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Review

Recent developments in the coordination and organometallic chemistry of Kläui oxygen tripodal ligands

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Abstract

The Kläui oxygen tripodal ligands $[(\eta^5\text{-}C_5H_5)Co\{P(O)(OR)_2\}_3]^-$ ($L_{OR}{}^-$ where R = alkyl group), which have been recognized as oxygen analogues of cyclopentadienyl, can form stable complexes with a range of main group and transition metal ions. This review reports on the recent developments in the coordination and organometallic chemistry of the Kläui tripodal ligands. Special attention will be paid to polynuclear M-L_{OEt} (M = Ti, Zr) oxo and hydroxo compounds that may serve as models for group 4 metal aqua ions.

Keywords: Oxygen ligand; Tripodal ligand; Metal complex; Cluster

1. Introduction

The mono-anionic oxygen tripodal ligands of the general formula $[CpCo(P(O)(X)_2)_3]^-$ ($L_x{}^-$), where Cp = cyclopentadienyl; X = alkyl, aryl, alkoxy or aryloxy (Scheme 1), developed by Kläui and co-workers [1–4] have been recognized as oxygen analogues of cyclopentadienyl. The

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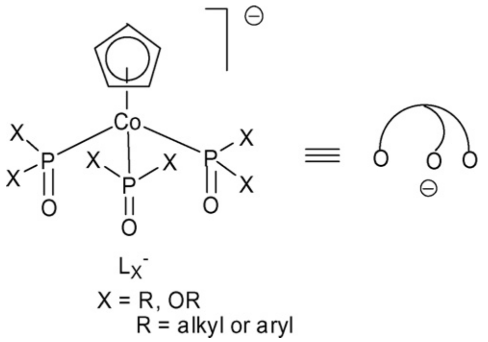


Scheme 1. Structure of the Kläui oxygen tripodal ligands.

Kläui tripodal ligands can form stable complexes with various main group and transition metal ions [1,5–10]. Owing to their hydrolytic stability, they have been used as models of facially coordinated aqua ligands in organometallic compounds [11]. Despite their hardness and strong π-donor strength, L_x^- are compatible with both hard and soft metal ions, exhibiting interesting organometallic chemistry. The use of M-L_x complexes in homogeneous catalysis has been reported [12].

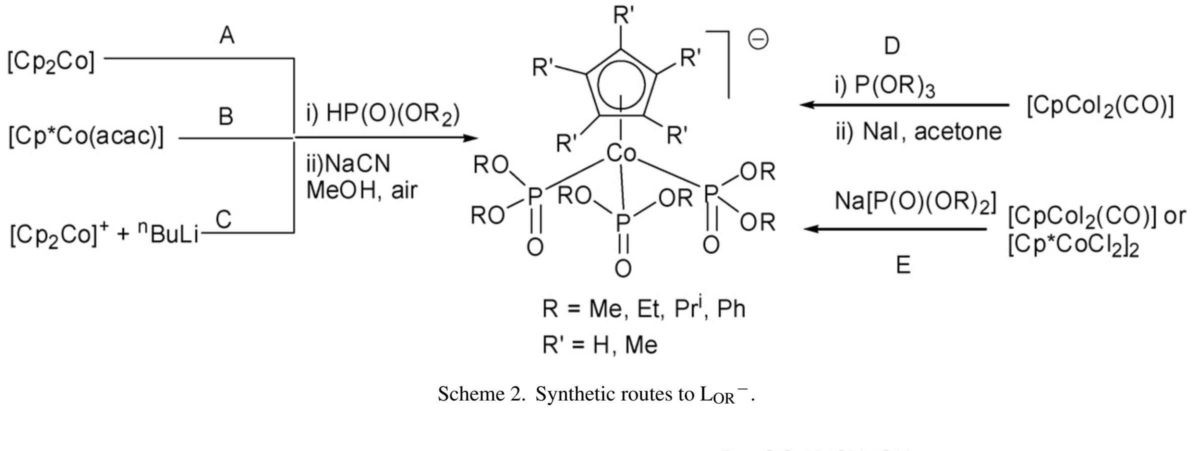
This review summarizes the recent developments in the coordination and organometallic chemistry of the Co(III)-based Kläui tripodal ligands $[CpCo\{P(O)(OR)_2\}_3]^-$, denoted as L_{OR}^-. In particular, the studies on polynuclear Ti(IV)- and Zr(IV)-L_{OEt} oxo and hydroxo complexes that are relevant to group 4 aqua ions will be highlighted. The review is organized into three sections: (i) Ligand syntheses, (ii) Survey of metal complexes, and (iii) Applications. The survey of complexes, which is organized by groups, will cover the works published after 1990. A detailed account on metal complexes with L_{OR}^- prepared prior to 1990 can be found in Kläui's review [1].

2. Ligand syntheses

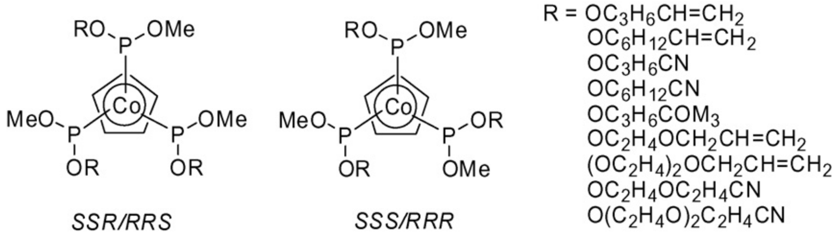
L_{OR}^- are generally synthesized by (i) reaction of $[CP_2Co]$ (method A), $[Cp^*Co(acac)]$ ($Cp^* = \eta^5\text{-}C_5Me_5$, $acac^-$ = acetylacetonate) (method B), or $[Cp_2Co]^{+/n}BuLi$ (method C) with $HP(O)(OR)_2$ followed by demetallation with NaCN in air; (ii) reaction of $[CpCoI_2(CO)_2]$ with $P(OR)_3$ followed by Arbuzov dealkylation with NaI (method D); or (iii) reaction of $[CpCoI_2(CO)_2]$ or $[Cp^*CoCl_2]_2$ with $NaP(O)(OR)_2$ (method E) (Scheme 2) [2–4,12–14].

The analogous Ir(III)-based tripodal ligand $[Cp^*Ir\{P(O)(OMe)_2\}_3]^-$ has been prepared by reaction of $[Cp^*IrCl_2]_2$ with $Ag(ClO_4)$ and $P(OMe)_3$ followed by NaI/acetone [15]. Di-anionic Ru(II)-based tripodal ligands $[Cp^*Ru\{P(O)(OR)_2\}_3]^{2-}$ ($L_{Ru,OR}^{2-}$), where R = Me, Et, Pr^i, have been synthesized by either (i) treatment of $[Cp^*Ru(OMe)]_2$ with $HP(O)(OR)_2$ (R = Me, Ph) followed by dealkylation with NaI, or (ii) direct reaction of $[Cp^*RuCl]_2$ with $NaP(O)(OEt)_2$. Similar to mono-anionic L_{OR}^-, $L_{Ru,OR}^{2-}$ reacted with metal halides to give stable complexes of the types $[M(L_{Ru,OR})_2]^{n-}$ (M = Si^{IV}, Ti^{IV}, Nb^{IV}, $n = 0$; Cr^{III}, Fe^{III}, $n = 1$; Co^{II}, $n = 2$) and $[MX(L_{Ru,OR})]$ (MX = BPh or $V^{IV}(O)$) [16,17].

Kläui tripodal ligands bearing functional groups in pendant side chains $[CpCo\{P(O)(OMe)(OR')_3\}]^-$, where $R = (C_2H_4O)_nCH_2CH{=}CH_2$, $(C_2H_4O)_nC_2H_4CN$, $(C_3H_6)CN$, $C_3H_6C(O)CH_3$, $(CH_2)_5CO_2Me$; $n = 1$ or 2, have been synthesized by reaction of $[CpCoI_2(CO)P(OMe)(OR')$ with $P(OMe)_2(OR)$ followed by dealkylation with NaI, and iso-



Scheme 2. Synthetic routes to L_{OR}^-.



Scheme 3. Newman projections of the *RRR*/*SSS* and *RRS*/*SSR* diasteromers of $L_{OMe,OR}^-$ (*R* and *S* refer to the configurations of the phosphorus centers).

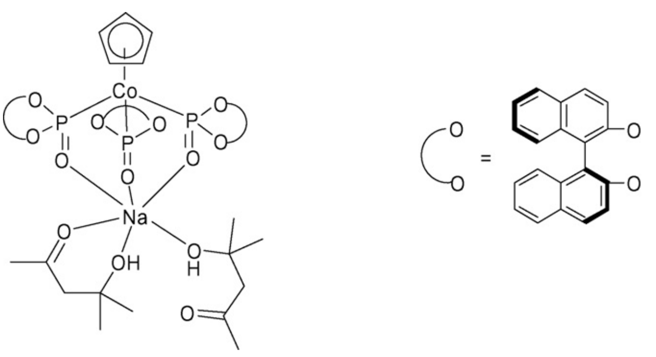
lated as two pairs of disastereomers, namely the *RRR*/*SSS* and *RRS*/*SSR* isomers (Scheme 3), according to NMR spectroscopy [12].

Hydrolysis of Na[CpCo{P(O)(OMe)(O(CH$_2$)$_5$CO$_2$Me)}$_3$] and Na[(η^5-C$_5$H$_4$CO$_2$Me)Co{P(O)(OMe)$_2$}$_3$] with KOH followed by protonation with H_2SO_4 afforded carboxy-substituted tripodal ligands Na[CpCo{P(O)(OMe)(O(CH$_2$)$_5$CO$_2$H)}$_3$] and Na[(η^5-C$_5$H$_4$CO$_2$H)Co{P(O)(OMe)$_2$}$_3$], respectively [18].

The chiral C$_3$-symmetric tripodal ligand $L_{\text{S-BINOL}}^-$ has been synthesized by reaction of the sodium salt of HP(O)(*S*-BINOL) (*S*-BINOLH$_2$ = (*S*-(-)-bi-2-napthol) with [CpCoI$_2$(CO)]. Recrystallization of Na($L_{\text{S-BINOL}}$) from acetone led to isolation of [($L_{R\text{-BINOL}}$)Na(C$_6$H$_{12}$O$_2$)$_2$] (Scheme 4), the diacetone alcohol ligands of which were derived from the aldol reaction of acetone. The chiral nature of $L_{S\text{-BINOL}}^-$ is indicated by its large measured optical rotation, $[\alpha]^{72}{}_D = -446°$ (CH$_2$Cl$_2$, *c* 0.36). The *R*-isomer $L_{R\text{-BINOL}}^-$ was prepared similarly from NaP(O)(*R*-BINOL) and [CpCoI$_2$(CO)] [19].

Na(L_{OR}) tends to aggregate in both the solid state and solutions, and the degree of aggregation is dependent upon the size of the R group. While Na(L_{OEt}) forms a trimeric aggregate [Na(L_{OEt})]$_3$·2H$_2$O containing the triangular Na$_3$ core capped by two μ_3-aqua ligands [10], the phenoxy analogue [Na(L_{OPh})]$_2$ is a dimer, in which each Na binds to four P=O groups [14]. Negative-ion electrospray mass spectra of Na(L_{OR}) (R = Me, Et, Pr^i) in Pr^{i}OH/H$_2$O (1:1) show peaks that can be assigned to [Na(L_{OR})$_2$]$^-$, [Na$_2$(L_{OR})$_3$]$^-$, and [Na$_3$(L_{OR})$_4$]$^-$ (for R = Me). Addition of NaCl to the solutions of Na(L_{OR}) resulted in the appearance of new peaks attributable to the NaCl adducts of the types {[L_{OR}]$^-$ + *n*(NaCl)} (*n* = 1–9) and {[Na(L_{OR})$_2$]$^-$ + *n*(NaCl)} (*n* = 1–8) [20].

