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Structurally Characterized Organometallic Hydroxo Complexes of the f- and d-Block Metals

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Contents

I. Introduction

Organotransition metal hydroxides have been known for a long time, and there has been interest in them for many years, primarily because of their role in catalysis.[1] However, this class of compounds has taken on increased importance with the growth of activity in materials-related chemistry. As organometallic precursors are now being used for the synthesis of oxide materials by sol–gel and related hydrothermal syntheses, an understanding organometallic hydroxides, which occur as intermediates or themselves function as precursors, becomes important. The primary purpose of this review is to summarize the structures found in the organometallic hydroxide complexes of the d- and f-block elements. While preparative methods will be mentioned, many of the complexes have formed adventitiously and there are gaps in the chemical understanding. Nonetheless, common structural features occur throughout the periodic chart and we hope this review will aid the development of both the pure and applied chemistry of this series of compounds.

We are unaware of another review of this area. However, terminal hydroxide complexes of the late transition metals and organometallic oxo–hydroxo compounds[1,2] are covered in reviews largely devoted to other topics.

II. Prologue

A Lewis dot formula shows three electron pairs residing on oxygen in the hydroxide ion. As might be expected from this representation, the hydroxo ligand is capable of a variety of coordination modes utilizing one or several electron pairs. Thus, even the terminal M–OH linkages are complicated by possible contribution from three resonance forms:

$$\mathrm{M{-}OH} \leftrightarrow \mathrm{M{=}OH} \leftrightarrow \mathrm{M{\equiv}OH}$$

In fact, M–OH units often possess short metal–oxygen distances which sometimes are interpreted in terms of metal–oxygen multiple bonding.

While terminal hydroxo coordination is found in complexes of metals throughout the transition series, doubly and triply bridging geometries are more common. While there is no clear separation between the various metals, doubly bridging complexes are encountered relatively most frequently with the early transition and the f-block metals while the triple bridge is somewhat more common with the later metals. There are a variety of different structures for each type of hydroxide coordination, but among the triply bridging complexes "cubanes" are the most frequently encountered type and are common from group 6 to 12.

In many cases the coordinated OH group is involved in hydrogen bonding. This can occur both in an intra- and/or intercomplex fashion or to solvents of crystallization. When no other sites are accessible, very weakly basic molecules, with which the hydroxo complex has co-crystallized, may be involved. Undoubtably, the tendency of these compounds to hydrogen bond may influence their chemistry. However, this has not yet been investigated. The compounds mentioned in this review are listed in Table 1 along with the metal–oxygen bond lengths.

III. Scandium, Yttrium, Lanthanides, and Actinides

Hydrolysis is a common mode of decomposition for the organometallic complexes of the electropositive metals, and all of the known group 3, lanthanide, and actinide organometallic hydroxo complexes have been prepared by this route.

The most common structural type of the organo–hydroxo complexes of the group 3 and lanthanide metals is the double-bridged $[(Cp)_2M]_2(\mu_2\text{-}OH)_2$, where Cp may be C_5H_5 or a derivative. If the two Cp and two OH ligands are each considered to occupy a single coordination site, the metals are distorted tetrahedral and the Cp(centroid)$_2$M planes are approximately perpendicular to the nearly planar $M_2(O)_2$ rings.

$[(C_5H_5)_2Y]_2(\mu_2\text{-}OH)_2$ was isolated from a mixture of $(C_5H_5)_2Y(Bu^t)(thf)$ and Ph—C≡C—Ph, in which it presumably formed by hydrolysis and from which it co-crystallizes with PhC≡CPh.[3] $[(C_5H_5)_2Y]_2(\mu_2\text{-}OH)_2$

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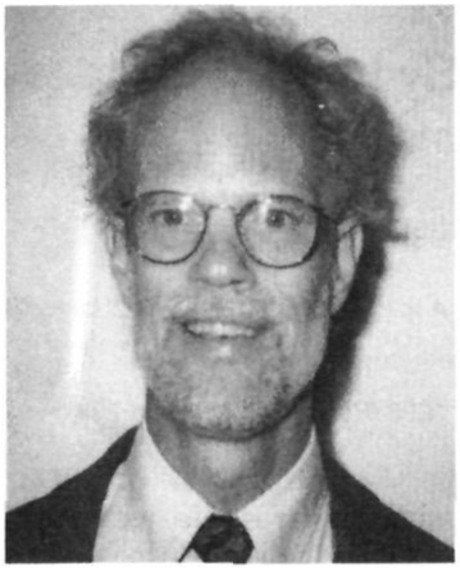


John W. Gilje grew up in St. Paul, MN, and in 1961 received B. Chem. degree from the University of Minnesota. He went on for graduate study at the University of Michigan, where he completed his Ph.D. in 1965, working with Robert W. Parry on boron hydride chemistry. In 1965 he joined the faculty of the University of Hawaii where he is now professor of chemistry. He has held visiting positions at the University of Texas, Austin, (1972/1973), Imperial College of Science and Technology, London, (1979/1980), Technical University at Braunschweig, Germany, (1980/1981), and Göttingen University, Germany (1990). He received an Alexander von Humboldt Research Fellowship (1980) and was awarded a Distinguished Senior Scientist Award from the Alexander von Humboldt Foundation (1990). Currently he is serving as a Program Officer in Inorganic Chemistry at the National Science Foundation. His research interests include the molecular chemistry of electropositive metals and phosphorus chemistry.

Herbert W. Roesky was born in 1935 in Laukischken. He studied chemistry at the university of Göttingen, Germany, where he obtained his Diplom in 1961 and his Ph.D. in 1963. After one year of postdoctoral work at DuPont in Wilmington, DE, he made his habilitation at Göttingen University. In 1971 he became full professor in Frankfurt and since 1980 he has been a full professor and director of the Institute of Inorganic Chemistry at Göttingen University. During this time he has also been a visiting professor at Tokyo Institute of Technology and at Kyoto University in Japan. He is member of the Academy of Sciences in Göttingen and of the Academy of Scientists "Leopoldina" in Halle. He has received many awards, e.g. the D.rer.nat.h.c. of Bielefeld University, Alfred-Stock-Memorial Award, and French Alexander-von-Humboldt award. More than 550 research publications, articles, patents and books document his activity.

consists of two $(C_5H_5)_2Y$ units bridged by OH groups and with Y–O distances of 233(2) and 236(2) pm. The PhC≡CPh molecules are located between layers of $[(C_5H_5)_2Y]_2(\mu_2\text{-}OH)_2$ molecules, which are oriented so that each O–H is directed toward the C≡C bond of an alkyne; the oxygen and carbon separations range between 344 and 355 pm, and a hydrogen binding interaction is proposed.[3] Subsequent attempts to obtain $[(C_5H_5)_2Y]_2(\mu_2\text{-}OH)_2$ by hydrolysis of $(C_5H_5)_2YR$ ($R = C_5H_5$, CH_3, or H) gave mixtures of products, as did the reaction of $(C_5H_5)_3Y$(thf) with a suspension of NaOH in thf. When $(NPCl_2)_n$ was added to scavange $C_5H_5^-$ a compound formulated as $(C_5H_5)_2Y(OH)$(thf) was isolated, but no structure was determined.[3]

With the lanthanides, $[\{[C_5H_3(SiMe_3)_2]\}_2Sm]_2(\mu_2\text{-}OH)_2$ and $\{[C_5H_4(SiMe_3)]_2Yb\}_2(\mu_2\text{-}OH)_2$ are obtained by careful, oxidative hydrolysis:[4]

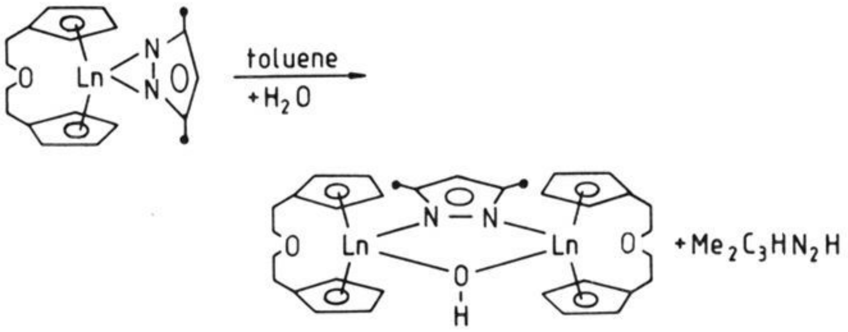
$$2\{[C_5H_{5-n}(SiMe_3)_n]\}_2Ln(L) + 2H_2O \rightarrow [\{[C_5H_{5-n}(SiMe_n)_2]\}_2Ln]_2(\mu_2\text{-}OH)_2 + 2L + H_2$$
$$Ln = Sm,\ n = 2,\ L = thf;\ Ln = Yb,\ n = 1,\ L = Et_2O$$

and $[\{[C_5H_4(Bu^t)]\}_2Ln]_2(\mu_2\text{-}OH)_2$ by[5]

$$Ln[C_5H_4(Bu^t)]_3 + 2H_2O \rightarrow \{[C_5H_4(Bu^t)]_2Ln\}_2(\mu_2\text{-}OH)_2 + 2C_5H_5(Bu^t)$$
$$Ln = Nd\ or\ Dy$$

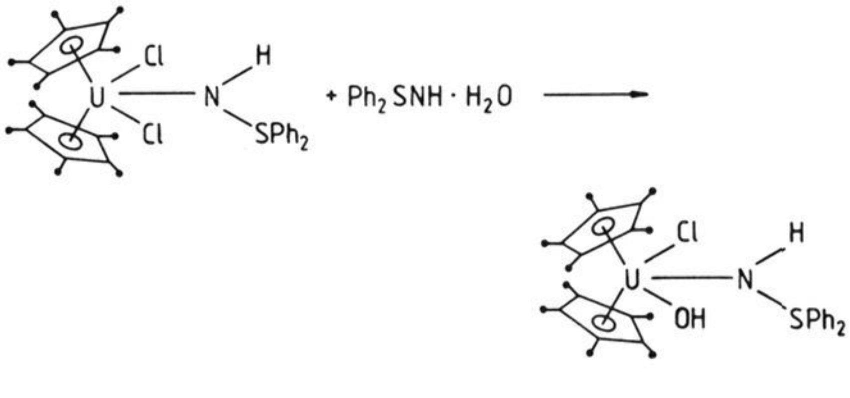
In each of these reactions dilute solutions of water in an ether are used for the hydrolysis. The mean metal–oxygen distances in these compounds are Sm–O = 240,[4] Yb–O = 229,[4] Nd–O = 232.9,[5] and Dy–O = 225.7 pm.[5]

Another Y and an analogous Lu complex, $\{[O(CH_2CH_2C_5H_4)_2]Ln\}_2(\mu_2\text{-}Me_2C_3H\text{-}N_2)(\mu_2\text{-}OH)$ (Ln = Y, Lu), form by



The M–OH distances are 220.2(2) and 215.4(3) pm for the Y and Lu complex, respectively.[6]

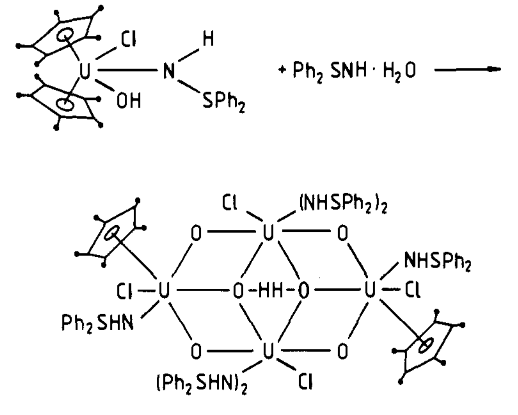
The generation and subsequent reactions of hydrogen halide may complicate hydrolysis reactions of organometallic halides. A novel solution to this problem has been the use of $Ph_2SNH\cdot H_2O$ as a reagent to provide stoichiometric amounts of water and to absorb HCl as it is formed. $(C_5Me_5)_2UCl_2(NHSPh_2)$, a product from the reaction between $(C_5Me_5)_2UCl_2$ and $HNSPh_2$, reacts with $Ph_2SNH\cdot H_2O$ in toluene:



$(C_5Me_5)_2U(OH)(NHSPh_2)(Cl)$ has a typical bent metallocene structure; the U–O bond distance, 210(2) pm, is quite short.[7] $(C_5Me_5)_2U(OH)(NHSPh_2)(Cl)$ decomposes slowly in the solid state or within a few days in solution

$$2(C_5Me_5)_2U(OH)(NHSPh_2)(Cl) \rightarrow (C_5Me_5)_2UCl_2(NHSPh_2) + 2(C_5Me_5H) + \text{“}UO_2(NHSPh_2)\text{”}$$

or reacts further with $Ph_2SNH{\cdot}H_2O$ to form a tetra-uranium–oxo–hydroxo cluster:[7]



The U–O bond distances range from 196 to 236 pm and the OH groups are assigned on the basis of symmetry and bond distances. The $U_4O_4(OH)_2$ core is a small segment of a common type encountered in uranium-oxide and uranium–oxy–halide chemistry. As the complete hydrolysis of $(C_5Me_5)_2UCl_2$ would undoubtedly yield an oxide or oxy chloride, $(C_5Me_5)_2U(OH)(NHSPh_2)(Cl)$ and $(C_5Me_5)_2U_4O_4(OH)_2Cl_4(NHSPh_2)_6$ can be viewed as intermediates in the conversion of an organometallic precursor to an oxide.

