Tantalum

Zi-Ling Xue[a] and Tabitha M. Cook[b]

[a] *Department of* Chemistry*, University of Tennessee, Knoxville, Tennessee 37996, USA*

[b] *Department of Chemistry and Biochemistry, Berry College, Mount Berry, Georgia 30149, USA*

Abstract. This review on coordination chemistry of tantalum covers the literature between 2003 and 2018. Tantalum complexes with ligands based on groups 15 (nitrogen, phosphorus, arsenic), 16 (oxygen, sulfur, selenium, tellurium), and 17 (fluorine, chlorine, bromine) as well as with mixed-donor ligands are the focus. Coverage of organometallic complexes is selective to give readers a more comprehensive understanding of the coordination chemistry of tantalum. Complexes with hydride and boron- and carbon-based ligands, including alkylidene, η^2-allyl, allene, vinyl, alkene, alkylidyne, η^3-allyl, alkyne, N-heterocyclic carbene (NHC), and CCC pincer ligands, are discussed. Complexes with alkyl, cyclopentadienyl, acyl, iminoacyl, and related ligands are generally not discussed. Tantalum is among the largest early transition elements and can easily form complexes with high coordination numbers, although six is the most common. In addition, the larger radii of tantalum ions lead to less tight coordination sphere and frequently observed stereodynamic properties of the complexes. Tantalum complexes have been used as precursors to make electronic materials through processes such as chemical vapor deposition or atomic layer deposition.

Tantalum

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1. INTRODUCTION

Tantalum is a third-row, group 5 transition element with two naturally occurring isotopes, Ta-180 and Ta-181 at natural abundance of 0.012% and 99.988%, respectively. The element was discovered by Swedish chemist Anders G. Ekeberg in 1802 who named it after Tantalus, a villain from Greek mythology.[1] Due to oxide film on its surface, tantalum is known to be very corrosion resistant but is ~~attached~~attacked by

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HF.[2] Ekeberg gave the element the name tantalum because of the difficulty he encountered in dissolving tantalum-containing minerals.[1]

Tantalum has similar atomic and ionic radii and chemical properties as the second-row, group 5 transition element niobium as a result of lanthanide contraction. In fact, the two elements, both present in the mineral columbite [$(Fe,Mn)(Ta,Nb)_2O_6$],[2] were thought to be one until at least 1845 when German mineralogist and chemist Heinrich Rose showed the presence of two distinct elements in the mineral.[1, 3] One was tantalum and the other Rose named niobium after Niobe, daughter of Tantalus.[1]

Several oxidation states of tantalum, from −III to V, are known. Tantalum is oxophilic and more often at the V oxidation in its coordination compounds. At lower oxidation states, tantalum atoms tend to form Ta-Ta bonds. Tantalum is among the largest early transition elements. It thus can easily form complexes with high coordination numbers, although six is the most common coordination number. In addition, the larger radii of tantalum ions lead to less tight coordination sphere and often observed stereodynamic properties of the complexes.

There is no known biological role of the element, although the daily dietary intake of tantalum by humans is about 1 μg, and it mainly exists in bones at ca. 0.03 ppm (parts per million).[2]

Tantalum oxide Ta_2O_5 is widely used as a capacitor material in electronic equipment such as mobile phones and computers mainly due to its large dielectric constant ($k = 27$ as amorphous solid). The need for better Ta-containing materials has led in part to the studies of tantalum complexes as precursors in the past 15 years, as discussed below.

This review on tantalum coordination chemistry covers the literature between 2003 and 2018. SciFinder searches of keywords “tantalum” and “Ta” in January and February 2019 were followed by sorting of the hits by CA (Chemical Abstracts) sections, leading to the selection of hits in the following CA sections: “Inorganic Chemicals and Reactions”, “Organometallic and Organometalloidal Compounds”, “Catalysis, Reaction Kinetics, and Inorganic Reaction Mechanisms”, “Benzene, Its Derivatives, and Condensed Benzenoid Compounds”, “General Organic Chemistry”, “Heterocyclic, Aliphatic & Alicyclic Compounds”, “Industrial Inorganic Chemicals”, and “Physical Organic Chemistry”. The abstracts of the hits in these CA sections and their original papers were then evaluated for the current review.

This review follows essentially the format of the last review of niobium and tantalum in Comprehensive Coordination Chemistry II (CCC II) which covered the literature till 2002.[4] As in CCC II, carbon-based ligands is selective - Alkyl, cyclopentadienyl, acyl, iminoacyl and related ligands are generally not discussed. Detailed surveys of the organometallic chemistry of Ta between 2003 and early 2005 are given in the review by Mashima in Comprehensive Organometallic Chemistry III.[5] Tatalum coordination chemistry was also reviewed in Annual Reports on the Progress of Chemistry till 2013.[6-8]

NMR chemical shifts of d^0 tantalum complexes, in comparison to those of vanadium and niobium analogs, have been found to follow the general trends for d^0 transition metal compounds:[9] (1) For single-bonded ligands such as M-*H*, M-*C*R$_3$, M←*N*R$_3$, M-*Si*R$_3$ and M←*P*R$_3$, ^{1}H, ^{13}C, ^{15}N, ^{29}Si and ^{31}P shifts of these α atoms in the complexes of both first- and third-row transition metals are typically *downfield shifted* from those of second-row analogs with a “V-shape” (Trend 1). (2) For multiple-bonded ligands including those with d-p π bonds, such as M=*C*HR, M≡*C*R, M=*N*R, M=*O* and M $\underline{\leftarrow}$ *F*, ^{13}C, ^{15}N, ^{17}O and ^{19}F shifts of the α atoms in the complexes of first-, second- and third-row transition metals move consecutively *upfield* (Trend 2).[9]

Common abbreviations are defined in the Abbreviations Section.

2. TANTALUM (V)

2.1. Selected Hydride Ligands

Complex (silox)$_2$TaH(κ^2-*O,C*-OSiBu$^t_2$CMe$_2$CH$_2$) (silox = Bu$^t_3$SiO$^-$, **1**) was produced via cyclometallation of (silox)$_3$Ta.[10] [NPN″**]Ta(H)(dmpe) (**2**, [NPN″**] = κ^5-*C,N,P,N,C*-[PhP(C$_6$H$_4$-*o*-CHNAr)$_2$]$^{4-}$, Ar = 3,5-Me$_2$C$_6$H$_3$) was made from [NPN″**]Ta(CH$_2$SiMe$_3$)(dmpe) exposed to high pressures of H$_2$.[11] Treatment of KHBEt$_3$ with [NPN*]Ta(RC≡CR)Cl ([NPN*]$^{2-}$ = PhP[2-(*N*-mesityl)-5-Me-C$_6$H$_3$)$_2$$^{2-}$]; R = Et, SiMe$_3$) yielded the corresponding hydrides [NPN*]Ta(RC≡CR)H (**3**).[12] Addition of H$_2$ gas to [NPN*]TaMe$_3$ and [NPN*]Ta(RC≡CR)CH$_2$Ph (R = Et, SiMe$_3$) yielded ([NPN*]Ta)$_2$(μ-H)$_4$.[13] Hydrogenolysis of [NPN*]Ta(RC≡CR)CH$_2$Ph took many days and the complexes [NPN*]Ta(η^2-*trans*-RHC=CHR)H (R = SiMe$_3$, Et; **4**) could be isolated. The ethyl complex (**4**) undergoes rearrangement to also form the terminal 1-hexene isomer.[13] Deuterated labeling studies were also conducted to help elucidate the reaction pathways of these reactions.[13]

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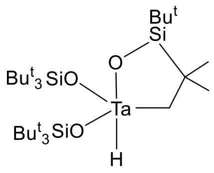

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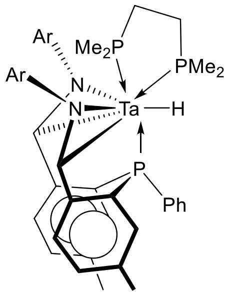
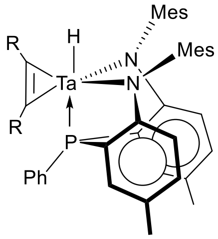


Ar = 3,5-Me$_2$C$_6$H$_3$

(**2**)



R = Et, SiMe$_3$

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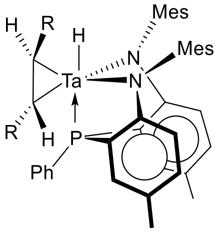

R = Et, SiMe$_3$

(**4**)

(Bu$^t{}_2$PhSiO)$_3$TaH$_2$ was synthesized from the reaction of (Bu$^t{}_2$PhSiO)$_3$TaCl$_2$ with Na/Hg in an H$_2$ environment.[14] Complexes [(bit-Bu^t-X)Ta]$_2$(μ-H)$_3$ML$_2$ (M = Li, L = thf, (**5a**, including the structure of the bit-Bu^t-X ligand); M = K, L = dme, **5b**) were prepared from the reactions of [(Bu^t-X)TaCl$_2$]$_2$ [H$_3$(Bu^t-X) = 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-tert-butyl-phenol] with MBHEt$_3$.[15] Treatment of [(bit-Bu^t-X)Ta]$_2$(μ-H)$_3$K(dme)$_2$ (**5b**) with 18-crown-6 in thf afforded (~~9~~6).[15]

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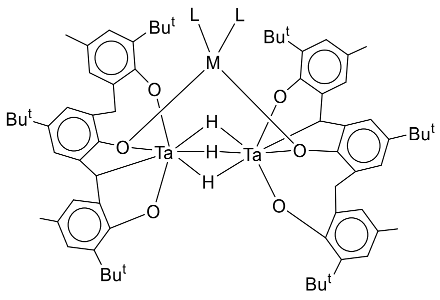

M = Li, L = thf; **5a**
M = K, L = dme; **5b**

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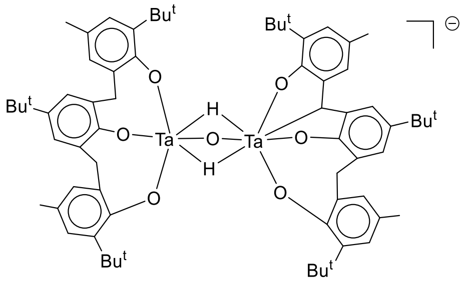
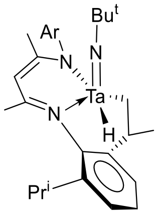


(**6**)

Complexes (silox)$_3$(H)Ta-EHR [E = N, R = H, Me, Bu^n, Ph, C$_6$H$_4$-*p*-X (X = H, Me, NMe$_2$); E = P, R = H, Ph; E = As, R = H, Ph] were prepared from the oxidative addition of REH$_2$ to (silox)$_3$Ta.[16]

Hydrogenolysis of [BDI^{Pr}]Ta(=NBu^t)Me$_2$ ([BDI^{Pr}]$^-$ = ~~bis-N,N′-(2,6-Pr$^i_2$-C$_6$H$_3$)-β-diketiminate~~ κ^2-ArNC(Me)CHC(Me)NAr, Ar = 2,6-Pr$^i_2$-C$_6$H$_3$) produced two diastereotopic isomers of cyclometallated tantalum hydride (**7**).[17] Refluxing (**7**) resulted in the elimination of H$_2$ to make [κ^4-*C,N,N,C*-BDI^{Pr}]Ta(=NBu^t) (**8**).[17]



Ar = 2,6-Pr$^i_2$-C$_6$H$_3$

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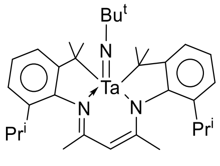

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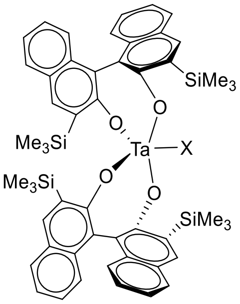
Reaction of Ta[O_2-3,3'-$(SiMe_3)_2C_{20}H_{10}$]$_2$(Ph) (**9a**) with diisobutylaluminum hydride yielded (R,R)-Ta[O_2-3,3'-$(SiMe_3)_2C_{20}H_{10}$]$_2$(H) (**9b**).[18]

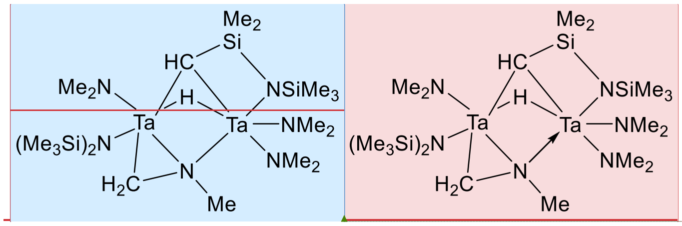


X = Ph, **9a**; H, **9b**

(**9**)

(silox)$_3$Ta(H)(η^3-BH_4) was prepared from a two-step process involving the exposure of (silox)$_3$Ta to H_2 to give (silox)$_3TaH_2$, followed by the reaction of (silox)$_3TaH_2$ with BH_3·thf.[19]

$(Me_2N)_2[(Me_3Si)_2N]Ta(\mu\text{-}H)_2(\mu\text{-}C\text{-}\eta^2\text{-}CHSiMe_2NSiMe_3)Ta(NMe_2)_2$ (**10**) was prepared, which is discussed in Section 2.3.1.[20]



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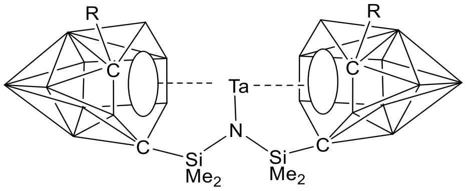
(**10**)

2.2. Selected Boron-based Ligands

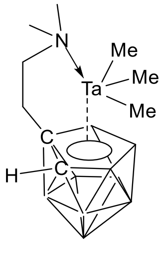
Dicarborane amide complexes [(*closo*-2-R-2,3-$C_2B_{10}H_{10}$)Me_2Si]$_2$NTa (R = Me, Ph, **11**) were afforded from the reaction of $TaCl_5$ with [(*closo*-1-R-1,2-$C_2B_{10}H_{10}$)Me_2Si]$_2$NH (R = Me, Ph) and sodium metal.[21] With MAO (methylaluminoxane) as a co-catalyst, these complexes were found to be active catalysts in ethylene polymerization.[21]



R = Me, Ph

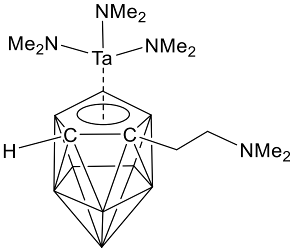
(**11**)

Refluxing ($Me_2NHCH_2CH_2$)$C_2B_9H_{11}$ with excess NaH in thf, followed by the addition of $TaMe_3Cl_2$ in toluene at room temperature, afforded [η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]$TaMe_3$ (**12**).[22]



(**12**)

Treatment of $Ta(NMe_2)_5$ with $(Me_2NHCH_2CH_2)C_2B_9H_{11}$ gave the product $[\eta^5$-$(Me_2NCH_2CH_2)C_2B_9H_{10}]Ta(NMe_2)_3$ (**13**).[23] When (**13**) was heated in the presence of py, the reaction is proposed to go through a Ta(III) intermediate before an intramolecular electron-transfer from the metal to the carborane ligand led to the final formation of $[\eta^1:\eta^6$-$(Me_2NCH_2CH_2)C_2B_9H_{10}]Ta(NMe_2)(py)$ (**14**).[23]



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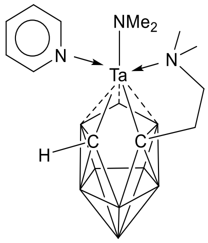
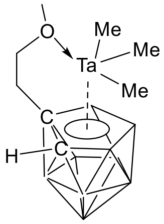


(**14**)

When $[(MeOCH_2CH_2)C_2B_9H_{10}]Na_2$ ~~reacted~~ was treated with ~~Me_3~~Ta~~Cl_2~~Me_3Cl_2, the reaction gave $[\eta^1:\eta^5$-$(MeOCH_2CH_2)C_2B_9H_{10}]TaMe_3$ (**15**).[24]



(**15**)

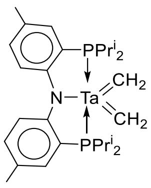
2.3. Selected Carbon-Based Ligands

In this section, alkyl, cyclopentadienyl, acyl, iminoacyl and related ligands are generally not discussed.

2.3.1. *Alkylidene, η²-allyl, allene, vinyl, and alkene ligands*

Alkyl complex [PNP]$TaMe_4$ was thermolytically and/or photochemically converted to the bis(methylidene) [PNP]$Ta(=CH_2)_2$ (**16**, $[PNP]^-$ = $N(2\text{-}PPr^i_2\text{-}4\text{-}Me\text{-}C_6H_3)_2^-$).[25] $[NPN^{Ph}]Ta(=CH_2)Me$ ($[NPN^{Ph}]^{2-}$ = $PhP(CH_2SiMe_2NPh)_2^{2-}$, **17**) was ~~also~~ made from irradiation of $[NPN^{Ph}]TaMe_3$ in toluene.[26]

As discussed in Section 2.1, C-H activation of $(Me_2N)_3Ta(\eta^2\text{-}CH_2SiMe_2NSiMe_3)$ in its reaction with H_3SiPh gave alkylidene/hydride complex $(Me_2N)_2[(Me_3Si)_2N]Ta(\mu\text{-}H)_2(\mu\text{-}C\text{-}\eta^2\text{-}CHSiMe_2NSiMe_3)Ta(NMe_2)_2$ (**10**).[20]



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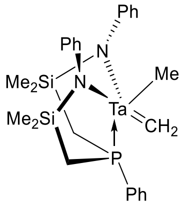

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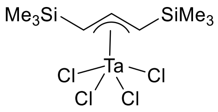

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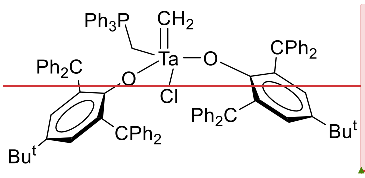
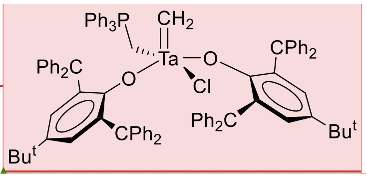
$Me_3SiCH=CHCH(SiMe_3)(SnMe_3)$ reacted neatly with $TaCl_5$ yielding $[\eta^3\text{-}1,3\text{-}(SiMe_3)_2C_3H_3]TaCl_4$ (**18**).[27] The methyledine complex $(Ar'O)_2Ta(=CH_2)(Cl)(CH_2PPh_3)$ [$(OAr')^-$ = 2,6-bis(diphenylmethyl)-4-tert-butylphenoxide$^-$, **19**] was produced by reaction of H_2CPPh_3 with $(Ar'O)_2TaMeCl_2$.[28] The deuterated alkyl complex $Ta(CD_2Bu^t)_5$ converts to alkylidene $(Bu^tCD_2)_3Ta{=}CDBu^t$ over time.[29] KIE studies on the conversion of $Ta(CD_2Bu^t)_5$ to $(Bu^tCD_2)_3Ta{=}CDBu^t$ and $Ta(CH_2Bu^t)_5$ to archetypical alkylidene $(Bu^tCH_2)_3Ta{=}CHBu^t$ gave a KIE = 14.1(0.8).[29]





(**19**)

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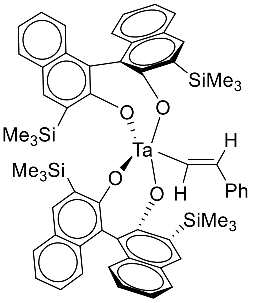
Addition of RC≡CH (R = Me, Ph) to (*R*,*R*)-Ta[O_2-3,3'-$(SiMe_3)_2C_{20}H_{10}$]$_2$(H) (**9b**) yielded (*R,R*)-Ta[O_2-3,3'-$(SiMe_3)_2C_{20}H_{10}$]$_2$[*E*-CH=C(H)Ph] (**20**) and isomers (*R,R*)-Ta[O_2-3,3'-$(SiMe_3)_2C_{20}H_{10}$]$_2$[*Z*-C(H)=C(H)Me] and (*R,R*)-Ta[O_2-3,3'-$(SiMe_3)_2C_{20}H_{10}$]$_2$[C(Me)=CH_2].[18]

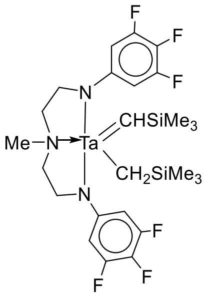


(**20**)

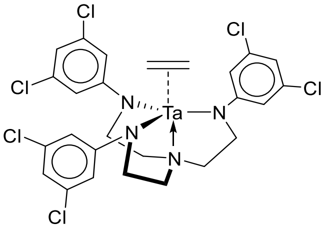
Thermolysis of $(silox)_3Ta(olefin)$ [silox$^-$ = $Bu^t{}_3SiO^-$; olefin = C_2H_4, C_2H_3Me,

C_2H_3Et, $^cC_5H_8$, $^cC_6H_{10}$, $H_2CCHC_6H_4$-*p*-X (X = H, OMe, CF_3)] yielded two Ta(V) species: the "tuck-in" alkyls $(silox)_2Ta(R)(\kappa^2$-*O,C*-$OSiBu^t{}_2CMe_2CH_2)$ [R = Et, Pr^n, Bu^n, ^cPen, ^cHex, $CH_2CH_2C_6H_4$-*p*-X (X = H, OMe, F)], and $(silox)_3Ta$(alkylidene) [alkylidene = =CHMe, =CHEt, =$CHPr^n$, =$^cC_5H_8$, =$^cC_6H_{10}$, =$CHCH_2C_6H_4$-*p*-X (X = H, OMe, F)].[10] During its thermolysis, the norbornene derivative, $(silox)_3Ta(\eta^2\text{-}^cC_7H_{10})$ converted to the norbornylidene $(silox)_3Ta{=}^cC_7H_{10}$.[10] The "tuck-in" alkyl $(silox)_2$(2-norbornyl)Ta(κ^2-*O,C*-$OSiBu^t{}_2CMe_2CH_2$) was not observed. Kinetic isotope effects (KIEs) were studied on a few of these systems.[10] Olefin substitution and association chemistry of adducts $(silox)_3Ta$(olefin) [olefin = C_2H_4 (as $^{13}C_2H_4$ or C_2D_4), C_2H_3Me, C_2H_3Et, *cis*-2-C_4H_8, *iso*-C_4H_8, C_2H_3Ph, $^cC_5H_8$, $^cC_6H_{10}$, $^cC_7H_{10}$ ~~(norborene)~~] were investigated via kinetic studies and theoretical calculations.[30] Reactions of both $(silox)_2Ta(pyrr)(\eta^2\text{-}C_2H_4)$ with ethylene and $(silox)_2Ta(pyrr)Cl_2$ with excess ethylene and Na/Hg gave $(silox)_2Ta(pyrr)[\kappa^2$-*C,C*-$CH_2(CH_2)_2CH_2]$.[31]

$[F_3N_2NMe]Ta(=CHSiMe_3)(CH_2SiMe_3)$ ($[F_3N_2NMe]^{2-}$ = $[(3,4,5\text{-}F_3C_6H_2NCH_2CH_2)_2NMe]^{2-}$, **21**) was the product of the reaction of Me_3SiCH_2MgCl with $[F_3N_2NMe]TaCl_3$.[32] Another alkylidene, $[F_3N_2NMe]Ta(=CHBu^t)Me$, was synthesized from treatment of $[F_3N_2NMe]Ta(CH_2Bu^t)Cl_2$ with MeMgCl.[32] $[F_3N_2NMe]Ta(\eta^2\text{-}C_2H_4)Et$ was produced from EtMgBr and $[F_3N_2NMe]TaCl_3$.[32] Treatment of $[Cl_2N_2NMe]TaCl_2$ ($[Cl_2N_2NMe]^{3-}$ = $[(3,5\text{-}Cl_2C_6H_3NCH_2CH_2)_3N]^{3-}$) with EtMgCl yielded $[Cl_2N_2NMe]Ta(\eta^2\text{-}C_2H_4)$ (**22**).[32]



(**21**)



(**22**)

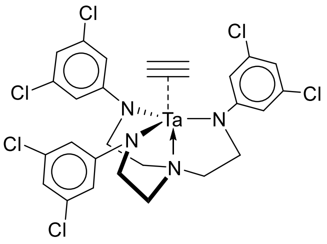
Addition of Ph_3PCH_2 to $(silox)_3Ta$ yielded $(silox)_3Ta{=}CH_2$ and phosphonio alkylidyne $(silox)_3Ta{=}C{\equiv}PPh_3$.[16]

2.3.2. *Alkylidyne, η^3-allyl, and alkyne ligands*

Many Ta atoms in the complexes in this section could be considered to be at the III oxidation state by the Dewar-Chatt bonding model but at the V oxidations state by the metalacyclopropene bonding model.[33]

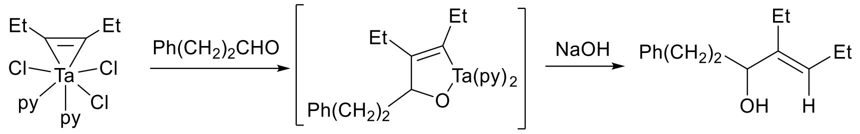
Commented [XZ(11]: Some of these complexes (in fact nearly all alkyne complexes) are Ta(III) by a different count. I added this paragraph to clarify.

Reaction of $[Cl_2N_2NMe]TaCl_2$ ($[Cl_2N_2NMe]^{3-} = [(3,5\text{-}Cl_2C_6H_3NCH_2CH_2)_3N]^{3-}$) with $H_2C{=}CHMgBr$ gave $[Cl_2N_2NMe]Ta(\eta^2\text{-}C_2H_2)$ (**23**).[32]

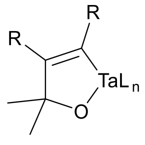


(**23**)

$TaCl_3(\eta^2\text{-}RC\equiv CR')(dme)$ (R = R′ = Et; R = R′ = *n*-C_5H_{11}; R = Ph, R′ = Me; R = R′ = Ph; R = R′ = $SiMe_3$; R = $SiMe_3$, R′ = Me; R = Bu^t, R′ = Me; R = $SiPr^i_3$, R′ = Me) were prepared from a one-pot reaction of $TaCl_5$, alkyne, and Zn powder in a mixed dme/toluene solvent.[34, 35] When the dme complexes were reacted with pyridine, $TaCl_3(\eta^2\text{-}RC\equiv CR')(py)_2$ (R = R′ = Et; R = R′ = *n*-C_5H_{11}; R = Ph, R′ = Me; R = R′ = Ph; R = R′ = $SiMe_3$; R = $SiMe_3$, R′ = Me) were formed.[34, 35] Thermodynamic and kinetic studies were conducted on the other alkyne exchange reactions with dme and py complexes.[35] Alkyne exchange reactions were also used to synthesize $Ta(PhC\equiv CR)(dme)$ (R = COOMe, $CONMe_2$).[35] $TaCl_3(\eta^2\text{-}EtC\equiv CEt)(dme)$ was ~~also~~ formed when the solids of the reaction of $TaCl_5$ with 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (btcd) were mixed with a solution containing toluene, dme, and 3-hexyne.[36] When using this method, $TaCl_3(\eta^2\text{-}EtC\equiv CEt)(dme)$ could not be isolated from the product mixture containing other products, $(TaCl_3)_x(dme)_y$ and hexamethylbenzene which was from alkyne trimerization.[36] Reactivities of $TaCl_3(\eta^2\text{-}EtC\equiv CEt)(dme)$, $TaCl_3(\eta^2\text{-}EtC\equiv CEt)py_2$, $TaCl_3(\eta^2\text{-}EtC\equiv CEt)(bipy)$ and $TaCl_3(\eta^2\text{-}EtC\equiv CEt)(tmeda)$ towards 3-phenylpropanal was also investigated.[34] Only $TaCl_3(\eta^2\text{-}EtC\equiv CEt)(py)_2$ reacted with aldehyde $Ph(CH_2)_2CHO$ to give an allylic alcohol (Scheme 1).[34] NMR-scale reactions of aldehydes RCHO with $TaCl_3(EtC\equiv CEt)(py)_2$ and $TaCl_3[\eta^2\text{-}(n\text{-}C_5H_{11})C\equiv C(n\text{-}C_5H_{11})](py)_2$ gave oxatantalacyclopentene complexes (**24**).[34] The L portions of these complexes are still unclear. Hydrolysis of the oxatantalacyclopentene product formed from $TaCl_3[(n\text{-}C_5H_{11})C\equiv C(n\text{-}C_5H_{11})](py)_2$ affords an allylic alcohol (Scheme 2).[34]

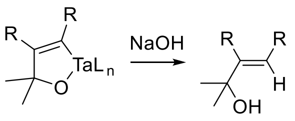


Scheme 1



R = Et or *n*-C_5H_{11}

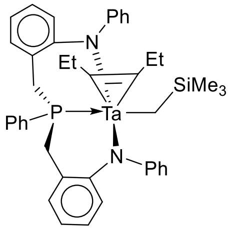
(**24**)



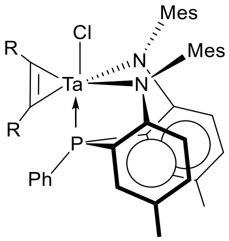
R = *n*-C_5H_{11}

Scheme 2

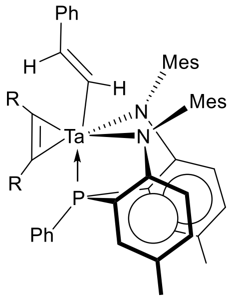
[NPN′]Ta(CH_2SiMe_3)(η^2-EtC≡CEt)] ($[NPN′]^{2-}$ = PhP(CHC_6H_4-*o*-NPh)$_2^{2-}$, **25**) was synthesized from the reaction of $TaCl_3$(η^2-EtC≡CEt)(dme) with the lithium salt [NPN′]Li_2(dioxane).[11] Addition of [NPN*]K_2(thf)$_{0.5}$ ($[NPN^*]^{2-}$ = PhP[2-(*N*-mesityl)-5-Me-$C_6H_3]_2^{2-}$) to $TaCl_3$(dme)(η^2-RC≡CR) (R = Et, $SiMe_3$) yielded [NPN*]Ta(RC≡CR)Cl (**26**).[12, 13, 37] When phenylacetylene was added to [NPN*]Ta(RC≡CR)(H), [NPN*]Ta(RC≡CR)(CH=CHPh) (**27**) was synthesized.[12] Reaction of [NPN*]Ta(RC≡CR)H (**3**) with ArN≡C (Ar = 2,6-$Me_2C_6H_3$) gave (**28**).[12]



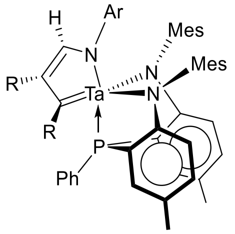
(**25**)



(**26**)



(**27**)



(**28**)

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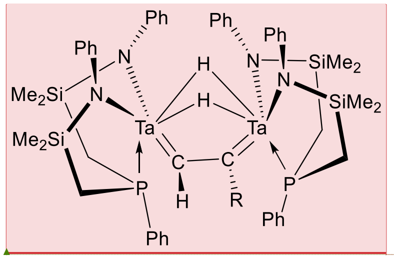
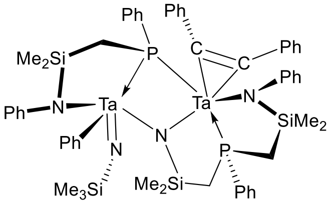
Heterobimetalic complex $TaCl_3(C_4H_2Bu^t{}_2)Ni(cod)$ was synthesized by adding 1 equiv $Ni(cod)_2$ to $TaCl_3(C_4H_2Bu^t{}_2)$.[38] Addition of PMe_2Ph, 1,2-bis(diphenylphosphino) ethane (dppe), 1,2-bis(diethylphosphino)ethane (depe), ~~and~~ or 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (~~IPR~~IPr) to $TaCl_3(C_4H_2Bu^t{}_2)Ni(cod)$ led to the formation $TaCl_3(C_4H_2Bu^t{}_2)Ni(PMe_2Ph)_2$, $TaCl_3(C_4H_2Bu^t{}_2)Ni(dppe)$, $TaCl_3(C_4H_2Bu^t{}_2)Ni(depe)$, ~~and~~ or $TaCl_3(C_4H_2Bu^t{}_2)Ni($~~IPR~~IPr), respectively. DFT calculations were report~~complet~~ed for the complex ~~on~~ $TaCl_3(C_4H_2Bu^t{}_2)Ni($~~IPR~~IPr).[38]

Complexes $\{[NPN^{Ph}]Ta\}_2(\mu\text{-RCCH})(\mu\text{-H})_2$ ($[NPN^{Ph}]^{2-} = PhP(CH_2SiMe_2NPh)_2{}^{2-}$; R = Ph, Pr^n, Bu^t; **29**) were produced via the reactions of $([NPN^{Ph}]Ta)_2(\mu\text{-H})_4$ with terminal alkynes.[39] In low pressure environments, ([NPN^{Ph}]Ta)$_2$(μ-PhCCH)(μ-H)$_2$ lost H_2 to form ([NPN^{Ph}]Ta)$_2$(μ-CH)(μ-CPh).[39] Reaction of {[PhP(CH_2SiMe_2NPh)$_2$]Ta}$_2$(μ-H)$_4$ ~~and~~ with PhC≡CPh gave the asymmetric complex (**30**).[39]



(**29**)



(**30**)

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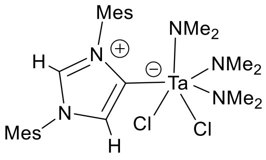
Field Code Changed

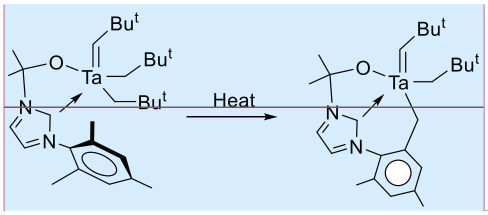
2.3.3. *N-Heterocyclic carbene (NHC) ligands*

TaX_5(IP~~p~~r) [X = F, Cl, Br; IP~~p~~r = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] were prepared from TaX_5 and free IPr in equimolar portions.[40, 41] [(IMes)$_2$$TaCl_4$]($TaCl_6$) (IMes = 1,3-dimesitylimidazol-2-yliden) was afforded from the reaction of $TaCl_5$ with IMes at low temperature.[41] Complexes $LTaF_3(NMe_2)_2$ (L = IMes, SIMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) were prepared via the reactions of L·HBF_4 with $Ta(NMe_2)_5$.[42] The salt [IMes–H···IMes][*fac*-$TaCl_3(NMe_2)_3$] was formed from IMes·HCl with $Ta(NMe_2)_5$ followed by a pentane extraction.[42] If the residue was extracted followed by a slow evaporation, crystals of (αIMes)$TaCl_2(NMe_2)_3$ (**31**) formed.[42] A more direct route to synthesize (αIMes)$TaCl_2(NMe_2)_3$ was found by reacting $TaCl_2(NMe_2)_3$ with IMes.[42]



(**31**)

Complexes Ta(=X-Bu^t)(L)(CH$_2$Bu^t)$_2$ (X = N, CH) (**32a,b**) were prepared from the reactions of Ta(=XBu^t)(CH$_2$Bu^t)$_3$ with HL [1-mesityl-3-(2-hydroxyisobutyl)imidazol-2-ylidene].[43] If the reaction were heated or left at room temperature for a couple of days, one of the ortho-methyl groups in the NHC mesityl substituent in Ta(=CHBu^t)(L)(CH$_2$Bu^t)$_2$ underwent C-H bond activation to form [Ta(L*)(=CHBu^t)(CH$_2$Bu^t)] (Scheme 3).[43]



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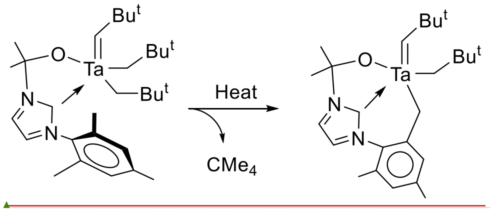

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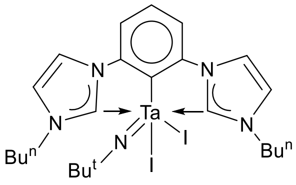
(**32b**)

