still contained traces of water. This is another example of the adventitious presence of moisture generating a hydroxo-product. The structure of the complex, shown in Figure 11, is that of two distorted Mo octahedra sharing an OH···OH edge, to form a folded four-membered $Mo(\mu\text{-}OH)_2Mo$ ring.[108] The pyrazole ligands are in the axial position and form bent N–H···O intramolecular hydrogen bonds to the bridging OH groups. The two sets of Mo–OH bonds differ significantly in length, with the two bonds in the five-membered hydrogen-bonded rings averaging 2.237 Å, while the two non-hydrogen bonded Mo–OH distances are 2.140 Å.

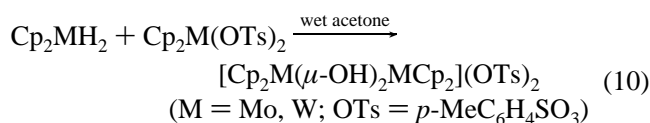**Figure 11.** ORTEP drawing of [Mo(CO)$_2$(OH)(η^3-C$_4$H$_7$)(3,5-diMepzH)]$_2$·C$_6$H$_6$. Solvent benzene molecule and hydrogen atoms except those involved in intramolecular N−H···O contacts have been omitted for clarity.

Prolonged treatment of the dimeric complex [Mo(H)Cp-(μ-(η^1:η^5-C$_5$H$_4$))]$_2$ with aqueous hexafluorophosphoric acid gives the hydroxo complex [{MoCp}$_2$(μ-OH)(μ-H){μ-(η^5-C$_5$H$_4$-η^5-C$_5$H$_4$)}]·2PF$_6$.[109] The cation consists of two MoCp moieties which are bridged by a H atom, the hydroxyl ligand, and the pentafulvalene ligand, which is η^5-bonded to the Mo atoms; the structure is similar to the Ti complex shown in Figure 4, except that a hydride replaces one of the hydroxides.[110] The molybdenum atoms are separated by 3.053 Å, indicating no Mo−Mo bonding. There is no direct evidence from the electron density distribution for the presence of the bridging hydrogen, but it was inferred on chemical grounds.

The reaction of [Cp$_2$Mo(SMe$_2$)Br]$^+$PF$_6^-$ with aqueous methylamine gives the complex [Cp$_2$Mo(NH$_2$Me)OH]$^+$PF$_6^-$. This compound on treatment with MeNH$_2$ in water results in the formation of [Cp$_2$Mo(NH$_2$Me)H]$^+$PF$_6^-$.[111] Reduction of Cp*MoCl(O)$_2$ with zinc in HCl gave a mixture of [Cp*Mo(O)(μ-O)]$_2$ and [(Cp*Mo)$_3$(μ-OH)$_n$(μ-O)$_{6-n}$]Cl$_2$. The latter compound was the major product of the reaction. Based on the ^{1}H NMR and magnetic moment observations, it was suggested that an equilibrium exists in the solution due to the redox disproportionation of the diamagnetic cluster with $n = 5$ into the paramagnetic cluster ($n = 4$) with $\mu_{eff} = 1.73$ μ_B and the paramagnetic cluster ($n = 6$) with $\mu_{eff} = 1.13$ μ_B.[112] Poli and co-workers have shown that reduction of [Cp*$_2$Mo$_2$O$_5$] with zinc in a MeOH/H$_2$O solution acidified with either CF$_3$COOH or CF$_3$SO$_3$H affords the triangular paramagnetic cluster [(Cp*Mo)$_3$(μ-O)$_2$(μ-OH)$_4$]$^{2+}$, where the three Mo atoms form a nearly equilateral triangle, each edge of which is symmetrically bridged by two oxygen atoms, with one above and one below the MoO$_3$ plane.[113] Based on the spectroscopic evidences, it has been shown that the solution structure of this molecule is identical to the solid-state structure. The anions CF$_3$COO$^-$ and CF$_3$SO$_3^-$ are involved in hydrogen bonding interactions with all four bridging OH groups.[113] The cations [(Cp*Mo)$_3$(μ-O)$_2$(μ-OH)$_4$]$^{2+}$ and [(Cp*Mo)$_3$(μ-O)$_{6-n}$(μ-OH)$_n$]$^{2+}$ are closely related to each other. Though they have been obtained by a similar route, the surprising fact about these cations is that, despite similar synthetic procedures, Poli reported [(Cp*Mo)$_3$-(μ-O)$_2$(μ-OH)$_4$]$^{2+}$ as the major product and no disproportionation in solution. However, Bottomley proposed [(Cp*Mo)$_3$(μ-O)(μ-OH)$_5$]$^{2+}$ with $n = 5$ as the major product, that results in a redox disproportionation equilibrium in solution with $n = 4$ and $n = 6$ (see above).[111−113] A stopped flow analysis of Cp*$_2$Mo$_2$O$_5$ in 20% MeOH/H$_2$O over the pH range 0−14 suggests that at low pH (<2.5) Cp*MoO$_2^+$

is the only species present in the solution. At pH > 6 Cp*MoO$_3^-$ anion is the dominant species. The ions in the equilibrium also contain a small amount of Cp*MoO$_2$(OH) (ca. 15% at pH 4), whose dissociation constant is p$K = 3.65$ $\pm$ 0.02. The three trioxygenated species Cp*MoO$_2^+$, Cp*MoO$_2$(OH), and Cp*MoO$_3^-$ establish rapid proton-transfer equilibria but transform to the dioxo species Cp*MoO$_2^+$ by two independent slow first-order pathways: loss of H$_2$O from Cp*MoO$_3$H$_2^+$ (at pH < 2) and loss of OH$^-$ from Cp*MoO$_2$(OH). The prevalent pathway at high pH is the addition of OH$^-$ to Cp*MoO$_2^+$, which is first order in [OH$^-$]. The kinetics of the equilibrium process at intermediate pH are affected by the buffer concentration, indicating a general acid/base equilibrium.[114]

A molybdenum carbonyl cluster of the composition K$_3$[Mo$_2$(OH)$_3$(CO)$_6$] has been obtained by the alkaline hydrolysis of Mo(CO)$_6$.[115] The complex [Cp$_2$Mo(μ-OH)$_2$-MoCp$_2$]$^{2+}$(OTs)$_2$ (OTs = p-MeC$_6$H$_4$SO$_3^-$) has been obtained in good yields by reaction of Cp$_2$MoH$_2$ with Cp$_2$Mo(OTs)$_2$ in aqueous acetone[116] (eq 10).

$$Cp_2MH_2 + Cp_2M(OTs)_2 \xrightarrow{\text{wet acetone}}$$
$$[Cp_2M(\mu\text{-OH})_2MCp_2](OTs)_2 \quad (10)$$
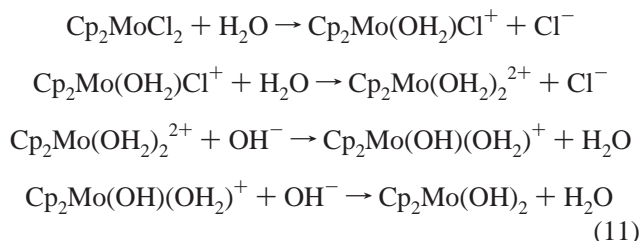$$(M = Mo, W; OTs = p\text{-MeC}_6H_4SO_3)$$

The presence of water in the solvent was thought to be responsible for these reactions, since under strict anhydrous conditions no formation of the hydroxide was observed.

The compounds are all isostructural, showing the metals bridged by OH ligands that result in a planar four-membered M$_2$O$_2$ ring core, which is typical for [(Cp$_2$M)$_2$(μ-OH)$_2$] dimers, such as that shown in Figure 1. The tosylates are hydrogen bonded to the hydroxide hydrogens. In methanol solution, the ^{1}H NMR chemical shifts for the cyclopentadienyl units of the complexes are significantly deshielded with respect to those for the neutral, parent dihydrides, presumably reflecting a withdrawal of electron density from the rings to the metals in the cationic complexes. The hydroxy groups in the complexes were sufficiently labile to undergo displacement by tertiary phosphines in alcoholic solvents to yield monomeric alkoxo complexes of the type [Cp$_2$M(PR$_3$)-(R′O)]$^+$(OTs)$^-$ (R = Et, nBu, and Ph; R′ = Me, Et, iPr, CF$_3$CH$_2$, and Ph).[116] In aqueous solution, there is an equilibrium between the dimeric molybdenocenes [(CpR)$_2$-Mo(μ-OH)$_2$Mo(CpR)$_2$]$^{2+}$ and their respective monomers [(CpR)$_2$Mo(OH$_2$)(OH)]$^+$.[117] From ^{1}H NMR dilution studies in D$_2$O, the equilibrium constants for the dimer dissociation (where R = Me and H) were determined to be 7.9×10^{-2} $\pm$ 1 $\times$ 10^{-3} M at pD 7 and $3.5 \times 10^{-2} \pm 1.3 \times 10^{-3}$ M at pD 3.5, respectively.[117] Dimer formation has also been used to account for the kinetics of the Cp$_2$MoCl$_2$ promoted hydrolysis of phosphate esters, which were found to be first order in phosphate and one-half order in the molybdenocene.[29] It was postulated that the Cp$_2$MoCl$_2$ complex underwent hydrolysis with loss of Cl$^-$ to give an OH/H$_2$O complex that dimerizes in solution, setting up a dimer/monomer equilibrium. The monomeric partner in this equilibrium coordinates with the phosphate esters, promoting hydrolysis.[29] The possibility of dimer formation is reasonable in the light of reports by Ito et al.[116,118] The investigation of the dimeric molybdenocene complex in water was reported in the context of C−H bond activation chemistry promoted by water soluble molybdenocenes.[119] The molecular structure of [(η^5-C$_5$H$_4$Me)$_2$Mo(μ-OH)$_2$Mo(η^5-C$_5$H$_4$Me)$_2$](OTs)$_2$ shows

only slight differences in the geometric parameters from the unsubstituted Cp analogue.[116] In fact, the two dimers are reported to be isostructural.

The aqueous chemistry of Cp_2MoCl_2 has been investigated in detail by Marks et al.[31] The titration of aqueous Cp_2MoCl_2 with NaOH exhibits two deprotonations with $pK_a(1) = 5.5$ and $pK_a(2) = 8.5$. Using the classical hydrolysis model for *cis*-platin[120] and Cp_2VCl_2, the hydrolytic steps were tentatively formulated as follows (eq 11):
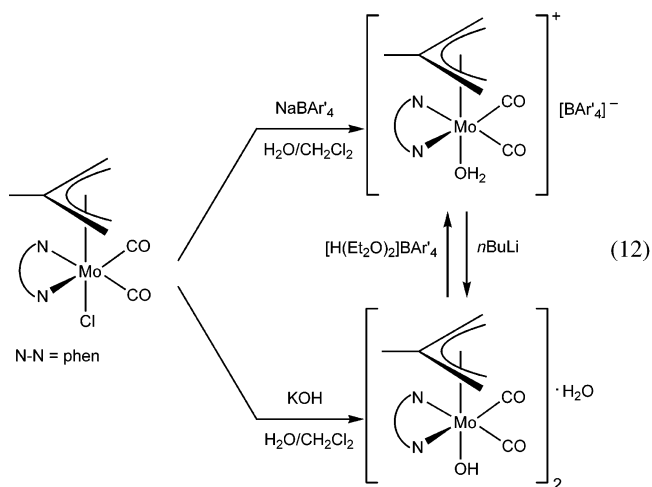
$$Cp_2MoCl_2 + H_2O \rightarrow Cp_2Mo(OH_2)Cl^+ + Cl^-$$

$$Cp_2Mo(OH_2)Cl^+ + H_2O \rightarrow Cp_2Mo(OH_2)_2^{2+} + Cl^-$$

$$Cp_2Mo(OH_2)_2^{2+} + OH^- \rightarrow Cp_2Mo(OH)(OH_2)^+ + H_2O$$

$$Cp_2Mo(OH)(OH_2)^+ + OH^- \rightarrow Cp_2Mo(OH)_2 + H_2O$$
$$(11)$$

These studies reveal that, at physiological pH, the predominant $Cp_2MoCl_2(aq)$ solution species is the monocation $Cp_2Mo(OH)(OH_2)^+$. In agreement with these observations, a hydroxo complex, $Cp_2Mo(OH)(OH_2)^+BPh_4^-\cdot^1/_2H_2O$, was precipitated from such solutions in high yield at pH 7.4. Cp_2MoCl_2, which has a clam-shell shape containing a tetrahedral Mo(IV) center with two chlorides in the equatorial girdle,[29] is known to promote the phosphoester bond cleavage of activated phosphate diesters and monoesters in aqueous solution. Under pseudo-first-order conditions, Cp_2MoCl_2 (110-fold excess) promotes the production of 4-nitrophenol from 4-nitrophenyl phosphate (NPP) and from bis(4-nitrophenyl)phosphate (BNPP).[30] As pointed out earlier, it is known that Cp_2VCl_2 is as active as *cis*-platin against human epidermoid tumor cells *in vitro* and against mouse mammary tumor cells *in vivo*.[121] Therefore, studies on the aqueous solution behavior of the analoguous Cp_2MoCl_2 are valuable in understanding the mechanism of carcinostatic activity of Cp_2MCl_2 compounds.

Another interesting method leading to the formation of hydroxide complexes is by way of the oxidation of hydride complexes. Poli and co-workers studied the oxidation of $CpMoH(PMe_3)_3$ with $[Cp_2Fe]^+$ (Fc^+) or Ag^+ in a number of solvents.[122,123] Under anhydrous conditions in MeCN, the initial product was $[CpMoH(PMe_3)_3]^+$, which then decomposed to give $[CpMo(PMe_3)_3(MeCN)]^+$.[122] The decomposition was thought to go through two parallel mechanisms. This disproportionation path is favored in strongly coordinating solvents such as MeCN, or a tandem deprotonation/oxidation mechanism is favored in coordinating solvents such as THF. Both theoretical and experimental evidence was presented in support of these mechanisms.[122,123] Since the disproportionation decomposition mode is involved in the formation of the solvo-intermediate $[CpMoH(PMe_3)_3(S)]^+$, it was speculated that the presence of a good coordinating agent, such as water, in a less coordinating solvent, such as THF or Me_2CO, could lead to the formation of an aqua-intermediate ($S = H_2O$), which would initiate the possibility of other decomposition products. Using wet THF or acetone, the Mo(III) hydroxo complex $[CpMo(OH)(PMe_3)_3][BF_4]$ and the Mo(IV) oxo complex $[CpMo(O)(PMe_3)_2][BF_4]$ were obtained.[123]
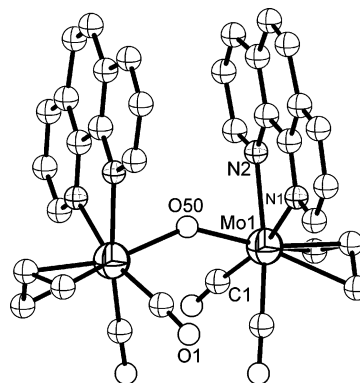
The oxidation of the trihydride complex $(C_5R_5)MoH_3$-(dppe) (dppe = 1,2-*bis*(diphenylphosphine)ethane, R = Me or Et) by Fc^+ in wet THF produced the bis(hydroxo) complex $(C_5R_5)Mo(OH)_2(dppe)$.[124] This reaction is interesting in that

oxidation of $(C_5R_5)MoH_3(dppe)$, in which the Mo is in a formal +4 state, results ultimately in the formation of (C_5R_5)-$Mo(OH)_2(dppe)$. The mechanism of the formation of the dihydroxo product is not known, but it is thought to involve a number of electron- and proton-transfer steps and reactions with coordinated water.[124]

Mononuclear hydroxo complexes of Mo(II) are very rare. However, the mononuclear organometallic compound of Mo(II) containing a terminal hydroxo ligand, $CpMo(OH)$-$(PMe_3)_2$, has been synthesized.[122] The reaction of $[Mo(\eta^3$-C_3H_4-Me-2)Cl(CO)_2(phen)]$ with $NaBAr'_4$ (Ar' = 3,5-bis-(trifluoromethyl)phenyl) and H_2O led to the isolation of the aqua complex $[Mo(\eta^3$-C_3H_4-Me-2)(OH_2)(CO)_2(phen)]BAr'_4\cdot$ $2Et_2O$.[125] Deprotonation of this complex gave a neutral hydroxo compound, $[\{Mo(\eta^3$-C_3H_4-Me-2)(OH)(CO)_2(phen)\}_2$-$(\mu$-$H_2O)]$, which also could be obtained by reaction of $[Mo$-$(\eta^3$-C_3H_4-Me-2)Cl(CO)_2(phen)]$ with KOH in a biphasic CH_2Cl_2/H_2O medium[125] (eq 12). The $[Mo(\eta^3$-C_3H_4-Me-2)-

$$(12)$$

$(OH_2)(CO)_2(phen)]BAr'_4\cdot2Et_2O$, when treated with $[\{Mo$-$(\eta^3$-C_3H_4-Me-2)(OH)(CO)_2(phen)\}_2(\mu$-$H_2O)]$, gave the binuclear hydroxo-bridged complex $[\{Mo(\eta^3$-C_3H_4-Me-2)(CO)_2$-$(phen)\}_2(\mu$-$OH)]BAr'_4$ (see eq 13 and Figure 12).[125]

Figure 12. ORTEP drawing of $[\{Mo(\eta^3$-$C_3H_5)(CO)_2(phen)\}_2(\mu$-$OH)]^+$. Hydrogen atoms are omitted for clarity.

