Highlight Review

Tridentate Aryloxide Ligands: New Supporting Ligands in Coordination Chemistry of Early Transition Metals

Tsukasa Matsuo and Hiroyuki Kawaguchi*

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Abstract

The use of covalently linked multidentate ligands is a very useful concept in coordination and organometallic chemistry. This article gives an account of the syntheses and structures of metal complexes supported by linear-linked aryloxide trimer ligands, in which aryloxide units are connected at *ortho* positions through methylene linkers.

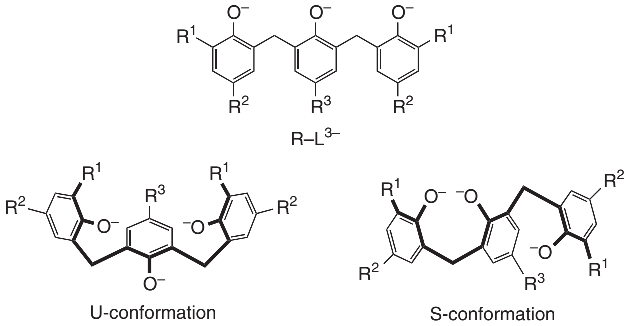
◆ Introduction

Development of ligands that play supporting roles in coordination and organometallic chemistry has been the subject of intense interest for many years. Studies of metal aryloxide chemistry have shown that aryloxide ligands can promote various important organic/inorganic reactions at metal centers.[1] Therefore, aryloxide ligands complement the well-studied cyclopentadienyl-based systems, with the major difference being the greater reactivity of the aryloxide complexes due to their relatively higher unsaturation and lower coordination numbers for a $(ArO)_nM$ fragment. However, coordinatively unsaturated metal complexes undergo facile ligand redistribution reactions, which are occasionally a severe obstacle to synthetic efforts.

One of strategies for overcoming this problem is the use of covalently linked ancillary ligands, thereby limiting ligand mobility and leaving little possibility to reorganize the molecule. This feature has led to the isolation and structural characterization of a number of metal complexes that are difficult to obtain with aryloxide monodentate ligands. In this context, we set out to investigate linear-linked aryloxide trimers $R\text{–}L^{3-}$ as new ancillary ligands, in which aryloxide units are connected at *ortho* positions through methylene linkers (Scheme 1). Although calix[*n*]arenes[2] and 2,2′-methylene-bisaryloxide derivatives[3] constitute an important class of multidentate ligands, there are few examples of metal complexes with linear-linked aryloxide trimers in coordination chemistry. This is surprising because the preparation of linear phenol trimers was reported by Koebner in 1933.[4]

In addition to preventing ligand redistribution, the use of $R\text{–}L^{3-}$ has the following three advantages. First, linear-linked aryloxide trimers exhibit the flexibility of their binding modes. For instance, they can adopt either an S- or a U-conformation, which is determined by a delicate balance of steric and/or electronic factors of the R–L ligands and incoming substrates. The coordination in an S-conformation often stabilizes the dimeric species, whereas a U-conformation of the ligand is reminiscent of a cone conformation of calix[4]arene. Secondly, compared to the related calix[4]arene system, there is the opportunity for coordinative unsaturation. Third, steric bulk can be manipulated through varying substituents (R^1) at *ortho* positions of the outer aryloxides.

The focus of this short review is to give a brief overview of the coordination chemistry of acyclic aryloxide tridentate ligands, paying particular attention to the structures and reactivity of their metal complexes.



Scheme 1.

◆ Ligand Synthesis

Syntheses of methylene-linked polyphenol derivatives have been well developed. Linear-linked phenol trimers $H_3(R\text{–}L)$ are readily prepared from commercially available starting materials, using a procedure modified from the literature (Scheme 2).[5] We routinely prepare $H_3(R\text{–}L)$ in a 40 g-scale using this methodology. All linear-linked phenol trimers listed in Scheme 2 can be obtained as colorless crystals.