IV. Titanium, Zirconium, and Hafnium

A. Titanium(III)

The reaction of the titanocene $[(C_5H_5)Ti(\mu_2\text{-}H)]_2[\mu\text{-}(C_5H_4)_2]$ with water in thf gives $[(C_5H_5)Ti(\mu_2\text{-}OH)]_2[\mu\text{-}C_5H_4)_2]$:[8]

$$[(C_5H_5)Ti(\mu_2\text{-}H)]_2[\mu\text{-}(C_5H_4)_2] + 2H_2O \rightarrow [(C_5H_5)Ti(\mu_2\text{-}OH)]_2[\mu\text{-}(C_5H_4)_2] + 2H_2$$

The crystal structure shows discrete molecules of $[(C_5H_5)Ti(\mu_2\text{-}OH)]_2[\mu\text{-}(C_5H_4)_2]$, with one OH in each molecule hydrogen bonded to a thf of solvation.

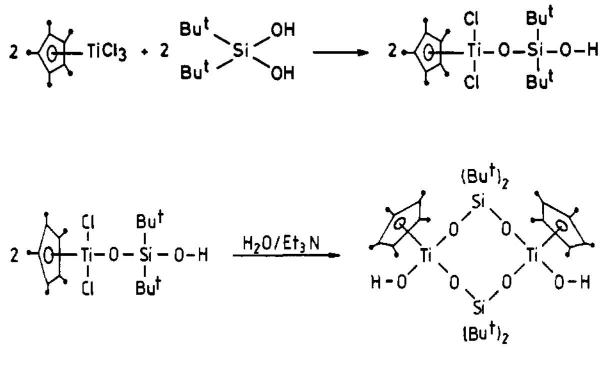
B. Titanium(IV)

Several Ti(IV) complexes containing a terminal hydroxo ligand have been characterized by X-ray diffraction. $[(C_5Me_5)_2Ti(OH)(HNCPh_2)]BPh_4{\cdot}Et_2O$, prepared by the reaction of $(C_5Me_5)_2TiN{=}CPh_2$ with $AgBPh_4$ in the presence of traces of moisture,[9] shows pseudotetrahedral titanium coordination with a short Ti–OH distance, 185.3(7) pm, which indicates substantial Ti–O double-bond character.

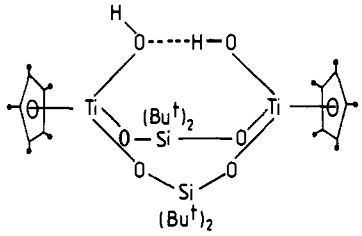
The reaction of $(C_5Me_5)_2TiMe$ with $AgBPh_4$ in thf gives the sterically congested $[(C_5Me_5)_2TiMe(thf)]BPh_4$. The thf is easily displaced by donor molecules[10] and in the presence of even traces of water $[(C_5Me_5)_2Ti(OH)(H_2O)]BPh_4{\cdot}2thf$ forms. The Ti–OH bond length, 185.3(5) pm, is identical to that in the previous cation.

The reaction of $(C_5Me_5)_2TiCl_2$ with $AgCF_3SO_3$ in moist thf produces $[(C_5Me_5)_2Ti(H_2O)_2][CF_3SO_3]_2$.[11] From aqueous solutions of this compound the monohydrate $[(C_5Me_5)_2Ti(OH)(H_2O)]CF_3SO_3{\cdot}H_2O$ and dihydrate $[(C_5Me_5)_2Ti(OH)(H_2O)]CF_3SO_3{\cdot}2H_2O$ have been isolated. All three compounds were characterized by X-ray diffraction and the Ti–OH distances are all nearly the same, 187-pm mean value for the three compounds.

The first titanium hydroxide containing an O–H–O bond was prepared according to the following equations:[12]

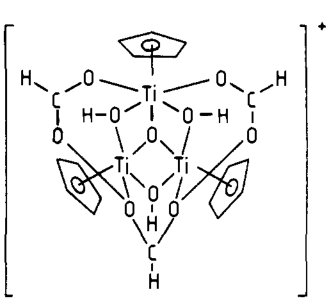


$[(C_5Me_5)Ti(OH)OSi(Bu^t)_2O]_2$ is a yellow crystalline solid showing characteristic OH absorptions in the IR. A side-on view of the structure shows an eight-membered ring in a boat form with one OH hydrogen bonding through a transannular bridge to the other, which is not involved in hydrogen bonding:



The hydrogen bridge increases the coordination number of O(1) and results in a long Ti(1)–O(1) bond, 187.2(2) pm. Normally the elimination of a water molecule would be expected, but in this case steric factors presumably prevent further reactions of the OH groups.

On hydrolysis of $(C_5H_5)_2TiCl_2$ in water at pH > 5 one cyclopentadienyl group is removed. Reaction of the product with formic acid gives the ionic trinuclear complex $[Ti_3(\mu_3\text{-}O)(\mu_2\text{-}OH)_3(\mu_2\text{-}HCOO)_3(C_5H_5)_3]^+[HCOO]^-{\cdot}2HCOOH$ whose structure was determined by X-ray:[13]



The complex cation is oxygen centered, with Ti–O–Ti

Table 1. The Structurally Characterized Organo–Hydroxo Complexes of the d- and f-Block Metals

	M–O distance (pm)	ref
Y		
$[(C_5H_5)_2Y]_2(\mu_2\text{-}OH)_2\cdot PhC{\equiv}CPh$	233, 236	3
$\{[O(CH_2CH_2C_5H_4)_2]Y\}_2(\mu_2\text{-}Me_2CHN_2)(\mu_2\text{-}OH)$	220.2	6
Ln		
$[\{[C_5H_3(SiMe_3)_2]\}_2Sm]_2(\mu_2\text{-}OH)_2$	240	4
$[\{[C_5H_4(SiMe_3)]\}_2Yb]_2(\mu_2\text{-}OH)_2$	229	4
$\{[C_5H_4(Bu^t)]_2Nd\}_2(\mu_2\text{-}OH)_2$	232.9	5
$\{[C_5H_4(Bu^t)]_2Dy\}_2(\mu_2\text{-}OH)_2$	225.7	5
$\{[O(CH_2CH_2C_5H_4)_2]Lu\}_2(\mu_2\text{-}Me_2C_3HN_2)(\mu_2\text{-}OH)$	215.4	6
An		
$(C_5Me_5)_2U(OH)(NHSPh_2)(Cl)$	210	7
$(C_5Me_5)_2U_4(\mu_2\text{-}O)_4(\mu_3\text{-}OH)_2(Cl)_4(NHSPh_2)_6$	see text	7
Ti(III)		
$[(C_5H_5)Ti(\mu_2\text{-}OH)]_2[\mu\text{-}(C_5H_4)_2]\cdot thf$	205, 210	8
Ti(IV)		
$[(C_5Me_5)_2Ti(OH)(HNCPh_2)]BPh_4\cdot Et_2O$	185.3	9
$[(C_5Me_5)_2Ti(OH)(H_2O)]BPh_4\cdot 2thf$	185.3	10
$[(C_5Me_5)_2Ti(OH)(H_2O)]CF_3SO_3\cdot H_2O$	187	11
$[(C_5Me_5)_2Ti(OH)(H_2O)]CF_3SO_3\cdot 2H_2O$	187	11
$[(C_5Me_5)Ti(OH)OSi(Bu^t)_2O]_2$	183.7, 187.2	12
$[Ti_3(\mu_3\text{-}O)(\mu_2\text{-}OH)_3(\mu_2\text{-}HCOO)_3(C_5H_5)_3]^+[HCOO]^-\cdot 2HCOOH$	201	13
Zr(IV)		
$[(C_5H_5)Zr(NO_3)_2(\mu_2\text{-}OH)]_2\cdot 2thf$	209.0, 216.7	14
$[(C_5H_5)Zr(OCOCF_3)(\mu_2\text{-}OH)]_2$	215	15
$[(C_5H_5)_2Zr_2(\mu_2\text{-}OH)_2(H_2O)_6](CF_3SO_3)_4\cdot 4thf$	219	16
$[(C_5H_5)_2Zr_2(\mu_2\text{-}OH)_2(H_2O)_6](ClO_4)_4\cdot 8thf$	218	16
$[Zr_3(\mu_3\text{-}O)(\mu_2\text{-}OH)_3(\mu_2\text{-}C_6H_5COO)_3(C_5H_5)_3]^+[C_6H_5COO]^-\cdot O(C_2H_5)_2$	213.3	17
$(C_5Me_5)_2Zr(OH)Cl$	195.0	18
$(C_5Me_5)_2Zr(OH)_2$	198.2	18
$(C_5Me_5)_2Zr(OH)(C_{16}H_{17}N_2)$	255.4	19
$[(C_5Me_5)ZrCl]_3(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)_3\cdot 2thf$	215	20
		21
$[(C_5Me_5)ZrCl_2(H_2O)(\mu_2\text{-}OH)]_2$	216	22
$[(C_5H_5)_2Zr(NC\text{-}Pr^n)(\mu_2\text{-}OH)]_2(BPh_4)_2$	208.1, 223.2	23
Nb(IV)		
$[(C_5H_5)NbOOCH]_3(\mu_2\text{-}OH)_2(\mu_3\text{-}O)(\mu_2\text{-}O)$	197	24
		25
$[(C_5H_4Me)NbCl]_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)$	220	26
Nb(IV,V)		
$[(C_5H_5)NbCl(\mu_2\text{-}Cl)]_3(\mu_3\text{-}OH)\cdot thf$	217.1, 220.1	27
$[(C_5Me_5)Nb(\mu_2\text{-}Cl)(\mu_2\text{-}O)]_3[(C_5Me_5)Nb]_3(\mu_2\text{-}Cl)_2(\mu_2\text{-}OH)(\mu_2\text{-}O)_3(Zn_4Cl_{10})$	218.5, 220.3, 223.4	28
Nb(V)		
$[(C_5Me_5)NbCl_2]_2(\mu_2\text{-}Cl)(\mu_2\text{-}OH)(\mu_2\text{-}O)$	219	28
$\{[(C_5Me_5)NbCl_2]_3(OH)_2(\mu_2\text{-}OH)(\mu_3\text{-}OH)(\mu_2\text{-}O)_2Cl\}Cl$	213.2, 220.2	29
Ta		
$\{[(C_5Me_5)Ta]_3(OH)_2(\mu_2\text{-}OH)(\mu_3\text{-}OH)(\mu_2\text{-}O)_2(\mu_3\text{-}O)Cl\}Cl$	213, 217	29
		30
		31
$[(C_5Me_5)Ta(\mu_2\text{-}O)]_4(\mu_3\text{-}O)_2(\mu_4\text{-}O)(OH)_2$	195.0	32
$[(C_5Me_5)TaCl_2]_2(\mu_2\text{-}O)(\mu_2\text{-}OH)_2$	213, 218	33
Cr		
$[(C_5Me_5)_4Cr_4(\mu_2\text{-}OH)_6](BF_4)_2$	195	55
$[Et_4N]_4[(OC)_3Cr(\mu_3\text{-}OH)]_4$	see text	49
$(C_5H_5)(ON)Cr(\mu_2\text{-}SeBu^t)(\mu_2\text{-}OH)Cr(NO)(C_5H_5)$	196	43
Mo		
$[Cr(en)_3]_3[(NC)_4Mo(O)(OH)]$	207.7	34
$[(C_5H_5)_2Mo(NH_2Me)(OH)]PF_6$	205	35
$[(C_7H_7)Mo(\mu_2\text{-}Br)(\mu_2\text{-}OH)_2Mo(C_7H_7)]^+$	208	40
$[(C_7H_7)Mo(\mu_2\text{-}Cl)_2(\mu_2\text{-}OH)Mo(C_7H_7)]^+$	208.5	41
$(C_5H_5)(Cl)_2Mo(\mu_2\text{-}OH)(\mu_2\text{-}SMe)_2Mo(Cl)(C_5H_5)$	196.5, 191.7	42
$[(C_5H_5)Mo(\mu\text{-}C_5H_4\text{-}C_5H_4)(\mu_2\text{-}H)(\mu_2\text{-}OH)Mo(C_5H_5)](PF_6)_2$	208	44
$[(MeC_3H_4)(OC)_2Mo]_2(\mu_2\text{-}OH)_2(C_3N_2H_4)_2\cdot H_2O$	223.7, 214.0	46
$[MeGa(3,5\text{-}Me_2HC_3N_2)_2](\mu_2\text{-}OH)Mo(CO)_2(MeC_3H_4)$	227.2	47
$[Et_4N]_4[(OC)_3Mo(\mu_3\text{-}OH)]_4$	see text	50
$K_4[(OC)_3Mo(\mu_3\text{-}OH)]_4$	see text	51
$[(ON)(OC)_2Mo(\mu_3\text{-}OH)]_4$	see text	52
$[(C_7H_7)Mo(\mu_3\text{-}OH)]_4$	see text	41
$Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6$		56