Prout and co-workers have considered the factors contributing to the structure of $[Cp_2Mo(OH)NH_2Me]PF_6$ and other early transition metal complexes of the type Cp_2MX_2.[126] They all have a clam-shell-type structure (see Figures 1, 4, and 7, for example) in which the salient structural features are the Cp(Cnt)-M-Cp(Cnt) and X-M-X angles (Cnt = ring centroid) and the M-Cp(Cnt) and M-X distances. They noted that, in general, the M-Cp(Cnt) distances and the

N-N = phen

Ar' = 3,5-bis(trifluoromethyl)phenyl

$[BAr'_4]^-$ (13)

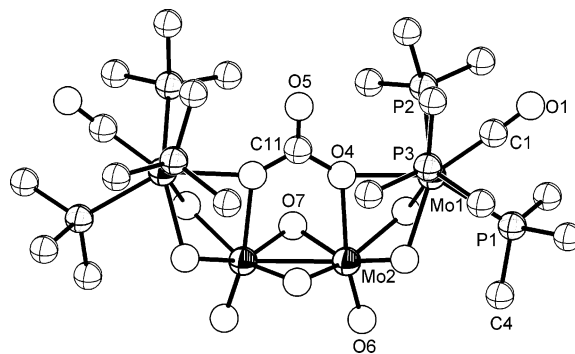M−X distances vary oppositely from one another. For example, in the Cp_2MCl_2 series (M = Zr, Nb, Mo) there is a marginal increase in the M−Cl distance with increasing atomic number (2.44 to 2.47 Å), accompanied by a much larger decrease in the M−Cp(Cnt) distances (2.19 to 1.98 Å). The Cp(Cnt)−M−Cp(Cnt) angles varied very little and were all less than 135°. On the other hand, the X−M−X angles fall into fairly discrete nonoverlapping groups according to the number of nonbonding electrons: d^0, 94−97°; d^1, 85−88°; d^2, 76−82°. This variation was accounted for on the basis of stereochemically active nonbonding electrons occupying orbitals outside of the MX_2 angle.[126] Other factors specific to a complex may also affect the geometry; for example, in the case of the d^2 complex $[Cp_2Mo(OH)\text{-}NH_2Me]PF_6$, a slightly low value of 72.2° for the MX_2 bond has been attributed to OH···N hydrogen bonding.

A tetrametallic mixed-valence Mo(II)/Mo(V) complex $[Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2 (\mu\text{-}O)_2(\mu\text{-}OH)_4(PMe_3)_6]$ containing a bidentate, quadruply bridging carbonato group was obtained as a minor product from the reaction of petroleum ether solutions of *cis*-$Mo(N_2)_2(PMe_3)_4$ with 50−60 psi of CO_2 at room temperature.[127] The structure given in Figure 13 shows that the carbonate ligand bridges all four Mo atoms, with two Mo atoms bonded to each of the carbonate oxygens of the symmetry axis. The outer Mo(II) atoms are seven-coordinate and are bonded to the inner Mo(V) atoms through two bridging OH ligands as well as an O (carbonate) bridge. The inner Mo(V) atoms are connected to one another via two oxo-bridges. The Mo(V)−Mo(V) distance is 2.552 Å, indicating metal−metal bonding.

7.3. Tungsten

The complex $[Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs)_2$ (OTs = p-$MeC_6H_4SO_3^-$) was prepared in good yields by the reaction
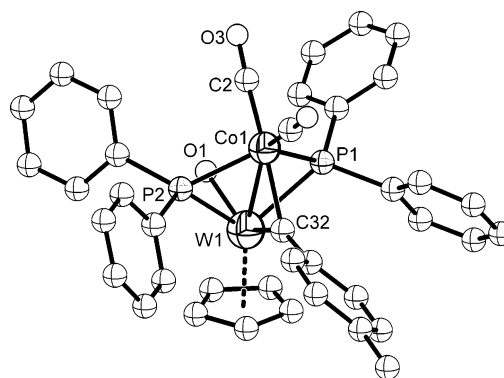

Figure 13. ORTEP drawing of $[Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu\text{-}O)_2(\mu\text{-}OH)_4(PMe_3)_6]$. Hydrogen atoms are deleted for clarity.

of Cp_2WH_2 with $Cp_2W(OTs)_2$ in aqueous acetone[116] (eq 10). Since no formation of the hydroxide was observed when the reaction was carried out under rigorous anhydrous conditions, the presence of water in the solvent was thought to be responsible for these reactions.

The neutral, protonated tungsten tetramer $[W(OH)(CO)_3H]_4\cdot$ $OPPh_2Et$,[128] a structurally characterized example of the so-called Hieber's acid,[129] has the same general structure of the type $[M_4(CO)_{12}(\mu\text{-}OR)_4]^{4-}$ that has already been discussed above for Cr and Mo complexes. Although the hydridic hydrogens could not be located in the electron density map, the NMR spectrum shows the presence of such hydrogens. The structure of the $[W(OH)(CO)_3H]_4\cdot OPPh_2Et$ exhibits that, unlike the case of $[M_4(CO)_{12}(\mu_3\text{-}OR)_4]^{4-}$, the local symmetry of the $W(CO)_3$ groups is not C_{3v} but one in which one of the C−W−C angles is much larger than the others. The authors argued that the location of the hydrido ligand is indicated by the opening of one of the C−W−C bond angles and that each W is better described as being heptacoordinated, with the geometry of a trigonal pyramid and a square pyramid sharing an apex.[128] A small tungsten hydroxocarbonyl cluster of the type $K_3[W_2(OH)_3(CO)_6]$ was prepared from the alkaline hydrolysis of the hexacarbonyls, $W(CO)_6$.[115] The $K_3[W_2(OH)_3(CO)_6]\cdot 2H_2O$ consists of two tungsten atoms, each having three terminal CO ligands held together by three bridging hydroxo groups, giving an overall D_{3h} symmetry to the anion and a trigonal antiprismatic coordination to each tungsten.[129] The Mo complex was reported to be isomorphous with the tungsten complex but very unstable.[130]

A heterobimetallic hydroxo complex $[WCo(OH)(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(\mu\text{-}PPh_2)_2(CO)_2Cp]$ could be prepared by the hydrolysis of the moisture sensitive complex $[WCo(Cl)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)_2(CO)_2Cp]$. The X-ray crystal structure of $[WCo\text{-}(OH)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)_2(CO)_2Cp]$ (Figure 14) shows

Figure 14. ORTEP drawing of $[WCo(OH)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)_2(CO)_2Cp]$. Hydrogen atoms are omitted for clarity
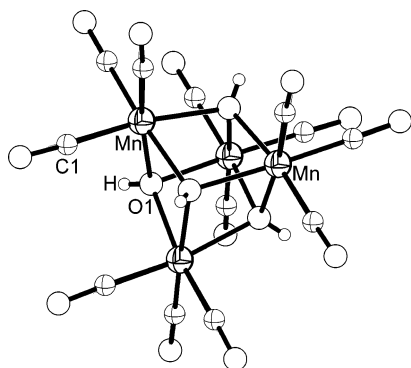
a W−Co bimetal alkylidine complex with two symmetrically disposed μ-PPh$_2$ ligands and a terminal hydroxo ligand attached to the W atom. This complex slowly isomerizes to the sterically less crowded oxo complex [WCo(O){μ-C(C$_6$H$_4$-Me-4)C(O)}(μ-PPh$_2$)(CO)(μ-PPh$_2$H)Cp], which on reaction with HBF$_4$·Et$_2$O gave [WCo(OH)(μ-CC$_6$H$_4$Me-4)(μ-PPh$_2$)-(CO)$_2$(PPh$_2$H)Cp]BF$_4$.[131] Crown ethers have been employed in the synthesis of [dibenzo-18-crown-6-K][W(CO)$_5$OH] by dissolving W(CO)$_6$ in dibenzo-18-crown-6 and treating with KOH under irradiation with a mercury vapor lamp at room temperature. The chromium analogue was also prepared, but its stability was low compared to that of the tungsten complex.[132] The reaction of Cp*WCl$_4$ with aqueous NaOH under exclusion of air affords two spectroscopically characterized intermediates, Cp*WCl$_3$(OH) and Cp*WCl$_2$(OH)$_2$. In the former the OH proton resonates at 10.1 ppm and the IR spectrum showed the OH band at 3447 cm^{-1}, whereas in the latter compound the hydroxyl groups appear at 29.1 ppm in the ^{1}H NMR and the OH stretching mode can be seen at 3431 cm^{-1} in the IR spectrum. However, in the presence of air, the reaction of Cp*WCl$_4$ and NaOH leads to the formation of Cp*W(O)$_2$Cl via the hydrolysis and oxidation reactions.[133]

8. Group 7 Organo-hydroxides

Most of the organometallic hydroxides reported in this group are of rhenium. Those of manganese are rare; the technecium ones are even rarer.

8.1. Manganese

Most of the organometallic hydroxides of Mn are based on a cubane-like Mn$_4$O$_4$ core. A synthetic route to several interesting manganese hydroxo-carbonyls is from the oxidation of Mn$_2$(CO)$_{10}$. Reaction with Me$_3$NO·2H$_2$O in THF produced the tetrameric [Mn(μ_3-OH)(CO)$_3$]$_4$ (see Figure 15)
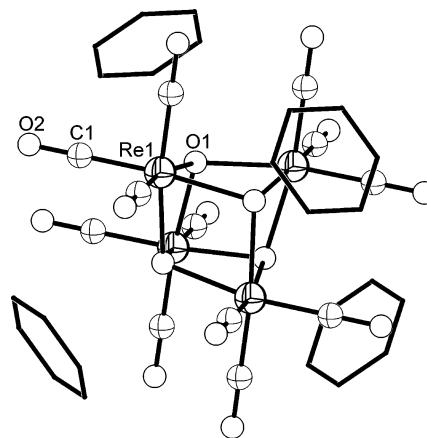

Figure 15. ORTEP drawing of [Mn(μ_3-OH)(CO)$_3$]$_4$.

in almost quantitave yield.[134] Me$_3$NO·2H$_2$O is known to facilitate carbonyl substitution reactions by the oxidation of a CO to CO$_2$.[135] On the other hand, in the presence of benzophenone, the mixed-valent heptanuclear complex [Mn$_7$(μ_3-OH)$_8$(CO)$_{18}$] was obtained in 71% yield. There are two different Mn atoms in the complex, formally, a central Mn(II) and six peripheral Mn(I) atoms bonded to three terminal carbonyls. The structure is of interest in that the geometry around the central Mn is essentially that of a trigonal prism. This complex was thought to arise from the oxidation of the [Mn(μ_3-OH)(CO)$_3$]$_4$.[134]

Reactions of Mn(CO)$_5$X (X = Cl, Br) with TlF or AgF in CH$_2$Cl$_2$ solution under water saturated nitrogen resulted in

the formation of the cluster species [Mn$_4$(CO)$_{12}$F$_x$(OH)$_{4-x}$].[136] The reactions with TlF give predominantly the species with $x = 1$ and 2, while AgF produced the species with $x = 2$ and 3. The individual species were identified in the mass spectrum. The $x = 2$ product from AgF could be separated from its $x = 3$ coproduct by crystallization from benzene to yield the pure solvate [Mn$_4$(CO)$_{12}$F$_2$(OH)$_2$]·2C$_6$H$_6$. X-ray quality crystals of the TlF product, [Mn(CO)$_3$F$_x$(OH)$_{4-x}$]$_4$·2C$_6$H$_6$, showed a cubane-type structure similar to that seen in Figure 15 with Mn(CO)$_3$ groups at one set of corners interpenetrated with fluoro or hydroxy groups at the other.[136] The product is predominantly the monofluoride species, but the other differently substituted ones form isomorphous crystals. Benzene molecules are on the cube diagonals between adjacent pairs of (F/OH) sites, similar to the case seen in Figure 16 (see below), consistent with OH···π(benzene)···HO bonding.

Figure 16. ORTEP drawing of [Re(CO)$_3$OH]$_4$·2C$_6$H$_6$. Hydrogen atoms are deleted for clarity.
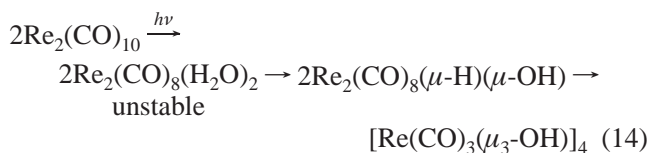
8.2. Technecium

Only two organotechnecium carbonyl hydroxide clusters Tc(CO)$_{12}$F(μ_3-OH)$_3$ and [Tc(μ_3-OH)(CO)$_3$]$_4$ have been reported.[137,138] The first cluster was prepared by the reaction of KTcO$_4$, HCOOH, and HF and essentially has a cubic core where alternate edges are occupied by Tc atoms and (μ_3-OH) groups, except one of the (μ_3-OH) groups is replaced by a fluoride ion.[137] Dissolution of [NEt$_4$]$_2$[TcCl$_3$(CO)$_3$] in water yielded [Tc(OH$_2$)$_3$(CO)$_3$], which, upon treatment with OH$^-$, afforded the [Tc(μ_3-OH)(CO)$_3$]$_4$ cubic cluster.[138] The Tc$_4$O$_4$ cubic core of this molecule is slightly distorted, with the Tc−OH distances in the range 2.180−2.191 Å,[138] and its edges are occupied by Tc atoms and μ_3-OH groups. Reaction of the complex [Tc(μ_3-OH)(CO)$_3$]$_4$ with Cp*H gave the compound Cp*Tc(CO)$_3$ as an important starting material on which the organometallic chemistry of Tc is ultimately based.[138]
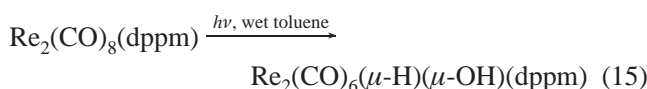
8.3. Rhenium

The reaction of either Re$_2$(CO)$_{10}$ or Re(CO)$_5$Cl with H$_2$O at 200 °C gives [Re(CO)$_3$(OH)]$_4$.[139] A pseudocubane structure without metal−metal bonds in which the Re(CO)$_3$ groups are linked by triply bridging OH ligands was proposed for this complex; the compound is of interest in that it is one of the few stable transition metal hydroxo carbonyl compounds. The structure was verified by X-ray crystallographic analysis

of the dibenzene complex, $[Re(CO)_3OH]_4 \cdot 2C_6H_6$, which was prepared by the photolysis of $Re_2(CO)_{10}$ in wet ether followed by recrystallization from benzene[135,139,140] (eq 14).

$$2Re_2(CO)_{10} \xrightarrow{h\nu}$$
$$2Re_2(CO)_8(H_2O)_2 \rightarrow 2Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH) \rightarrow$$
$$\text{unstable}$$
$$[Re(CO)_3(\mu_3\text{-}OH)]_4 \quad (14)$$

The structure (Figure 16) consists of discrete tetramers, in which four rhenium and four oxygen atoms occupy the corners of a distorted cube. The benzene rings of crystallization are oriented perpendicularly to the four 3-fold axes of the unit cell, stabilized by $OH\cdots\pi$ hydrogen bonds.[135] Each benzene ring uses both faces as acceptors for $OH\cdots\pi$ hydrogen bonding. The $[Re(CO)_3(OH)]_4$ complex can be used as a starting material for other complexes, through the formal substitution of the hydroxy hydrogen by other single bonding groups. For example, reaction of $[Re(CO)_3(OH)]_4$ with $RCHN_2$ (R = H, Me) gives $[Re(CO)_3OCH_2R]_4$, deuteration in D_2O/ether results in the adduct $[Re(CO)_3OD\cdot OEt_2]_4$, and metalation with Li gives the salt $[Re(CO)_3OLi]_4$, which is stable in THF solution for only a short period of time.[139] Lewis bases can be attached to $[Re(CO)_3(OH)]_4$ via H bonds to give the very stable complexes $[Re(CO)_3OH\cdot L]_4$ (L = THF, $OPPh_3$, and Et_4NBr).[139] The photochemical decomposition of $Re_2(CO)_{10}$ was believed to go through the formation of an unstable $Re_2(CO)_8(H_2O)_2$ intermediate that undergoes a loss of one water molecule, followed by the oxidative addition of the second water to give a $(\mu\text{-hydrido})(\mu\text{-hydroxo})$-dirhenium octacarbonyl, $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)$, that immediately decomposes to give the $[Re(CO)_3(\mu_3\text{-}OH)]_4$ product.[28]

Indirect support for the postulate of an unstable $Re_2(CO)_8$-$(\mu\text{-}H)(\mu\text{-}OH)$ intermediate comes from the synthesis and crystal structure of $[Re_2(CO)_6(\mu\text{-}H)(\mu\text{-}OH)](dppm)$ (dppm = bis(diphenylphosphino)methane).[141] The compound, made from the photolysis of $Re_2(CO)_8(dppm)$ in wet toluene, consists of a $[Re(CO)_3]_2(\mu\text{-}H)(\mu\text{-}OH)$ core, bridged by the dppm molecule (eq 15).

$$Re_2(CO)_8(dppm) \xrightarrow{h\nu,\ \text{wet toluene}}$$
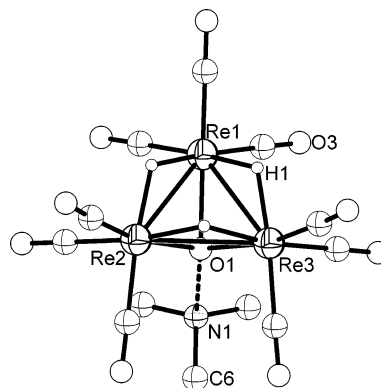$$Re_2(CO)_6(\mu\text{-}H)(\mu\text{-}OH)(dppm) \quad (15)$$

The rigid bridging group holds the two Re centers in proximity to one another, thereby stabilizing the complex, relative to $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)$.[142] Metal carbonyl bridging group stabilization has been noted in $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)$, $FeRu_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)(PPh_3)_2$, and $FeRu_2(CO)_8(\mu\text{-}OH)_2L_2$ (L = PPh_3, PMe_3, and $AsPh_3$).[143]

An unusual hydrogen bond stabilized anion, $[Re_3(\mu\text{-}H)_3$-$(CO)_9(\mu_3\text{-}O\cdots H\cdots NMe_3)]^-$, was isolated as one of several products of the reaction of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with Me_3NO in a solvent, such as acetone or THF.[144] The structure, given in Figure 17, shows a triangular $[Re(CO)_3]_3$ core capped on one side with an OH ligand and having three bridging hydrides on the other between the Re atoms; such a structure is typical for other $[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}X)]^-$ anions.[144] The $O-H\cdots N$ hydrogen bond is short $(O\cdots N$ distance 2.502(10) Å) and almost linear, indicating an unusually strong $O\cdots H\cdots N$ bond.