Protonation of Na(L_{OMe}) with HCl(g) in CH$_2$Cl$_2$ afforded NaCl and [CpCo{P(O)(OMe$_2$)}$_3$H$_2$]Cl that reacted with 1 equivalent of Na(L_{OMe}) to give [CpCo{P(O)(OMe)$_2$}$_3$H] and NaCl. Hydrolysis of [CpCo{P(O)(OMe)$_2$}$_3$H] in boiling water gave MeOH and the highly water-soluble tris-phosphonic acid ligand [CpCo{P(O)(OH)$_2$}$_3$H] (H(L_{OH})). Reaction of HL_{OH} with K$_2$CO$_3$ in water gave K(L_{OH}), which is a two-dimensional coordination polymer in the solid state with each K being coordinated by twelve oxygen atoms of six tris-phosphonic acids. Attempts to crystallize H(L_{OH}) from H$_2$O/acetone in a glass vessel led to [(L_{OH})$_2$Si] characterized by X-ray crystallography. The ligand H(L_{OH}) is a rather strong Brønsted acid with measured pK_a values of 2.0, 4.0, 6.3 and 9.6, respectively [21].



Scheme 4. Structure of [($L_{S\text{-BINOL}}$)Na(C$_6$H$_{12}$O$_2$)$_2$].

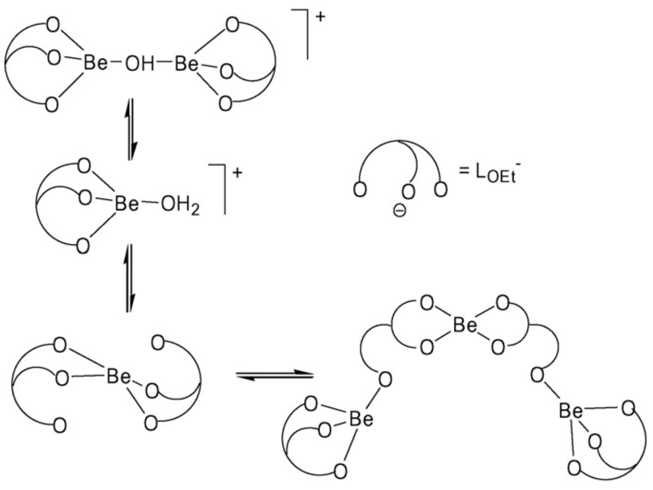
3. Survey of metal complexes with L_{OR}^-

3.1. s-and p-Block elements

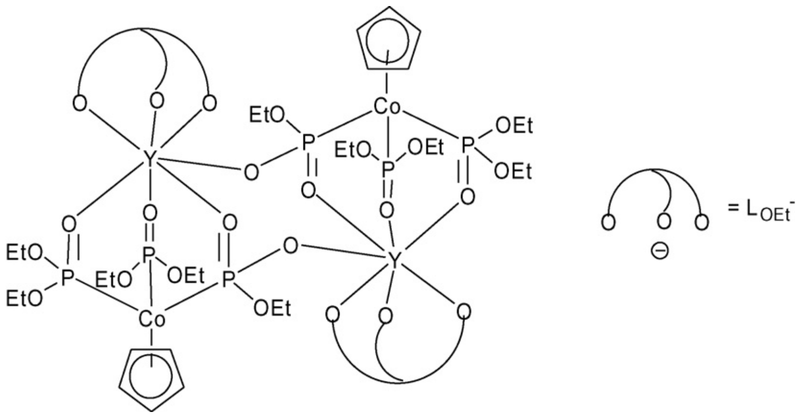
L_{OR}^- react with main group metal ions to give [M(L_{OR})$_2$]$^{n+}$ (M = third-row element) or [M(L_{OR})(X)]$^{n+}$ (M = second-row element) compounds. Potentiometric, NMR, and electrospray mass spectrometric studies suggested that aqueous mixtures of BeSO$_4$ with Na(L_{OEt}) are composed of monomeric and dimeric species, presumably [Be(L_{OEt})(H$_2$O)]$^+$ and [Be$_2$(L_{OEt})$_2$(μ-OH)]$^+$, respectively. Although [Be(L_{OEt})(H$_2$O)]$^+$has not been isolated, [Be(L_{OEt})(OPPh$_3$)]$^+$ was obtained by reaction of Be(ClO$_4$)$_2$ with Na(L_{OEt}) in the presence of OPPh$_3$. Reaction of Be(ClO$_4$)$_2$ with Na(L_{OEt}) in water afforded trinuclear [Be$_3$(L_{OEt})$_4$][ClO$_4$], in which the two bridged L_{OEt}^- ligands bind to the central Be in a μ-$\kappa^1 O$:$\kappa^2 O'O''$ mode (Scheme 5) [22].

Treatment of AlMe$_3$ with Na(L_{OEt}) or Tl(L_{OEt}) afforded a yellow compound that was formulated as [(L_{OEt})AlMe$_2$(AlMe$_3$)] on the basis of NMR spectroscopy [23]. Anhydrous MCl$_3$ (M = Ga and In) reacted with Na(L_{OEt}) in THF in 1:1 and 2:1 molar ratios afforded [M(L_{OEt})$_2$][MCl$_4$] and [M(L_{OEt})$_2$]Cl, respectively. Similar reactions with [M(Me)Cl$_2$] gave [M(L_{OEt})$_2$][M(Me)Cl$_3$] [24]. Treatment of [GeCl$_2$C$_4$H$_8$O$_2$)] (C$_4$H$_8$O$_2$ = 1,4-dioxane) with Na(L_{OEt}) afforded [(L_{OEt})GeCl] that reacted with NaN$_3$ to give [(L_{OEt})Ge(N$_3$)]. Both [(L_{OEt})GeCl] and [(L_{OEt})Ge(N$_3$)] exhibit pseudo trigonal bipyramidal coordination geometry around the Ge with one long Ge–O bond and two considerably short Ge–O bonds. Oxidation of [(L_{OEt})Ge(N$_3$)] with 2 equivalents of HN$_3$ afforded [(L_{OEt})Ge(N$_3$)$_3$] that exhibits approximately octahedral geometry [25].

Treatment of [(Tp*)InCl$_2$(MeCN)] (Tp* = hydrotris(3,5-dimethylpyrazol-l-yl)borate) with Ag(L_{OMe}) and Tl(L_{Et}) afforded the heteroleptic compounds [(L_{OMe})In(Tp*)][AgCl$_2$] and [(L_{Et})In(Tp*)]Cl, respectively. Equilibrating [(Tp*)$_2$ln]



Scheme 5. Monomeric and dimeric Be(L_{OEt})$^+$ species in aqueous solutions.



Scheme 6. Structure of $[(L_{OEt})Y]_2(\mu\text{-L}')_2$ (**1**).

$[PF_6]$ and $[(L_{OMe})_2In][PF_6]$ in a 1:1 molar ratio produced $[In(L_{OMe})_2][PF_6]$, suggestive of the preference of In(III) for an anti-symbiotic arrangement of hard (L_{OMe}^-) and soft $[(Tp^{*-})_2]$ ligands [26]. $[(L_{OEt})Pb(Tp^*)]$ prepared from $PbCl_2$ and equimolar amounts of $Na(L_{OEt})$ and KTp in water [27] was found to be a mixture of $[Pb(L_{OEt})_2]$ and $[Pb(Tp^*)_2]$ according NMR analysis [26]. The organotin(IV) compounds $[(L_{OMe})SnR_{3-n}Cl_n]$ (R = Me, Ph; n = 0–3) synthesized from $[SnR_{3-n}Cl_n]$ and $Na(L_{OMe})$ display complex NMR spectra at room temperature, indicative of fluxional behavior in solutions [28].

3.2. d-Block elements

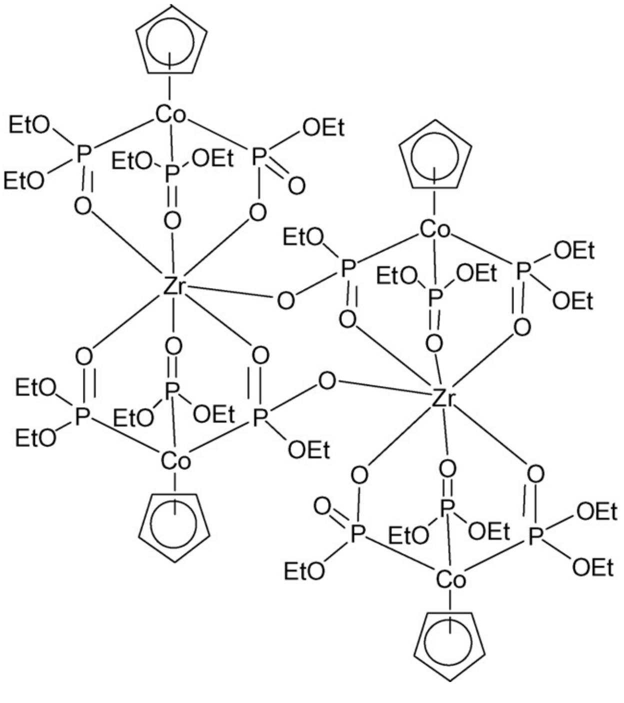
3.2.1. Groups 3 and 4

Treatment of $YbCl_3$ with $Na(L_{OEt})$ in THF gave dinuclear $[(L_{OEt})Y]_2(\mu\text{-L}')_2$ (**1**) ($[L']^{2-} = [CpCo\{P(O)(OEt)_2\}\{P(O)_2(OEt)\}]^{2-}$) containing two dealkylated L_{OEt}^- as bridged ligands (Scheme 6) [29] whereas $YbCl_3$ reacted with $Na(L_{OEt})$ and Na(OAc) in a 1:1:2 molar ratio to give $[(L_{OMe})Yb]_2(\mu\text{-OAc})_2$, the two acetate ligands of which exhibit the μ-κO:$\kappa O'$ and μ-κO:$\kappa^2 O'$ binding modes [30]. The crystal structure of $[(L_{OMe})_2La(H_2O)_2]Cl$ showing an approximate square prismatic O_8 ligand environment around La has been determined [31].

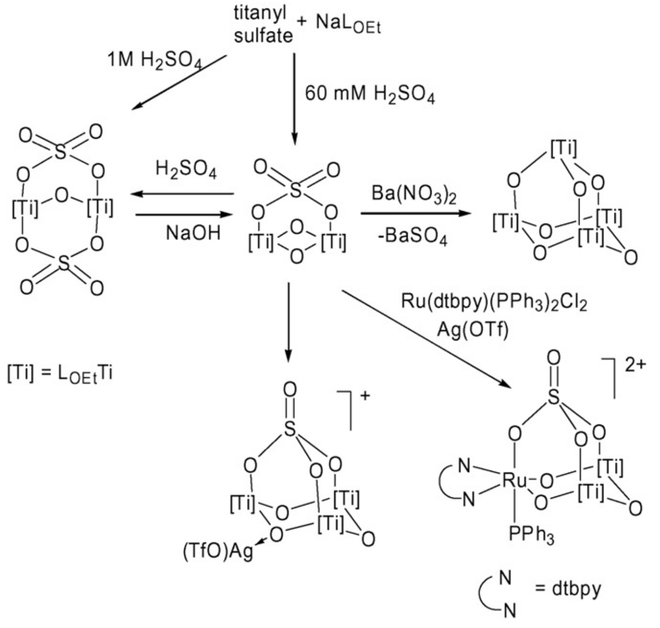
Treatment of $[ZrCl_4(THF)_2]$ with two equivalents of $Na(L_{Et})$ afforded $[Zr(L_{Et})_2]Cl_2$ whereas that with $Na(L_{OEt})$ gave labile $[(L_{OEt})_2ZrCl_2]$ that underwent Arbuzov dealkylation to give dinuclear $[(L')Zr]_2(\mu\text{-L}')_2$ (**2**) (Scheme 7) [32,33]. Reaction of $[CpZrCl_3]$ with $Na(L_{OEt})$ led to Cp^- displacement and the formation of $[(L_{OEt})ZrCl_3]$ [32].

