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# Aryloxide-based multidentate ligands for early transition metals and f-element metals

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## Abstract

This article presents an overview of the chemistry of early transition metal and f-element complexes stabilized by aryloxide-based multidentate ligands. Preparations and reactivity studies of these compounds are discussed. The presence of the bridging units in this ligand system imposes a strong geometry constraint to the aryloxide groups, which leads the way to novel patterns of structure and reactivity.
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*Keywords:* Aryloxide complexes; Multidentate ligands; Chelate effect; Early transition metals; f-Element metals

## 1. Introduction

Aryloxide (and alkoxide) ligands are known to support and promote various important organic/inorganic reactions at metal centers [1]. In this context, they complement the well-studied cyclopentadienyl-based ancillary ligands, with the major difference being the greater reactivity of aryloxide complexes due to their relatively higher unsaturation and lower coordination numbers for $(ArO)_nM$ fragments. However, in addition to coordinative unsaturation, the propensity of the oxygen for bridging metal atoms renders aryloxide complexes prone to dimerization. A consequence of this ability to aggregate is low energy pathways for ligand exchange, resulting in facile ligand redistribution. This is a common process through which coordinatively unsaturated metal complexes decompose. This undesired ligand redistribution reaction is occasionally a severe obstacle to synthetic efforts. One of strategies for overcoming this problem and controlling stoichiom-

etry is to bury the metal inside large and inert organic matrices of bulky ligands [2], and the chemistry of metal aryloxides grew dramatically with the use of sterically bulky aryloxide ligands [3].

Another approach is to use covalently linked ancillary ligands, thereby limiting ligand mobility and leaving little possibility to reorganize the molecule. The chelate effect in coordination and organometallic chemistry has most pronounced kinetic and thermodynamic consequences. Furthermore, complexes supported by multidentate aryloxide ligands have intriguing coordination and reactivity compared to metals supported by monodentate aryloxide ligands, because the presence of the bridging units imposes a strong geometry constraint to the aryloxide groups.

Linked aryloxide ligands are accessible by various synthetic methods. The introduction of alkyl substituents onto the *ortho* positions of *para*-substituted phenols can be readily achieved by electrophilic substitution reactions. For example, the condensation of *para*-substituted phenols with formaldehyde produces the calix[*n*]arenes [4]. The strong *ortho*-metallation directing effect of the phenolic group can be used to build linked

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aryloxide ligands [5]. Therefore, in aryloxide-based multidentate ligands, aryloxide units are almost exclusively connected at *ortho* positions through the bridge units. Steric bulk can be manipulated through the *ortho*-substituents, whereas *para*-substituents could help to control solubility and modify the spectroscopic properties of metal complexes without little steric influence on the coordination sphere.

The focus of this review is to give an overview of selected current results from the chemistry of linked aryloxide ligands, paying particular attention to the synthesis and reactivity of their early transition metal and f-element metal complexes. Their applications as polymerization catalysts are mentioned only briefly, because these systems have been partially covered in other reviews in the context of the exploration of non-metallocene catalysts [6]. We will exclude metal complexes containing Schiff base derivatives and 2,2′-biphenol/ binaphthol derivatives, because this area has also been covered elsewhere [6b–8].

## 2. Bis(aryloxide) ligands

### 2.1. Bis(aryloxide) ligands bridged by the carbon chain

One of the first chelating aryloxide ligands to support early transition metals is the 2,2′-methylene-bis(phenol) derivatives $H_2[1^R]$ (Scheme 1). The direct reactions of various titanium(IV) precursors with 1 equiv. of $H_2[1^{tBu}]$ led to monomeric mono-ligand complexes formulated as $[1^{tBu}]TiX_2$ [9–11]. Organometallic derivatives $[1^{tBu}]TiR_2$ could be prepared via standard alkylation procedures [9a,10]. The eight-membered chelate ring of the $[1^{tBu}]^{2-}$ ligand adopts a boat or a chair conformation. NMR spectra of $[1^{tBu}]TiX_2$ indicated a dynamic behavior that could be explained by boat-chair interconversion as well as inversion of the eight-membered chelate ring. Though somewhat dependent on the nature of the ligand X, the activation barrier to this process is high (see Scheme 2).

The reaction of $[1^{tBu}]TiCl_2$ with $LiBH_4$ afforded the bis-tetrahydroborate complex, in which both $BH_4^-$ anions act as a tridentate ligand [9b]. Dissolution of $[1^{tBu}]$-$TiCl_2$ in THF gave the THF adduct due to the Lewis
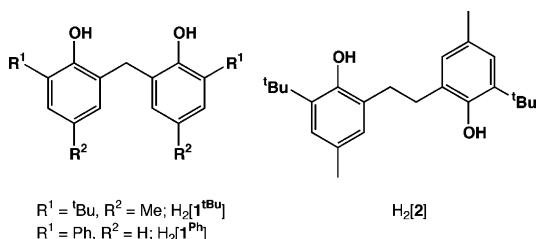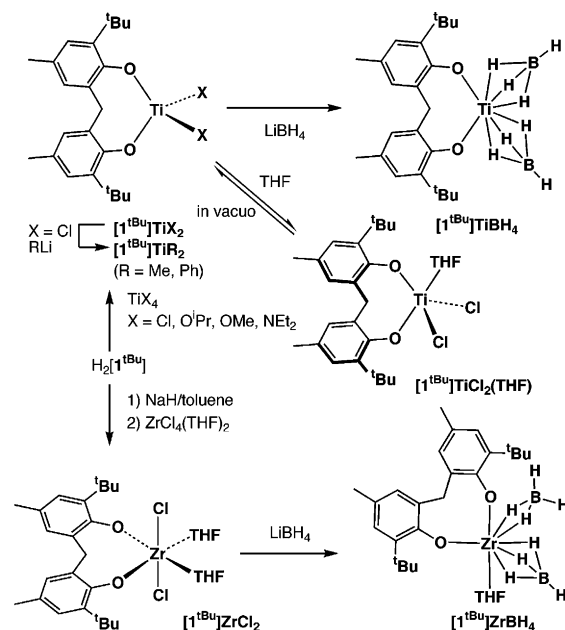
acidity of the titanium center [10]. The THF molecule in $[1^{tBu}]TiCl_2(THF)$ was readily lost on warming in vacuo. The related dibromo and diiodo derivatives, which were prepared by the reaction of $[1^{tBu}]TiCl_2$ with $Me_3$-SiX (X = Br, I), did not form isolable THF adducts. Likewise, the dialkyl and dialkoxy complexes exhibit no interaction with THF according to $^1H$ NMR spectroscopy. This was attributed to the large steric requirement of the $[1^{tBu}]^{2-}$ ligand.

The zirconium complex containing the $[1^{tBu}]^{2-}$ ligand was obtained as a bis-THF adduct via salt elimination [9b], in contrast to the labile mono-THF adduct obtained for the smaller titanium congener. The reaction with $LiBH_4$ proceeded with loss of one THF molecule to yield the tetrahydroborate complex. The X-ray analysis reveals that the zirconium center is bound to a tridentate and a bidentate $BH_4^-$ ligand. In these complexes of group four metals, the O–M–O angle of the $[1^{tBu}]^{2-}$ ligand has to be constrained to be *cis*.

The catalytic activity of $[1^{tBu}]TiX_2$ for the polymerization was investigated, mimicking the strategy used to develop *ansa*-metallocene catalysts. Although the $[4E]TiX_2$/MAO combinations (M = Ti, Zr; vide infra) are reasonably active catalysts for α-olefin polymerization, the related methylene-linked bis(aryloxide) complexes $[1^{tBu}]TiX_2$ showed only low activity [12,13]. This is partially due to the rigid ligand structure that blocks one segment of the coordination sphere. On the other hand, $[1^{tBu}]TiX_2$ are highly active initiators for the living ring-opening polymerization of ε-caprolactone [14] and cyclic six- and seven-membered carbonates [15], the copolymerization of cyclic acid anhydrides with oxetane [16], and the sequential

Scheme 2.

Scheme 1.

cationic and anionic polymerization of oxetane and ε-caprolactone [17]. The polymers obtained possess narrow molecular weight distributions. In comparison to linked-aryloxide complexes, monodentate aryloxide titanium complexes produced polymers with broader molecular weight distributions. While the [1^tBu]Ti unit is retained during the polymerization process, the monodentate aryloxide ligand is observed to be partially incorporated into the resulting polymers.