9. Group 8 Organo-hydroxides

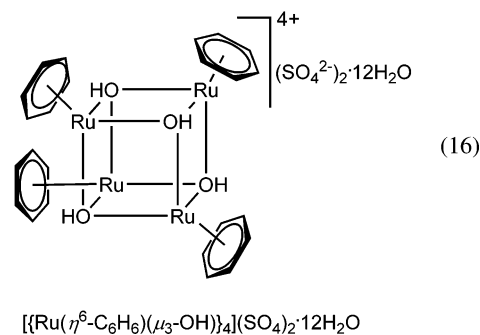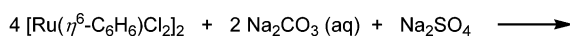The majority of the hydroxo complexes reported in this group are organometallic hydroxides of ruthenium.

Figure 17. ORTEP drawing of $[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}O\cdots H\cdots NMe_3)]^-$. Hydrogen atoms except the hydrides are omitted for clarity. The $O\cdots N$ contact is 2.502(10) Å.

9.1. Iron

There have been only a few organoiron hydroxides prepared; most are of the form $Fe_2(CO)_6XY$, where X and Y are anionic bridiging groups.[145,146] $Fe_2(CO)_6\{\mu\text{-}P(H)[CH\text{-}(SiMe_3)_2]\}(\mu\text{-}OH)$ was one of the products obtained in the reaction of $[NEt_4]_2[Fe_2(CO)_8]$ with $Cl_2PCH(SiMe_3)_2$.[145]

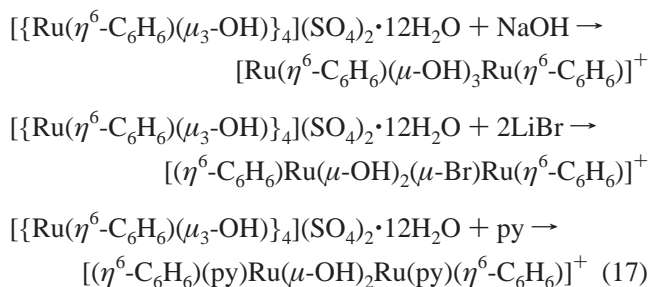### 9.2. Ruthenium

The reactions of $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ with aqueous bases produced several different hydroxo complexes, depending on the nature of the base and the stoichiometry of the reaction; all retained the $(\eta^6\text{-}C_6H_6)Ru$ grouping.[147−149] The reaction of $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ with aqueous Na_2CO_3 (1:1 molar ratio) and excess Na_2SO_4 produced the tetrameric $[\{Ru(\eta^6\text{-}C_6H_6)(\mu_3\text{-}OH)\}_4]^{4+}$ cationic complex as its sulfate salt, $[\{Ru(\eta^6\text{-}C_6H_6)(\mu_3\text{-}OH)\}_4](SO_4)_2\cdot 12H_2O$.[147,149] Its structure consists of discrete $[Ru(\eta^6\text{-}C_6H_6)(\mu_3\text{-}OH)]_4^{4+}$ cations and sulfate anions (eq 16). The cations have a cubane-type Ru_4O_4

$$4\ [Ru(\eta^6\text{-}C_6H_6)Cl_2]_2\ +\ 2\ Na_2CO_3\ (aq)\ +\ Na_2SO_4\ \longrightarrow$$

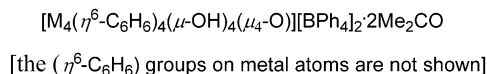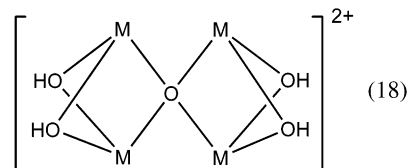$$[\{Ru(\eta^6\text{-}C_6H_6)(\mu_3\text{-}OH)\}_4](SO_4)_2\cdot 12H_2O$$

core, similar to the Mn_4O_4 core shown in Figure 15, that can be described as containing interpenetrating tetrahedrons of $(\eta^6\text{-}C_6H_6)Ru$ and OH groups. Each Ru atom has bonds to three OH groups of equal length (2.12 Å) and the $O-Ru-O$ and $Ru-O-Ru$ angles are 76.3° and 102.2°, respectively.[149] Each cation may be regarded as bonded to eight others through the cube corners and through strong van der Waals bonding between benzene molecules at the metal vertexes. Additional stabilization is achieved through hydrogen bonding between the OH vertexes and the sulfate ions.[149] The water molecules, which were poorly defined, were thought to occupy positions in the van der Waals gap between the benzene molecules. The synthesis could not be extended to

other (η^6-arene)Ru systems. Reaction of [Ru(η^6-arene)Cl$_2$]$_2$ (arene = C$_6$Me$_6$, 1,3,5-C$_6$Me$_3$H$_3$, p-MeC$_6$H$_4$(CHMe$_2$)) with stoichiometric amounts of Na$_2$CO$_3$ in the presence of excess Na$_2$SO$_4$ produced only unreacted starting material and/or the triply OH-bridged [Ru$_2$(η^6-arene)$_2$(μ_3-OH)$_3$]$^+$ cations.[149] It was speculated that the bulky arenes did not furnish sufficient van der Waals interactions to stabilize a tetramer. The tetramer can be destroyed by reaction with aqueous NaOH to give [Ru(η^6-C$_6$H$_6$)(μ-OH)$_3$Ru(η^6-C$_6$H$_6$)]$^+$, which with aqueous LiBr (1:2 molar ratio) leads to [(η^6-C$_6$H$_6$)Ru(μ-OH)$_2$-(μ-Br)Ru(η^6-C$_6$H$_6$)]$^+$.[147] Bases (L), such as pyridine, also decompose the tetramer[147] to give [(η^6-C$_6$H$_6$)(L)Ru(μ-OH)$_2$-Ru(L)(η^6-C$_6$H$_6$)]$^+$ (eq 17).

$$[\{Ru(\eta^6\text{-C}_6H_6)(\mu_3\text{-OH})\}_4](SO_4)_2 \cdot 12H_2O + NaOH \rightarrow$$
$$[Ru(\eta^6\text{-C}_6H_6)(\mu\text{-OH})_3Ru(\eta^6\text{-C}_6H_6)]^+$$

$$[\{Ru(\eta^6\text{-C}_6H_6)(\mu_3\text{-OH})\}_4](SO_4)_2 \cdot 12H_2O + 2LiBr \rightarrow$$
$$[(\eta^6\text{-C}_6H_6)Ru(\mu\text{-OH})_2(\mu\text{-Br})Ru(\eta^6\text{-C}_6H_6)]^+$$

$$[\{Ru(\eta^6\text{-C}_6H_6)(\mu_3\text{-OH})\}_4](SO_4)_2 \cdot 12H_2O + py \rightarrow$$
$$[(\eta^6\text{-C}_6H_6)(py)Ru(\mu\text{-OH})_2Ru(py)(\eta^6\text{-C}_6H_6)]^+ \quad (17)$$

Treatment of [Ru(η^6-C$_6$H$_6$)Cl$_2$]$_2$ with an excess of sodium carbonate or hydroxide, followed by the addition of Na[BPh$_4$] and recrystallization from acetone, produced the tetranuclear cation [Ru$_4$(η^6-C$_6$H$_6$)$_4$(μ-OH)$_4$(μ_4-O)]$^{2+}$, isolated as [Ru$_4$(η^6-C$_6$H$_6$)$_4$(μ-OH)$_4$(μ_4-O)][BPh$_4$]$_2$·2Me$_2$CO[148] (eq 18). The struc-

$$2\ [M(\eta^6\text{-C}_6H_6)Cl_2]_2 \ + \ Na_2CO_3 \text{ or NaOH} \ + \ 2\ NaBPh_4 \xrightarrow{\text{acetone}}$$

(M = Ru, Os)

$$(18)$$

[M$_4$(η^6-C$_6$H$_6$)$_4$(μ-OH)$_4$(μ_4-O)][BPh$_4$]$_2$·2Me$_2$CO
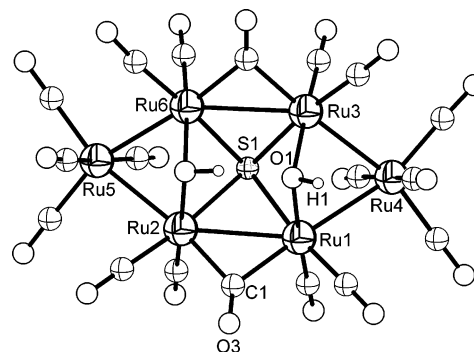
[the (η^6-C$_6$H$_6$) groups on metal atoms are not shown]

ture is that of two Ru$_2$(C$_6$H$_6$)$_2$(μ-OH)$_2$ units sharing a common tetrahedrally coordinated O atom and is believed to arise from the condensation of two [Ru(η^6-C$_6$H$_6$)(OH)(μ-OH)$_2$Ru-(H$_2$O)(η^6-C$_6$H$_6$)]$^+$ cations with the loss of three water molecules. This compound is presumably the product from the reaction of [{Ru(η^6-C$_6$H$_6$)(μ_3-OH)}$_4$]$^{4+}$ with aqueous NaOH.

The proposition that base hydrolysis of the unsubstituted arene [Ru$_2$(η^6-C$_6$H$_6$)Cl$_2$]$_2$ gives rise to the tetranuclear cation [{Ru(η^6-C$_6$H$_6$)(μ_3-OH)}$_4$]$^{4+}$, while the more sterically crowded arenes produce only the triply OH-bridged [Ru$_2$(η^6-arene)$_2$-(OH)$_3$]$^+$ cations (or condensation products thereof), is appealing. However, it is limited. The reaction of [Ru$_2$(η^6-C$_6$H$_6$)Cl$_2$]$_2$ with TlOPh (1:3 molar ratio) leads to the triple-phenoxo-bridged product [Ru$_2$(η^6-C$_6$H$_6$)$_2$(μ-OPh)$_3$]$^+$ in 86% yield.[150] This compound on reaction with water at room temperature gives [Ru$_2$(η^6-C$_6$H$_6$)$_2$(μ-OH)$_3$]$^+$ in essentially quantitative yield. The crystal structure of the chloride salt [Ru$_2$(η^6-C$_6$H$_6$)$_2$(μ-OH)$_3$]Cl·3H$_2$O showed the cation to be a triply bridged hydroxo complex having essentially D_{3h} symmetry.[150] It was speculated that the very basic medium

of the original synthesis resulted in nucleation of the dimer to give the tetranuclear product. It has also been reported that the dimeric hydroxoruthenium [Ru$_2$(η^6-C$_6$H$_6$)$_2$(OH)$_3$]Cl·2H$_2$O was obtained from the reaction of [Ru(η^6-C$_6$H$_6$)Cl$_2$]$_2$ with aqueous NaOH.[151]

A number of organometallic hydroxides have been prepared by the reaction of water with complexes having good leaving groups. For example, the room-temperature hydrolysis of the cyclometalated hydride RuH(η^2-CH$_2$PMe$_2$)-(PMe$_3$)$_3$[152] produced the hydrido(hydroxo)ruthenium compound [(PMe$_3$)$_4$Ru(H)(OH)] in low yield.[10] The yield could be increased by reacting [(PMe$_3$)$_4$Ru(C$_2$H$_4$)] with stoichiometric amounts of water. Excess water (>2 equiv) produced the hydroxide salt [(PMe$_3$)$_3$Ru(μ-OH)$_3$Ru(PMe$_3$)$_3$]$^+$OH$^-$.[10] The hydrido(hydroxo)ruthenium compound is thermally unstable, decomposing in benzene at 45 °C; the corresponding [(PMe$_3$)$_4$(Me)Ru(OH)] was found to be thermally stable up to 70 °C. Hydrolysis of the bis(bidentate)ruthenium compound [Ru(dmpe)$_2$(C$_2$H$_4$)] (dmpe = bis(dimethylphosphine)ethane) produced the interesting dimer [$trans$-Ru(H)-(OH)(dmpe)$_2$·H$_2$O]$_2$, in which two $trans$-(H)(OH)(dmpe)$_2$Ru octahedral complexes are held together by two bridging hydrogen bonding water molecules. The solid-state structure shows that both hydrogens on the two water molecules form hydrogen bonding to the OH ligands. However, the ^{1}H NMR shows the dimer to be fluxional, equilibrating the water and hydroxide protons.[10]

In addition to forming hydrogen bonds with neighboring Lewis bases, hydroxide ligands can also form stabilizing intramolecular hydrogen bonds. This is seen in the cluster [Ru$_6$(CO)$_{16}$(μ-CO)$_2$(μ-OH)$_2$(μ_4-S)], shown in Figure 18.[153]

Figure 18. ORTEP drawing of [Ru$_6$(CO)$_{16}$(μ-CO)$_2$(μ-OH)$_2$(μ_4-S)].