Half-sandwich $[(L_{OEt})TiCl_3]$ was prepared conveniently by reacting $[Ti(OPr^i)_2Cl_2]$ with $Na(L_{OEt})$ followed by chlorination with HCl in Et_2O. Treatment of $[(L_{OEt})TiCl_3]$ with tetrachlorocatechol $(C_6C1_4(OH)_2)$ afforded $[(L_{OEt})Ti(C_6Cl_4O_2)Cl]$, which was hydrolyzed to give $[(L_{OEt})Ti(C_6Cl_4O_2)]_2(\mu\text{-O})$. Treatment of $[(L_{OEt})TiCl_3]$ with Na_2(*S*-BINOL) afforded dinuclear $[(L_{OEt})_2Ti_2](\mu\text{-O})$ (μ-*S*-BINOL), in which the *S*-BINOL ligand binds to the two Ti in a μ-O,O' mode [34].

In an attempt to model the aqueous chemistry of Ti^{4+} and Zr^{4+}, interactions of titanyl and zirconyl compounds with $Na(L_{OEt})$ in the presence of oxyanions in aqeuous solutions have been studied [35–38]. Reaction of titanyl sulfate with $Na(L_{OEt})$ in 0.6 mM and 1 M sulfuric acid afforded the dinuclear sulfato compounds $[(L_{OEt})Ti]_2(\mu\text{-O})_2(\mu\text{-SO}_4)$ and $[(L_{OEt})Ti]_2(\mu\text{-O})_2(\mu\text{-SO}_4)$, respectively, which can be interconverted to each other by addition of H_2SO_4 or NaOH. Treatment $[(L_{OEt})Ti]_2(\mu\text{-O})_2(\mu\text{-SO}_4)$ with Ag(OTf) (OTf = triflate) afforded the trinuclear μ_3-sulfato complex $[\{(L_{OEt})Ti\}_3(\mu\text{-O})_3(\mu_3\text{-SO}_4)\{Ag(OTf)\}][OTf]$, whereas that with $Ba(NO_3)_2$ led to isolation of tetranuclear $[(L_{OEt})Ti]_4(\mu\text{-O})_6$ containing an adamantane-like Ti_4O_6 core. Reaction of $[(L_{OEt})Ti]_2(\mu\text{-O})_2(\mu\text{-SO}_4)$ with $[Ru(dtbpy)(PPh_3)_2Cl_2]$ (dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) in the presence of Ag(OTf) afforded a trinuclear Ti(IV)/Ru(IV) complex, $[\{(L_{OEt})Ti\}_2(\mu\text{-O})_3(\mu_3\text{-SO}_4)\{Ru(dtbpy)(PPh_3)\}][OTf]_2$, which has a measured magnetic moment of 2.4 μ_B. (Scheme 8) [36].



Scheme 7. Structure of $[(L')Zr]_2(\mu\text{-L}')_2$ (**2**).



Scheme 8. Dinuclear and trinuclear Ti(IV)-L_{OEt} sulfato complexes.

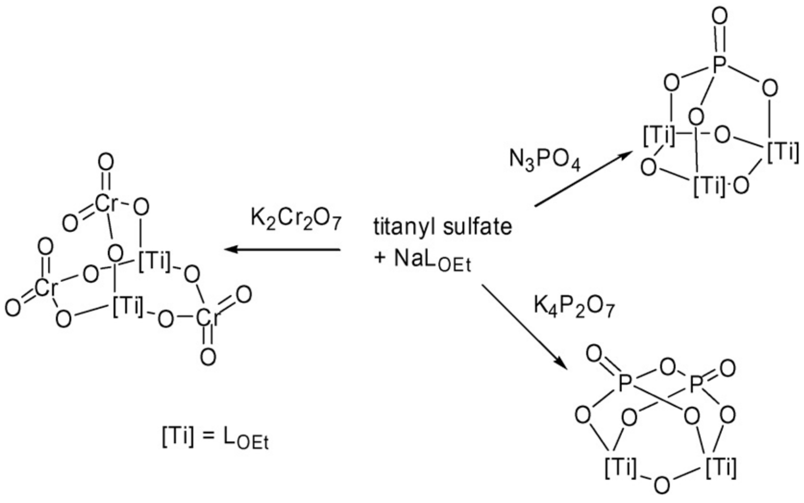
Treatment of titanyl sulfate with $Na(L_{OEt})$ in dilute H_2SO_4 the presence of Na_3PO_4, $Na_4P_2O_7$, $K_2Cr_2O_7$ led to isolation of $[\{(L_{OEt})Ti\}_3(\mu\text{-}O)_3(\mu_3\text{-}PO_4)]$, $[\{(L_{OEt})Ti\}_2(\mu\text{-}O)(\mu\text{-}P_2O_7)]$, and $[\{(L_{OEt})Ti\}_3(\mu\text{-}CrO_4)_3]$, respectively (Scheme 9) [35].

Zirconyl nitrate reacted with $Na(L_{OEt})$ in dilute nitric acid (pH 2.1) to give a ca. 1:1 mixture of tetranuclear $[(L_{OEt}Zr)_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_4(H_2O)_2][NO_3]_4$ and $[(L_{OEt})_2Zr(\kappa^2\text{-}NO_3)][NO_3]$ [38]. At lower pH (<1), the same reaction yielded a ca. 2:3 mixture of $[(L_{OEt})_2Zr(\kappa^2\text{-}NO_3)][NO_3]$ and $[(L_{OEt})Zr(\kappa^2\text{-}NO_3)_3]$. The Zr_4 core (**3**) in $[(L_{OEt}Zr)_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_4(H_2O)_2]^{4+}$ is reminiscent of the $[Zr_4(OH)_8]^{8+}$ core (**4**) found in $ZrOCl_2\cdot 8H_2O$ (Scheme 10) [39]. In acidic solutions, $[(L_{OEt})Zr(\kappa^2\text{-}NO_3)_3]$ and $[(L_{OEt}Zr)_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_4(H_2O)_2]^{4+}$ can be inter-converted to each other by treatment with NaOH or HNO_3.

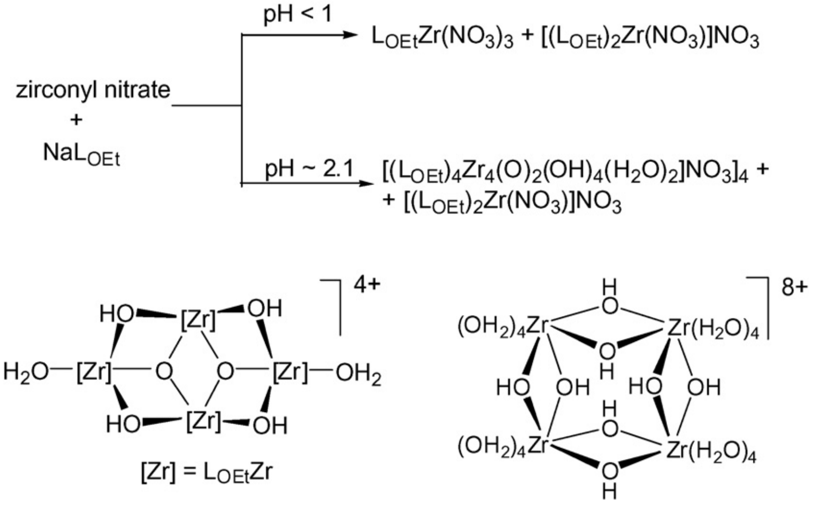
The electrospray mass spectrum of $[(L_{OEt})Zr(\kappa^2\text{-}NO_3)_3]$ in weakly acidic solutions displays a molecular ion peak at *m*/*z* 1320, assignable to $[(L_{OEt}Zr)_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_4(H_2O)_2]^{2+}$, suggesting that in aqueous solutions Zr(IV)-L_{OEt} compounds predominantly exists as tetrameric species. It should be noted that aqueous solutions of Zr^{4+} contain predominantly the tetranuclear species $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, which is in equilibrium with octanuclear $[Zr_8(OH)_{20}(H_2O)_{24}]^{12+}$ [40]. In acetone/H_2O solution, **3** can hydrolyze the phosphodiester $(4\text{-}NO_2C_6H_4O)_2P(O)H$ to give a cubane cluster $[L_{OEt}Zr]_4(\mu\text{-}PO_4)_4$ along with $4\text{-}NO_2C_6H_4OH$. Treatment of zirconyl nitrate with $Na(L_{OEt})$ in the presence of Na_3PO_4 afforded $[(L_{OEt})Zr]_3(\mu\text{-}OH)_3(\mu_3\text{-}O)(\mu_3\text{-}PO_4)$ (Scheme 11) [38].

Efforts have been made to prepare L_{OEt}Zr(IV) sulfato compounds in oxygen-rich ligand environments that are relevant to sulfated zirconia materials. Treatment of zirconyl nitrate with $Na(L_{OEt})$ in 3.5 M sulfuric acid afforded $[(L_{OEt})_2Zr(\kappa^2\text{-}NO_3)][L_{OEt}Zr(\kappa^2\text{-}SO_4)(\mu\text{-}NO_3)]$. The nitrate-free Zr(IV) sulfato compound $[(L_{OEt})Zr(\kappa^2\text{-}SO_4)(H_2O)]_2(\mu\text{-}SO_4)$ was prepared by reaction of $ZrCl_4$ with $Na(L_{OEt})$ and Na_2SO_4 in 1.8 M H_2SO_4. Treatment of $[(L_{OEt})Zr(\kappa^2\text{-}SO_4)(H_2O)]_2(\kappa\text{-}SO_4)$ with triflic acid afforded $[Zr(L_{OEt})_2][OTf]_2$ whereas that with Ag(OTf) gave a mixture of trinuclear $[\{(L_{OEt})Zr(\kappa^2\text{-}SO_4)(H_2O)\}3(\mu_3\text{-}SO_4)][OTf]$ and $[Zr(L_{OEt})_2][OTf]_2$ (Scheme 12) [36].

Reaction of titanyl sulfate with $Na(L_{OEt})$ in dilute sulfuric acid followed by HBF_4(aq) led to isolation of $[(L_{OEt})TiF_3]$. Similarly, $[(L_{OEt})ZrF_3]$ was obtained by the reaction of zirconyl nitrate with $Na(L_{OEt})$ followed by HBF_4(aq) [34]. Although $[(L_{OEt})MF_3]$ (M = Ti, Zr) are very stable compounds due to the strong M(IV)–F bonds, the fluoride ligands can be removed easily by using trimethylsilyl compounds. Thus, treatment of $[(L_{OEt})MF_3]$ with Me_3SiOTf (OTf = triflate) afforded $[(L_{OEt})M(OTf)_3]$ whereas that with $[ReO_3(OSiMe_3)]$ gave $[(L_{OEt})Ti(ReO_4)_3]$ and $[(L_{OEt})Zr(ReO_4)_3(H_2O)]$ [35]. $[(L_{OEt})M(OTf)_3]$ hydrolyzed readily to give hydroxo and oxo complexes. The outcome of hydrolysis of $[(L_{OEt})Zr(OTf)_3]$ was found to be dependent upon the source of moisture and reaction conditions. While reaction of $[(L_{OEt})Zr(OTf)_3]$ with $Na_2WO_4\cdot xH_2O$ gave din-



Scheme 9. Ti(IV)-L_{OEt} chromato and phosphate compounds.