Group 4 cationic species have been so important in the field of olefin polymerization. Stable cationic four coordinate titanium complexes supported by the linked-bis(aryloxide) ligands could be isolated by using aryl or benzyl groups with an additional Lewis base functionality attached [18]. For example, treatment of [1^tBu]TiCl_2 with LiR [R = C_6H_4(o -CH_2NMe_2)] followed by the methylation with MeLi gave [1^tBu]TiMe[η^2-R] (Scheme 3). The NMR studies show that the cationic species was generated by reacting the methyl complex with B(C_6F_5) in C_6D_5Br. The $^{19}$F NMR spectrum indicates that the MeB(C_6F_5) anion is non-coordinating. This cationic species underwent a single insertion of ethene and propene into the Ti–C bond. In the case of ethene, the reaction give a subsequent rearrangement that is likely to proceed through β-H elimination and 2,1-reinsertion of the substituted styrene ligand thus formed. This rearrangement is driven by formation of a thermodynamically more favorable benzylic species. The geometry around the metal center enforced by the two chelating ligands might inhibit further olefin insertion.
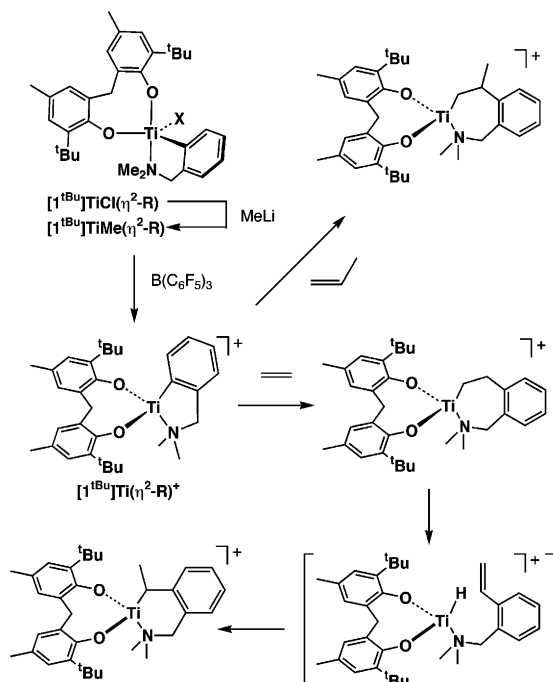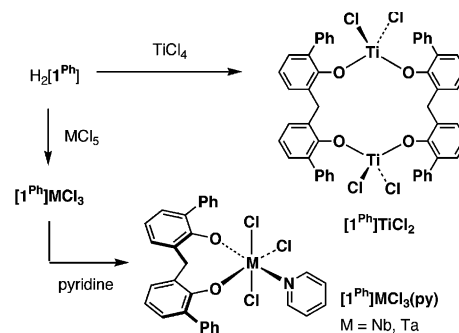
Modifications of the parent [1^tBu]^2− ligand system have the significant influence on structures and catalytic performance of the complexes. Two potential sites for ligand modification are the ortho-substitute groups and the linker units. When the phenyl-substituted [1^Ph]^2− ligand was used, the dimeric compound was prepared by the direct reaction of TiCl_4 with H_2[1^Ph] (Scheme 4) [19]. In contrast to the cis-coordination mode observed for monomeric complexes containing the [1^tBu]^2− ligand, the X-ray analysis of [1^Ph]TiCl_2 shows that the bis(aryloxide) ligands can span two tetrahedral titanium centers.

The use of the ethylene-linked bis(aryloxide) [2]^2− ligand increases the chelate size of the complex [20,21]. A series of titanium complexes with the [2]^2− ligand were prepared via the direct synthesis (Scheme 5) [20]. The nine-membered ring of [2]TiX_2 is fluxional in solution at ambient temperatures, which contrasts with the high barrier to inversion of the eight-membered chelate ring of the [1^tBu]^2− ligand. In the presence of MAO, [2]TiX_2 copolymerized ethene and styrene with high incorporation of styrene. The X-ray analysis reveals that both phenyl rings of the [2]^2− ligand are coplanar with the tert-butyl groups directed away from the metal center. This allows the incoming styrene easy access, resulting in a higher incorporation of styrene monomer.

Bis(aryloxide) complexes of group 5 transition metals are accessible by direct synthesis and salt metathesis [11,19,21b,22]. For example, treatment of MCl_5 (M = Nb, Ta) with H_2[1^Ph] result in formation of [1^Ph]MCl_3, which reacted with pyridine to provide the pyridine adduct [19] (Scheme 4). The structures of these
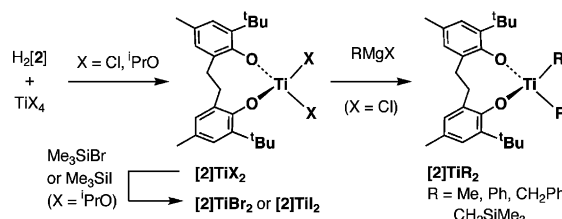


Scheme 4.



Scheme 3.



Scheme 5.

linked-bis(aryloxide) complexes are similar to those of the related monodentate aryloxide complexes. However, comparison of the reactivity of the linked bis(aryloxide) complexes and the monodentate-aryloxide complexes reveals significant differences. The hydrogenation of benzene was carried out by mixing [1$^{Ph}$]NbCl$_3$ with 3 equiv. of BuLi followed by exposure to H$_2$ (1200 psi) to produce cyclohexane (80 equiv. per Nb). Although the catalytic activity was about three times lower than reported for the monodentate-aryloxide precursor Nb(2,3,5,6-OC$_6$HPh$_4$)$_2$Cl$_3$, the chelation of the [1$^{Ph}$]$^{2-}$ ligand at the metal center inhibits the hydrogenation of the *ortho*-phenyl rings of the ligand during the catalysis [19]. This intramolecular hydrogenation readily takes place for monodentate *ortho*-phenylphenoxides [23].

The bis(aryloxide) ligand was used for the preparation of Mo$_2^{6+}$ and W$_2^{6+}$ compounds [24]. The reaction of 2 equiv. of H$_2$[1$^{tBu}$] with Mo$_2$(NMe$_2$)$_6$ gave a mixture of two isomers, [1$^{tBu}$]Mo-a and [1$^{tBu}$]Mo-b (Scheme 6). These isomers are thermally stable and show no sign of interconversion in solution, indicating that their formation is kinetically controlled. However, addition of Lewis bases such as pyridine promotes the isomerization of [1$^{tBu}$]Mo-b to [1$^{tBu}$]Mo-a. Therefore, [1$^{tBu}$]Mo-a is the thermodynamic isomer. In the similar amine elimination
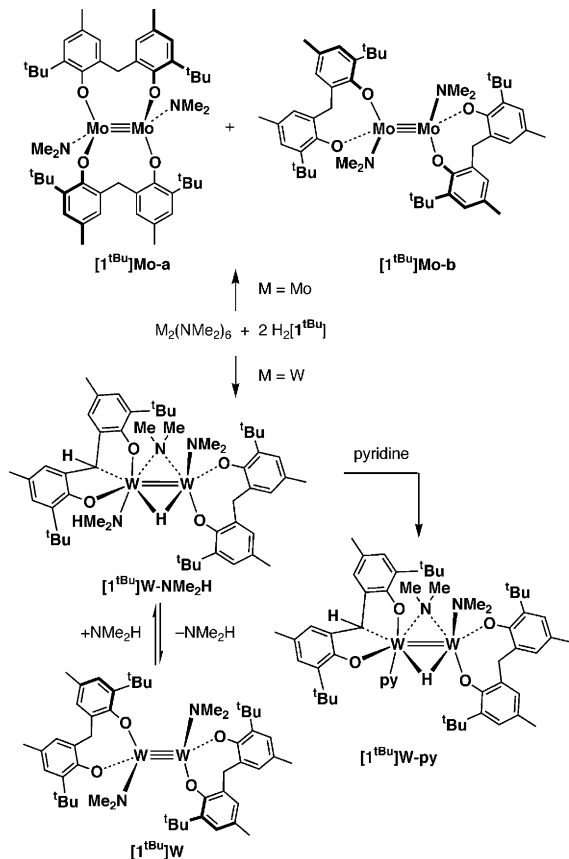
using W$_2$(NMe$_2$)$_6$, the C–H activation of the ligand took place to provide the amine adduct [1$^{tBu}$]W-NMe$_2$H. Removal of NMe$_2$H from the reaction mixture led to formation of [1$^{tBu}$]W, which is similar to [1$^{tBu}$]Mo-b. The transformation of [1$^{tBu}$]W-NMe$_2$H into [1$^{tBu}$]W was observed in the solid state upon heating in vacuo. The $^1$H NMR studies provide evidence that [1$^{tBu}$]W is in equilibrium with [1$^{tBu}$]W-NMe$_2$H in the presence of NMe$_2$H in solution. A pre-equilibrium coordination of Lewis bases is proposed as the initial step in the conversion of [1$^{tBu}$]W into [1$^{tBu}$]W-NMe$_2$H, because the PMe$_3$ adduct has been observed at −60 °C upon addition of PMe$_3$ into a solution of [1$^{tBu}$]W. This adduct was found to undergo C–H oxidative addition to the metal–metal bond between −20 and 20 °C, according to $^1$H and $^{31}$P NMR spectroscopy. In these dinuclear systems, coordination of the Lewis base to the metal center induces isomerization or C–H activation.

Amine elimination has been also useful for the synthesis of lanthanide(II) complexes. The reaction of M{N(SiMe$_3$)$_2$}$_2$(THF)$_2$ (M = Sm, Yb) with H$_2$[1$^{tBu}$] afforded the dimeric compounds [25]. These complexes showed moderate activity for the ring-opening polymerizations of ε-caprolactone and dimethyltrimethylene carbonate and their copolymerization. Addition of a monomer to the Sm(II) complexes resulted in an immediate color change from dark purple to pale yellow, implying that the active species is the lanthanide(III) complex in polymerization.