The course and outcome of the reaction chemistry are dependent on the identity of the *ortho* substituents (R^1) of the outer aryloxide rings in the R–L ligand (as described below). The solubility properties of their complexes can be tuned by the choice of *para* substituents of aryloxide units without large changes in the electronic features of the metal/donor atom chemistry. To date, in addition to the chemistry described here, the main synthetic uses of phenol trimers have been directed towards the preparation of macrocyclic compounds such as calixarenes.[6] Recently, independent from us, three groups demonstrated the synthesis of compounds having linear linked aryloxide trimers for lithium, sodium, aluminum, titanium, and uranium.[7–9]

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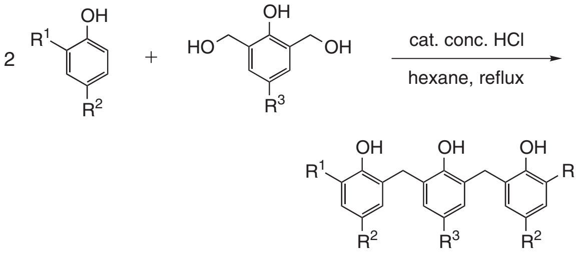
*Dr. Tsukasa Matsuo, Prof. Hiroyuki Kawaguchi**
Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan
E-mail: hkawa@ims.ac.jp



$R^1 = R^2 = R^3 = Me$; $H_3(Me–L^{Me})$ 35%
$R^1 = R^2 = Me$, $R^3 = t$-Bu; $H_3(Me–L)$ 55%
$R^1 = t$-Bu, $R^2 = R^3 = Me$; H_3 (t-Bu–L^{Me}) 52%
$R^1 = R^3 = t$-Bu, $R^2 = Me$; H_3(t-Bu–L) 74%
$R^1 = R^2 = t$-Bu, $R^3 = Me$; H_3(t-Bu_4–L) 60%
$R^1 = R^2 = R^3 = t$-Bu; H_3(t-Bu–$L^{t\text{-}Bu}$) 56%

Scheme 2.

◆ Lithium and Aluminum Complexes

Since the lithium compounds are expected to be a useful synthon for delivery of the R–L^{3-} anion to other metals, we examined the reactions between linear-linked phenol trimers and n-BuLi. The phenol trimers H_3(R–L) are found to be deprotonated in a stepwise manner. For example, deprotonation of H_3(R–L) with 1 equiv. of n-BuLi resulted in the formation of monolithium compounds shown in Figure 1.[10] The selective mono-deprotonation of the inner phenol moiety may be ascribed to the formation of intramolecular hydrogen bonds between the inner aryloxide oxygen atom and two outer phenolic oxygen atoms.

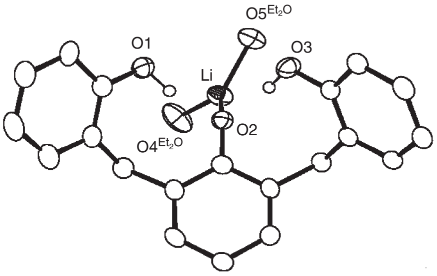


Figure 1. Structure of LiH_2(t-Bu–L)$(Et_2O)_2$ (**1**). Methyl and *tert*-butyl groups of t-Bu–L^{3-} ligand and the Et_2O groups (except for the oxygen atoms) have been omitted for clarity.

When the amount of n-BuLi was increased to 3 equiv., the trilithium salts of R–L^{3-} were obtained. The trilithium salts have been crystallographically characterized by Scott[7] and us.[10] When the compounds are recrystallized from Et_2O, they exist as a dimer in the solid state (Figure 2).[10] The two halves of dimer are related by a center of symmetry, and each t-Bu–L ligand assumes a U-conformation. The molecule contains the fused open-cubane Li_6O_6 core, in which the coordination of the Et_2O molecules to lithium [Li(1)] requires that one edge of each cubane is open. The lithium cations are found in three distinct coordination environments. The ^{7}Li NMR spectrum of $[Li_3(t\text{-}Bu–L)(Et_2O)]_2$ (**2**) in benzene-d_6 shows three signals with the same intensity at 1.31, 0.47, and −2.82 ppm, suggesting that the crystal structure is retained in solution. The upfield resonance is due to anisotropy shielding effects induced by the close proximity of Li1 to the center of the phenyl rings of the ligand.