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Scheme 10. Zr(IV)-L$_{\mathrm{OEt}}$ nitrato compounds.

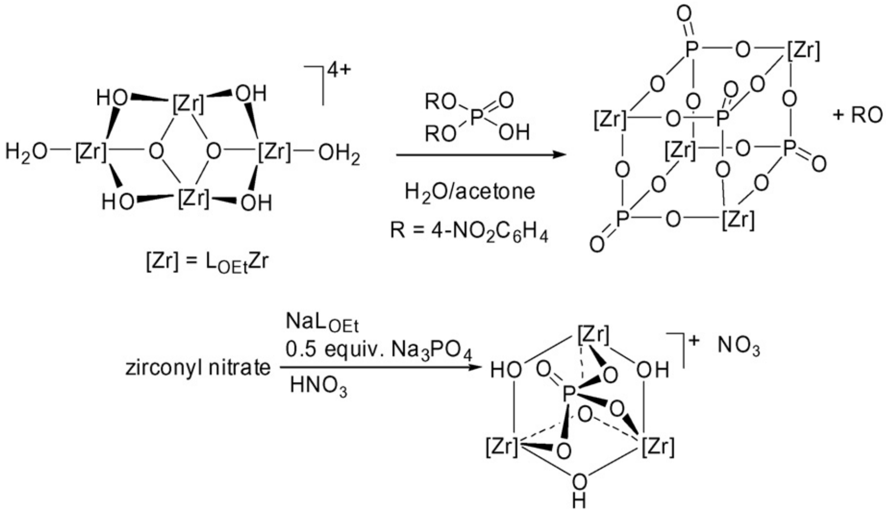
uclear $[\{(\mathrm{L_{OEt}})\mathrm{Zr(H_2O)_2}\}_2(\mu\text{-OH})_2][\mathrm{OTf}]_4$, recrystallization of $[(\mathrm{L_{OEt}})\mathrm{Zr(OTf)_3}]$ from wet $\mathrm{CH_2Cl_2}$ in air led to isolation of trinuclear $[\{(\mathrm{L_{OEt}})\mathrm{Zr(H_2O)}\}_3(\mu_3\text{-O})\text{-}(\mu\text{-OH})][\mathrm{OTf}]_4$ [29]. Treatment of $[(\mathrm{L_{OEt}})\mathrm{Ti(OTf)_3}]$ with *S*-binapO$_2$ and $\mathrm{K[N(Ph_2PO)_2]}$/CsOH afforded the terminal hydroxo complexes $[(\mathrm{L_{OEt}})\mathrm{Ti}(S\text{-binapO}_2)(\mathrm{OH})][\mathrm{OTf}]_2$ (*S*-binapO$_2$ (*S*)-(-)-2,2′-bis(diphenylphosphinoyl)-1,1′-binaphthyl) and $[(\mathrm{L_{OEt}})\mathrm{Ti\{N(Ph_2PO)_2\}(OH)}][\mathrm{OTf}]$, respectively (Scheme 13) [37].

3.2.2. *Groups 5 and 6*

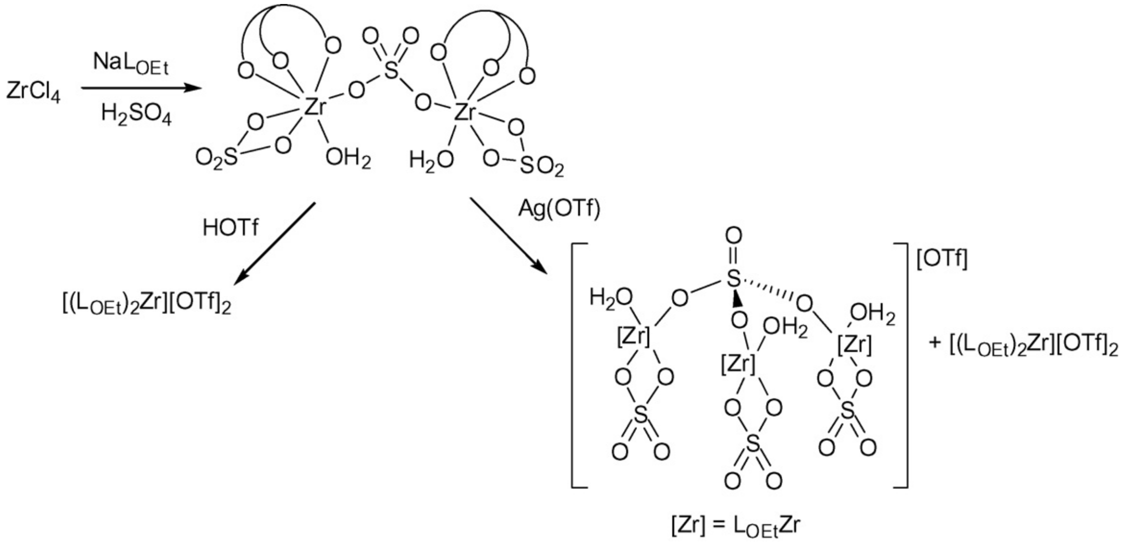
A number of groups 5–8 $\mathrm{L_{OR}}^-$ complexes with metal–ligand multiple bonds have been synthesized. Treatment of $[\mathrm{V(O)X_3}]$ (X = Cl, F) with $\mathrm{Na(L_{OR})}$ (*R* = Me, Et) afforded $[(\mathrm{L_{OR}})\mathrm{V(O)X_2}]$. Reaction of $[(\mathrm{L_{OMe}})\mathrm{V(O)X_2}]$ with Br$_2$ in $\mathrm{CH_2Cl_2}$ afforded $[\mathrm{V(O)(L_{OMe})_2}][\mathrm{V(O)Br_4}]$ [41]. Treatment of $[\mathrm{Cr(NBu}^t\mathrm{)Cl_2(dme)}]$ (dme = 1,2-dimethoxyethane) with $\mathrm{Na(L_{OEt})}$ afforded the imido-Cr(V) complex $[(\mathrm{L_{OEt}})\mathrm{Cr(NBu}^t\mathrm{)Cl_2}]$ [42].

Reactions of $[(\mathrm{L_{OR}})\mathrm{(CO)_2M{=}C}\text{-}p\text{-tol}]$ (M = Mo, W; *p*-tol = *p*-tolyl) with oxidizing agents have been investigated (Scheme 13). Treatment of $[(\mathrm{L_{OR}})\mathrm{(CO)_2M{=}C}\text{-}p\text{-tol}]$ (M = Mo, W) with I$_2$ and Br$_2$ afforded $[(\mathrm{L_{OR}})\mathrm{(CO)(I)_2M{=}C}\text{-}p\text{-tol}]$ (R = Me, Et) and $[(\mathrm{L_{OR}})\mathrm{MoBr_4}]$ (R = Pr^i), respectively. Reaction of $[(\mathrm{L_{OR}})\mathrm{(CO)_2W{\equiv}C}\text{-}p\text{-tol}]$ with S$_8$ and moist air afforded $[(\mathrm{L_{OR}})\mathrm{(CO)_2W(S_2C}\text{-}p\text{-tol})]$ and $[(\mathrm{L_{OR}})\mathrm{W(O)}]_2(\mu\text{-O})$, respectively. Treatment of $[(\mathrm{L_{OR}})\mathrm{(CO)_2M{\equiv}C}\text{-}p\text{-tol}]$ with $[\mathrm{Pd}(\eta^3\text{-allyl})\mathrm{Cl}]_2$ gave $[\{(\mathrm{L_{OR}})\mathrm{(CO)_2M{\equiv}C}\text{-}p\text{-tol}\}_2\mathrm{Pd}]$, in which the W≡C units bind to Pd like an alkyne. Reaction of $[\{(\mathrm{L_{OMe}})\mathrm{(CO)_2W{\equiv}C}\text{-}p\text{-tol}\}_2\mathrm{Pd}]$ with $[\mathrm{Pd}(\eta^3\text{-allyl})\mathrm{Cl}]_2$ and C$_2$Cl$_6$ in boiling THF afforded $[(\mathrm{L_{OMe}})\mathrm{Cl_2W{\equiv}C}\text{-}p\text{-tol}]$ (Scheme 14) [43].

Chlorination of $[(\mathrm{L_{OR}})\mathrm{(CO)_2W{\equiv}C}\text{-}p\text{-tol}]$ (R = Me, Pr^i) with PhICl$_2$ afforded $[(\mathrm{L_{OR}})\mathrm{Cl_2W{=}C}\text{-}p\text{-tol}]$. A similar reac-

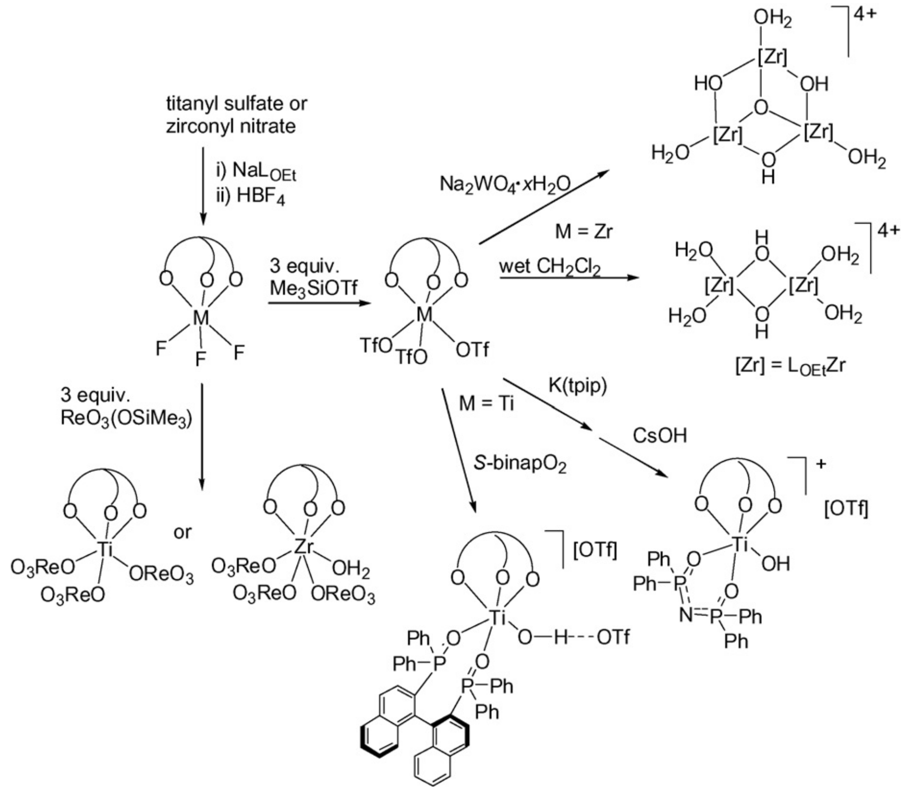


Scheme 11. Tetranuclear and trinuclear Zr(IV)-L$_{\mathrm{OEt}}$ phosphato compounds.