The actinide complex supporting by the bis(aryloxide) ligand was found to facilitate cleavage and hydrogenation of dinitrogen (Scheme 7) [26]. Complex [1$^{tBu}$]Th was prepared by the reaction of K$_2$[1$^{tBu}$] with ThCl$_4$(DME)$_2$. Reduction of [1$^{tBu}$]Th with 1 equiv. of potassium naphthalenide under N$_2$ for three days produced the
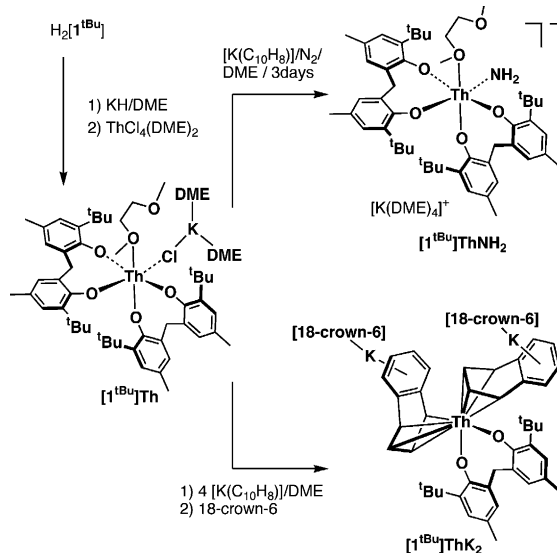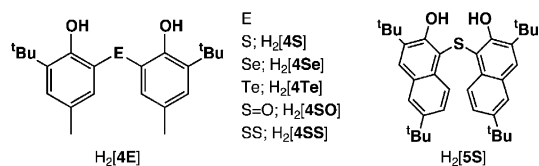


Scheme 6.
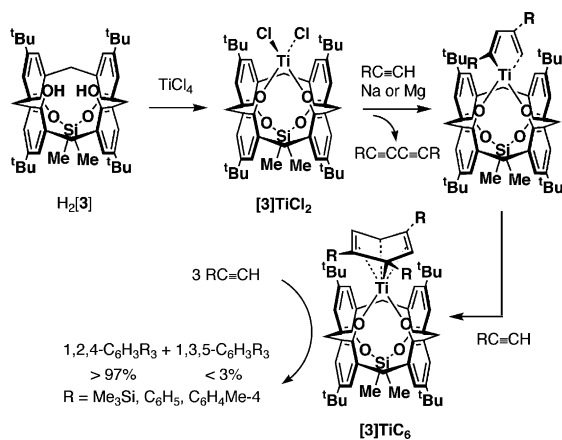


Scheme 7.

Scheme 8.



Scheme 9.

thorium(IV) amide complex [1$^{tBu}$]ThNH$_2$ as colorless crystals, in which cleavage of dinitrogen and subsequent H-abstraction from DME might take place. In the initial stage of the reaction, the solution turned dark-red. Attempts to isolate any intensely colored complex from the (1:1) K(napthalenide)/[1$^{tBu}$]Th reaction under Ar have been unsuccessful. When the amount of potassium napthalenide was increased to 4 equiv., the mono-ligand complex [1$^{tBu}$]ThK$_2$ was isolated as dark red crystals. The X-ray analysis displays the distortion of the naphthalenes moiety, indicating that [1$^{tBu}$]ThK$_2$ acts as low-valent thorium synthon. In light of the isolation of [1$^{tBu}$]ThK$_2$, the reaction between [1$^{tBu}$]Th and [1$^{tBu}$]ThK$_2$ is proposed to trigger the transformation resulting in dinitrogen cleavage and partial hydrogenation.

The 1,2-alternate conformer of the calix[4]arene could be utilized as a bis(aryloxide) ligand to sterically define the reaction sites at the metal center (Scheme 8). In the calix[4]arene-derived bis(aryloxide) [3]$^{2-}$ ligand, two proximal oxygen atoms of the 1,2-alternate conformer are bridged by the SiMe$_2$ group [27]. Metalation of this Si-bridged 1,2-conformer H$_2$[3] was accomplished by treating H$_2$[3] with TiCl$_4$. Complex [3]TiCl$_2$ under reducing conditions catalyzed highly regioselective alkyne cyclotrimerizations [27b]. This regioselectivity is a result of steric effects imposed by the *tert*-butyl groups and the phenyl rings attached to the Si-bridged aryloxides in the 1,2-alternate conformer [3]$^{2-}$ ligand. In the catalytic cycle, the metalanorbornadiene [3]TiC$_6$ was formed. This intermediate underwent the insertion of aldehydes and ketones into a Ti–C bond [27e].

## 2.2. Bis(aryloxide) ligands linked by the heteroatom group

The heteroatom-bridged bis(aryloxide) [4E]$^{2-}$ ligands (Scheme 9) have played an important role in exploring non-metallocene catalysts for the polymerization of ethene, α-olefins, and butadiene, as well as for the copolymerization of ethene and styrene [28–30]. One

of the earliest examples was reported by Miyatake and Kakugo [29], in which the replacement of a methylene linker of the [1$^{tBu}$]$^{2-}$ ligand by a sulfur atom dramatically improved group 4 metal catalysts when activated with MAO. The heteroatom E linker of the [4E]$^{2-}$ ligand acts as an additional donor, and further works have shown the importance of the additional intramolecular E donor for catalytic activity. Theoretical calculations have suggested that, in the putative alkyl cation, the coordinating additional donor decreases the activation barrier for the olefin insertion into the metal–alkyl bond [31]. Of the three chalcogenide bridging atoms, electron-donating capacity of the bridging E atom to the metal center increases on going from S to Se to Te. Therefore, the ability of the bridging E atom to lower the barrier to ethene insertion follows the order S > Se > Te. Although the catalyst system based on [4Te]TiCl$_2$ shows 20–50 times higher activity in ethene polymerization than that based on the methylene-bridged [1$^{tBu}$] analogue, its activity is three times lower relative to the sulfur-bridged complex [32]. The lower activity of the tellurium-bridged complex might be ascribed to the instability of active species as well as tellurium–aluminum exchange reaction [33].

A series of titanium complexes containing the [4E]$^{2-}$ ligand (E = S, Se, Te, SO) could be prepared by the
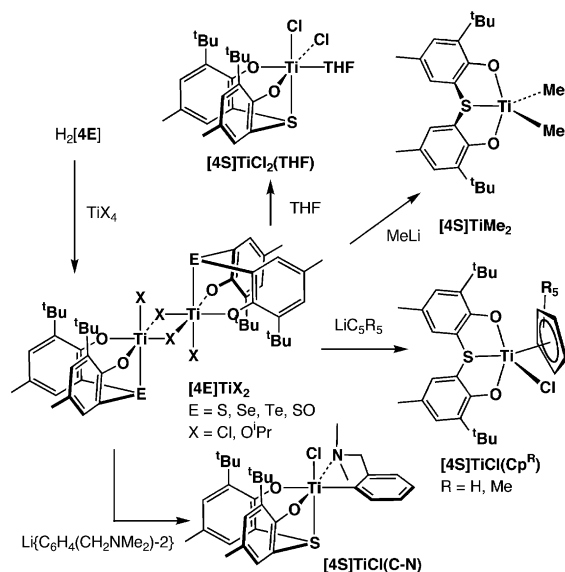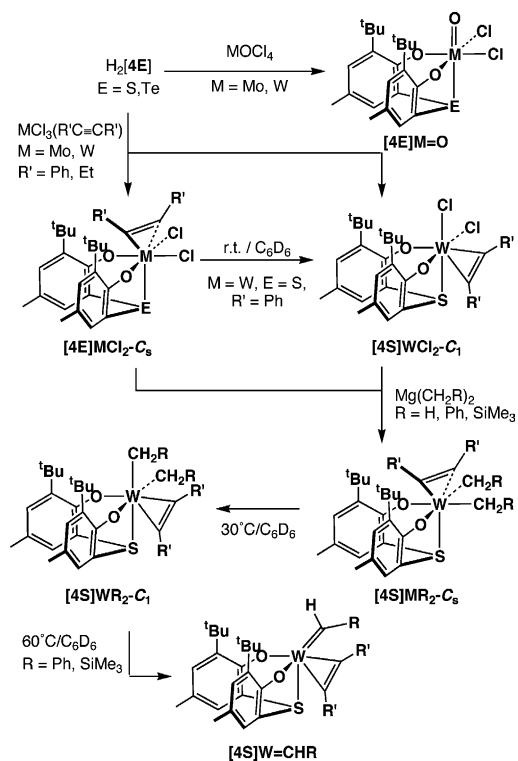


Scheme 10.

direct reactions with appropriate precursors with H$_2$[4E] (Scheme 10) [32,34,35]. In contrast to the monomeric structures found for [1$^{tBu}$]TiX$_2$, [4E]$^{2-}$ derivatives (E = S, Te, SO) are dimeric in the solid-state structure. In each case, the [4E]$^{2-}$ ligand is coordinated to the metal in a facial fashion and the E bridging unit exhibits weak interaction with the metal center. All the structurally characterized metal complexes reported to date show a facial coordination mode as seen in these titanium complexes, except for the copper(II) derivative in which the coordination geometry is intermediate between planar and tetrahedral [36]. In a comparison between the structures of the sulfur- and tellurium-bridged complex, as expected, the Ti–Te interaction is stronger than the Ti–S interaction [32].

Alkylation of the [4S] complex with MeLi afforded the five-coordinated monomer complex [4S]TiMe$_2$ [34b]. Attempts to isolate a cationic species by the reaction of [4S]TiMe$_2$ with Lewis acidic activators B(C$_6$F$_5$)$_3$, [NPhMe$_2$H][B(C$_6$F$_5$)$_4$] or [Ph$_3$C][B(C$_6$F$_5$)$_4$] led to considerable decomposition above −20 °C, due to the extreme electrophilicity and instability of the 4-coordinate alkyl cation as the putative catalyst for olefin polymerization. However, this methyl complex activated with Lewis acids was capable of polymerizing ethene, albeit in low yield.