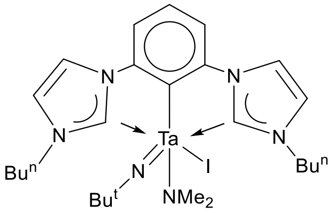
Scheme 3

2.3.4. *CCC pincer ligands*

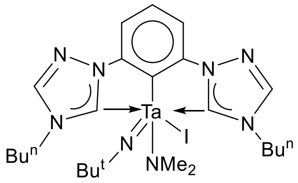
When 1.1 equiv of $\mathrm{Ta(=NBu^t)(NMe_2)_3}$ was combined with 1,3-bis(3-*n*-butylimidazol-1-yl)benzene diiodide ($\mathrm{[^{Bu}C^iC^iC^{Bu}]I_2}$), a mixture of bis(NHC)-CCC imido products, $\mathrm{[^{Bu}C^iC^iC^{Bu}]Ta(=NBu^t)I_2}$ (**33**) and $\mathrm{[^{Bu}C^iC^iC^{Bu}]Ta(=NBu^t)(NMe_2)I}$ (**34**) were observed.[44] When $\mathrm{Ta(=NBu^t)(NMe_2)_3}$ was added in excess to ($\mathrm{[^{Bu}C^iC^iC^{Bu}]I_2}$), $\mathrm{[^{Bu}C^iC^iC^{Bu}]Ta(=NBu^t)(NMe_2)I}$ (**34**) was the sole product. A similar approach was used to make pure $\mathrm{[^{Bu}C^tC^tC^{Bu}]Ta(=NBu^t)(NMe_2)I}$ (**35**) using $\mathrm{Ta(=NBu^t)(NMe_2)_3}$ and 1,3-bis(3-*n*-butyltriazol-1-yl)benzene diiodide ($\mathrm{[^{Bu}C^tC^tC^{Bu}]I_2}$).[44] The dimeric (($\mathrm{[^{Bu}C^iC^iC^{Bu}]Ta(=NBu^t)_2 \cdot LiI)_2}$ (**36**) was afforded by the treatment of (**34**) with $\mathrm{Bu^tNHLi}$.[45, 46] This dimer was found to have catalytic activity for oxidative amination reactions.[45, 46] After a few months, ($\mathrm{[^{Bu}C^iC^iC^{Bu}]Ta(=NBu^t)_2 \cdot LiI)_2}$ was found to transform to an asymmetric CCC-NHDC/NHC (NHDC = anionic N-heterocyclic dicarbene, **37**).[46] Heating ($\mathrm{[^{Bu}C^iC^iC^{Bu}]Ta(=NBu^t)_2 \cdot LiI]_2}$ for a few days produced (**34**) instead of the desired product (**37**).[46] Reaction (**34**) with excess $\mathrm{LiNHBu^t}$, followed by heating, gave an oxo product (**129**) in Section 2.~~6~~7.9.[46]



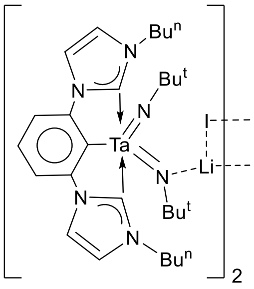
(**33**)



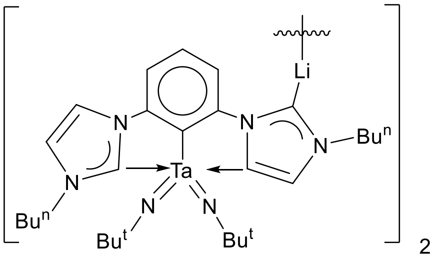
(**34**)



(**35**)

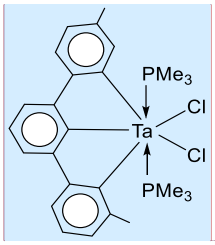


(**36**)



(**37**)

NMR-scale reactions of $[\mathrm{Ar}^{\mathrm{Tol2}}]\mathrm{TaMe_3Cl}$ ($[\mathrm{Ar}^{\mathrm{Tol2}}]^-$ = 6-di-p-tolylphenyl) containing a CCC-pincer ligand with $\mathrm{PMe_3}$ or $\mathrm{Ta(PMe_3)_2Me_3Cl_2}$ with $[\mathrm{Ar}^{\mathrm{Tol2}}]\mathrm{Li}$ both yielded $[\kappa^3\text{-}\mathrm{Ar}^{\mathrm{Tol*2}}]\mathrm{Ta(PMe_3)_2MeCl}$ (**38;** Tol* = $\mathrm{C_6H_3Me}$).[47] $[\kappa^3\text{-}\mathrm{Ar}^{\mathrm{Tol*2}}]\mathrm{Ta(PMe_3)_2Cl_2}$ could be made from the reaction of $\mathrm{ZnCl_2}$ with $[\kappa^3\text{-}\mathrm{Ar}^{\mathrm{Tol*2}}]\mathrm{Ta(PMe_3)_2MeCl}$.[47]



(**38**)

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2.4. Selective Silicon-Based Ligands

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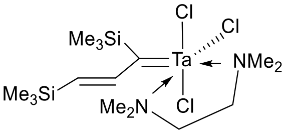
$Ta[Si(SiMe_3)_3]_2(NMe_2)_3$ and $Ta(SiBu^tPh_2)_2(NMe_2)_3$ were synthesized via addition of $Li(thf)_3Si(SiMe_3)_3$ or $Li(thf)_2(SiBu^tPh_2)$, respectively, to $TaCl_2(NMe_2)_3$.[48] When $TaCl(SiBu^tPh_2)(NMe_2)_3$ was treated with $Li(thf)_3Si(SiMe_3)_3$, $Ta[Si(SiMe_3)_3](SiBu^tPh_2)(NMe_2)_3$ formed.[48] $Ta[Si(SiMe_3)_3](SiBu^tPh_2)(NMe_2)_3$ and $Ta(SiBu^tPh_2)_2(NMe_2)_3$ were found to be thermally unstable and kinetic studies on the decomposition of these complexes were conducted.[48, 49]

2.45. Nitrogen-Based Ligands

2.45.1. *Neutral ligands*

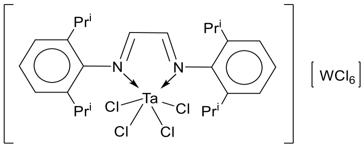
$Sr(HF)_3(TaF_6)_2$ reacted with liquid NH_3 to give eight-coordinate $TaF_5(NH_3)_3$ with a square antiprismatic structure.[50] $[TaF_4(py)_4](TaF_6)$ and $[TaF_4(2,2'\text{-bipy})_2](TaF_6)$ were produced from addition of the neutral donor ligands to TaF_5 via ligand promoted self-ionization.[51]

Treatment of $[\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3]TaCl_4$ with $NH_2(CH_2)_4NH_2$ (tmeda) led to the formation of the allyl $[Me_3SiCH{=}CHC(SiMe_3){=}]TaCl_3(tmeda)$ (**39**).[27] The tmeda ligand is unsymmetrically bonded to the Ta center. The Ta-N bond *trans* to the alkylidene ligand is significantly longer than the Ta-N bond *trans* to a chloride ligand.[27]

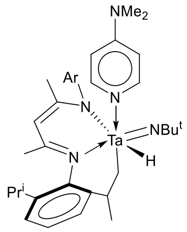


(**39**)

Oxidation of [DAD^{Dip}]TaCl$_4$ (DAD = 1,4-diaza-1,3-dienes or α-diimines; DAD^{Dip} = ArN=CHCH=NAr; Ar = 2,6-Pr$^i_2$C$_6$H$_3$) with WCl$_6$ yielded ([DAD^{Dip}]TaCl$_4$)(WCl$_6$) (**40**).[52] ([DAD^{Dip}]TaBr$_4$)(TaBr$_6$) was made from TaBr$_5$ and DAD^{Dip}.[53] Addition of 4-dimethylaminopyridine (dmap) to (**7**) yielded octahedral complex (**41**).[17]



(**40**)



(**41**)

The dme ligand of diphenylhydrazide TaCl$_3$(=NNPh$_2$)(dme) was found to be labile. Treatment of this complex with pyridine, tmeda, 2,2'-bipyridine, or thf gave TaCl$_3$(=NNR$_2$)(L$_2$) (L$_2$ = py$_2$, tmeda, bpy, thf$_2$).[54] {[κ^3-~~(~~MeN~~[~~(CH$_2$~~)~~CH$_2$N~~(~~SiMe$_3$)~~]~~$_2$~~}~~]Ta(=NNPh$_2$)(py)$_n$~~]~~~~(~~}(BArF$_{24}$) (n = 1, 2) were produced when [~~(~~κ^3-MeN~~[~~(CH$_2$CH~~)~~$_2$N~~(~~SiMe$_3$)~~]~~$_2$]~~)~~TaCl(=NNPh$_2$) was treated with Na(BArF$_{24}$) (BArF$_{24}^-$ =

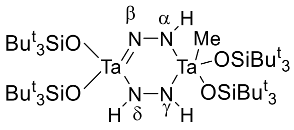
Commented [XZ(19]: I've deleted one "layer" of parehthesis, making κ^3-MeN[(CH$_2$)$_2$N(SiMe$_3$)]$_2$ -> [κ^3-MeN(CH$_2$CH$_2$NSiMe$_3$)$_2$].

$B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$) and pyridine.[54] The bispyridne complex was ~~projected to be~~ a decomposition product of the monopyridine complex.[54] Treatment of $Ta(=NBu^t)Cl_3py_2$ with tmeda gave $Ta(=NBu^t)Cl_3(tmeda)$.[55]

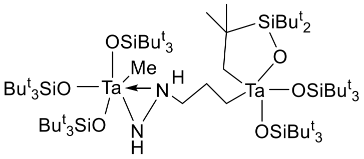
Adduct $TaCl_5(4\text{-}Bu^tpy)$ was formed from the addition of $4\text{-}Bu^tpy$ to $TaCl_5$.[56]

2.~~4~~5.2. *Amide ligands*

Exposure of hydrazine ~~or~~ and N-amino-2-methylaziridine to $(silox)_3Ta=CH_2$ afforded $(silox)_3(Me)TaNHNH_2$ and $(silox)_3(Me)TaNH(\text{-}^cNCHMeCH_2)$, respectively.[16] These complexes were precursors to $[(silox)_2TaMe](\mu\text{-}N_\alpha HN_\beta)(\mu\text{-}N_\gamma HN_\delta H)[Ta(silox)_2]$ (**42**) and $[(silox)_3MeTa](\mu\text{-}\eta^2\text{-}N,N{:}\eta^1\text{-}C\text{-}NHNHCH_2CH_2CH_2)Ta(\kappa\text{-}O,C\text{-}OSiBu^t_2CMe_2CH_2)(silox)_2$ (**43**), respectively.[16]



(**42**)



(**43**)

Reaction of $(Me_2N)_3TaCl_2$ with 1 equiv of $LiN(SiMe_3)_2$ gave a mixed amide complex $(Me_2N)_3Ta(Cl)[N(SiMe_3)_2]$ which, in the solid state, adopted a distorted trigonal bipyramidal geometry with the $\text{-}N(SiMe_3)_2$ and $\text{–}Cl$ ligands in the equatorial and axial positions, respectively~~.~~.[57] Studies of reactions of $TaCl(NMe_2)_4$ with $LiNR_2$ (R = Et, $SiMe_3$) suggest the presence of an equilibrium among $TaCl(NMe_2)_4$, $Ta(NMe_2)_5$ and $Ta_2(\mu\text{-}Cl)_2(NMe_2)_6Cl_2$: $2\ TaCl(NMe_2)_4 \rightleftharpoons Ta(NMe_2)_5 + \tfrac{1}{2}\ Ta_2(NMe_2)_6Cl_2(\mu\text{-}Cl)_2$.[58] For

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example, $TaCl(NMe_2)_4$ reacted with $LiNEt_2$, affording $Ta(NMe_2)_5$, $Ta(NMe_2)_4(NEt_2)$, and $Ta(NMe_2)_3(NEt_2)_2$.[58] Similarly, the reaction of $TaCl(NMe_2)_4$ with $LiN(SiMe_3)_2$ gives $Ta(NMe_2)_4[N(SiMe_3)_2]$, $Ta(NMe_2)_5$, and $(Me_2N)_3\overline{TaN(SiMe_3)SiMe_2CH_2}$ (Section 2.~~9~~10.9).[58] $Ta(NMe_2)_4(NEt_2)$, $Ta(NMe_2)_5$, and $Ta(NMe_2)_3(NEt_2)_2$ are in a slow exchange: $2\ Ta(NMe_2)_4(NEt_2) \rightleftharpoons Ta(NMe_2)_5 + Ta(NMe_2)_3(NEt_2)_2$ with an equilibrium constant of $K_{eq} = 0.25(0.01)$ at 90 °C.[58]

In studying the amine exchange of $Ta(NMe_2)_5$ with 5 equiv of *N*-methyl-*p*-toluidine [(*p*-tol)MeNH], a mixture of products $[(p\text{-tol})MeN]Ta(NMe_2)_4$ and $[(p\text{-tol})MeN]_2Ta(NMe_2)_3$ were formed.[59] When 25 equiv of (*p*-tol)MeNH was used in the reaction, $[(p\text{-tol})MeN]_2Ta(NMe_2)_3$ and $[(p\text{-tol})MeN]_3Ta(NMe_2)_2$ were made. $[(p\text{-tol})MeN]_2Ta(NMe_2)_3$ and $[(p\text{-tol})MeN]_3Ta(NMe_2)_2$ could also be synthesized via a reaction of $Ta(NMe_2)_5$, (*p*-tol)MeNH, and 1-octene. Alkylaniline was produced in this reaction as well.[59]

Complexes $(silox)_2TaCl_2(NR_2)$ [NR_2 = pyrrolidine (pyrr), piperidine (pip), NMe_2] were made via addition of lithium amides to $(silox)_2TaCl_3$.[31] $Cl_4Ta(NMePh)(OEt_2)$ and $Ta_2Cl_4(NMePh)_2(\mu\text{-}Cl)_2$ were prepared as precursors for hydroaminoalkylation catalysts.[60]

Phosphinoamido-imido complex $(Ph_2PNPr^i)_3Ta{=}NBu^t$ was prepared from $LiNPr^iPPh_2$ and $Ta({=}NBu^t)Cl_3py_2$.[61] Addition of CoI_2 to $(Ph_2PNPr^i)_3Ta{=}NBu^t$ produced the heterobimetallic complex $ICo(PPh_2NPr^i)_3Ta{=}NBu^t$ (**44**). Reaction of $ICo(PPh_2NPr^i)_3Ta{=}NBu^t$ with Na/Hg under N_2 yielded $[(thf)_5Na][N_2Co(Ph_2PNPr^i)_3Ta{=}NBu^t]$ (**45**).[61]

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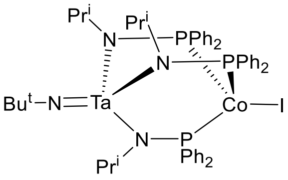
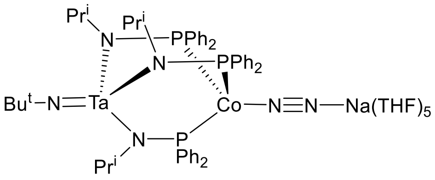
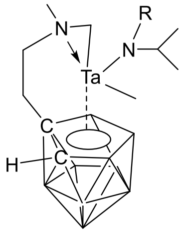

(**44**)


(**45**)

Treatment of [η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]$TaMe_3$ (**12**) with 1 equiv of CyNC ~~and~~ or Pr^iNC gave amide {σ:η^1:η^5-[MeN(CH_2)CH_2CH_2]$C_2B_9H_{10}$}Ta[N(Pr^i)R](Me) (R = Cy, Pr^i; **46**).[24]



R = Cy, Pr^i

(**46**)

Amide imide complex Ta(=NBu^t)($NHBu^t$)Cl_2(p~~p~~y)$_2$ was made via the reaction of $TaCl_5$ with Bu^tNH_2 in the presence of pyridine.[62]

2.~~4~~5.3. *Azide and hydroazide ligands*

Hepta-coordinated complexes $A_2[Ta(N_3)_7]$ (A^+ = PPh_4^+, Cs^+) were isolated form the reactions of $Ta(N_3)_5$ with AN_3.[63] Preparation of [TaF_4(2,2'-bipy)$_2$][$Ta(N_3)_6$] was conducted by mixing 2,2′-bipyridine (2,2′-bipy) and TaF_5, which was followed by addition of 3 equiv of Me_3SiN_3.[64] If the molar ratio of of TaF_5 to Me_3SiN_3 was 1:6, the self-ionization product $[Ta(N_3)_4(2,2'\text{-bipy})_2][Ta(N_3)_6]$ formed.[64] $[Ta(N_3)_4(1,10\text{-phen})_2][Ta(N_3)_6]$ could be synthesized via a similar route.[64] When 3,3′-bipy or 4,4′-bipy was used, even with great excesses of Me_3SiN_3, only complexes $[Ta(N_3)_5]_2(\mu\text{-L})$ (L = 3,3′-bipy, 4,4′-bipy) were produced.[64]

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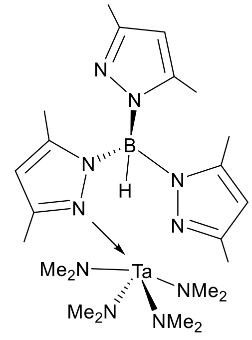
$Ta_2(NMe_2)_8(\mu\text{-}N_3)_2$ was synthesized from $TaCl(NMe_2)_4$ and NaN_3.[65] Reaction of $Ta_2(NMe_2)_8(\mu\text{-}N_3)_2$ with formamidine $Pr^iNC(H)NHPr^i$ or *p*-toluidine afforded *fac*-$Ta(NMe_2)_3(\eta^1\text{-}N_3)[Pr^iNC(H)NPr^i]$ or $Ta_3(NMe_2)_5(\mu\text{-}NMe_2)(\mu\text{-}NC_6H_4Me\text{-}4)_2(NC_6H_4Me\text{-}4)(\mu\text{-}N_3)_2(\eta^1\text{-}N_3)$, respectively.[65]

$TaCl_3[N(Pr^i)NMe_2]_2$ was synthesized via addition of $LiN(Pr^i)NMe_2$ to $TaCl_5$.[66] $TaCl(NMe_2)_3[N(SiMe_3)NMe_2]$ was produced from hydrazinolysis of $TaCl(NMe_2)_4$ using $(Me_3Si)NHNMe_2$.[67] $Ta(NMe_2)_4[N(SiMe_3)NMe_2]$ was synthesized via metathesis using $TaCl(NMe_2)_3[N(SiMe_3)NMe_2]$ and $LiNMe_2$.[67] ALD experiments were conducted using $Ta(NMe_2)_4[N(SiMe_3)NMe_2]$ as a precursor to make Ta_2O_5 films.[67] Treatment of $TaCl_5$ with tmeda and either 1,1-dimethyl-2-trimethylsilylhydrazine or 1-trimethylsilyl-1-aminopiperidine gave $[Ta(=NNMe_2)Cl_2(NH_2NMe_2)(tmeda)]Cl\cdot CH_2Cl_2$ or $\{Ta(=NNC_5H_{10})Cl_2[NH_2N(C_5H_{10})](tmeda)\}Cl\cdot CH_2Cl_2$.[68] $[Ta(=NN(C_5H_{10})Cl_2[NH_2N(C_5H_{10})]_2]Cl\cdot[(CH_2Cl_2)(C_6H_{14})_{0.5}]$ was synthesized in a similar method using $TaCl_5$ with 1-aminopiperidine and 1-trimethylsilyl-1-aminopiperidine.[68] Complexes $(dme)TaCl_3(=NNR_2)$ [R_2 = Ph_2, $C_{12}H_8$ (carbazole), $(p\text{-}ClPh)_2$, $(p\text{-}BrPh)_2$, $(p\text{-}MePh)_2$, $(p\text{-}MeOPh)_2$] were prepared from $TaCl_5$ and the corresponding disubstituted hydrazine H_2NNR_2.[54, 69] $Ta(=NBu^t)(NR_2)_2(tdmh)$ (R = Me, Et) were made from the addition of $H(Me_3Si)NNMe_2$ (Htdmh = *N*-trimethylsilyl-*N′N′*-dimethylhydrazine) with $Ta(=NBu^t)(NR_2)_3$.[70] The ethyl analogue was used for CVD of TaN(Si) thin films.[70] $TaCl_3(tdmh)_2$ was made from the reaction of H-tdmh with $Ta(=NBu^t)Cl_3(py)_2$.[71] Treatment of $Ta(=NBu^t)Cl_3(py)_2$ with 1 equiv of XMg(tdmh) (X = Br, Cl) yielded $Ta(=NBu^t)(tdmh)_2X$.[71] $Ta(=NBu^t)(tdmh)_2X$ was reacted with several amines ($H_2NC_6F_5$) and salts (KCH_2Ph, $LiNMe_2$, $LiNHBu^t$) to prepare $Ta(=NC_6F_5)(tdmh)_2Cl$, $Ta(=NBu^t)(tdmh)_2(CH_2Ph)$, $Ta(=NBu^t)(tdmh)_2(NMe_2)$, and $Ta(=NBu^t)(tdmh)_2(NHBu^t)$.[71] $Ta(=NBu^t)(tdmh)_2(NHBu^t)$ was also prepared from the reaction of $Ta(=NBu^t)Cl_3(py)_2$ with 2 equiv of XMg(tdmh) (X = Br, Cl).[71]

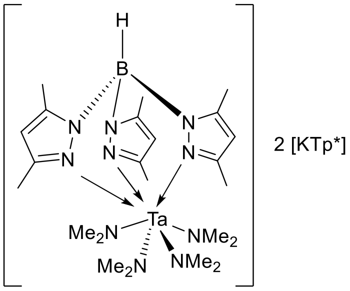
2.~~4~~5.4. *Tris(pyrazolyl)borohydride ligands*

Solutions containing KTp* [Tp^{*-} = HB(3,5-dimethylpyrazolyl)$_3^-$] and $TaCl(NMe_2)_4$ were added together to afford the mixture of (κ^1-Tp*)$Ta(NMe_2)_4$ (**47**) and [(κ^3-Tp*)$Ta(NMe_2)_4$]·2KTp* (**48**).[72] When KTp [Tp^- = HB(pyrazolyl)$_3^-$] reacted with $TaCl(NMe_2)_4$, only (κ^2-Tp)$Ta(NMe_2)_4$ (**49**) formed.[72] Reactions of $TaCl_3(\eta^2\text{-}EtC{\equiv}CEt)(dme)$ with KTp* and $TlTp^{Mes*}$ [Tp^{Mes*-} = HB(3-mesitylpyrazolyl)$_2$(5-mesitylpyrazolyl)$^-$] yielded $Tp^*TaCl_2(\eta^2\text{-}EtC{\equiv}CEt)$ and $Tp^{Mes*}TaCl_2(\eta^2\text{-}EtC{\equiv}CEt)$ (**50**), respectively.[73] When $TaCl_3(=N\text{-}2,6\text{-}Pr^i{}_2C_6H_3)(dme)$ was used to react with $TlTp^{Mes*}$, the product was $Tp^{Mes*}TaCl_2(=N\text{-}2,6\text{-}Pr^i{}_2C_6H_3)$ (**51**). Treatment of $TaCl_3(=NBu^t)(dme)$ with $TlTp^{Mes}$ [Tp^{Mes-} = HB(3-mesitylpyrazolyl)$_3^-$] yielded both $Tp^{Mes}TaCl_2(=NBu^t)$ (**52a**) and its isomer $Tp^{Mes*}TaCl_2(=NBu^t)$ (**52b**).[73] Reaction of $LiNMe_2$ with $Tp^*Ta(=NBu^t)Cl_2$ gave $Tp^*Ta(=NBu^t)(NMe_2)Cl$ if the $LiNMe_2$ was in slight excess, whereas $Tp^*Ta(=NBu^t)(NMe_2)_2$ was formed if a larger excess was used.[74] Equimolar reactions of

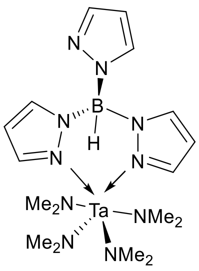
$B(C_6F_5)_3$ with Tp*Ta(=NBu^t)Me(NMe_2) and Tp*Ta(=NBu^t)(NMe_2)$_2$ gave [Tp*Ta(NMe_2)(=NBu^t)][BMe(C_6F_5)$_3$] and {Tp*Ta(NMe_2)[κ^1-*N*-N(CH_2)Me](=NBu^t)}[BH(C_6F_5)$_3$], respectively.[74]



(**47**)



(**48**)



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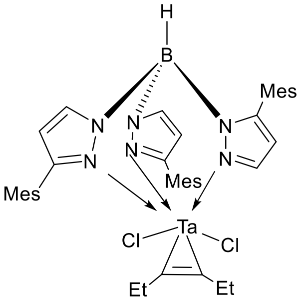
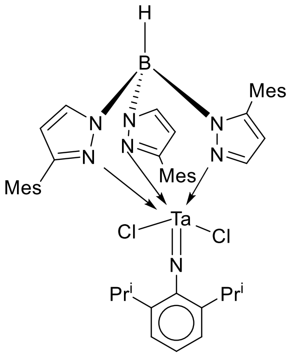


(**50**)



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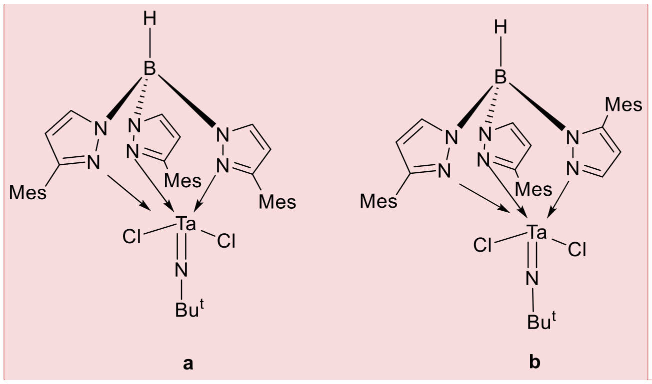

a

b

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(**52**)

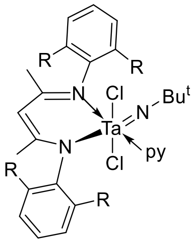
2.~~4~~5.5. *Ketimide Ligands*

Reaction of $TaCl_4$(tmeda) with Li($N=CBu^t_2$) resulted in the formation of Ta(Cl)($N=CBu^t_2$)$_4$.[75]

2.~~4~~5.6. *Diketiminate ligands*

Complexes $[BDI^R]Ta(=NBu^t)Cl_2$(p~~p~~y) ($[BDI^R]^-$ = $ArNCMeCHCMeNAr^-$, Ar = 2,6-

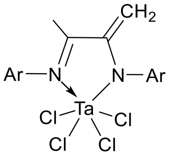
$R_2C_6H_3$; R = Pr^i, Cl; **53**) were synthesized via addition of Li[BDI^R] to Ta(=NBu^t)Cl$_3$(p~~p~~y)$_2$.[76, 77]



(**53**)

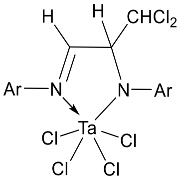
2.~~4~~5.7. *Miscellaneous monoanionic bidentate nitrogen-based ligands*

$CHCl_3$ and CCl_4 abstracted an H atom from one of the methyl groups on α-diimine ligand DAD^{Dip}-R [DAD = 1,4-diaza-1,3-dienes; DAD^{Dip}-R,R′ = ArN=C(R)C(R′)=NAr; Ar = 2,6-Pr$^i_2C_6H_3$] of [DAD^{Dip}-CH_3,CH_3]TaCl_4 to produce the asymmetric complex (**54**).[52] Reactions of [DAD^{Dip}-H,H]TaCl_4 with $CHCl_3$ and CCl_4 yielded (**55**) and (**56**), respectively, where the organic compound attached to one side of the ligand backbone.[52] [DAD^{Dip}-H,H]TaCl_4 also reacted with styrene and CCl_4 to make (**57**).[52]



Ar = 2,6-Pr$^i_2C_6H_3$

(**54**)



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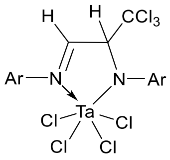
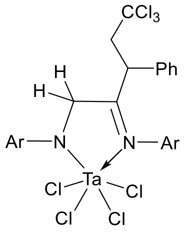
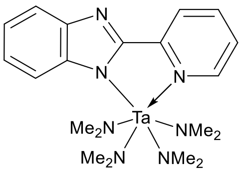


(**56**)

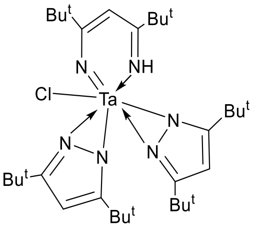


(**57**)

[BzImPy]Ta(NMe_2)$_4$ ([BzImPy$^-$] = 2-(2-pyridin)benzimidazolate$^-$, **58**) was prepared from Ta(NMe_2)$_5$ and H[BzImPy].[78] Treatment of $TaCl_4$(4-Bu^{t}py)$_2$ with potassium 3,5-di-t-butylpyrazolate (KBu$^t_2$pz) yielded Ta(tmkh)$_2$(Bu$^t_2$pz)Cl (tmkh = 2,2,6,6-tetramethyl-5-ketimidehept-3-en-3-imide) (**58**).[79]



(**58**)



(**59**)

2.5.8. *Diamide ligands*

Diamido-arsenine complex [NAsN]TaMe$_3$ [NAsN^{2-} = PhAs(CH_2SiMe_2NPh)$_2^{2-}$] was prepared from the reaction of [NAsN]Li_2(thf)$_2$ with Ta(Me)$_3Cl_2$.[80] ~~Hydrolysis~~ Hydrogenation of [NAsN]TaMe$_3$ only yielded free ligand.[80] Reactions of Ta(Me)$_3Cl_2$ with 1,8-(RNH)$_2C_{10}H_6$ and Li_2R_2DAN (R_2DAN^{2-} = [1,8-(RN)$_2C_{10}H_6$]$^{2-}$; R = Ph, 3,5-$Me_2C_6H_3$)

afforded $TaCl_3[1,8-(RN)_2C_{10}H_6]$ and $TaMe_3[1,8-(RN)_2C_{10}H_6]$, respectively.[81] Similarly, reactions of $Li_2(Pr^i)_2$DAN with $Ta(NEt_2)_2Cl_3$ and $Li_2(3,5-Me_2C_6H_3)_2$DAN with $Ta(NEt_2)_2Cl_3$py both yielded $TaCl(NEt_2)_2[1,8-(RN)_2C_{10}H_6]$ (R = Pr^i, 3,5-$Me_2C_6H_3$; **60**).[81] Addition of $LiNMe_2$ to (**60**) gave metathesis products $Ta(NEt_2)_2(NMe_2)[1,8-(RN)_2C_{10}H_6]$ (R = Pr^i, R = 3,5-$Me_2C_6H_3$).[81] $[\eta^2\text{-}RN(CH_2)_nNR]Ta(NMe_2)_3$ (R = Me, n = 2 or 3; R = Et, n = 2 or 3) were made from the addition of diamine lithium salts $[RN(CH_2)_nNR]Li_2$, generated in situ, to the dinuclear complex $(Me_2N)_3TaCl_2$.[82] $Ta[1,2\text{-}(NCH_2Bu^t)_2C_6H_4]_2Cl$ was generated from the treatment of $TaCl_5$ with $Li_2[1,2\text{-}(NCH_2Bu^t)_2C_6H_4]$.[83]

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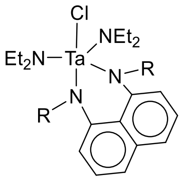
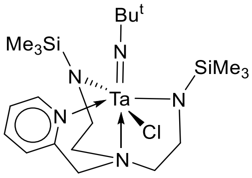


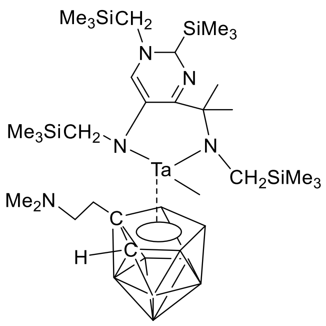
(**60**)

Reaction of $Ta(=NBu^t)Cl_3$(p~~p~~y)$_2$ with $Li_2(2\text{-}C_5H_4N)CH_2N\text{-}[CH_2CH_2N(SiMe_3)]_2$ gave the tetradentate complex $Ta(=NBu^t)Cl(N_2NN')$ [N_2NN' = $(2\text{-}C_5H_4N)CH_2N(CH_2CH_2NSiMe_3)_2$] (**61**).[84]

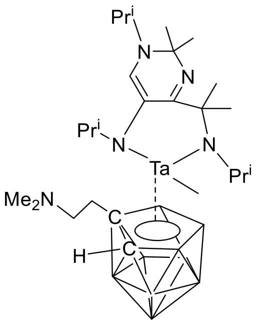


(**61**)

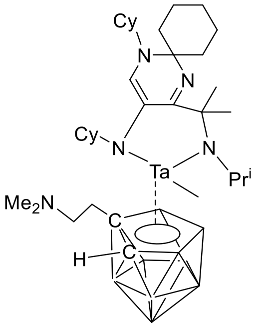
Treatment of [η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]$TaMe_3$ (**12**) with 4 equiv of isonitriles Me_3SiCH_2NC, Pr^{i}NC, or 1 equiv of Pr^{i}NC, followed by 3 equiv of CyNC yielded fused six-membered *N*-heterocycles (**62**), (**63**), and (**64**), respectively.[24]



(**62**)



(**63**)

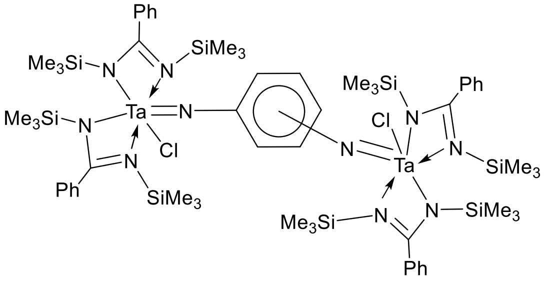


(**64**)

2.45.9. *Amidinate and guanidinate ligands*

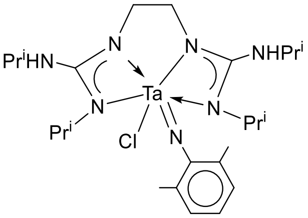
Reactions of Ta(=NBu^t)Cl_3(py)$_2$ with 2 equiv of Li[(NR)$_2$(CMe)] (R = Pr^i, Bu^t) gave Ta(=NBu^t)[NR)$_2$(CMe)]$_2$Cl.[85] Treatment of Ta(=NBu^t)[(NR)$_2$(CMe)]$_2$Cl with various lithium amides LiNR′R″ gave a family of amidinate amide complexes, Ta(=NBu^t)[NR)$_2$(CMe)]$_2$(NR′R″) (For R = Pr^i, R′ = R″ = Me; R′ = R″ = Et; R′ = Et, R″ = Me; For R = Bu^t , R′ = R″ = Me; R′ = R″ = Et; R′ = Et, R″ = Me).[85] These complexes were used as candidates for thin film growth.[85] Ta(MeCN)$_2$Cl$_3$]$_2$(μ-1,n-NC_6H_4N) (n = 3, 4) reacted with two equiv of Li[PhC($NSiMe_3$)$_2$] to give benzamidinato complexes {Ta[($NSiMe_3$)$_2$(CPh)]$_2$Cl}$_2$(μ-1,n-NC_6-H_4N)] (**65**).[56] Reaction of Ta(=NBu^t)(CH_2Ph)$_3$ with diisopropylcarbodiimide gave the amidinate complex

$Ta[(NPr^i)_2C(CH_2Ph)]_2(=NBu^t)(CH_2Ph)$, which could only be characterized via NMR spectroscopic studies.[86]



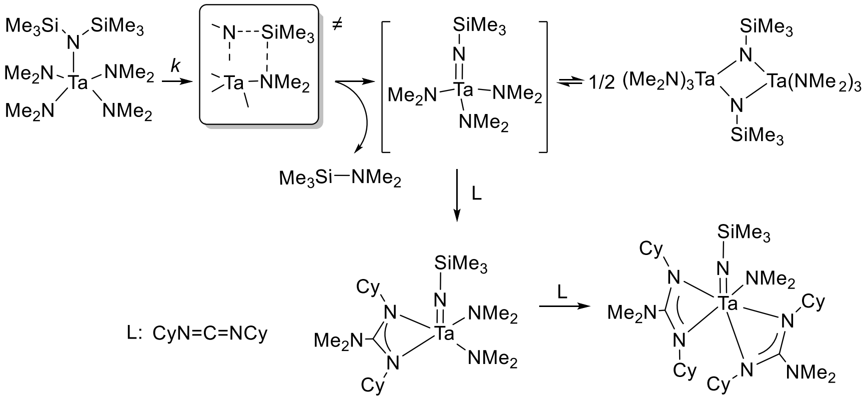
(**65**)