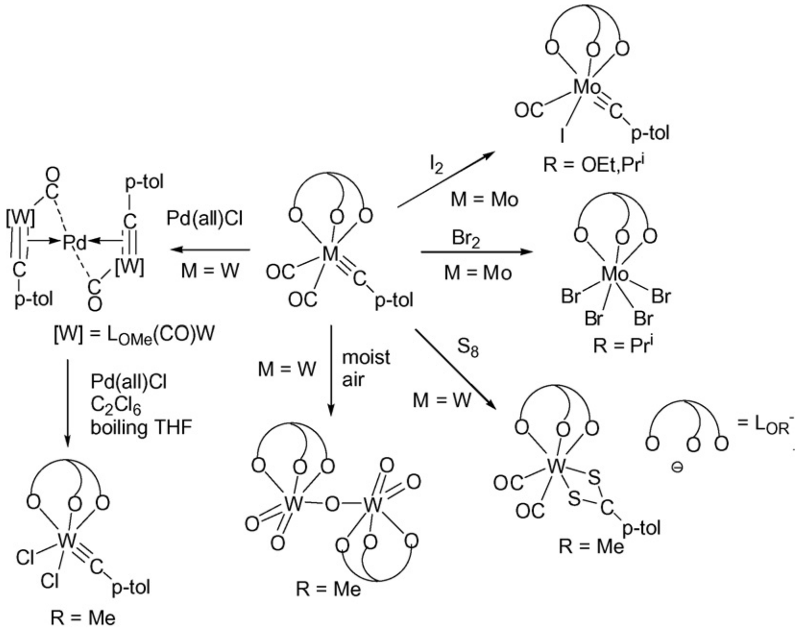


Scheme 12. Dinuclear and trinuclear Zr(IV)-$\mathrm{L_{OEt}}$ sulfato compounds.

tion with $[(\mathrm{L_{OR}})(\mathrm{CO})_2\mathrm{Mo}{\equiv}\mathrm{C}$-*p*-tol] yielded $[\mathrm{L_{OMe}MoCl_2}]_2$ and $[\mathrm{L_{OR}MoCl_4}$. Treatment of $[(\mathrm{L_{OMe}})\mathrm{Cl_2W}{\equiv}\mathrm{C}$-*p*-tol] with $\mathrm{Me_3SnF}$ afforded $[(\mathrm{L_{OMe}})\mathrm{F_2W}=\mathrm{C}$-*p*-tol] that reacted with NaOEt and $\mathrm{Me_3SiNMe_2}$ to give $[(\mathrm{L_{OMe}})(\mathrm{OEt})_2\mathrm{W}{\equiv}\mathrm{C}$-*p*-tol] and $[(\mathrm{L_{OMe}})\mathrm{F}(\mathrm{NMe_2})\mathrm{W}=\mathrm{C}$-*p*-tol], respectively [44]. $[(\mathrm{L_{OMe}})\mathrm{Cl_2W}{\equiv}\mathrm{C}$-*p*-tol] reacted with ROH to yield $[(\mathrm{L_{OMe}})\mathrm{Cl}(\mathrm{OR})\mathrm{W}{\equiv}\mathrm{C}$-*p*-tol] ($\mathrm{R = OMe, OEt, OCH_2CH_2OH}$) whereas the dimethoxy compound $[(\mathrm{L_{OMe}})(\mathrm{MeO})_2\mathrm{W}=\mathrm{C}$-*p*-toi] was prepared from $[(\mathrm{L_{OMe}})\mathrm{Cl_2W}{\equiv}\mathrm{C}$-*p*-tol] and KOMe. Reaction of $[(\mathrm{L_{OMe}})\mathrm{Cl_2W}{\equiv}\mathrm{C}$-*p*-tol] with aqueous $\mathrm{Et_3N}$ or alumina gave two isomeric oxocarbene complexes $[(\mathrm{L_{OMe}})\mathrm{Cl}(\mathrm{O})\mathrm{W}{\equiv}\mathrm{CH}$-*p*-tol], which reacted with $\mathrm{Al_2O_3}$ to give the dioxo-alkyl complex $[(\mathrm{L_{OMe}})(\mathrm{O})_2\mathrm{W}$-CH-*p*-tol]. Treatment of $[(\mathrm{L_{OMe}})\mathrm{Cl_2W}{\equiv}\mathrm{C}$-*p*-tol] with $\mathrm{Et_2NH}$ and $\mathrm{Pr}^n\mathrm{NH_2}$ afforded $[(\mathrm{L_{OMe}})\mathrm{Cl}(\mathrm{NHEt})\mathrm{W}{\equiv}\mathrm{C}$-*p*-tol] and the imido-carbene complex $[(\mathrm{L_{OMe}})(\mathrm{Pr^nN})\mathrm{W}{\equiv}\mathrm{CH}$-*p*-tol], respectively. Air oxidation of $[(\mathrm{L_{OMe}})\mathrm{Cl}(\mathrm{X})\mathrm{W}{\equiv}\mathrm{CH}$-*p*-tol] yielded $[(\mathrm{L_{OMe}})\mathrm{W}(\mathrm{O})(\mathrm{X})\mathrm{Cl}]$ ($\mathrm{X = OMe, OPr}^i$, NPr^n) (Scheme 15) [45].

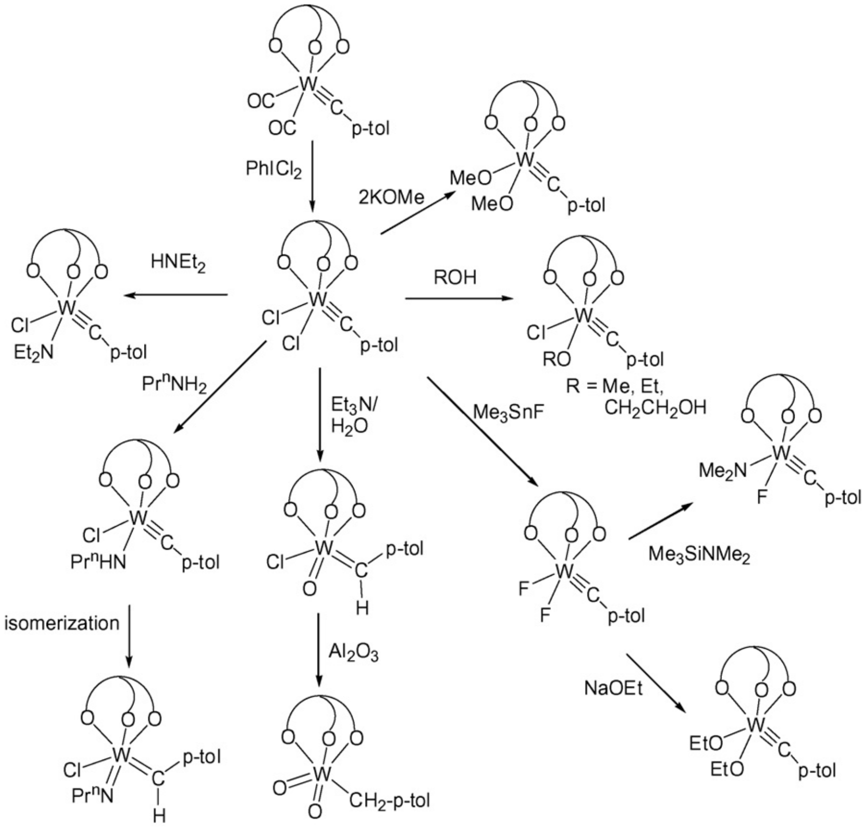


Scheme 13. Ti(IV) and Zr(IV) triflato and perrhenato complexes.



Scheme 14. Oxidation of W(VI)- and Mo(VI)-L$_{OEt}$ carbyne complexes.

Treatment of [Mo(Nmes)$_2$Cl$_2$(dme)] (mes = 2,4,6-trimethylphenyl) with Na(L$_{OEt}$) afforded the bis-imido complex [(L$_{OEt}$)Mo(Nmes)$_2$Cl] that reacted with HCl in Et$_2$O to give [(κ^2-HL$_{OEt}$)Mo(Nmes)$_2$Cl$_2$]. Reaction of [Mo(Nmes)(O)Cl$_2$(dme)] and [Mo(Nmes)Cl$_3$(dme)] with Na(L$_{OEt}$) afforded [(L$_{OEt}$)Mo(Nmes)(O)Cl] and [(L$_{OEt}$)Mo(Nmes)Cl$_2$], respectively [46]. Treatment of [(L$_{OMe}$)Mo(O)Cl$_2$] with NaOMe and 30% H$_2$O$_2$ in THF gives [(L$_{OMe}$)Mo(O)$_2$Cl] and [(L$_{OMe}$)Mo(O)$_2$(OH)], respectively [47]. Reaction of [MoCl$_4$(THF)$_2$] with Me$_3$SiN$_3$ followed by treatment with Na(L$_{OEt}$) led to isolation of the Mo(VI) nitrido complex [(L$_{OEt}$)Mo(N)Cl$_2$] [48].



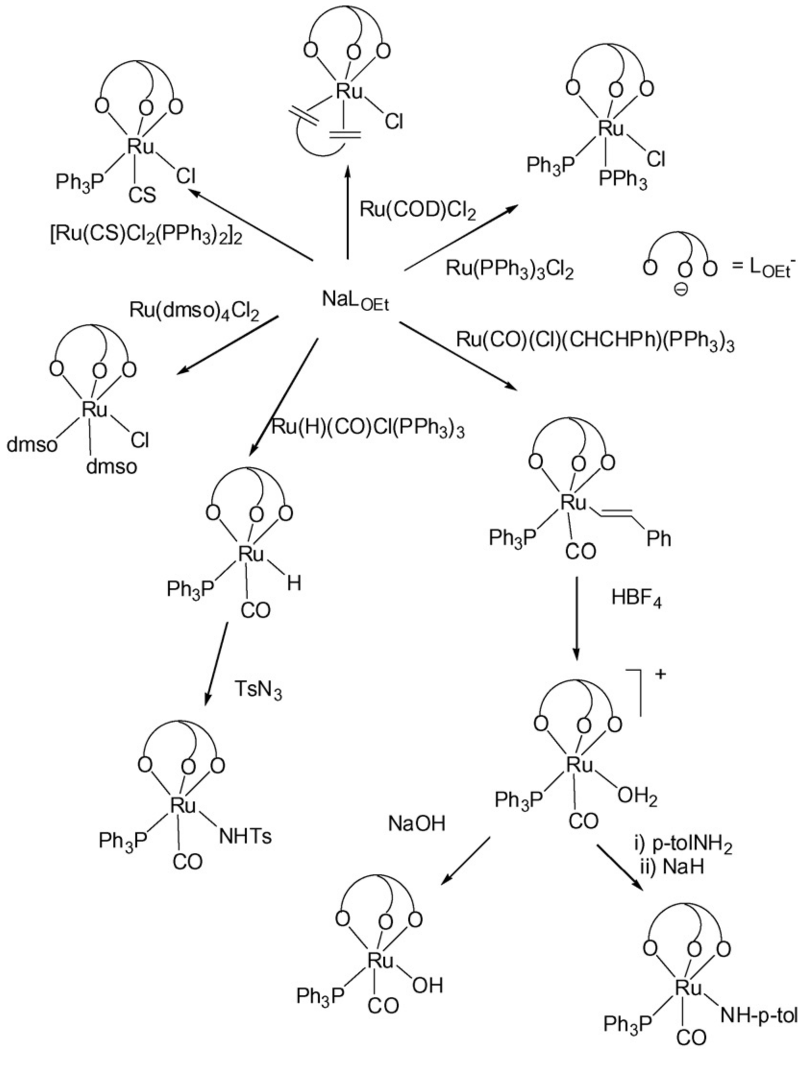
Scheme 15. L$_{OMe}$W(VI) oxo, carbene, and imido complexes.