When the number of sulfur in the linker unit was increased to two, the disulfide-bridged bis(aryloxide) [4SS]$^{2-}$ ligand can adopt various coordination modes [37]. Attempts to alkylate the dihalo complexes containing the [4SS]$^{2-}$ ligand have been failure, and activation of the complexes with MAO gave no significant activity in ethene polymerization. The coordination of the disulfide unit facilitates the reduction of the metal center, which may be a reason for these difficulties.

The direct reactions of H$_2$[4E] with MOCl$_4$ and MCl$_3$(R′C≡CR′) (M = Mo, W) afforded the corresponding complexes of group 6 metals (Scheme 11) [38,39]. When the alkyne adducts were used, the structures of products formed are $C_1$- and/or $C_s$-symmetric with depending on the nature of the metal and the ligands. The $C_s$-isomer was transformed into the $C_1$ isomer in solution at room temperature. The alkylation using dialkyl magnesium led to formation of the corresponding $C_s$-symmetric complexes. These $C_s$-symmetric alkyl complexes were found to convert into the $C_1$-symmetric isomer in solution, which underwent subsequent α-H elimination to give the alkylidene species. The reactions of the alkylidene complexes with norbornene afforded poly(norbornene)s with high *cis*-contents [39b]. On the other hand, the oxo complex exhibited higher activity for the ring-opening metathesis polymerization (ROMP) of norbornene than the corresponding alkyne adduct [38b]. The activation of the oxo complexes with AlMe$_3$ and AlEt$_3$ afforded the catalysts that showed strong dependence of *cis–trans* selectivity on the catalyst con-



Scheme 11.

centration and temperature. The interaction between the W=O bond and the aluminum center is proposed to enhance the *cis*-selectivity as well as the catalytic activity.

The samarium(III) complexes having [4S]$^{2-}$ and [5S]$^{2-}$ ligands were prepared by the direct synthesis and the salt metathesis using Sm(OAr)$_3$ (Scheme 12) [40]. The [4S]$^{2-}$ ligand stabilizes the monomeric Sm(III)
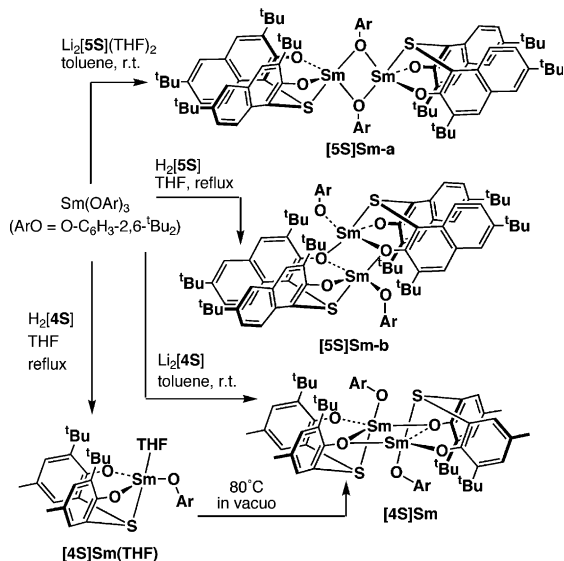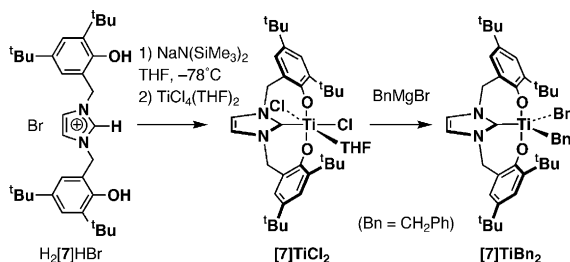


Scheme 12.
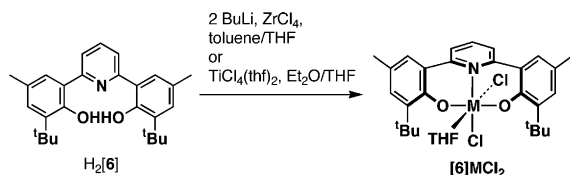
Scheme 13.

complex as a THF adduct, which could be converted into a THF-free dimer by heating in vacuo. The dimeric bis(naptholate) $[5S]^{2-}$ derivatives were isolated free of THF, even though the reactions were performed in this media. There are no evidence for interconversion between two dimers [5S]Sm-a and -b on the NMR time-scale up to 380 K in the absence of coordinating solvents, because of the rigidity of the bis(naptholate) conformation coordinated to the samarium metal. These dimeric complexes were tested as catalysts for the one-step monoacylation of *meso*-hyrobenzoin.

The bis(aryloxide) ligands linked by pyridine [41] and N-heterocyclic carbene (NHC) [42] were reported in the synthesis of titanium and zirconium complexes as shown in Schemes 13 and 14, respectively. While X-ray analysis reveals that the conformation of the pyridine-linked ligand is $C_s$-symmetric, the NHC-linked ligand adopts a $C_2$-symmetric conformation. Alkylation of the NHC dichloro complex with PhCH$_2$MgBr afforded the $C_2$-symmetric benzyl complex, whose activation parameters for the enantiomerization [$\Delta H^{\ddagger} = 64.8$ kJ mol$^{-1}$; $\Delta S^{\ddagger} = -6.2$ J mol$^{-1}$K$^{-1}$] was determined by variable-temperature NMR studies. The titanium-pyridine complex [6]TiCl$_2$ with MAO were poor catalysts for the polymerization of ethene, whereas the zirconium congener showed a very high activity [41]. For the NHC complex, the activation with MMAO produced catalysts gave rise to a high activity in the polymerization of ethene. High activities observed for [6]ZrCl$_2$ and [7]TiCl$_2$ are intriguing despite the presence of the THF ligand that normally suppresses catalytic efficiency.

## 2.3. Tripod ligands having two aryloxide groups and two additional donors

The combination of an amine-bis{(2-hydroxyaryl)methyl} with a sidearm function leads to a family of dianionic tetradentate ligands $[8E]^{2-}$ (Scheme 15).
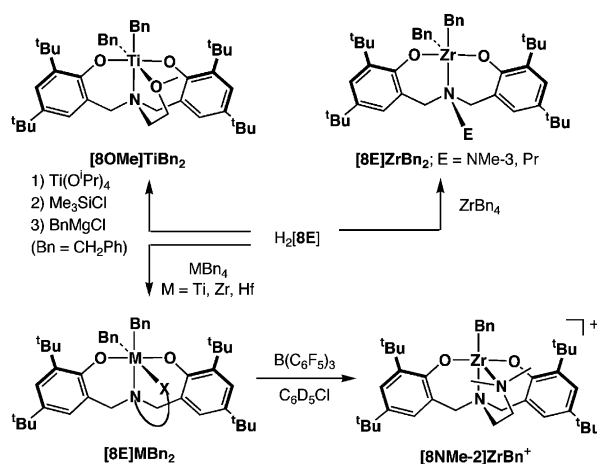


Scheme 14.
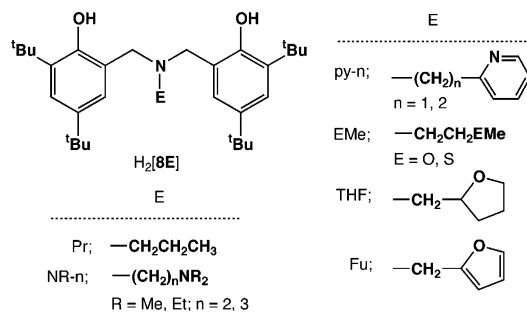


Scheme 15.

The titanium complexes have been prepared by the direct reactions of H$_2$[8E] with Ti(O$^i$Pr)$_4$ and Ti(CH$_2$Ph)$_4$ [43,44] (Scheme 16). For the *iso*-propoxide derivative, treatment with Me$_3$SiCl and subsequent alkylation with PhCH$_2$MgCl afforded [8OMe]TiBn$_2$ [43a]. The X-ray analyses show that the complexes have an octahedral geometry with $C_s$ symmetry, and two labile X groups are forced into a *cis* geometry. The benzyl complex, when activated with B(C$_6$F$_5$)$_3$ in neat 1-hexene, was capable of polymerizing 1-hexene in a living fashion to produce very high molecular weight monodisperse poly-1-hexene [a]. It should be noted that, even at 65 °C, the catalyst provided poly-1-hexene with narrow molecular weight distribution. This system could be applied to the block copolymerization of 1-hexene and 1-octene by sequential addition of the corresponding monomers. In comparison with zirconium and hafnium congeners described below, these titanium complexes exhibit a low activity for α-olefin polymerization but a prolonged living character.