The cluster was obtained by the UV-irradiation of a solution of Ru$_3$(CO)$_9$(μ_3-CO)(μ_3-S) and Ru$_3$(CO)$_{12}$ in the presence of H$_2$O, but in only 8% yield.[153] The structure exhibits a Ru$_4$ rectangular core capped on one side with an μ_4-S atom and on the other by two oppositely facing μ-hydroxyls and two bridging carbonyls. In addition, the sides having the bridging hydroxides also have bridging (CO)$_4$Ru groups. The structure shows that two hydroxide hydrogens, which were located, are not equivalent; one (H(2)) is hydrogen bonded to its oppositely facing hydroxide oxygen (O(1)), resulting in a O(1)···H(2) distance of 1.83 Å. This was also consistent with the infrared spectrum, which showed two O−H stretching vibrations. The room temperature ^{1}H NMR spectrum of the compound in toluene-d_8 exhibited a single broad resonance, indicating fluxionality. The Ru−Ru distances in the Ru$_4$ core are not equal; those spanned by the (CO)$_4$Ru groups (3.057 and 2.970 Å) are longer than the other two (2.876 and 2.887 Å). It was speculated that the internal hydrogen bonding could, among other things, contribute to the differ-

ences in Ru−Ru distances. Intramolecular hydrogen bonds between the bridging OH and coordinating $CF_3SO_3^-$ in Ru_4-$(C(O)Et)_4(OH)_2(CF_3SO_3)_2(CO)_8$ are also expected to assist in stabilizing the compound.[154]

A different core was found in the tetranuclear cluster [Ru$_4$-(CO)$_{10}$(C=CHiPr)(OH)(PPh$_2$)], which was prepared in 30% yield by the fragmentation of [Ru$_3$(CO)$_{11}$(Ph$_2$PC≡CiPr)] in wet THF.[155] The Ru$_4$ core is a butterfly arrangement of metal atoms with an unusual multisite-bound μ_4-vinylidene, a face-bridging μ_3-OH, and an edge-bridging μ-PPh$_2$ group (eq 19).
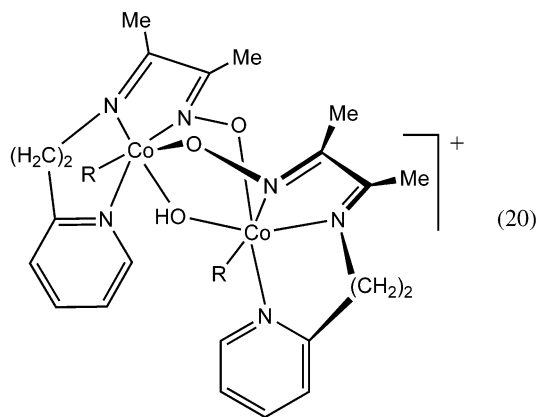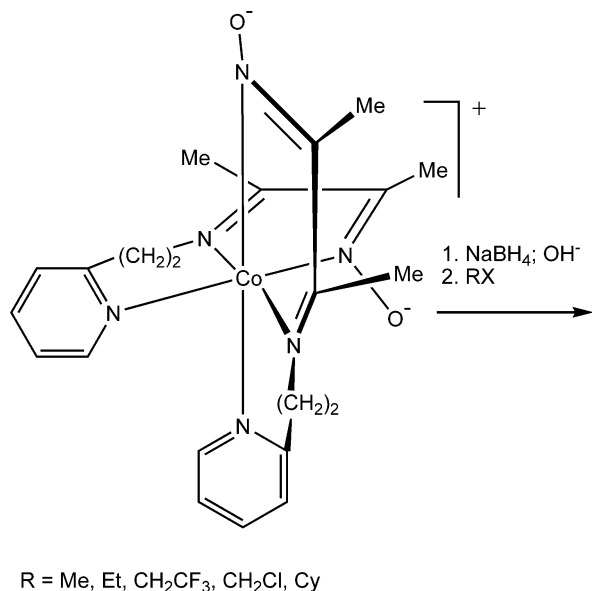

(R = H, Et)

[Ru$_4$(CO)$_{10}$(Ph$_2$P)(C=CH-iPr)(OR)
the CO groups are omitted

9.3. Osmium

Reaction of the Os compound [Os$_2$(η^6-C$_6$H$_6$)Cl$_2$]$_2$ with excess NaOH or Na$_2$CO$_3$ produced the corresponding [Os$_4$(η^6-C$_6$H$_6$)$_4$(μ-OH)$_4$(μ_4-O)][BPh$_4$]$_2$·2Me$_2$CO.[148] Reaction of OsH(Ph)(CO)(P-tBu$_2$Me)$_2$ with 1 equiv of water leads to the formation of OsH(OH)(CO)(P-tBu$_2$Me)$_2$, or alternatively, KOH in methanol converts OsHCl(CO)(P-tBu$_2$Me)$_2$ to OsH-(OH)(CO)(P-tBu$_2$Me)$_2$. Due to the reductive nature of the KOH/MeOH system, the latter route is not very satisfactory, as is the case for OsH(Ph)(CO)(P-tBu$_2$Me)$_2$ and water. The Os atom resides in a square pyramidal environment with the phosphines oriented *trans* to teach other. The hydride group was located at the apical site, but the angles to two P were unreasonably unequal.[156]

10. Group 9 Organo-hydroxides

The organometallic hydroxides of the two heavier members of this group are observed more.
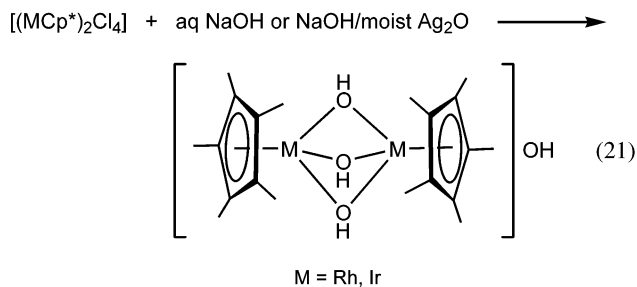
10.1. Cobalt

Organocobalt hydroxo complexes have been reported relatively recently compared to other group 9 elements. Binuclear cobalt(III) hydroxides of general composition [(RCoL)$_2$(μ-OH)]$^+$ (R = Me, Et, CH$_2$CF$_3$, CH$_2$Cl, or Cy) supported by the tridentate ligand L have recently been reported (L = 2-(2-pyridylethyl)imino-3-butanone oximato). The synthetic strategy consists of the oxidative addition of an alkyl halide to the nucleophilic Co(I) species generated by reduction, with NaBH$_4$, of the parent Co(III) complex (eq 20). The R = CH$_2$CF$_3$ and Cy derivatives have been structurally elucidated as perchlorate salts, which reveals that the ligand L occupies three equatorial positions in a *mer* arrangement and that the bridging hydroxide group resides in the fourth position. The alkyl group and the oxime O atom of the ligand L are located at the apical positions as shown in eq 20, which also depicts the tridentate ligation of the L.[157] Another Co hydroxide [{MeCo(LE-py)}$_2$(μ-OH)]ClO$_4$·0.5H$_2$O (LE-py = 2-(2-pyridyl)imino-3-butanone oximato) was obtained by the reaction of [Co(LE-py)$_2$]ClO$_4$ with NaOH followed by treatment with NaBH$_4$, water, and MeI.[158]

R = Me, Et, CH$_2$CF$_3$, CH$_2$Cl, Cy
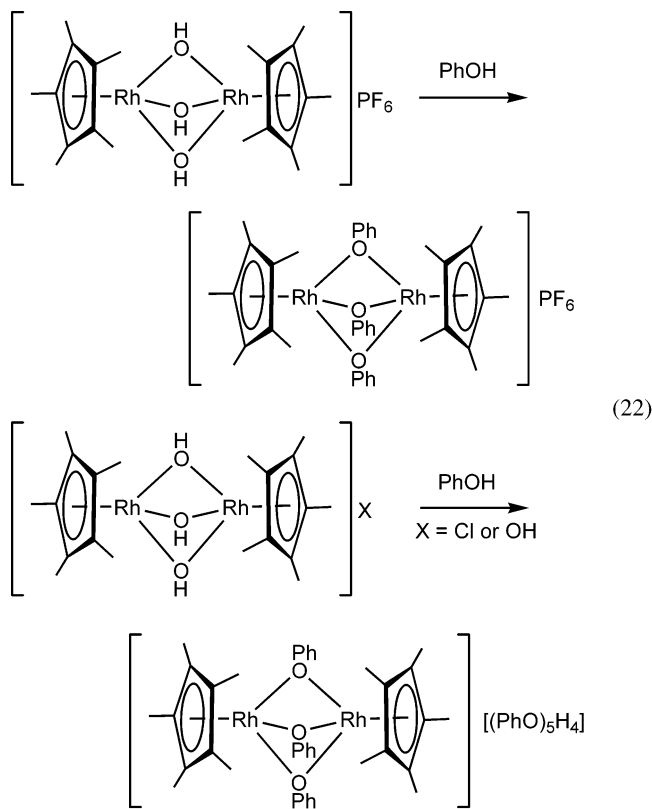

A cobalt hydroxide complex derived from the ligand *N,N′*-(3-mercapto-3-methylbutyryl)-*o*-phenylendiamine, (Et$_4$N)$_2$-[Co(N$_2$S$_2$)(CN)(MeCN)], by air oxidation leads to the formation of the mixed valence Co(III)−Co(II)−Co(III) trinuclear complex (Et$_4$N)$_2$[Co{Co{N$_2$(SO$_2$)}(CN)(OH)}$_2$]. The product formation proceeds through the oxidation of thiolate to the sulfinates. The mixed valence nature of the complex has been established by temperature-dependent magnetic susceptibility measurements and by EPR spectroscopy both in the solid state and in solution, which agrees with the high-spin Co(II) species. The crystal structure of this molecule exhibits a linear arrangement of cobalt ions connected together by bridging hydroxides and sulfinate ligands in a distorted octahedral environment.[159]
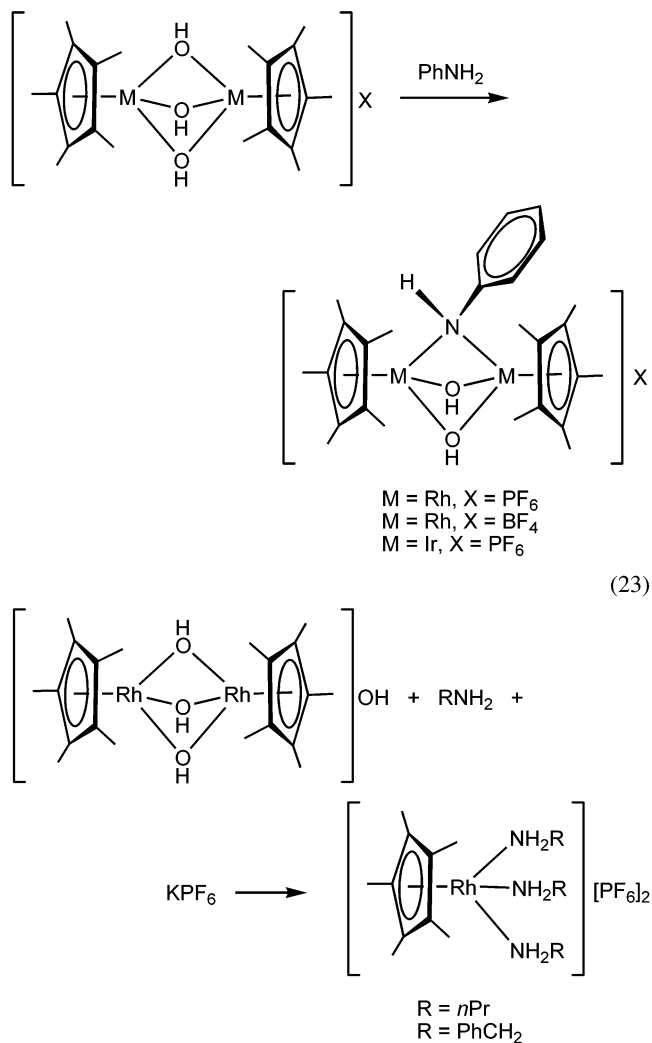
10.2. Rhodium

Reaction of [(RhCp*)$_2$Cl$_4$] with aqueous NaOH or NaOH/moist Ag$_2$O affords the corresponding dimeric cation [(RhCp*)$_2$(μ-OH)$_3$]$^+$.[160−162] The structural analysis showed it to be composed of two (Cp*)Rh units bridged by three hydroxo ligands[160] (eq 21). Maitlis and co-workers have studied the reactions of different salts of [(RhCp*)$_2$(μ-OH)$_3$]$^+$ with various Lewis bases. They reported that the reaction of [(RhCp*)$_2$(μ-OH)$_3$]PF$_6$ with PhOH gave the corresponding (μ-OPh) dimer, [(RhCp*)$_2$(μ-OPh)$_3$]PF$_6$, while the Cl$^-$ or OH$^-$ salts gave [(RhCp*)$_2$(μ-OPh)$_3$][(PhO)$_5$H$_4$][162] (eq 22). Although the cations in both salts were the same, the methyl groups in the latter salt underwent a facile H/D exchange

[(MCp*)$_2$Cl$_4$]   +   aq NaOH or NaOH/moist Ag$_2$O $\longrightarrow$

$$\left[\quad \right] \text{OH} \qquad (21)$$

M = Rh, Ir

with d_6-acetone, (CD$_3$)$_2$CO, at room temperature.[162] The reactions of the [(RhCp*)$_2$(μ-OH)$_3$]X complexes with Lewis bases result in different products, depending on the nature of the base, the identity of X, and, in some cases, the reaction time. Treatment of [(RhCp*)$_2$(μ-OH)$_3$]OH with aniline in the presence of PF$_6^-$ or BF$_4^-$ yielded the μ-anilido complex

$$\left[\quad \right] \text{PF}_6 \xrightarrow{\text{PhOH}} \left[\quad \right] \text{PF}_6 \qquad (22)$$

$$\left[\quad \right] \text{X} \xrightarrow[\text{X = Cl or OH}]{\text{PhOH}} \left[\quad \right] [(\text{PhO})_5\text{H}_4]$$

[(RhCp*)$_2$(μ-NHPh)(μ-OH)$_2$]X (X = PF$_6$ or BF$_4$); the corresponding Ir compound reacts similarly.[163] On the other hand, [(RhCp*)$_2$(μ-OH)$_3$]OH reacts with the primary amines, RNH$_2$ (R = nPr, PhCH$_2$), to give the fully substituted [Cp*Rh(NH$_2$R)$_3$]$^{2+}$, which rapidly decomposed in solution[163] (eq 23). The difference in the reactivities of aniline and other primary amines was thought to be due to the higher acidity of the aniline, affording the anilide ion, which then undergoes complexation. Other amines and conditions gave different products. For example, the reaction of [(RhCp*)$_2$(μ-OH)$_3$]$^+$ with aqueous HClO$_4$ or HBF$_4$ and the pyridine-type bases (L) gave [(Cp*RhL)$_2$(μ-OH)$_2$]$^{2+}$ (L = py, 2-Mepy, 4-Etpy, 2-MeOpy) in acetone, while, in MeOH, pyridine yielded [{RhCp*(py)}$_2$(μ-OMe)$_2$]X$_2$ (X = ClO$_4$, BF$_4$).[164] [(Cp*Rh)$_2$-(μ-OH)$_3$]ClO$_4$ reacts with pyrazole bases (HL) in which hydroxides are progressively substituted by bridging L$^-$ ligands. The neutral HL can also act as a monodentate ligand, giving complexes of the type [(RhCp*HL)$_2$(μ-OH)$_2$]-(ClO$_4$)$_2$.[165,166] Similar to these organometallic hydroxides,

$$\left[\quad \right] \text{X} \xrightarrow{\text{PhNH}_2}$$

M = Rh, X = PF$_6$
M = Rh, X = BF$_4$
M = Ir, X = PF$_6$

$$\left[\quad \right] \text{OH} + \text{RNH}_2 + \qquad (23)$$

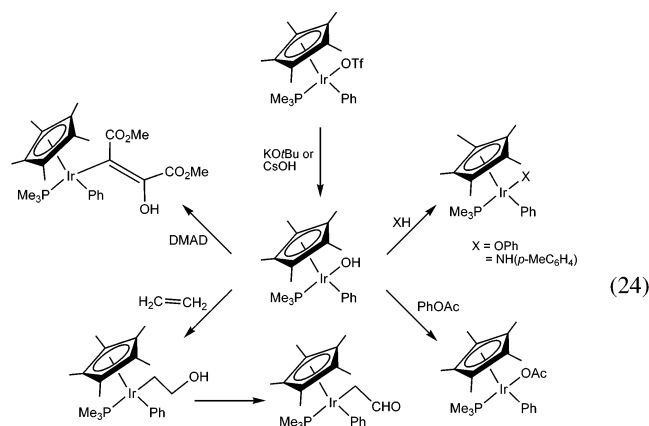$$\xrightarrow{\text{KPF}_6} \left[\quad \right] [\text{PF}_6]_2$$

R = nPr
R = PhCH$_2$

Wieghardt et al.[167] reported that the related hydroxo cation [{(tacn)Rh}$_2$(μ-OH)$_3$]$^{3+}$ (tacn = 1,4,7-triazacyclononane) can be protonated in aqueous solution, leading to the formation of the dihydroxo solvated cation [{(tacn)Rh(H$_2$O)$_2$}$_2$(μ-OH)$_2$]$^{4+}$. This explains that such a type of substitution pattern is not limited to the organometallic hydroxo complexes but can also occur in inorganic coordination complexes.