3.2.3. Groups 7 and 8

The homogeneous self-exchange rate constant for $[(L_{OEt})_2Mn]^{0/+}$ was estimated to be $4.25 \times 10^{-3}\,M^{-1}\,s^{-1}$ from the cross reaction with ferrocenium salts, whereas the heterogeneous electron transfer rate constant for the couple was determined to be ca. 7–8 × $10^{-7}\,cm\,s^{-1}$ by cyclic voltammetry. The solid-state structure of $[(L_{OEt})_2Mn]^+$ shows a sizeable Jahn-Teller distortion with three distinctly different Mn–O distances [1.981(5), 2.053(4) and 1.923(4) Å]. Nevertheless, the kinetic inertness of the $[(L_{OEt})_2Mn]^{0/+}$ couple has been attributed to the thermodynamic stability of the Mn(II) state with a half-filled d shell, rather than the geometric/structural rearrangement accompanying the redox changes [49].

Treatment of $[M(CO)_3(H_2O)_3]^+$ (M = Tc, Re) with $Na(L_{OR})$ (R = Me, Et) afforded $[(L_{OR})M(CO)_3]$ [50]. The Re(VIII) trioxo compounds $[(L)Re(O)_3]$ were synthesized from $[Re_2O_7]$ and NaI ($L^- = [CpCo\{P(O)(OMe)(O(CH_2)_5CO_2Me)\}_3]^-$, $L_{OMe}{}^-$, or $L_{OEt}{}^-$) [18,51]. Treatment of $[Re(O)X_3(PPh_3)_2]$ with Na(L) afforded $[(L)Re(O)X_2]$ (X = Cl, Br, I). $[(L)Re(O)X_2]$ slowly hydrolyzed in water to give perrhenic acid [18]. Treatment of $[Re(N)Cl_2(PPh_3)_2]$ with $Na(L_{OEt})$ afforded the nitrido complex $[(L_{OEt})Re(N)Cl(PPh_3)]$ that reacted with MeOTf, $PhCH_2Br$, $[Ph_3C]BF_4$, $[Au(PPh_3)(OTf)]$, $[Re(Me)(O)_3]$, and $[Ru(S_2CNEt_2)(PPh_3)_2(CO)(OTf)]$ to give the imido complexes $[(L_{OEt})Re(NMe)Cl(PPh_3)]$, $[(L_{OEt})Re(NCH_2Ph)Cl(PPh_3)]$, and $[(L_{OEt})Re(NCPh_3)Cl(PPh_3)]$, and the nitrido-bridged bimetallic complexes $[(L_{OEt})Cl(PPh_3)Re(\mu\text{-}N)\{Au(PPh_3)\}]$, $[(L_{OEt})Cl(PPh_3)Re(\mu\text{-}N)\{Re(Me)(O)_3\}]$ and $[(L_{OEt})Cl(PPh_3)Re(\mu\text{-}N)Ru(S_2CNEt_2)(PPh_3)(CO)(H_2O)]$, respectively. The cyclic voltammograms of $[(L_{OEt})Re(N)Cl(PPh_3)]$ and $[(L_{OEt})Re(O)Cl_2]$ in CH_2C1_2 displayed reversible Re(VI/V) couples at −0.296 and 0.470 V versus $Cp_2Fe^{+/0}$ whereas the oxidation of $[L_{OEt}Re(NMe)Cl(PPh_3)]$ is irreversible with $E_{pa} = 0.620$ V [52].

Treatment of RuO_4 in CCl_4 with $Na(L_{OR})$ (R = Me, Et) in 1% H_2SO_4 followed by afforded the oxo-bridged dinuclear Ru(IV) compounds $[(L_{OR})Ru(OH)]_2(\mu\text{-}O)_2$. Protonation of $[(L_{OR})Ru(OH)]_2(\mu\text{-}O)_2$ with HOTf afforded $[\{(LoR)Ru(H_2O)\}_2(\mu\text{-}O)_2][OTf]_2$. The Ru(V) oxo compounds $[(L_{OR})Ru(O)]_2(\mu\text{-}O)_2$ have been prepared by oxidation of $[(L_{OR})Ru(OH)]_2(\mu\text{-}O)_2$ with RuO_4 (R = Et) or $PhIO/NEt_4OH$ (R = Me) [53,54]. The Ru-O(terminal) and average Ru-



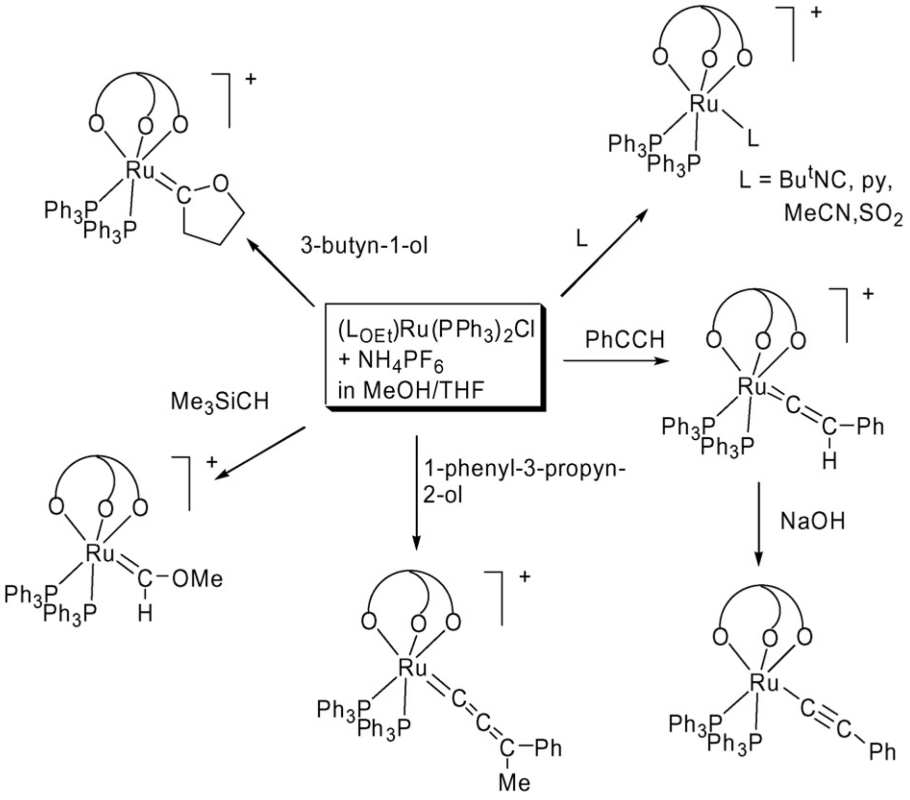
Scheme 16. Organoruthenium complexes supported by $L_{OEt}{}^-$.

O(bridged) distances in $[(L_{OEt})Ru(O)]_2(\mu\text{-}O)_2$ are 1.725(3) and 1.886(3) Å, respectively. The Ru–Ru separation of 2.912(1) Å in $[(L_{OMe})Ru(O)]_2(\mu\text{-}O)_2$ is considerably longer than that in $[(L_{OEt})Ru(OH)]_2(\mu\text{-}O)_2$ (2.452(1) Å), indicating that there is little or very weak metal–metal interaction in the Ru(V)–Ru(V) dimer. The lack of Ru-Ru interaction in the edge-sharing bioctahedral Ru(V)–Ru(V) dimer has been attributed to the $\sigma^2\pi^2\delta^{*2}$ configuration (cf. $\sigma^2\pi^2\delta^2\delta^{*2}$ for the Ru(IV)–Ru(IV) counterpart) [53].

A series of organoruthenium compounds with L_{OEt}^- have been synthesized (Scheme 16) [55–58]. Treatment of $Na(L_{OEt})$ with $[Ru(PPh_3)_3Cl_2]$, $[Ru(H)(Cl)(CO)(PPh_3)_3]$, $[Ru(CH=CHPh)(CO)Cl(PPh_3)_3]$, $[Ru(Me_2SO)_4Cl_2]$, $[Ru(COD)Cl_2]_x$ (COD = cyclooctadiene), $[Ru(CS)(PPh_3)_2Cl_2]_2$ afforded $[(L_{OEt})Ru(PPh_3)_2Cl]$, $[(L_{OEt})Ru(H)(PPh_3)(CO)]$, $[(L_{OEt})Ru(CH=CHPh)(PPh_3)(CO)]$, $[(L_{OEt})Ru(Me_2SO)_2Cl]$, $[(L_{OEt})Ru(COD)Cl]$, and $[(L_{OEt})Ru(CS)(PPh_3)Cl]$, respectively. The cyclic voltammogram of $[(L_{OEt})Ru(PPh_3)_2Cl]$ displayed a reversible Ru(III/II) couple at ca. −0.02 V versus $Cp_2Fe^{+/0}$, which is less anodic than that for $[CpRu(PPh_3)_2Cl]$ (0.45 V) [55], indicating that L_{OEt}^- is a stronger donor than Cp^-. Oxidation of $[CpRu(PPh_3)_2Cl]$ with I_2 afforded the Ru(III) compound $[CpRu(PPh_3)_2Cl]^+$, isolated as the triiodide salt. Migratory insertion of $[(L_{OEt})Ru(H)(PPh_3)(CO)]$ with tosylazide afforded the tosylamido compound $[(L_{OEt})Ru(NHTs)(PPh_3)(CO)]$ (Ts = tosyl). Protonation of $[(L_{OEt})Ru(CH=CHPh)(PPh_3)(CO)]$ with HBF_4 afforded $[(L_{OEt})Ru(\eta^2\text{-}PhCH=CH_2)(PPh_3)(CO)][BF_4]$, which lost the styrene ligand in wet CH_2Cl_2 to give $[(L_{OEt})Ru(H_2O)(PPh_3)(CO)][BF_4]$. Chloride abstraction of $[(L_{OEt})Ru(COD)Cl]$ with $Ag(BF_4)$ in acetone/H_2O afforded cationic $[(L_{OEt})Ru(COD)(H_2O)]^+$, which can also be prepared from $[(COD)Ru(H_2O)_4]^{2+}$ and $Na(L_{OEt})$ [59]. Deprotonation of $[(L_{OEt})Ru(H_2O)(L)_2][BF_4]$ and $[(L_{OEt})Ru(NH_2\text{-}p\text{-tol})(L)_2][BF_4]$ afforded the Ru(II) hydroxo $[(L_{OEt})Ru(OH)(L)_2]$ and amido $[(L_{OEt})Ru(NHtol)(L)_2]$ complexes (L_2 = (CO)(PPh_3) or COD), respectively.

$[(L_{OEt})Ru(PPh_3)_2Cl]$ underwent chloride dissociation in polar solvents such as MeOH to give $[(L_{OEt})Ru(PPh_3)_2(solv)]^+$, which reacted with Lewis bases L to form the adducts $[(L_{OEt})Ru(PPh_3)_2(L)]^+$ (L = Bu^tNC, pyridine, Me_2SO, SO_2). Treatment of $[(L_{OEt})Ru(PPh_3)_2Cl]$ with PhC≡CH, $Me_3SiC{\equiv}CH$, 3-butyn-l-ol, and l-phenyl-3-propyn-2-ol in MeOH/THF in the presence of NH_4PF_6 afforded $[(L_{OEt})(PPh_3)_2Ru=C=CHPh][PF_6]$, $[(L_{OEt})(PPh_3)_2Ru=CH(OMe)][PF_6]$, $[(L_{OEt})(PPh_3)_2Ru=CH(CH_2)_3O][PF_6]$, and $[(L_{OEt})(PPh_3)_2Ru=C=C=CMePh][PF_6]$, respectively. Deprotonation of $[(L_{OEt})(PPh_3)_2Ru=C=CHPh]$ $[PF_6]$ with NaOH gave the σ-acetylide compound $[(L_{OEt})(PPh_3)_2Ru(C{\equiv}CPh)]$ (Scheme 17) [55,56].