A series of zirconium and hafnium dibenzyl complexes having various $[8E]^{2-}$ ligands were analogously prepared by the direct reactions of corresponding tetrabenzyl complexes with the ligand precursors, revealing
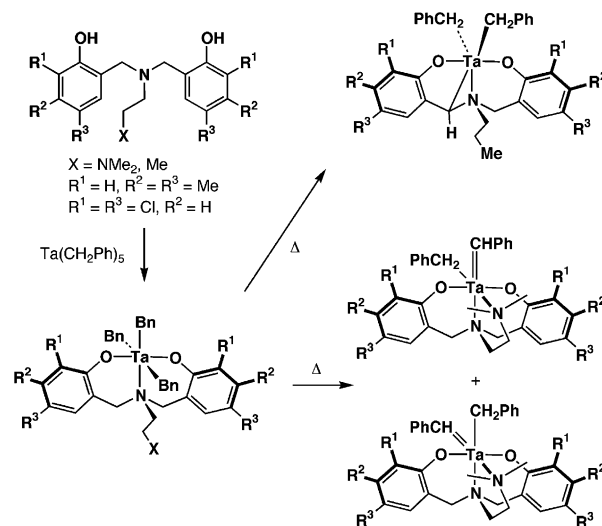


Scheme 16.

interesting correlations of catalyst structure with activity for polymerization [44–46]. The X-ray structures of these complexes show that the amine-bis(aryloxide) cores of the ligands assume a very similar meridional geometry with the sidearm donor binding to the metal center, except for the **[8NMe-3]**$^{2-}$ ligand in which the amine sidearm group is non-coordinating. According to NMR studies, treatment of **[8NMe₂-2]ZrBn₂** with B(C₆F₅)₃ in C₆D₅Cl leads to formation of a well-separated ion pair, in which the sidearm function of the ligand remains ligated to the metal. This cationic species is stable for hours at room temperature and for days at −35 °C.

Although the sidearm donor plays a minor structural role, the reactivity of complexes having the **[8E]**$^{2-}$ ligand is dependent on the nature of the sidearm moiety. Activities of these complexes for 1-hexene polymerization were investigated upon activation with B(C₆F₅)₃ in neat 1-hexene, indicating that a strong donation of a sidearm group led to highly reactive polymerization catalysts. The activity order as a function of the sidearm donor is OMe > NMe₂ > SMe for zirconium complexes and SMe > OMe > NMe₂ for hafnium complexes [46b]. The interaction between the metal and the sidearm donor can be modified by the combination of the tether length and the substituents on the sidearm donor atom. Complex **[8NMe₂-2]ZrBn₂** shows high activity for 1-hexene polymerization, while the ethyl substituents on the N-donor of the **[8NEt₂-2]**$^{2-}$ ligand reduced the reactivity dramatically and led to oligomers. The steric congestion between the sidearm group and the *tert*-butyl substituent in the *ortho*-position of the aryloxide moiety results in a weaker binding of the sidearm donor. When the sidearm donor is not coordinated to the metal center (such as **[8NMe₂-3]ZrBn₂** and **[8Pr]ZrBn₂**), this system produces a trace amount of oligomers.

The related dichloride complex **[8py-1]ZrCl₂** was prepared by the direct synthesis of Zr(CH₂SiMe₃)₂Cl₂(Et₂O)₂ with H₂**[8py-1]** or the salt metathesis of ZrCl₄(THF)₂ with Na₂**[8py-1]** [47]. The variable-temperature NMR studies indicate that this dichloride complex is an equilibrium mixture of two isomers having $C_1$ and $C_s$ symmetry in solution. The **[8py-1]**$^{2-}$ complexes of zirconium shows poor activity for the polymerization of ethene with MAO or B(C₆F₅)₃ activation, in contrast to their high activity for 1-hexene polymerization described above.

In the case of tantalum, the reactions of Ta(CH₂Ph)₅ with the related bis(aryloxide) ligand precursors are found to depend on the size of the *ortho*-substituent of the aryloxide group [48]. Although bulky H₂**[8NMe-2]** did not react with Ta(CH₂Ph)₅, the related ligand precursors having the small *ortho*-substituent (Me, Cl, H) on the aryloxide rings could be incorporated into tantalum's coordination sphere via toluene-elimination reactions (Scheme 17). In the resulting tribenzyl complexes,
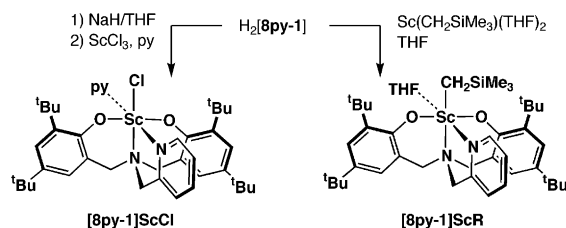


Scheme 17.

the ligands are coordinated in a meridional manner with the non-coordinating sidearm. These tribenzyl complexes undergo an α-abstraction from the benzyl ligand or a β-abstraction from the ligand backbone along with toluene elimination. The structural features that promote each of these two processes have been investigated [48b].

The scandium complexes containing the **[8py-1]**$^{2-}$ ligand were accessible by the salt metathesis of ScCl₃ with Na₂**[8py-1]** in the presence of pyridine and the direct synthesis of Sc(CH₂SiMe₃)(THF)₂ with H₂**[8py-1]** (Scheme 18) [49]. In the solid-state structure of **[8py-1]ScCl**, the geometry at scandium is best described as an octahedron with the Cl ligand positioned *trans* to the amine donor of the ligand.

*2.4. Open-chain bis(aryloxide) ligands having two additional donors*

The connectivity of the donor atoms in dianionic tetradentate bis(aryloxide) ligands is changed from the branched mode of the **[8E]**$^{2-}$ ligand to the sequential mode of the ethylenediamine-linked bis(aryloxide) **[9]**$^{2-}$ ligand (Scheme 19). The direct reaction of Zr(CH₂Ph)₂ with H₂**[9]** afforded the dibenzyl complex
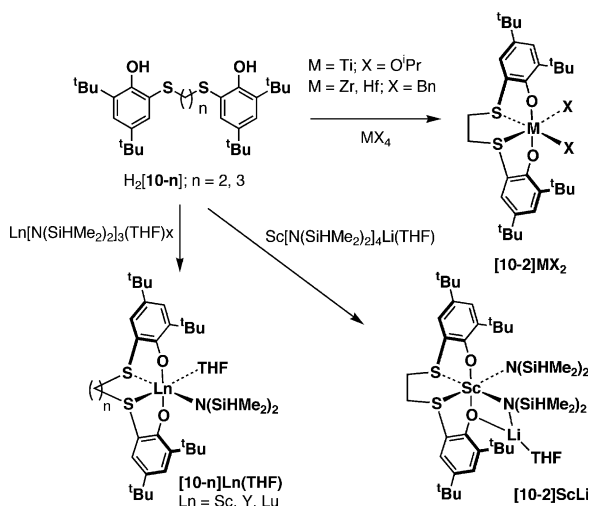


Scheme 18.
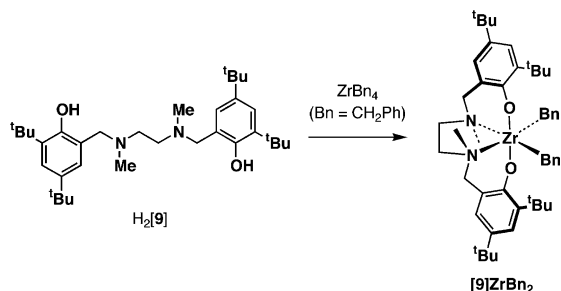
Scheme 19.

[50]. The X-ray analysis shows that it adopts a $C_2$-symmetrical structure, which is retained in solution according to its ^{1}H NMR data. Upon activation with $B(C_6F_5)$, this complex produced highly isotactic poly(1-hexene) (>95%) in a living fashion at room temperature. Since replacing the *tert*-butyl groups of the ligand with the methyl groups resulted in formation of atactic poly(1-hexene), the steric bulk of the *ortho*-aryloxide substituent may play an important role in achieving isospecific living-polymerization of 1-hexene.

The open-chain tetradentate bis(aryloxide) ligands linked through a dithiaalkane-bridge $[10\text{-}n]^{2-}$ were also used as an ancillary ligand for group 4 metals and rare earth metals (Scheme 20). Treatment of $H_2[10\text{-}n]$ with appropriate precursors of group 4 metals afforded the corresponding [10-n] complexes [51]. The NMR data of complexes having the [10-2] ligand are consistent with the $C_2$-symmetric structure, and the X-ray analysis has confirmed that **[10-2]HfBz₂** possesses an octahedral structure with $C_2$-symmetry. When the bridging unit is changed from 1,2-dithia-ethane to 1,3-dithia-propane, **[10-3]TiCl₂** adopts a $C_1$-symmetric structure in the solid state and is fluxional in solution according to NMR spectroscopy. The **[10-2]** complexes, in combination with MAO, are active for isospecific polymerization of

styrene. The titanium complex **[10-2]TiCl₂** is also shown to be an active catalysts precursor for the polymerization of 4-metyl-1,3-pentadiene (4-MPD), yielding highly isotactic poly-1,2-(4-MPD) [52]. On the other hand, the $C_1$-symmetric octahedral complexes **[10-3]TiX₂** exhibit low activity for syndiospecific styrene polymerization.

Amine elimination of $Ln[N(SiHMe_2)_2]_3(THF)_x$ and $Sc[N(SiHMe_2)_2]_4Li(THF)$ with $H_2[10\text{-}n]$ gave monomeric rare earth metal complexes [53]. The X-ray analyses confirm that these complexes adopt an octahedral or a trigonal-prismatic geometry with $C_1$-symmetry, in which two oxygen atoms of the ligand are mutually *trans* or *cis*. The $C_1$-symmetric structures of **[10-n]Ln(THF)** are not retained in solution and show $C_s$- or $C_2$-symmetry according to NMR spectroscopy. This fluxional behavior is attributed to the reversible THF-dissociation process, which leads to a pseudo-five-coordinated metal center with either $C_s$- or $C_2$-symmetry. The mono-amide complexes were active initiators for the ring-opening polymerization of L-lactide, affording high molecular weight polymers with narrow molecular weight distributions.