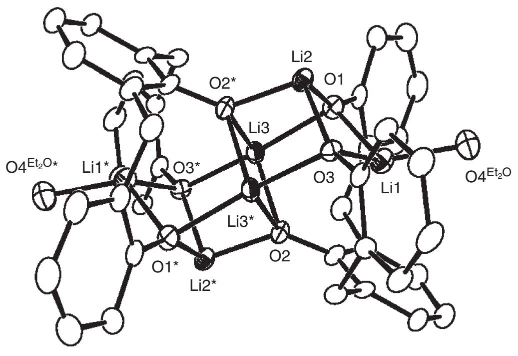
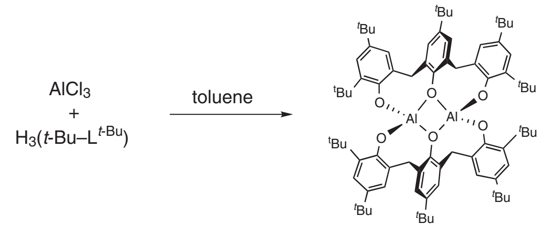


Figure 2. Structure of $[Li_3(t\text{-}Bu–L)(Et_2O)]_2$ (**2**). Methyl and *tert*-butyl groups of t-Bu–L^{3-} ligands and the Et_2O groups (except for the oxygen atoms) have been omitted for clarity.

The synthesis of the aluminum species **3** was reported by Hofmeister and coworkers (Scheme 3). A structure determination shows that the linked aryloxide ligands are coordinated to two tetrahedral aluminum centers in an S-shape conformation, in which the central aryloxide group of the ligand bridges two metals and each terminal aryloxide group is coordinated to a different metal center.



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Scheme 3.

◆ Titanium and Zirconium Complexes

Aryloxides complexes of early transition metals are typically synthesized by reactions of metal chlorides with either ArOH, ArOM (M = Li, Na, K), or $ArOSiMe_3$. In this study, we began to examine the reactions between $TiCl_4$ and H_3(R–L) (Scheme 4). Reaction of $TiCl_4$ with H_3(Me–L) in refluxing toluene gave a Ti(IV) dimer **4** as red crystals in high yield.[11] Each titanium center has a distorted trigonal bipyramidal geometry bridged by the central aryloxides of the Me–L^{3-} ligands, and the Me–L ligands assume a U-conformation.

When H_3(t-Bu–L) was used instead of H_3(Me–L), the analogous reaction produced an inseparable mixture of **5** and ill-defined compound(s). The problem arose from partial loss of the t-Bu groups at the *ortho* positions in the t-Bu–L ligand. The leaving t-Bu group is captured by a Cl^- nucleophile, because 2-chloro-2-methylpropane 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 t-Bu group in some manner in calixarene and phenol derivatives.[12] The retro-Friedel–Crafts reaction may be promoted by the acidic Ti(IV) metal center. Thus we feel that a less acidic $TiCl_4(THF)_2$ prevents the de-*tert*-butylation of the ligand. This proved to be the case, as shown in Scheme 4. In contrast to the Me–L ligands in **4**, the t-Bu–L ligands adopt a highly twisted S-conformation and span