Table 1 (Continued)

	M–O distance (pm)	ref
W		
$[\mathrm{Ph_2B(C_3H_3N_2)}](\mu_2\text{-OH})\mathrm{W(CO)_2(C_5H_8N_2C_3H_3)}$	219.4	48
$\mathrm{(OC)_2Co}(\mu_2\text{-PPh}_2)_2[\mu\text{-C(C}_6\mathrm{H_4Me)}]\mathrm{W(C_5H_5)(OH)}$	208.7	37
$[\mathrm{Et_4N}]_4[\mathrm{(OC)_3W}(\mu_3\text{-OH})]_4$	see text	50
$\mathrm{K_3}[\mathrm{(OC)_3W}(\mu_2\text{-OH})_3\mathrm{W(CO)_3}]$	216	39
$[\mathrm{(OC)_3W}(\mu_3\text{-OH})\mathrm{(H)}]_4$	see text	53
Mn		
$[\mathrm{Mn(CO)_3}(\mu_3\text{-OH})_4]_4$		57
$[\mathrm{Mn(CO)_3F}_x(\mu_3\text{-OH})_{4-x}]_4$	205	59
$\mathrm{Mn_7(CO)_{18}}(\mu_3\text{-OH})_{18}$	see text	57
Re		
$\mathrm{(PPh_4)_2[ReO(OH)(CN)_4]\cdot 5H_2O}$	190	60
$\mathrm{Re_2(CO)_6(Ph_2PCH_2PPh_2)}(\mu_2\text{-H})(\mu_2\text{-OH})$	216.0, 217.5	61
$[\mathrm{NEt_4}]^+[\mathrm{Re_3}(\mu_2\text{-H})_3\mathrm{(CO)_9}(\mu_3\text{-OH})]^-\cdot\mathrm{NEt_3}$	212.6	62
$[\mathrm{(OC)_3Re}(\mu_3\text{-OH})]_4\cdot 2\mathrm{C_6H_6}$	220.7	64
$\mathrm{F_3B}(\mu_2\text{-OH})\mathrm{Re(CO)_5}$	216.7	65
Fe		
$\mathrm{Fe_2(CO)_6}(\mu_2\text{-PRR}')(\mu_2\text{-OH})$		
R = R′ = p-$\mathrm{C_6H_4Me}$	197.2	66
R = $\mathrm{CH(SiMe_3)_2}$, R′ = H	199.0	67
Ru		
$[\mathrm{(arene)Ru}(\mu_2\text{-OH})_3\mathrm{Ru(arene)]Cl}$		
arene = $\mathrm{C_6H_6}$	208	70
arene = 1,3,5-$\mathrm{Me_3C_6H_3}$	209	68
$[\mathrm{(C_6H_6)_4Ru_4}(\mu_2\text{-OH})_4(\mu_4\text{-O})]\mathrm{(BPh_4)_2}$	209	68
$[\mathrm{(C_6H_6)Ru}(\mu_3\text{-OH})]_4\mathrm{(SO_4)_2}$	212	69
$\{[(p\text{-}\mathrm{MeC_6H_4CHMe_2)Ru}]_2(\mu_2\text{-OH})(\mu_2\text{-pz})_2\}\mathrm{BPh_4}$, pz = pyrazolate, $\mathrm{N_2C_3H_3}$	208.8	71
$[\mathrm{(Bu^n{}_3P)(OC)_2Ru}](\mu_2\text{-OH})(\mu_2\text{-MeCO}_2\text{-}O)(\mu\text{-MeCO}_2\text{-}O,O')[\mathrm{Ru(CO)(MeCO_2)(PBu^n{}_3)}]$	207	73
$\mathrm{FeRu_2(CO)_8(PPh_3)_2}(\mu_2\text{-OH})_2$	212	79
$\mathrm{Ru_4(CO)_{10}(C{=}CHPr^i)}(\mu_3\text{-OH})(\mu_2\text{-PPh}_2)$	215	83
$\mathrm{Ru_6(CO)_{18}}(\mu_2\text{-OH})_2(\mu_4\text{-S})$	212	84
$[\mathrm{Ru_3Cl_3(CO)_6(COEt)_2}(\mu_3\text{-OH})]_2$	216	85
Os		
$[\mathrm{(C_6H_6)_4Os_4}(\mu_2\text{-OH})_4(\mu_4\text{-O})]\mathrm{(BPh_4)_2}$	208	68
$\{[(p\text{-}\mathrm{MeC_6H_4CHMe_2)Os}]_2(\mu_2\text{-OH})(\mu_2\text{-H})(\mu_2\text{-O}_2\mathrm{CH})\}\mathrm{PF_6}$	206	72
$\mathrm{Os_3(CO)_9(L)}(\mu_2\text{-OH})(\mu_2\text{-H})$		
L = $\mathrm{PPh_3}$		74
L = $\mathrm{PMe_2Ph}$	213	75
$\mathrm{Os_3(CO)_{10}}(\mu_2\text{-OH})(\mu_2\text{-NCMe}_2)$	216	77
$\mathrm{Os_3(CO)_9}(\mu_3\text{-C}_2\mathrm{CPh_2})(\mu_2\text{-OH})(\mu_2\text{-H})$	213	78
$\mathrm{Os_3(CO)_8(NMe_3)}(\mu_2\text{-OH})(\mu_3\text{-S})(\mu_2\text{-H})$	214	80
$[\mathrm{Os_4(CO)_{12}H_4}(\mu_2\text{-OH})]^+[\mathrm{Os(CO)_3(NO_3)_3}]^-$	209	81
$\mathrm{Os_4(CO)_{12}H_3}(\mu_2\text{-OH})$	209	82
$\mathrm{Os_6(CO)_{18}}(\mu_2\text{-OH})(\mu_4\text{-S})(\mu_3\text{-S})(\mu_2\text{-H})$	214	80
Rh		
$\mathrm{(C_3H_5)_2Rh}(\mu_2\text{-OH})_2\mathrm{Rh(C_3H_5)_2}$	217.7	88
$\mathrm{(C_5Me_5)(L)Rh}(\mu_2\text{-OH})_2\mathrm{Rh(C_5Me_5)(L)(ClO_4)_2}$		
L = $\mathrm{NC_5H_5}$	211	89
L = $\mathrm{Me_2CHN_2}$	217.9	90
$[\mathrm{(C_5Me_5)Rh}(\mu_2\text{-OH})_3\mathrm{Rh(C_5Me_5)}]^+\mathrm{OH}^-$	210.9	91
$[\mathrm{Rh_2(CO)_2}(\mu_2\text{-OH})\mathrm{(Me_2PCH_2PMe_2)]PF_6\cdot OCMe_2}$	206.8	95
Ir		
$\mathrm{Ir(OH)(CO)(PPh_3)_2}$	211.0	86
$\mathrm{(C_8H_{12})Ir(Cl)}(\mu_2\text{-O})(\mu_2\text{-OH})_2\mathrm{Ir(Cl)(C_8H_{12})}$	209.8	92
$\mathrm{(C_5Me_5)Ir}(\mu_2\text{-OH})(\mu_2\text{-PPh}_2)(\mu_2\text{-C}_6\mathrm{H_4})\mathrm{Ir(C_5Me_5)}$	214	93
$[\mathrm{Ir_2(CO)_2}(\mu_2\text{-OH})\mathrm{(Ph_2PCH_2PPh_2)]Cl}$	207	94
$[\mathrm{(C_5Me_5)Ir}(\mu_2\text{-OH})_3\mathrm{Ir(C_5Me_5)}]^+\mathrm{(O_2CMe)}^-$	212	91
Ni		
$\mathrm{(MeC_6H_4CH_2)(Me_3P)Ni}(\mu_2\text{-OH})_2\mathrm{Ni(PMe_3)(CH_2C_6H_4Me)}$	191.9	97
$[\mathrm{Bu^t{}_4N}]_2[\mathrm{(C_6F_5)_2Ni}(\mu_2\text{-OH})_2\mathrm{Ni(C_6F_5)_2}]$	189	99
$[\mathrm{Bu^t{}_4N}]_2[\mathrm{(C_6F_5)_2Ni}(\mu_2\text{-C}_3\mathrm{H_3N_2})(\mu_2\text{-OH})\mathrm{Ni(C_6F_5)_2}]$	189.1	99
$\mathrm{Ni_3(CH_2C_6H_4Me)_4(PMe_3)_2}(\mu_3\text{-OH})_3$	193.1, 199.9	98
Pd		
$[\mathrm{Bu^t{}_4N}]_2[\mathrm{(C_6F_5)_2Pd}(\mu_2\text{-OH})_2\mathrm{Pd(C_6F_5)_2}]$	207.3	100
$\{[\mathrm{(8\text{-}mq)Pd}]_3(\mu_3\text{-Ph}_2\mathrm{PCHCO_2Et})(\mu_3\text{-OH})\}\mathrm{PF_6}$	228, 226.1, 214.4	103

Table 1 (Continued)

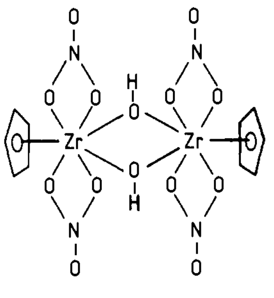
	M–O distance (pm)	ref
Pt		
$(dppe)PtMe(OH)$	202.5	2
$[Bu^t_4N]_2[(C_6F_5)_2Pt(\mu_2\text{-}OH)_2Pd(C_6F_5)_2]$	207.2	101
$[Bu_4N]_2[(C_6F_5)_2Pt(\mu_2\text{-}Me_2C_3HN_2)(\mu_2\text{-}OH)Pt(C_6F_5)_2]$	210	102
$[Me_3Pt(\mu_3\text{-}OH)]_4$	see text	104 105 106 107
Au		
$\{[(Ph)C{=}C(Ph){-}C(Ph){=}C(Ph)]Au(\mu_2\text{-}OH)\}_2$	see text	110
$[Me_2Au(\mu_2\text{-}OH)]_4$	see text	111
Zn		
$(Me_3Si)_3CZn(\mu_2\text{-}OH)_2ZnC(SiMe_3)_3$	189.9	112
Cd		
$[(C_6F_5)Cd(\mu_3\text{-}OH)]_4$	see text	113

angles around the central oxygen [106.9(2) to 107.6(2)°] being close tetrahedral. Each pair of Ti atoms is bridged by a formato and an hydroxo ligand.

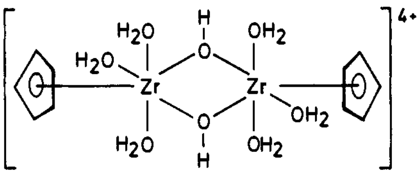
C. Zirconium

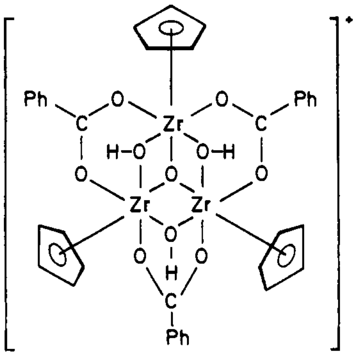
We are not aware of any hydroxide complexes of zirconium or hafnium in oxidation states other than IV.