$[Bu^tNC(NMe_2)NEt]Ta(NMe_2)_4$ was synthesized from the addition of 1-t-butyl-3-ethylcarbodiimide to $Ta(NMe_2)_5$.[82] Reaction of isopropylcarbodiimide with $Ta(=NBu^t)(NRR')_3$ ($R = R' = Me$; $R = Me$, $R' = Et$; $R = R' = Et$) gave complexes $Ta[NPr^i)_2C(NRR')]_2(=NBu^t)(NRR')$.[87] MOCVD experiments were conducted with these complexes to make TaN thin films.[87] Similar guanidinate complexes $Ta(=NR)(NR''R''')[C(NR''R''')(NR')_2]_2$ (For $R = Bu^t$, $R' = Pr^i$, $R'' = R''' = Me$; $R'' = Me$, $R''' = Et$; $R'' = R''' = Et$; For $R = Bu^t$, $R' = Cy$, $R'' = R''' = Me$; $R'' = Me$, $R''' = Et$; $R'' = R''' = Et$; For $R = Pr^n$, $R' = Pr^i$, Cy, $R'' = R''' = Et$) were also prepared via similar methods using different carbodiimides.[88] Biguanidinate $[L_4^{Pr}]Ta(=N\text{-}2,6\text{-}Me_2C_6H_3)Cl$ ($L_4^{Pr} = \kappa^4$-*N,N,N,N*- $[Pr^iNC(NHPr^i)N(CH_2)_2NC(NHPr^i)NPr^i]^{2-}$, **66**) was synthesized by reaction of $Li_2[L_4^{Pr}]$ with the imide $Ta(=N\text{-}2,6\text{-}Me_2C_6H_3)Cl_3(thf)_2$.[89] Crystal structure was solved for the thf adduct obtained from a solution mixture of thf-Et_2O.[89]



(**66**)

Reaction of $TaCl_5$ with $LiNMe_2$, in addition to giving $Ta(NMe_2)_5$, unexpectedly afforded $M(NMe_2)_4(\kappa^2$-*N,N*-$MeNCH_2NMe_2)$ containing a chelating ligand in ca. 5–10% yield.[90] $Ta(NMe_2)_4[N(SiMe_3)_2]$ undergoes the elimination of Me_3Si-NMe_2, converting the amide $N(SiMe_3)_2$ ligand to the imide $=NSiMe_3$ ligand, to give "$Ta(NMe_2)_3(NSiMe_3)$" which was observed as its dimer (Scheme 4).[91] Kinetic study of the α-$SiMe_3$ abstraction gives $\Delta H^{\neq}$ = 21.3(1.0) kcal/mol and $\Delta S^{\neq}$ = –17(2) eu. CyN=C=NCy captures "$Ta(NMe_2)_3(=NSiMe_3)$" to yield guanidinates $Ta(NMe_2)_{3-n}(=NSiMe_3)[CyNC(NMe_2)NCy]_n$ (n = 1, 2).[91] The dimer $Ta_2(NMe_2)_6(\mu$-$NSiMe_3)_2$ could also be prepared from $Ta(=NSiMe_3)Cl_3(py)_2$ and $LiNMe_2$.[91]

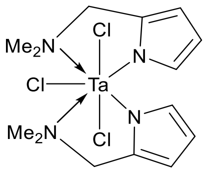


Scheme 4

DFT calculations were used to model the rare α-elimination of square pyramidal $Ta(NMe_2)_4[N(SiMe_3)_2]$ to form $Ta(=NSiMe_3)(NMe_2)_3$ and Me_3SiNMe_2.[92] In the presence of the carbodiimde, MeN=C=NMe, $Ta(=NSiMe_3)(NMe_2)_3$ was trapped as the mono- and biguanidinate-substituted products $Ta(=NSiMe_3)(NMe_2)_2[MeNC(NMe_2)NMe]$ and $Ta(=NSiMe_3)(NMe_2)[MeNC(NMe_2)NMe]_2$.[92]

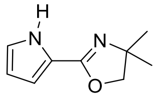
2.5.10. *Pyrrole and oxazoline ligands*

Reaction of $Li[N\text{-}2\text{-}(CH_2NMe_2)C_4H_3]$ with $TaCl_5$ yielded $[N\text{-}2\text{-}(CH_2NMe_2)C_4H_3]_2TaCl_3$ (**67**).[93] The two pyrrolyl ligands are fluxional as shown via variable-temperature (VT) NMR spectroscopic studies.[93]



(**67**)

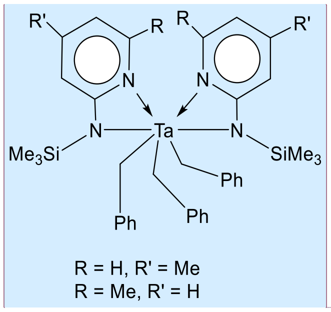
Oxazoline complexes $[OX]Ta(NMe_2)_4$ and $[OX]_2Ta(NMe_2)_3$ (HOX = 4,4-dimethyl-2-pyrrole-2-oxazoline) were synthesized via reaction of $Ta(NMe_2)_5$ with HOX.[94] The crystal structures of both complexes show a distorted octahedral geometry involving the κ^2-*N,N*-OX ligand.[94]



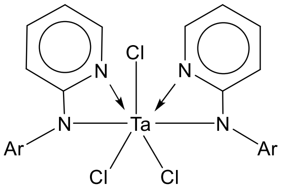
4,4-Dimethyl-2-pyrrole-2-oxazoline (HOX)

2.5.11. *Aminopyridinate ligands*

Reaction of (4-methylpyridin-2-yl)(trimethylsilyl)amine or (6-methylpyridin-2-yl)(trimethylsilyl)amine with $Ta(CH_2Ph)_5$ gave complexes (**68**) (R = H, R′ = Me; R = Me, R′ = H).[95] (2,6-diisopropylphenyl)(pyridin-2-yl)amine was treated with Bu^nLi, followed by its slow addition to $TaCl_2(CH_2Ph)_3$. The process resulted in the formation of $Ta[NC_5H_5NAr]_2(CH_2Ph)_3$ (Ar = $2,6\text{-}Pr^i{}_2C_6H_3$), which has ~~with~~ an analogous structure to those of (**68**).[95] Direct reaction of $TaCl_5$ with either (2,6-diisopropylphenyl)(pyridin-2-yl)amine or lithiated reagent [from adding Bu^nLi to (2,6-diisopropylphenyl)(pyridin-2-yl)amine, as described above] afforded $Ta[NC_5H_5NAr]_2Cl_3$ (**69**) which, after activated by polymethylaluminoxane, has low activity as ethylene polymerization catalysts.[95]



(**68**)



(**69**)

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2.~~4~~5.12. *Imide ligands*

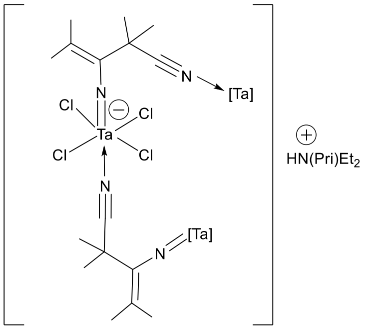
As indicated in Section 2.~~4~~5.2, reaction of $TaCl_5$ with Bu^tNH_2 in the presence of pyridine yielded the amide imide complex $Ta(=NBu^t)(NHBu^t)Cl_2$(p~~p~~y)$_2$.[62]

$(silox)_3Ta=NR$ were prepared through 1,2-H_2 elimination by heating amide hydride complexes $(silox)_3(H)TaNHR$ (R = H, Me, Bu^n, C_6H_4-*p*-X, Li, $SiMe_3$; X = H, Me, NMe_2, CF_3).[16] Though the imido complexes $(silox)_3Ta=N-N=Ta(silox)_3$ could not be synthesized, similar complexes $(silox)_2(Cl)Ta=N-N=Ta(Cl)(silox)_2$ and $(silox)_2(Me)Ta=N-N=Ta(Me)(silox)_2$ were prepared ~~Imido complex $(silox)_3Ta=N-N=Ta(silox)_3$ was synthesized from $(silox)_3Ta$~~.[16]

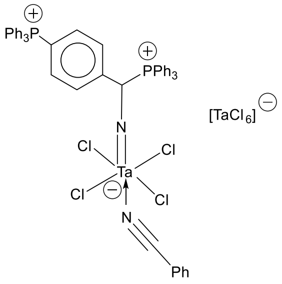
NMR-scale reaction of $(silox)_2Ta(pyrr)(\eta^2$-*N,C*-$NC_5H_5)$ or $(silox)_2Ta(pip)Ta(\eta^2$-*N,C*-$NC_5H_5)$ with H_2NMe led to the formation of imido complexes $(silox)_2Ta(pyrr)(=NMe)$ and $(silox)_2Ta(pip)(=NMe)$, respectively.[31]

Zwitterionic vinylimido complexes $Ta[=NC(=CRR')NEt_3]Cl_4(L)$ (R = R′ = H, L = Cl; R = H, R′ = Me, L = MeCN; R = R′ = Me, L = Pr^iCN) were synthesized from the reactions of $TaCl_5$ and NEt_3 with nitriles MeCN, EtCN, and Pr^iCN.[96] Reaction of $TaCl_5$

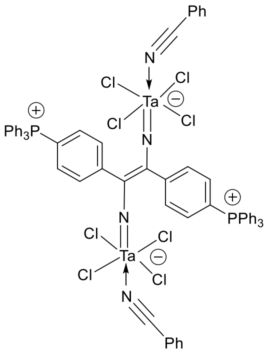
with NPr$^{i}_{2}$Et in the presence of excess Pr^{i}CN yielded the polymer (**70**).[96] Reaction of $TaCl_5$ with PhCN and PPh_3 gave zwitterionic compound (**71**).[97] The formation of this compound was followed by EPR at different stages.[97] Addition of NPr$^{i}_{2}$Et to (**71**) gave (**72**).[97] $Ta[NC(PPh_3)CH_2]Cl_4(CH_3CN)$ (**73**) and $(TaCl_4\{NC(PPh_3)CHCH(PPh_3)CN\}TaCl_4)(NCC_2H_4CN)_2$ (**74**) were prepared from reactions of $TaCl_5$ and PPh_3 with either acetonitrile and succinonitrile, respectively.[97]



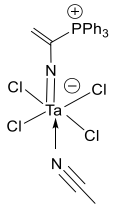
(**70**)



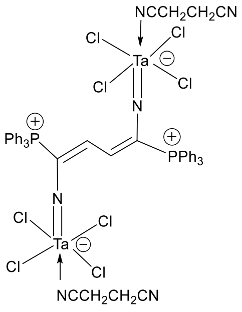
(**71**)



(**72**)



(**73**)



(**74**)

Reaction of H_2 with complex (**7**) and 4-dimethylaminopyridine (dmap) gave (mad)Ta(=NBu^t)(=NAr)(dmap) (mad = monoazabutadiene; Ar = 2,6-$Pr^i_2C_6H_3$) (**75**).[17] $(TaL_2Cl_3)_2(\mu\text{-}1,n\text{-}NC_6H_4N)$ (L = MeCN, 4-Bu^{t}py, n = 2, 3, 4; **76**) were synthesized via reactions of $TaCl_5$ with the applicable *N,N,N′,N′*-tetrakis(trimethylsilyl) -1,4-, -1,3- or -1,2-phenylenediamine and free MeCN or 4-Bu^{t}py.[56] Treatment of $TaCl_5$ with 3,5-lutidine (3,5-$Me_2C_5H_3N$) and $HN(SiMe_3)_2$ yielded $Ta(=NSiMe_3)Cl_3(NC_5H_3Me_2\text{-}3,5)_2$, which was found to be an effective precursor for low pressure chemical vapor deposition (LPCVD) of TaN thin films.[98]

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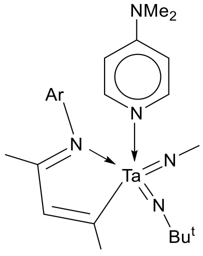
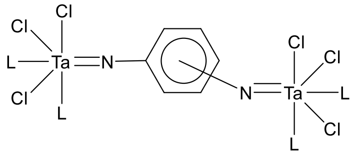
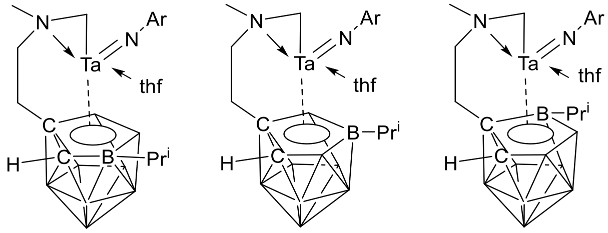




n = 2 (1,2 or ortho)
n = 3 (1,3 or meta)
n = 4 (1,4 or para)

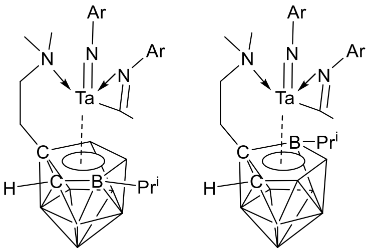
(**75**) (**76**)

Reaction of [η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]$TaMe_3$ (**12**), discussed in Section 2.2, with 2,6-dimethylphenyl isonitrile (Ar-NC) afforded three regioisomers of {σ:η^1:η^5-[MeN(CH_2)CH_2CH_2]($CHMe_2$)$C_2B_9H_9$}Ta(=N-Ar)(thf) (Ar = 2,6-$Me_2C_6H_3$, **77**).[22] When (**12**) reacted with 2-3 equiv of ArNC, two isomers of [η^1:η^5-($Me_2NCH_2CH_2$)($CHMe_2$)$C_2B_9H_9$]Ta(=N-Ar)(η^2-*C,N*-MeC=N-Ar) (**78**) were synthesized.[22] When (**12**) was treated with bulkier 2,6-diisopropylphenyl isonitrile (Ar′NC, Ar′ = 2,6-Pr^i_2-C_6H_3), the reaction gave afford [η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Ta(=N-Ar′)(η^2-*C,N*-MeC=N-Ar′) (**79**).[22]



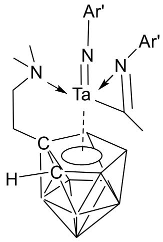
Ar = 2,6-$Me_2C_6H_3$

(**77**)



Ar = 2,6-$Me_2C_6H_3$

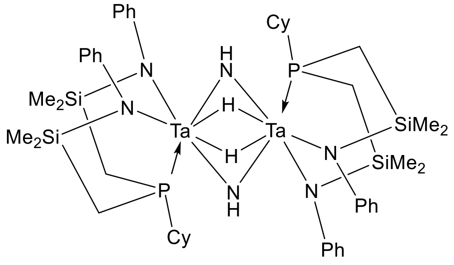
(**78**)



Ar' = 2,6-$Pr^i_2C_6H_3$

(**79**)

Imide $([NPN^{Cy}]Ta)_2(\mu\text{-}NH)_2(\mu\text{-}H)_2$ (**80**, $[NPN^{Cy}]^{2-}$ = $CyP(CH_2SiMe_2NPh)_2{}^{2-}$) was formed from the addition of hydrazine H_2NNH_2 to Ta(IV) dimer $([NPN^{Cy}]Ta)_2(\mu\text{-}H)_4$.[99] Reaction of the phenyl analog $([NPN^{Ph}]Ta^{IV})_2(\mu\text{-}H)_4$ ($[NPN^{Ph}]^{2-}$ = $PhP(CH_2SiMe_2NPh)_2{}^{2-}$] with H_2NNH_2 gave an analogous product $([NPN^{Ph}]Ta)_2(\mu\text{-}NH)_2(\mu\text{-}H)_2$.[99]

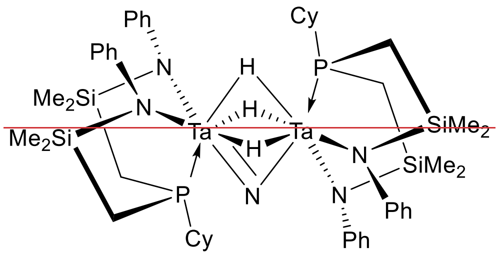


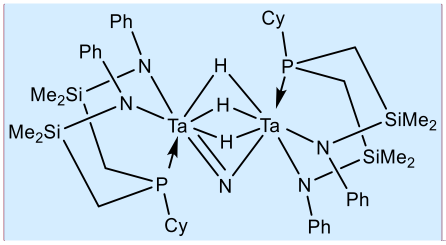
(**80**)

As discussed later in Section 2.~~6~~7.10, hexatantalum tetradecaimido clusters $(ArN)_{14}Ta_6O$ (**130**), Ar = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-$Bu^tC_6H_4$, *p*-BrC_6H_4, *m*-ClC_6H_4) and $(Cp^*{}_2Co)[(ArN)_{14}Ta_6O]$ were prepared.[100, 101]

2.~~4~~5.13. *Nitride complexes*

Nitride ([NPN^{Cy}]Ta)$_2$(μ-N)(μ-H)$_3$ (**81**, [NPN^{Cy}]$^{2-}$ = CyP(CH$_2$SiMe$_2$NPh)$_2$$^{2-}$) was formed from the addition of 1,1-dimethylhydrazine Me$_2$NNH$_2$ to Ta(IV) dimer ([NPN^{Cy}]Ta)$_2$(μ-H)$_4$.[99]





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(**81**)

Cluster compound Ta$_5$(μ$_5$-N)(μ$_3$-NPr^i)$_2$(μ-NPr^i)$_6$(η^1-NPr^i)$_4$(η^1-NHPr^i)$_2$ (**82**) was prepared from the reaction of Ta(NMe)$_5$ with excess Pr^{i}NH$_2$.[102] The cluster contains 76 valence electrons, assuming that the edge-bridging imide ligands, located around a basal–apical Ta–Ta vectors, serve as 2e donating ligands. The molecular framework was rationalized by polyhedral skeletal electron pair (PSEP) theory.[102]

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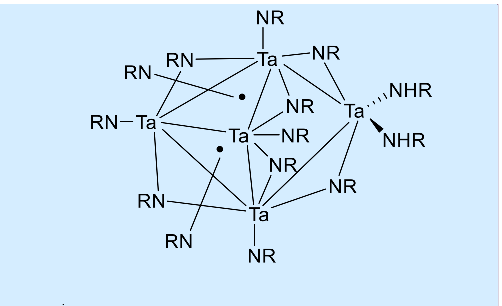


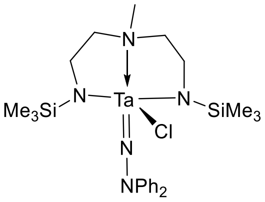
R = Pr^i; Interstitial nitrides have been omitted for clarity

(**82**)

DFT calculations were also performed on the reduction of CO_2 gas by $(Bu^tArN)_3M{\equiv}N$ (M = V, Ta, Nb; Ar = 3,5-$Me_2C_6H_3$).[103] Amongst the metal complexes studied, the Ta complex had the strongest activity to activate CO_2.[103]

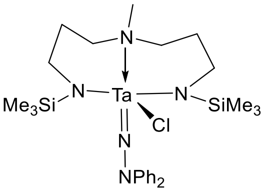
2.~~4~~5.14. *Dianionic tridentate ligands*

$(dme)Ta(=NNPh_2)Cl_3$ reacted with $MeN[(CH_2)_nN(SiMe_3)]_2Li_2$ (n = 2, 3), affording the bis(amide)amine hydrazido complexes (κ^3-$MeN[(CH_2)_nN(SiMe_3)]_2$)$Ta(=NNPh_2)Cl$ (**83, 84**).[54]



n = 2

(**83**)



n = 3

(**84**)

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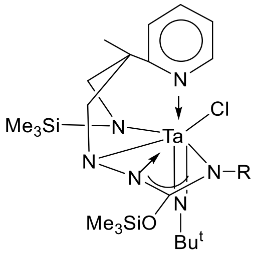
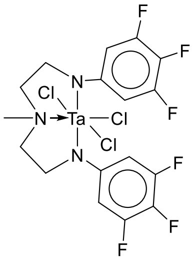
Complexes (**85**) were prepared via reactions of Ta(=NBu^t)(N$_2$N$_{py}$)Cl(py) [N$_2$N$_{py}$ = MeC(2-C$_5$H$_4$N)(CH$_2$NSiMe$_3$)$_2$] with Bu^{t}NCO or *p*-tolyl isocyanate.[104] These complexes were compared against similar cationic W complexes including DFT calculations.[104, 105]



R = Bu^t, *p*-C$_6$H$_4$Me

(**85**)

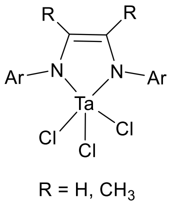
[F$_3$N$_2$NMe]TaCl$_3$ ([F$_3$N$_2$NMe]$^{2-}$ = [(3,4,5-F$_3$C$_6$H$_2$NCH$_2$CH$_2$)$_2$NMe]$^{2-}$, **86**) was prepared via slow addition of TaCl$_5$ to H$_2$[F$_3$N$_2$NMe].[32]



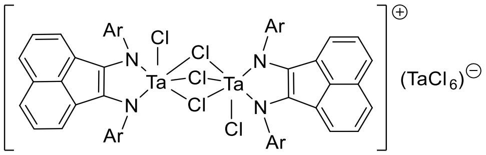
(**86**)

2.~~4~~5.15. *Miscellaneous dianionic ligands*

Reactions of α-diimines DAD^{Dip} or DAD^{Dip}-Me,Me [DAD = 1,4-diaza-1,3-dienes; DAD^{Dip} = ArN=C(H)C(H)=NAr; DAD^{Dip}-R,R' = ArN=C(R)C(R')=NAr; Ar = 2,6-$Pr^i_2C_6H_3$] with $TaCl_5$, followed by the addition of reductant 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (mbtcd), gave [DAD^{Dip}]$TaCl_3$ or (DAD^{Dip}-Me,Me)$TaCl_3$ (**87a,b**), respectivley.[52] When R and R′ belong to a single acenaphthene group, [DAD^{Dip}-acenaphthene]TaCl]$_2$(μ-Cl)$_3$]($TaCl_6$) was prepared (**88**).[52] (Cp_2Co){[DAD^{Dip}]$TaCl_4$} was prepared from the reduction of (DAD^{Dip})$TaCl_4$, as discussed in Section 3.3.1. [52]



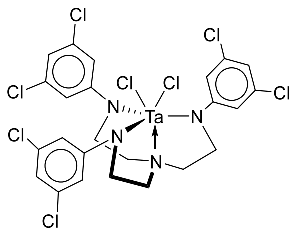
(**87a,b**)



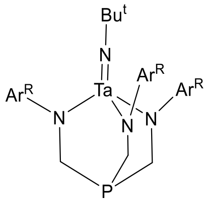
(**88**)

2.~~4~~5.16. *Other trianionic ligands*

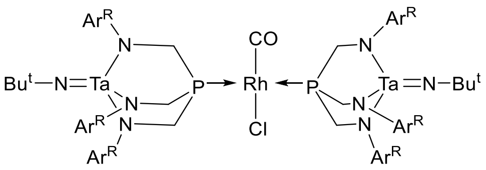
Reaction of $TaCl_5$ to $H_3[Cl_2N_2NMe]$ ($[Cl_2N_2NMe]^{3-}$ = $[(3,5\text{-}Cl_2C_6H_3NCH_2CH_2)_3N]^{3-}$) produced $[Cl_2N_2NMe]TaCl_2$ (**89**).[32] [P(CH$_2$NAr^R)$_3$]Ta=NBu^t (Ar^R = 3,5-$R_2C_6H_3$; R = H, Me, CF_3) (**90**) were prepared from the precursors [P(CH$_2$NAr^R)$_3$]H_3 with Ta(=NBu^t)(NEt$_2$)$_3$.[106] When P(CH$_2$NAr^R)$_3$Ta=NBu^t was reacted with $Rh_2(CO)_4$(μ-Cl)$_2$, *trans*-Cl(CO)Rh[P(CH$_2$NAr^R)$_3$Ta(=NBu^t)]$_2$ formed (**91**).[106]



(**89**)



(**90**)



(**91**)

[κ^3-N(CH$_2$in)$_2$(CH$_2$inH)]Ta(NMe$_2$)$_3$ (**92**, N(CH$_2$inH)$_3$ = tris[(2-indole)methyl]amine~~,~~ ~~**92**~~) was prepared via the reaction of equimolar portions of Ta(NMe$_2$)$_5$ and N(CH$_2$inH)$_3$.[107] Reaction of [κ^3-N(CH$_2$in)$_2$(CH$_2$inH)]Ta(NMe$_2$)$_3$ with MeLi yielded the tetradentate, tripodal complex [κ^4-N(CH$_2$in)$_3$]Ta(NMe$_2$)$_2$ (**93**), where the third inldolyl group coordinated to the Ta center.[107] [κ^4-N(CH$_2$in)$_3$]Ta(NMe$_2$)Cl was made from Me$_3$SiCl and (**93**).[107] Amino-imido complex [κ^4-N(CH$_2$in)$_3$]Ta(=NAr)(NHMe$_2$) (Ar = 2,6-Pr$^i_2$C$_6$H$_3$) was synthesized from the addition of N(CH$_2$inH)$_3$ to a solution of Ta(=NAr)(NMe$_2$)$_3$.[107] If [κ^4–N(CH$_2$in)$_3$]Ta(=NAr)(NHMe$_2$) were treated with MeI, a rapid equilibrium was established between that complex and [(κ^4-N(CH$_2$in)$_3$]Ta=NAr and (Me$_3$NH)I, which was monitored via ^{1}H NMR spectroscopy.[107]

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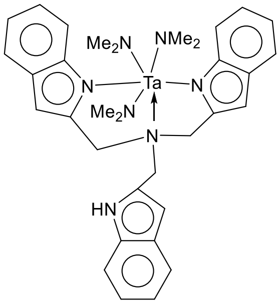
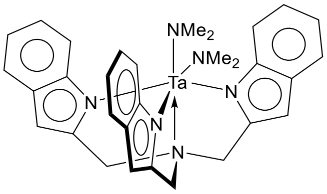


(**92**)

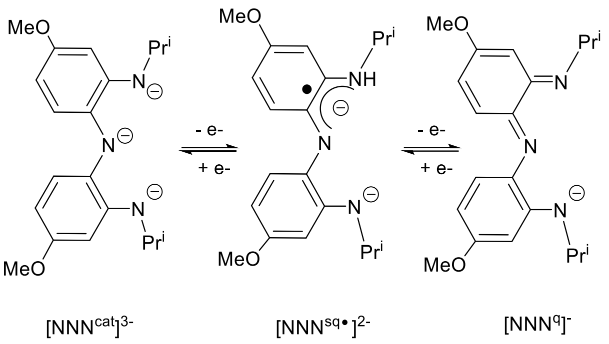


(**93**)

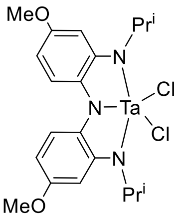
[NNN^{cat}]TaCl$_2$ ([NNN^{cat}]H$_3$ = bis(2-isopropylamino-4-methoxyphenylamine, **94**) was made via the reaction of [NNN^{cat}]H$_3$ with ~~TaCl$_2$(MMe)$_3$~~ TaMe$_3$Cl$_2$.[108] Reaction of [NNN^{cat}]TaCl$_2$ with Bu^{t}NC, a σ-donating ligand, formed [NNN^{cat}]TaCl$_2$(CNBu^t).[108] [NNN^{cat}]$^{3-}$ could be oxidized by one electron to form the radical, semiquinone ligand [NNN$^{sq\bullet}$]$^{2-}$. The removal of one more electron formed the quinone form [NNN^{q}]$^{-}$ (Scheme 5). [NNN^{cat}]TaCl$_2$ reacted with PhICl$_2$, Ar′N$_3$ (Ar′ = Ph, *p*-tolyl, *p*-C$_6$H$_4$Bu^t), and Ph$_2$CN$_2$ to form [NNN$^{sq\bullet}$]TaCl$_3$, [NNN^{q}]TaCl$_2$(=NAr’), and [NNN^{q}]TaCl$_2$(NNCPh$_2$), respectively. EPR and CV studies were conducted on [NNN$^{sq\bullet}$]TaCl$_3$.[108] ^{X,R}[NNN^{cat}]H$_3$ (For R = Pr^i, X = F, H, Me, Bu^t, OMe; For R = dmp, X = OMe) and derivatives of the [NNN^{cat}]$^{3-}$ complexes, where electron-donating groups were on the 4,4′ positions, were prepared in order to probe the electronic effects on the ligands. From the reactions of these derivatives with ~~TaCl$_2$(MMe)$_3$~~ TaMe$_3$Cl$_2$, ^{X,R}[NNN^{cat}]TaCl$_2$ (**95**) were prepared.[109] ^{OMe,dmp}[NNN^{cat}]TaCl$_2$ complex shows an affinity for weakly coordinating solvents and has one OEt$_2$ ligand coordinating to the Ta center in its crystal structure. ^{X,R}[NNN^{cat}]TaCl$_2$ reacted with [N(CH$_2$Ph)Et$_3$]Cl, yielding [N(CH$_2$Ph)Et$_3$][^{X,R}(NNN^{cat})]TaCl$_3$.[109]

Commented [TC39]: Added for more information

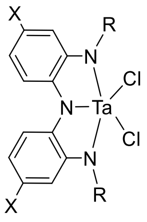
^{X,R}[NNN^{cat}]TaCl$_2$(CNBu^t), ^{X,R}[NNN$^{sq\bullet}$]TaCl$_3$, and ^{X,R}[NNN^q]TaCl$_2$(=NPh-*p*-R′) (For R = Pr^i, R′ = Bu^t, X = F, H, Me, Bu^t, OMe; For R = Pr^i, R′ = CF$_3$, X = F, OMe; For R = dmp, R′ = CF$_3$, X = OMe) were prepared using (**95**) with CNBu^t, PhICl$_2$, or (NPh-*p*-R′)N$_3$, respectively.[109]



Scheme 5



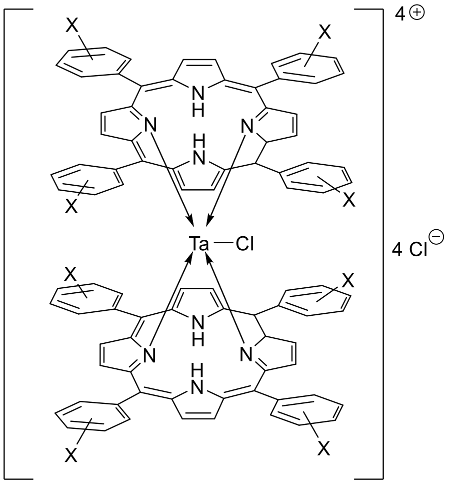
(**94**)



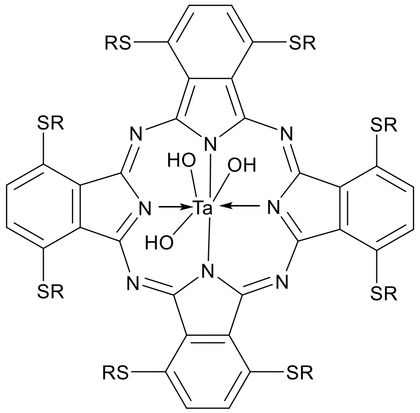
(**95**)

2.45.17. *Porphyrin, phthalocyanine, and corrole ligands*

H$_2$t(Xp)p (meso-tetraarylporphyrins) and TaCl$_5$ were ground together with a small amount of toluene to give {[H$_2$t(4-Xp)p]$_2$TaCl}Cl$_4$ (X = H, OMe, Me, Pr^i, Br, Cl) or {[(H$_2$t(3-X′p)p]$_2$TaCl}Cl$_4$ (X′ = OMe, Me, Cl, Br) complexes (**96**).[110] (HO)$_3$Ta[OPT-Pc] and $(OH)_3Ta[OOT\text{-}Pc]$ (Pc = phthlocyanine, OPT = octa-pentylthio, OOT = octa-octylthio; **97**) were synthesized by the reactions of substituted 3,6-dicyanobenzenes with anhydrous $Ta(OBu^n)_5$ in 1-pentanol in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU).[111]



(**96**)



R = $(CH_2)_4CH_3$ for OPT; $(CH_2)_7CH_3$ octyl (OOT)

(**97**)

[Mes$_2$(*p*-OMePh)corrole]TaCl$_2$ (**98**) was synthesized via the addition of [Mes$_2$(*p*-OMePh)corrole]H$_3$ and ~~Ta(MMe)$_3$Cl$_2$~~TaMe$_3$Cl$_2$.[112] [Mes$_2$(*p*-OMePh)corrole]Ta=NBu^t was prepared via a similar method using Ta(=NBu^t)(CH$_2$Ph)$_3$.[112] Several alkoxyl derivatives were also prepared from [Mes$_2$(*p*-OMePh)corrole]TaMe$_2$ and [Mes$_2$(*p*-OMePh)corrole]Ta=NBu^t, which is discussed in Section 2.~~6~~7.2.[112]

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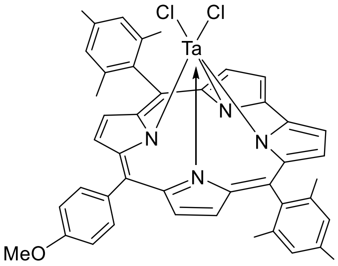
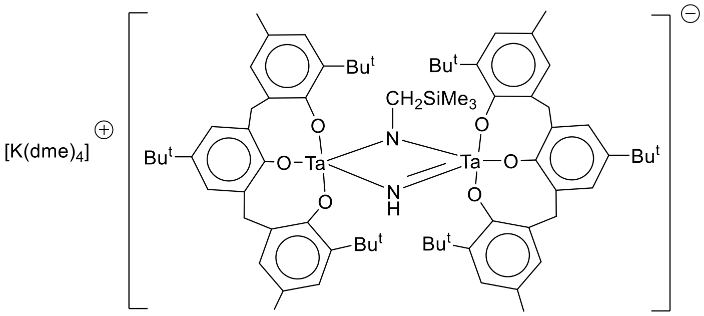


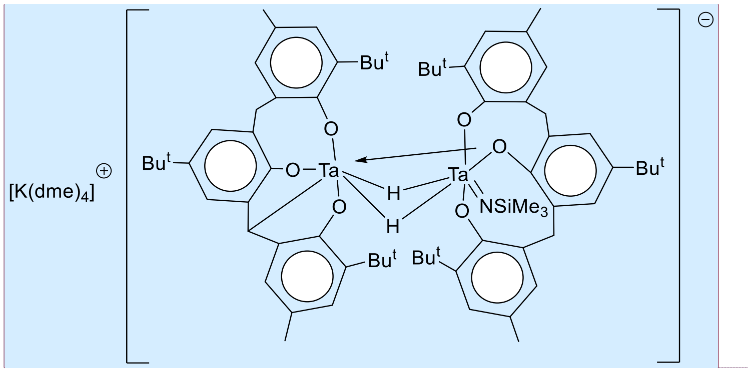
(**98**)

2.~~4~~5.18. *Imide-nitride ligands*

$\mathrm{[K(dme)_4]\{([OOO]Ta)_2(\mu\text{-}N)(\mu\text{-}NCH_2SiMe_3)\}}$ ($\mathrm{[OOO]^{3-}}$ = 2,6-bis(3-tert-butyl-5-methyl-2-oxybenzyl)-4-tertbutylphenolate, **99**) was synthesized from the addition of $\mathrm{Me_3SiCHN_2}$ to $\mathrm{[K(dme)_2]\{([OOCO]Ta)_2(\mu\text{-}H)_3\}}$ ($\mathrm{[OCOO]^{4-}}$ = cyclometalated $\mathrm{[OOO]^{3-}}$ ligand).[113] Imido $\mathrm{[K(dme)_4]\{[OOO]Ta({=}NSiMe_3)\}([OCOO]Ta)(\mu\text{-}H)_2}$ (**100**) was prepared from the reaction of $\mathrm{[K(dme)_2]\{([OOCO]Ta)_2(\mu\text{-}H)_3\}}$ with $\mathrm{Me_3SiN_3}$.[113] Upon addition of $\mathrm{Me_3SiN_3}$ to $\mathrm{[K(dme)_4]\{[OOO]Ta({=}NSiMe_3)\}([OCOO]Ta)(\mu\text{-}H)_2}$, $\mathrm{[K(dme)]\{[OOO]Ta({=}NSiMe_3)\}\{([OOO]Ta)\}(\mu\text{-}NSiMe_3)(\mu\text{-}H)}$ was preapred.[113] Treatment of $\mathrm{[K(dme)_2]\{([OOCO]Ta)_2(\mu\text{-}H)_3\}}$ with $\mathrm{NaN_3}$ yielded $\mathrm{[Na(dme)]_2\{([OOO]Ta)([OCOO]Ta)(\mu\text{-}H)_2(\mu\text{-}N)\}}$, which was unstable at room temperature, yielding $\mathrm{[Na(dme)]\{[OOO]Ta(H)\}\{[OCO]Ta(\mu\text{-}O)\}(\mu\text{-}N)[Na(dme)]}$ over time.[113]



(**99**)



(**100**)

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2.~~4~~5.19. *Precursors to solid-state materials*

The *in-situ* mechanism of the formation of Ta_2O_5 thin films by ALD using $Ta(=NBu^t)(NEt_2)_3$ and D_2O or O_3 was explored using quartz crystal microbalance (QCM) and quadrupole mass spectrometry.[114]