Reactions with alcohols also occur in different ways. For example, [(RhCp*)$_2$(μ-OH)$_3$]X (X = Cl, PF$_6$, BF$_4$) reacts with iPrOH to give the trimeric complex [(RhCp*)$_3$(μ-H)$_3$O]X. X-ray studies show a triangular (Cp*Rh)$_3$ core surmounted on one side by an O atom with each pair of Ru atoms bridged by hydrides on the other side.[168] Prolonged reaction leads ultimately to the tetrahydrido compound [(RhCp*)$_4$(H)$_4$]$^{2+}$. The reaction of [(RhCp*)$_2$(μ-OH)$_3$]PF$_6$ with primary alcohols (RCH$_2$OH) produced mixtures of [(RhCp*)$_2$(O$_2$CR)$_2$H]PF$_6$ and [(RhCp*)$_2$(O$_2$CR)(H)$_2$]PF$_6$. X-ray diffraction studies on the latter compound (R = Me) showed it to be a dinuclear compound with two rhodiums, each bonded to a Cp* and bridged by two hydrides and one acetate.[166,167] The reaction of [(RhCp*)$_2$(μ-OH)$_3$]Cl with P(OMe)$_3$ gave a mixture of 34% of the methylrhodium compound [(RhCp*)(Me){P(OMe)$_3$}$_2$]$^+$ and 53% of the expected [(RhCp*)(Me){P(OMe)$_3$}$_3$]$^{2+}$.[160] In addition, [(RhCp*)$_2$(μ-OH)$_3$]Cl·4H$_2$O was found to catalyze the oxygenation of THF to γ-butyrolactone in the presence of small amounts of water. It also catalyzes the oxidation of Ph$_3$P to Ph$_3$PO. The reaction of P(OEt)$_3$ with [(RhCp*)$_2$(μ-OH)$_3$]Cl

did not lead to oxidation, but it instead gave the substitution product $[RhCp^*\{P(OEt)_3\}_3]^{2+}$.[169]

10.3. Iridium

Several terminal hydroxo complexes of both Ir(I) and Ir(III) have been characterized. The hydroxo complex Cp*Ir-(Ph)(PMe₃)(OH), prepared by the addition of CsOH to a solution of Cp*(PMe₃)₃(Ph)Ir(OTf) (OTf = CF₃SO₃⁻) in THF,[170] was found to react with a number of nucleophilic and electrophilic agents, with the reaction centered at the Ir−O−H bond[170] (eq 24). Treatment with XH (X = PhO,
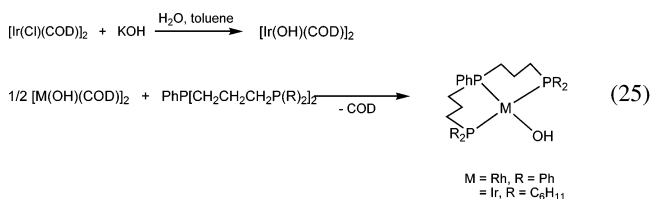

$$(24)$$

NH(p-MeC₆H₄)) gave complete conversion to the corresponding Cp*Ir(Ph)(PMe₃)(X), while reaction with the weaker electrophile, phenyl acetate, gave an equimolar mixture of Cp*Ir(Ph)(PMe₃)(OPh) and Cp*Ir(Ph)(PMe₃)-(O₂CMe). The complex was also found to undergo insertion reactions with dimethylacetylenedicarboxylate (MeO₂CC≡CCO₂Me) and H₂C=CH₂ to yield Cp*Ir(Ph)(PMe₃)C-(CO₂Me)=C(CO₂Me)OH and Cp*Ir(Ph)(PMe₃)(CH₂CH₂-OH), which quickly transforms to Cp*Ir(Ph)(PMe₃)(CH₂C-(O)H)[170] (eq 24). A mechanism for the latter insertion/oxidation sequence has been proposed.[171] An iridium hydrido hydroxo complex IrH(OH)[C₆H₃-2,6-(CH₂P-tBu₂)₂] was synthesized by the dehydrogenation of IrH₂[C₆H₃-2,6-(CH₂P-tBu₂)₂] using $tert$-butylethylene followed by the treatment with an excess of water. The isotopic labeling with D₂O indicates that the 16-electron hydrido hydroxo complex IrH-(OH)[C₆H₃-2,6-(CH₂P-tBu₂)₂] was formed from the oxidative addition of water to the intermediate 14-electron complex Ir[C₆H₃-2,6-(CH₂P-tBu₂)₂]. The single-crystal X-ray structure of IrH(OH)[C₆H₃-2,6-(CH₂P-tBu₂)₂] shows that the Ir center has a square-pyramidal coordination environment in which two phosphorus atoms are oriented $trans$ to each other, as expected for the chelate PCP pincer ligand. The metalated carbon and the hydroxo ligand constitute another pair of basal ligands, whereas the hydrido ligand occupies the apical site. Moreover, the complex IrH(OH)[C₆H₃-2,6-(CH₂P-tBu₂)₂] is an efficient catalyst for the transfer dehydrogenation of cyclooctane to cyclooctene.[172] [(IrCp*)₂Cl₄] reacts with aqueous NaOH or NaOH/moist Ag₂O to give the corresponding dimeric cation $[(IrCp^*)_2(\mu\text{-OH})_3]^+$.[160−162] This molecule has a structure analogous to that of the rhodium complex $[(RhCp^*)_2(\mu\text{-OH})_3]^+$, which is composed of two (Cp*)Rh units bridged by three hydroxo ligands[160] (see above and eq 21). The reaction of $[(IrCp^*)_2(\mu\text{-OH})_3]^+$ with aqueous HClO₄ or HBF₄ and the pyridine-type bases (L) gave $[(Cp^*IrL)_2(\mu\text{-OH})_2]^{2+}$ (M = Ir, L = py) in acetone.[164]

The reaction of Vaska's complex, $trans$-[Ir(CO)Cl(PR₃)₂] with NaOMe, followed by hydrolysis, gives rise to the Ir(I)

complexes $trans$-[Ir(CO)(OH)(PR₃)₂].[173] The complexes can undergo phosphine exchange reactions. $trans$-[Ir(CO)(OH)-(PPh₃)₂] can be oxidized to the Ir(III) sulfato complex [Ir(CO)(OH)(SO₄)(PPh₃)₂] by the reaction with SO₂/O₂, in which the sulfato group acts as a bidentate ligand and the two phosphines are oriented $trans$ to each other.[174] The [Ir(CO)(OH)(SO₄)(PPh₃)₂] in turn reacts with CO to give the trigonal bipyramidal Ir(I) compound [Ir(CO)₃(PPh₃)₂][HSO₄]; the corresponding P(p-tolyl)₃ complexes react similarly.[174] The Ir(I) complex [Ir(PMe₃)₄][PF₆] undergoes oxidative addition with water to give cis-[IrH(OH)(PMe₃)₄][PF₆].[175]

[Ir(OH)(COD)]₂ was synthesized in the reaction of [Ir(Cl)(COD)]₂ with KOH in water and acetone, and was isolated as a yellow solid (COD = 1,5-cyclooctadiene) (eq 25). Reaction of [Ir(OH)(COD)]₂ with chelating phosphine

$$(25)$$

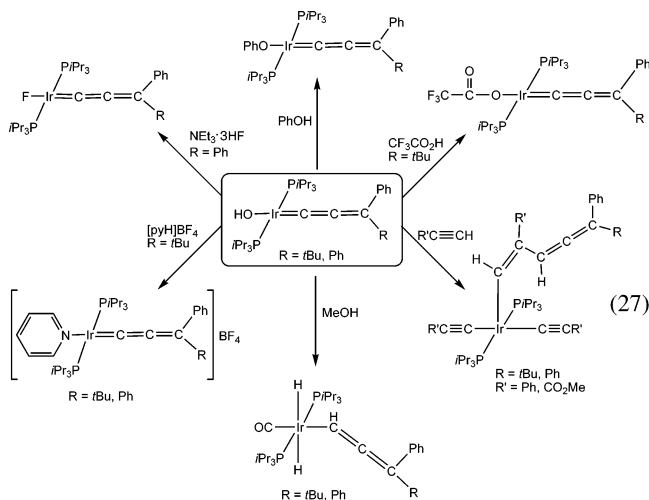Cyttp (Cyttp = PhP[CH₂CH₂CH₂P(C₆H₁₁)₂]₂) leads to the substitution of COD and formation of the complex Ir(OH)-(Cyttp) as a highly soluble compound that was isolated from hexane solution[176] (eq 25). [Ir(OH)(COD)]₂ serves as a useful synthon in the preparation of several interesting iridium compounds; for example, treatment of [Ir(OH)(COD)]₂ with aqueous HF affords [Ir(F)(COD)]ₙ, which was isolated as [Ir(F)(COD)PPh₃].[177]

The (allenylidene)iridium(I) complexes $trans$-[IrOH-{=C=C=C(Ph)R}(iPr₃P)₂] (R = tBu, Ph), prepared by salt metathesis of the corresponding chloro derivatives, $trans$-[IrCl{=C=C=C(Ph)R}(iPr₃P)₂], with KOH, have been shown to be versatile starting materials for OH/ligand substitution reactions[178] (eq 26). They undergo acid/base

$$(26)$$

reactions with PhOH, CF₃CO₂H, and NEt₃·3HF, to give the corresponding $trans$-[IrX{=C=C=C(Ph)R}(iPr₃P)₂] (X = PhO, CF₃CO₂, and F), while pyH[BF₄] afforded $trans$-[Ir-{=C=C=C(Ph)tBu}py(iPr₃P)₂][BF₄].[178] Reactions with methanol resulted in the complete fragmentation of the MeOH to give the carbonyl(dihydrido)iridium(III) compound [IrH₂-(CO)(iPr₃P)₂(CH=C=CPhR)] in high yields (88−91%). The (hydroxo)vinylidine complexes also react with the acetylenes, HC≡CR′ (R′ = Ph, CO₂Me), to give novel alkyne insertion reactions leading to the formation of [Ir(iPr₃P)₂(C≡CR′)₂-(CH=C(R′)CH=C=CPhR)]. The stucture of the compound (R = R′ = Ph) shows a square pyramidal geometry around the metal, with $trans$-disposed acetylenes and iPr₃P ligands in the basal plane and the (CH=C(Ph)CH=C=CPh₂) in the axial position. The complex is coordinatively unsaturated and reacts with CO to give the octahedral (carbonyl)iridium(III) complex in 93% yield[178] (eq 27).

The hydroxy ligand can also play a spectator role, as seen in the phosphine ligand exchange reaction of $trans$-Ir(CO)-(P(p-tolyl)₃)₂OH with PCy₃ (PCy₃ = tricyclohexylphosphine) in benzene to produce $trans$-Ir(CO)(PCy₃)₂OH.[173] This

(27)

Figure 20. ORTEP drawing of Ni$_3$(CH$_2$C$_6$H$_4$-o-Me)$_4$(PMe$_3$)$_2$(μ_3-OH)$_2$. Hydrogen atoms are deleted for clarity.
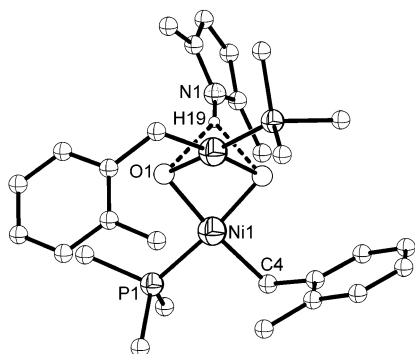
exchange reaction has been used to produce a number of Vaska-type complexes with different phosphines; it works best when the incoming phosphine ligand is more electron-rich than the leaving phosphine moiety.[173]
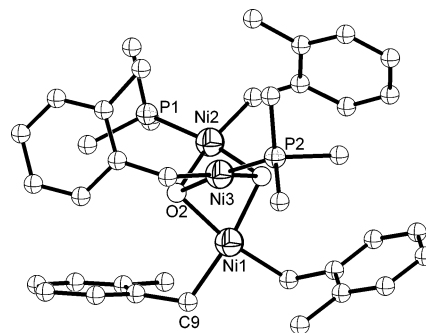
11. Group 10 Organo-hydroxides

A large number of organometallic hydroxides have been reported for metals in this group. Many of the hydroxo complexes have been suggested as intermediates in catalytic reactions.[3]

11.1. Nickel

Because of their ease in forming bridged bonds, most of the (hydroxo)nickel compounds are multimetallic clusters. The complex [NiMe$_2$(PMe$_3$)$_3$] is a very versatile starting compound in that it reacts with HX molecules to give CH$_4$ and X substitution. Treatment with water produces the bridged complex [NiMe(PMe$_3$)(OH)]$_2$.[179] Low temperature ^{1}H NMR shows that the compound exists in solution as an equilibrium mixture of *cis* and *trans* isomers. A number of other (hydroxo)nickel complexes of the type [Ni(R)(PMe$_3$)-(OH)]$_2$ (R = CH$_2$SiMe$_3$, CH$_2$CMe$_2$Ph, CH$_2$Ph) have been reported from the reaction of Ni(R)Cl(PMe$_3$)$_2$ with NaOH.[180] Except where R = CH$_2$Ph, all show *cis/trans* equilibria. A very similar complex, [Ni(CH$_2$C$_6$H$_4$-o-Me)(PMe$_3$)(μ-OH)]$_2$, synthesized by the reaction of KOH with [Ni(η^3-CH$_2$C$_6$H$_4$-o-Me)(Cl)(PMe$_3$)], also showed only a *trans* isomer.[181] The structure of its 2,5-dimethylpyrrole adduct [Ni(CH$_2$C$_6$H$_4$-o-Me)(PMe$_3$)(μ-OH)]$_2$·HNC$_4$H$_2$Me$_2$, shown in Figure 19, demonstrates the basicity of the bridged hydroxides in their strong

Figure 19. ORTEP drawing of [Ni(CH$_2$C$_6$H$_4$-o-Me)(PMe$_3$)(μ-OH)]$_2$·2,5-HNC$_4$H$_2$Me$_2$. Hydrogen atoms except on pyrrolic nitrogen are deleted for clarity.

hydrogen bonding interactions with the N−H bond of the dimethylpyrrole.[180] The donor properties of the bridging hydroxides are also seen in the structure of the trimetallic cluster [Ni$_3$(CH$_2$C$_6$H$_4$-o-Me)$_4$(PMe$_3$)$_2$(μ_3-OH)$_2$], given in Figure 20.[181] The structure consists of a [Ni(CH$_2$C$_6$H$_4$-o-Me)-(PMe$_3$)(OH)]$_2$ dimer, with a Ni(CH$_2$C$_6$H$_4$-o-Me)$_2$ moiety bridging the two OH ligands. A binuclear anionic complex of Ni, (NBu$_4$)$_2$[(C$_6$F$_5$)$_2$Ni(μ-OH)$_2$Ni(C$_6$F$_5$)$_2$] has been prepared by the reaction of *cis*-Ni(C$_6$F$_5$)$_2$(PhCN)$_2$ and NBu$_4$OH[182] (eq 28).

$$2cis\text{-}M(C_6F_5)_2(PhCN)_2 + 2NBu_4OH \rightarrow$$
$$(NBu_4)_2[(C_6F_5)_2M(\mu\text{-}OH)_2M(C_6F_5)_2] + 4PhCN$$
$$(M = Ni, Pd)$$

$$(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(C_6F_5)_2] + 2NBu_4OH \rightarrow$$
$$(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}OH)_2Pt(C_6F_5)_2] + 2NBu_4Cl \quad (28)$$

The bridging OH ligands are quite reactive and can be replaced by using weak acids HL [L = pyrazolate (pz), 3-methylpyrazolate (mpz), 3,5-dimethylpyrazolate (dmpz), indazolate (indz), or triazolate (tz)] to give the corresponding complexes (NBu$_4$)$_2$[{Ni(C$_6$F$_5$)$_2$}$_2$(μ-OH)(μ-L)] and (NBu$_4$)$_2$-[Ni(C$_6$F$_5$)$_2$(μ-L)]$_2$ (except for L = dmpz) for Ni/HL molar ratios of 1 and 2, respectively.[183]

11.2. Palladium

Palladium(II) hydroxides also exist mainly as dimers possessing hydroxide bridges. Dimers of the form [PdLR-(μ-OH)]$_2$ (L = tertiary phosphine; R = alkyl or aryl group) have been synthesized by the reaction of (L)$_2$PdCl$_2$, KOH, and the particular alkyl or aryl halide.[184−186] It was found that the presence of excess phosphine (iPr$_3$P, Cy$_3$P) (Cy = cyclohexyl) in a solution of [L$_2$Pd$_2$(Ph)$_2$(μ-OH)$_2$] (L = iPr$_3$P or Cy$_3$P) produced the corresponding monohydroxide [L$_2$Pd(Ph)(OH)], indicating the establishment of an equilibrium involving the dimer, base, and monomer. The equilibrium for the reaction was studied using variable temperature ^{31}P NMR spectroscopy.[187] It was found that K_{eq} decreased in the order Cy$_3$P ∼ iPr$_3$P > Ph$_3$P, while the replacement of Ph with Me indicated no great change. These observations were consistent with the fact that, while both [(iPr$_3$P)$_2$Pd-(Ph)(OH)] and [(Cy$_3$P)$_2$Pd(Ph)(OH)] could be isolated, [(Ph$_3$P)$_2$Pd(Ph)(OH)] could not be obtained. The OH ligands in the [L$_2$Pd$_2$(R)$_2$(μ-OH)$_2$] dimers can be replaced with other ligands to give the analogous [L$_2$Pd$_2$(R)$_2$(μ-X)$_2$] complexes.[184−186] Such ligand exchanges were also found in the [M$_2$(C$_6$F$_5$)$_4$(μ-OH)$_2$]$^{2-}$ (M = Pd, Pt) dimers.[188,189] The

complexes $[L_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$ (L = Ph$_3$P, Cy$_3$P) not only undergo ligand metathesis but also react with $[CpM(CO)_3H]$ (M = W, Mo, Cr) to give the trimetallic clusters $[L_2Pd_2\text{-}(Ph)_2(\mu\text{-}OH)(\mu\text{-}CO)_2(\mu_3\text{-}CO)MCp]$ in high yields[190] (eq 29).
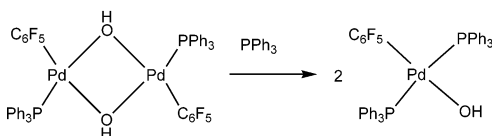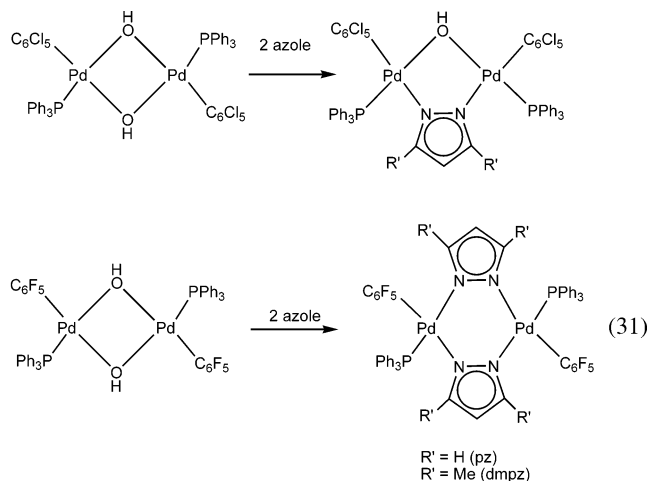
(29)