## 3. Tris(aryloxide) ligands

### 3.1. Open-chain tridentate tris(aryloxide) ligands

Early transition metal complexes with open-chain aryloxide trimers $[11^R]^{3-}$ show remarkable reaction behavior as well as interesting structural chemistry [54]. In the tridentate $[11^R]^{3-}$ ligands, aryloxide units are connected at *ortho* positions through methylene linkers (Scheme 21). These ligand systems have been found to be flexible in their mode of binding. While U-shape arrangements are perhaps favored, in sterically more demanding situations, S-shape coordination modes are possible. In particular, a U-conformation of the ligand is reminiscent of a cone conformation of the calix[4]arene.

The exploration of some aspects of coordination chemistry of the $[11^R]^{3-}$ ligands was started with tita-
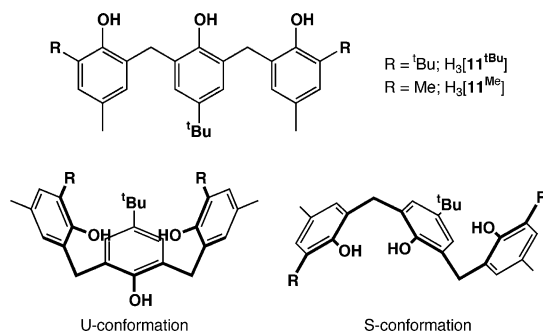


Scheme 20.



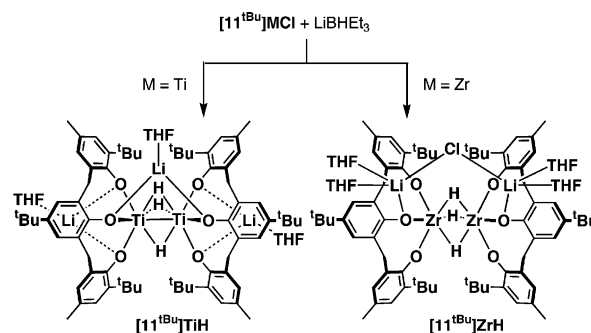Scheme 21.

nium for comparison to well-studied titanium complexes of $[\mathbf{1^R}]^{2-}$ and $[\mathbf{4E}]^{2-}$ ligands (vide supra). Reaction of $TiCl_4$ with $H_3[\mathbf{11^{Me}}]$ in refluxing toluene gave $[\mathbf{11^{Me}}]\mathbf{TiCl}$ (Scheme 22) [55], whereas attempts to prepare the $[\mathbf{11^{tBu}}]$ derivative by the similar direct synthesis resulted in an inseparable mixture of $[\mathbf{11^{tBu}}]\mathbf{TiCl}$ and ill-defined compound(s) [56]. The problem arose from partial loss of the $^t$Bu groups at the *ortho* positions in the ligand. The leaving *tert*-butyl group is captured by a $Cl^-$ nucleophile, because 2-chloro-2-methyl-propane was detected in the reaction mixture. This retro-Friedel–Crafts reaction is one example of what is likely to be a general tendency to lose a *tert*-butyl group in some manner in calixarene and phenol derivatives [57]. Thus the use of a less acidic $TiCl_4(THF)_2$ as a precursor prevents the de-*tert*-butylation of the ligand, yielding the desired product. The X-ray analysis of $[\mathbf{11^{Me}}]\mathbf{TiCl}$ shows that it is a dimer bridged by the central aryloxides of the U-shape ligands, in which each titanium center has a distorted trigonal bipyramidal geometry. In $[\mathbf{11^{tBu}}]\mathbf{TiCl}$, the ligands adopt a highly twisted S-conformation and span two tetrahedral metal centers. The direct reaction of the phenol trimer with $Ti(OR)_4$ ($R = {}^t$Bu, $^i$Pr) afforded the dimers similar to $[\mathbf{11^{Me}}]\mathbf{TiCl}$ [58]. Complexes $[\mathbf{11^R}]\mathbf{TiCl}$ showed moderate activities for the polymerization of ethene if activated with MMAO [56].

These titanium complexes readily forms a bis-THF adduct, because of the Lewis acidity of the titanium center. The $[\mathbf{11^R}]$Ti moiety is robust towards reduction chemistry, and the reaction of $[\mathbf{11^{Me}}]\mathbf{TiCl}$ with 2 equiv. of potassium metal to afford a paramagnetic Ti(III)
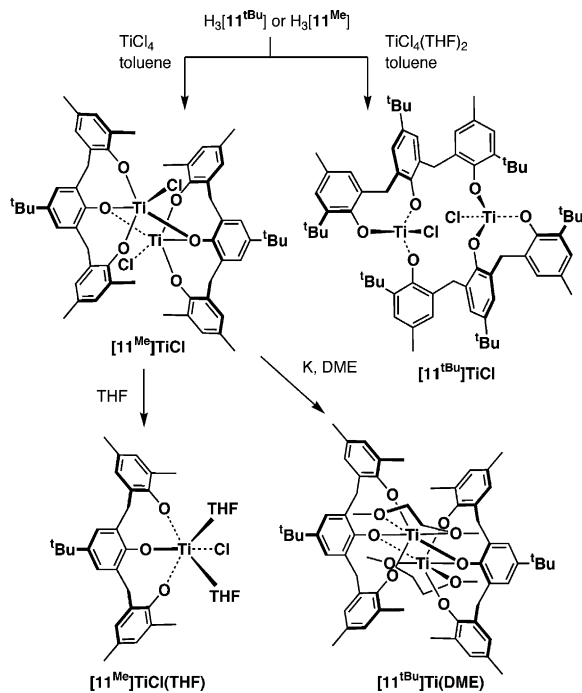
dimer with a long Ti–Ti distance of 3.113(1) Å ($\mu_{eff} = 0.90\ \mu_B$ per Ti atom) [55]. Treatment of $[\mathbf{11^{tBu}}]$-**TiCl** with $LiBHEt_3$ in toluene/THF produced another Ti(III) dimer, in which $LiBHEt_3$ acts as a hydride transfer reagent as well as a reductant (Scheme 23) [59]. A striking feature of the structure of $[\mathbf{11^{tBu}}]\mathbf{TiH}$ is the presence of the $[([\mathbf{11^{tBu}}]Ti)_2(\mu\text{-H})_3]^{3-}$ unit, which adopts a face-sharing bioctahedral geometry. From the measurement of the magnetic susceptibility (Evans method) as well as the valuable temperature $^1H$ NMR studies, the hydride-bridging dimer was found to be diamagnetic in solution. Additionally, the short Ti–Ti distance of 2.621(1) Å might be explained by the formation of a metal–metal $\sigma$ bond. In contrast, the zirconium complex was analogously treated with $LiBHEt_3$ to provide a Zr(IV) dimer, in which no reduction took place.

Like the $TiCl_4/H_3[\mathbf{9^{tBu}}]$ reaction system, treatment of $MCl_5$ (M = Nb, Ta) with $H_3[\mathbf{11^{tBu}}]$ resulted in the de-
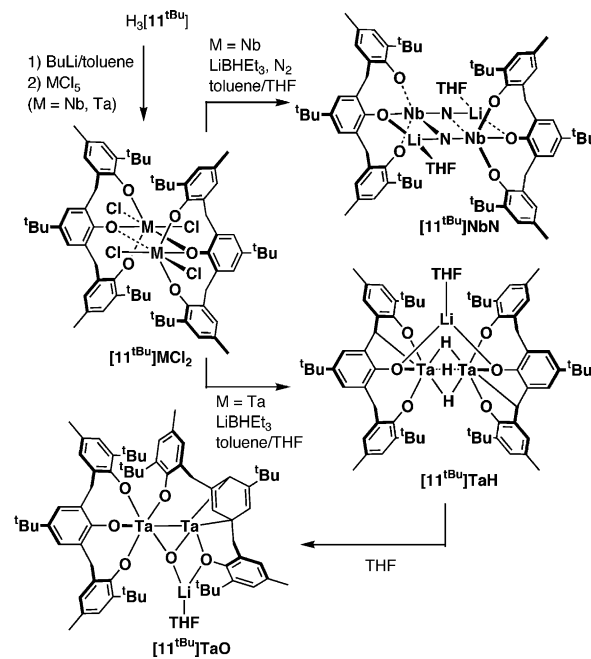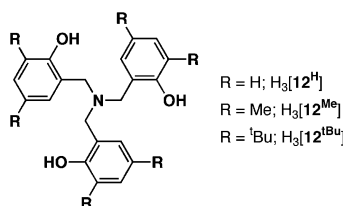


Scheme 23.



Scheme 22.



Scheme 24.

*tert*-butylation of the ligand [60]. The salt metathesis has proven to be efficient for the synthesis of **[11^tBu]MCl_2**. Lithiation of $H_3[\mathbf{11^{tBu}}]$ and subsequent reaction of NbCl_5 and TaCl_5 gave the corresponding chloride complexes **[11^tBu]MCl_2** (Scheme 24). The niobium complex was treated with LiBHEt_3 in toluene/THF under N_2 to produce the nitride-bridging dimer [61]. The $^{15}N$ NMR spectrum of the isotopically enriched compound, analogously prepared under an atmosphere of $^{15}N_2$, exhibits a single peak at $\delta$ 312. This unambiguously confirms that the bridging ligands of **[11^tBu]NbN** originate from dinitrogen.