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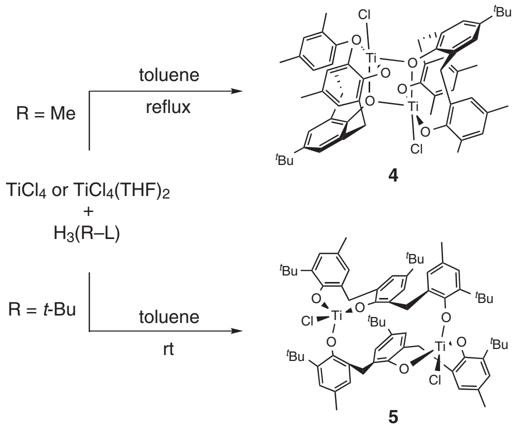
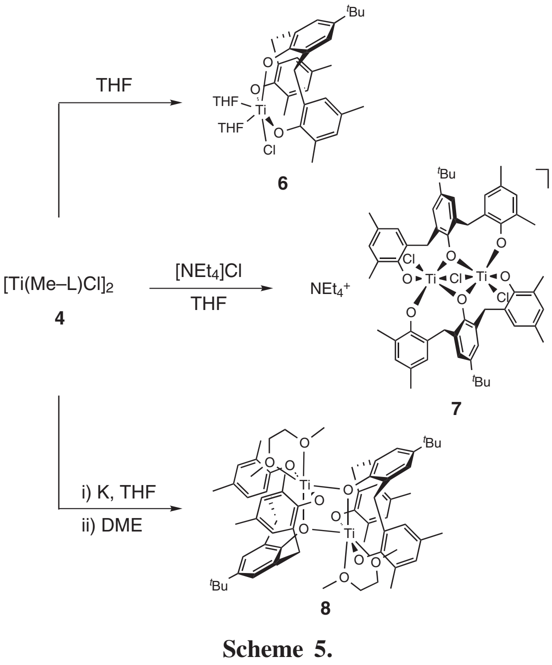
two tetrahedral metal centers.[10] Hofmeister and coworkers reported that the related complexes $[\mathrm{Ti}(t\text{-Bu–L}^{t\text{-Bu}})(\mathrm{OR})]_2$ (R = *i*-Pr, *t*-Bu) was prepared by the reaction of $\mathrm{Ti(OR)_4}$ with $\mathrm{H_3}(t\text{-Bu–L}^{t\text{-Bu}})$.[8]



Scheme 4.

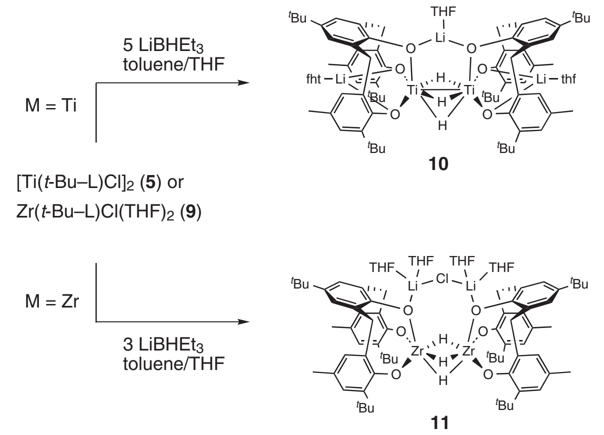
Complex **4** readily adds external ligands because of the Lewis acidity of the titanium center (Scheme 5).[11] For example, dissolving **4** in THF resulted in the formation of a monomer **6**. On the other hand, treatment of **4** with $\mathrm{NEt_4Cl}$ in THF produced a dimer **7** with two distorted octahedral metal centers connected through facial bridging. To examine the robustness of Ti(Me–L) moiety towards reduction chemistry, we carried out the reaction of **4** with 2 equiv. of potassium metal to afford a Ti(III) dimer **8** as apple-green crystals in high yield. The long Ti–Ti distance of 3.113(1) Å rules out any possible metal–metal bonding interaction, which is consistent with the paramagnetic nature of **8** ($\mu_{\mathrm{eff}} = 0.90\ \mu_{\mathrm{B}}$ per Ti atom).

Owing to the flexibility of the binding modes of $\mathrm{R–L^{3-}}$, titanium complexes described above may act model systems to study how substrate binding changes the coordination mode of the linear-linked aryloxide trimer core. An adaptation of the coordination mode of the Me–L ligand can be examined by comparing the structures of **4**, **6**, **7**, and **8**. For **6**, the ligand facially coordinates to the octahedral metal center in the U-conformation, in which the O–Ti–O angle involving the outer aryloxides [100.2(1)°] is smaller than those of the parent dimer **4** (av. 114°). In contrast to the facial mode observed in **4** and **6**, the ligand of **8** is coordinated in a meridional manner and assumes a U-conformation, and the corresponding O–Ti–O angle is opened up [167.3(1)°]. In the case of **7**, the Me–L ligands span two octahedral titanium centers in an S-conformation in order to accommodate one external chloride anion.