Relatively few Os–L_{OR} complexes have been isolated. Treatment of $[^nBu_4N]$ $[Os(N)Cl_4]$ with $Na(L_{OEt})$ afforded $[(L_{OEt})Os(N)Cl_2]$ that reacted with PPh_3 to give the Os(IV) phosphoraminato complex $[(L_{OEt})Os(NPPh_3)Cl_2]$ [52]. Reaction of $[Os(CBu^t)(CH_2CMe_3)_2(py)_2(OTf)]$ with $Na(L_{OEt})$ afforded $[(L_{OEt}(CH_2(CMe_3)_2Os{\equiv}CBu^t]$ [60].



Scheme 17. Ru-L_{OEt} carbene, vinylidene, and allenylidene compounds.

3.2.4. Groups 9–12

Treatment of Na(L_{OMe}) with excess $COCl_2$ in MeOH afforded dinuclear [L_{OMe}Co(μ-L_{OMe})$CoCl_2$] in which the bridged L_{OMe}^- ligands bind to the two Co(II) in a μ-κ^3,κ^1 fashion. By contrast, reaction $M(NO_3)_2\cdot 6H_2O$ (M = Co, Ni) with Na(L_{OMe}) in MeOH followed by recrystallization from acetone gave [(L_{OMe})M(κ^2-NO_3)(Me_2CO)]. Substitution of [(L_{OMe})Ni(κ^2-NO_3)(Me_2CO)] with L and py (pyridine) afforded [(L_{OMe})Ni(κ^2-NO_3)(L)][NO_3] (L = PPh_3, 2,5-dimethylpyridine, 3,5-dimethylpyrazole) and [(L_{OMe})Ni$(py)_3$][NO_3], respectively. Treatment of [(L_{OMe})M(κ^2-NO_3)(acetone)] (M = Co and Ni) with NaN_3 afforded the tetrameric μ_3-azido complexes [(L_{OMe})M(μ_3-N_3)]$_4$. While reactions of [(L_{OMe})M(κ^2-NO_3)(Me_2CO)] with NaOAr gave the μ-aryloxo compounds [(L_{OMe})M]$_2$(μ-OAr)$_2$ (Ar = 2,4,6-$Me_3C_6H_2$, 2,6-$Me_2C_6H_3$, or 2-$NO_2C_6H_4$) and [(L_{OMe})M(L)]$_2$(μ-OAr)$_2$ (Ar = 4-nitrophenyl or pentaflurophenyl, L = MeOH or H_2O), similar reactions with NaOH and NaOR' (R′ = alkyl, Ph, 4-tol, 2,6-$X_2C_6H_4$ where X = F, Cl) led to isolation of [M(L_{OMe})$_2$]. Treatment of [(L_{OMe})M(κ^2-NO_3)(L)] (L = acetone or PPh_3) with bidentate ligands N^N afforded [(L_{OMe})M(N^N)(κ^1-NO_3)] (N^N = 2,2′-bipyridine, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). Analogous Mn(II) complexes [(L_{OMe})Mn(μ_3-N_3)]$_4$, [(L_{OMe})Mn]$_2$(μ-OAr)$_2$ (Ar = 2,6-$Me_2C_6H_3$, 2-$NO_2C_6H_4$) and [(L_{OMe})Mn(bpy)(NO_3)] have been prepared similarly [61,62].

Treatment of [(η^5-C_5Ph_5)Ni(CO)Br] and [(η^5-C_5Ph_5)Ni(CO)(ClO_4)] with Na(L_{OR}) (R = Me, Et, Pr^i) afforded the 20-electron complexes [(η^5-C_5Ph_5)Ni(L_{OR})], which can be oxidized quasi-reversibly at ca. +0.26 V versus SCE (standard cal$_{ome}$l electrode). Oxidation of [(η^5-C_5Ph_5)Ni(L_{oR})] led to dissociation of the C_5Ph_5 ligand and formation of [$(L(oR)_2Ni$] [63].

The Pd(IV) alkyl compounds [(L_{OR})Pd$(Me)_2$(R′)] were prepared by oxidative addition of *cis*-[$PdMe_2$(bpy)] with R′X(R′X = MeI, $PhCH_2Br$, C_3H_3Br) in the presence of Na(L_{OR}) or Ag(L_{OR}) [64]. The solid-state structure of [(L_{OMe})$PdMe_3$], which is iso-structural with [(L_{OMe})$PtMe_3$] [65], has been determined. Treatment of [Pd(all)Cl]$_2$ (all = propenyl, 2-methylpropenyl, 2-*tert*-butylpropenyl, 1,1,2-trimethylpropenyl) with Ag(L_{OR}) afforded the π-allyl compounds [(κ^2-L_{OR})Pd(all)]. Reaction of [(L_{OMe})Pd(C_4H_7)] with PPh_3 in CH_2Cl_2 and toluene led to formation of [(C_4H_7)Pd$(PPh_3)_2$](L_{OMe}) and [(C_4H_7)Pd(PPh_3)(L_{OMe})], respectively [66]. Treatment of [$PdCl_2(MeCN)_2$] and [Pd(PPh_3)Cl]$_2$(μ-Cl)$_2$ with Ag(L_{OMe}) afforded [(κ^2-L_{OMe})$_2$Pd] and [(κ^2-L_{OMe})PdCl(PPh_3)], respectively. Reaction of [(κ^2-L_{OMe})$_2$Pd] with PPh_3 led to displacement of one L_{OMe}^- ligand and formation of [(κ^2-L_{OMe})Pd$(PPh_3)_2$](L_{OMe}). Carbonylation of [(κ^2-L_{OMe})PdCl(PPh_3)] with CO (40 bar) afforded [Pd(CO_2Me)(PPh_3)]$_2$(μ-Cl)$_2$, which reacted with PPh_3 and Ag(L_{OMe}) to give [Pd(CO_2Me)Cl$(PPh_3)_2$] and [(L_{OMe})Pd(COMe)(PPh_3)], respectively [67]. Alkylation of [(κ^2-L_{OMe})PdCl(PPh_3)] with Me_4Sn afforded [(κ^2-L_{OMe})Pd(Me)(PPh_3)] that reacted with CO to give [(κ^2-L_{OMe})Pd(COMe)(PPh_3)] [68].

Treatment of [(L_{OR})Cu(MeCN)] with L afforded [(L_{OR})Cu(η^2-L)] (L = olefin, alkynes, and *p*-benzoquinone) [69]. Analogous complexes containing a chiral tripodal ligand [($L_{S\text{-}BINOL}$)Cu(η^2-L)] (L = PhC≡CH, Me_3SiC≡CH) have been prepared and structurally characterized. The solid-state structures of [L_{or}Cu(η^2-L)] feature the “2 + 1” distorted tripod ligand coordination, in which one Cu–O bond is significantly longer than the other two, indicative of a tendency of a Cu(I) alkene and alkyne compounds to be three-coordinated [69,19].

Treatment of [ZnR_2] (R = Me, Et, Pr^i) with Tl(L_{OEt}) afforded [(L_{OEt})ZnR]. Reaction of [(L_{OEt})ZnEt] with I_2, HCl, HNO_3 and HOAc afforded [(L_{OEt})ZnX] (X = I, Cl, NO_3 and OAc), which were alternatively prepared from Tl(L_{OEt}) and ZnX_2 [23].

3.3. f-Block elements

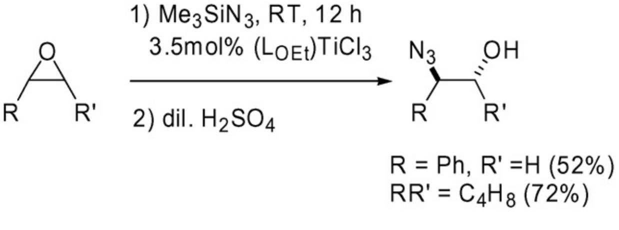
Interactions of L_{OR}^- with trivalent lanthanide ions in aqueous media gave stable cationic [Ln$(L_{OR})_2(H_2O)_2$]$^+$ compounds [5]. Solid samples of [Eu$(L_{OEt})_2(H_2O)_2$]BF_4 underwent reversible dehydration to give [Eu$(L_{OEt})_2(H_2O)_2$]BF_4 and during the reaction the crystallinity of the substance was retained [70]. Treatment of [(η^8-C_8H_8)Sm(μ-Cl)(THF)]$_2$ with two equivalents of Na(L_{OEt}) afforded [(η^8-C_8H_8)Sm(L_{OEt})] [71]. [Ln(por)(L_{OEt})] have been prepared by treatment of [Ln(por)$(H_2O)_3$]$^+$ (H_2por = tetrakis(3,4,5-trimethoxyphenyl)porphyrin, tetrakis(4-methoxyphenyl)porphyrin, tetraphenylporphyrin, or tetra(*p*-tolyl)porphyrin; Ln = Er or Yb) with Na(L_{OEt}). [72]. Interaction of [Ln{N$(SiMe_3)_2$}$_3$]·[LiCl(THF)]$_x$ (Ln = Er, Yb) with N-confused tetraphenylporphyrin (H_2NCTPP) followed by Na(L_{OMe}) afforded [(L_{OMe})Ln(NCTPP)]. The solid-state structure of [(L_{OMe})Yb(NCTPP)] shows an η^2-agostic interaction between Yb and the inter C–H bond of the NCTPP ligand [73].

Treatment of UX_4 (X = BH_4, Cl) and $ThCl_4$ with Na(L_{OEt}) afforded [(L_{OEt})UX_3] and [(L_{OEt})$ThCl_3$], respectively [74]. Reaction of [(L_{OEt})UCl_3] with Na(L_{OEt}) and TlCp gave [$(L_{OEt})_2UCl_2$] and [(L_{OEt})(Cp)UCl_2], respectively [75]. An attempt to alkylate [$(L_{OEt})_2UCl_2$] with Me_3CCH_2Li resulted in nucleophilic attack of the Cp ring in L_{OEt}^- by the neopentyl group with concomitant reduction of Co(III) to Co(I), and the formation of [(η^4-$C_5H_5CH_2CMe_3$)Co{P(O)$(OEt)_2$}$_3$]$_2$U that has been characterized by X-ray crystallography [76].

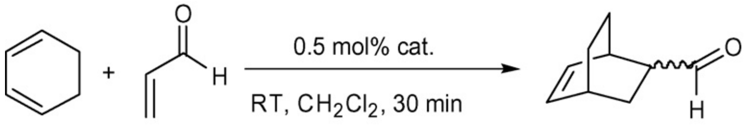
4. Applications of metal complexes with Kläui’s tripodal ligands

4.1. Electrocatalysis [54]

Reduction of [{(L_{OMe})Ru(H_2O)}$_2$(μ-O)][OTf]$_2$ with alcohols, aldehydes, or PPh_3 in MeCN afforded the



Scheme 18. Ti(IV)-catalyzed ring opening of epoxides.



cat.	yield (%)	*endo*:*exo*
$L_{OEt}Ti(OTf)_3$	85	95:5
$L_{OEt}Zr(OTf)_3$	68	90:10

Scheme 19. Ti(IV)- and Zr(IV)-catalyzed Diels–Alder reaction of cyclohexadiene and acrolein.

hydroxo-bridged Ru(III) dimer $[\{(L_{OMe})Ru(MeCN)\}_2(\mu\text{-}OH)_2][OTf]_2$. In buffered aqueous solutions, the reduction of $[\{(L_{OMe})Ru(H_2O)\}_2(\mu\text{-}O)][OTf]_2$ by formaldehyde to give the formate adduct $[\{(L_{OMe})Ru\}_2(\mu\text{-}OH)(\mu\text{-}O_2CH)][OTf]_2$ was found to be auto-catalytic via an inner-sphere mechanism. Oxidation of $[\{(L_{OMe})Ru\}_2(\mu\text{-}OH_2)(\mu\text{-}O_2CH)][OTf]_2$ with Ag(OTf) gave the Ru(IV) dimer $[\{(L_{OMe})Ru\}_2(\mu\text{-}O)(\mu\text{-}O_2CH)][OTf]_2$ that reacted with formaldehyde to regenerate the Ru(III)–Ru(III) dimer and formate. The $[(L_{OMe})Ru(OH)]_2(\mu\text{-}O)_2$ can function as an electrocatalyst for oxidation of formaldehyde through its Ru^{IV}–$Ru^{IV}/Ru^{III}Ru^{III}$ couple at relatively low potentials (near 0 V versus SCE).