In contrast to the niobium species capable of activating dinitrogen, the tantalum complex was found to undergo C–O cleavage of the $[\mathbf{11^{tBu}}]^{3-}$ ligand [62]. The analogous reaction of **[11^tBu]TaCl_2** with LiBHEt_3 gave the cyclometalated complex, in which intramolecular addition of a methylene CH bond to a Ta(III)–Ta(III) intermediate may take place. The NMR data show that the methylene CH activation process is reversible. The tantalum hydride complex is thermally unstable and gradually undergoes rearrangement, yielding the oxo-bridging dimer. The X-ray analysis shows that one tantalum is bounded to the deoxygenated $\eta^6$-phenyl ring. For the analogous complex containing a potassium cation, the C–O bond cleavage smoothly proceeded in the presence of 18-crown-6 to provide the dimer bridged by one oxo and two hydride ligands. This suggests that the counter cations play an important role in stabilizing the ditantalum hydride species.

The uranium complexes with the linearly linked aryl-oxide trimers have been reported [63]. The aryloxide trimers act as a bidentate diphenoxide-monophenol ligand or a trianionic tridentate ligand. In the latter case, the ligand facially coordinates to the uranium center in a U-conformation.

## 3.2. Tri(aryloxide)-amine tripod ligands

The replacement of the sidearm donor of the $[\mathbf{8E}]^{2-}$ ligand with one aryloxide unit leads to tripodal tetradentate tris(aryloxide) ligands, $[\mathbf{12^R}]^{3-}$ (Scheme 25). The titanium complexes **[12^R]Ti(OR′)** were straightforwardly prepared as shown in Scheme 26 [64–67]. The structures of these mono-ligand complexes can be described as a 3-bladed turbine of $C_3$ symmetry and are maintained in solution on the NMR time scale at ambient tempera-
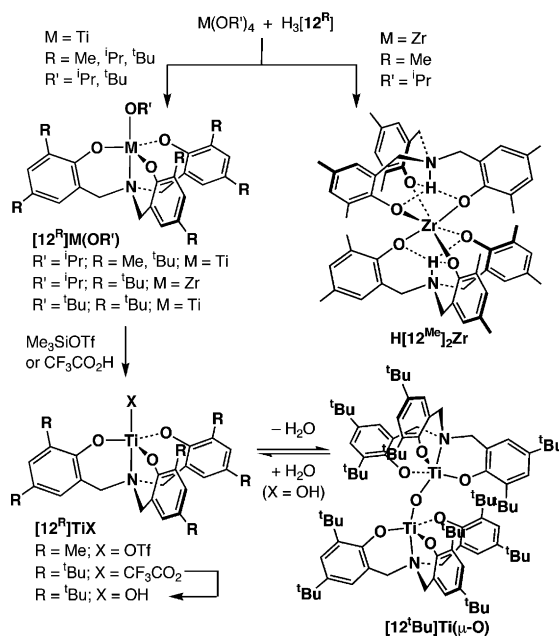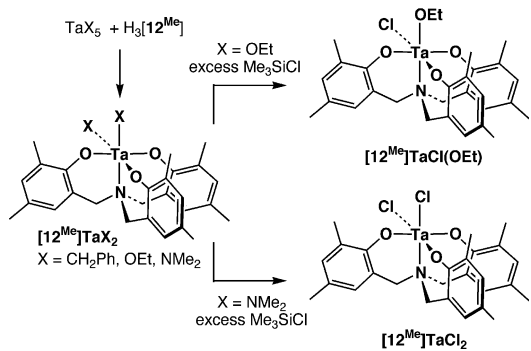


Scheme 26.

ture. High barriers to inversion between their enantiomers were observed [64,67b]. The apical alkoxide group can be readily substituted by more acidic reagent such as CF_3CO_2H and CF_3SO_3SiMe_3 [65a,66]. Remarkably, these titanium complexes are air- and moisture-stable. Therefore, attempts to prepare **[12^tBu]Ti(OH)** by the direct hydrolysis have been failure [66]. The hydroxide complex was prepared by treating the trifluoroacetate complex with aqueous NaOH, whereas the isolated hydroxide complex readily underwent alcoholysis to yield the corresponding alkoxide complex. In the absence of water, the hydroxide complex condenses to form the μ-oxo dimer.

On the other hand, treatment of $Zr(O^iPr)_4$ with $H_3[\mathbf{12^{Me}}]$ gave the bis-ligand complex, in which the amine nitrogen of the ligand was protonated to form the zwitterionic tri-aryloxide ligand [65b]. The X-ray analyses of **H[12^Me]_2Zr** reveal that the ammonium center of the $H[\mathbf{12^{Me}}]^{2-}$ ligand has significant hydrogen-bonding interactions with three aryloxide groups. The formation of this bis-ligand complex is attributable to the larger ionic radii of zirconium compared to titanium. Thus the sterically bulky $[\mathbf{12^{tBu}}]^{3-}$ ligand is required to afford the mono-ligand zirconium complexes.

Titanium complexes incorporating the $[\mathbf{12^R}]^{3-}$ ligand were tested for activity as a Lewis acid catalyst. The *iso*-propoxide complexes are found to be poor catalysts, while weaker metal–ligand coordination of the triflate relative to the *iso*-propoxide enhances activity for the formal aza-Diels–Alder reaction between imine and diene [65a]. Complexes **[12^R]Ti(OR′)** initiated the ring-open polymerization of *L*- and *rac*-lactide, producing isotactic and atactic polymers, respectively [65]. It is
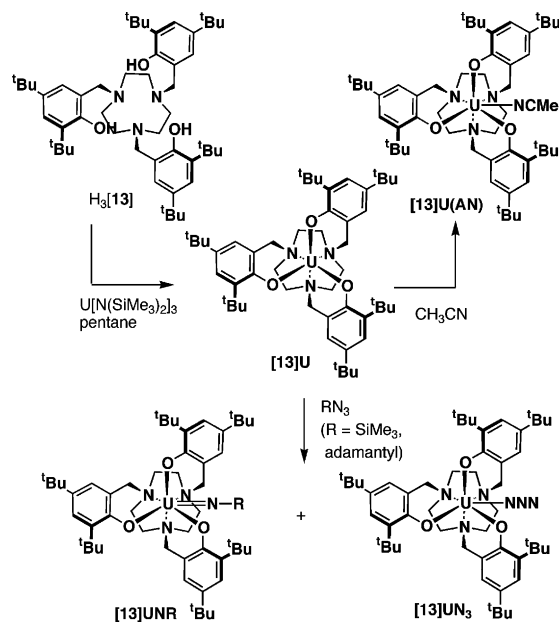


Scheme 25.

Scheme 27.

noteworthy that these Lewis acid catalysts containing the [12$^R$]Ti moiety are air- and moisture-stable.

Although difficulty has been reported in using salt metathesis to attach the [12$^{Me}$]$^{3-}$ ligand to tantalum, the direct reactions with Ta(OEt)$_5$, Ta(NEt$_2$)$_5$, and Ta(CH$_2$Ph)$_5$ have proven to be efficient for the synthesis of tantalum complexes (Scheme 27) [48a,68,69]. The ethoxide complex undergoes substitution with methanol to give the bis-methoxide complex [68]. However, only one of the ethoxide groups was chlorinated by treating with a large excess of Me$_3$SiCl, in which the remaining ethoxide ligand is *trans* to the amine group [69]. The dichloride complex is obtained along with the mono-chloride complex by the reaction of the amide complex with 10 equiv. of Me$_3$SiCl over four days. The structures of these complexes assume an octahedral geometry with $C_s$ symmetry. These tantalum alkoxido complexes show no activity in the ring-open polymerization of lactide, in contrast to the related $C_3$-symmetric titanium complexes [12$^R$]Ti(OR′) [68].

### 3.3. Triazacyclononane-derived tris(aryloxide) ligands

Another $C_3$ symmetric tri-aryloxide ligand system, which is based on the 1,4,7-triaza-cyclononane macrocyclic amine backbone, has been utilized to support uranium(III) complexes (Scheme 28). Structural investigations indicate that these ligand systems generate exclusively coordinatively saturated octahedral complexes with first-low transition metals [70], while the large uranium ion supported by the hexadentate [13]$^{3-}$ ligand could provide a platform for reactivity studies at the seventh axial position. Amine elimination using U[N(SiMe$_3$)$_2$]$_3$ gave the six-coordinate uranium(III) complex [71]. Since this complex is highly reactive, recrystallization from pentane and Et$_2$O or THF at room temperature resulted in formation of uranium(IV) complexes via ligand degradation and oxygen atom abstraction [71a]. When [13]U was carefully recrystallized from *n*-pentane containing trace amounts of alkanes (e.g., cyclohexane, cyclopentane, neohexane), X-ray analyses of crystals obtained reveal that one alk-



Scheme 28.

ane molecule occupies the axial position of the metal center with an η$^2$-H,C fashion (U–C distances, average 3.798 Å) [71b].

Complex [13]U also forms the acetonitrile adduct [71c]. Treatment of the uranium(III) complex with Me$_3$SiN$_3$ afforded the uranium(V) imide complex with evolution of N$_2$ and the uranium(IV) azide complex as a side product. When 1-adamantyl azide was used, the analogous reaction produced the corresponding imide complex exclusively. The DFT calculations show that [13]U(AN) and [13]UNSiMe$_3$ display significant π-bonding involving uranium f-orbitals and the axial acetonitrile ligand and the imide ligand, respectively. In contrast, the bonding in the azide complex is almost ionic in nature, exhibiting no π-interaction with the axial azide ligand.