Scheme 5.

With the aim of preparing non-metallocene hydrides of group 4 metals, we carried out the reaction of the *t*-Bu–L complexes **5** and **9** with $\mathrm{LiBHEt_3}$.[13] Treatment of **5** with $\mathrm{LiBHEt_3}$ in toluene/THF produced the triple-hydrogen-bridged dimer **10** as brown crystals, in which the metal center was reduced from Ti(IV) to Ti(III) (Scheme 6). During the reaction, $\mathrm{LiBHEt_3}$ acts as a hydride transfer reagent as well as a reductant. A striking feature of the structure of **10** is the presence of the $[\{\mathrm{Ti}(t\text{-Bu–L})\}_2(\mu\text{-H})_3]^{3-}$ dimer, which adopts a face-sharing bioctahedral geometry (Figure 3). The three lithiums are not innocent counterions but are bound strongly to the aryloxides. The structure of **10** observed in the solid state is persistent in solution, and the ^{7}Li NMR spectrum in toluene-d_8 consists of two singlets at 0.42 and −2.65 ppm in a 1:2 ratio. From the measurement of the magnetic susceptibility (Evans method) as well as the valuable temperature ^{1}H NMR studies, **10** was found to be diamagnetic in solution. When the diamagnetism of **10** is taken into account, the short Ti–Ti distance of 2.621(1) Å might be explained by the formation of a metal–metal σ bond.



Scheme 6.

On the other hand, the analogous reaction of the zirconium complex **9** with $\mathrm{LiBHEt_3}$ afforded colorless crystals of **11**, in which the Zr(IV) oxidation state is retained. The molecule contains the triple-hydrogen-bridged dinuclear fragment, which is comparable to that found in **10**. For **11**, one $[\mathrm{Li–Cl–Li}]^+$ moiety spans the two central aryloxides of the ligands. The facile synthesis of **10** and **11** provides us with a good opportunity to examine differences in the reactivity between d^1–d^1 and d^0–d^0 metal systems and to compare this reactivity with that of complexes bearing cyclopentadienyl ligands.

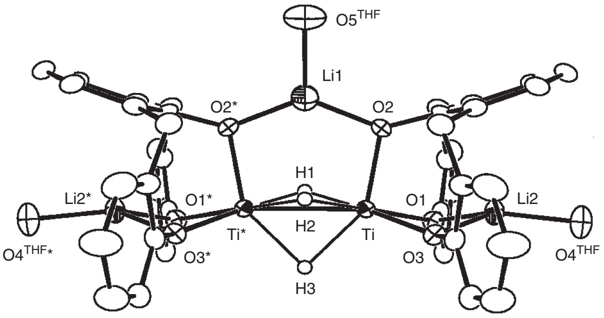
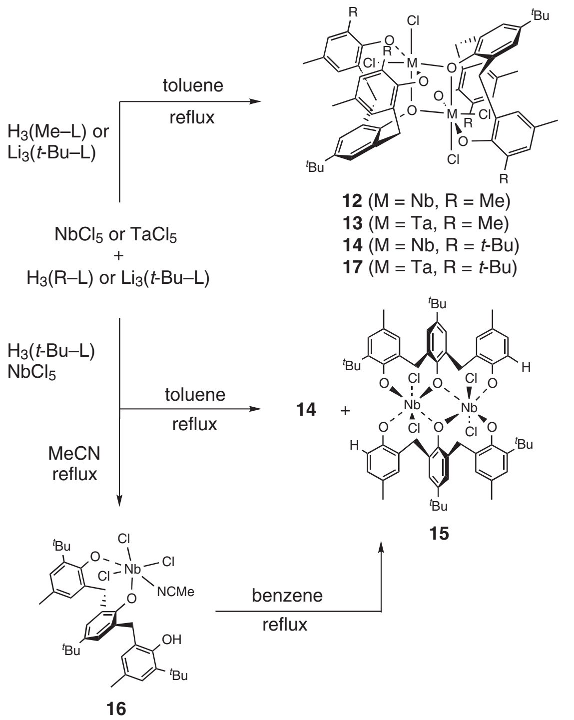