A number of hydroxide complexes of zirconium have been obtained from $(C_5H_5)_2ZrCl_2$. With nitric acid in $CHCl_3$ a dinuclear doubly OH-bridged complex $[(C_5H_5)Zr(NO_3)_2(\mu_2\text{-}OH)]_2{\cdot}2thf$ is formed. The Zr atom has pentagonal-bipyramidal geometry with a C_5H_5 and an OH group occupying the axial positions and the equatorial plane containing two chelating NO_3 ligands and one OH group:[14]



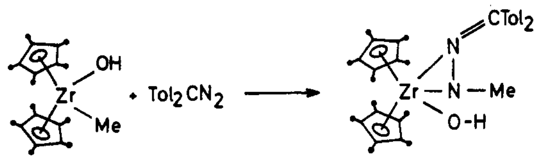
The reaction of $(C_5H_5)_2ZrCl_2$ with CF_3COOH in a two-phase $CHCl_3/H_2O$ system yields a dinuclear complex, $[(C_5H_5)_2Zr(OCOCF_3)(\mu_2\text{-}OH)]_2$, in which the 18-electron Zr atoms are five-coordinate.[15] Salts of $[(C_5H_5)_2Zr_2(\mu_2\text{-}OH)_2(H_2O)_6]^{4+}$, a dihydroxy-bridged cation, have been obtained in the reaction of $(C_5H_5)_2ZrCl_2$ with $AgCF_3SO_3$ or $AgClO_4$ followed by addition of water. X-ray structures of $[(C_5H_5)_2Zr_2(\mu_2\text{-}OH)_2(H_2O)_6](CF_3SO_3)_4{\cdot}4thf$ and $[(C_5H_5)_2Zr_2(\mu_2\text{-}OH)_2(H_2O)_6](ClO_4)_4{\cdot}8thf$ show that the Zr atoms have a distorted octahedral coordination geometry with a C_5H_5 group being trans to OH.[16] Reaction of $(C_5H_5)_2ZrCl_2$ with an aqueous sodium benzoate solution yields the trinuclear complex $[Zr_3(\mu_3\text{-}O)(\mu_2\text{-}OH)_3(\mu_2\text{-}C_6H_5COO)_3(C_5H_5)_3]^+[C_6H_5COO]^-{\cdot}O(C_2H_5)_2$. The complex cation is oxygen centered, and the Zr–O–Zr angles [107.3(1) to 108.9(2)°] at the central oxygen are close to the tetrahedral angle. Each pair of Zr atoms is bridged by a benzoato and a hydroxo ligand. The coordination octahedron around each Zr atom is completed by a C_5H_5 group:[17]





$(C_5Me_5)_2Zr(OH)Cl$ and $(C_5Me_5)_2Zr(OH)_2$ were synthesized in high yield via treatment of $(C_5Me_5)_2Zr(Bu^n)Cl$ and $(C_5Me_5)_2Zr(Me)_2$ in hexane solution, respectively, with 1 and 2 equiv of water. Confirmation of the two compounds as discrete, monomeric hydroxo compounds was provided by X-ray diffraction.[18]

Another structurally characterized complex containing a terminal Zr–OH is a hydroxo-*N,N'*-hydrazinoate produced by treatment of $(C_5Me_5)_2ZrMe(OH)$ with bis(*p*-tolyl)diazomethane:[19]



Base hydrolysis of $(C_5Me_5)ZrCl_3$ in thf yields $[(C_5Me_5)ZrCl]_3(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)_3{\cdot}2thf$. This cluster contains a nearly equilateral triangle of three Zr atoms capped above and below by μ_3-O and μ_3-OH groups and symmetrically edge bridged by three μ_2-OH groups which are coplanar with the three Zr atoms. The octahedral coordination sphere about Zr is completed by a terminal Cl and a C_5Me_5. Two chloride ligands and one C_5Me_5 group lie on one side of the $(-ZrO-)_3$ ring while the remaining Cl and the two C_5Me_5 groups are on the other, which produces a molecule with near C_5-m symmetry.[20,21]

The hydrolysis of $(C_5Me_5)ZrCl_3$ with $LiOH{\cdot}H_2O$ in thf gives $[(C_5Me_5)ZrCl_2(H_2O)(\mu_2\text{-}OH)]_2$. This complex is also formed by hydrolysis of zirconium alkyls.

$$2(C_5Me_5)ZrCl_2R + 4H_2O \rightarrow [(C_5Me_5)ZrCl_2(H_2O)(\mu_2\text{-}OH)]_2 + 2RH$$
$$R = CH_2C_6H_5,\ SiMe_3$$

The dimer is centrosymmetric.[22] $[(C_5H_5)_2Zr(NC\text{-}Pr^n)(\mu_2\text{-}OH)]_2(BPh_4)_2$ contains a similar $Zr_2(\mu_2\text{-}OH)_2$ unit.[23]

D. Hafnium

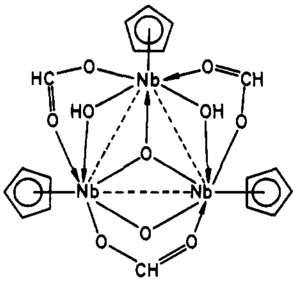
We are not aware of any structural characterized organohafnium hydroxo complexes.

V. *Vanadium, Niobium, and Tantalum*

A majority of the structurally characterized hydroxo organometallic compounds of the group 5 metals are those of niobium. None have been reported for vanadium.

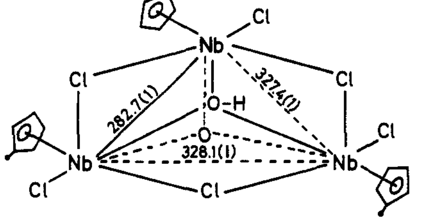
A. Niobium

The first structurally characterized niobium complex is the trinuclear[24,25] $[(C_5H_5)NbOOCH]_3(\mu_2\text{-}OH)_2(\mu_3\text{-}O)(\mu_2\text{-}O)$ which was prepared by heating $(C_5H_5)Nb(CO)_3PPh_3$ with anhydrous HCOOH in xylene:



In this d^1 niobium compound the metal atoms are located at the vertices of an almost regular triangle with short Nb–Nb distances (314 pm, average).

$[(C_5H_4Me)Nb(CO)_2Cl_2]_2$ undergoes decarbonylation[26] in refluxing thf to give a dark paramagnetic intermediate which reacts with atmospheric oxygen to produce another Nb(IV) trinuclear cluster $[(C_5H_4Me)NbCl]_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}OH)(\mu_3\text{-}O)$. Within the triangular array there is one short, 282.7(1) pm, and two longer, 327.4(1) and 328.1(1) pm, Nb–Nb separations:[24,26]



Each edge of the triangle is bridged by a chloride while a (μ_3-O) and a (μ_3-OH) triply bridge opposite faces of the Nb_3 triangle. Terminal C_5H_4Me and Cl ligands on each Nb complete the coordination sphere. In this conformation two of the Nb atoms are bonded, while the third is not bonded to the others. The odd electron is coupled to a single Nb nucleus as indicated by a characteristic 10-line ESR spectrum.

The very similar $[(C_5H_5)NbCl]_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}OH)(\mu_3\text{-}O)$ is formed by hydrolysis of $(C_5H_5)NbCl_4$ to $[(C_5H_5)NbL_4]_2(\mu_2\text{-}O)$, where L_4 is a combination of H_2O and terminal or bridging Cl such that the niobium remains eight-coordinate and pentavalent,[27] followed by reduction with aluminum, zinc powder, or sodium amalgam in thf.

$[(C_5Me_5)NbCl_2]_2(\mu_2\text{-}Cl)(\mu_2\text{-}OH)(\mu_2\text{-}O)$ and polymeric $[Nb_2Cl_2O_4{\cdot}3thf]_x$ are obtained by oxidation of $(C_5Me_5)_2NbCl_2$ with O_2 in the presence of H_2O.[28] Reduction of $[(C_5Me_5)NbCl_2]_2(\mu_2\text{-}Cl)(\mu_2\text{-}OH)(\mu_2\text{-}O)$ by zinc powder in the presence of zinc oxide produces a double salt:

$$3[(C_5Me_5)NbCl_2]_2(\mu_2\text{-}Cl)(\mu_2\text{-}OH)(\mu_2\text{-}O) + 2Zn + 2ZnO \rightarrow [(C_5Me_5)Nb(\mu_2\text{-}Cl)(\mu_2\text{-}O)]_3{\cdot}[(C_5Me_5)Nb]_3(\mu_2\text{-}Cl)_2(\mu_2\text{-}OH)(\mu_2\text{-}O)_3][Zn_4Cl_{10}] + H_2O$$

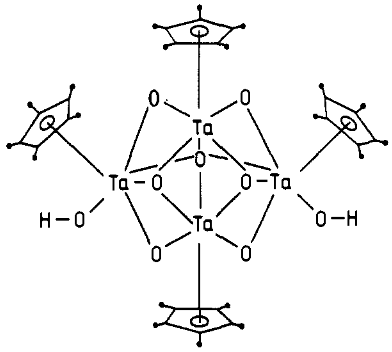
Structurally $[(C_5Me_5)Nb(\mu_2\text{-}Cl)(\mu_2\text{-}O)]_3^+$ and $[(C_5Me_5)Nb]_3(\mu_2\text{-}Cl)_2(\mu_2\text{-}OH)(\mu_2\text{-}O)_3]^+$ are very similar only differing by the replacement of a bridging Cl in the first by an OH in the second.

Hydrolysis of $(C_5Me_5)NbCl_4$ with excess water leads to a mixture of products.[29] Heating the crude mixture produces $[(C_5Me_5)NbCl(\mu_2\text{-}O)]_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)$ which yields $\{[(C_5Me_5)Nb]_3(OH)(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)(\mu_2\text{-}O)_2(\mu_3\text{-}O)Cl\}Cl$ upon treatment with water.[29]

B. Tantalum

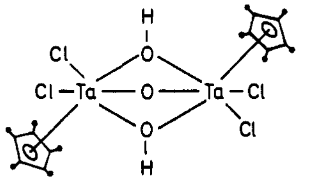
There are few structures on hydroxotantalum complexes. $(C_5Me_5)TaCl_4$ is quantitatively converted to $[(C_5Me_5)TaCl_2(OH)_2]_2(\mu_2\text{-}O)$ with excess of water. When this complex is heated in the solid state it loses water and HCl to form $[(C_5Me_5)Ta]_3(\mu_2\text{-}O)_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)Cl_3$, which hydrolyzes in excess water to form the trinuclear cluster $\{[(C_5Me_5)Ta]_3(OH)_2(\mu_2\text{-}OH)(\mu_3\text{-}OH)(\mu_2\text{-}O)_2(\mu_3\text{-}O)Cl\}Cl$.[30,31] While this is not the formulation proposed in the original publication,[30,31] the compound almost certainly possesses the same structure as the analogous niobium complex.[29]

$(C_5Me_5)Ta(H)_2(\eta^2\text{-}CHPMe_2)PMe_3$ reacts with deoxygenated water in benzene to give the butterfly oxo cluster $[(C_5Me_5)Ta(\mu_2\text{-}O)]_4(\mu_3\text{-}O)_2(\mu_4\text{-}O)(OH)_2$. The tetranuclear core is surrounded by seven oxo ligands, four of which are doubly bridging, two of which cap the triangular faces of each wing, and one of which quadruply bridges the hinge and wing-tip tantalums:[32]



The two terminal hydroxo ligands are attached to the wing-tip Ta atoms. Direct metal–metal bonds are not required to interpret the structure.

The hydrolysis of $(C_5Me_5)TaCl_4$[31] and the air oxidation of $(C_5Me_5)TaCl_2(CO)_2{\cdot}thf$[33] produces $[(C_5Me_5)TaCl_2]_2(\mu_2\text{-}O)(\mu_2\text{-}OH)_2$. The molecule consists of two $C_5Me_5TaCl_2$ units bridged by one oxo and two hydroxo ligands:[33]



In contrast to niobium, no hydroxo complexes in which the oxidation state of tantalum is less than V have been structurally characterized.

VI. Chromium, Molybdenum, and Tungsten

There are many similarities between the chromium group metals, and it makes little sense to separate them in this discussion. Among these elements a few terminal hydroxo organometallic complexes are encountered. However, doubly or triply bridging hydroxo ligands are far more common.