M = Cr or Mo, L = Ph$_3$P
M = W, L = Ph$_3$P or Cy$_3$P

Dimeric palladium(II) hydroxo complexes are expected to play a role in the carbonylation reactions of aromatic halides catalyzed by $[L_2PdCl_2]$ (L = tertiary phosphine).[184,186] In the presence of a base, the Pd(II) complex forms an initial (monohydroxo)palladium complex of the type $[L_2PdCl(OH)]$ which disproportionates to give phosphine oxide and a Pd(0) species [LPd]. The Pd(0) complex can then undergo oxidative addition with PhI to give $[L_2Pd_2(Ph)_2(\mu\text{-}I)_2]$, which further reacts with OH$^-$ to give the dihydroxo complex $[L_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$. In the presence of CO, OH$^-$, and PhI, the $[L_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$ enters into a cyclic process involving, sequentially, $[L_2Pd_2(COPh)_2(\mu\text{-}I)_2]$ and $[L_2Pd_2(Ph)_2\text{-}(\mu\text{-}I)_2]$ with the production of PhCOO$^-$.[186] The palladium hydroxo-dimeric cation $[(DAB)Pd_2(\mu\text{-}OH)_2]^{2+}$ (DAB = ArN=C(Me)=C(Me)=NAr; Ar = 3,5-di-*tert*-butylphenyl or 3,5-bis(trifluoromethyl)phenyl) was found to be a coproduct, along with biphenyl, in the stoichiometric activation of the benzene C−H bonds in the presence of HBF$_4$ by the Pd(II) complexes of the type (DAB)PdMe$_2$ under 1 atm of O$_2$.[191]

The dinuclear anionic complex of palladium (NBu$_4$)$_2$-$[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]$ has been synthesized in a manner similar to that of the nickel derivative[182] (eq 28). In addition to this bridged binuclear anionic complex, neutral hydroxo complexes of the form $[PdR(PPh_3)(\mu\text{-}OH)]_2$ (R = C$_6$F$_5$, C$_6$Cl$_5$) have been prepared and characterized.[192] Their syntheses were via metathesis reactions of the corresponding $[PdR(PPh_3)(\mu\text{-}Cl)]_2$ complexes with NBu$_4$OH (eq 30). Proton,

$$[PdR(PPh_3)(\mu\text{-}Cl)]_2 + 2NBu_4OH \rightarrow$$
$$[PdR(PPh_3)(\mu\text{-}OH)]_2 + 2NBu_4Cl$$
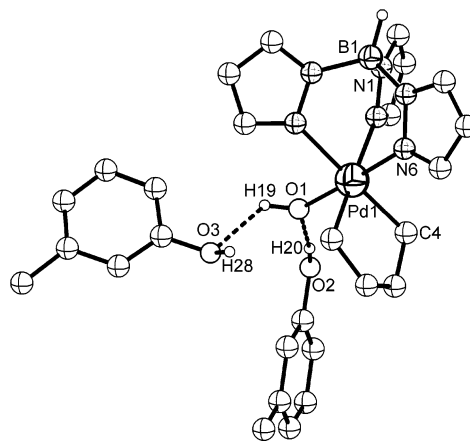$$(R = C_6F_5 \text{ or } C_6Cl_5) \quad (30)$$

fluorine-19, and phosphorus-31 NMR studies in trichloromethane show that the hydroxo-bridged complexes assume a *trans* configuration across the Pd$_2(\mu\text{-}OH)_2$ core.

The reaction of the hydroxo-bridged complexes with 2 equiv of pyrazole (Hpz) or 3,5-dimethylpyrazole (Hdmpz) produced either the disubstituted product $[Pd(C_6F_5)(PPh_3)\text{-}(\mu\text{-}azolate)]_2$ or the monosubstituted one $[\{Pd(C_6Cl_5)(PPh_3)\}_2\text{-}(\mu\text{-}OH)(\mu\text{-}azolate)]$ (azolate = pz or dmpz), depending on the nature of the R group.[192] In the $[Pd(C_6F_5)(PPh_3)(\mu\text{-}azo}\text{-}late)]_2$ product, the C$_6$F$_5$ ligands are *trans* to one another, while, in $[\{Pd(C_6Cl_5)(PPh_3)\}_2(\mu\text{-}OH)(\mu\text{-}azolate)]$, the C$_6Cl_5$ ligands occupy *cis* positions. It was also reported that the reaction of $[Pd(C_6F_5)(PPh_3)(\mu\text{-}OH)]_2$ with excess PPh$_3$ gave the mononuclear complex *trans*-$[Pd(C_6F_5)(OH)(PPh_3)_2]$, while the corresponding pentachlorophenylhydroxo complexes did not react with PPh$_3$, even under forcing conditions (eq 31). The difference in the reactivities of both the mononuclear

(31)

R' = H (pz)
R' = Me (dmpz)

and the binuclear Pd complexes was rationalized to be a result of the increased steric requirements of the C$_6$Cl$_5$ ligands, compared to the C$_6$F$_5$ ligands.[192] The oxidation of the pallada(II)cyclopentane reagent $[Pd(C_4H_8)\{(pz)_3BH\}]^-$ ((pz)$_3$BH$^-$ = tris(pyrazol-1-yl)borate) by water or H$_2$O$_2$ produces the palladium(IV) complex $[Pd(OH)(C_4H_8)\{(pz)_3\text{-}BH\}]$.[193] The structure of the compound, which could be isolated as $[Pd(OH)(C_4H_8)\{(pz)_3BH\}]\cdot2(3\text{-MeC}_6H_4OH)$, given in Figure 21, showed the Pd atom to be at the center of a

Figure 21. ORTEP drawing of $[Pd(OH)(C_4H_8)\{(pz)_3BH\}\cdot2(3\text{-}MeC_6H_4OH)]$. Hydrogen atoms except those involved in intramolecular contacts are deleted for clarity.

distorted octahedron with the metal-bound OH ligand hydrogen bonded to one μ-cresol through its H and the other through its oxygen.[194] Protonation of $[Pd(OH)(C_4H_8)\{(pz)_3\text{-}BH\}]$ with pentafluorophenol (C$_6$F$_5$OH) gave $[Pd(OH_2)\text{-}(C_4H_8)\{(pz)_3BH\}\cdot C_6F_5O]_2$, which has a similar octahedral geometry around the metal.[194]

Gogoll and co-workers isolated an adamantanoid hexanuclear cluster $[\{(1,3\text{-}\eta^3\text{-}propenyl)Pd\}_6(\mu_3\text{-}OH)_4](CF_3SO_3)_2$ in an attempt to synthesize a complex of the sterically hindered *N*,*N'*-bis(diphenylmethyl)-3,7-diazabicyclo[3,3,1]nonane with a (π-allyl)palladium species. X-ray structure analysis of $[\{(1,3\text{-}\eta^3\text{-}propenyl)Pd\}_6(\mu_3\text{-}OH)_4](CF_3SO_3)_2$ exhibits that the cluster pairs bonded via two CF$_3$SO$_3^-$ ions are linked into strands via two other CF$_3$SO$_3^-$ ions[195] (eq 32).

(32)

11.3. Platinum

In contrast to the case of the lighter group 10 metals, there are a number of reports of monomeric Pt(II) and Pt(IV) hydroxide complexes. As with the Pd(II) complexes, [PtR$_2${(pz)$_3$BH}]$^-$ (R = Me, p-tolyl) can be oxidized by water to give the corresponding hydroxoplatinum(IV) complexes [Pt(OH)R$_2${(pz)$_3$BH}].[193,196,197] Other Pt(II) complexes having tridentate ligands, such as tris(pyridin-2-yl)methanol and py$_3$COH, react similarly.[197] As expected, the metal exhibits a distorted octahedral geometry.[193,196] In the same way, the Pt(II) complexes [PtMe$_2$(N–N)] (N–N = 2,2′-bipyridyl, 1,10-phenanthroline) react with alcohols, ROH (R = Me, Et, iPr), to form [PtMe$_2$(N–N)(OR)(OH$_2$)]OH or with water to form a similar complex where OH replaces OR.[198] It is of interest that the Pt–OR bonds in these compounds are quite inert and do not undergo alcohol exchange or hydrolysis with either water or dilute perchloric acid.[198] Other platinum(II) hydroxo complexes such as methyl- and phenyl-bis(tertiaryphosphine)hydroxo derivatives of general composition Pt(OH)RL$_2$ have been synthesized by the reaction of KOH with cationic acetone complexes [PtR(OCMe$_2$)L$_2$]$^+$ where the cationic complex was generated in situ (R = Ph and L = PCy$_3$, P-tBu$_2$Me, P-tBuMe$_2$, PEt$_3$, PMePh$_2$, PMe$_2$Ph; R = Me and L = P-tBu$_2$Me, P-iPr$_3$). These complexes have been shown to catalyze the hydration of acetonitrile to acetamide at 80 °C. However, the efficiency was less than that of the trialkylphosphine platinum(0) complexes.[11,199] The monomeric hydroxo(methyl)platinum(II) complex Pt(OH)(Me)(dppe) {dppe = 1,2-bis(diphenylphosphino)ethane, Ph$_2$PCH$_2$CH$_2$PPh$_2$} was prepared by the reaction of the cation [Pt(MeOH)(Me)(dppe)]$^+$ with aqueous methanolic sodium hydroxide. Reaction with weak carbon acids, e.g. acetone and acetonitrile, leads to anion formation of the complexes and provides a convenient route to unsymmetrically substituted bis(alkyls) of platinum(II), Pt(CH$_2$COMe)(Me)(dppe) and Pt(CH$_2$CN)(Me)(dppe). The ^{31}P{^{1}H} NMR spectra of these complexes suggest the *trans* influence of OH$^-$ and of σ-carbon donors. However, in this case, the generally high *trans* influence of σ-carbon donors is lowered due to the presence of conjugated electron-withdrawing groups on the ligating carbon atom.[200] The binuclear anionic complex of platinum (NBu$_4$)$_2$[(C$_6$F$_5$)$_2$Pt-(μ-OH)$_2$Pt(C$_6$F$_5$)$_2$] has a composition similar to its Ni and Pd analogues but is synthesized in a different manner by the reaction of (NBu$_4$)$_2$[(C$_6$F$_5$)$_2$Pt(Cl)$_2$M(C$_6$F$_5$)$_2$] and

NBu$_4$OH[182] (eq 28). The reaction of NBu$_4$OH with PtI(Ph)-(COD) formed a platinum diphenyl complex Pt(Ph)$_2$(COD) along with the complex Pt(OH)(X)(COD). The reaction involves the isolable dinuclear platinum intermediate [{Pt(Ph)(COD)}$_2$(μ-OH)]X (COD = 1,5-cyclooctadiene; X = I$^-$, OH$^-$) and proceeds through an intermolecular phenyl ligand transfer as shown in eq 33.[201] The complex [{Pt(Ph)-

(33)

(COD)}$_2$(μ-OH)]BF$_4$ was prepared by an independent route using AgBF$_4$, water, and PtI(Ph)(COD).[201]

Platinum(IV) hydroxo complexes having only monodentate ligands can similarly be obtained by the oxidative addition of ROH to cis-PtMe$_2$Py$_2$ to give [PtMe$_2$Py$_2$(OR)(OH)].[202] The complexes cis-PtMe$_2$L$_2$ [L$_2$ = 2,2′-dipyridine or 1,10-phenanthroline] undergo an oxidative addition reaction with water or alcohols to form PtMe$_2$L$_2$(OH)$_2$.[198,202,203] Oxidizing agents other than water can be used to form the Pt(IV)(OH) compounds. For example, (TMEDA)PtMe$_2$ (TMEDA = N,N,N′,N′-tetramethylethylenediamine) reacts with dioxygen in methanol to give (TMEDA)PtMe$_2$(OMe)(OH).[204] The reaction is believed to occur in two steps: the first involves the addition of O$_2$ and MeOH to give the hydroperoxoplatinum(IV) intermediate (TMEDA)PtMe$_2$(OOH)(OMe), which then reacts with another (TMEDA)PtMe$_2$ to give 2 equiv of (TMEDA)PtMe$_2$(OMe)(OH); other α-diimines react similarly.[204] The structures of both the intermediates and final products have been reported.[204] It has been demonstrated that the use of crown ethers as phase transfer catalyst assists in the formation of the complexes [L$_2$Pt$_2$Cl$_2$(OH)$_2$] (L = PEt$_3$, PMe$_2$Ph, and PEt$_2$Ph), [Pt$_2$(OH)$_2$(C$_6$H$_4$Me$_4$)$_2$(PEt$_2$Ph)$_2$], and [Pt(OH)Ph(dppe)] from the corresponding chloro complexes and KOH. Crown ethers have been the key reactant in this strategy, since crown ether/KOH reacts with Pt(II) complexes in benzene, whereas, in the presence of hydroxide, alcohols as solvents become strongly reducing and offer either Pt metal, Pt(0) complexes, or Pt(II) hydrides.[205]

Small-ring alkynes, cyclohexyne and cycloheptyne (ac), can be trapped in the stable zerovalent metal complexes $M(ac)L_2$ [M = Pd, Pt; L_2 = 2PPh$_3$, Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe)], from which the alkynes are not readily displaced by other unsaturated ligands.[12] The cyclohexyne complex [Pt(C$_6$H$_8$)(dppe)] reacts with H$_2$O to give stable, monomeric hydroxo-platinum(II) complexes [Pt(OH)(C$_6$H$_9$)(dppe)]. The complex is soluble in aromatic hydrocarbons, dichloromethane, and trichloromethane to give air stable solutions. The ^{1}H NMR spectrum of the hydroxo complex exhibits the expected doublet of vinyl resonance with ^{195}Pt satellites. However, the hydroxyl resonance could not be observed; the absence of this resonance was attributed to the masking by the methylene resonances. The hydroxo-metal formulation is supported by the observation that the complex catalyzes the hydration of nitriles to amides, a property that is exhibited by the known hydroxo complexes.[13]
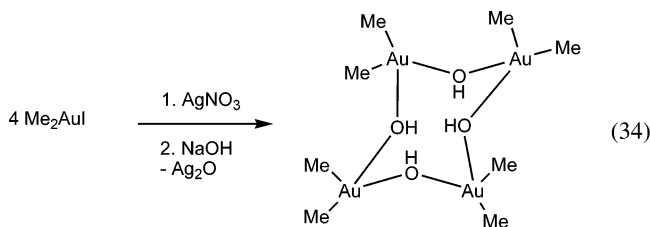
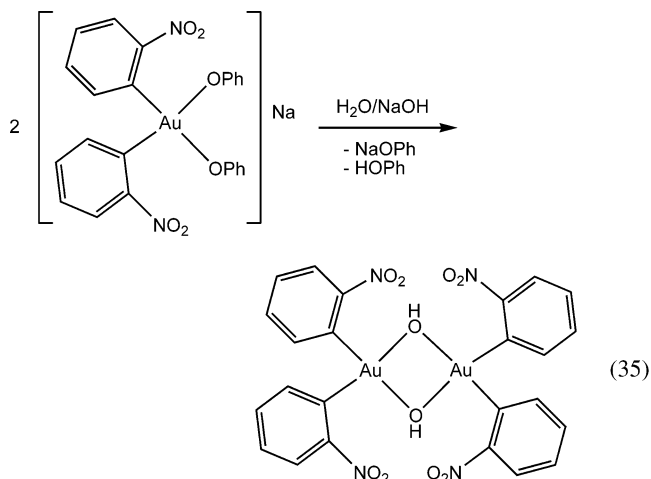## 12. Group 11 Organo-hydroxides

12.1. Copper and Silver

To our knowledge, there are no reports of structurally characterized organometallic hydroxides of copper or silver. One Cu hydroxide is reported, but structural characterization has not been done. Reaction of CuCl$_2$·2H$_2$O with N,N,N',N'-tetramethylethylenediamine (tmen) results in the formation of [Cu(tmen)Cl$_2$]. The latter compound on dissolution in water yields [Cu(tmen)(OH$_2$)$_2$]$^{2+}$. Treatment of this diaquo Cu complex with 1 equiv of NaOH results in the formation of the copperaquo-hydroxo complex [Cu(tmen)(OH)(OH$_2$)]$^+$. Due to steric effects, N-methylation of ethylenediamine leads to the formation of a mono rather than bis complex of Cu(II). This copper hydroxo complex is useful in promoting hydrolysis of 2,4-dinitrophenyldiethylphosphate and O-isopropylmethylphosphonofluoridate.[206]

12.2. Gold

Only three hydroxides of gold are reported, di-μ-hydroxo-bis(1,2,3,4-tetraphenyl-1,3-butadien-1,4-diyl)digold(III), [{PhC=C(Ph)C(Ph)=C(Ph)}Au(μ-OH)]$_2$,[207] and [Me$_2$Au(μ-OH)]$_4$.[208,209] The dimethylgold(III) hydroxide has been used to prepare aqueous solutions of Me$_2$AuNO$_3$, Me$_2$AuClO$_4$, and Na[Me$_2$Au(OH)$_2$].[208] The X-ray crystal structure of the dimethylgold(III) hydroxide shows that it exists in the solid state as gold tetramers consisting of eight-membered rings with the local geometry around each Au being a square planar one in which the methyl groups are *cis* to one another; in solution the tetramer is stereochemically rigid[209] (eq 34).

$$4 \text{ Me}_2\text{AuI} \xrightarrow[\substack{\text{2. NaOH} \\ - \text{Ag}_2\text{O}}]{\text{1. AgNO}_3} \quad (34)$$

Treatment of Na[Au(C$_6$H$_4$NO$_2$-2)$_2$(OPh)$_2$] in acetone with NaOH yielded [Au(C$_6$H$_4$NO$_2$-2)$_2$(μ-OH)]$_2$ (eq 35). The X-ray crystal structure of the ether adduct of this molecule shows that it is a centrosymmetric dimer with two hydroxy groups bridging two Au(C$_6$H$_4$NO$_2$-2) moieties. The bridging OH

$$(35)$$

groups are also involved in the hydrogen bonding with ether molecules.[210]

13. Group 12 Organo-hydroxides

13.1. Zinc

Several non-organometallic hydroxides of Zn are known. Most of these are supported by the N-donor ligands.[211−215] The only known organozinc hydroxide is [(Me$_2$PhSi)$_3$-CZnOH]$_2$, which was synthesized by the reaction of (Me$_2$PhSi)$_3$CZnCl with NaOH in THF; its structure shows that each Zn is coordinated to two bridging OH's and a (Me$_2$PhSi)$_3$C$^-$ group.[216] It was speculated that the large steric bulk of the (Me$_2$PhSi)$_3$C prevented its protonation by the OH protons and the compound is stable even in moist air.