Figure 3. Structure of $[Li_3(THF)_3\{Ti(t\text{-Bu–L})\}_2(\mu\text{-H})_3]$ (**10**). Methyl and *tert*-butyl groups of t-Bu–L^{3-} ligands and the THF groups (except for the oxygen atoms) have been omitted for clarity.

◆ Niobium and Tantalum Complexes

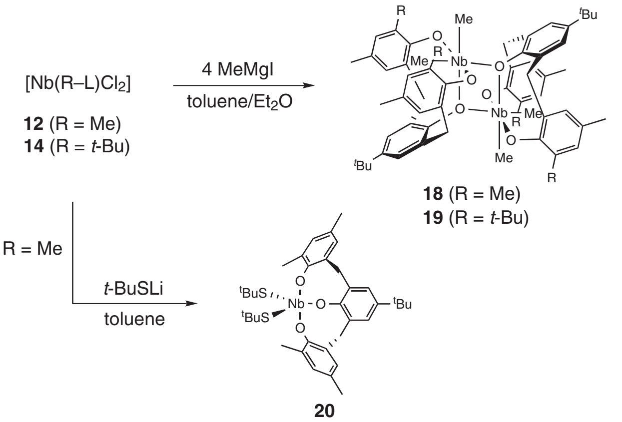


Scheme 7.

Syntheses of a series of niobium and tantalum chloride complexes derived from linear-linked aryloxide trimers are summarized in Scheme 7.[14] Treatment of MCl_5 (M = Nb, Ta) with H_3(Me–L) in toluene gave the corresponding chloride complexes **12** and **13**. Like the de-*tert*-butylation observed in titanium complexes, the reaction of $NbCl_5$ with H_3(t-Bu–L) in toluene resulted in a mixture of **14** and **15**. When the $NbCl_5/H_3$(t-Bu–L) reaction was carried out in CH_3CN, **16** was isolated as dark red crystals. As expected, the retro-Friedel–Crafts reaction was inhibited by the coordination of acetonitrile. However, once isolated, **16** is found to be labile in solution. Upon heating a benzene-d_6 solution of **16** at 80 °C in sealed tube, we noticed the formation of **14** and **15** in a 1:4 ratio according to the ^1H NMR spectra.

The elimination of HCl as a byproduct from the $NbCl_5/H_3$(t-Bu–L) reaction may cause the de-*tert*-butylation of the ligand in the presence of the Nb(V) Lewis acid, so we have sought an alternative synthetic method for **14** and the tantalum congener **17**. For our purpose, we examined the reactions of MCl_5 with solvent-free Li_3(t-Bu–L) in toluene under reflux. Multigram quantities of the t-Bu–L derivatives **14** and **17** were prepared in moderate yields through this metathesis.

The chloride complexes **12**–**14** and **17** proved to be versatile precursors to organometallic and coordination complexes via halide displacement reactions with MeMgI, t-BuSLi, and $LiBHEt_3$ as shown in Scheme 8. Addition of MeMgI in Et_2O to **12** and **14** in toluene afforded the methyl derivatives **18** and **19** as yellow crystals. The formation of the methyl complexes was found to be sensitive to the alkylating reagent, as the analogous reactions with methyllithium resulted in a mixture of **18** (or **19**) and the corresponding trilithium salt of R–L^{3-} (**2**). Alkylation of **16** with 3 equiv. of MeMgI provided an alternative route to the methyl complex **19**.



Scheme 8.