4.2. Organic transformations

Treatment of sodium malonate with $[(L_{OMe})Pd(all)]$ (all = propenyl, 2-methylpropenyl) resulted in the formation of the C–C bond coupling products $(allyl)CH(CO_2Et)_2$ whereas that with $[(L_{OMe})Pd(3\text{-oxo-chlestenyl})]$ and $[(L_{OMe})Pd(4,6\text{-}\eta\text{-(cholestenyl)}]$ led to elimination of the corresponding cholestadienes. Reaction of $[(L_{OMe})Pd(all)]$ with sodium 2-acetylcyclopentanoate (Na(acp)) resulted in substitution of the acp^- for the L_{OMe}^- ligand [77].

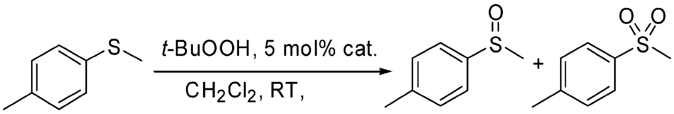
Ti(IV)-L_{OEt} complexes have been used as Lewis acid catalysts for organic transformations. For example, $[(L_{OEt})TiCl_3]$ can catalyze the ring-opening of styrene oxide and cyclohexene oxide with Me_3SiN_3 to give the corresponding azidohydrins in 52 and 72%, respectively (Scheme 18) [34].

In the presence of 0.5 mol% of $[(L_{OEt})Ti(OTf)_3]$, 1,3-cyclohexadiene reacted with acrolein to give the Diels–Alder product in 83% yield with an *endo*:*exo* ratio ofca. 19:1. A slightly lower yield was found for the Zr catalyst $[(L_{OEt})Zr(OTf)_3]$ (68% yield, *endo*:*exo* ratio ofca. 9:1) (Scheme 19) [35].

The Ti(IV) perrhenate complex $[(L_{OEt})Ti(ReO_4)_3]$ is capable of catalyzing oxidation of sulfides with *tert*-butylhydroperoxide (TBHP) (Table 1). For example, treatment of methyl *p*-tolylsulfide with TBHP with 5 mol% of $[(L_{OEt})Ti(ReO_4)_3]$ afforded a ca. 20:1 mixture of the sulfoxide and sulfone in 95% yield. $[(L_{OEt})Ti(ReO_4)_3]$ is a considerably more active catalyst than $[(L_{OEt})Ti(OTf)_3]$ and $[(L_{OEt})Ti]_2(\mu\text{-}CrO_4)_3$, suggesting that a different and more reactive intermediate, presumably a Re alkylperoxo species, is involved in the Ti/Re catalyst system. $[n\text{-}NBu_4]$ $[ReO_4]$ is inactive in the sulfide oxidation, indicating that in the bimetallic Ti/Re system, the Ti(IV) center may act as a Lewis acid activating the Re *tert*-butylperoxo moiety that undergoes oxo transfer to the sulfide. The Zr(IV) perrhenato complex $[(L_{OEt})Zr(ReO_4)_3(H_2O)]$ can also catalyze the sulfide oxidation but with a much lower selectivity (ca. 2.3). Thus, it appears that for the M/Re bimetallic catalysts, the $L_{OEt}M(IV)$ moiety has an influence on the reactivity/selectivity of the Re alkyperoxo active intermediates [35].

Table 1

Ti(IV) and Zr(IV)-catalyzed oxidation of methyl *p*-tolylsulfide with TBHP[a]



Catalyst	Time (h)	%Yield	Selectivity[b]
$[L_{OEt}Ti(OTf)_3]$[c]	24	46	14.3
$[(L_{OEt}Ti)_2(\mu\text{-}O)(\mu\text{-}SO_4)_2]$[c]	24	71	16.8
$[(L_{OEt}Ti)_2(\mu\text{-}CrO_4)_3)]$	5	44	13.7
$[L_{OEt}Ti(ReO_4)_3]$	0.25	93	17.6
$[L_{OEt}Zr(ReO_4)_3(H_2O)]$	0.5	85	2.3
$[n\text{-}Bu_4N][ReO_4]$	3	2	N.D.[d]

[a] Conditions: methyl *p*-tolyl sulfide (0.3 mmol), TBHP (0.36 mmol), catalyst (0.015 mmol), CH_2Cl_2 (2 mL).

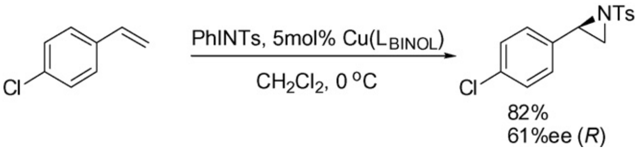
[b] Sulfoxide/sulfone ratio.

[c] 20 mol% of catalyst was used.

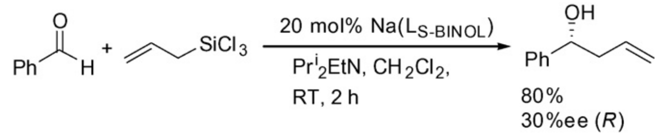
[d] Not determined.

The use of the chiral tripodal ligand $L_{S\text{-BINOL}}^-$ in asymmetric catalysis has been reported. For example, treatment of 4-chlorostyrene with PhINTs in the presence of 5 mol% of $[(L_{S\text{-BINOL}})Cu(MeCN)]$ afforded the aziridines in 82% yield and 65% yield (Scheme 20) [19].

Reaction of benzaldehyde with allyltrichlorosilane in the presence of 20 mol.% of $Na(L_{S\text{-BINOL}})$ afforded the homoallyl alcohol 4-phenyl-l-buten-4-ol in 80% yield and 30% yield (Scheme 21) [19]. It seems likely that the catalytic allylation of aldehydes involves the activation of the silyl group by the P=O chelate, although it is not clear whether $L_{S\text{-BINOL}}^-$ binds to the Si in a bidentate or tridentate fashion.



Scheme 20. Cu(I)-catalyzed asymmetric aziridination of 4-chlorostyrene with PhINTs.



Scheme 21. Asymmetric allylation of benzaldehyde with allyltrichlorosilane.

4.3. Homogeneous catalysis

Rh(I) complexes with Kläui tripodal ligands can catalyze hydrogenation of alkenes such as cyclohexene. For the hydrogenation of cyclohexene in CH_2Cl_2 with $[(L_{OMe})_2Rh_2(CO)_3]$, precipitation of Rh metal was observed, suggesting that the catalytic activity of the Rh compound may be the result of a heterogeneous reaction. However, no Rh precipitate was formed when acetone was added to the reaction mixture presumably because the acetone can stabilize the catalytically active species. Consistent with this suggestion, $[(L_{OMe},_{OR'})Rh(CO)_2]$ ($R = OC_3H_6C(O)CH_3$) containing keto groups in the ligand pendant arms can catalyze hydrogenation of cyclohexene homogeneously in CH_2Cl_2 without precipitation of Rh metal [12].

Rh(I) complexes supported by functionalized tripodal ligands $L_{OMe,OR'}{}^-$ are more efficient hydroformylation catalysts than those with $L_{OMe}{}^-$. In the presence of PPh_3 additive, $[(L_{OMe,OR'})Rh(CO)_2]$ can catalyze hydroformylation of propene with a turnover number of 690 (cf. 50 for $[(L_{OMe})_2Rh_2(CO)_3]$). The enhanced catalytic activity of $[(L_{OMe,OR'})Rh(CO)_2]$ compared with that of the $L_{OMe}{}^-$ analogue has been attributed to the coordinative bonding of the keto functionality to the Rh center [12]. The bis-acyl complexes $[(L_{OMe})Rh(COR)_2]$ ($R = C_2H_5$ or C_6H_{13}) have been isolated during the hydroformylation of alkenes with $[(L_{OMe})_2Rh_2(CO)_3]$, although it is not clear where the bis-acyl compounds come to play in the catalytic cycle of Rh-catalyzed hydroformylation. Analogous bis-acyl compounds supported by a sulfonated tri-pyrazolyl ligand $[(Tpms)Rh(COR)_2]$ ($TpmS^- =$ tris(pyrazolyl)methanesulfonate) have also been characterized [78].

4.4. Catalytic polymerization

In the presence of $AlCl_3$ activator, $[(L_{OPr})(O)ClW{=}CH_2$-*p*-tol] is an active catalyst for ring-opening metathesis polymerization of cycloctene [45]. $[(L_{OEt})TiCl_3]$ is capable of catalyzing polymerization of vinyl chloride with methyl aluminoxane co-catalyst with activity comparable to that for $[Cp^*TiCl_3]$. The poly(vinylchloride) prepared with the Ti-L_{OEt} catalyst showed bimodal molecular weight distribution, and the molecular weight decreases as polymerization temperature increases [79].

4.5. Extraction and separation of metal ions

Owing to their high affinity for hard metal ions, $L_{OR}{}^-$ have been used as ionophores for extraction and separation of metal ions. The extraction of Li^+, Na^+, Mg^{2+} and Ca^{2+} with $L_{OEt}{}^-$ has been studied and the effects of pH and ligand concentration examined. Li^+ could be specifically separated from Na^+ and K^+. Separation of Li^+ from Mg^{2+} and Ca^{2+} was achieved by masking the and Ca^{2+} with EDTA or precipitation of them with $L_{OEt}{}^-$ before the extraction [80]. Resins containing $L_{OEt}{}^-$ on Amberlite® XAD-7 were found to sorb Am(III) and Pu(IV) strongly but exhibit low affinity for U(VI) due to the geometrical mismatch of tripodal $L_{OEt}{}^-$ and the pentagonal or hexagonal planar coordination environment preferred by the linear $UO_2{}^{2+}$ ion. The sorption for both Am^{3+} and Pu^{4+} by the resins was found to decrease with increasing nitric acid concentration, but the effect is more pronounced for the former. Thus, Am^{3+} could be separated from Pu^{4+} by adjusting the nitric acid concentration. Although Fe(III) severely suppresses the Pu(IV) sorption under equilibrium conditions, the ability of the resins to separate Pu(IV) under dynamic conditions is maintained [81].

5. Conclusion

The Kläui oxygen tripodal ligands are versatile ligands that can bind tightly to both hard and soft metal ions, exhibiting interesting coordination and organometallic chemistry. Owing to their high hydrolytic stability, water-soluble M-L_{OR} complexes may serve as models for metal aqua ions. Interactions of hydroxo/oxo-bridged M(IV)-L_{OEt} (M = Ti and Zr) compounds with oxyanions in aqueous media give clusters that have core structures similar to those of oxide-based materials. The study of aqueous solution chemistry of water-soluble M(IV)-L_{OEt} complexes offers an opportunity to better understand some reactions of metal aqua ions that are otherwise difficult to follow by conventional spectroscopic methods. The investigation of structures and reactivity of polynuclear hydroxo/oxo-bridged M-L_{OR} complexes in aqueous and non-aqueous media provides new insights into the aqueous chemistry of tetravalent metal ions.

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