DFT calculations were conducted to investigate the transamination of alkylamide ligands during MOCVD conditions to make TaN films.[115] Energetics and rate constants for the ligand exchange of $Ta(=NBu^t)(NMe_2)_3$ with NH_3, the proton transfer, and dissociation of $HNMe_2$ to afford net transamination of the dimethylamido ligand were calculated to be facile at ~300 °C. The increased nitrogen content and deposition of N-rich films were consistent with the calcuated increased strength of the Ta–NH_2 bonds.[115] The mechanisms of the growth of TaN films by ALD using $Ta(=NBu^t)(NEt_2)_3$ and NH_3 were also investigated via B3LYP hybrid density functional theory.[116]

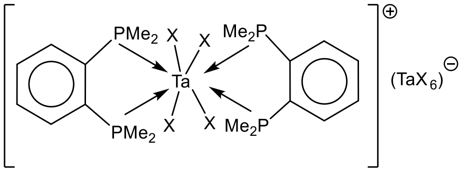
Thin TaS_2 films have been fabricated from $Ta(NMe_2)_5$ and Bu^tSH by aerosol-assisted chemical vapor deposition (AACVD) on glass at 225–450 °C. Hexanes or dichloromethane were used as solvents.[117] In order to investigate possible compounds within the aerosol mist, five equiv. of Bu^tSH was used in the reaction with $Ta(NMe_2)_5$. From this reaction, crystals of $Ta(S\text{-}Bu^t)_2(NMe_2)_3$ were isolated and its crystal structure was determined.[117]

Thin films using $Ta(=NBu^t)(NEt_2)_3$ and H_2 prepared via plasma plasma-enhanced atomic layer deposition (PEALD) were studied using various temperatures, plasma power, and duration time.[118] The film made was a homogeneous mixture of TaC, TaN, Ta_3N_5, and Ta_2O_5 phases, where O_2 from the air was incorporated into the film.[118]

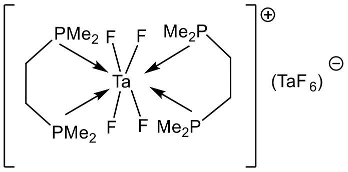
2.6. Phosphorus- and Arsenic-Based Ligands

The complex $[TaF_4(dppe)_2](TaF_6)\cdot½CH_3CN$ was produced from addition of dppe to TaF_5.[51] The adduct complex $TaCl_5\cdot PPh_3$ was prepared by adding PPh_3 slowly to a solution containing $TaCl_5$.[97]

Hepta-coordinated $Ta(PMe_3)_2Me_3Cl_2$ was produced by the addition of PMe_3 to $TaMe_3Cl_2$.[119] $\{TaX_4[o\text{-}C_6H_4(PMe_2)_2]_2\}(TaX_6)$ (X = F, Cl) (**101**), $[TaF_4(dmpe)_2](TaF_6)$ (**102**), $\{TaF_4[Et_2P(CH_2)_2PEt_2]_2\}(TaF_6)$, and $\{TaF_4[o\text{-}C_6H_4(PPh_2)_2]_2\}(TaF_6)$ were prepared from TaX_5 and phosphines $o\text{-}C_6H_4(PMe_2)_2$, $Me_2P(CH_2)_2PMe_2$, $Et_2P(CH_2)_2PEt_2$ and $o\text{-}C_6H_4(PPh_2)_2$, respectively.[120]



(**101**)



(**102**)

Phosphinidenes $(silox)_3Ta{=}PR$ was prepared through 1,2-H_2 elimination from heating $(silox)_3(H)Ta\text{-}PHR$ (R = H, Ph).[16]

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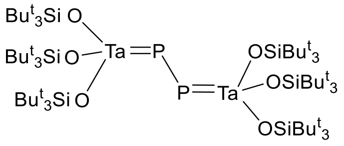
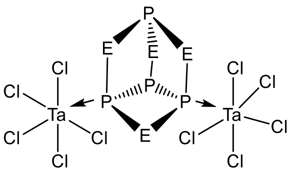
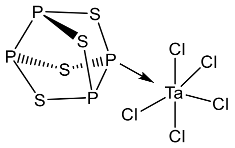
Diphosphorus-bridged complex $[(silox)_3Ta]_2(\mu\text{:}\eta^1,\eta^1\text{-}P_2)$ (**103**) was synthesized via the reaction of $(silox)_3Ta$ with P_4.[121] Complexes $(TaCl_5)_2(\beta\text{-}P_4E_4)$ (E = S, Se) (**104**) were made from P_4E_4 with $TaCl_5$.[122] $(TaCl_5)(\alpha\text{-}P_4S_4)$ (**105**), $(TaCl_5)(\alpha\text{-}P_4S_5)$ (**106**), $(TaCl_5)(\beta\text{-}P_4S_5)$ (**107**), and $(TaCl_5)(\beta\text{-}P_4S_6)$ (**108**) were prepared from $TaCl_5$.[123] $\{[BDI^{Pr}]Ta(=NBu^t)\}_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}P_4)$ (**109**) ($[BDI^{Pr}]^-$ = bis-*N,N′*-(2,6-Pr^i_2-C_6H_3)-β-diketiminate) was synthesized from a heated reaction of $[BDI]Ta(=NBu^t)(CO)_2$ with P_4.[124]



(**103**)



(**104**)



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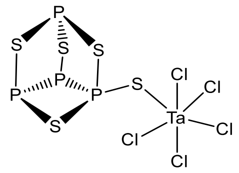

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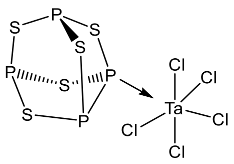
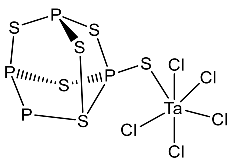
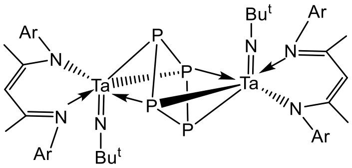


(**107**)



(**108**)



(**109**)

Arsinidenes $(silox)_3Ta{=}AsR$ was made through H_2 elimination by heating $(silox)_3(H)Ta$-$AsHR$ (R = H, Ph).[16]

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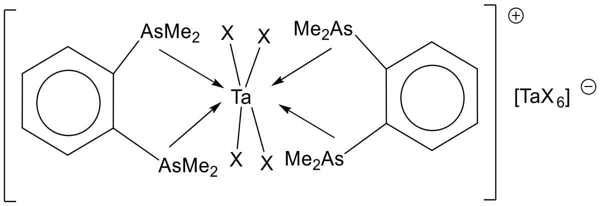
$\{TaX_4[(o\text{-}C_6H_4(AsMe_2)_2]_2\}(TaX_6)$ (X = Cl, F) (**110**) were synthesized via the addition of $o\text{-}C_6H_4(AsMe_2)_2$ to TaF_5.[120]



(**110**)

2.~~6~~7. Oxygen-Based Ligands

2.~~6~~7.1. *Ether ligands*

Dimethoxybenzenes and 1,2-diphenoxyethane acted as bidentate bridging ligands in their reactions with TaX_5 (X = F, Cl) in 1:2 molar ratio, yielding dinuclear complexes $(TaX_5)_2(\mu\text{-}\kappa^2\text{-}[O–O])$ ([O–O] = $1,4\text{-}(OMe)_2C_6H_4$, $1,4\text{-}(OMe)_2\text{-}2,5\text{-}C_6H_2F_2$, $1,3\text{-}(OMe)_2C_6H_4$, $PhO(CH_2)_2OPh$).[125] When 1,2-dimethoxybenzene reacted with TaX_5 (X = Cl, Br) in ca. 1:1 molar ratio, C–O bond cleavage occurred yielding $TaX_4[\kappa^2\text{-}OC_6H_4(2\text{-}$

OMe)] as the products.[125] Similarly when $TaBr_5$ reacted with 1,4-$(OMe)_2C_6H_4$, C-O bond cleavage led to the formation of $TaBr_4[\kappa^1\text{-}OC_6H_4(4\text{-}OMe)]$.[125]

Reactions of TaX_5 (X = Cl, Br) with other ethers (L = 2,5-dimethyltetrahydrofuran and tetrahydropyran) as well as the reaction of $TaCl_5$ with 1,4-dioxane led to the formation of hexacoordinated adducts $TaX_5(L)$.[126]

TaF_5 reacted with diethers $ROCH_2CHR'OR''$ [diethers = $MeO(CH_2)_2OMe$ (dme), $MeOCH_2CH(Me)OMe$, and $EtO(CH_2)_2OEt$] to give ionic derivatives $[MF_4(\kappa^2\text{-}ROCH_2CHR'OR'')_2](TaF_6)$ or $[TaF_4(ROCH_2CHR'OR'')_2](Ta_2F_{11})$ according to the metal/diether molar ratios.[127]

Reactions of thf with TaX_5 gave adducts $TaX_5(thf)$ (X = F, Cl).[126]

2.~~6~~7.2. *Alkoxide, hydroxyl, enolate, and related ligands*

$Ta(OCPh_2R)_3(=NBu^t)$ (R = $CH_2CMe=CH_2$) was synthesized via the reaction of $COPh_2$ with $Ta(\eta^3\text{-}CH_2CMeCH_2)_3(=NBu^t)$.[55] $(Ar'O)_2TaMe_3$ [$(OAr')^-$ = 2,6-bis(diphenylmethyl)-4-tert-butylphenoxide] and $(Ar'O)_2$Ta~~(~~M~~M~~e~~)~~Cl_2 were produced from the addition of $TaMe_3Cl_2$~~(MMe)$_3$~~ to NaOAr′ and HOAr′, respectively.[28]

Commented [XZ(47]: “Me” should not have (…).

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Reaction of hydride complex (*R*,*R*)-$Ta[O_2\text{-}3,3'\text{-}(SiMe_3)_2C_{20}H_{10}]_2(H)$ with acetophenone yielded (*R*,*R*,*R*) and (*R*,*R*,*S*) isomers of $Ta[O_2\text{-}3,3'\text{-}(SiMe_3)_2C_{20}H_{10}]_2(OCHMePh)(O=CMePh)$.[18] Upon addition of more (*R*,*R*)-$[Ta(O_2C_{20}H_{10}(SiMe_3)_2\text{-}3,3')_2(H)]$ to the NMR reaction tube, free acetophenone was consumed, leaving the complexes (*R,R,S*)/(*R,R,R*) $Ta[O_2\text{-}3,3'\text{-}(SiMe_3)_2C_{20}H_{10}]_2(OCHMePh)$ and (*R*,*R*)-$Ta[O_2\text{-}3,3'\text{-}(SiMe_3)_2C_{20}H_{10}]_2[OC(=CH_2)Ph]$ behind.[18]

In the reactions of thf with TaX_5, in addition to adducts $TaX_5(thf)$ (X = F, Cl) discussed in the previous section, $\{TaX_4(thf)[O(CH_2)_4O(CH_2)_3CH_2]\}(TaX_6)$ (X = Cl, Br, I; **111**) were also products.[126] Complexes (**111**), containing a new 4-(tetrahydrofuran-1-ium)-butan-1-oxo ligand, are believed to play a role in ~~THF~~ thf polymerization catalyzed by TaX_5.[126]

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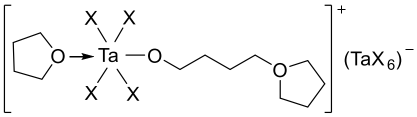


X = Cl, Br, I

(**111**)

Reactions of TaF_5 with $ROSiMe_3$ (R = Me, Et, Ph) in 1:1 and 1:2 molar ratios gave alkoxides $TaF_4(OR)$ and $TaF_3(OR)_2$, respectively.[128] When TaF_5 reacted with $MeOSiMe_3$ in 1:3 molar ratio, $TaF_2(OMe)_3$ was the product.[128]

When $EtOSiMe_3$ reacted with $TaCl_5$, elimination of $ClSiMe_3$ was observed, yielding $TaCl_4(OEt)$.[129]

Reactions of TaX_5 (X = Cl, Br) with dimethoxymethane $CH_2(OMe)_2$ afforded $TaX_5[OMe(CH_2X)]$ and $[TaX_3(OMe)(\mu\text{-}OMe)]_2$.[130]

Reactions of $TaCl_5$ with 3 equiv of epoxides (1,2-epoxybutane and epoxycyclohexane) and $TaBr_5$ with 3 equiv of ethylene oxide gave dinuclear dihalide tris(2-haloalcoholato) complexes $[TaX_2(OR)_2(\mu\text{-}OR)]_2$ [X = Cl, R = $-CH(Et)CH_2Cl$, $-CH(CH_2)_4CHCl$; X = Br, R = $-CH_2CH_2Br$] through multiple epoxide insertion into metal–

halide bonds.[131]

$Li\{Ta[OCH(CF_3)_2]_6\}$ was synthesized from $TaCl_5$ and $Li[OCH(CF_3)_2]$.[132]

Alkyl amide imide complex $Ta(=NSiMe_3)[N(SiMe_3)_2](CH_2Bu^t)_2$ reacted with O_2, leading to the selective insertion of oxygen into the two Ta-alkyl bonds to yield alkoxy complex $Ta(=NSiMe_3)[N(SiMe_3)_2](OCH_2Bu^t)_2$.[133] In reactions of O_2 with these d^0 complexes, oxidation of the ligands was the prevailing pathway.[133-136] $Ta(=NSiMe_3)[N(SiMe_3)_2](OCH_2Bu^t)_2$ underwent the following ligand exchange to give $Ta_2(\mu\text{-}NSiMe_3)_2(OCH_2Bu^t)_6$ and $Ta(=NSiMe_3)[N(SiMe_3)_2]_2(OCH_2Bu^t)$,[133] reaching the equilibrium:

2 $Ta(=NSiMe_3)[N(SiMe_3)_2](OCH_2Bu^t)_2$ $\rightleftharpoons$ ~~=~~ ½ $Ta_2(\mu\text{-}NSiMe_3)_2(OCH_2Bu^t)_6$ + $Ta(=NSiMe_3)[N(SiMe_3)_2]_2(OCH_2Bu^t)$

$[K_{eq} = 2.10(11) \times 10^{-4}$ at 296 K; $\Delta G^o_{296K} = 4.98(3)$ kcal].[133]

$Ta(=NSiMe_3)[N(SiMe_3)_2](OCH_2Bu^t)_2$ and $Ta(=NSiMe_3)[N(SiMe_3)_2]_2(OCH_2Bu^t)$ were also prepared from the reactions of $\{Ta(\mu\text{-}Cl)Cl(=NSiMe_3)[N(SiMe_3)_2]\}_2$ with $LiOCH_2Bu^t$ and $LiN(SiMe_3)_2/LiOCH_2Bu^t$, respectively.[133] When $TaMe_2(=NSiMe_3)[N(SiMe_3)_2]$, methyl analog of $Ta(=NSiMe_3)[N(SiMe_3)_2](CH_2Bu^t)_2$, was exposed to 1 equiv of O_2, the reaction also led to the formation of dialkoxy dimer $Ta_2(\mu\text{-}OMe)_2(OMe)_2(=NSiMe_3)_2[N(SiMe_3)_2]_2$ as *cis*/*trans* isomers.[137] However, when only 0.5 equiv of O_2 was used, the alkoxy-bridged alkyl dimer $Ta_2(\mu\text{-}OMe)_2Me_2(=NSiMe_3)_2[N(SiMe_3)_2]_2$ was the product as *cis*/*trans* isomers.[137] Only the *trans* alkoxy-bridged alkyl dimer crystalized in the solid. When dissolved, the *trans* isomer was converted to the *cis* isomer till the equilibrium: *trans* ~~$\rightleftarrows$~~$\rightleftharpoons$ *cis* was established with K_{eq} = 0.79(0.02) at 2~~3.1~~5.0(0.1) °C.[137] Kinetic studies of the exchange gave the rate constants k = 0.018(0.002) min^{-1} for the *trans* → *cis* conversion and k' = 0.022(0.002) min^{-1} for the reverse *cis* → *trans* conversion at ~~23~~25.~~1~~0(0.1) °C for $Ta_2(\mu\text{-}OMe)_2Me_2(=NSiMe_3)_2[N(SiMe_3)_2]_2$.[137]

$Ta(=NBu^t)Cl_2(O\text{-}2,6\text{-}Pr^i{}_2C_6H_3)(py)_2$ was prepared from $TaCl_3(=NBu^t)(py)_2$ and $LiO\text{-}2,6\text{-}Pr^i{}_2C_6H_3\cdot thf$.[138]

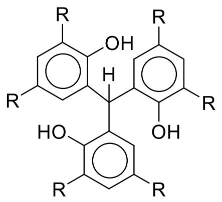
Treatment of $Ta(OMe)_5$ with $CoCl_2$ or the reaction of ~~$[Na][Ta(OMe)_6]$~~ $NaTa(OMe)_6$ with $CoCl_2$ produced ionic complex $[Co_2Ta_2(OMe)_{12}(MeCN)_4][CoCl_3(MeCN)]_2$ containing a planar $M_4(\mu_3\text{-}OMe)_2(\mu\text{-}OMe)_4$ core.[139]

Commented [XZ(51]: I have used this formula in other places of the manuscript, including, e.g., $KTa(OPr^i)_6$ and $KOPr^i$ on p. 67 below the structure of **113**. Also, Tl(OTf) on p. 69.

Mixing $Ta(OEt)_5$ and $SnCl_4$ in a mixture of toluene and EtOH gave $(EtOH)(EtO)_3Ta(\mu\text{-}OEt)_2SnCl_4$, which, when was recrystalized from a solution in toluene and Pr^iOH, yielded $(Pr^iOH)(OPr^i)_3Ta(\mu\text{-}OEt)_2SnCl_4$ retaining the heterometallic $Ta(\mu\text{-}OEt)_2Sn$ core.[140] These complexes may be used to make halide-free spinodal form of Ta(V)-doped $TiO_2\text{-}SnO_2$ as a potential thermoelectric material.[140]

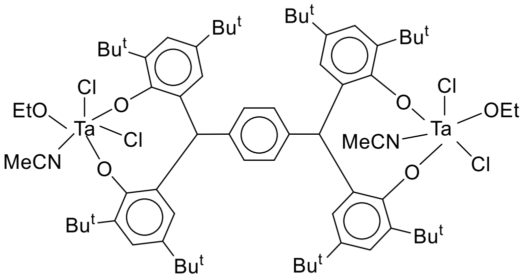
Reactions of $Ta(OR)_5$ (R = Me, Et) with pinacol and Et_3N gave $Ta(O_2C_6H_{12})_2(OC_6H_{12}OH)$.[141]

Reaction of $TaCl_5$ with tris(3,5-di-t-butyl-2-hydroxy)methane and Et_3N gave $(Et_2NH_2)[TaCl_3(O\text{-}2,4\text{-}Bu^t{}_2C_6H_2)_3CH]$, in which the Ta(V) center is coordinated by three Cl^- and three phenoxides of the tripodal ligand.[142]

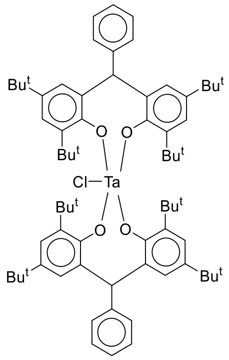


tris(3,5-di-t-butyl-2-hydroxy)methane

$TaCl_5$ reacted with α,α,α′,α′-tetra(3,5-di-t-butyl-2-hydroxyphenyl-*p*-)xylene-*para*-tetraphenol (*p*-LH_4), yielding $[TaCl_2(OEt)(NCMe)]_2(\mu\text{-}p\text{-}L)$ (**112**).[143] When $TaCl_5$ reacted with two equiv of 2,2′-$PhCH(4,6\text{-}Bu^t{}_2C_6H_2OH)_2$, $TaCl[2,2'\text{-}PhCH(4,6\text{-}Bu^t{}_2C_6H_2O)_2]_2$ (**113**) was the product.[144]



(**112**)



(**113**)

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Reactions of KTa~~2~~$(OPr^i)_6$, prepared from~~10~~ $Ta_2(OPr^i)_{10}$ with $KOPr^i$, and CdI_2 under slightly different conditions gave heterobimetallic alkoxides $[I_2Cd_2Ta(OPr^i)_7]_2$ or $\{I_2Cd[Ta(OPr^i)_6]K(HOPr^i)_2\}_4$.[145] $Ta_2(OPr^i)_{10}$ reacted with CdI_2 in thf and $Cd[N(SiMe_3)_2]_2$ in Pr^iOH/toluene, yielding $I_2CdTa(OPr^i)_5$•thf and $[CdTa(OPr^i)_7]_2$, respectively.[145]

Thermogravimetric and differential thermal analysis (TGA/DTA) of $[CdTa(OPr^i)_7]_2$ showed that it decomposed to $Cd_2Ta_2O_7$.[145]

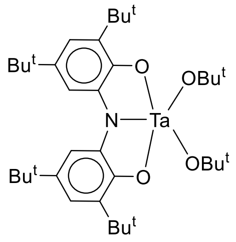
When $Ta_2(OPr^i)_{10}$ reacted with a series of glycols [HO-gly-OH = 2-methyl-2,4-pentanediol, (±)2,3-butanediol, 2,2-dimethyl-1,3-propanediol, 2-methyl-1,3-propanedio~~i~~l, 2,2-diethyl-1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol], yielding $Ta_2(O\text{-gly-}O)_4(\mu\text{-}OPr^i)_2$ based NMR spectra.[146]

Reaction of $Ta_2(OPr^i)_{10}$ with $Sr(OPr^i)_2$, prepared *in-situ* from Sr metal and $HOPr^i$, gave $SrTa_2(OPr^i)_8(\mu\text{-}OPr^i)_4(Pr^iOH)_2$.[147] When dimethyl~~ethanol~~amineethanol $Me_2NCH_2CH_2OH$ (dmae-OH) was added to solution of $SrTa_2(OPr^i)_8(\mu\text{-}OPr^i)_4(Pr^iOH)_2$, Sr–Ta complex $Sr[(\mu\text{-}OPr^i)(\mu\text{-O-dmae})Ta(OPr^i)_4]_2$ was the product.[147] $[Nb(OPr^i)_6]Pb[Ta(OPr^i)_6]$ was also reported.[148]

$([NPN^{Ph}]Ta)_2(\mu\text{-}H)_4$ ($[NPN^{Ph}]^{2-} = PhP(CH_2SiMe_2NPh)_2{}^{2-}$) reacted with CO_2 to give $([NPN^{Ph}]Ta)_2(\mu\text{-}H)_2(\mu\text{-}OCH_2O)$.[149]

Addition of 4-methylbenzyl alcohol and triphenylmethanol to [Mes_2(*p*-OMePh)corrole]Ta(=NBu^t) yielded the bis-alkoxide [Mes_2(*p*-OMePh)corrole]Ta(OCH_2-*p*-$MeC_6H_4)_2$ and the amido-alkoxide [Mes_2(*p*-OMePh)corrole]Ta($OCPh_3$)($NHBu^t$), respectively.[112]

Reaction of $[ONO^{cat}]TaMe_2$ ($[ONO^{cat}]^{3-}$ = N,N-bis(3,5-di-t-butyl-2-phenoxide)amide) with Bu^tOH gave $[ONO^{cat}]Ta(OBu^t)_2$ (**114**).[150]



(**114**)

Reaction of $Ta(OPr^i)_2[OSi(OBu^t)_3]_3$ with silica led to the formation of surface-supported hydroxide $(\equiv SiO)_3Ta(OH)_2$, which then reacted with RMe_2Si-NMe_2 (R = Me, Bu^n and Oc^n), affording $(\equiv SiO)_2Ta(OH)(OSiMe_2R)[OSi(OSiMe_2R)(OSi\equiv)_2]$ that contains the siloxide $\equiv OSiMe_2R$ ligand.[151] When silica reacted with $Ta(OPr^i)_2[OSi(OBu^t)_3]_3$ in the presence of RMe_2Si-NMe_2, the grafted complex was $(\equiv SiO)_2Ta(OH)_2[OSi(OSiMe_2R)$-$(OSi\equiv)_2]$.[151] These Ta(V) centers were catalysts for highly selective olefin epoxidation with aqueous H_2O_2.[151] Kinetic and mechanistic studies of the catalytic olefin epoxidation were conducted.[152]

Oxalate complexes $(Hphen)[Ni(phen)_3][Ta(C_2O_4)_4]$, $[Ni(phen)_3][Ta(OH)(C_2O_4)_3]$, $[Ni(phen)_3][Ta(OEt)(C_2O_4)_3]$ and $[Ni(phen)_3][Ta(OMe)(C_2O_4)_3]$ (phen = 1,10-phenanthroline) were ~~prepared~~ synthesized from tantalate(V) oxalate solutions and $[Ni(phen)_3]Cl_2$, which was prepared in-situ, ~~with~~ in different solvents.[153] Oxalatate complexes $[M(phen)_3][Ta(OEt)(C_2O_4)_3]\cdot H_2O$ (M = Fe, Co; phen = 1,10-phenanthroline) were ~~prepared~~ similarly synthesized from the reactions of $[M(phen)_3]Cl_2$ prepared in-situ and ~~an~~ aqueous (oxalato)tantalate(V) solutions containing EtOH.[154]

Bis-enolate complexes $TaMe_3(OX)_2$ (**115**; X = enolate ligands) were prepared from the K^+ salts of the enolates and ~~$Ta(MMe)_3Cl_2$~~ $TaMe_3Cl_2$.[155] Hydrogenolysis of (**115**) in pyridine led to the formation of Ta(III) complex *cis*-$Ta(OX)_2Me(py)$(2,2′-bipyridine) and Ta(V) bis-pyridyl complex *cis*-$Ta(OX)_2Me(py)(pyridyl)_2$.[155]

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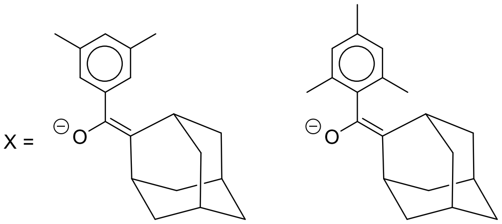


OX ligands in (**115**)

Reaction of ketimide chloride Ta~~(~~Cl~~)~~$(N{=}CBu^t_2)_4$ with Tl(OTf) gave $Ta(OTf)(N{=}CBu^t_2)_4$.[75]

Dinuclear complexes $[(\eta^2\text{-}RC{\equiv}CR)TaCl_2]_2(\mu\text{-}OMe)_2(\mu\text{-thf})$ (R = Et or Pr^n) were synthesized by treating $(\eta^2\text{-}RC{\equiv}CR)TaCl_3(dme)$ (R = Et or Pr^n) with NaOMe in thf.[156] When a mixture of $[(\eta^2\text{-}(EtC{\equiv}CEt)TaCl_2]_2(\mu\text{-}OMe)_2(\mu\text{-thf})$ and $[(\eta^2\text{-}(Pr^nC{\equiv}CPr^n)TaCl_2]_2(\mu\text{-}OMe)_2(\mu\text{-thf})$ was monitored via ^1H NMR spectroscopy, spontaneous dissociation and dimerizatation occurred to yield a mixed dinuclear tantalum−alkyne complex $[(\eta^2\text{-}(EtC{\equiv}CEt)TaCl_2][(\eta^2\text{-}(Pr^nC{\equiv}CPr^n)TaCl_2](\mu\text{-}OMe)_2(\mu\text{-thf})$.[156]

As discussed earlier in Section 2.3.3, the reactions of $Ta(=XBu^t)(CH_2Bu^t)_3$ with an NHC containg an OH group, HL (1-mesityl-3-(2-hydroxyisobutyl)imidazol-2-ylidene), yielded $Ta(=XBu^t)(L)(CH_2Bu^t)_2$ (X = N, CH; **32a,b**).[43]

Extended X-ray absorption fine structure (EXAFS) and Raman spectroscopy were used to investigate hydrolysis and condensation behavior of $Ta(OEt)_5$, revealing that it was dimeric and instantaneously underwent hydrolysis and condensation reaction upon water addition.[157] For the mixed solutions of $Ta(OEt)_5$ and prehydrolyzed $Si(OEt)_4$, EXAFS results show that the two species remain as separate entities in the solution.[157]

2.~~6~~7.3. *Siloxide ligands*

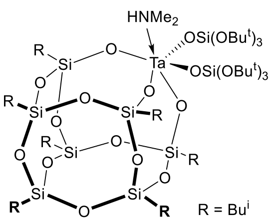
Siloxide complexes $(R_3SiO)_3TaCl_2$ (R_3 = Cy_3, Bu^t_2Ph, Bu^t_2Me, $Pr^i_2Bu^t$, Pr^i_3, Bu^t_2H) with various sized ligands have been prepared from $TaCl_5$ and R_3SiONa.[14] Studies of the reduction of these complexes and $(Bu^t_3SiO)_3TaCl_2$ by sodium amalgam suggest that $Ta^{IV}_2(OSiR_3)_6(\mu\text{-}Cl)_2$ may be a common intermediate. When the siloxide ligand was large~~ in $(Bu^t_3SiO)_3TaCl_2$~~, disproportionation of the Ta(IV) intermediate $Ta_2(OSiBu^t{}_3)_6(\mu\text{-}Cl)_2$ gave the Ta(III) species $(Bu^t_3SiO)_3Ta$ and the Ta(V) complex $(Bu^t_3SiO)_3TaCl_2$~~.~~ When the siloxide ligand was small, the Ta(IV) intermediate Ta~~^{IV}~~$_2(OSiPr^i_3)_6(\mu\text{-}Cl)_2$ was stable.[14]

$\{[BID^{Pr}](Ph_3SiO)Ta(=NBu^t)\}[B(C_6F_5)_4]$ ($[BDI^{Pr}]^-$ = bis-*N,N′*-(2,6-Pr^i_2-C_6H_3)-β-diketiminate) was synthesized via reaction of Ph_3SiOH with $\{[BDI^{Pr}]MeTa(=NBu^t)\}[B(C_6F_5)_4]$.[76, 77]

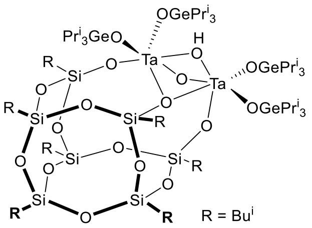
$\{Ta[OSi(SiMe_3)_3](\mu\text{-}OEt)(OEt)_3\}_2$ and $Ta[OSi(SiMe_3)_3]_3(OEt)_2$ were synthesized from the reactions of $HOSi(SiMe_3)_3$ with $Ta(OEt)_5$ in different molar ratios.[158]

$Ta(NMe_2)_3[OSi(OBu^t)_3]_2$ and $[(Pr^i_3GeO)_3Ta]_2(\mu\text{-}OH)_2(\mu\text{-}O)$ were prepared from the reactions of $Ta(NMe_2)_3Cl_2$ with $KOSi(OBu^t)_3$ and of $Ta(NMe_2)_5$ with $HOGePr^i_3$, respectively.[159] Their reactions with silsesquioxane yielded $[(Bu^tO)_3SiO]_2Ta(POSS)(HNMe_2)$ (**116**) and $[(Pr^i_3GeO)_2Ta]_2(\mu\text{-}OH)(\mu\text{-}O)(\mu\text{-}$

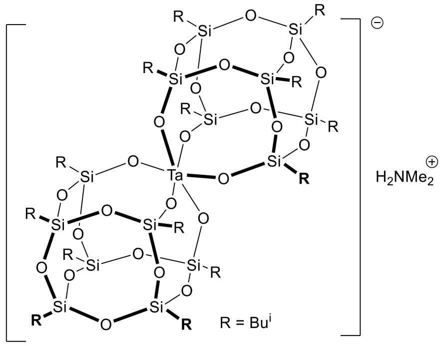
OSi)(POSS)(HNMe$_2$) (**117**), respectively.[159] In the presence of H_2O_2 and urea, (**116**) was converted to (H_2NMe_2)[Ta(POSS)$_2$] (**118**) containing two POSS ligands bridged by an octahedral TaO_6 center.[159] (**118**) was prepared independently via reaction of 2 equiv of silsesquioxane with 1 equiv of Ta(NMe$_2$)$_5$.[159] Germanoxy-containing (**117**) was efficient for the epoxidation of cyclooctene by H_2O_2.[159]



(**116**)



(**117**)



(**118**)

Ta(OEt)$_5$ reacted with 1 equiv of 1,1,3,3-tetraphenyl-disiloxane-1,3-diol, (HO)SiPh$_2$OSiPh$_2$(OH) and incompletely condensed silsesquioxane precursor $Cy_7Si_7O_9(OH)_3$ (Cy = cyclohexyl), giving disiloxanediolate

$Ta_2(OEt)_4(\mu\text{-}OEt)_2[\mu\text{-}\kappa^2\text{-}(O\text{-}Ph_2Si)_2O]_2$ and tantalasilsesquioxane derivative $Ta_2(OEt)_2(\mu\text{-}OEt)_2(Cy_7Si_7O_{12})_2$, respectively.[160]

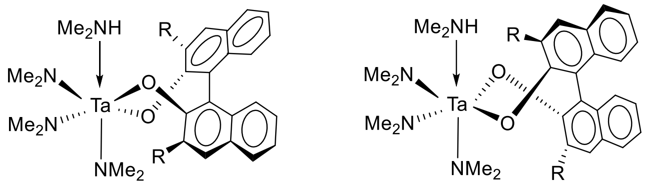
Reaction between $Ta(OEt)_5$ and 1,1,3,3-tetramethyl-1,3-disiloxanediol ($HOSiMe_2OSiMe_2OH$) gave siloxy complexes $Ta_2(OEt)_4(\mu\text{-}OEt)_2(\mu\text{-}\kappa^2\text{-}OSiMe_2OSiMe_2O)_2$ and $[Ta(\kappa^2\text{-}OSiMe_2OSiMe_2OSiMe_2O)]_2(\mu\text{-}OEt)_2(\mu\text{-}\kappa^2\text{-}OSiMe_2OSiMe_2O)_2$.[161] These products catalyzed the transformation of $HOSiMe_2OSiMe_2OH$ to polysiloxanes.[161]

As discussed earlier, amide silyl complex $(Me_2N)_4Ta$(~~-~~$SiBu^tPh_2$) ~~-~~reacted with O_2 to yield siloxy aminoxy $(Me_2N)_3Ta(\eta^2\text{-}ONMe_2)(OSiBu^tPh_2)$, siloxy $(Me_2N)_4Ta(OSiBu^tPh_2)$ and the unusual μ-oxo amino $Ta_2(NMe_2)_2(OSiBu^tPh_2)_2(\mu,\kappa^2\text{-}Me_2NCH_2NMe)_2(\mu\text{-}O)_2$ with two bridging chelating (aminomethyl)amide $-N(Me)CH_2NMe_2$.[135]

Silica supported complex $\equiv Si\text{-}O\text{-}Ta(NMe_2)_4$ was formed from the reaction of silica $SiO_{2\text{-}(700)}$ with $Ta(NMe_2)_5$.[162]

2.~~6~~7.4. *Aryloxide ligands*

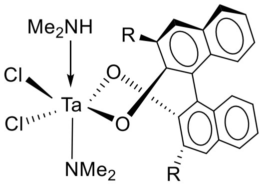
Reactions of $Ta(NMe_2)_5$ and *mer,cis*-$Ta(NMe_2)_2Cl_3(HNMe_2)$ with optically resolved 3,3′-disubstituted-2,2′-dihydroxy-1,1′-binaphthyl gave amine adducts $Ta(\kappa^2\text{-}O,O\text{-}R_2\text{-}C_{20}H_{10})(NHMe_2)(NMe_2)_3]$ (**119**, R = $SiMe_3$, $SiMe_2Ph$, $SiMePh_2$, $SiPh_3$) and $Ta(\kappa^2\text{-}O,O\text{-}R_2\text{-}C_{20}H_{10})(NHMe_2)(NMe_2)Cl_2$ (**120**, R = $SiMe_3$, $SiMe_2Ph$, $SiMePh_2$, $SiPh_3$), respectively.[163] Heating ***S*-(119)** (R = $SiMe_3$) under vacuum leads to the elimination of $HNMe_2$ and formation of $Ta[\kappa^2\text{-}O,O\text{-}3,3'\text{-}(SiMe_3)_2\text{-}C_{20}H_{10}](NMe_2)_3$ (**121**). When mixed with $SiCl_4$, ***S*-(119)** (R = $SiMe_3$) was converted to a mixture of $Ta[\kappa^2\text{-}O,O\text{-}3,3'\text{-}(SiMe_3)_2\text{-}C_{20}H_{10}](NHMe_2)Cl_3$ (**122**) and $(Me_2NH_2)Ta[\kappa^2\text{-}O,O\text{-}3,3'\text{-}(SiMe_3)_2\text{-}C_{20}H_{10}]Cl_4$ (**123**).[163]



(*R*) (*S*)

(*S*), R = SiMe$_3$
(*R*), R = SiMe$_2$Ph
(*R*), R = SiMePh$_2$
(*R*,*S*), R = SiPh$_3$

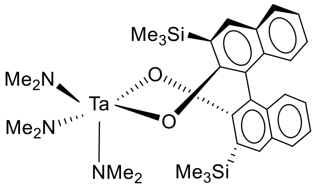
(**119**)



(*S*)