Treatment of **12** with t-BuSLi in toluene at 60 °C gave **20** as orange crystals in high yield. Although attempts to prepare mixed thiolate/alkoxide complexes frequently result in complicated mixtures, **20** shows no sign of ligand redistribution reactions. In contrast to the dimeric structures of **12** and **18**, the structural analysis confirms the monomeric nature of **20** and the coordination geometry of the complex is best described as a trigonal bipyramidal. The ancillary Me–L ligand assumes an S-shaped conformation and is bound in a meridional fashion with the outer aryloxide donors occupying axial positions. Solution NMR data show that its structure, although fluxional, is maintained in solution.

The Me–L ligand also serves to stabilize the Nb(III) center. Reaction of **12** with $LiBHEt_3$ in THF afforded **21** as green crystals in good yield.[15] The molecule contains a $[Nb(\text{Me–L})(THF)]_2(\mu\text{–Cl})(\mu\text{–H})^{2-}$ core, in which each Nb atom possesses an octahedral geometry and the two Me–L ligands are arranged in a U-conformation (Figure 4). This dimeric unit carries four lithiums coordinating at aryloxides and two chlorine atoms bridging three lithiums. Taking into account the observed diamagnetism of **21**, the short Nb–Nb distance of 2.647(1) Å suggests the presence of the Nb–Nb double bond.

The use of t-Bu–L^{3-} instead of Me–L^{3-} introduced a significant modification in the reactivity pattern of niobium complexes

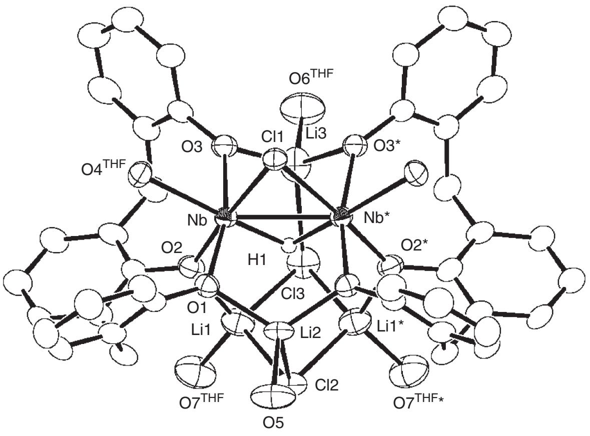
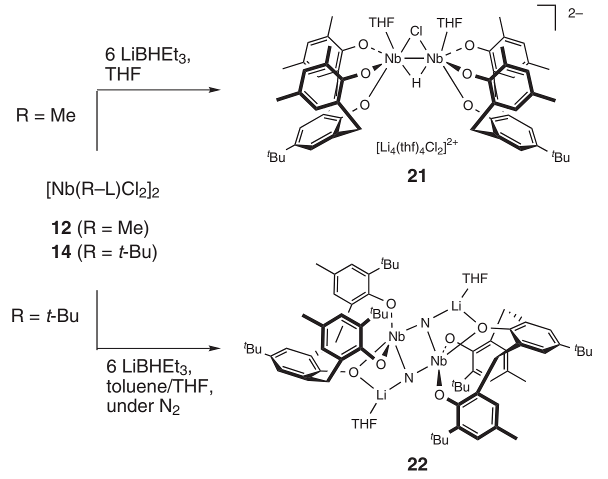


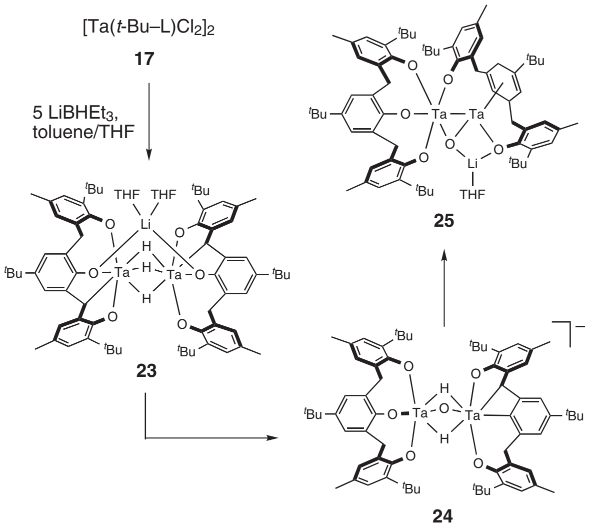
Figure 4. Structure of $[\{Li_4Cl_2(THF)_4\}\{Nb_2(Me–L)_2(\mu\text{-}Cl)(\mu\text{-}H)(THF)_2\}$ (**21**). Methyl and *tert*-butyl groups of Me–L^{3-} ligands and the THF groups (except for the oxygen atoms) have been omitted for clarity.