## 4. Cyclic polyaryloxide ligands

### 4.1. Carixarenes

An important class of poly-phenol is calix[*n*]arenes, in which *n* represents the number of phenol units. In particular, metal complexes of calix[4]arene H$_4$[14], which provide an oxo-quasiplanar ligand environment, have received much attention due to their potential as models for organometallic fragments grafted onto metal-oxo-surfaces. Since metal calixarene complexes have been amply covered in the review literature [72], they are mentioned only briefly in this article. Particularly noteworthy is the activation of small molecules in low-valent complexes supported by calix[4]arene. A set of oxygen

donor atoms provides both σ and π donation to a metal center, resulting in very reactive low-valent metalla-calix[4]arene complexes.

The direct reaction of NbCl₅ with H₄[**14**] afforded the chloride complex (Scheme 29). Reduction of [**14**]NbCl with 4 equiv. of sodium under Ar gave the diamagnetic niobium(III) dimer. In the absence of a suitable substrate, the reactive fragment collapses to form the dimeric species, which temporarily stores four electrons in the Nb–Nb double bond [Nb–Nb, 2.659(1) Å] [73]. This dimer was found to perform the four-electron reduction of dinitrogen, resulting in formation of the linear diazenide complex [Nb–N, 1.747(12) Å; N–N, 1.390(17) Å]. Addition of two electrons to [**14**]NbN₂ using sodium led to the complete cleavage of N–N bond. The core structure of the resulting nitride complex is similar to that observed in the related triaryloxide complex [**11^tBu**]NbN (vide supra).

The stepwise reduction of carbon monoxide was carried out by using the niobium calix[4]arene complex [74].
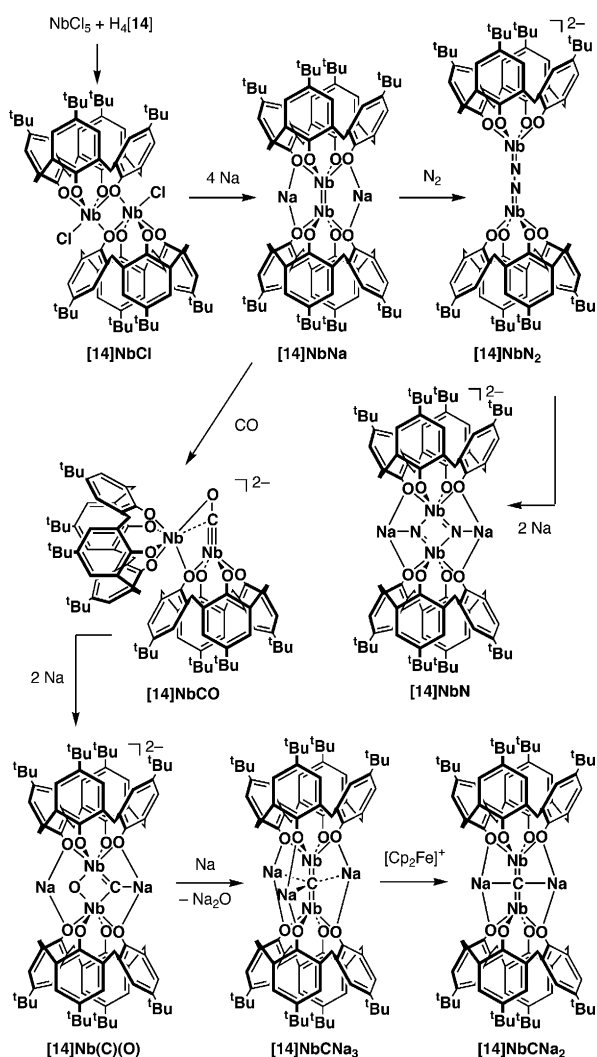
Treatment of the Nb(III)–Nb(III) dimer with carbon monoxide at −40 °C gave the oxyalkylidyne species, in which the geometrical parameters of the Nb₂CO unit proves the four-electron reduction of carbon monoxide. The resulting alkylidyne complex accepts two additional electrons from sodium, facilitating complete C–O bond cleavage and rearrangement to a Nb₂(μ-carbide)(μ-oxo) core. The X-ray analysis shows the bent bonding mode of a carbide unit bridging two niobium metals. Further one-electron reduction of the bent-carbide complex with sodium results in formation of the linear-carbide complex along with the loss of μ-oxo ligand. This paramagnetic Nb(IV)–Nb(V) complex was oxidized with 1 equiv. of [Cp₂Fe][BPh₄] to produce the diamagnetic carbide species, which exhibits a resonance due to the bridging carbide at 257 ppm in its ¹³C NMR spectrum.

### 4.2. Thiacarixarenes

The methylene groups of calix[*n*]arenes are replaced by the thioether sulfur atoms, yielding thiacalix[*n*]arenes. These compounds are also regarded as the macrocyclic analogues of the [**4S**]²⁻ ligand. The replacement of the methylene bridge by sulfur causes the macrocycle expansion of ca. 0.5 Å of the distance between two adjacent bridging atoms, allowing the incorporation of the large metal ion in the ligand cavity. For example, thiacalix[4]arene was shown to be a selective ligand for the uranyl ion [75]. The exploration of coordination and organometallic chemistry of this molecule has been initiated by the recent discovery of the high-yield synthesis of thiacalix[4]arene, H₄[**15**] [76].

Treatment of H₄[**15**] with an excess of TiCl₄ gave the mixture of cone- and 1,2-alternate-isomers containing two titanium metals, and the [**15**]⁴⁻ moiety acts as a binulceating ligand (Scheme 30) [77]. This contrasts with the cavity size of calix[4]arene, which is too small to accommodate two titanium metal [78]. Since the 1,2-alternate isomer is sparingly insoluble in the solvent, they could be separated. The solid-state structure of the cone-isomer shows that the ligand is facially coordinated to each titanium through two aryloxides and one thioether. This coordination mode is similar to those found in metal complexes having the [**4S**]²⁻ ligand. Octahedral coordination spheres are completed by one adventitious H₂O bridging molecule. The cone-complex showed high catalytic activity in the Mukaiyama–Aldol reaction of aromatic aldehydes with silyl enol ethers, because the close proximity of two metal centers in the cone conformation allows cooperative binding of a substrate.

The [**15**]⁴⁻ ligand also allows the preparations of heterobimetallic complexes. Treatment of CpTiCl₃ with H₄[**15**] in the presence of NEt₃ afforded **H[15]TiCp** [79]. This titanium complex was found to react with the molybdenum dinitrogen complex to yield the TiMo



Scheme 29.

Scheme 30.
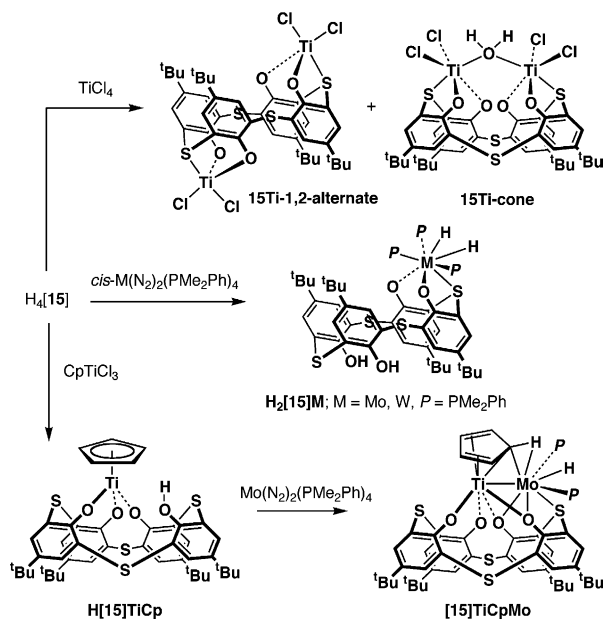
heterobimetallic complex, in which the Cp ligand is $\eta^5$-bonded to Ti and $\eta^2$-bonded to Mo. On the other hand, the reaction of $M(N_2)_2(PMe_2Ph)_4$ (M = Mo, W) with $H_4[\mathbf{15}]$ cleanly proceeded to give the corresponding dihydride complexes with the loss of the coordinated dinitrogen molecules. During the reaction, oxidation from M(0) to M(IV) took place. The X-ray analysis shows that the ligand is coordinated to the metal center as a bis(aryloxide)-thioether tridentate ligand in a facial fashion. The 1,2-alternate and partial cone conformations of the ligand were found to exist in the solid-state, indicating that the $H_2[\mathbf{15}]^{2-}$ ligand are conformationally fluxional.

## 5. Conclusions and outlook

In this review, it has been shown that aryloxide-based multidentate ligands can coordinate a variety of early transition metals and f-element metals in the strained modes. This ligand system hold the potential for controlling the reactivity and the nuclearity of the metal complexes through adjustment of the steric and electronic properties of the substituents on the phenyl rings and the bridging units between the aryloxide moieties. This strategy has found its way into the systematic design of olefin polymerization catalysts. In addition to the strained geometry forced by this ligand system, the combination of aryloxide groups with different types of donor functionalities will lead the way to novel patterns of structure and reactivity [80]. Thus, it can be emphasized that aryloxide-based multidentates ligands offer a pathway to a rich organometallic and coordina-

tion chemistry, which includes the exploration of the catalytic and stoichiometric reactivity.

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