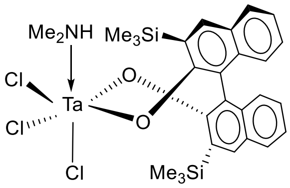
(*S*), R = SiMe$_3$
(*S*), R = SiMe$_2$Ph
(*S*), R = SiMePh$_2$
(*S*), R = SiPh$_3$

(**120**)



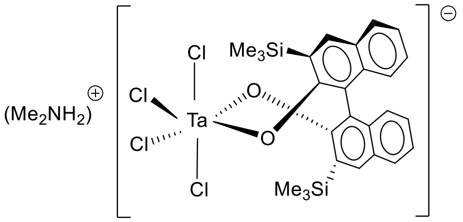
(*S*)

(**121**)



(*S*)

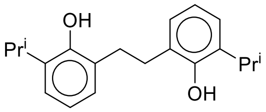
(**122**)



(*S*)

(**123**)

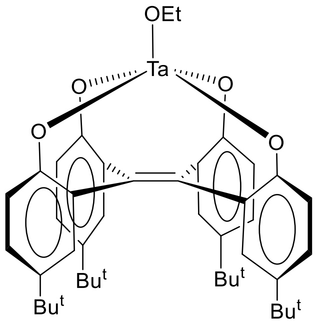
2,2′-Ethylenebis(6-isopropylphenol) (H_2bipp) reacted with $TaCl_5$ to give (bipp)$TaCl_3$ containing a chelating bis(aryloxide) ligand. Addition of RMgCl (R = CH_2Ph, Me) and S (S = thf, Et_2O) gave (bipp)TaR_3 and (bipp)$TaCl_3$(S), respectively.[164]



2,2'-Ethylenebis(6-isopropylphenol)

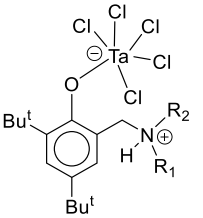
$[K(H_2O)(MeOH)_3]_2(PPh_4)_2[Ta_6Cl_{12}(p\text{-}OC_6H_4\text{–}F)_6]$ containing *p*-fluorophenolate ligands was prepared from $[Ta_6Cl_{14}(MeOH)_4]$•6MeOH, K(*p*-OC_6H_4–F) and (PPh_4)Br in MeOH.[165]

Treatment of 2,2′,2″,2‴-(1,2-ethenediylidene)tetrakis(4-tert-butylphenols) [(tpo)H_4] with $Ta(OEt)_5$ and $Ta(NMe_2)_5$ afforded Ta(V) square pyramidal complexes (tpo)Ta(OEt) (**124**) and dimethylamide (tpo)Ta(NMe_2), respectively, which are supported by the tpo^{4-} spectator ligand.[166] When (tpo)Ta(OEt) or (tpo)Ta(NMe_2) was treated with $AlMe_3$, the methyl derivative (tpo)TaMe was the product.[166] (tpo)Ta(OEt) and (tpo)Ta(NMe_2) were cleanly regenerated by addition of EtOH and $HNMe_2$ to (tpo)TaMe, respectively.[166]



(**124**)

Reactions of the aminophenols with $TaCl_5$ yielded zwitterionic aminophenolate complexes (**125**) with protonated N atom of the ligand and negative charged metal center. The complexes show moderate activities for the ring opening polymerization of lactides.[167]



R_1 = Et, R_2 = Et
R_1-R_2 = (-CH_2CH_2)$_2$O
R_1-R_2 = (-CH_2)$_5$

(**125**)

2.~~6~~7.5. *Ketone ligands or ligands containing N–C=O, As-C=O, and P=O functionalities*

TaX_5 (X = F, Cl, Br) reacted with ketones, yielding adducts TaX_5(ketone) (X = F, Cl, ketone = Me_2C=O, MePhC=O, Ph_2C=O; X = Cl, ketone = HPhC=O; X = Br, ketone =

$Me_2C{=}O$).[168]

TaF_5 reacted with benzophenone Ph_2CO, (2-diphenylphosphino)phenol (dppph), and 4-fluorobenzonitrile NCC_6H_4(*p*-F) to give $[TaF_4(Ph_2CO)_2](TaF_6)$, $[TaF_4(dppph)_2](TaF_6)$, and $TaF_5[NCC_6H_4(p\text{-}F)]$, respectively.[169]

Reactions of $TaCl_5$ with ethers OR_2 [$R_2 = Me_2$, Et_2, $Me(CH_2Cl)$] and *N,N*-diethyl methyl carbamate gave adducts $TaCl_5(OR_2)$ and $TaCl_5(Et_2NCO_2Me)$, respectively.[129]

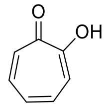
Reactions of TaX_5 (X = F, Cl) with ligands L containing N–C=O and P=O functionalities (tetramethylurea, tetraethylurea, dimethylformamide, diethylformamide, *N*-phenylacetam~~nil~~ide, ~~triphenylphosphane~~ triphenylphosphine oxide, and trimethyl phosphate) gave complexes $MX_5(L)$.[170] Reactions of $TaBr_5$ with *N*-phenylacetanilide and tetramethylurea yielded $TaBr_5$(*N*-phenylacetanilide) and $[TaBr_4(\text{tetramethylurea})_2](TaBr_6)$, respectively.[170]

$TaCl_5$ reacted with $Li(dme)^+[RC(=O)\text{-}As\text{-}C(=O)R]^-$ (R = Ph, mesityl), giving not the substituted product but $[R(O=)C]_2As\text{-}As[C(=O)R]_2$, presumably via oxidative coupling of the arsadionate ligands.[171]

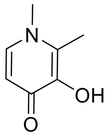
2.~~6~~7.6. *O,O-monoanionic and dianionic bidentate ligands and O,O,O-dianionic tridentate ligands*

Reaction of $TaBr_5$ with $MeOCH_2CH_2OMe$ (dme) led to single C-O bond cleavage, yielding *O,O*-monoanionic alkoxyether complex $TaBr_4(\kappa^2\text{-}OCH_2CH_2OMe)$ and MeBr.[172] Similar reaction of $TaCl_5$ with 1 equiv of dme gave alkoxyether $TaCl_4(\kappa^2\text{-}OCH_2CH_2OMe)$ as well as oxo-bridged adduct $Cl_3(dme)Ta(\mu\text{-}O)TaCl_5$.[173]

Reaction of $TaCl_5$ with tropolone (Htro) gave $[Ta(\kappa^2\text{-}O,O\text{-}tro)_4]Cl$ containing an eight-coordinated Ta(V) cation.[174] Its crystal structure was compared with that of its less stable Nb(V) analog, showing more distorted square antiprismatic geometry.[174] Reaction of $Ta(OEt)_5$ with deferiprone (Hdef) gave tris(1,2-dimethyl-3-hydroxy-4(*1H*) pyridone)oxotantalum $TaO(\kappa^2\text{-}O,O\text{-}C_7H_8O_2N)_3$.[175]



Tropolone (Htro)



Deferiprone (Hdef)

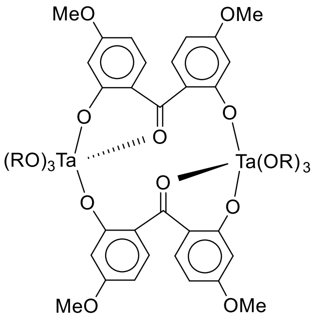
TaX_5(acetone) (X = F, Cl) were reactive towards acetone, acetophenone or benzophenone, giving the aldolate species $TaF_4[\kappa^2\text{-(O)-OC(Me)}CH_2CPh_2O]$ and $TaCl_4[\kappa^2\text{-(O)-OC(Me)}CH_2CPh(Me)O]$.[168] Reactions of TaX_5 (X = F, Cl, Br) with acetylacetones yielded $TaX_4[\kappa^2\text{-(O)-OC(Me)C(R)C(Me)O}]$ (X = F, Cl, R = H, Me; X = Br, R = Me).[168]

$BiPh_3$ reacted with salicylic acid and $Ta(OEt)_5$, giving $Bi_2Ta_2(\mu\text{-}O)(sal)_4(Hsal)_4(OEt)_2$.[176] When $BiPh_3$ reacted with salicylic acid, $HOPr^i$, $Mg(OAc)_2$, and $Ta(OEt)_5$, the product was $BiTa_4(\mu\text{-}O)_4(sal)_4(Hsal)_3(OPr^i)_4$ (sal = $O_2CC_6H_4\text{-}2\text{-}O^{2-}$, Hsal = $O_2CC_6H_4\text{-}2\text{-}OH^-$).[176] Pyrolysis and hydrolysis of $Bi_2Ta_2(\mu\text{-}O)(sal)_4(Hsal)_4(OEt)_2$ yielded bimetallic oxides.[176]

Reactions of Bi-Ta salicylate complexes $Bi_2Ta_2(sal)_4(Hsal)_4(OEt)_4$ and $BiTa_4(\mu\text{-}O)_4(sal)_4(Hsal)_3(OPr^i)_4$ with $NaBPh_4$ in alcoholic solutions gave heterobimetallic oxide $[PhBi(Hsal)Ta(sal)_2(OEt)_2\cdot EtOH]_2$ and $PhBiTa_4(\mu\text{-}O)_4(Hsal)_2(sal)_4(OEt)_4\cdot CH_2Cl_2$.[177]

$Ta(OEt)_5$ reacted with 3 equiv of bidentate catechol 1,3-$(OH)_2C_6H_3$ (cat-H_2), yielding Ta(cat)$_2$(cat-H)(py).[178]

Reactions of $Ta(OEt)_5$ and $Ta(OEt)(OCH_2Bu^t)_4$ with 4,4′-dimethoxy-2,2′-diol-benzophenone (H_2-Obzp) gave $[(RO)_3Ta(\mu,\mu_c\text{-Obzp})]_2$ (**126**, R = Et, Bu^tCH_2).[179] The complexes adopt the ‘bridging, chelating bridging’ (μ,μ_c-Obzp) mode.[179]



R = Et, Bu^tCH_2

(**126**)

Bisphenoxide-supported trimethyl complex (**127**) was prepared by the reaction of ~~Me_3~~$TaMe_3Cl_2$ with dipotassium salt of $[(2,5\text{-}HOC_6H_2\text{-}2,4\text{-}Bu^t{}_2)_2OC_4H_2]$ containing a furan linker.[180] If the bisphenol directly reacts with ~~Me_3~~$TaMe_3Cl_2$, the product was dichloro methyl complex (**128**).[180]

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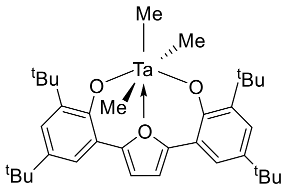
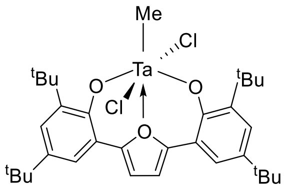


(**127**)



(**128**)

2.~~6~~7.7. *Carboxylate, carboxylic acid and related ligands*

When TaF_5 was mixed with acetic anhydride, ^{19}F NMR spectroscopic studies showed the formation of adduct $TaF_5[O{=}C(Me)OC({=}O)Me]$ and $TaF_5[OC(O)Me]^-$ anion, along with MeC(=O)F and $MeC({=}O)O^-$ anion.[181]

Reactions of TaX_5 (X = Cl, Br) with acetic acid and halo-substituted acetic acids gave dinuclear complexes $Ta_2X_8(\mu\text{-OOCMe})_2$ and $Ta_2Cl_8(\mu\text{-OOCR})_2$ (R = CH_2Cl, $CHCl_2$, CCl_3, CF_3).[182] TaF_5 reacted with acetic acid and halo-substituted acetic acids RCOOH (R = Me, CH_2Cl) to give ionic complexes $[MF_4(RCOOH)_2](MF_6)$.[182]

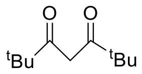
When freshly prepared $Ta(OH)_5{\cdot}nH_2O$ was dissolved in aqueous oxalic acid, followed by addition of dimethylformamide $HC({=}O)NMe_2$ and NH_4Cl, the process afforded oxalate complex $(NH_4)(Me_2NH_2)_2[Ta(C_2O_4)_4]$.[183]

2.~~6~~7.8. *β-Diketonate ligands*

β-Diketonate complexes $[TaX(NH_3)_3F_2]F_2$ (X^- = tta, hfa, bfa) were prepared from the reactions of basic aqueous solution of TaF_7^{2-} with thenoyltrifluoroacetone (Htta), hexafluoroacetylacetone (Hhfa), and benzoyltrifluoroacetylacetone (Hbfa).[184]

Reaction of $TaCl_5$ with neat 2,2,6,6-tetramethylheptane-3,5-dione (Htmhd) (in the absence of solvent) gives $[Ta(tmhd)_4](TaCl_6)$ containing the 8-coordinate Ta(V) cation,

$[Ta(tmhd)_4]^+$.[185]



Htmhd

Reaction of $Co(acac)_2$ with 1.5 eq. of Ta~~$_2$~~(OPr^i)$_5$~~$_{10}$~~ gave $Co_2Ta_2(OPr^i)_{14}$ and $Ta(acac)(OPr^i)_4$.[186]

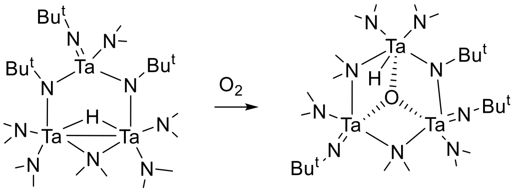
EXAFS and Raman spectroscopic studies showed that the reaction of $Ta(OEt)_5$ with Hacac gave $Ta(OEt)_x(acac)_{5-x}$ (x = 4, 3, 2), where Ta ion was 6- (x = 4), 7- (x = 3), or 8-coordinated (x = 2), respectively.[157]

2.~~6~~7.9. *Oxo ligands*

When $TaCl_5$ reacted with 2 or more equiv of dme, multiple C–O bond cleavages occurred, giving $Ta(=O)Cl_3(dme)$.[173]

$TaCl_5$ promoted coordinated urea dehydration of *N,N′*-dicyclohexylurea [CyNH-C(=O)-NHCy] by NEt_3 to carbodiimide CyN=C=NCy with the formation of $TaOCl_3(NEt_3)_2$ in a process similar to that by $NbCl_5$.[187]

$Ta_3(\mu\text{-}H)(\mu\text{-}NMe_2)(\mu\text{=}NBu^t)_2(\text{=}NBu^t)(NMe_2)_5$ with a Ta(IV)–Ta(IV) bond reacted with O_2, affording the oxo product in Scheme 6.[188]

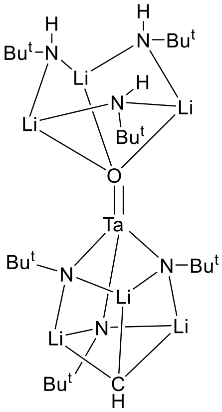


Scheme 6

Mixing $Ta(OEt)_5$ with $Ba_4(OEt)_4(thd)_4(EtOH)_4$ (Hthd = tetramethylheptanedion), followed by slow hydrolysis with air, gives $Ba_4Ta_4O_3(thd)_4(OEt)_{18}$.[189] Similarly, slow hydrolysis of $Ba_2Ta_2(Pr^iacac)_2(OEt)_{12}$ ($HPr^iacac = Pr^iOCOCH_2COMe$; isopropyl acetoacetate) in air afforded $Ba_4Ta_4O_4(Pr^iacac)_4(OEt)_{16}$. Both clusters were characterized by single-crystal diffraction.[189]

Hydrolysis of ortho-pinacolate $Ta(O_2C_6H_{12})_2(OC_6H_{12}OH)$ yielded $Ta_2O(O_2C_6H_{12})_2(OC_6H_{12}OH)_4$.[141]

The unusual oxo complex (**129**) was prepared from reacting complex (**34**) with excess $LiNHBu^t$, followed by heating.[46]



(**129**)

Reaction of $TaCl(NMe_2)_4$ with H_2O gave $Ta_2(\mu\text{-}Cl)_2(\mu\text{-}O)(NMe_2)_6$ with elimination of $HNMe_2$.[58]

Reduction of perox complexes $\alpha\text{-}K_5SiW_{11}[Ta(O_2)]O_{39}\cdot 18H_2O$ and $\alpha_2\text{-}K_7P_2W_{17}[Ta(O_2)]O_{61}\cdot 16H_2O$ by $NaHSO_3$ yielded oxo complexes $\alpha\text{-}K_5SiW_{11}TaO_{40}\cdot 14H_2O$ and $\alpha_2\text{-}K_7P_2W_{17}TaO_{62}\cdot 14H_2O$, respectively.[190]

Mixed-metal complex $[Ni(bpy)_3]_2[TaO(C_2O_4)_3]Cl\cdot nH_2O$ (n = 11, 12) was prepared from (oxalato)tantalite(V) solution and $[Ni(bpy)_3]Cl_2$.[191] Reaction of $Ni(NO_3)_2$, bpy and (oxalato)tantalite(V) solution gives $[Ni_2(bpy)_4(\mu\text{-}C_2O_4)]_{1.5}[TaO(C_2O_4)_3]\cdot 13H_2O$.[191]

$[Cr(bpy)_2(H_2O)(\mu\text{-}O)Ta(C_2O_4)_3]_2\cdot 3.5H_2O$ (bpy = 2,2'-bipyridine) and $[H_2(terpy)][Cr(terpy)(C_2O_4)(\mu\text{-}O)Ta(C_2O_4)_3]\cdot 0.5H_2C_2O_4\cdot 2.5H_2O$ (terpy = 2,2':6',2"-terpyridine) were prepared from the reactions of the (oxalato)tantalate(V) solution with $[Cr(bpy)_2(H_2O)_2](NO_3)_3$ and $[Cr(terpy)(H_2O)_3](NO_3)_3$, respectively.[192] These complexes contain Cr–O–Ta ~~bridges~~cores.

Adding a mixture from dissolving tantalum metal in aqueous $HF\text{-}H_2O_2$ solution to a solution of $FeCl_2\cdot 4H_2O$ and 1,10-phenanthroline (phen) yielded $[Fe(phen)_3][Ta_2(\mu\text{-}O)F_{10}]$.[193] If $RuCl_3\cdot 4H_2O$ was used instead of $FeCl_2\cdot 4H_2O$, the reaction afforded $[Ru(phen)_3]_2[Ta_2(\mu\text{-}O)F_{10}](TaF_6)_2$.[193]

Reaction of $TaCl_5$ with imine $Ph_2C{=}NH$ gave $(Ph_2C{=}NH_2)_2[Ta_2(\mu\text{-}O)Cl_{10}]$, presumably the result of adventitious water.[194]

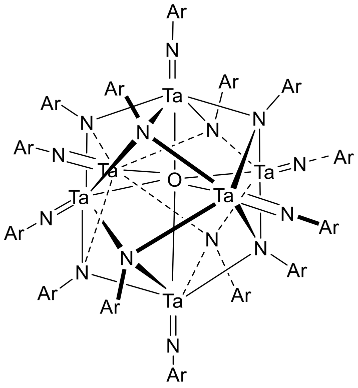
Reactions of $Ta(NMe_2)_5$ and $TaCl(NMe_2)_4$ with H_2O gave cage complex $Ta_4(Me_2N)_{12}(\mu_3\text{-}O)_4$[195] and dimer $Ta_2(NMe_2)_6(\mu\text{-}Cl)_2(\mu\text{-}O)$,[58] respectively.

Reactions of TaF_5 with Ti(=O)$(acac)_2$ and V(=O)$(acac)_2$ yielded Ta(=O)F_3 with an oxo ligand and $[V(acac)_3](TaF_6)$ with no oxo ligand, respectively.[196]

Relativistic quantum chemistry studies of TaO_3^- showed that the oxidation state Ta was the expected V with divalent oxygen O(-II).[197] Optimized geometrical and electronic structures of TaO_3^- as well as its relative energies, vibrational frequencies, and energy of decomposition were provided from the calculations.

2.~~6~~7.10. *Polynuclear oxo ligands*

O-centered hexatantalum tetradecaimido clusters $(ArN{=})_{14}Ta_6O$ (**130**, Ar = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-$Bu^tC_6H_4$, *p*-BrC_6H_4, *m*-ClC_6H_4) were prepared from the reactions of either $Bn_3Ta{=}N\text{-}Bu^t$ or $Ta(NMe_2)_5$ with an excess of the aniline and stoichiometric water (or Ta_2O_5).[100, 101] Reduction with $Cp^*{}_2Co$ gave stable salts of $(Cp^*{}_2Co)[(ArN)_{14}Ta_6O]$ (Ar = Ph, *p*-MeC_6H_4).[100]



(**130**)

Mixed-metal oxoalkoxide complexes $(Nb_xTa_{1-x})_4(\mu\text{-}O)_2(OMe)_{14}(ReO_4)_2$ (x = 0.3, 0.5, 0.7) were obtained by the reactions of Re_2O_7 with $M_2(OMe)_{10}$ (M = Nb, Ta).[198] Similarly oxo-ethoxo-perrhenate $Ta_4(\mu\text{-}O)_2(\mu\text{-}OR)$~~$_{14}$~~$(OR)_{10}(ReO_4)_2$ (R = Me, Et), containing a tetranuclear $M_4(\mu\text{-}O)_2(\mu\text{-}OR)_4$ core, was obtained via interaction of $Ta(OR)_5$ with Re_2O_7 ~~containing a tetranuclear $M_4(\mu\text{-}O)_2(\mu\text{-}OR)_4$ core~~.[199, 200]

2.~~6~~7.11. *Polyoxometalates (POMs)*

Hexatantalate Lindqvist compound $Na_8Ta_6O_{19}\cdot 26H_2O$, a polyoxometalate with a layered structure, was prepared from H_2TaF_7 and NaOH.[201]

$Cs_3[H_9P_4Ta_6(O_2)_6O_{25}]\cdot 9H_2O$ and guanidinium salt $(CN_3H_6)_6[H_4P_4Ta_6(O_2)_6O_{24}]\cdot 4H_2O$ were prepared from the reaction of $K_8(Ta_6O_{19})\cdot 16H_2O$, H_2O_2, H_3PO_4, with NaOH, followed by the addition of CsCl and guanidine hydrochloride $(CN_3H_5\cdot HCl)$, respectively.[202]

Mixed polyoxometalates $Cs_4Na(Ta_3W_3O_{19})\cdot 6H_2O$, $Cs_5(TaW_9O_{32})\cdot 6.5H_2O$ and $Cs_6(Ta_2W_8O_{32})\cdot 6H_2O$ were prepared from $[Ta(O_2)_4]^{3-}$, $Na_2WO_4\cdot 2H_2O$, HCl, Cs^+ and water/H_2O_2 under strict pH control. $(Ta_3W_3O_{19})^{5-}$ adopts the Lindqvist-type structure. $(TaW_9O_{32})^{5-}$ and $(Ta_2W_8O_{32})^{6-}$ were isostructural with $(W_{10}O_{32})^{4-}$.[203]

Hydrothermal method led to the synthesis of polytantalotungstate $Cs_{12.5}K_{4.5}H(Ta_{12}Si_4W_{37}O_{158})\cdot 25H_2O$ whose structure was based on the $(SiW_9Ta_3O_{40})^{7-}$ cluster.[204] This polytantalotungstate showed significant photocatalytic water splitting activity to give H_2 and O_2 from water.[204] Two other polytantalotungstates $Cs_5K_4[Cr_3(Ta_3P_2W_{15}O_{62})_2(H_2O)_{12}]\cdot 15H_2O$ and $Cs_{8.5}K_8Na_2H_{5.5}[Cr_4(Ta_3P_2W_{15}O_{62})_4(H_2O)_{12}]\cdot 53H_2O$, which were based on Cr_3Ta_6 and

Cr_4Ta_{12} clusters, were also prepared.[205] Both polytantalotungstates also demonstrated significant photocatalytic water splitting activities.[205]

Polyoxometalate $(Bu^n{}_4N)_4[(TaW_5O_{18})_2(\mu\text{-}O)]$ was synthesized by the reaction of $(Bu^n{}_4N)_3(TaW_5O_{19})$ with Bu^nSnCl_3 or PhC(=O)Cl.[206]

Small-angle X-ray scattering (SAXS) studies of $Rb_8(Ta_6O_{19})$ and $Cs_8(Ta_6O_{19})$ in aqueous RbOH, CsOH or NMe_4OH solutions showed solvent-separated ion-pairing between $(Ta_6O_{19})^{8-}$ and counterions. In contrast, Nb(V) analogs revealed that contact ion-pairing dominates between $[Nb_6O_{19}]^{8-}$ and its counter ions.[207]

The reactivity of peroxide H_2O_2 with $(NMe_4)_6H_2Ta_6O_{19}\cdot 21H_2O$ was investigated. Small and wide-angle as well as total X-ray scattering showed that peroxide ligand promoted the linking of the hexameric tantalate clusters probably through bridging of bound peroxide or hydrogen bonding.[208]

A solution route to $(Ta_6O_{19})^{8-}$ [in $Na_8(Ta_6O_{19})\cdot 15H_2O$] was developed by using peroxo complex $[Ta(O_2)_4]^{3-}$ in adequately alkaline conditions in order to block the formation of Ta_2O_5, followed by catalytic decomposition of the peroxide ligands by $(VO_4)^{3-}$. Terminal M(η=O) bond lengths and M-μ~~$_2$~~-O–M angles of $(Ta_6O_{19})^{8-}$ were larger than those in its Nb analog, while bridging μ~~η~~^{2}-O–M bond lengths in the tantalum complex was smaller and the central η^6-O–M bond lengths were identical within experimental error.[209]

Kinetics of the oxygen-isotope exchange between ^{17}O-enrich $(H_xTa_6O_{19})^{x-8}$ Lindqvist i~~I~~on and aqueous solutions was studied using ^{17}O NMR spectroscopy, revealing that the terminal η=O ligands reacted faster than the μ~~$_2$~~-O(H) ligands. Oxygen sites in the Ta complex and its Nb analog reacted via different pathways.[210]

Heating of $(Me_4N)_6(H_2Ta_6O_{19})\cdot xH_2O$ coating led to the formation of the Ta_2O_5 film, along with NMe_3, OMe_2 and water. The approach precluded abrupt nanoparticle formation, giving films with densities near 95% of single-crystal values.[211]

Reaction between $(\eta^6\text{-}C_6H_6)_2Ru_2Cl_2(\mu\text{-}Cl)_2$ and $Na_8(Ta_6O_{19})$ gave two new hybrid POM complexes, $Na_{10}[(\eta^6\text{-}C_6H_6)RuTa_6O_{18}]_2(\mu\text{-}O)\cdot 39.4H_2O$ and $Na_4[\textit{trans}\text{-}(\eta^6\text{-}C_6H_6)Ru]_2Ta_6O_{19}]\cdot 20H_2O$.[212] $Na_{10}[(\eta^6\text{-}C_6H_6)RuTa_6O_{18}]_2(\mu\text{-}O)\cdot 39.4H_2O$ dissociated in water to give $[(\eta^6\text{-}C_6H_6)RuTa_6O_{19}]^{6-}$.[212] Reaction of $Cp^*{}_2Ir_2Cl_2(\mu\text{-}Cl)_2$ with $Na_8(Ta_6O_{19})$ gave hybrid POM complexes $Na_6[(Cp^*Ir)Ta_6O_{19}]\cdot 27H_2O$ and $Na_4[\textit{trans}\text{-}[(Cp^*Ir)_2Ta_6O_{19}]\cdot 24H_2O$~~$4^{-}$~~.[213] Similarly reactions of $Cp^*{}_2Rh_2Cl_2(\mu\text{-}Cl)_2$ with sodium hexatantalate and cesium hexatantalate $M_8(Ta_6O_{19})$ (M = Na,[214] Cs[215]) yielded the *trans* complex $[(Cp^*Rh)_2Ta_6O_{19}]^{4-}$, which was isolated as $M_4[(Cp^*Rh)_2Ta_6O_{19}]\cdot nH_2O$ (M = Na, n = 24;[214] M = Cs, n = 18~~.~~[214, 215]).

Ta-containing POMs $[Ln_3(H_2O)_{22}](P_2W_{15}Ta_3O_{62})\cdot nH_2O$ (Ln = La, Ce, Pr, Nd) were prepared from the self-assembly of Wells–Dawson type Ta/W mixed-addendum POM and lanthanide ions.[216] The La complex showed proton conduction ~~performance~~ at high relative humidity.[216]

Hydrothermal reactions of hydrous tantalum oxide and NMe_4OH with two different amounts of $Ti(OPr^i)_4$ gave two polyoxotantalates $(NMe_4)_8(Ti_2Ta_8O_{28})\cdot 21H_2O$ and $(NMe_4)_{10}(Ti_{12}Ta_6O_{44})\cdot 39H_2O$.[217] Both were kinetically stable over a much wider range of pH range than the more familiar hexatantalate cluster $Ta_6O_{19}{}^{8-}$.[217]

Rare-earth polyoxometalates $[M(H_2O)_7]_3(P_2W_{15}Ta_3O_{62})\cdot nH_2O$ (M = Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) were prepared through self-assembly of $K_5Na_4[P_2W_{15}O_{59}(TaO_2)_3]\cdot 17H_2O$ and rare-earth salts in water.[218]

Base catalytic activity of $(H_4Ta_6O_{19})^{4-}$ (with $Bu^n{}_4N^+$ cation) for, *e.g.*, Knoevenagel condensation and CO_2 fixation reactions was higher than its Nb^V and Mo^{VI}/W^{VI} analogs.[219] This was likely due to the large number of negative charges on the surface O atoms in the $(H_4Ta_6O_{19})^{4-}$ ion.[219]

2.~~6~~7.12. *Peroxo ligands*

Water-soluble peroxo complex $(gu)_3[Ta(O_2)_4]$ (gu = guanidinium) was prepared from $TaCl_5$, H_2O_2, and $(gu)_2CO_3$ in water.[220] Reactions of the peroxo complex in H_2O_2 solution with ethylenediaminetetraacetic acid (H_4edta),[220] propylenediaminetetraacetic acid (H_4pdta),[220] diethylenetriaminepentaacetic acid (H_5dtpa),[221] and triethylenetetraminehexaacetic acid (H_6ttha)[221] gave peroxo-polyaminocarboxylato complexes $(gu)_3[Ta(O_2)_2(edtaO_2)]\cdot 2.32H_2O\cdot 0.68H_2O_2$,[220] $(gu)_3[Ta(O_2)_2(pdtaO_2)]\cdot H_2O$,[220] $(gu)_3[Ta_2(O_2)_4(dtpaO_3)]\cdot 5H_2O$,[221] and $(gu)_3[Ta_2(O_2)_4(HtthaO_4)]\cdot 3H_2O$,[221] respectively. In these complexes, N atoms of the polyaminocarboxylates were oxidized into N-oxide derivatives.[220, 221] When 1:1 solutions of $(gu)_3[Nb(O_2)_4]$ and $(gu)_3[Ta(O_2)_4]$ were used in the reactions with H_5dtpa and H_6ttha, the reactions yielded heterometallic $(gu)_3[NbTa(O_2)_4(dtpaO_3)]\cdot 2.5H_2O$ and $(gu)_3[NbTa(O_2)_4(HtthaO_4)]\cdot 2H_2O$.[221]

Water-soluble bimetallic peroxo-tartrato complex $(gu)_6[Ta_2(O_2)_4(tart)_2]\cdot 4H_2O$ (tart = tartrate) was obtained from $(gu)_3[Ta(O_2)_4]$, DL-H_4tart, and H_2O_2.[222] Reaction of 1:1 aqueous solution of $(gu)_3[Nb(O_2)_4]$ and $(gu)_3[Ta(O_2)_4]$ with DL-H_4tart and H_2O_2 yielded the mixed Nb/Ta complex $(gu)_5[NbTa(O_2)_4(tart)(Htart)]\cdot 4H_2O$.[222] Crystal structure of $(gu)_6[Ta_2(O_2)_4(tart)_2]\cdot 6H_2O$ showed two ~~8-fold~~octa-coordinated Ta atoms, each surrounded by O atoms of two bidentate peroxo, two monodentate carboxylato, and two alkoxo groups from both bridging tartrate ligands.[222]

IR and Raman spectra of several peroxotantalates $M_3[Ta(O_2)_4]$ ($M = NH_4^+$, K^+, Rb^+, Cs^+) were studied and discussed with respect to the internal vibrations of the peroxogroup and the dodecahedral $[Ta(O_2)_4]^{3-}$ ion.[223] Powder X-ray diffraction of the complexes and single-crystal structure of $Rb_3[Ta(O_2)_4]$ showed that these compounds were isotypic.[223]

Reactions of a mixture of $K_8Ta_6O_{19}\cdot16H_2O$ and H_2O_2 with α-$K_8SiW_{11}O_{39}\cdot13H_2O$ and α_2-$K_{10}P_2W_{17}O_{61}\cdot20H_2O$ afforded perox complexes α-$K_5SiW_{11}[Ta(O_2)]O_{39}\cdot18H_2O$ with the Keggin structure and α_2-$K_7P_2W_{17}[Ta(O_2)]O_{61}\cdot16H_2O$ with the Wells–Dawson structure, respectively.[190]

Actinyl polyoxometalate nanoclusters $Cs_{15}\{[Ta(O_2)_4]Cs_4K_{12}[UO_2(O_2)_{1.5}]_{28}\}\cdot20H_2O$ and $Na_6K_9\{[Ta(O_2)_4]Rb_4Na_{12}[UO_2(O_2)_{1.5}]_{28}\}\cdot20H_2O$ were synthesized by incorporating a central $Ta(O_2)_4^{3-}$ anion templating a shell of 28 uranyl peroxide polyhedra.[224]

Catalytic activity for selective epoxidation of olefins by binuclear peroxo $[SeO_4WO(O_2)_2TaO(O_2)_2]^{3-}$ anion was investigated by DFT computations and compared with analogous anions.[225]

2.~~6~~7.13. *Isocyanate ligand*

TaF_5 reacted with methyl isocyanate MeN=C=O to give adduct TaF_5(MeN=C=O) and the heterocyclic cation $[(\mu\text{-F})(\mu\text{-MeN=C=O})(TaF_4)_2]_n^+$ (n = 1, 2), as shown by ^{19}F NMR and IR spectra.[226] In TaF_5(MeN=C=O), the methyl isocyanate ligand was coordinated in the monodentate mode via N or O atom as bond isomers.[226]

2.~~6~~7.14. *Phosphinylamine ligands*

Reaction of TaF_5 with bis(diphenylphosphinyl)amine $Ph_2P(=O)NHP(=O)Ph_2$ (LH) was studied by ^{19}F and ^{31}P NMR spectroscopy, showing the formation of several species including $(F_5Ta)_2(\mu\text{-}\kappa^2\text{-LH})$, $(LH_2)[(TaF_5)_2(\mu\text{-}\kappa^2\text{-L})]$, $TaF_4(\kappa^2\text{-L})$, $[TaF_5(\kappa^2\text{-L})]^-$, and $TaF_3(\kappa^2\text{-L})_2$.[227]

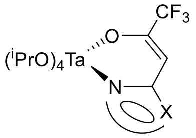
2.~~6~~7.15. *Precursors to solid-state materials*

The general approaches to make electronic metal oxide materials were reviewed.[228]

$(Pr^iO)_2Ta[OSi(OBu^t)_3]_3$ was prepared from the reaction of $Ta(OPr^i)_5$ with $(Bu^tO)_3SiOH$.[229] The complex was used as a structural and spectroscopic model of Ta(V) on silica. Its thermolysis in solution afforded homogeneous, high-surface-area xerogels ($Ta_2O_5\cdot 6SiO_2$).[229]

Reaction of 3 equiv of ~~[~~K~~]~~$[Ta(OPr^i)_6]$ ~~-~~with $ErCl_3$ gave alkoxide $Er[Ta(OPr^i)_6]_3$ which reacted with MCl_4 (M = Si, Ti, Zr) to give mixed complexes $Er[TaM(OPr^i)_2$~~(~~O~~)~~$_4]_3$ and Pr^iCl.[230] Thermogravimetric and differential thermal analyses of the mixed complexes were conducted with interest to form metal oxides.[230]

Monomeric heteroleptic Ta(V) complexes $Ta(OPr^i)_4(ArTFP)$ (**131**) were prepared from $Ta_2(OPr^i)_{10}$ and bidentate chelating ligands 3,3,3-trifluoro-1-(heteroar-2-yl)propen-2-oles (ArTFP-H; TFP-H = trifluoropropenol; Ar = pyridine, 4,5-dimethyloxazole, 4,5-dimethylthiazole, benzimidazole, benzoxazole, benzthiazole).[231] These complexes showed better stability and volatility than $Ta_2(OPr^i)_{10}$, simplifying chemical vapor deposition of Ta_2O_5 from the precursors.[231]



X = CH, NH, O, S

(**131**)

The growth characteristics of Ta_2O_5 thin film from $Ta(=NBu^t)(NEt_2)_3$ and H_2O by atomic layer deposition (ALD) was studied.[232]

Crystals of borate $KTa[B_4O_6(OH)_4](OH)_2 \cdot 1.33H_2O$ were prepared from Ta_2O_5, B_2O_3, SiO_2 in molar ratio of 2:1:1 by the hydrothermal method.[233] The crystals showed second-order nonlinear optical properties.