Only two monometallic organo–hydroxo complexes of the chromium group have been structurally characterized. The Mo is octahedrally coordinated in $[Cr(en)_3{}^+]_3[(NC)_4Mo(O)(OH)]^{3-}$ with the oxo and hydroxo ligands being trans.[34] While the proton was not located in the structure, the two Mo–O distances are 207.7(7) and 166.8(5) pm and the OH is assumed to have the longer bond. This distance is comparable to 205.0(5) pm in $[(C_5H_5)_2Mo(NH_2Me)(OH)]^+PF_6^-$ in which the cation has a typical bent metallocene structure.[35] $[(NC)_4Mo(O)(OH)]^{3-}$ is prepared from $[(NC)_4MoO_2]^{4-}$ by an acid–base reaction with water in methanol,[34] and $[(C_5H_5)_2Mo(NH_2Me)(OH)]^-$ by hydrolysis of $[(C_5H_5)_2Mo(SMe_2)Br]^-$ in dilute, aqueous NH_2Me.[36]

A terminal OH is also encountered in $(OC)_2Co(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}C\text{-}C_6H_4Me)W(C_5H_5)(OH)$, where the W–O distance, 208.7(6) pm, is nearly the same as the distances mentioned above. This compound is obtained from the corresponding chloride by hydrolysis on deactivated alumina.[37]

There are several examples of hydroxo bridges. $K_3[(OC)_3M(\mu_2\text{-}OH)_3M(CO)_3]$ forms during alkaline hydrolysis of $M(CO)_6$, M = Mo or W,[38] and an X-ray structure has been determined on the tungsten derivative.[39] While the W–W distance, 323.0(5) pm, implies a metal–metal bond, such bonding is not required to produce an 18-electron count about the metals and the short separation may reflect geometric constraints imposed by the necessity of minimizing O–O repulsions between bridging OH groups. The mean W–O distance, 216(2) pm, is long, the W–O–W angle, 97(1)°, is relatively narrow, and the O···O contacts, 245 pm, are less than the sum of oxygen van der Waals radii, 280 pm.

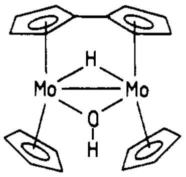
$[(C_7H_7)Mo(\mu_2\text{-}Br)(\mu_2\text{-}OH)_2Mo(C_7H_7)]^+$ was obtained from a reaction between $Mo(CO)_3(C_7H_7)^+BF_4^-$ and $C_8H_7SiMe_3$ in thf; the bromine was probably an impurity in the $C_8H_7SiMe_3$ and the source of the OH is uncertain.[40] Usual electron-counting conventions imply a Mo–Mo bond, which is also indicated by the Mo–Mo separation, 288.2(2) pm. The average Mo–O distance, 208 pm, and Mo–O–Mo angle, 88.1°, are consistent with this description.

Closely related is $[(C_7H_7)Mo(\mu_2\text{-}Cl)_2(\mu_2\text{-}OH)Mo(C_7H_7)]^+$, which was one of several products from reactions between LiCl and $[(C_7H_7)Mo(toluene)][PF_6]$ in methanol.[41] The Mo–O, 208.4 pm (av), and Mo–Mo, 309.1(1) pm, distances as well as the Mo–O–Mo angle, 95.8(3)°, resemble those in $[(C_7H_7)Mo(\mu_2\text{-}Br)(\mu_2\text{-}OH)_2Mo(C_7H_7)]^+$.[41]

$(C_5H_5)(Cl)_2Mo(\mu_2\text{-}OH)(\mu_2\text{-}SMe)_2Mo(Cl)(C_5H_5)$, isolated from a reaction between $(C_5H_5)MoCl_4$ and CH_3SH in diethyl ether, consists of a $(C_5H_5)MoCl_2$ moiety linked to $(C_5H_5)MoCl$ through one OH and two SMe bridges.[42] The Mo–Mo distance, 272.6(1) pm, indicates metal–metal bonding. The molecule is asymmetric and the $(C_5H_5)Cl_2Mo$–O distance, 196.5(5) pm, is longer than $(C_5H_5)ClMo$–O, 191.7(5) pm. Interestingly, the opposite trend occurs with the Mo–S bonds, where those to $(C_5H_5)Cl_2Mo$ are about 15 pm shorter than the ones to $(C_5H_5)ClMo$.

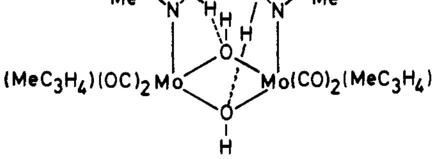
A structure has been determined for $(C_5H_5)(ON)Cr(\mu_2\text{-}SeBu^t)(\mu_2\text{-}OH)Cr(NO)(C_5H_5)$, a minor product from the reaction of $(C_5H_5)(ON)_2CrCl$ with $Mg(SeBu^t)_2$.[43] The Cr–O distance, 196 pm (av), and Cr–O–Cr angle, 93.9(2)°, are comparable to those in (μ_2-OH)-bridged Mo and W compounds, when size differences between the metals is taken into account. The H atom on oxygen was located and refined in the X-ray structure.

Three as of yet uncharacterized compounds were obtained in a reaction of $[(C_5H_5)_2Mo(H)(Li)]_4$ with NO. Prolonged treatment of each with aqueous HPF_6 gives $[(C_5H_5)Mo(\mu\text{-}C_5H_4\text{-}C_5H_4)(\mu_2\text{-}H)(\mu_2\text{-}OH)Mo(C_5H_5)](PF_6)_2$:[44]



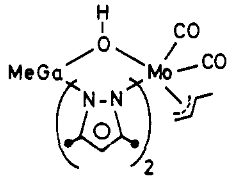
The OH group symmetrically bridges the two Mo atoms, Mo–O = 208 pm (av), Mo–O–Mo = 94.3(6)°, and a Mo–Mo bond is indicated.

Pyrazoleborate and -galate chemistry has led to three novel organo Mo and W hydroxides. Attempts to form a methylallyl complex analogous to $[Me_2Ga(3,5\text{-}Me_2HC_3N_2)_2]Mo(CO)_2(MeC_3H_4)$ failed,[45] rather



forms, apparently by hydrolysis of an intermediate with "adventitious" water. The X-ray structure, in which hydrogen atoms were located and refined, reveals distorted octahedral coordination about Mo and a folded Mo(μ_2-OH)$_2$Mo ring (dihedral angle 28°) with the oxygen atoms being displaced toward the pyrazole ligand to which they are hydrogen bonded. Two different Mo–O distances occur in the molecule: 223.7(2) pm, to the Mo to which the hydrogen-bonding pyrazolate ligand is coordinated and 214.0(2) pm to the other.[46]

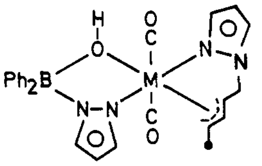
Hydrolysis involving water of unknown origin also occurs in attempted preparations of [MeGa(3,5-Me$_2$-HC$_3$N$_2$)$_2$](μ_2-OH)M(CO)$_2$(RC$_3$H$_4$), M = Mo or W; R = H or Me. A structure of the Mo compound with R = Me shows[47]



An interesting feature of this structure is that the hydroxyl hydrogen has been precisely enough located to show that the oxygen is pyramidal. The Mo–O distance, 227.2(4) pm, is somewhat longer than these involved in typical Mo(μ_2-OH)Mo bridges.

An unusual bridging hydroxide forms in the hydrolysis of a (pyrazol-1-yl)borate complex

$$Ph_2B(H_3C_3N_2)_2M(CO)_2(C_5H_7) + H_2O \longrightarrow$$



While the details of the reaction are beyond the scope of this review, an initial coordination of water to the metal is postulated.[48] A structure was determined for the W derivative and the W–O bond, 219.4(6) pm, is in the usual range.

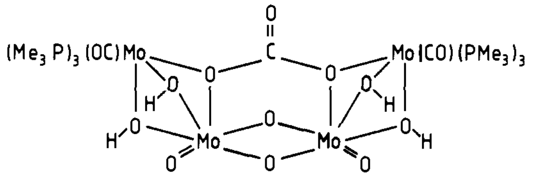
From the viewpoint of this review, the preceding two compounds are particularly interesting as they are among the very few examples of an OH group bridging transition and main group metals.

The most common structure encountered in the organo–hydroxo complexes of the group 6 metals is a cubane-like arrangement with metal and hydroxide oxygen atoms occupying alternate corners of a distorted M$_4$O$_4$ cube. In general these clusters are electron precise, with OH$^-$ utilizing three lone pairs to bond three metals. The structurally characterized examples are [(OC)$_3$M(μ_3-OH)]$_4^{4-}$ (M = Cr,[49] Mo,[50,51] W[50]), [(ON)(OC)$_2$Mo(μ_3-OH)]$_4$,[52] [(C$_7$H$_7$)Mo(μ_3-OH)]$_4$,[41] and [(OC)$_3$W(μ_3-OH)(H)]$_4$.[53] The cores of all of these are typical of A$_4$B$_4$ cubane complexes.[54] The Mo–O and W–O bond lengths range between 215 and 228 pm while the Cr–O range is 211–215 pm.

While details of the individual syntheses vary, the M(CO)$_3$ compounds are formed by reactions of M(CO)$_6$ or related carbonyl derivatives with base,[49–51,53] the NO complex from [(OC)$_3$Mo(μ_3-OH)(H)]$_4$, and NO.[52] [(C$_7$H$_7$)Mo(μ_3-OH)]$_4$ formed, along with [(C$_7$H$_7$)Mo(μ_2-Cl)$_2$(μ_2-OH)Mo(C$_7$H$_7$)]$^+$, during attempts to crystallize (C$_7$H$_7$)Mo(Cl)(MeC$_6$H$_5$).[41]

In addition to the cubane complexes there is a Cr$_4$ compound with the adamantane structure. (C$_5$Me$_5$)$_2$Cr$_2$(CO)$_4$ reacts with H$_2$O in refluxing toluene to produce [(C$_5$Me$_5$)$_4$Cr$_4$(μ_2-OH)$_6$]$^{2+}$ in moderate yield.[55] A structure, determined on the BF$_4^-$ salt, shows a tetrahedral arrangement of (Me$_5$C$_5$)Cr units with each edge bridged by an OH. This deep blue ion is paramagnetic and has been formulated as a Cr(III) complex. The Cr–O distance is 195.7 pm (av) and Cr–O–Cr is 140.4(4)°.

Finally, if *cis*-[Mo(N$_2$)$_2$(PMe$_3$)$_4$] and CO$_2$ are allowed to react in a 2:1 acetone/toluene mixture for 15–20 days "small amounts" of red-orange Mo$_4$(μ_4-CO$_3$)(CO)$_2$(O)$_2$(μ_2-O)$_2$(μ_2-OH)$_4$(PMe$_3$)$_6$ were isolated.[56] The structure of this unusual Mo^{II}–Mo^V species is



VII. Manganese, Technecium, and Rhenium

A. Manganese

The characterized organomanganese hydroxides have structures based on the cubane core. When conducted in thf Mn$_2$(CO)$_{10}$ and Me$_3$NO·2H$_2$O give [Mn(CO)$_3$(μ_3-OH)$_4$]$_4$.[57] Structures have been determined on bis adducts with toluene[57] and ethylenediamine,[58] with which it forms a hydrogen-bonded diamondoid network. [Mn(CO)$_3$F$_x$(μ_3-OH)$_{4-x}$]$_4$ which was isolated from the reaction of Mn(CO)$_5$X (X = Cl or Br) with TlF or AgF. A structure was determined on a crystal where x = 1.4. Apparently the fluorides and hydroxides are disordered.[59]

A complex with higher nuclearity, Mn$_7$(CO)$_{18}$(μ_3-OH)$_{18}$, forms when benzophenone is present during the reaction of Mn$_2$(CO)$_{10}$ with Me$_3$NO·2H$_2$O.[57] This Mn$_7$ species consists of two cubane units joined through a common corner Mn atom. The geometries and Mn–O bond distances involving [Mn(CO)$_3$(μ_3-OH)$_4$]$_4$, [Mn(CO)$_3$F$_x$(μ_3-OH)$_{4-x}$]$_4$, and the outer six Mn atoms in Mn$_7$(CO)$_{18}$(μ_3-OH)$_{18}$ are essentially identical. However, coordination of the central Mn, which joins the two cubane units, in Mn$_7$(CO)$_{18}$(μ_3-OH)$_{18}$ is intermediate between octahedral and trigonal prismatic and its Mn–O distances, 216.9(2) pm (av), are longer than the 205-pm Mn–O separations seen in the other complexes and in the outer atoms of the Mn$_7$ species. This unique atom is assigned as Mn(II) on the basis of its structure and a charge balance criterion.[57]

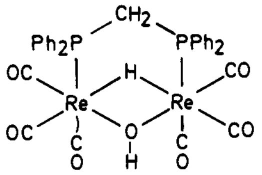
B. Technecium

We are not aware of any structures for organometallic hydroxides of this element.