13.2. Cadmium

Bis(pentafluorophenyl)cadmium(II) was found to react in toluene containing small amounts of water to give (C$_6$F$_5$)-CdOH. The solid-state structure showed it to crystallize as a tetramer with a cubane-like structure with the cadmium and oxygen atoms occupying alternate edges of the cube.[217] The Cd−O distances lie within the range 2.209−2.285 Å. Starting from Cd(C$_6$F$_5$)$_2$ and treatment with TrtSH generates the complex [Cd(C$_6$F$_5$)(STrt)$_4$]·1.5toluene (TrtSH = triphenylmethanethiol). This complex exhibits the characteristic reactivity of a ligand deficient complex toward potential ligands and can easily be degraded by reaction with an appropriate amount of hydroxide to the hydroxo complex [{Cd(C$_6$F$_5$)(STrt)}$_3$(μ_3-OH)]K(THF)$_3$, as shown in eq 36. In

R = C$_6$F$_5$
TrtSH = triphenylmethanethiol

$$(36)$$
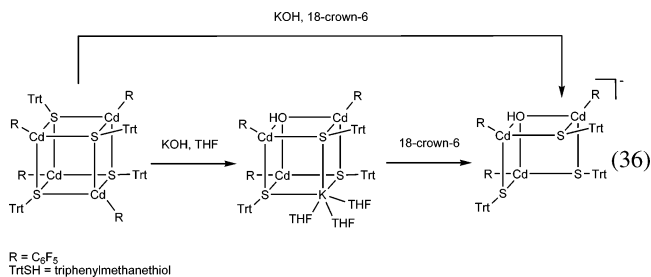
the presence of 18-crown-6, the compound [K(18-crown-6)(THF)$_2$][{Cd(C$_6$F$_5$)(STrt)}$_3$(μ_3-OH)]·THF was isolated, which is a cyclic trimer of the [{Cd(C$_6$F$_5$)(STrt)}] unit stabilized by a (μ_3-OH) ligand.[218]

Slow diffusion of acetonic solutions of $(NBu_4)_2[Pt(C≡CPh)_4]$ and $Cd(ClO_4)_2·6H_2O$ under aerobic conditions produced an unusual decanuclear platinum/cadmium cluster $[Pt_4Cd_6(C≡CPh)_4(\mu-C≡CPh)_{12}(\mu_3-OH)_4]$. This cluster is composed of a hexanuclear cation $[Cd_6(\mu_3-OH)_4]^{8+}$ and four $[Pt(C≡CPh)_4]^{2-}$ anions held together by Pt⋯Cd and π⋯Cd acetylide interactions.[219]

13.3. Mercury

The simplest organometallic hydroxides of mercury are MeHgOH and PhHgOH. The former undergoes a ready loss of water to produce $(MeHg)_2O$ and $[(MeHg)_3O](OH)$.[220] PhHgOH when reacted with strong acids easily affords $[(PhHg)_2OH]^+$. The X-ray structure of the BF_4^- salt $[(PhHg)_2OH][BF_4]$ shows that the cation has an Hg−O−Hg angle of 126°.[220]

Mercuration of acetaldehyde with mercuric nitrate containing an excess of nitric acid leads to the formation of $[(OH)Hg_2(NO_3Hg)CCHO]NO_3$. The solid-state structure of this molecule consists of a dimercurated oxonium cation $[(OH)Hg_2(NO_3Hg)CCHO]_n^{n+}$ in the form of an infinite helical chain.[221] The $CF_3SO_3^-$ salt of hydroxo[μ-(3,4,5,6-tetramethyl-1,2-phenylene)] dimercury was obtained by the treatment of the corresponding oxo derivative with CF_3SO_3H, in which the 1,2-phenylenedimercury units are bridged by hydroxyl groups. This μ-hydroxide defines an approximately planar symmetric ten-membered $C_4Hg_4O_2$ ring,[222] as shown in eq 37.

(37)

The first monomeric organomercury hydroxide $4-Me_2NC_6H_4HgOH$ was obtained in a metathesis reaction of $4-Me_2NC_6H_4HgOAc$ and NaOH. The molecule is essentially planar with a linear coordinated Hg atom, and surprisingly, it has no intermolecular H-bonding contacts between the −OH group and either of the acceptor sites $(Me_2N$ or the oxygen atom).[223]
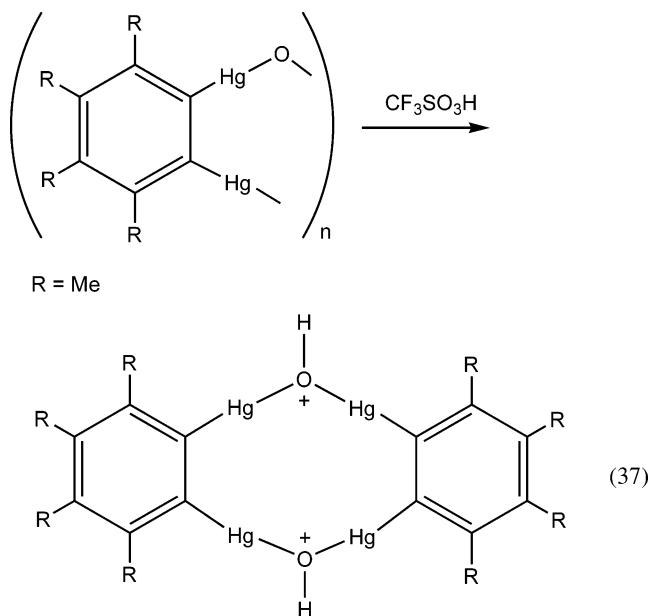
14. Future Scope

There is only a limited number of reports on organometallic hydroxides in the literature, and many of these are older references. A review of the synthetic routes to these compounds reveals that many were not the main target but

were formed accidentally due to the traces of moisture in the reaction system. Despite the adventitious nature of such syntheses, many of the compounds have interesting polynuclear structures. Because of the tendency of the OH ligand to act as a bridging group, a majority of the organometallic hydroxides are dimeric, although trimers, tetramers, and higher order aggregates are known (*vide supra*). Many of the monomeric hydroxides are stabilized by bulky ligands that prevent further reaction or conglomeration.

Since the M−O bonds with metals in low oxidation states are not particularly strong and are labile because of the soft acid/hard base interactions, organometallic hydroxides can react with electrophilic organic substrates. They can form strong hydrogen bonds with organic acceptors and, hence, increase the basicity of the compounds. The presence of electron pairs on the OH group gives them additional capabilities in terms of interacting with molecules and weak acids, and these interactions can result in lowering activation barriers for bimolecular reactions.

As many of these organometallic hydroxides are soluble in organic solvents, they may find application as catalysts in biphasic catalysis. Even though most of them are not soluble in water, they could induce catalytic reactions in water and find application in green catalysis due to their hydrogen bonding capabilities. However, these types of studies have not yet been properly exploited. Thus, the future studies on the hydroxo complexes should be concentrated on using the systems for generating hetero-bimetallic compounds and on understanding the role they could play in a wide range of catalytic processes, due to their cooperative properties of the different metal atoms.

16. References

(1) Roesky, H. W.; Haiduc, I.; Hosmane, N. S. *Chem. Rev.* **2003**, *103*, 2579.
(2) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339.
(3) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.
(4) Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44.
(5) Roesky, H. W.; Singh, S.; Jancik, V.; Chandrasekhar, V. *Acc. Chem. Res.* **2004**, *37*, 969.
(6) Gilje, J. W.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 895.
(7) *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 1−14.
(8) Anastas, P. T.; Kirchhoff, M. M. *Acc. Chem. Res.* **2002**, *35*, 686.
(9) Roesky, H. W.; Walawalkar, M. G.; Murugavel, R. *Acc. Chem. Res.* **2001**, *34*, 201.
(10) Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 5875.
(11) Arnold, D. P.; Bennet, M. A. *J. Organomet. Chem.* **1980**, *199*, 119.
(12) Bennet, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.
(13) Bennet, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3030.

(14) Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 723.
(15) Jensen, C. M.; Trogler, W. C. *Science* **1986**, *233*, 1069.
(16) Masters, C. *Homogeneous Transition Metal Catalysis*; Chapman & Hall: New York, 1981.
(17) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027.
(18) Choudhury, D.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1885.
(19) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941.
(20) Zudin, V. N.; Chinakov, V. D.; Nekipelov, V. M.; Rogov, V. A.; Likholobov, V. A.; Ermakov, Yu. I. *J. Mol. Catal.* **1989**, *52*, 27.
(21) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130.
(22) Milstein, D. *J. Chem. Soc., Chem. Commun.* **1986**, 817.
(23) Zahalka, H. A.; Alper, H.; Sasson, Y. *Organometallics* **1986**, *5*, 2497.
(24) Cole-Hamilton, D. J.; Bruce, D. W. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, 1987; Vol. 6, p 487.
(25) Yoshida, T.; Otsuka, S. *Adv. Chem. Ser.* **1982**, No. 196, 135.
(26) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472.
(27) Gargano, M.; Giannoccaro, P.; Rossi, M. *J. Organonomet. Chem.* **1977**, *129*, 239.
(28) Gard, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 6340.
(29) Kuo, L. Y.; Barnes, L. A. *Inorg. Chem.* **1999**, *38*, 814.
(30) Kuo, L. Y.; Kuhn, S.; Ly, D. *Inorg. Chem*, **1995**, *34*, 5341.
(31) Kuo, L. Y.; Kanatzidis, M. G.; Sabat, M.; Tipton, A. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 9027.
(32) Braga, D.; Grepioni, F. *J. Chem. Soc., Dalton Trans.* **1999**, 1.
(33) Williams, J. M.; Wang, H. H.; Emge, T. J.; Geiser, U.; Beno, M. A.; Leung, P. C. W.; Carson, K. D.; Thorn, R. J.; Schultz, A. J.; Whangbo, M.-H. *Prog. Inorg. Chem.* **1987**, *35*, 51.
(34) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385.
(35) Miller, J. S.; Epstein, A. J. *Chem. Eng. News* **1995**, *73*, 30.
(36) Khan, O. *Molecular Magnetism*; VCH: New York, 1993.
(37) Müller, A.; Peters, F.; Pope, M. T.; Gatteschi, D. *Chem. Rev.* **1998**, *98*, 239.
(38) Mardar, S. R. *Inorg. Mater.* **1992**, 115.
(39) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21.
(40) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155.
(41) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.
(42) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.
(43) Evans, W. J.; Allen, N. T.; Greci, M. A.; Ziller, J. W. *Organometallics* **2001**, *20*, 2936.
(44) Xie, Z.; Liu, Z.; Chui, K.; Xue, F.; Mak, T. C. W. *J. Organomet. Chem.* **1999**, *588*, 78.
(45) Schumann, H.; Görlitz, F. H.; Hahn, F. E.; Pickardt, J.; Qian, C.; Xie, Z. *Z. Anorg. Allg. Chem.* **1992**, *609*, 131.
(46) Hitchcock, P. B.; Lappert, M. F.; Prashar, S. *J. Organomet. Chem.* **1991**, *413*, 79.
(47) Deng, D.; Jiang, Y.; Qian, C.; Wu, G.; Zheng, P. *J. Organomet. Chem.* **1994**, *470*, 99.
(48) Deng, D.; Song, F.; Wang, Z.; Qian, C. *Polyhedron* **1992**, *11*, 2883.
(49) Evans, W. J.; Hozbor, M. A.; Bott, S. G.; Robinson, G. H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 1990.
(50) Schumann, H.; Loebel, J.; Pickardt, J.; Qian, C.; Xie, Z. *Organometallics* **1991**, *10*, 215.
(51) Lin, J.; Wang, Z. *J. Organomet. Chem.* **1999**, *589*, 127.
(52) Berthet, J.-C.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1993**, *460*, 47.
(53) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Neculai, D.; Neculai, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1419.
(54) Bai, G.; Peng, Y.; Roesky, H. W.; Li, J.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1132.
(55) Bai, G.; Singh, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2005**, *127*, 3449.
(56) Jancik, V.; Pineda, L. W.; Stueckl, A. C.; Roesky, H. W.; Herbst-Irmer, R. *Organometallics* **2005**, *24*, 1511.
(57) Chai, J.; Jancik, V.; Singh, S.; Zhu, H.; He, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hosmane, N. S. *J. Am. Chem. Soc.* **2005**, *127*, 7521.
(58) Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium and Hafnium*; Academic Press: New York, 1974.
(59) Giddings, S. A. *Inorg. Chem.* **1964**, *3*, 684.
(60) Demerseman, B.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1981**, 665.
(61) Toney, J. H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 947 and references therein.
(62) Thewalt, U.; Lasser, W. *J. Organomet. Chem.* **1984**, *276*, 341.
(63) Thewalt, U.; Klein, H.-P. *J. Organomet. Chem.* **1980**, *194*, 297.
(64) Thewalt, U.; Schleussner, G. *Angew. Chem.* **1978**, *90*, 559.
(65) Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1976**, *98*, 4137.
(66) Döppert, K. *J. Organomet. Chem.* **1979**, *178*, C3.
(67) Döppert, K.; Thewalt, U. *J. Organomet. Chem.* **1986**, *301*, 41.
(68) Thewalt, U.; Honold, B. *J. Organomet. Chem.* **1988**, *348*, 291.
(69) Bochmann, M.; Jaggar, A. J.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1989**, *8*, 1838.
(70) Aslan, H.; Eggers, S. H.; Fischer, R. D. *Inorg. Chim. Acta* **1989**, *159*, 55.
(71) Bochmann, M.; Jaggar, A. J.; Hursthouse, M. B.; Mazid, M. *Polyhedron* **1990**, *9*, 2097.
(72) Liu, F. Q.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1992**, *11*, 2965.
(73) Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829.
(74) Thewalt, U.; Döppert, K.; Lasser, W. *J. Organomet. Chem.* **1986**, *308*, 303.
(75) Klima, S.; Thewalt, U. *J. Organomet. Chem.* **1988**, *354*, 77.
(76) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.
(77) Lasser, W.; Thewalt, U. *J. Organomet. Chem.* **1984**, *275*, 63.
(78) Babcock, L. M.; Day, V. W.; Klemperer, W. G. *Inorg. Chem.* **1989**, *28*, 806.
(79) Morris, S.; Almond, M. J.; Cardin, C. J.; Drew, M. G. B.; Rice, D. A.; Zubavichus, Y. *Polyhedron* **1998**, *17*, 2301.
(80) Babcock, L. M.; Day, V. W.; Klemperer, W. G. *J. Chem. Soc., Chem. Commun.* **1988**, 519.
(81) Bai, G.; Roesky, H. W.; Li, J.; Labahn, T.; Cimpoesu, F.; Magull, J. *Organometallics* **2003**, *22*, 3034.
(82) Bai, G.; Roesky, H. W.; Lobinger, P.; Noltemeyer, M.; Schmidt, H.-G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2156.
(83) Bai, G.; Ma, Q.; Roesky, H. W.; Vidovic, D.; Herbst-Irmer, R. *Chem. Commun.* **2003**, 898.
(84) Hughes, R. P.; Lindner, D. C.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **2001**, *20*, 363.
(85) Lasser, W.; Thewalt, U. *J. Organomet. Chem.* **1986**, *311*, 69.
(86) Hidalgo, G.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1118.
(87) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93.
(88) Bortolin, R.; Patel, V.; Munday, I.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 456.
(89) Vaughan, G. A.; Rupert, P. B.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1987**, *109*, 5538.
(90) Choukroun, R.; Lorber, C.; Vendier, L.; Lepetit, C. *Organometallics* **2006**, *25*, 1551.
(91) Bunker, M. J.; De Cian, A.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1977**, 59.
(92) Kirillova, N. I.; Gusev, A. I.; Pasynskii, A. A.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1973**, *14*, 1075.
(93) Sharp, P. R. *J. Chem. Soc., Dalton Trans.* **2000**, 2647.
(94) Bottomley, F.; Karslioglu, S. *Organometallics* **1992**, *11*, 326.
(95) Bottomley, F.; Karslioglu, S. *J. Chem. Soc., Chem. Commun.* **1991**, 222.
(96) Curtis, M. D.; Real, J. *Inorg. Chem.* **1988**, *27*, 3176.
(97) Bottomley, F.; Keizer, P. N.; White, P. S.; Preston, K. F. *Organometallics* **1990**, *9*, 1916.
(98) Jernakoff, P.; De Meric de Bellefon, C.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 1362.
(99) Jernakoff, P.; De Meric de Bellefon, C.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *New J. Chem.* **1988**, *12*, 329.
(100) Kwon, D.; Curtis, M. D.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, *31*, 3489.
(101) Wormsbächer, D.; Nicholas, K. M.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1985**, 721.
(102) McNeese, T. J.; Mueller, T. E.; Wierda, D. A.; Darensbourg, D. J.; Delord, T. J. *Inorg. Chem.* **1985**, *24*, 3465.
(103) McNeese, T. J.; Cohen, M. B.; Foxman, B. M. *Organometallics* **1984**, *3*, 552.
(104) Bazhenova, T. A.; Ioffe, M. S.; Kachapina, L. M.; Lobkovskaya, R. M.; Shibaeva, R. P.; Shilov, A. E.; Shilova, A. K. *Zh. Strukt. Khim.* **1978**, *19*, 1047.
(105) Lin, J. T.; Yeh, S. K.; Lee, G. H.; Wang, Y. *J. Organomet. Chem.* **1989**, *361*, 89.
(106) Albano, V. G.; Bellon, P. L.; Ciani, G.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1969**, 1242.
(107) Rott, J.; Guggolz, E.; Rettenmeier, A.; Ziegler, M. L. *Z. Naturforsch.* **1982**, *37B*, 13.
(108) Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1988**, *66*, 97.
(109) Cooper, N. J.; Green, M. L. H.; Couldwell, C.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1977**, 145.
(110) Prout, K.; Couldwell, M. C. *Acta Crystallogr., Sect. B* **1977**, *33*, 2146.
(111) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1244.