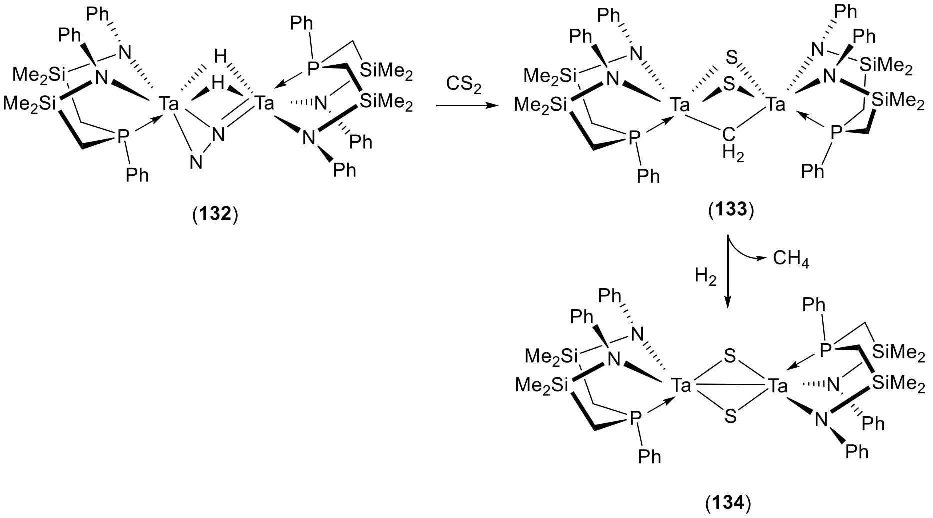
Thermal decomposition of mixed-metal oxo methoxide $(Nb_{1-x}Ta_x)_4O_2(OMe)_{14}(ReO_4)_2$ (x = 0, 0.3, 0.5, 0.7, 1) at ca. 160 °C led to the formation of Re–Nb–O and Re–Ta–O oxides.[234]

2.~~7~~8. Sulfur-, Selenium-, and Tellerium-Based Ligands

2.~~7~~8.1. *Sulfide ligands*

In the reaction of CS_2 with $([NPN^{Ph}]Ta)_2(\mu\text{-}H)_2(\mu\text{-}\eta^2{:}\eta^1\text{-}N_2)$ (**132**; $[NPN^{Ph}]^{2-}$ = $PhP(CH_2SiMe_2NPh)_2^{2-}$) containing a side-on end-on dinitrogen ligand, cleavage of both C=S double bonds was observed with the formation of $([NPN^{Ph}]Ta)_2(\mu\text{-}S)_2(\mu\text{-}CH_2)$ (**133**) with one bridging methylene and two bridging sulfide ligands (Scheme 7).[235] Reduction of the product with H_2 led to $([NPN^{Ph}]Ta^{IV})_2(\mu\text{-}S)_2$ (**134**) containing a Ta-Ta bond

(Scheme 7).[235]



Scheme 7

When TaBr$_5$ reacted with NiBr$_2$, PPh$_3$, and S(SiMe$_3$)$_2$, cluster Ta$_2$Ni$_2$(μ_3-S)$_4$Br$_4$(PPh$_3$)$_2$(MeCN)$_2$ was the product. Based on the crystal structure of its Nb/Cl analog, the compound takes a cubane structure.[236] Reaction of TaCl$_5$ and NiCl$_2$ with PMe$_3$, followed by addition of S(SiMe$_3$)$_2$, gave [Ni$_3$S$_2$(PMe$_3$)$_6$][Ta$_3$Ni(μ_3-S)$_4$(PMe$_3$)$_4$Cl$_6$]$_2$.[236] Similar reaction of FeCl$_2$, TaCl$_5$, (diphenylphosphanyl)methane (dppm), and S(SiMe$_3$)$_2$ afforded [Fe(dppm)$_2$(MeCN)$_2$][TaFe$_3$(μ_3-S)$_4$Cl$_3$(dppm)(MeCN)]$_2$. The anions in both products [Ta$_3$Ni(μ_3-S)$_4$(PMe$_3$)$_4$Cl$_6$]$^-$ and [TaFe$_3$(μ_3-S)$_4$Cl$_3$(dppm)(MeCN)]$^-$ also adopt the cubane structure with bridging sulfide ligands.[236] When FeCl$_2$ reacted with TaCl$_5$, PMe$_3$ and S(SiMe$_3$)$_2$, cluster [Cl(Me$_3$P)Ta(μ-S)$_2$(μ_3-S)$_2$Fe(PMe$_3$)$_2$]$_2$ was produced.[237] In the cluster, the two [Cl(Me$_3$P)Ta] units are arranged around one central $Fe_2(\mu\text{-}S)_2$ unit. Selenide analogs are discussed in the section on selenide ligands (Section 2.7.7).

Reaction of $TaCl_5$ with $NiCl_2(PPh_3)_2$ and $S(SiMe_3)_2$ in MeCN gave $[TaCl_2(MeCN)]_2[Ni(PPh_3)]_2(\mu_3\text{-}S)_4$.[238] If $Ta(NCS)_5$ reacted with $Co(NCS)_2$, PBu^t_3, and $S(SiMe_3)_2$, the product was $[Ta(NCS)_3][Co(PBu^t_3)]_3(\mu_3\text{-}S)_4$.[238] Both adopt the cubane structure.

Reaction of $Cu(NCS)_2$ with PPh_3 and $Li_3(TaS_4)(tmeda)_2$ (tmeda = tetramethylethylenediamine $Me_2NCH_2CH_2NMe_2$) yielded $Cu_3Ta(\mu\text{-}S)_2(\mu_3\text{-}S)_2(PPh_3)_4$.[239] When $(Et_4N)_2[Fe(SPh)_4]$ reacted with $Li_3(TaS_4)(MeCN)_4$, the product was $(Et_4N)_3\{Ta(\mu\text{-}S)_4[Fe(SPh)_2]_2\}$.[239]

Reaction of $S{=}Mo[NBu^t(3,5\text{-}Me_2C_6H_3)]_3$ with $Ta(OSiBu^t_3)_3$ yielded $S{=}Ta(OSiBu^t_3)_3$ and $Mo[NBu^t(3,5\text{-}Me_2C_6H_3)]_3$.[240]

DFT calculations of the reaction $Re(NH_2)_3 + CS_2 + 2Ta(NH_2)_3$, leading to the forming $S{=}Ta(NH_2)_3$ and $C{\equiv}Re(NH_2)_3$, showed that this was a promising reaction for the cleavage of CS_2.[241]

2.~~7~~8.2. *Thioether ligands*

Adding SBu^n_2 to $TaCl_5$ afforded $TaCl_5(SBu^n_2)$.[242] When bidentate $o\text{-}C_6H_4(CH_2SEt)_2$ was used instead, the reaction gave dimer $Ta_2Cl_{10}[\mu,\eta^2\text{-}o\text{-}C_6H_4(CH_2SEt)_2]$.[242]

Reaction of TaF_5 with SMe_2 and $RS(CH_2)_2SR$ (R = Me, Et or Pr^i) in anhydrous CH_2Cl_2 solution produced $[TaF_4(SMe_2)_4](TaF_6)$ and $\{TaF_4[\kappa^2\text{-}RS(CH_2)_2SR]_2\}(TaF_6)$, respectively.[243] In neat SR_2 (R = Me, Et), TaF_5 formed adducts $TaF_5(SR_2)$.[243]

Treatment of the imido complexes TaCl$_3$(=NR)(p~~P~~y)$_2$ (R = Bu^t, 2,6-Me$_2$C$_6$H$_3$) with S(SiMe$_3$)$_2$ afforded sulfide clusters Ta$_4$Cl$_4$(=NR)$_4$Py$_4$(μ$_3$-S)$_4$ with cubane structures.[244]

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2.~~7~~8.3. *Thione ligand*

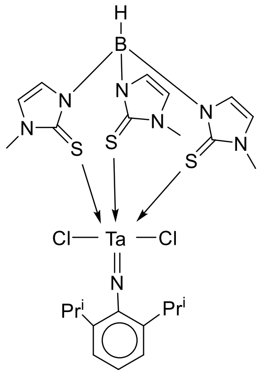
When TaX$_5$ (X = Cl, OEt) was mixed with 3-(4'-pyridyl)-4-phenyl-1,2,4-triazole-5-thione (L), adduct TaX$_5$(L) was the product in which the S atom of the ligand is coordinated to the Ta(V) ion.[245]

2.~~7~~8.4. *Dithiocarbamate ligands*

Reaction of Ta(NMe$_2$)$_5$ with CS$_2$ in toluene and thf gave the Ta(V) dimethyldithiocarbamate (dtc) complex [Ta(dtc)$_4$](dtc).[246] If the solvent was CH$_2$Cl$_2$, the product was [Ta(dtc)$_4$]Cl.[246]

2.~~7~~8.5. *(Methimazolyl)borate ligands*

Tris(methimazolyl)borate complex Ta(=N-2,6-~~^{i}~~Pr$^i_2$C$_6$H$_3$)Cl$_2${HB(mt)$_3$}] (**135**, mt = methimazolyl) was obtained from the reaction of Ta(=NR)Cl$_3$(thf)$_2$ with Na[HB(mt)$_3$].[247] The work showed that the HB(mt)$_3^-$ ligand can bind to "hard" metals in high oxidation states. When Ta(η^2-RC≡CR)Cl$_3$(dme) (R = Et, Ph) reacted with Na[HB(mt)$_3$], the products were Ta(η^2-RC≡CR)Cl$_2$[HB(mt)$_3$].[248]



(**135**)

2.~~7~~8.6. *Trifluorosulfane ligand*

DFT calculations showed that the dissociation of $Ta(SF_3)(CO)_5$ to $Ta(SF_2)(F)(CO)_5$ was thermodynamically favored by 32.3 kcal/mol.[249]

2.~~7~~8.7. *Selenide ligands*

As the formation of sulfide analog, when $TaBr_5$ reacted with $NiBr_2$, PPh_3, and $Se(SiMe_3)_2$, cluster ~~$Ta_2Ni_2(\mu_3\text{-}Se)_4Br_4(PPh_3)_2(MeCN)_2$~~ $[TaBr_2(MeCN)]_2[Ni(PPh_3)]_2(\mu_3\text{-}Se)_4$ was the product.[236] Adding $TaCl_5$ to $Fe_8Se_9(dppm)_3$ afforded $[FeCl(dppmSe)_2][TaFe_3(\mu_3\text{-}Se)_4Cl_3(dppm)(MeCN)]$. The anions in the products adopt the cubane structure.[236]

Reaction of LiOMe with $Se(SiMe_3)_2$ and $Ta(OEt)_5$ in MeCN and Et_2O gave 1-D polymeric $1/_\infty[Li_3(TaSe_4)(MeCN)_4]_\infty$ containing chelating Li^+ cations via four of the six edges of the tetrahedral $(TaSe_4)^-$ building blocks and the $Li(MeCN)_2^+$ cations.[239]

Reaction of $TaCl_5$ with $NiCl_2(PPh_3)_2$ and $Se(SiMe_3)_2$ in MeCN afforded

$[TaCl_2(MeCN)]_2[Ni(PPh_3)]_2(\mu_3\text{-}Se)_4$.[238]

Reaction of $Se{=}Mo[NBu^t(3,5\text{-}Me_2C_6H_3)]_3$ with $Ta(OSiBu^t{}_3)_3$ yielded $Se{=}Ta(OSiBu^t{}_3)_3$ and $Mo[NBu^t(3,5\text{-}Me_2C_6H_3)]_3$.[240] $Se{=}Ta(OSiBu^t{}_3)_3$ was also prepared from the reaction of Se with $Ta(OSiBu^t{}_3)_3$.[240]

2.~~7~~8.8. *Selenoether ligands*

Reaction of $SeBu^n{}_2$ with $TaCl_5$ gave $TaCl_5(SeBu^n{}_2)$.[242] When TaF_5 reacted with $SeMe_2$ and $MeSe(CH_2)_2SeMe$, the products were $TaF_5(SeMe_2)$ and $(TaF_5)_2[\mu\text{-}MeSe(CH_2)_2SeMe]$.[243]

2.~~7~~8.9. *Telluroether ligands*

Adding $TeBu^n{}_2$ to $TaCl_5$ or $TeMe_2$ to TaX_5 (X = F, Cl, Br) yielded $TaCl_5(TeBu^n{}_2)$ and $TaX_5(TeMe_2)$, respectively.[242] $TaCl_5$ led to the decomposition of ditelluroether $CH_2(CH_2TeBu^t)_2$. One of the products was the dealkylated $[Bu^tTe(CH_2)_3Te](TaCl_6)$.[242]

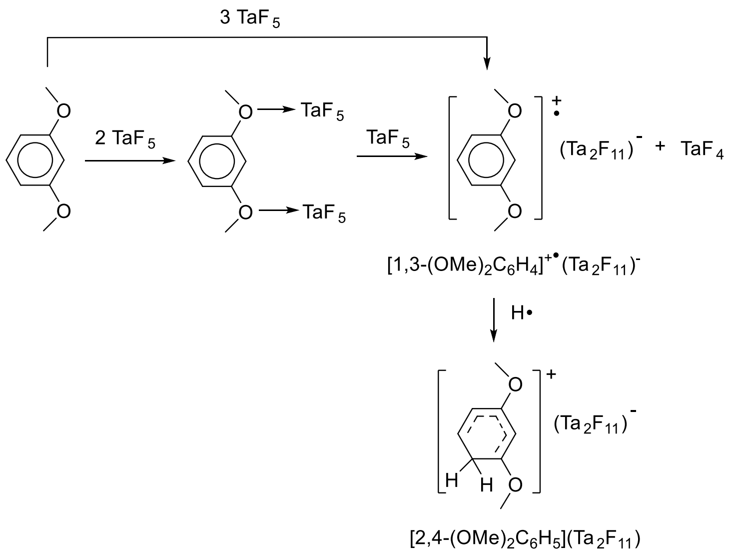
2.~~7~~8.10. *Reactions of $TaCl_3(=S)$*

$TaCl_3(=S)$ catalyzed trimerization of alkyne $PhC{\equiv}CH$, giving 1,2,~~5~~4-triphenylbenzene and 1,3,5-triphenylbenzene, along with small amounts of 2,4-diphenylthiophene and 2,5-diphenylthiophene.[250] When $MeC{\equiv}CMe$ was used, the products were hexamethylbenzene and a small amount of 2,3,4,5-tetramethylthiophene.[250]

2.~~8~~9. Halogen-Based Ligands

2.~~8~~9.1. *Fluoride ligands*

Reaction of $Ta(OH)_5$ with 4-amino-1,2,4-triazole in aqueous HF solution gave $(C_2H_5N_4)TaF_6$ containing protonated 4-amino-1,2,4-triazolium cation.[251] The 3:1 molar reaction of TaF_5 with 1,3-dimethoxybenzene initially gave adduct $(TaF_5)_2[\kappa^2\text{-1,3-}(OMe)_2C_6H_4]$. Subsequent single-electron oxidation of the arene ligand by TaF_5 yielded TaF_4 and radical $[1,3\text{-}(OMe)_2C_6H_4]^{+\bullet}(Ta_2F_{11})^{-}$. The radical takes an H atom to give arenium salt $[2,4\text{-}(OMe)_2C_6H_5](Ta_2F_{11})$ (Scheme 8).[252] Similar products formed when 3 equiv of TaF_5 reacted with $1,4\text{-}(MeO)_2C_6H_4$ and $1,4\text{-}F_2\text{-}2,5\text{-}(MeO)_2C_6H_2$ to give long-lived radical cation salts $[1,4\text{-}(MeO)_2C_6H_4]^{+\bullet}(Ta_2F_{11})^{-}$ and $[1,4\text{-}F_2\text{-}2,5\text{-}(MeO)_2C_6H_2]^{+\bullet}(Ta_2F_{11})^{-}$, respectively, which were ~~quantified~~ characterized by EPR.[253] Radical TaF_4 formed in the reaction with CH_3CN as solvent was observed in EPR as $TaF_4(NCMe)_2$.[253] When non-alkoxy-substituted arenes (arene = C_6H_5Me, $1,4\text{-}C_6H_4Me_2$, C_6H_5F, $C_6H_5NO_2$) were used in the reactions with 3 equiv of TaF_5, radical cation salts $[\text{arene}]^{+\bullet}(Ta_2F_{11})^{-}$ and TaF_4 were the products.[253]



Scheme 8. Formation of arenium salt $[2,4\text{-}(OMe)_2C_6H_5](Ta_2F_{11})$.

Reactions of TaF_5 with 4-hydroxy-3-methoxybenzaldehyde (vanillin) and N,N-dimethylaniline gave protonated salts $[4\text{-}(OH)\text{-}3\text{-}(OMe)C_6H_3CH(=O\text{-}H)][4\text{-}(OH)\text{-}3\text{-}(OMe)C_6H_3\text{-}CHO](TaF_6)$ and $[TaF_4(NPhMe_2)_2](TaF_6)$, respectively.[254] Attempts of crystallization of the latter product resulted in the isolation of the ammonium salt $(PhNHMe_2)(TaF_6)$.[254]

Using $N(C_2H_4NH_2)_3$ (tren) as a template, reaction of Ta_2O_5 with aqueous HF solution led to the formation of $(H_4tren)(TaF_7)_2{\cdot}H_2O$ and $(H_4tren)(TaF_7)_2$ containing isolated TaF_7^{2-} anions as distorted monocapped trigonal prisms and pentagonal bipyramids, respectively.[255] If ZrF_4 (or ZrO_2), Ta_2O_5, and tren in 40% HF aqueous-EtOH solution were heated to 190 °C in an autoclave, the reaction yielded hydrate $(H_3tren)_6(TaOF_6)_4(ZrF_7)_2{\cdot}3H_2O$ ~~containing $(H_3tren)_2(MX_7)_2{\cdot}H_2O$ (M = Zr, Ta; X = F, O)~~

~~sheets in the structure~~.[256] In addition, when tren was used as a template, solvothermal reaction of Ta_2O_5 with aqueous HF at 170 °C yielded $(H_3tren)(TaF_7)F$.[257] The hydrogen bond network in the compound gives a layered structure.[257]

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Commented [XZ(60R59]: Correct. $(H_3tren)^{3+}$ is a trication.

Two-step hydrothermal process using Ta_2O_5, aqueous HF solution, $Cu(acetate)_2{\cdot}H_2O$, 2-oxidopyridinium-3-carboxylic acid (opdcH), and 1,10-phenanthroline (phen) affords a blue fluorescent, zigzag chain coordination polymer $\{[Cu_2(opdc)_2(phen)_2][F_5Ta(\mu\text{-}O)TaF_5]\}_n$.[258] A similar process using Ta_2O_5, aqueous HF and piperazine yields $[H_2N(C_2H_4)_2NH_2](TaF_7)$.[259]

Reactions of TaF_5 with hydrazinium difluoride $(N_2H_6)F_2$ and NaF in aqueous HF solution yield $(N_2H_6)_3[(TaF_8)(TaF_7)]HF_2$ and $Na_7TaF_8(TaF_7)_2$, respectively. Both compounds contain discrete TaF_8^{3-} and TaF_7^{2-} anions in their crystal structures.[260]

When TaF_5 reacted with $[S(NMe_2)_3](SiMe_3F_2)$, salts $[S(NMe_2)_3](TaF_6)$ and $[S(NMe_2)_3](Ta_2F_{11})$ were obtained. $TaF_5[(Me_2N)_2CO]$ was detected in solution mixture of TaF_5 and $(Me_2N)_2CO$.[261] When two equiv of L = $HCONMe_2$ or thf were mixed with TaF_5, NMR revealed the formation of $(TaF_4L_4)(TaF_6)$.[261]

N-alkyl-*N*-methylpyrrolidinium ($RMePyr^+$, R = Et, Bu^n, and hexyl) and *N*-Bu^n-pyridinium (Bu^nPy^+) salts of TaF_6^- were prepared.[262] Their thermal behaviors (by DSC), ionic conductivity, and viscosity were studied.[262] ^{19}F, ^1H NMR spectroscopy and DSC studies of $(NMe_4)TaF_6$ were performed, showing that, e.g., the NMR spectral changes were associated with changes in the character of ion motions in the anion and cation sublattices of compounds.[263]

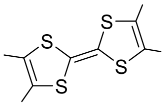
Crystals of salts $[H_2(2,2'\text{-bpy})]TaOF_5$ (2,2′-bpy = 2,2′-bipyridyl), $(Hdpa)TaF_6$ (dpa = 2,2′-dipyridylamine), and $(H_2en)TaF_7$ (en = ethylenediamine) were prepared from

Ta_2O_5 in aqueous HF solutions using the organic bases with different pK_a values.[264]

$(NH_4)_2TaF_7$, Na_3TaF_8, and K_2TaF_7 were obtained from a Ta(V) extract in tributyl phosphate, which had been prepared by dissolving Ta_2O_5 in aqueous fluoride–sulfuric acid solutions.[265] Mixed-cation complexes $NaMTaF_7$ ($M^+ = K^+$, Rb^+, Cs^+, NH_4^+) were prepared from Ta_2O_5 in HF solutions of MF and NaF.[266]

$Cd(BF_4)(TaF_6)$ is prepared from a solution of $Cd(BF_4)_2$, CdF_2, and TaF_5 In anhydrous HF. Eight F^- ions from 4 BF_4^- and 4 TaF_6^- anions surround each Cd^{2+} ion as a distorted square antiprism.[267]

Electrochemical oxidation of tetramethyltetrathiafulvalene in a solution of $(Bu^n{}_4N)TaF_6$ in CH_2Cl_2 leads to the formation of $(TMTTF)_2^+$ cation which is then crystalized with TaF_6^- anion to give $(TMTTF)_2TaF_6$.[268] The compound undergoes an antiferromagnetic transition around 9 K.[268]



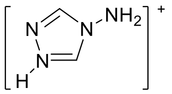
tetramethyltetrathiafulvalene

TaF_5 dissolved in aqueous HF solution reacted with *cis-syn-cis*-dicyclohexano-18-crown-6 (crown) to give $[H_3O^+(crown)]TaF_6$.[269] Ta_2O_5 reacts with HF and aza-15-crown-5, giving $[H(aza\text{-}15\text{-}crown\text{-}5)]_2(Ta_2F_{10}O)$ containing two azonia-15-crown-5 cations.[270] Similarly, when Ta_2O_5 is dissolved in HF solution and then added 18-crown-6, 15-crown-5, benzo-15-crown-5, and benzo-12-crown-4, the products are $[(18\text{-}crown\text{-}6)\cdot H_3O](TaF_6)$, $[(15\text{-}crown\text{-}5)\cdot H_5O_2](TaF_6)$, $[(benzo\text{-}15\text{-}crown\text{-}5)_2\cdot H_5O_2][$(benzo-15-

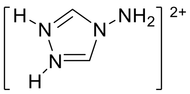
crown-5)$_2$·H_3O]$(TaF_6)_2$, and [(benzo-12-crown-4)$_2$·H_3O](TaF_6), respectively.[271] Tantalum oxyfluoride clusters $(Ta_8O_{12}F_{24})^{\cancel{8-}}\cdot 8(N_2C_3H_5)^{\cancel{+}}$, $(Ta_8O_{12}F_{24})^{\cancel{8-}}\cdot 2[(C_2H_4NH_3)_3NH]^{\cancel{4+}}\cdot 6H_2O$, and $(Ta_4O_4F_{16})^{\cancel{4-}}\cdot 4(NC_5H_6)^{\cancel{+}}$ were prepared.[272]

$M(Ta_2F_{11})_2$ (M = Cd, Hg) have been synthesized from MF_2 and four equiv of TaF_5 in anhydrous HF as solvent.[273] Cations are connected through two anions forming 1-D chains.

Addition of 4-amino-1,2,4-triazole to a solution of $Ta(OH)_5$ in aqueous HF solution led to the protonation of 4-amino-1,2,4-triazole and formation of $(C_2H_5N_4)_2TaF_7$ and $(C_2H_6N_4)TaF_7\cdot H_2O$ containing mono-cation $C_2H_5N_4^+$ and di-cation $C_2H_6N_4^{2+}$, respectively.[274] The TaF_7^{2-} anions in the two complexes adopt monocap trigonal prismatic and pentagonal bipyramidal geometries, respectively.



mono-cation $C_2H_5N_4^+$



di-cation $C_2H_6N_4^{2+}$

1-Alkyl-3-methylimidazolium hexafluoro complex salts (R-Im-Me)(TaF_6) (R = *n*-tetradecanyl, *n*-hexadecanyl, *n*-octadecanyl) are prepared from (R-Im-Me)Cl and $KTaF_6$ containing a liquid crystalline mesophase.[275]

Amidinate $Ta(=NBu^t)(Bu^tNCMeNBu^t)_2F$ was made from the treatment of $Ta(=NBu^t)(Bu^tNCMeNBu^t)_2Cl$ with $AgBF_4$.[85]

Reaction of $[PNP]Ta(=NSiMe_3)Cl_2$ ($[PNP]^- = N(2\text{-}PPr^i_2\text{-}4\text{-}Me\text{-}C_6H_3)_2^-$), whose preparation is discussed in Section 2.9.8, with $FSnMe_3$ gave $\{[PNP]_2Ta_2(=NSiMe_3)_2(\mu$-

F)$_3$}[$Me_3ClSn(\mu\text{-}X)SnClMe_3$] (X = F, Cl).[276]

XPS, ^{19}F SSNMR spectroscopy, and DSC studies were performed on $KTaF_6$, K_2TaF_7, and K_3TaF_8 to obtain electronic binding energies of accessible orbitals, correlate SSNMR spectral shifts with structures and XPS data, and characterize phase transitions in the compounds.[277]

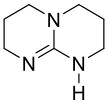
Molecular modelling of the stepwise hydrolysis of TaX_5 (X = F, Cl) to $Ta(OH)_5$ and Ta_2O_5 shows that this is an endothermic reaction, while the formation of $Ta(H_2O)F_5$ and TaF_4(O~~O~~H) is exothermic.[278]

2.~~8~~9.2. *Chloride and bromide ligands*

Reaction of $TaCl_5$ with (~~[~~hpp~~]~~)$SiMe_3$ in 1:~~1~~ 2 molar ratio (~~[~~hpp~~]~~H = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine) or with in-situ generated (hpp)Li afforded [(hpp~~]~~)~~$_2$~~$_4$Ta](TaCl$_6$)~~$_2$ which was identified by mass spectral analysis of the crude solid product~~.[279] ~~However, ([hpp]H$_2$)$_2$(TaCl$_6$)(Cl) and ([hpp]H$_2$)$_3$(TaCl$_6$)$_2$(Cl)·MeCN in low yield were isolated, presumably generated as a result of adventitious moisture.~~[278]

Commented [XZ(61]: The change here is to make the abbreviated names consistent. For example, earlier "Hdpa" is used.

I didn't change [NPN^{Ph}]$^{2-}$ et al. (by Fryzuk et al.) as it's based on binding atoms (rather than abbreviated names. In addition, it seems to be widely used. Making a change may cause confusion.

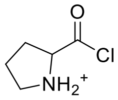


hppH

When Ta(=NBu^t)Cl_3(py)$_2$ reacted with non-heterocyclic carbene (NHC) 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), the product was ionic complex (IPrH)[Ta(=NBu^t)Cl_4(py)].[280]

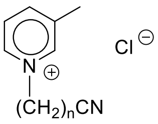
Reactions of IMes:CO_2 and IPr:CO_2, which are carboxylation products of NHCs 1,3-dimesitylimidazol-2-yliden (IMes) and IPr, respectively, with $TaCl_5$ gave (IMes:CO_2)$TaCl_5$ and $[(IPr:CO_2)_2TaCl_3](TaCl_6)_2$, respectively, with O-Ta bonds. The metal centers in the two complexes adopt distorted octahedral and pentagonal bipyramidal geometries, respectively.[281]

Thermally-stable salts of (pyrrolidinium-2-carbonylchloride)(TaX_6) (X = F, Cl), as *L*-proline derivatives, were reported.[282]



pyrrolidinium-2-carbonyl chloride

Mixings of nitrile-functionalized pyridinium chlorides with $TaCl_5$ gave salts of the nitrile-functionalized pyridinium cations and $TaCl_6^-$ anions as ionic liquids which were characterized by X-ray diffraction.[283] (~~bmpy~~bmPy)($TaCl_6$) (~~bmpy~~ bmPy = 1-butyl-4-methylpyridinium) was similarly synthesized.[284] When water is present, the reactions of (~~bmpy~~bmPy)Cl and (emIm)Cl (emIm = 1-ethyl-3-methylimidazolium) with $TaCl_5$ give (~~bmpy~~bmPy)$_4[(TaCl_6)_2[Ta_2(\mu\text{-}O)Cl_{10}]$ and $[(emIm)_2][Ta_2(\mu\text{-}O)Cl_{10}]$, respectively.[284]



n = 1, 3

nitrile-functionalized pyridinium chlorides

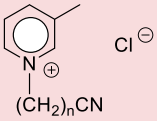
Reaction of $TaCl_5$ with α-diimine DAD^{Dip} produced $[DAD^{Dip}(H)]$[Ta~~M~~Cl_6].[53]

Radical salt $(1,4\text{-}Me_2C_6H_4)^{+\bullet}(Ta_2Cl_{11})^-$ was produced by reaction of $TaCl_5$ with 1,4-xylene, and the product was identified by EPR.[253]

$TaCl_3(=O)$ reacts with phosphaalkynes P≡C-R (R = Bu^t, 1-adamantyl), yielding 1,2-dichloro-phosphaalkenes Cl~P=C(Cl)R.[250] The tantalum-containing product was not identified but is probably a reduced species.

Cluster-containing 3-D heterotrimetallic frameworks $(H_3O)\{Ta_6Cl_{12}(CN)_6[Mn(salen)]_6Fe(CN)_6\}\cdot 4H_2O$ and $\{Ta_6Cl_{12}(CN)_6[Mn(salen)]_6Cr(CN)_6\}\cdot 7H_2O$ were prepared from the self-assembly of the paramagnetic octahedral metal cluster $[Ta_6Cl_{12}(CN)_6]^{3-}$, $[Mn(salen)]^+$ [salen = *N,N′*-ethylenebis~~-~~(salicylidene)iminate] and polycyanometallates ($[Fe(CN)_6]^{4-}$ and $[Cr(CN)_6]^{3-}$, respectively~~)~~.[285] $[Ta_6Cl_{12}(CN)_6]^{3-}$ consists of a Ta_6 octahedral metal core supported by 12 edge-bridging μ~~$_2$~~-Cl^- as inner ligands and 6 apical CN^- ligands.[285]

186, 284



n = 1, 3

nitrile-functionalized pyridinium chlorides

~~Ionic liquids with $TaCl_6^-$ anion and two nitrile-functionalized pyridinium cations have been prepared and characterized by X-ray diffraction.~~[282]

Commented [MDJ62]: Not clear what this is, phosphaalkyne?

Commented [XZ(63R62]: Yes. Name added.

Commented [MDJ64]: What is this for?

Commented [XZ(65R64]: The product is an organophosphorus compound. The sentence here indicates the reactivity of $TaCl_3(=O)$..

Commented [XZ(66]: Moved 5 paragraphs earlier (after the combined text).

Commented [XZ(67]: Combined with an earlier paragraph (5 paragraphs before this one).

Amidinate $\mathrm{Ta(=NBu^t)(Bu^tNCMeNBu^t)_2Br}$ was made from the treatment of $\mathrm{Ta(=NBu^t)(Bu^tNCMeNBu^t)_2Cl}$ with $\mathrm{BBr_3}$.[85]

$\mathrm{[Ta_6Br_{12}(H_2O)_6](BPh_4)_2\cdot 4H_2O}$ was obtained from the reaction of $\mathrm{Ta_6Br_{14}\cdot 7H_2O}$ with $\mathrm{NaBPh_4}$ in water.[286]

2.~~9~~10. Mixed-Donor Ligands

2.10~~9~~.1. *η^2-Aminoxy (N,O) ligands*

d^0 $\mathrm{Ta(NMe_2)_5}$ reacted with $\mathrm{O_2}$ to give aminoxy complexes $\mathrm{(Me_2N)_nTa(\eta^2\text{-}ONMe_2)_{5-n}}$ (n = 4, 3) as well as $\mathrm{(Me_2N)_4Ta_2[\kappa^2\text{-}N(Me)CH_2NMe_2]_2(\mu\text{-}O)_2}$ and $\mathrm{(Me_2N)_6Ta_3[\kappa^2\text{-}N(Me)CH_2NMe_2]_2(\eta^2\text{-}ONMe_2)(\mu\text{-}O)_3}$ with ~~novel~~ chelating (aminomethyl)amide $\mathrm{\text{-}N(Me)CH_2NMe_2}$ ligands.[134]

As discussed earlier, $\mathrm{(Me_2N)_4Ta\text{-}SiBu^tPh_2}$ reacted with $\mathrm{O_2}$ to yield aminoxy complex $\mathrm{(Me_2N)_3Ta(\eta^2\text{-}ONMe_2)(OSiBu^tPh_2)}$ as well as $\mathrm{(Me_2N)_4Ta(OSiBu^tPh_2)}$ and $\mathrm{Ta_2(NMe_2)_2(OSiBu^tPh_2)_2(\mu,\kappa^2\text{-}Me_2NCH_2NMe)_2(\mu\text{-}O)_2}$ with two chelating, bridging-$\mathrm{N(Me)CH_2NMe_2}$ ligands.[135]

Reaction of 3 equiv of $\mathrm{HONEt_2}$ with $\mathrm{Ta(NMe_2)_5}$ gave η^2-hydroxylamido oxo dimer $\mathrm{Ta_2(\mu\text{-}O)_2(\eta^2\text{-}ONEt_2)_6}$.[287]

2.10~~9~~.2. *Amino-acidate (N,O) ligands*

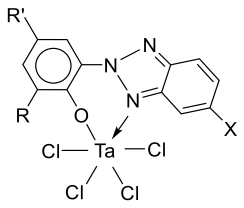
When $\mathrm{Ta(OEt)_5}$ reacted with *L*-α-amino acids including~~,~~ *L*-phenylalanine, *L*-proline, and *L*-methionine (MetH), $\mathrm{Ta(OEt)_4(\kappa^2\text{-}amino\ acidato)}$ complexes were the products in which the amino acidate ligands were bidentate using both the N and O binding sites.[288]

2.10~~9~~.3. *Aminophenol (N,O) and aminothiophenol (N,S) ligands*

Reaction of 2-aminophenol or 2-aminothiophenol (2-HX-$C_6H_4NH_2$; X = O, S) with $TaCl_5$ afforded the product $Ta(\kappa^2\text{-}XC_6H_4NH_2)Cl_4$ containing a bidentate ligand.[289]

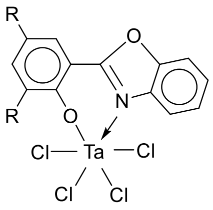
2.10~~9~~.4. *Benzotriazole and benzoxazole phenoxide (N,O) ligands*

Complexes with benzotriazole phenoxide (**136**) and benzoxazole phenoxide (**137**) ligands were prepared from the reactions of $TaCl_5$ with benzotriazole~~s~~ phenols and benzoxazole phenols, respectively.[290] These complexes were tested as catalysts for the ring-opening polymerization of glycidol to synthesize hyperbranched polyglycerols using 1,1,1-tris(hydroxymethyl)propane as an initiator.[290]



R = H, R' = Me, X = H
R = R' = Bu^t, X = Cl
R = R' = t-pentyl, X = H

(**136**)

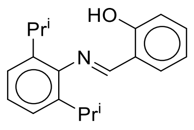


R = Bu^t
R = Cl
R = Br

(**137**)

2.10~~9~~.5. *Iminomethylphenol (N,O) ligand*

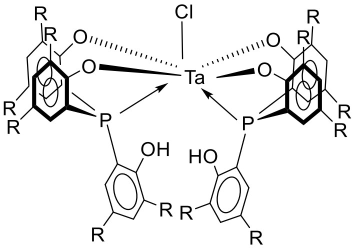
$[TaCl_2(\kappa^2\text{-dpimp})_2](TaCl_6)$ is prepared from $TaCl_5$ and 2-[(2,6-diisopropylphenyl)iminomethyl]phenol (dpimpH).[291]



dpimpH

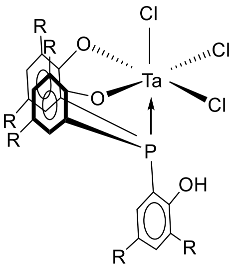
2.10~~9~~.6. *Phosphine alkoxide (O,P) ligand*

Reaction of triphenol phosphine (2-HO-3,5-$Bu^t_2C_6H_2)_3P$ ($H_3[O_3P]$) with 3 equiv of Bu^nLi and 1 equiv of $TaCl_5$ gave 7-coordinate $Ta[O_2P(OH)]_2Cl$ (**138**).[292] If $H_3[O_3P]$ or (**138**) reacted with $TaCl_5$, the product was $Ta[O_2P(OH)]Cl_3$ (**139**).[292]



R = Bu^t

(**138**)



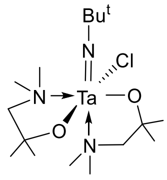
R = Bu^t

(**139**)

2.10~~9~~.7. *Other monoanionic bidentate ligands*

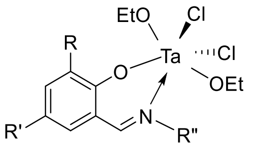
Imine complex $(silox)_2Ta(\eta^2\text{-}NC_5H_9)Me$ was tentatively identified in the thermolysis of $(silox)_2Ta(pip)Me_2$.[31]

Reaction of 2 equiv of $NaOCMe_2CH_2NMe_2$ with $Ta(=NBu^t)Cl_3(py)_2$ gave $Ta(=NBu^t)Cl(\kappa^2\text{-}OCMe_2CH_2NMe_2)_2$ (**140**).[293]



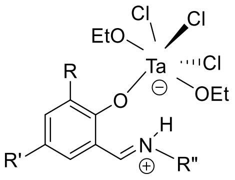
(**140**)

$TaCl_5$ reacts with imino phenols in EtOH-toluene solution to give imino phenolate complexes (**141**) and (**142**), which are catalysts for the polymerization of lactides, ε-caprolactone and ethylene.[294]



R = R' = Bu^t; R" = 4-OMe-C_6H_4
R = Bu^t; R' = Me, R" = 4-OMe-C_6H_4

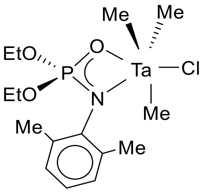
(**141**)



R = R' = R" = Bu^t
R = Bu^t; R' = Me, R" = 4-OMe-$C_6H_4CH_2$

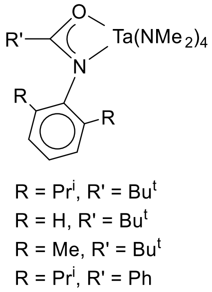
(**142**)

Complex (**143**) with a κ^2-*N,O*-phosphoramidate ligand was prepared and it was a precatalyst for room-temperature hydroaminoalkylation.[295]

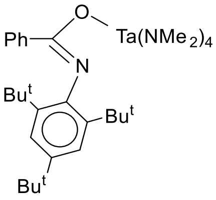


(**143**)

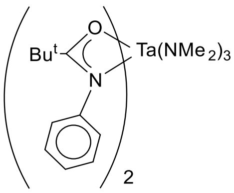
~~Several a~~Amidates (**144**) and (**145**) were prepared from the reactions of $Ta(NMe_2)_5$ with organic amides.[296, 297] These amidates were precatalysts for hydroaminoalkylation.[296, 297] Bis(amidate) amide (**146**)[296] and bis(amidate) aziridine complex (**147**)[294] were also reported.