C. Rhenium

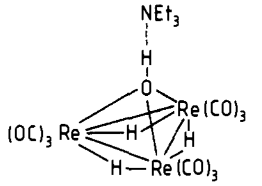
trans-(Dioxo)(tetracyano)rhenium(V), [ReO$_2$(CN)$_4$]$^{3-}$, can be protonated to [ReO(OH)(CN)$_4$]$^{2-}$ which can be crystallized as the [PPh$_4$]$^+$ salt. The [ReO(OH)(CN)$_4$]$^{2-}$ ion has a distorted octahedral geometry. Bond distances are Re=O = 170(1), Re—OH = 190(1), and Re—C (av) = 212(2) pm. The Re atom is displaced 8 pm out of the plane formed by the four carbon atoms toward the terminal oxo ligand, and the O=Re—OH unit is nearly linear, 175.7(5)°.[60]

Photolysis of $Re_2(CO)_8(Ph_2PCH_2PPh_2)$ in wet toluene or benzene leads to a 35% yield of $Re_2(CO)_6(\mu_2\text{-}H)(Ph_2PCH_2PPh_2)(\mu_2\text{-}OH)$ and a 35% yield of $Re_2(CO)_6(Ph_2PCH_2PPh_2)(\mu_2\text{-}OH)_2$. A crystal structure, which locates the OH, CH_2, and hydride hydrogens, shows the first of these to be



The Re–O distances are 217.7(5) and 216.0(5) pm and Re–O–Re is 88.6(2)°, within the slightly asymmetric $Re_2O(OH)$ ring.[61]

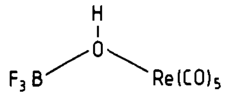
A Re_3 cluster containing a μ_3-OH, $[Re_3(\mu_2\text{-}H)_3(CO)_9(\mu_3\text{-}OH)]^-$, has been isolated as an NMe_3 adduct from reactions of $[Re_3(\mu_2\text{-}H)_3(CO)_9(\mu_2\text{-}O)]^{2-}$ with $Me_3NH^+Cl^-$, by protonation of $[Re_3(\mu_2\text{-}H)_3(CO)_9(\mu_2\text{-}O)]^{2-}$ followed by treatment with NMe_3, or by reaction of $[Re_3(\mu_2\text{-}H)_4(CO)_{10}]^-$ with $ONMe_3$. In the $ONMe_3$ reaction the (μ_2-OH) comes either from water present in the amine oxide or by attack of a hydride on the oxygen of coordinated amine oxide. The structure of the anion is



with Re–O = 212.6 (av), Re–Re = 297.9 pm (av), and Re–O–Re = 88.9° (av). The O–H is hydrogen bonded to a triethylamine.[62]

$[(OC)_3Re(\mu_3\text{-}OH)]_4$, from the reaction of $Re_2(CO)_{10}$ or $Re(CO)_5Cl$ with H_2O at 200 °C,[63] possesses a distorted "cubane" structure. The Re atoms are approximately octahedral, and Re–O = 220.7(8) pm, O–Re–O = 73.9°, and Re–O–Re = 104.0(5)°. Each of the O–H groups hydrogen bonds to a benzene molecule which lies perpendicular to a crystallographic 3-fold axis which passes through the OH group. Each benzene is involved in two of these hydrogen bonds and, as such, uses both faces in its interaction with O–H groups.[64]

A final organorhenium hydroxide is the unusual

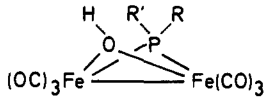


which formed by partial hydrolysis during the crystallization of $\{[(OC)_5Re]_3O\}BF_4$. The two compounds cocrystallize. The OH of $F_3B(\mu_2\text{-}OH)Re(CO)_5$ hydrogen bonds to a BF_4^- anion and Re–O = 216.7 and B–O = 147.6 pm.[65]

VIII. Iron, Ruthenium, and Osmium

A. Iron

The two structurally characterized organoiron hydroxides are $Fe_2(CO)_6(\mu_2\text{-}PRR')(\mu_2\text{-}OH)$ with R = R' = $p\text{-}C_6H_4Me$[66] and R = $CH(SiMe_3)_2$, R' = H:[67]



Both structures are typical of $Fe_2(CO)_6(\mu_2\text{-}X)_2$ compounds but are unusual in that they have two different bridging groups. $Fe_2(CO)_6\{\mu_2\text{-}P(H)[CH(SiMe_3)_2]\}(\mu_2\text{-}OH)$ possesses the additional unusual feature of cocrystallizing with $Fe_2(CO)_6(\mu_2\text{-}CO)(\mu_2\text{-}H)\{\mu_2\text{-}P[CH(SiMe_3)_2](OH)\}$, which hydrogen bonds through its P–OH group to the O(H) of $Fe_2(CO)_6\{\mu_2\text{-}P(H)[CH(SiMe_3)_2]\}(\mu_2\text{-}OH)$.[67] In $Fe_2(CO)_6\{\mu_2\text{-}P(H)[CH(SiMe_3)_2]\}(\mu_2\text{-}OH)$ the Fe–O = 199.0(2) pm and Fe–O–Fe = 76.6(1)°[67] and in $Fe_2(CO)_6[\mu_2\text{-}P(C_6H_4Me)_2](\mu_2\text{-}OH)$ the corresponding values are 197.2 pm (av) and 79.1(2)°.[66]

$Fe_2(CO)_6(\mu_2\text{-}PR_2)(\mu_2\text{-}OH)$ (R = $p\text{-}C_6H_4Me$) forms in low yield as a side product during direct reactions of $Fe_2(CO)_9$ with PR_2H or in 60% yield by

$$Fe(CO)_4(PR_2H) + BuLi \rightarrow Fe(CO)_4(PR_2)Li$$

$$Fe(CO)_4(PR_2)Li + Fe_2(CO)_9 \xrightarrow{\text{thf}} \xrightarrow[\text{over alumina}]{\text{chromatography}} Fe_2(CO)_6(\mu_2\text{-}PR_2)(\mu_2\text{-}OH)$$

The sources of the OH^- is unknown, but the relatively high yield argues against reactions involving minor impurities.[66]

$Fe_2(CO)_6\{\mu_2\text{-}P(H)[CH(SiMe_3)_2]\}(\mu_2\text{-}OH)$ is one of a large number of products formed in the reaction of $[NEt_4]_2[Fe_2(CO)_8]$ with $Cl_2PCH(SiMe_3)_2$.[67]

B. Ruthenium and Osmium

Apparently no monometallic organo hydroxides of ruthenium or osmium have been structurally characterized. Rather a number of remarkable clusters are encountered.

In the simpler complexes which contain μ_2-OH ligands the M–O distances are typically between about 207 and 210 pm, while in higher clusters about 212–216 pm is more typical. Within many complexes there are small differences in apparently similar M–O bonds, and some structures contain several molecules per asymmetric unit, each with somewhat different bond lengths and angles. There are no significant differences between Ru–O and Os–O bond lengths, and the angles involving the OH groups often appear to be influenced more by the geometric constraints of the cluster than by intrinsic interactions between the hydroxo ligand and the metals to which it is most closely associated.

The hydrolysis of $[(arene)MCl_2]_2$ (M = Ru or Os) provides a variety of hydroxo complexes depending on the arene and the exact conditions of the reaction. With the bulky $1,2,5\text{-}Me_3C_6H_3$, C_6Me_6, or $p\text{-}MeC_6H_4CHMe_2$ and aqueous Na_2CO_3 or NaOH, $[(arene)Ru(\mu_2\text{-}OH)_3Ru(arene)]^+$ is obtained:[68]

$$[(arene)RuCl_2]_2 \xrightarrow[\text{(or NaOH)}]{Na_2CO_3} [(arene)Ru(\mu_2\text{-}OH)_3Ru(arene)]^+$$

With arene = C_6H_6 the reactions of $[(C_6H_6)MCl_2]_2$ are more complex. In aqueous solution with approximately equal metal and CO_3^{2-} concentrations a tetrameric cation forms:

$$2[(C_6H_6)RuCl_2]_2 + 2Na_2CO_3 \rightarrow [(C_6H_6)Ru(\mu_3\text{-}OH)]_4^{4+}$$

$[(C_6H_6)Ru(\mu_3\text{-}OH)]_4^{4+}$ contains a cubane core of alternating ruthenium and oxygen atoms.[69] In contrast, a tetranuclear oxo-centered cation forms with excess NaOH or Na_2CO_3:

$$2[(C_6H_6)MCl_2]_2 \xrightarrow[\text{(or NaOH)}]{\text{excess } Na_2CO_3} [(C_6H_6)_4M_4(\mu_2\text{-}OH)_4(\mu_4\text{-}O)]^{2+}$$

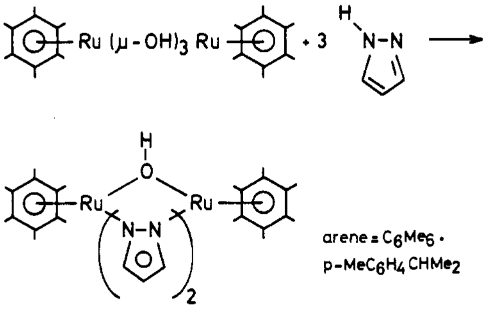
In this compound two binuclear $[(C_6H_6)M(\mu_2\text{-}OH)_2M(C_6H_6)]^{2+}$ units share a tetrahedrally coordinated oxide ion.[68]

A triply OH bridged ion has been obtained by the hydrolysis of a phenoxide complex:[70]

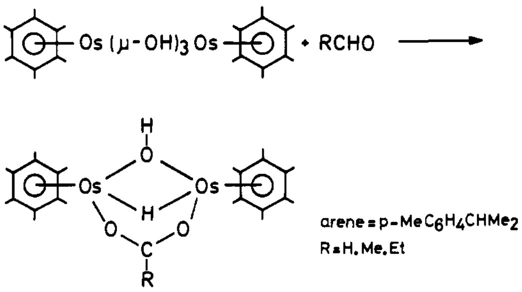
$$[(C_6H_6)Ru(\mu_2\text{-}OPh)_3]_2^+ \xrightarrow{H_2O} [(C_6H_6)Ru(\mu_2\text{-}OH)_3Ru(C_6H_6)]^+$$

Perhaps this method succeeds because it avoids basic media employed in the reaction of $[(C_6H_6)MCl_2]_2$, and which may favor formation of the tetranuclear species.

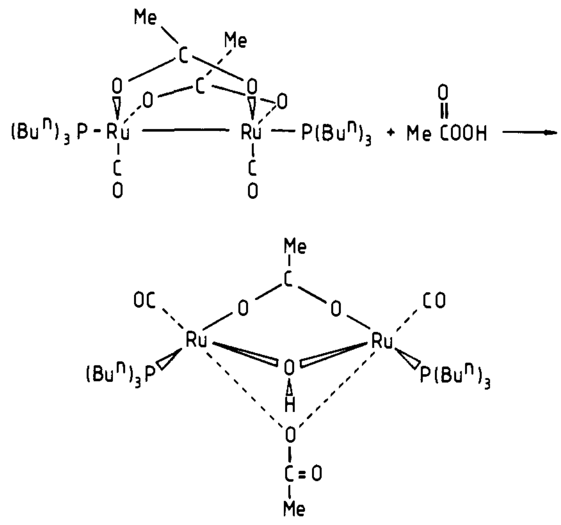
The $[(arene)M(\mu_2\text{-}OH)_3M(arene)]^+$ complexes themselves can serve as precursors to binuclear hydroxo complexes. With pyrazole[71]



and with aldehydes[72]

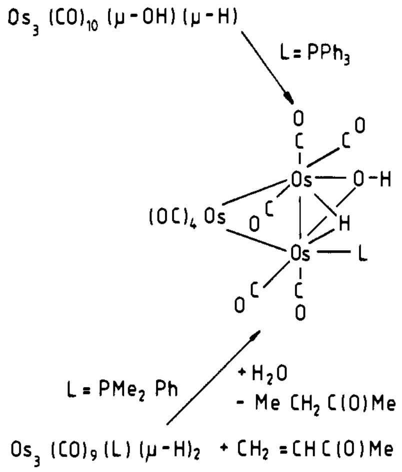


Another bimetallic ruthenium complex, which contains a single, doubly bridging hydroxide, forms in an oxidation using peracetic acid.[73]



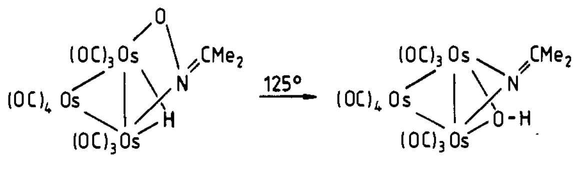
The hydroxo hydrogen was located in the final difference map but was not refined.