(112) Bottomley, F.; Chen, J.; Preston, K. F.; Thompson, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 7989.
(113) Demirhan, F.; Caatay, B.; Demir, D.; Baya, M.; Daran, J.-C.; Poli, R. *Eur. J. Inorg. Chem.* **2006**, 757.
(114) Collange, E.; Gracia, J. A.; Poli, R. *New J. Chem.* **2002**, *26*, 1249.
(115) Hieber, W.; Englert, K.; Rieger, K. *Z. Anorg. Allg. Chem.* **1959**, *300*, 295.
(116) Ren, J.-G.; Tomita, H.; Minato, M.; Ito, T.; Osakada, K.; Yamasaki, M. *Organometallics* **1996**, *15*, 852.
(117) Balzarek, C.; Weakley, T. J. R.; Kuo, L. Y.; Tyler, D. R. *Organometallics* **2000**, *19*, 2927.
(118) Minato, M.; Tomitaq, H.; Ren, J.-G.; Ito, T. *Chem. Lett.* **1993**, 1191.
(119) Balzarek, C.; Tyler, D. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 2406.
(120) Lippard, S. J. *Science* **1982**, *218*, 1075.
(121) Rosenberg, B. *Cancer* **1985**, *55*, 2303.
(122) Fettinger, J. C.; Kraatz, H.-B.; Poli, R.; Quadrelli, E. A.; Torralba, R. C. *Organometallics* **1998**, *17*, 5767.
(123) Fettinger, J. C.; Kraatz, H.-B.; Poli, R.; Quadrelli, E. A. *J. Chem. Soc., Dalton Trans.* **1999**, 497.
(124) Morales, D.; Pleune, B.; Poli, R.; Richard, P. *J. Organomet. Chem.* **2000**, *596*, 64.
(125) Morales, D.; Elena Navarro Clemente, M.; Perez, J.; Riera, L.; Riera, V.; Miguel, D. *Organometallics* **2002**, *21*, 4934.
(126) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *30*, 2290.
(127) Carmona, E.; Gonzalez, F.; Poveda, M. L.; Marin, J. M.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3365.
(128) Albano, V. G.; Ciani, G.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* **1972**, *34*, 353.
(129) Hieber, W.; Englert, K.; Rieger, K. *Z. Anorg. Allg. Chem.* **1959**, *300*, 304.
(130) Albano, V. G.; Ciani, G.; Manassero, M. *J. Organomet. Chem.* **1970**, *25*, C55.
(131) El Amin, E. A. E.; Jeffery, J. C.; Walters, T. M. *J. Chem. Soc., Chem. Commun.* **1990**, 170.
(132) Cihonski, J. L.; Levenson, R. A. *Inorg. Chem.* **1975**, *14*, 1717.
(133) Rau, M. S.; Kretz, C. M.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3447.
(134) Clerk, M. D.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1607.
(135) Shen, J. K.; Gao, Y.-C.; Shi, Q.-Z.; Basolo, F. *Organometallics* **1989**, *8*, 2144.
(136) Horn, E.; Snow, M. R.; Zeleny, P. C. *Aust. J. Chem.* **1980**, *33*, 1659.
(137) Miroslavov, A. E.; Gorshkov, N. I.; Grigor'ev, M. S.; Lumpov, A. A.; Sidorenko, G. V.; Suglobov, D. N. *Radiokhimiya* **1997**, *39*, 41.
(138) Alberto, R.; Schibli, R.; Egli, A.; Abram, U.; Abram, S.; Kaden, T. A.; Schubiger, P. A. *Polyhedron* **1998**, *17*, 1133.
(139) Herberhold, M.; Suss, G.; Ellermann, J.; Gaebelein, H. *Chem. Ber.* **1978**, *111*, 2931.
(140) Herberhold, M.; Suss, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 700.
(141) Jones, D. F.; Dixneuf, P. H.; Benoit, A.; Le Marouille, J.-Y. *Inorg. Chem.* **1983**, *22*, 29.
(142) Lee, K. W.; Pennington, W. T.; Cordes, A. W.; Brown, T. L. *Organometallics* **1984**, *3*, 404.
(143) Johnson, B. F. G.; Lewis, J.; Kilty, P. A. *J. Chem. Soc. A* **1968**, 2859.
(144) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Molinari, H. *J. Organomet. Chem.* **1986**, *311*, 177.
(145) Arif, A. M.; Cowley, A. H.; Pakulski, M.; Pearsall, M.-A.; Clegg, W.; Norman, N. C.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1988**, 2713.
(146) Treichel, P. M.; Dean, W. K.; Calabrese, J. C. *Inorg. Chem.* **1973**, *12*, 2908.
(147) Gould, R. O.; Jones, C. L.; Robertson, D. R.; Stephenson, T. A. *J. Chem. Soc., Chem. Commun.* **1977**, 222.
(148) Gould, R. O.; Jones, C. L.; Stephenson, T. A.; Tocher, D. A. *J. Organomet. Chem.* **1984**, *264*, 365.
(149) Gould, R. O.; Jones, C. L.; Robertson, D. R.; Tocher, D. A.; Stephenson, T. A. *J. Organomet. Chem.* **1982**, *226*, 199.
(150) Kim, T. D.; McNeese, T. J.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 2554.
(151) Robertson, D. R.; Stephenson, T. A. *J. Organomet. Chem.* **1976**, *116*, C29.
(152) Werner, H.; Werner, R. *J. Organomet. Chem.* **1981**, *209*, C60.
(153) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1987**, *26*, 2561.
(154) Funaioli, T.; Cavazza, C.; Marchetti, F.; Fachinetti, G. *Inorg. Chem.* **1999**, *38*, 3361.
(155) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Chem. Soc., Chem. Commun.* **1981**, 476.
(156) Renkema, K. B.; Huffman, J. C.; Caulton, K. G. *Polyhedron* **1999**, *18*, 2575.

(157) Bigotto, A.; Felluga, A.; Dreos, R.; Nardin, G.; Randaccio, L.; Tauzher, G.; Peressini, S.; Tavagnacco, C. *J. Chem. Soc., Dalton Trans.* **2002**, 99.
(158) Dreos, R.; Tauzher, G.; Trendafilova, D. H.; Nardin, G.; Randaccio, L. *Inorg. Chem.* **1996**, *35*, 2715.
(159) Rat, M.; Alves de Sousa, R.; Tomas, A.; Frapart, Y.; Tuchagues, J.-P.; Artaud, I. *Eur. J. Inorg. Chem.* **2003**, 759.
(160) Nutton, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1997.
(161) Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *30*, 127.
(162) Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2335.
(163) Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2339.
(164) Lahoz, F. J.; Carmona, D.; Oro, L. A.; Lamata, M. P.; Puebla, M. P.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1986**, *316*, 221.
(165) Oro, L. A.; Carmona, D.; Lamata, M. P.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1823.
(166) Oro, L. A.; Carmona, D.; Lamata, M. P.; Foces-Foces, C.; Cano, F. H. *Inorg. Chim. Act,* **1985**, *97*, 19.
(167) Wieghardt, K.; Schmidt, W.; Nuber, B.; Prikner, B.; Weiss, J. *Chem. Ber.* **1980**, *113*, 36.
(168) Nutton, A.; Bailey, P. M.; Maitlis, P. M. *J. Organomet. Chem.* **1981**, *213*, 313.
(169) Hirai, K.; Nutton, A.; Maitlis, P. M. *J. Mol. Catal.* **1981**, *10*, 203.
(170) Woerpel, K. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7888.
(171) Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 2580.
(172) Morales-Morales, D.; Lee, D. W.; Wang, Z.; Jensen, C. M. *Organometallics* **2001**, *20*, 1144.
(173) Miller, C. A.; Janik, T. S.; Lake, C. H.; Toomey, L. M.; Churchill, M. R.; Atwood, J. D. *Organometallics* **1994**, *13*, 5080.
(174) Randall, S. L.; Thompson, J. S.; Buttery, L. A.; Ziller, J. W.; Churchill, M. R.; Atwood, J. D. *Organometallics* **1991**, *10*, 683.
(175) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387.
(176) Green, L. M.; Meek, D. W. *Organometallics* **1989**, *8*, 659.
(177) Gorol, M.; Mösch-Zanetti, N. C.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Eur. J. Inorg. Chem.* **2004**, 2678.
(178) Ilg, K.; Werner, H. *Organometallics* **2001**, *20*, 3782.
(179) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1973**, *106*, 1433.
(180) Carmona, E.; Marin, J. M.; Palma, P.; Paneque, M.; Poveda, M. L. *Inorg. Chem.* **1989**, *28*, 1895.
(181) Carmona, E.; Marin, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1987**, *6*, 1757.
(182) López, G.; García, G.; Ruiz, J.; Sánchez, G.; García, J.; Vicente, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1045.
(183) López, G.; García, G.; Sánchez, G.; García, J.; Ruiz, J.; Hermoso, J. A.; Vegas, A.; Martínez-Ripoll, M. *Inorg. Chem.* **1992**, *31*, 1518.
(184) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890.
(185) Grushin, V. V.; Benisnom, C.; Alper, H. *Organometallics* **1995**, *14*, 3259.
(186) Grushin, V. V.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4305.
(187) Grushin, V. V.; Alper, H. *Organometallics* **1996**, *15*, 5242.
(188) Ruiz, J.; Rodríguez, V.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *Organometallics* **1996**, *15*, 1662.
(189) Ruiz, J.; Rodríguez, V.; López, G.; Casabó, J.; Molins, E.; Miravitlles, C. *Organometallics* **1999**, *18*, 1177.
(190) Kuznetsov, V. F.; Bensimon, C.; Facey, G. A.; Grushin, V. V.; Alper, H. *Organometallics* **1997**, *16*, 97.
(191) Ackerman, L. J.; Sadighi, J. P.; Kurtz, D. M.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2003**, *22*, 3884.
(192) Ruiz, J.; Vicente, C.; Martí, J. M.; Cutillas, N.; García, G.; López, G. *J. Organomet. Chem.* **1993**, *460*, 241.
(193) Canty, A. J.; Fritsche, S. D.; Jin, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1995**, *490*, C18.
(194) Canty, A. J.; Jin, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1995**, *503*, C16.
(195) Gogoll, A.; Toom, L.; Grennberg, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 4729.
(196) Canty, A. J.; Fritsche, S. D.; Jin, H.; Patel, J.; Skelton, B. W.; White, A. H. *Organometallics* **1997**, *16*, 2175.
(197) Canty, A. J.; Honeyman, R. T.; Roberts, A. S.; Traill, P. R.; Colton, R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1994**, *471*, C8.
(198) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444.
(199) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110.
(200) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738.
(201) Suzaki, Y.; Osakada, K. *Organometallics* **2004**, *23*, 5081.
(202) Appleton, T. G.; Hall, J. R.; Neale, D. W.; Williams, M. A. *J. Organomet. Chem.* **1984**, *276*, C73.

(203) Appleton, T. G.; D'Alton, C. J.; Hall, J. R.; Mathieson, M. T.; Williams, M. A. *Can. J. Chem*. **1996**, *74*, 2008.

(204) Rostovtsev, V. V.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 3608.

(205) Fakley, M. E.; Pidcock, A. *J. Chem. Soc., Dalton Trans*. **1977**, 1444.

(206) Hay R. W.; Govan, N. *Polyhedron* **1998**, *17*, 2079.

(207) Peteau-Boisdenghien, M.; Meunier-Piret, J.; van Meerssche, M. *Cryst. Struct. Commun.* **1975**, *4*, 375.

(208) Miles, M. G.; Glass, G. E.; Tobias, R. S. *J. Am. Chem. Soc.* **1966**, *88*, 5738.

(209) Glass, G. E.; Konnert, J. H.; Miles, M. G.; Britton, D.; Tobias, R. S. *J. Am. Chem. Soc.* **1968**, *90*, 1131.

(210) Vicente, J.; Bermudez, M. D.; Carrion, F. J.; Jones, P. G. *J. Organomet. Chem.* **1996**, *508*, 53.

(211) Alsfasser, R.; Trofimenko, S.; Looney, A.; Parkin, G.; Vahrenkamp, H. *Inorg. Chem.* **1991**, *30*, 4098.

(212) Bauer-Siebenlist, B.; Meyer, F.; Farkas, E.; Vidovic, D.; Cuesta-Seijo, J. A.; Herbst-Irmer, R.; Pritzkow, H. *Inorg. Chem.* **2004**, *43*, 4189.

(213) Bauer-Siebenlist, B.; Meyer, F.; Farkas, E.; Vidovic, D.; Dechert, S. *Chem.—Eur. J.* **2005**, *11*, 4349.

(214) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738.

(215) Sakai, K.-I.; Imakubo, T.; Ichikawa, M.; Taniguchi, Y. *J. Chem. Soc., Dalton Trans*. **2006**, 881.

(216) Al-Juaid, S. S.; Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Roberts, A. T. L.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 908.

(217) Weidenbruch, M.; Herrndorf, M.; Schäfer, A.; Pohl, S.; Saak, W. *J. Organomet. Chem.* **1989**, *361*, 139.

(218) Duhme, A.-K.; Strasdeit, H. *Eur. J. Inorg. Chem.* **1998**, 657.

(219) Forniés, J.; Gómez, J.; Lalinde, E.; Moreno, M. T. *Inorg. Chem.* **2001**, *40*, 5415.

(220) Nicholson, B. K.; Whitton, A. J. *J. Organomet. Chem.* **1986**, *306*, 139.

(221) Grdeniæ, D.; Matkoviæ-Èalogoviæ, D.; Sikirica, M. *J. Organomet. Chem.* **1987**, *319*, 1.

(222) Vaugeois, J.; Simard, M.; Wuest, J. D. *Organometallics* **1998**, *17*, 1215.

(223) Nicholson, B. K.; Whitley, S. K. *J. Organomet. Chem.* **2004**, *689*, 515.