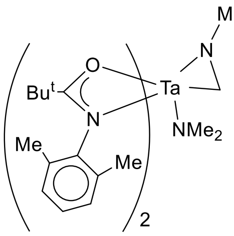
(**144**)



(**145**)



(**146**)

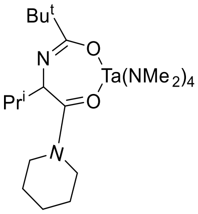


(**147**)

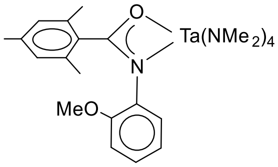
A series of 2-pyridonate complexes $LTa(NMe_2)_3X$ (X = Cl, L = 3-mesityl-2-pyridonate,[298] 3-methyl-2-pyridonate,[298] 3-trifluoromethyl-2-pyridonate,[298] 2-pyridonate,[298] 6-phenyl-2-pyridonate,[298] 6-methyl-2-pyridonate,[298] 3-phenyl-2-pyridonate;[298] X- = OTf, L = 3-phenyl-2-pyridonate[298]) and (3-phenyl-2-pyridonate)$Ta(NMe_2)_4$[299] were prepared and found to be precatalysts for

Commented [XZ(68]: If the negative sign "-" is used here, should we add "-" to other places such as "X = Cl" (just 3 lines) above and "X = O, S"?

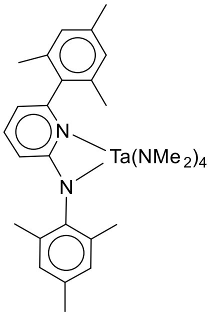
hydroaminoalkylation.[298, 299] Also alkyl ureates prepared in situ from $Ta(CH_2SiMe_3)_3Cl_2$ and ~~a~~ ureate *N,O* chelating ligand salts were catalytic systems for hydroaminoalkylation.[300] Other *N,O*-heteroatom containing-chelating ligands ~~derived from~~including *N*-[3-methyl-1-oxo-1-(piperidin-1-yl)butan-2-yl]pivalamide, *N*-(2-methoxyphenyl)-2,4,6-trimethylbenzamide, and *N*,6-dimesitylpyridin-2-amine were used to react with $Ta(NMe_2)_5$, giving (*Z*)-(2,2-dimethyl-1-{[3-methyl-1-oxo-1-(piperidin-1-yl)butan-2-yl]imino}propoxy)$Ta(NMe_2)_4$ (**148**), mono[*N*-(2-methoxyphenyl)-2,4,6-trimethylbenzamidate]$Ta(NMe_2)_4$ (**149**) and mono(*N*,6-dimesityl-2-aminopyridinate)$Ta(NMe_2)_4$ (**150**), respectively.[301]



(**148**)

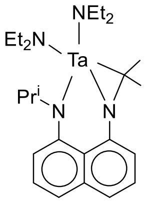


(**149**)



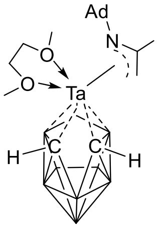
(**150**)

If MeLi were added to $TaCl(NEt_2)_2[1,8\text{-}(Pr^iN)_2C_{10}H_6]$, aziridine $[\kappa^3\text{-}(Me_2CN)(Pr^iN)C_{10}H_6]Ta(NEt_2)_2$ (**151**) formed after the elimination of methane.[81]



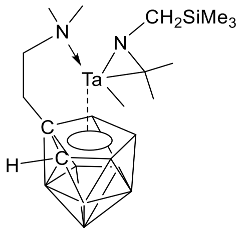
(**151**)

Treatment of (η^5-$C_2B_9H_{11}$)$TaMe_3$ with adamantyl isonitrile in dme produced (η^6-$C_2B_9H_{11}$)Ta[η^3-*C,C,N*-CH_2C~~(CH_3)~~MeNAd](dme) (**152**).[23]



(**152**)

Treatment of [η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]$TaMe_3$ (**12**) with 1 equiv of isonitrile Me_3SiCH_2NC to give aziridine [η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Ta[η^2-*C,N*-C(Me_2)NCH_2SiMe_3]Me (**153**).[24]



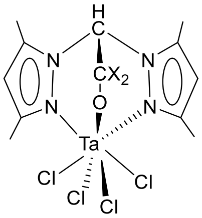
1~~153~~

Silica surface grafted ≡Si-O-Ta(NMe_2)$_4$ was found to be susceptible to β-H elimination. When heated under reduced pressure, ≡Si-O-Ta(NMe_2)$_4$ gave ≡Si-O-Ta(η^2-$NMeCH_2$)(NMe_2)$_2$ directly.[162] Treatment of ≡Si-O-Ta(NMe_2)$_4$ with HNMePh at room temperature yielded ≡Si-O-Ta(η^2-$NPhCH_2$)(NMe_2)$_2$.[162] These complexes were tested as catalysts for hydroaminoalkylation of alkenes~~ation reactions.~~ [161]

As discussed in Section 2.4.12 on imide ligands, reactions of carborane complex [η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]$TaMe_3$ (**12**) with 2,6-dimethylphenyl isonitrile and 2,6-diisopropylphenyl isonitrile yielded imide aziridine complexes (**77, 78, 79**).

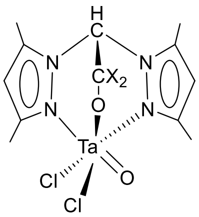
2.10~~9~~.8. *Monoanionic tridentate ligands*

Reaction of $TaCl_5$ with lithium 2,2-bis(3,5-dimethylpyrazol-1-yl)ethoxide gave (**154**) with a heteroscorpionate ligand.[302] Complexes (**154**) were converted to (**155**) in thf probably through hydrolysis.[302]



$X_2 = H_2$, O

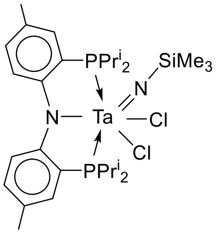
(**154**)



$X_2 = H_2$, O

(**155**)

Reaction of $Ta(=NSiMe_3)Cl_3(py)_2$ with $Li[N(2\text{-}PPr^i_2\text{-}4\text{-}Me\text{-}C_6H_3)_2]$ (Li[PNP]) gave $[PNP]Ta(=NSiMe_3)Cl_2$ (**156**), which reacted with $Na(O\text{-}2,6\text{-}Pr^i_2C_6H_3)$, affording $[PNP]Ta(=NSiMe_3)Cl(O\text{-}2,6\text{-}Pr^i_2C_6H_3)$.[276] When $FSnMe_3$ was added to the alkoxide derivative, the reaction yielded the fluoride imide complex $[PNP]Ta(=NSiMe_3)F(O\text{-}2,6\text{-}Pr^i_2C_6H_3)$.[276]



(**156**)

2.10~~9~~.9. *Dianionic bidentate ligands*

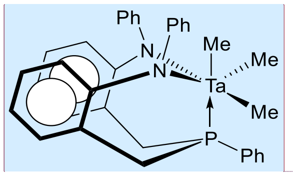
$(Me_2N)_3Ta(Cl)[N(SiMe_3)_2]$ reacted with 1 equiv of $LiN(SiMe_3)_2$ gave

$(Me_2N)_3\overline{TaN(SiMe_3)SiMe_2CH_2}$ with a four-membered metallaheterocyclic ring through γhydrogen abstraction.[57] The cyclic product could also be prepared from the reactions of $(Me_2N)_3TaCl_2$[57] or $(Me_2N)_4TaCl$[58] with $LiN(SiMe_3)_2$ or direct γ-H activation of the $N(SiMe_3)_2$ ligand in $(Me_2N)_3Ta[N(SiMe_3)_2](SiPh_2Bu^t)$ by the silyl ligand.[303] Kinetics of the γ-H abstraction by the silyl ligand was found to follow first-order kinetics with $\Delta H^\ddagger$ = 23.6(1.6) kcal/mol and $\Delta S^\ddagger$ = 3(5) eu between 288 and 313 K.[303] DFT studies of the γ-H abstraction by silyl ligands revealed that the formation of the metallacyclic complex through γ-H abstraction was entropically driven.[303]

2.10~~9~~.10. *N,P,N-dianionic tridentate ligand*

Complexes containing *N,P,N*-dianionic tridentate ligands, such as $[NPN^R]^{2-}$ (R = Ph, Cy, Ad), $[NPN']^{2-}$, $[NPN^*]^{2-}$ were used as starting materials to make other derivatives containing the tridentate ligands. These studies are discussed in other sections of this review. The current section is focused on the reaction forming new bonds between a Ta(V) ion and a tridentate ligand.

$[NPN']TaMe_3$ ($[NPN']^{2-} = PhP(CH_2C_6H_4\text{-}o\text{-}NPh)_2^{2-}$) (**157**) was synthesized via treatment of $TaCl_2Me_3$ with $[NPN']Li_2(dioxane)$.[11]



(**157**)

Commented [MDJ69]: Please fix bent C-N bonds

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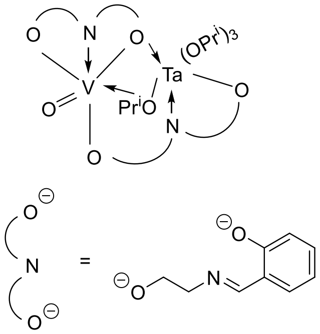
2.10~~9~~.11. *O,N,O-dianionic tridentate ligands*

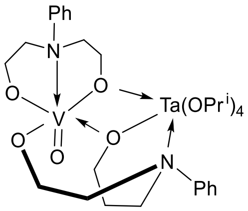
$Ta_2(\mu\text{–}pdm)_2(OCH_2Bu^t)_6$ ($pdmH_2$ = 2,6-dimethanol pyridine) was prepared from Ta~~$_2$~~$(OCH_2Bu^t)_5$~~$_8$(μ-OEt)$_2$~~ and $pdmH_2$.[304]

$Ta_2(OPr^i)_{10}$ reacted with V(=O)(OsaeO)(HOsaeO) (HOsaeOH = N-salicylidene-2-aminoethanol), giving (**158**) which was believed to have the following structure.[305]

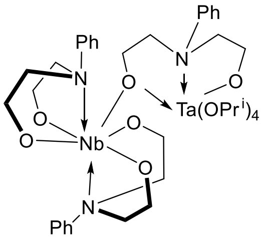


(**158**)

Mixed-metal complexes $V(=O)[PhN(CH_2CH_2O)]_2[Ta(OPr^i)_4]$ (**159**)[306] and $Nb[PhN(CH_2CH_2O)]_3[Ta(OPr^i)_4]$ (**160**)[307] have been reported.



(**159**)

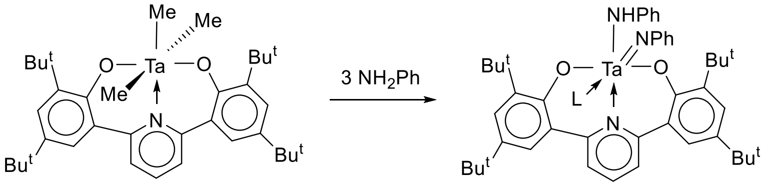


(**160**)

Reactions of $Ta_2(OPr^i)_{10}$ with diethanolamines $RN(CH_2CH_2OH)_2$ (R = H, Me, Bu^n, Ph) gave $[RN(CH_2CH_2O)_2]_2Ta(OPr^i)$.[308]

Reaction of $Ta(OEt)_5$ with salicylaldoxime 2-(HO)$C_6H_4CH{=}NOH$~~-2-OH~~ afforded dimer $Ta_2(\mu\text{-}O)(\mu\text{-}\kappa^3\text{-}O,N,O\text{-salicylaldoximate})_2(OEt)_4$.[309]

Complexes $[ONO]TaCl_3$ and $[ONO]TaCl_2Me$ supported by a pyridine-linked bisphenoxide ligand were prepared by the reactions of Me_2TaCl_3 and ~~Me_3~~$TaMe_3Cl_2$ with bis(phenol)pyridine 2,6-$(HOC_6H_2\text{-}2,4\text{-}Bu^t{}_2)_2NC_5H_3$ ($[ONO]H_2$), respectively.[180] In $[ONO]TaCl_2Me$, the Me and pyridinyl ligands are *trans* to each other. When dipotassium salt $[ONO]K_2$ reacts with ~~Me_3~~$TaMe_3Cl_2$, the product is the trimethyl derivative $[ONO]TaMe_3$,[180] which reacts with NH_2Ph, yielding $[ONO]Ta(=NPh)(NHPh)(NH_2Ph)$ (Scheme 9).[310] When $[ONO]H_2$ reacted with $Ta(NMe_2)_5$, the product was $[ONO]Ta(NMe_2)_3$, which formed $[ONO]Ta(NMe_2)_2Cl$ in the reaction with Me_3SiCl.[310] Reaction of $[ONO]Ta(NMe_2)_2Cl$ with $PhNH_2$ gave $[ONO]Ta(=NPh)Cl(L)$ (L = NH_2Ph or $HNMe_2$) in which the Cl^- ligand is *trans* to the pyridinyl ligand.[310] When added $HNMe_2$, $[ONO]TaCl_2Me$ was converted to $[ONO]Ta(Cl)(Me)(NMe_2)$, in which the Me ligand retains its trans position to the pyridinyl ligand.[310] Hydrazinolysis of $[ONO]Ta(NMe_2)_2Cl$ with H_2NNMe_2 gave $[ONO]Ta(=NNMe_2)Cl(HNMe_2)$.[54]



$[ONO]TaMe_3$

L = NH_2Ph
$[ONO]Ta(=NPh)(NHPh)(NH_2Ph)$

Scheme 9

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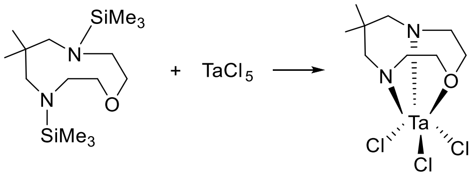
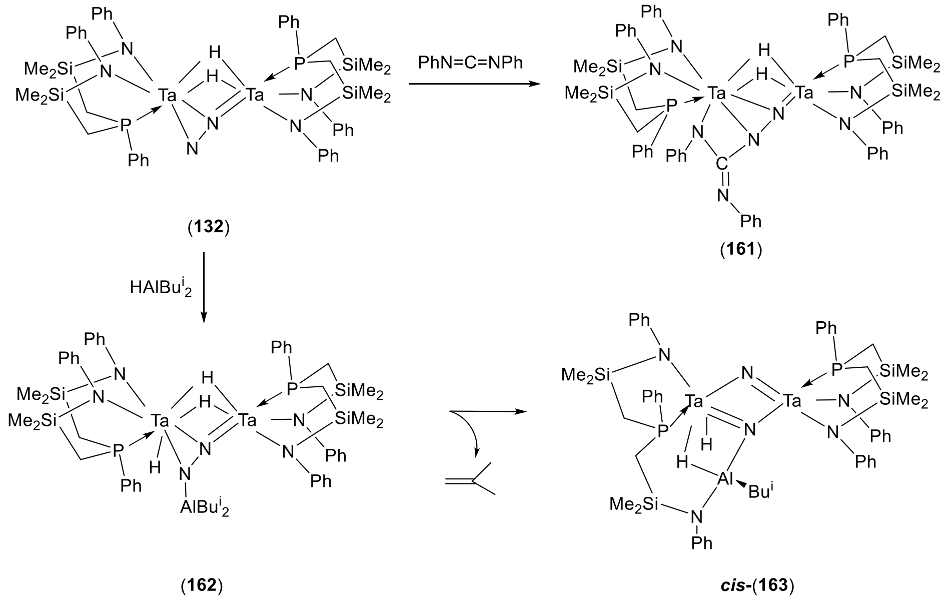
Reaction of dipotassium salt $[ONO]K_2$ with $(dme)Ta(=NNPh_2)Cl_3$ gave $[ONO]TaCl(=NNPh_2)(py)$.[54]

A bis-*N,N′*-trimethylsilyl functionalized macrocycle was used to prepare a complex with a dianionic diamido macrocyclic ligand (Scheme 10).[311] The identity of the complex was based on microanalysis.



Scheme 10

N,N′-diphenyl carbodiimide PhN=C=NPh reacted with $([NPN^{Ph}]Ta)_2(\mu\text{-}H)_2(\mu\text{-}\eta^2{:}\eta^1\text{-}N_2)$ (**132**) to give $([NPN^{Ph}]Ta)_2(\mu\text{-}H)_2[\mu\text{-}PhNC$~~(:~~(=NPh)$N_2]$ (**161**, Scheme 11).[312]

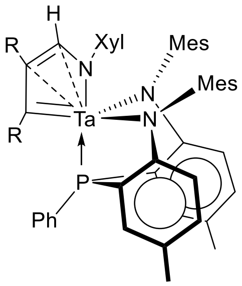


Scheme 11

When adding HAlBu$^i_2$ to ([NPN^{Ph}]Ta)$_2$(μ-H)$_2$(μ-η^1:η^2-N$_2$), the initial product was thermally unstable (**162**) in Scheme 11 which was converted to ~~*cis*-~~(**163**) and a diastereomeric rotational isomer of (**163**).[313] Reactions of (**132**) with secondary and primary boranes led to the cleavage of coordinated dinitrogen ligands.[314] For example, in the reaction with 9-borabicyclo[3.3.1]nonane (9-BBN), hydroboration of the Ta$_2$N$_2$ unit occurred, triggering a cascade of reactions that eventually generated a imide–nitride derivative.[314] When Lewis acid ER$_3$ [ER$_3$ = GaMe$_3$, AlMe$_3$ or B(C$_6$F$_5$)$_3$] was used in the reaction with (**132**), adduct ([NPN^{Ph}]Ta)$_2$(μ-H)$_2$(μ-η^1:η^2-NNER$_3$) was the product.[315]

2.10~~9~~.12. *C,N-trianionic bidentate (carbene-amide)*

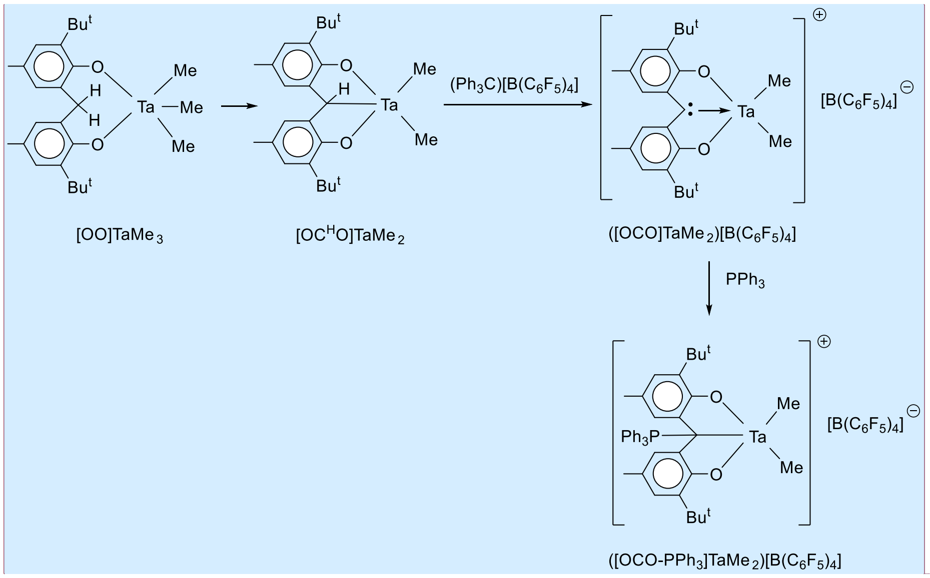
Reaction of [NPN*]Ta(RC≡CR)H (**164**; ([NPN*]$^{2-}$ = PhP[2-(*N*-mesityl)-5-Me-C$_6$H$_3$)$_2$$^{2-}$]; R = Et, SiMe$_3$) with 2,6-dimethylphenyl isocyanide yielded a five-membered tantallacyclic product (**164**).[12]



(**164**)

2.10~~9~~.13. *O,C,O-dianionic tridentate [carbene-bis(phenoxide)]*

Chelating bis(phenoxide) trimethyl complex [OO]TaMe$_3$ in Scheme 12 under heating yielded [OC^{H}O]TaMe$_2$ with a tridentate trianionic ligand.[316] [OC^{H}O]TaMe$_2$ then reacted with (Ph$_3$C)[B(C$_6$F$_5$)$_4$] to give ([OCO]TaMe$_2$)[B(C$_6$F$_5$)$_4$] in Scheme 12 containing a carbene-bis(phenoxide) ligand.[316] PPh$_3$ binds to the carb~~i~~ene C atom in ([OCO]TaMe$_2$)[B(C$_6$F$_5$)$_4$], yielding ([OCO-PPh$_3$]TaMe$_2$)[B(C$_6$F$_5$)$_4$].[316]



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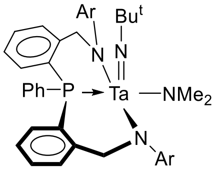
Scheme 12

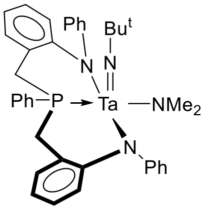
2.10~~9~~.14. *O,P,O-dianionic tridentate ligands*

Bu^{t}N=Ta(NMe$_2$)$_3$ reacted with benzylene-linked ~~tr~~diaminophosph~~a~~ine~~s~~ (H$_2$[NPN]), yielding [NPN](=NBu^t)(NMe$_2$) ([NPN]$^{2-}$ = PhP[C$_6$H$_4$-*o*-CH$_2$N(3,5-Me$_2$C$_6$H$_3$)]~~$_3^2$~~$_2^{2-}$, **165a**; PhP(CH$_2$C$_6$H$_4$-*o*-NPh)$_2$~~$_3$~~$^{2-}$, **165b**).[317]



Ar = 3,5-Me$_2$C$_6$H$_3$

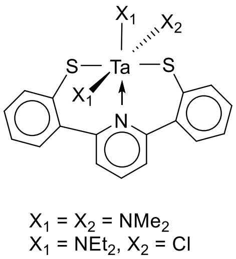
(**165a**)



(**165b**)

2.10~~9~~.15. *S,N,S-dianionic tridentate ligand*

Reaction of (2-C_6H_4SH)$_2$-2,6-C_5H_3N ([SNS]H_2) with Ta(NMe_2)$_5$ gave bis(thiophenolate)pyridine complex [SNS]Ta(NMe_2)$_3$ (**166a**).[318] Using the salt K_2[SNS] and $TaCl_3(NEt_2)_2$ yielded [SNS]TaCl(NEt_2)$_2$ (**166b**).[318]



(**166a,b**)

2.10~~9~~.16. *O,C,O-trianionic tridentate ligand*

Benzene-linked diphenol (HOC_6H_2-Bu^t_2)$_2C_6H_4$ reacts with ~~Me_3~~Ta$Me_3$$Cl_2$, yielding dichloro methyl complex $TaMeCl_2$[(OC_6H_2-Bu^t_2)$_2C_6H_4$] (**167**), which under heating eliminates CH_4 to give $TaCl_2$[(OC_6H_2-Bu^t_2)$_2C_6H_3$] (**168a**).[180, 319] Deuterium labeling of the phenol hydrogen atoms has been used, revealing the mechanism of the reaction.[319] When the dipotassium salt of the benzene-linked diphenol was reacted with ~~Me_3~~Ta$Me_3$$Cl_2$, the product is (**168b**), the dimethyl derivative of (**168a**).[180]

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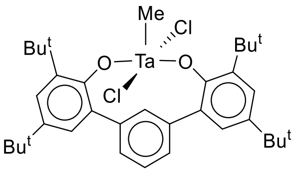
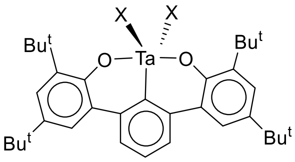


(**167**)



X = Cl, Me

(**168a,b**)

2.10~~9~~.17. *O,N,O-trianionic tridentate ligands*

Reactions of the *N,N*-bis(3,5-~~di-t-butyl~~Bu^t-2-phenoxide)amide trianion ($[ONO^{cat}]^{3-}$) with $TaCl_5$[320] and bis(3,5-Bu^t~~di-t-butyl~~-2-phenol)amine with ~~Me_3~~TaMe_3Cl_2[321] yielded [~~$ONO^{cat}]TaCl_2$~~[321] ~~and~~ $[ONO^{cat}]TaCl_2(L)$ (L = OEt_2,[150, 320] py[321]). The Et_2O ligand is replaced by Cl^- to give $[ONO^{cat}]TaCl_3^-$.[320] The N,O,N trianionic ligand in $[ONO^{cat}]TaCl_2$[321] or $[ONO^{cat}]TaCl_2(OEt_2)$ was oxidized by 0.5 equiv of $PhICl_2$ to give a radical semiquinonate ligand $[ONO^{sq}]^{2-}$ in $[ONO^{sq}]TaCl_3$.[320] $[ONO^{sq}]TaCl_3$ was further oxidized by 0.5 equiv of $PhICl_2$ to yield quinonate form of the ligand, $[ONO^q]^-$ in $[ONO^q]TaCl_4$.[321] $[ONO^{cat}]TaCl_2(OEt_2)$ reacted with 2 equiv of diazoalkane Ph_2CN_2 to form the ketazine adduct $[ONO^{cat}]TaCl_2[\eta^2(N,N')Ph_2C{=}NN{=}CPh_2]$.[322]

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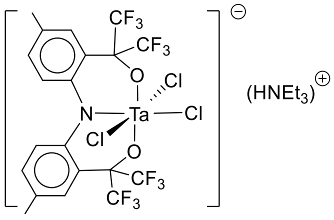
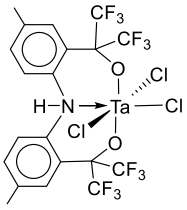
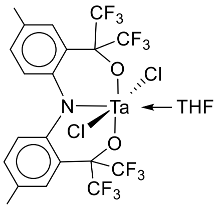
$TaCl_5$ reacted with 2,2′-[azanediylbis(3-methyl-6,1-phenylene)]bis(1,1,1,3,3,3-hexafluoropropan-2-ol) and NEt_3 to give (**169**) containing the pincer ligand.[323] Without NEt_3, the reaction in toluene afforded (**170**), which then in thf was converted (**171**).[323] The two remaining Cl^- ligands in (**171**) were replaced by $PhCH_2MgCl$ to yield dibenzyl complex (**172a**), which is also prepared from the reaction of $Ta(CH_2Ph)_5$ with the pre-ligand 2,2′-[azanediylbis(3-methyl-6,1-phenylene)]bis(1,1,1,3,3,3-hexafluoropropan-2-ol).[323] Reaction of the pre-ligand with $Ta(NMe_2)_5$, followed by vacuum to remove coordinated $HNMe_2$, yield (**172b**).[323]



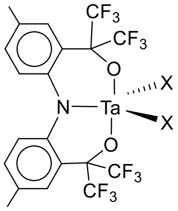
(**169**)



(**170**)



(**171**)

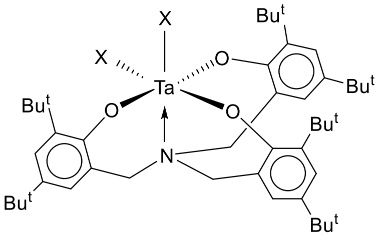


X = CH_2Ph
NMe_2

(**172a,b**)

2.10~~9~~.18. *O,O,O,N-trianionic tetradentate ligands*

Reactions of tris(2-hydroxy-3,5-di-t-butylbenzyl)amine with $Ta(NMe_2)_5$ and $Ta(OEt)_5$ yielded complexes (**173**).[324]



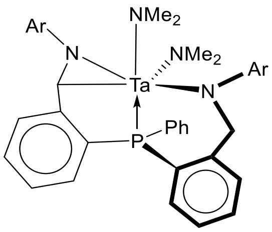
X = NMe_2, OEt

(**173**)

2.10~~9~~.17. *Other trianionic tetradentate ligands*

Reaction of $Ta(NMe_2)_5$ with $[NPN'']H_2$ ($[NPN'']H_2$ = $PhP(C_6H_4$-*o*-$CH_2NHAr)_2$; Ar = 3,5-$Me_2C_6H_3$) afforded $[NPN''{*}]Ta(NMe_2)_2$ (**174**, $[NPN''{*}]^{3-}$ = κ^4-*N,P,N,C*-[PhP(C_6H_4-*o*-

$CH_2NAr)](C_6H_4$-*o*-$CHNAr)^{3-}$).[11] With the addition of Me_3SiI to (**174**), [NPN″*]TaI_2 was formed.

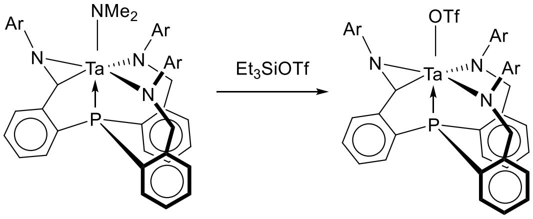


Ar = 3,5-$Me_2C_6H_3$

(**174**)

2.10~~9~~.19. *Tetraanionic pentadentate ligands*

Ta(NMe_2)$_5$ reacted with triamidophosphine to give a cyclometalated triamidophosphine amide complex which, when added Et_3SiOTf, afforded triflate derivative (Scheme 13).[325]



Ar = 3.5-$Me_2C_6H_3$

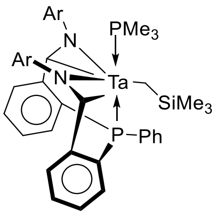
Scheme 13

Addition of PMe_3 or dmpe to [NPN″*]Ta(CH_2SiMe_3)$_2$ [see complex (**174**) for the

Commented [MDJ81]: was this defined

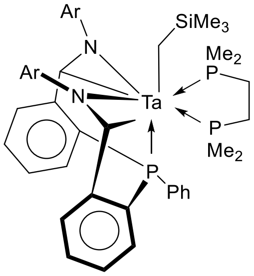
Commented [XZ(82R81]: Just defined for compound **174** above.

definition of the [NPN″*] ligand] afforded [NPN″**]Ta(CH_2SiMe_3)(PMe_3) ([NPN″**] = κ^5-*C,N,P,N,C*-[PhP(C_6H_4-*o*-CHNAr)$_2$]$^{4-}$, Ar = 3,5-$Me_2C_6H_3$) (**175**) and [NPN″**]Ta(CH_2SiMe_3)(dmpe) (**176**), respectively.[11]



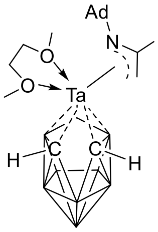
Ar = 3,5-$Me_2C_6H_3$

(**175**)



(**176**)

Treatment of (η^5-$C_2B_9H_{11}$)$TaMe_3$ with adamantyl isonitrile in dme produced (η^6-$C_2B_9H_{11}$)Ta[η^3-*C,C,N*-CH_2C~~(CH_3)~~MeNAd](dme) (**177**).[23]



(**177**)

2.10~~9~~.20. *Aryloxy phosphine ligand*

Reactions of PhP(3,5-$Bu^t{}_2C_6H_2OH$)$_2$ (^{Ph}[OPO]H_2) with $TaCl_5$ and ~~Me_3~~Ta$Me_3$$Cl_2$

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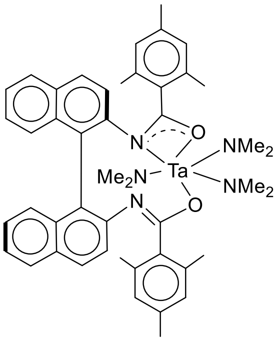
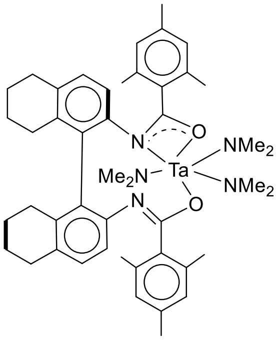
gave ^{Ph}[OPO]TaCl$_3$ and ^{Ph}[OPO]Ta(Me)Cl$_2$ (and ^{Ph}[OPO]Ta(Me)~~$_2$~~Cl$_2$), respectively.[326] When (^{Ph}[OPO]K$_2$)$_2$(thf)$_6$ reacted with Ta(Me)$_3$Cl$_2$, the product was ^{Ph}[OPO]TaMe$_3$.[326] Pr^{i}P(3,5-Bu$^t_2$C$_6$H$_2$OH)$_2$ (^{Pr}[OPO]H$_2$) reacted with TaCl$_5$ to give ^{Pr}[OPO]TaCl$_3$.[326]

2.10~~9~~.21. *O,N,N,O-dianionic tetradentate ligand*

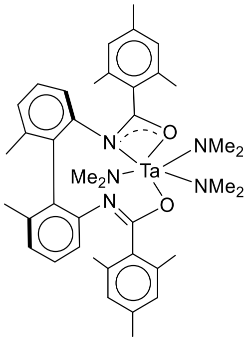
Amide complexes with chiral biaryl-based chiral multidentate ligands (**178**, **179**, **180**, **181**) were prepared from Ta(NMe$_2$)$_5$ with C_2-symmetric ~~amidates~~bis-amides or bis-sulfonylamide.[327]



(**178**)



(**179**)



(**180**)

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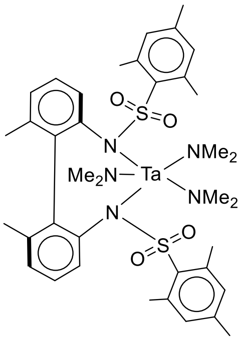
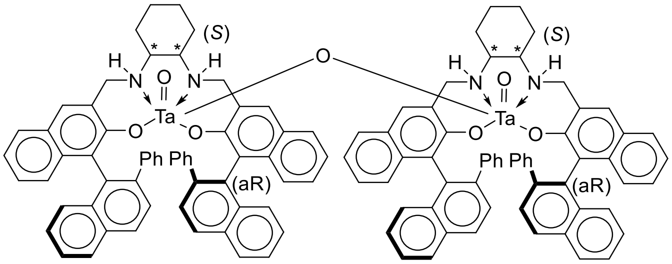


(**181**)