Structural confirmation is available for a number of hydroxo M_3 carbonyl clusters. Among the simplest of these is $Os_3(CO)_9(L)(\mu_2\text{-}OH)(\mu_2\text{-}H)$ which is obtained from the as of yet structurally uncharacterized $Os_3(CO)_{10}(\mu_2\text{-}OH)(\mu_2\text{-}H)$ by ligand exchange[74] or by an unusual route from $Os_3H_2(CO)_9(PMe_2Ph)$:[75]

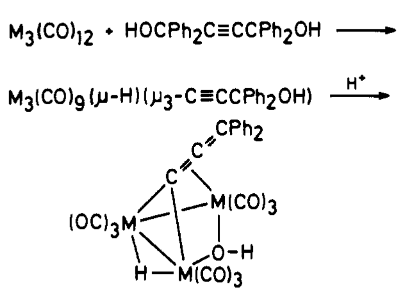


An analogous reaction of $Os_3(CO)_{10}(\mu_2\text{-}OH)(\mu_2\text{-}H)$ with $Ph_2PCH_2PPh_2$ (dppm) produces $Os_3(CO)_8(dppm)(\mu_2\text{-}OH)(\mu_2\text{-}H)$ in which the dppm, OH, and H all bridge the same edge of the Os_3 triangle.[76]

More unexpected pathways to M_3 hydroxo clusters include an isomerization of the product of the reaction between $Os_3(CO)_{10}(NCMe)_2$ and $Me_2C{=}NOH$:

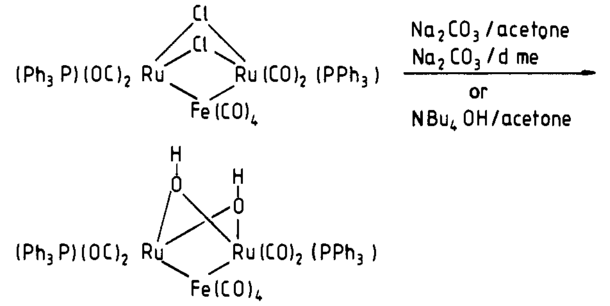


The structures of all of these clusters are normal. In each the Os–Os distances lie between about 270 and 300 pm, which are typical for Os–Os bonds. However, there are several trimetallic clusters in which the metals bridged by hydroxide are not directly bonded. Thus



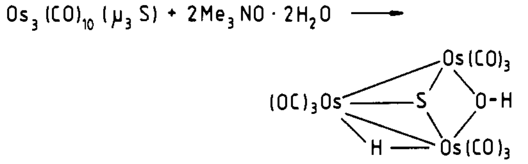
in which the distance between the two osmiums bridged by OH is 337 pm, indicating there is no direct bond between these metals.[77,78]

In another trimetal cluster, $FeRu_2(CO)_8(PPh_3)_2(\mu_2\text{-}OH)_2$, the Ru–Ru edge is bridged by two OH groups and the ruthenium atoms are not bonded. This complex forms by chloride substitution in weakly basic solution:



In Na_2CO_3/PrOH a lower yield is obtained, along with a side product which may be the mixed hydrido–hydroxo complex.[79]

One of the more successful methods of activating metal carbonyls involves the use of Me_3NO which converts CO to CO_2. $Me_3NO{\cdot}2H_2O$ also has been successfully employed to prepare an osmium–hydrido–hydroxo complex:



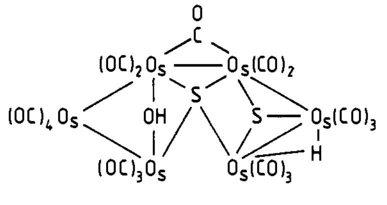
The osmiums which are bridged by OH are not bonded as indicated by their 370.7(6)-pm separation.[80]

Several M_4 hydroxo clusters are known. With the exception of $[(C_6H_6)_4M_4(\mu_2\text{-}OH)_4(\mu_4\text{-}O)]^+$, which was mentioned earlier, they all possess a "butterfly" conformation of the metal atoms in which, with one exception, the "wing tips" are connected by a bridging OH.

$[Os_4(CO)_{12}H_4(\mu_2\text{-}OH)]^+[Os(CO)_3(NO_3)_3]^-$ has been obtained in high yield by reaction of $Os_4(CO)_{12}H_4$ with N_2O_4. The first step apparently involves oxidation to $[Os_4(CO)_{12}H_4]^{2+}$, followed by a series of proton dissociations and the addition of water, whose source is unknown.[81] In a similar process $[Os_4(CO)_{12}H_3]^-$ is oxidized by $NO^+PF_6^-$ in wet MeCN to several products including $Os_4(CO)_{12}H_3(\mu_2\text{-}OH)$.[82] The heavy-atom structures of $[Os_4(CO)_{12}H_4(\mu_2\text{-}OH)]^+$ and $Os(CO)_{12}H_3(\mu_2\text{-}OH)$ are the same. While the hydride locations are not unambiguously established, they are thought to lie along the "wing tips" of the Os_4 butterfly.

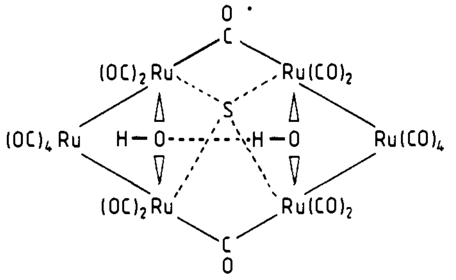
A different disposition of ligands about the M_4 butterfly core is encountered in $Ru_4(CO)_{10}(C{=}CHPr^i)(\mu_3\text{-}OH)(\mu_2\text{-}PPh_2)$ where one of the Ru_3 triangles is capped by the OH. The same Ru_3 unit is edge bridged by PPh_2 and capped on the side opposite the OH by the vinylidene group which itself complexes the remaining wing-tip Ru. The hydrogen on the OH was located in a difference map. The compound was formed by hydrolysis of $Ru_3(CO)_{11}(Ph_2PC{\equiv}CPr^i)$ in moist thf.[83]

While no M_5 hydroxo clusters have been characterized for the iron group several M_6 complexes are known. $Os_3(CO)_8(NMe_3)(\mu_2\text{-}OH)(\mu_3\text{-}S)(\mu_2\text{-}H)$, which is mentioned above, reacts with $Os_3(CO)_{10}(\mu_3\text{-}S)$ to produce $Os_6(CO)_{18}(\mu_2\text{-}OH)(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu_2\text{-}H)$:[80]



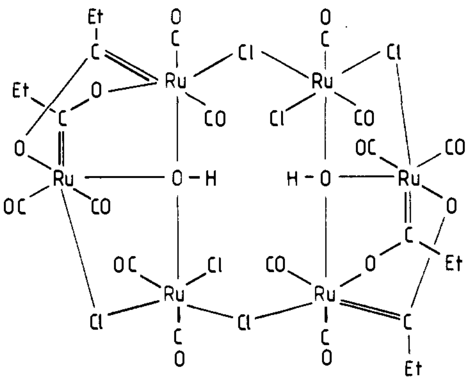
The O–H proton was located in a difference map, but was not refined. The hydride was not located but is assumed to bridge the longest Os–Os bond.

UV radiation of a mixture of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ and $Ru_3(CO)_{12}$ in wet thf produces $Ru_6(CO)_{18}(\mu_2\text{-}OH)_2(\mu_4\text{-}S)$:



The hydroxyl hydrogens were located and refined and one hydrogen bonds to the second oxygen. Formal electron counting indicates this to be a 94-electron, rather than a 92-electron precise complex. Two low-energy absorptions which are responsible for the compound's blue color are attributed to the extra two electrons occupying antibonding orbitals within the core of the molecule.[84]

A final M_6 complex is $[Ru_3Cl_3(CO)_6(COEt)_2(\mu_3\text{-}OH)]_2$.[85] The three ruthenium atoms in each half of the dimeric unit are octahedrally coordinated. The octahedra share a common vertex occupied by a hydroxo group:



The complex is prepared by the reaction of $Ru(C_3H_5)Cl(CO)_3$ with $CH_2{=}CH_2$ in benzene. The Ru–OH distances are 216 pm (av).

IX. Cobalt, Rhodium, and Iridium

A. Cobalt

We are unaware of any structurally characterized organocobalt hydroxides.

B. Rhodium and Iridium

$Ir(CH_2EMe_3)(CO)(PPh_3)_2$ (E = C or Si) can be hydrolyzed to $Ir(OH)(CO)(PPh_3)_2$. Befitting a derivative of Vaska's compound, the coordination about Ir is trans-square planar. The Ir–O distance, 211.0(9) pm, is close to the sum of the covalent radii of O and Ir.[86] This is the only structure of a terminal hydroxo complex of Rh or Ir.

There are a number of neutral or cationic dirhodium or iridium complexes containing bridging hydroxo groups. $[(C_3H_5)_2RhCl]_2$ reacts with KO_2 in CH_2Cl_2 to form $(C_3H_5)_2Rh(\mu\text{-}OH)_2Rh(C_3H_5)_2$ in 70% yield. The reaction is thought to proceed through a dioxygen intermediate which abstracts hydrogen from the solvent, forming the final product.[87] In $(C_3H_5)_2Rh(\mu\text{-}OH)_2Rh(C_3H_5)_2$ rhodium is cis-octahedral if the coordination sphere is defined by the terminal carbons in the allyl groups and the two bridging hydroxide oxygen atoms. The average metrical parameters in the Rh_2O_2 core are Rh–O = 217.7 pm, O–Rh–O = 81.8°, Rh–O–Rh = 98°.[88]

Cationic $[(C_5Me_5)(L)Rh(\mu\text{-}OH)_2Rh(C_5Me_5)(L)]^{2+}$ forms with a variety of pyridine type ligands by

$$[(C_5Me_5)Rh(\mu_2\text{-}OH)_3Rh(C_5Me_5)]ClO_4 + HClO_4 + 2L \rightarrow [(C_5Me_5)(L)Rh(\mu_2\text{-}OH)_2Rh(C_5Me_5)(L)](ClO_4)_2 + H_2O$$

A structure has been determined for the pyridine adduct. The coordination around the rhodium atoms is pseudo-octahedral with the C_5Me_5 occupying three *fac* positions, pyridine one, and the hydroxides the remaining two sites. Distances and angles are Rh–O = 211 pm (av), O–Rh–O = 76.8(2)°, and Rh–O–Rh = 103.1(2)°. The bridging OH groups are hydrogen bonded to the ClO_4^-.[89]

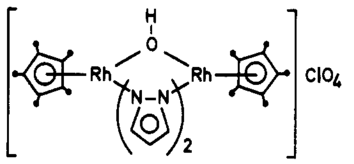
The very similar complex with L = 3,5-dimethylpyrazole, Me_2CHN_2H, has also been structurally investigated. In this compound Rh–O = 217.9 pm (av), O–Rh–O = 129.8° (av), and Rh–O–Rh = 99.3°.[90]

There are several complexes in which two Rh or Ir atoms are connected by triple bridges, at least one of which is an OH. Tris-μ_2-hydroxo structures are known for $[(C_5Me_5)M(\mu_2\text{-}OH)_3M(C_5Me_5)]^+X^-$ with M = Rh and X = OH^- and for M = Ir and X = $MeCO_2^-$. Assuming the C_5Me_5 ligands each occupy three coordination sites the metal atoms are pseudo-octahedral and the two C_5Me_5 rings are approximately parallel. Mean distances are Rh–O = 210.9 and Ir–O = 212.0 pm, and angles are Rh–O–Rh = 89.5°, O–Rh–O = 75.0°, Ir–O–Ir = 92.8°, and O–Ir–O = 73.3°. In both cases the bridging hydroxides are hydrogen bonded to the anion and, in the Rh compound, to waters of crystallization.[91]

The hydroxo ligands in $[(C_5Me_5)Rh(\mu_2\text{-}OH)_3Rh(C_5Me_5)]^+$ can be substituted by acid–base reactions

$$[(C_5Me_5)Rh(\mu_2\text{-}OH)_3Rh(C_5Me_5)]^+ + 2HL \rightarrow [(C_5Me_5)Rh(\mu_2\text{-}OH)(\mu_2\text{-}L)_2Rh(C_5Me_5)]^+ + 2H_2O$$

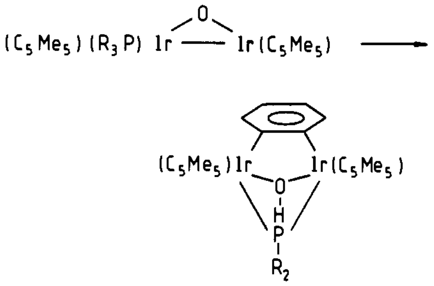
and the structure of one of these has been solved; the



Rh–O distance is 211.0(4) pm and the Rh–O–Rh angle is 111.7(2)°.[90]

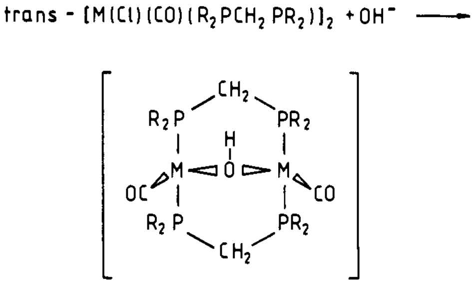
Air oxidation of $Ir_2(C_8H_{12})_2Cl_2$ produces $(C_8H_{12})(Cl)Ir(\mu_2\text{-}O)(\mu_2\text{-}OH)_2Ir(C_8H_{12})(Cl)$ in low yield. In this complex the octahedrally coordinated metal atoms are joined by three bridging oxygens, two of which have been assigned as OH and one an O. While an unambiguous determination of the bridging groups was not possible the two symmetry-related groups whose Ir–O distances, 209.8(1) pm, exceed the remaining Ir–O separation, 202.4(8) pm, are thought to be the hydroxo ligands.[92]

A bis-iridium μ_2-oxo complex undergoes a dramatic, rearrangement upon heating in benzene or toluene to produce a (μ_2-OH) linkage:



The reaction occurs when R is $3\text{-}MeC_6H_4$ or Ph and a structure has been determined for the Ph derivative. The Ir–O distance of 214 pm is considerably longer than either of the two Ir–O distances in the starting oxo complex.[93]

Finally, two very similar Rh and Ir "A frame" complexes, prepared by



have been structurally characterized.[94,95] The basic structures of the two anions are very similar: Ir–O = 207(2) pm, Ir–O–Ir = 99.4(8)° and Rh–O = 206.8(4) pm, Rh–O–Rh = 99.1(1)°. In the structure of the Ir complex the OH hydrogen was located in the difference map, but was not refined. In both complexes the hydroxide hydrogen bonds, in the Ir case,[94] to a Cl^- counterion and, with Rh,[95] to an acetone of solvation.

X. Nickel, Palladium, and Platinum

A. Nickel

Structures have been reported for four organohydroxide complexes of nickel. Three of these were prepared by metathesis reactions and a rational synthetic route has been designed for the fourth, which originally was found as a minor side product in another reaction.

The treatment of *trans*-$Ni(PMe_3)_2(R)(X)$, R = alkyl, with H_2O or OH^- yields alkylnickel dimers containing bridging hydroxides. While a variety of alkyl groups have been utilized[96-98] a structure is only available for R = $CH_2C_6H_4Me$, which was synthesized by

$$2(MeC_6H_4CH_2)(Me_3P)_2Ni(NC_4H_2Me_2) + 2H_2O \rightarrow (MeC_6H_4CH_2)(Me_3P)Ni(\mu_2\text{-}OH)_2Ni(PMe_3)(CH_2C_6H_4Me) + 2PMe_3 + 2HNC_4H_2Me_2$$

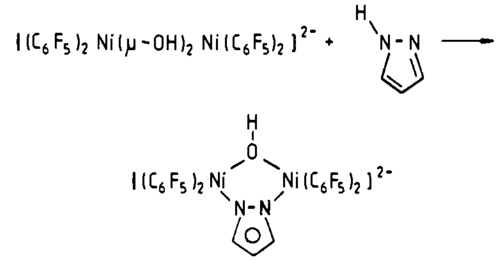
The Ni atoms are approximately square planar, and the $Ni_2(OH)_2$ core is folded (dihedral angle = 133.6°) with the oxygen atoms oriented toward and apparently hydrogen bonded to a 2,5-dimethylpyrrole molecule of crystallization. The Ni–O separation is 191.9 pm (av).

An anionic doubly OH bridged complex is also obtained by metathesis:

$$2cis\text{-}[Ni(C_6F_5)_2(NCPh)_2] + 2Bu^t_4NOH \rightarrow [Bu^t_4N]_2[(C_6F_5)_2Ni(\mu_2\text{-}OH)_2Ni(C_6F_5)_2] + 4PhCN$$

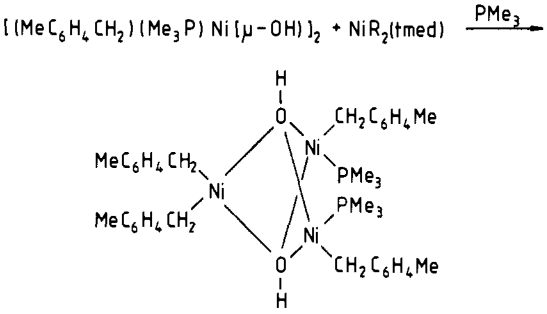
Distances and angles within the planar $Ni_2(OH)_2$ core are Ni–O = 189 pm (av), Ni–O–Ni = 99.2(4)°, and Ni–O–Ni = 80.8(4)°.[99]

The hydroxides in this anion are labile, and mono or disubstituted derivatives can be obtained from reactions with various bases. A monohydroxo complex forms from the reaction with pyrazole, $C_3H_3N_2H$:



A structure on the $[Bu^t_4N]^+$ salt shows the five-membered ring, containing the two Ni atoms, has an envelope conformation. The average Ni–O distance is 189.1(4) pm.[99]

The final structurally characterized Ni complex is $Ni_3(CH_2C_6H_4Me)_4(PMe_3)_2(\mu_3\text{-}OH)_2$ which originally was obtained as a minor side product during the work up of reactions between $NiCl_2(PMe_3)_2$ and $Mg(CH_2C_6H_4Me)(Cl)$. Subsequently it was prepared in 70–80% yields by[98]



Each Ni is approximately square planar with the three planes' edges joined through the (μ_3-OH) groups. The Ni–O distances to the nickel which is also bonded to two alkyl groups are 199.9 (av) and 193.1 pm (av) to the other two.

B. Palladium and Platinum

A Pt complex, (dppe)PtMe(OH), whose Pt–O bond distance is 202.5(8) pm has been mentioned in a review article, without details.[2]

$[(C_6F_5)_2Pd(\mu_2\text{-}OH)_2Pd(C_6F_5)_2]^{2-}$ can be prepared by a route analogous to that for $[(C_6F_5)_2Ni(\mu_2\text{-}OH)_2Ni(C_6F_5)_2]^{2-}$:[100]

$$2cis\text{-}(C_6F_5)_2Pd(NCPh)_2 + 2Bu_4NOH \rightarrow [Bu^t_4N]_2(C_6F_5)_2Pd(\mu_2\text{-}OH)_2Pd(C_6F_5)_2$$

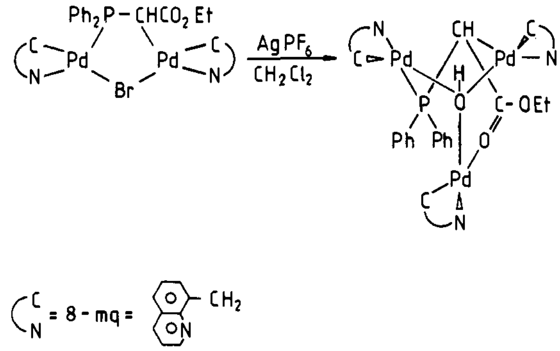
with platinum this method fails as coordinated benzonitrile undergoes nucleophilic attack by hydroxide. However, the bis(μ_2-OH) platinum complex has been obtained by chloride metathesis:[101]

$$[Bu_4N]_2[(C_6X_5)_2Pt(\mu_2\text{-}Cl)_2Pt(C_6X_5)_2] + 2Bu_4NOH \rightarrow [Bu_4N]_2[(C_6X_5)_2Pt(\mu_2\text{-}OH)_2Pt(C_6X_5)_2] + 2Bu_4NCl$$
$$X = F \text{ or } Cl$$

All three $[Bu_4N]_2[(C_6F_5)_2M(\mu_2\text{-}OH)_2M(C_6F_5)_2]$ compounds (M = Ni[102], Pd[100], Pt[101]) are isomorphous, with square-planar metals forming a planar M_2O_2 ring. The metrical parameters are nearly the same for the Pd (Pd–O 207.3 pm (av), O–Pd–O 81.2(4)°, Pd–O–Pd 98.8(4)°) and Pt compounds (Pt–O 207(2) pm, O–Pt–O 78.6(5)°, Pt–O–Pt 101.4(6)°) and are similar to those in the Ni compound when allowance is made for the different sizes of the metals.

The reactions of $[(C_6F_5)_2Pt(\mu_2\text{-}OH)_2Pt(C_6F_5)]^{2-}$ with azoles are very similar to those of $[(C_6F_5)_2Ni(\mu_2\text{-}OH)_2Ni(C_6F_5)_2]^{2-}$. A structure has been determined for $[Bu_4N]_2[(C_6F_5)_2Pt(\mu_2\text{-}3,5\text{-}Me_2C_3HN_2)(\mu_2\text{-}OH)Pt(C_6F_5)_2]$.[102] The central five-membered Pt_2N_2O ring is puckered, the average Pt–O distance is 210 pm (av) and the overall structure closely resembles the nickel–pyrazolate complex.

A tripalladium complex, $\{[(8\text{-}mq)Pd]_3(\mu_3\text{-}Ph_2PCHCO_2Et)(\mu_3\text{-}OH)\}^+PF_6^-$, has been characterized from



The OH is thought to originate from traces of water in solvents or on the silica gel used to purify the compound. There are three different Pd–O distances: 228(1) pm to the Pd which is also bonded to phosphorus, 226.1(8) pm to the carbon-bonded Pd, and 214.4(9) pm to the Pd which is coordinated by two oxygens. The differences in bond lengths may be due to differences in the trans ligand.[103]

In 1947 a structure of "tetramethylplatinum" was published.[104] Later the crystals used in this early study were shown to be $[Me_3Pt(\mu_3\text{-}OH)]_4$.[105] In 1968 X-ray[106] and neutron diffraction[107] studies appeared on $[Me_3Pt(\mu_3\text{-}OH)]_4$, precipitated from solutions containing Me_3Pt^+ upon the addition of base. While none of these is precise by modern standards, they establish that $[Me_3Pt(\mu_3\text{-}OH)]_4$ possesses a cubane like structure with Pt–O bond distances of about 220–222 pm. In the neutron structure the hydrogen atoms have been located and the O–H bond, 93(8) pm, is directed away from the Pt_4O_4 cluster.[107]

XI. Copper, Silver, and Gold

A. Copper and Silver

There is much interest in hydroxo-bridged copper complexes, which are important in establishing magnetic interactions between d^9 ions.[108] Nonetheless, there do not appear to be any structures available for organocopper hydroxides. Likewise organosilver hydroxides have not been structurally investigated.

B. Gold

Structures are known for two organogold hydroxides. In both, square-planar gold atoms are joined through double hydroxo bridges. $\{[PhC{=}C(Ph)C(Ph){=}C(Ph)]Au(\mu_2\text{-}OH)\}_2$, isolated from the reaction of $LiC(Ph){=}C(Ph)C(Ph){=}C(Ph)Li$ and $AuCl_3$,[109] is planar with the exception of the phenyl groups.[110] In contrast, the four square-planar gold atoms in $[Me_2Au(\mu_2\text{-}OH)]_4$ are tilted with respect to one another giving the molecule approximate S_4 symmetry.[111] The Au–O distances in both compounds are varied and range between 184 and 227 pm in $[Me_2Au(\mu_2\text{-}OH)]_4$ and 209 and 226 pm in $\{[PhC{=}C(Ph)C(Ph){=}C(Ph)]Au(\mu_2\text{-}OH)\}_2$. However, both structures were determined using photographic data and final R values are above 10%, so detailed analysis of the metrical data is probably not valid.

XII. Zinc, Cadmium, and Mercury

An alkylzinc hydroxide has been obtained by the hydrolysis of $(Me_3Si)_3CZnCl$ with NaOH in wet thf:

$$2(Me_3Si)_3CZnCl + 2H_2O \rightarrow (Me_3Si)_3CZn(\mu_2\text{-}OH)_2ZnC(SiMe_3)_3$$

In contrast to other organozinc hydroxides, $(Me_3Si)_3CZn(\mu_2\text{-}OH)_2ZnC(SiMe_3)_3$ is stable in moist air. The $C{-}Zn(\mu_2\text{-}OH)_2Zn{-}C$ fragment is planar (Zn–O = 189.9(9) pm, O–Zn–O = 77.5(3)°, and Zn–O–Zn = 102.3(3)°).[112]

A tetrameric, distorted cubane, somewhat unstable cadmium hydroxide forms in the hydrolysis of $(C_6F_5)_2Cd$ in moist toluene:

$$4Cd(C_6F_5)_2 + 4H_2O \xrightarrow{\text{toluene}} [(C_6F_5)Cd(\mu_3\text{-}OH)]_4 + 4C_6F_5H$$

Cd–O distances range from 220 to 229 pm and the Cd–O–Cd angles are about 100° while the O–Cd–O angles are near 80°.[113]

No organomercury hydroxo complex has been structurally characterized.

XIII. Acknowledgments

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