Salan complex (**182**), a stereoisomer, was studied as catalyst for the asymmetric epoxidation of geraniol.[328] The reaction catalyzed by the Ta complex was found to be slower and less selective than that with its Nb analog.[328]

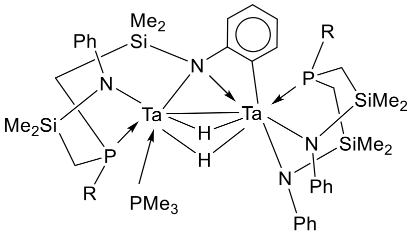


(**182**)

3. TANTALUM (IV)

3.1. Hydride Ligands

$[(Bu^t_2MeSiO)_3Ta]_2(\mu\text{-}H)_2$ and $[(Pr^i_2Bu^tSiO)_3Ta]_2(\mu\text{-}H)_2$ were prepared from reductions of $(Bu^t_2MeSiO)_3TaCl_2$ or $(Pr^i_2Bu^tSiO)_3TaCl_2$, respectively, with Na/Hg in an H_2 atmosphere.[14] In an attempt to isolate the Ta=Ta dihydride complex $([NPN^{Cy}]Ta)_2(\mu\text{-}H)_2(PMe_3)_2$ ($[NPN^{Cy}]^{2-} = CyP(CH_2SiMe_2NPh)_2^{2-}$), a low-temperature reaction of $([NPN^{Cy}]Ta)_2(\mu\text{-}H)_4$ with PMe_3 was conducted. However upon characterization, the orthometallation of the $[NPN^{Cy}]^{2-}$ ligand was found to occur, yielding (**183a**).[329] The $[NPN^{Ph}]^{2-}$ analog (**183b**) ($[NPN^{Ph}]^{2-} = PhP(CH_2SiMe_2NPh)_2^{2-}$) was also prepared in a similar manner.[329]



R = Cy (**a**), Ph (**b**)

(**183**~~a,b~~)

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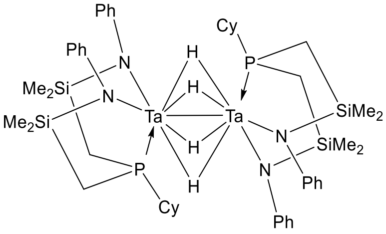
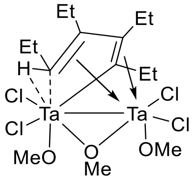
{[NPN^{Cy}]Ta}$_2$(μ-H)$_4$ (**184**) was synthesized from addition of H_2 gas to [NPN^{Cy}]TaMe$_3$.[330]



(**184**)

3.2. Selected Carbon-Based Ligand

When heated with 3-hexyne and 4-octyne, [(η^2-RC≡CR)TaCl$_2$]$_2$(μ-OMe)$_2$(μ-thf) (R = Et, Pr^n), respectively, underwent alkyne coupling reactions to form Ta$_2$Cl$_4$(OMe)$_2$(μ-C$_4$R$_4$)(thf) (R = Et or Pr^n).[156] Reaction of Ta$_2$Cl$_4$(OMe)(μ-OMe)(μ-C$_4$Et$_4$)(thf) with methanol yielded Ta$_2$Cl$_4$(OMe)$_3$(μ-HC$_4$Et$_4$) (**185**).[156]



(**185**)

$[(\text{bit-Bu}^t\text{-X})\text{Ta}]_2(\mu\text{-H})_3\text{Li(thf)}_2$ (**5a**), discussed in Section 2.1, was found to be thermally unstable and formed Ta(IV) complex (**186**) over a period of weeks.[15]

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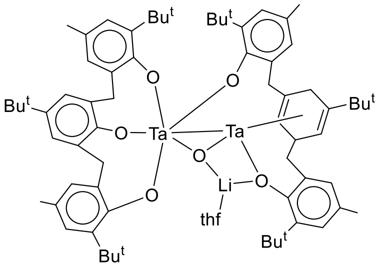


(**186**)

3.3. Nitrogen-Based Ligands

3.3.1. *Neutral ligands*

$\text{TaCl}_4\text{(tmeda)}$ was prepared from TaCl_5, Et_3SiH, and tmeda.[75] Reactions of $(\text{TaCl}_4)_n$ with α-diimines $\text{DAD}^{\text{Dip}}\text{-R}$ [$\text{DAD}^{\text{Dip}}\text{-R} = \text{ArN=C(R)C(R)=NAr}$, R = H, Me, acenaphthene; Ar = $2,6\text{-Pr}^i{}_2\text{C}_6\text{H}_3$] gave $(\text{DAD}^{\text{Dip}}\text{-R})\text{TaCl}_4$.[52] Reduction of $(\text{DAD}^{\text{Dip}})\text{TaCl}_4$

with Cp_2Co yielded $(Cp_2Co)\{[DAD^{Dip}]TaCl_4\}$ (**10**).[52]

The DAD^{Dip} ligand was found to be reactive (Sections 2.~~4~~5.1, 2.~~4~~5.7, and 2.~~4~~5.15).[52] EPR spectra confirmed that these compounds contain either neutral or π-radical α-diimine ligands. These Ta centers can be either Ta^{IV} or Ta^{V} depending on where the electron is located.[52]

3.3.2. *Amido ligands*

$Ta(NEt_2)_2(NCy_2)_2$ and $Ta(NEt_2)_2Cl_2(p\text{-}Me_2Npy)_2$ were prepared by adding $LiNCy_2$ and *p*-dimethylaminopyridine ($p\text{-}Me_2Npy$), respectively, to $[Ta(NEt_2)_2Cl_3]_2$, followed by use of Na/Hg. $Ta(NEt_2)_2Cl_2(p\text{-}Me_2Npy)_2$ adopts an octahedral structure with *trans* chloride and *cis* amido ligands. Thin films with the approximate composition $TaN_{1.5}H_{0.3–0.5}$ were prepared using CVD with $Ta(NEt_2)_2(NCy_2)_2$.[331]

3.3.3. *Ketimide ligands*

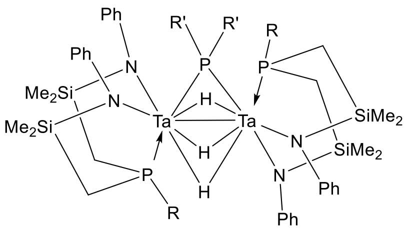
$Ta(N{=}CBu^t_2)_4$ was generated in situ via the reduction of $Ta(OTf)(N{=}CBu^t_2)_4$ by Cp^*_2Co. EPR spectroscopic studies were conducted on this complex and its vanadium and niobium analogs.[75]

3.3.4. *Hydrazido, and hydrazidium ligands*

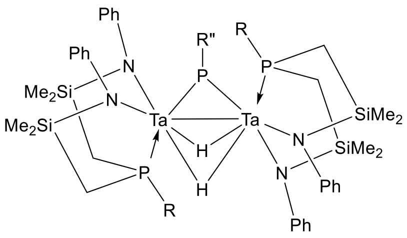
DFT calculations were used to elucidate the mechanism for the cleavage of the N-N bonds in Ta(IV) hydrazido and hydrazidium complexes for N_2 activation.[332]

3.5. Phosphrous Ligands

Reactions of ([NPN^{R}]Ta)$_2$(μ-H)$_4$ ([NPN^{R}]$^{2-}$ = PR(PhNSiMe$_2$CH$_2$)$_2$$^{2-}$; R = Cy, Ad) with HPR′$_2$ (R′ = Cy, Ad) and H$_2$PR″ (R″ = Cy, Ad) gave Ta(IV) complexes ([NPN^{R}]Ta)$_2$(μ-H)$_3$(μ-PR″$_2$) (**187**) and ([NPN^{R}]Ta)$_2$(μ-H)$_2$(μ-PR″) (**188**), respectively.[330]



(**187**)



(**188**)

3.4. Sulfur-Based Ligands

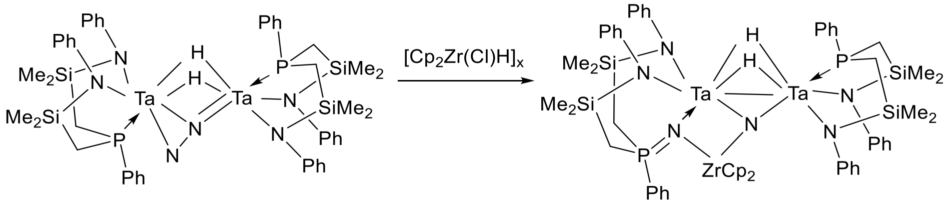
~~When FeCl$_2$ reacted with TaCl$_5$, PMe$_3$ and S(SiMe$_3$)$_2$, cluster [Cl(Me$_3$P)Ta(μ-S)$_2$(μ$_3$-S)$_2$Fe(PMe$_3$)$_2$]$_2$ was produced.~~[236] ~~In the cluster, the two [Cl(Me$_3$P)Ta] units are arranged around one central Fe$_2$(μ-S)$_2$ unit. If~~ Reaction of FeBr$_2$ with TaCl$_5$, PMe$_3$ and S(SiMe$_3$)$_2$ in MeCN afforded cluster [(Me$_3$P)$_2$Ta^{IV}Fe^{II}$_3$(μ$_3$–S)$_4$Br$_4$][(Me$_3$P)$_4$(MeCN)$_2$Fe^{II}] with a reduced, Ta^{IV}-containing [TaFe$_3$S$_4$]$^{2+}$ cubane structure.[237]

Commented [XZ(89]: (1) The section “S” has been moved to after the section on “P”, as in the Ta(VI) complexes earlier.
(2) The 1st two sentences have been moved to the Ta(V)-S section 2.7.1.

3.6. Mixed-Donor Ligands

Dinitrogen complex ([NPN^{Ph}]Ta)$_2$(μ-H)$_2$(μ-η^1:η^2-N$_2$) (**132,** [NPN^{Ph}]$^{2-}$ = PhP(CH$_2$SiMe$_2$NPh)$_2$$^{2-}$) reacted with hydride [Cp$_2$Zr(Cl)H]$_x$ or Cp$_2$M^{II}(py)(Me$_3$SiC≡CSiMe$_3$) (M = Ti, Zr) to give a phosphinimide (**189**) in Scheme

14.[333] In the reaction, the coordinated N_2 was cleaved to form a triply bridging nitride and a phosphinimide bridging between Ta and M~~ and a triply bridging nitride~~.[333]



(**132**) (**189**)

Scheme 14

Reactions of complex (**132**) with 1 equiv of silanes H_3SiR (R = Bu^n, Ph, $CH_2CH_2SiH_3$) yielded disilylimide dimer (**190**), (**191**), (**192**) (Scheme 15).[334] ~~-~~(**190**) reacted with another 1 equiv of silanes to give (**193**), (**194**), (**195**) with a Ta^{IV}-Ta^{IV} bond.[334, 335] ~~DFT studies were conducted to determine the energetics of the reaction in forming ([NPN^{Ph}]Ta)$_2$(μ-NSiH$_2$Bu^n)$_2$ (**194**).[336] I~~ In the presence of a catalytic amount of H_3SiBu^n, (**194**) was converted to (**196**).[334] For (**191**) (R = Ph), its reaction with additional H_3SiPh gave (**197**).[334] For (**192**, ~~(~~R = $CH_2CH_2SiH_3$), it underwent conversion to give (**198**).[334]

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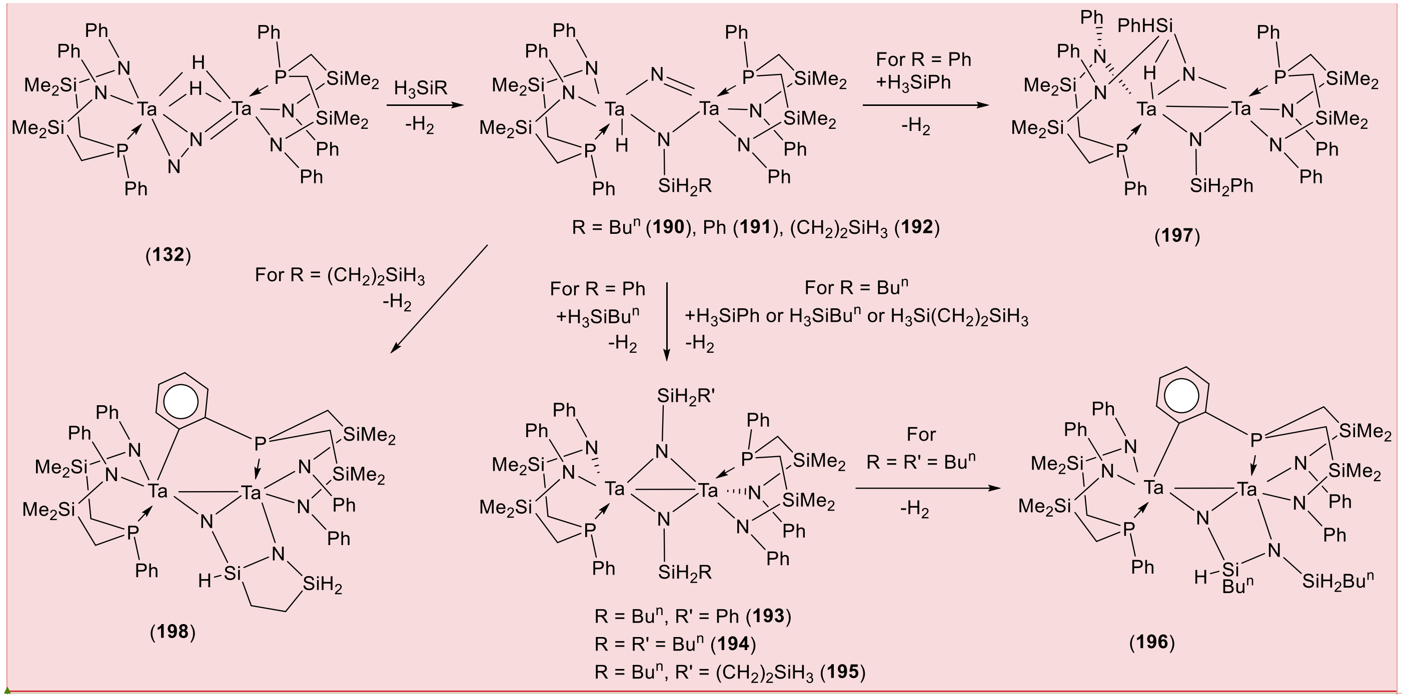

Scheme 15. In Ref. 334, authors indicated that a Ta-Ta bond in (**197**) is necessary to explain its the observed diamagnetic behavior.

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Commented [XZ(92]: Please use this for Scheme 15 (not the one above which should be deleted).

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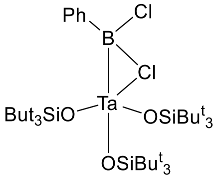
4. TANTALUM (III)

4.1. Boron-Based Ligands

$(silox)_3Ta(BH_3)$ and $(silox)_3Ta(\eta^2$-*B,Cl*-$BCl_2Ph)$ (**199**) were synthesized from the reaction of $(silox)_3Ta$ with $BH_3{\cdot}thf$ and BCl_2Ph, respectively.[19]



(**199**)

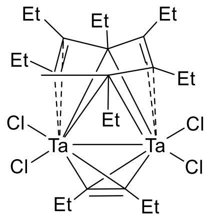
4.2. Carbon-Based Ligands

4.2.1. *Alkylidene, alkylidyne, alkene, and alkyne ligands*

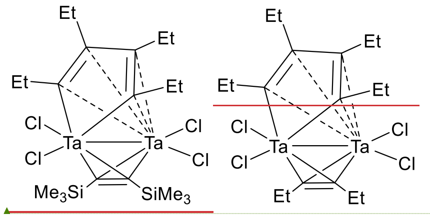
Thermolysis of $(silox)_2Ta(pyrr)Et_2$ (pyrr = pyrrolidine) afforded the alkene adduct complex $(silox)_2Ta^{III}(pyrr)(\eta^2$-$C_2H_4)$.[31] Treatment of $(silox)_2Ta(pyrr)Cl_2$ and $(silox)_2Ta(pip)Cl_2$ with Na/Hg in the presence of pyridine gave $(silox)_2Ta(pyrr)(\eta^2$-*N,C*-$NC_5H_5)$ and $(silox)_2Ta(pip)Ta(\eta^2$-*N,C*-$NC_5H_5)$, respectively.[31]

$Ta_2Cl_4(\mu$-η^4:η^4-$C_6Et_6)(\mu$-η^2:η^2-$EtC{\equiv}CEt)$ (**200**) was prepared by either treating $Ta_2Cl_6(\mu$-$C_4Et_4)(thf)$ with 10 equiv of 3-hexyne or by reducing $Ta_2Cl_6(\mu$-$C_4Et_4)$ with 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (Me_4-btdp), followed by adding 2 equiv of 3-hexyne.[336] If 3-hexyne was not added after the reduction, the polymer $[Ta_2Cl_4(\mu$-$C_4Et_4)]_n$ was produced. $Ta_2Cl_4(\mu$-$C_4Et_4)(\mu$-η^2:η^2-$Me_3SiC{\equiv}CSiMe_3)$ (**201**) was synthesized from Me_4-btdp, $Me_3SiC{\equiv}CSiMe_3$, and $Ta_2Cl_6(\mu$-$C_4Et_4)$.[336] $Ta_2Cl_4(\mu$-η^4:η^4-$C_6Et_4R_2)(\mu$-η^2:η^2-$Me_3SiC{\equiv}CSiMe_3)$ (R = Me or Pr^n) and

$Ta_2Cl_4(\mu\text{-}\eta^4:\eta^4\text{-}C_6Et_4RH)(\mu\text{-}\eta^2:\eta^2\text{-}Me_3SiC\equiv CSiMe_3)$] (R = Bu^n, *p*-tolyl) were synthesized by treating $Ta_2Cl_4(\mu\text{-}C_4Et_4)(\mu\text{-}\eta^2:\eta^2\text{-}Me_3SiC\equiv CSiMe_3)$ with 4-octyne, 2-butyne, 1-hexyne, and *p*-tolylacetylene at low-temperatures.[336] Complexes $Ta_2Cl_4(\mu\text{-}\eta^4:\eta^4\text{-}C_6Et_4Me_2)(\mu\text{-}\eta^2:\eta^2\text{-}Me_3SiC\equiv CSiMe_3)$ and $Ta_2Cl_4(\mu\text{-}\eta^4:\eta^4\text{-}C_6Et_4RH)(\mu\text{-}\eta^2:\eta^2\text{-}Me_3SiC\equiv CSiMe_3)$ (R = Bu^n, *p*-tolyl) underwent isomerization at 80 °C and room temperature, respectively.[336]



(**200**)



(**201**)

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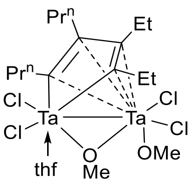
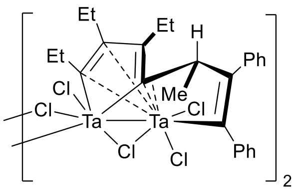
$Ta_2Cl_4(OMe)_2(\mu\text{-}C_4R_4)(thf)$ and $Ta_2Cl_5(OMe)(\mu\text{-}C_4R_4)(thf)$ (R = Et, Pr^n) were the thermal decomposition products of $Ta_2Cl_4(\eta^2\text{-}RC\equiv CR)_2(\mu\text{-}OMe)_2(\mu\text{-}thf)$ (R = Et, Pr^n).[156] Pure $Ta_2Cl_5(OMe)(\mu\text{-}C_4R_4)(thf)$ (R = Et, Pr^n) was formed when $Ta_2Cl_4(OMe)_2(\mu\text{-}C_4R_4)(thf)$ (R = Et or Pr^n) was heated in toluene with $SiCl_4$.[156] If MeOH was added to $Ta_2Cl_4(OMe)_2(\mu\text{-}C_4Et_4)(thf)$ at -78 °C, $Ta_2Cl_4(OMe)_3(\mu\text{-}HC_4Et_4)$ was formed. $Ta_2Cl_4(OMe)_2(\mu\text{-}C_4R_4)(thf)$ (R = Et, Pr^n) was reacted with 4-dimethylaminopyridine (dmap) to yield $Ta_2Cl_4(OMe)_2(\mu\text{-}C_4R_4)(dmap)$ (R = Et, Pr^n).[156] $Ta_2Cl_4(OMe)_2(\mu\text{-}C_4\text{-}2,3\text{-}Pr^n{}_2\text{-}4,5\text{-}Et_2)(thf)$ (**202**) was formed from $Ta_2Cl_4(\eta^2\text{-}EtC\equiv CEt)_2(\mu\text{-}OMe)_2(\mu\text{-}thf)$ and 4-octyne.[156] $Ta_2Cl_6(\mu\text{-}C_4Et_4)$ was made by reacting $TaCl_3(\eta^2\text{-}EtC\equiv CEt)(dme)$ with $AlCl_3$ in toluene and heated.[336] Lewis bases were added to $Ta_2Cl_6(\mu\text{-}C_4Et_4)$ to make the adducts

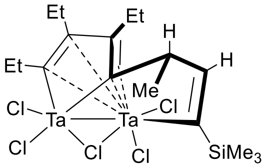
$Ta_2Cl_6(\mu\text{-}C_4Et_4)L$ [L = thf, py, tetrahydrothiophene (tht)]. Several of these dinuclear complexes were found to be active catalyst in cyclotrimerization of internal and terminal alkynes.[156, 336, 337] Polymeric $\{Ta_2Cl_5[\mu\text{-}C_4Et_3(CHMe)]\}_n$ was formed from the reaction of $Ta_2Cl_6(\mu\text{-}C_4Et_4)$ with $PhSiH_3$, which was formed from selective C-H bond activation and loss of H_2. Tetrahydrofuran (thf) reacted with the polymer to give monomeric $Ta_2Cl_5(thf)_2[\mu\text{-}C_4Et_3(CHMe)]$ which, in the reactions with PhC≡CPh and $HC{\equiv}CSiMe_3$, yielded $\{Ta_2Cl_5[C_4Et_3(CHMeCPh{=}CPh)]\}_2$ (**203**) and $Ta_2Cl_5[C_4Et_3(CHMeCH{=}CSiMe_3)]$ (**204**), respectively.[338] Benzaldehyde, 2-vinylpyridine, and PMe_2Ph also reacted with $Ta_2Cl_5(THF)_2[\mu\text{-}C_4Et_3(CHMe)]$ to form $Ta_2Cl_5[C_4Et_3(CHMeCHPhO)]$, $Ta_2Cl_5[C_4Et_3(CHMeCH_2CHpy)]$, and $Ta_2Cl_5(PMe_2Ph)_2[\mu\text{-}C_4Et_3(CHMe)]$, respectively.[338]



(**202**)



(**203**)

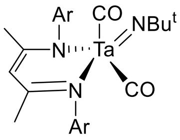


(**204**)

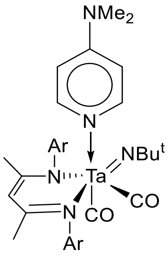
4.2.2. *Carbonyl ligands*

Reactions of CO with cyclometallated tantalum hydride (**7**) and

{ArNC(Me)CHC(Me)N[2-(CHMeCH$_2$)-6-Pr^i-C$_6$H$_3$]}Ta(=NBu^t)(dmap)H (Ar = 2,6-Pr$^i_2$C$_6$H$_3$) yielded [BDI^{Pr}]Ta(=NBu^t)(CO)$_2$ (**205**) and [BDI^{Pr}]Ta(=NBu^t)(CO)$_2$(dmap) (**206**), respectively.[17]



(**205**)



(**206**)

DFT studies were performed about whether Re(NH$_2$)$_3$ and Ta(NH$_2$)$_3$ could activate CO with the strongest bond in chemistry.[339] The computations showed that CO bounded to Re(NH$_2$)$_3$ without a barrier, forming OC-Re(NH$_2$)$_3$. The binding of Ta(NH$_2$)$_3$ to the O atom of CO had a barrier of 20 kJ mol^{-1}~~ and was followed by spontaneous cleavage of the C-O bond to form the products C-Re(NH$_2$)$_3$ and O-Ta(NH$_2$)$_3$~~.[339]

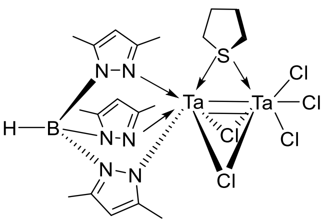
4.3. Nitrogen-Based Ligands

4.3.1. *Neutral ligands*

Treating TaCl$_3$(η^2-EtC≡CEt)(dme) with bidentate ligands bipyridine and tmeda gave TaCl$_3$(η^2-EtC≡CEt)(bipy) and TaCl$_3$(EtC≡CEt)(tmeda), respectively.[34]

4.3.2. *Tris(pyrazolyl)borohydride and (methimazolyl)borate ligands*

Dinuclear complex (Tp*Ta)(TaCl$_3$)(μ-Cl)$_2$(μ-tht) (tht = tetrahydrothiophene) (**207**), containg a Ta=Ta double bond, was synthesized from refluxing $[TaCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht)$ with KTp*.[340] The X-ray structure of a previously reported complex Tp*$TaCl_2$(PhC≡CMe) was also obtained.[340]



207

4.3.3 *Amide ligands*

Pathways ~~of~~ in the formation of (H_2N)~~R~~$_3$Ta=C=C=Ta(NH_2)~~R~~$_3$ by the reactions of CO with 3-coordinate compounds ~~TaR_3~~ $Ta(NH_2)_3$ ~~(R = silox, NH_2)~~ were investigated via DFT studies.[341] The stable intermediate $(H_2N)_3$Ta ~~silox)$_3$Ta~~-(CO)$_2$-Ta$(NH_2)_3$~~(silox)$_3$~~ was identified. Mixed metal systems $(H_2N)_3$~~(silox)$_3$~~Ta-(CO)$_2$-M(NH_2~~silox~~)$_3$ (M = La, Hf, W, Re) were modeled.[341] Geometries of intermediates with Ta[N(Bu^t)Ph]$_3$ were also modeled.[341]

Calculations of the mononuclear and dinuclear pathways of the cleavage of CO_2 by Ta[N(Bu^t)Ph]$_3$ were performed.[342] It was found that in the Ta-Ta system successfully bind to CO_2 in a mononuclear η^2 arrangement and would strongly activate one C–O bond to a point where spontaneous C–O bond cleavage occurs.[342]

4.4. Sulfide and Selenide Ligands

Reduction of $TaCl_5$ by Mg in the presence of SR_2 (R = Me, ~~or~~ Bu^n) gave $Ta^{III}{}_2Cl_4(SR_2)_2(\mu\text{-}Cl)_2(\mu\text{-}SR_2)$ with Ta=Ta double bonds.[343]

Reactions of $TaCl_5$ with Mg and thioethers SMe_2, tetrahydrothiophene C_4H_8S (thiolane), and tetrahydrothiopyran $C_5H_{10}S$ (thiane) gave Ta(III) dimers $Ta_2Cl_4L_2(\mu\text{-}Cl)_2(\mu\text{-}L)$ (L = thioether) containing Ta=Ta double bonds.[344] A similar reaction involving $TaBr_5$, Mg and SMe_2 yielded analogous complex $Ta_2Br_4(SMe_2)_2(\mu\text{-}$~~Cl~~Br$)_2(\mu\text{-}SMe_2)$.[344]

When $Ta^{III}{}_2Cl_4(SMe_2)_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)$ was added $MeSe(CH_2)$~~$_n$~~$_2$SeMe~~ (n = 2, 3)~~, SMe_2 ligands were replaced to give $Ta^{III}{}_2Cl_4[\eta^2\text{-}MeSe(CH_2)$~~$_n$~~$_2SeMe]_2(\mu\text{-}Cl)_2$ retaining the Ta=Ta double bond. If Bu^n~~R~~$SeCH_2CH_2CH_2Se$~~R (R = Me,~~ Bu^n~~)~~ was used instead, the reaction afforded the tetramer $[Ta^{III}{}_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)]_2(\mu\text{-}$$Bu^n$~~R~~$SeCH_2CH_2CH_2SeBu^n)_2$.[343]

5. TANTALUM (I)

Commented [MDJ93]: But there are some Ta-1 complexes shown here too.

Commented [XZ(94R93]: I've added a note in the section below on Ta(-I) about this point.

5.1. Carbon-Based Ligands

5.1.1. *Isocyanide ligands*

Reaction of $[Et_4N][Ta(CO)_6]$, CNDipp (Dipp = 2,6-$Pr^i{}_2C_6H_3$), and $AgBF_4$ in thf afforded the salt $[Ta(CNDipp)_7][BF_4]$.[345] The air-sensitive $TaI(CNDipp)_6$ was synthesized via the reaction of I_2 with Ta(-I) species $[Et_4N][Ta(CO)_6]$ in the presence of 6 equiv of CNDipp in a procedure similar to that for the synthesis of its analog $TaI(CNXyl)_6$.[345, 346] $TaI(CNDipp)_6$ was also the product of the reaction of the zerovalent $Ta(CNDipp)_6$ with SnI_2. ~~The~~ A ditantalum complex $[Ta(CNDipp)_7]^+[Ta(CO)_5(CNDipp)]^-$ containing Ta(I) and Ta(-I) moieties was prepared from zerovalent $Ta(CNDipp)_6$ heated with CO as a result of a disproportionation reaction. The crystal structure of the product showed the well-defined ions of $[Ta(CNDipp)_7]^+$ and $[Ta(CO)_5(CNDipp)]^-$ in the ~~crystal~~ lattice.[345]

6. TANTALUM (0)

6.1. Carbon-Based Ligands

6.1.1. *Homoleptic isocyanide ligands*

Zerovalent homoleptic Ta complexes are rare and more unstable than their vanadium and niobium analogs.[345] $Ta(CNDipp)_6$ was prepared wither from the reaction of $[Et_3NH][BPh_4]$ with $K[Ta(CNDipp)_6]$, $[Ta(CNDipp)_7)][BF_4]$ with $K[Ta(CNDipp)_6]$, or from the oxidation of $K[Ta(CNDipp)_6]$ by MoO_3. When in the presence of pyridine, $Ta(CNDipp)_6$ experiences reversible disproportionation to $[Ta(CNDipp)_6(py)]^+$ and $[Ta(CNDipp)_6]^-$.[345]

6.2 Nitrogen-Based Ligands

When tropylium tetrafluoroborate was added to $[Na(thf)_5][Ta(^tbpy)_3]$, neutral $Ta(^tbpy)_3$ (^tbpy = 4,4-di-t-butyl-2,2-bipyridine) was made.[347]

7. TANTALUM (-I)

Please see Section 5.1.1 on Ta(I) complexes with isocyanide ligands about the use of Ta(-I) $[Et_4N][Ta(CO)_6]$ as a starting material and the formation of $[Ta(CNDipp)_7]^+[Ta(CO)_5(CNDipp)]^-$ as a result of a disproportionation reaction of $Ta(CNDipp)_6$ under CO.[345]

7.1 Hydride Ligands

$[Li(tmed)]_3[TaHEt(C_2H_4)_4]\cdot 1/2$ tmed (tmed = *N,N,N′,N′*-tetramethylethylenediamine) was produced by first alkylating $TaCl_2(OMe)_3$ with LiEt, filtering, and adding tmed to that solution. The crystal structure shows that the Ta-H bond was relatively long, which was attributed to the presence of lithium cations.[348]

7.2. Carbon-Based Ligands

7.2.1. *Homoleptic and alkene ligands*

[~~$N(PPh_3)_2$~~PPN]$[Ta(\eta^4\text{-}C_4H_6)_3]$ [PPN^{+} = $N(PPh_3)_2^{+}$] was prepared from the reaction of $[Na(thf)_2][Ta(\eta^4\text{-}C_{10}H_8)_3]$ with excess 1,3-butadiene followed by the addition of [PPN]Cl to the resulting solid.[349] Analogous salts $[Na(dibenzo\text{-}18\text{-}crown\text{-}6)(thf)_2][Ta(\eta^4\text{-}C_4H_6)_3]$ and $[Na(18\text{-}crown\text{-}6)][Ta(\eta^4\text{-}C_4H_6)_3]$ were also synthesized using a similar procedure.[349] In thf, these salts undergo facile protonation by $[Et_3NH]Cl$ to afford $[Ta(\eta^3\text{-}1\text{-}MeC_3H_4)(\eta^4\text{-}C_4H_6)_2]$.[349]

Commented [MDJ95]: Please check

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[PPN]$Ta(C_{10}H_8)$~~(PPN)~~ was synthesized from the reaction of $[Na(thf)_2][Ta(\eta^4\text{-}C_{10}H_8)_3]$ with [PPN]Cl, in which two phenyl groups on one PPh_3 substituent of $[PPN]^+$ are *ortho*-metallated, while the third phenyl ring is hydrogenated to provide a tantalum bound 1,3-cyclohexadiene group.[350] Ta(I) complex [PPN]$Ta(C_{10}H_8)$~~(PPN)~~$[P(OMe)_3]$ was prepared from the treatment of [PPN]$Ta(C_{10}H_8)$~~(PPN)~~ with $P(OMe)_3$ in thf. Crystal structures show that these complexes are the thf adducts [PPN]$Ta(C_{10}H_8)$~~(PPN)~~$[P(OMe)_3](thf)_{0.5}$ and [PPN]$Ta(C_{10}H_8)$~~(PPN)~~(thf).[350]

7.2.2. *Isocyanide ligands*

$[Na(2.2.2\text{-}cryptand)][Ta(CN\text{-}2,6\text{-}Me_2C_6H_3)_6]$ was synthesized via the reaction of

$[Na(2.2.2\text{-cryptand})][Ta(\eta^4\text{-}C_{10}H_8)_3]$ with 6 equiv of $CN\text{-}2,6\text{-}Me_2C_6H_3$.[346] IR spectral features of the product were essentially identical to those of its potassium analog $[K(2.2.2\text{-cryptand})][Ta(CN\text{-}2,6\text{-}Me_2C_6H_3)_6]$.[351] $[Et_4N][Ta(CO)_5(CN\text{-}2,6\text{-}Me_2C_6H_3)]$ was made in order to compare it to the homoleptic complex $Cs[Ta(CN\text{-}2,6\text{-}Me_2C_6H_3)_6]$.[346] Several $Ta(CNDipp)_6^-$ (Dipp = $2,6\text{-}Pr^i_2C_6H_3$) complexes were synthesized by Chakarwet and coworkers.[345] A solution of $TaI(CNDipp)_6$ was stirred in the presence of a suspension of KC_8 to give $K[Ta(CNDipp)_6]$.[345] The hepta-coordinated complex $(Ph_3P)AuTa(CNDipp)_6$ could be prepared from $K[Ta(CNDipp)_6]$ and Ph_3PAuCl. The complex was apparently the first gold adduct of a homoleptic metal isocyanide reported at the time.[345] Treatment of $K[Ta(CNDipp)_6]$ with Ph_3SnCl gave $Ph_3SnTa(CNDipp)_6$.[345] When $Ta(CNDipp)_6$ was reacted with $[K(18\text{-crown-}6)][SnPh_3]$, a mixture of $Ph_3SnTa(CNDipp)_6$ and $[K(18\text{-crown-}6)][Ta(CNDipp)_6]$ was prepared.[345]

7.3 Nitrogen-Based Ligands

$[Na(thf)_5][Ta(^tbpy)_3]$ was synthesized from $TaCl_5$, ^{t}bpy (4,4′-di-tert-butyl-2,2′-bipyridine), and Na/Hg amalgam.[347] Treatment of $Cs[Ta(CN\text{-}2,6\text{-}Me_2C_6H_3)_6]$ with Diazald (*N*-methyl-*N*-nitroso-p-toluenesulfonamide) afforded $Ta(CN\text{-}2,6\text{-}Me_2C_6H_3)_5NO$.[346]

8. TANTALUM IN MIXED OXIDATION STATES

When $[Ta_6Br_{12}(EtOH)_6]Br_2$ was treated with Et_4NBr, followed by recrystallization in water in air, the process gave $(Et_4N)[Ta_6Br_{12}(H_2O)_6]Br_4\cdot 4H_2O$.[352] The $(Ta_6Br_{12})^{2+}$ cluster in $[Ta_6Br_{12}(EtOH)_6]Br_2$ was oxidized by O_2 in air to $(Ta_6Br_{12})^{3+}$ in the product.[352]

Oxidation of ~~$(Ta_6Cl_{12})Cl_2\cdot 6EtOH$~~ $[Ta_6Cl_{12}(EtOH)_6]Cl_2$ in ~~*n*-~~Bu^nCN solution leads to the formation of $2[(Ta_6Cl_{12})Cl_3($~~*n*-~~$Bu^nCN)_3]\cdot[(Ta_6Cl_{12})Cl_4($~~*n*-~~$Bu^nCN)_2]\cdot$~~*n*-~~$Bu^nCN$ containing different charged clusters $(Ta_6Cl_{12})^{3+}$ and $(Ta_6Cl_{12})^{4+}$.[353] Its structure consists of layers formed by the intergrown 1-D chains of the different cluster components.

9. ACKNOWLEDGMENTS

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