(Scheme 9). The analogous reaction of **14** with $LiBHEt_3$ in toluene/THF under N_2 produced the nitride compound **22**. The ^{15}N NMR spectrum of the isotopically enriched compound **22**-^{15}N, analogously prepared under an atmosphere of $^{15}N_2$, exhibits a single peak at δ 312. This unambiguously confirms that the bridging ligands of **22** originate from dinitrogen. Coupled with the isolation of **21**, the formation of **22** presumably proceeds via a $Nb(III)_2(\mu\text{-}H)_2$ dimer. This intermediate could bind and cleave N_2 concomitant with the reductive elimination of H_2 to produce **22**.[16]

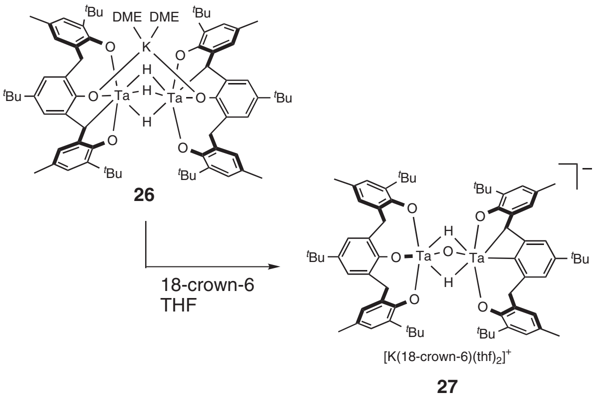


Scheme 9.

In contrast to the niobium species capable of activating dinitrogen, the tantalum complex undergoes C–O cleavage of the aryloxide group (Scheme 10).[17] Treatment of **17** with $LiBHEt_3$ in toluene/THF gave the cyclometalated complex **23** as yellow crystals, in which intramolecular addition of a methylene CH bond to a Ta(III)–Ta(III) intermediate may take place. The NMR data of **23** show that the methylene CH activation process is reversible, and thus **23** could provide a masked form of a low-valent tantalum dimer. Complex **23** is thermally unstable and gradually undergoes rearrangement. The first step is likely the migration of one hydride to the methine carbon of the *bit-t*-Bu–L ligand, giving a dihydride Ta(IV)–Ta(IV) intermediate. Subsequent C–O scission occurs across the metal–metal bond, in which two electrons stored in metal-metal bonding is used to yield an oxo-dihydride dimer **24**. The final formation of **25** requires the migration of two hydrides to a methine and an aryl carbon, respectively. The overall transformation implies an internal redox process and dose not require electrons to be added to or removed from **23**.



Scheme 10.

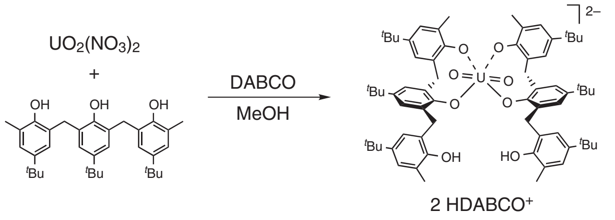


Scheme 11.

Isolation of **23** as a lithium salt and its transformation into **25** prompted us to explore the effect of other alkali cations. A similar reaction with $KBHEt_3$ afforded **26**, in which the potassium was incorporated as a counter cation. Treatment of **26** with 18-crown-6 in THF produced light yellow crystals of **27** (Scheme 11). Like **25**, the solid structure of **27** shows the μ-oxo ditantalum moiety associated with C–O bond cleavage of the ligand. One hydride has migrated back to the methine carbon, restoring the tridentate *t*-Bu–L ligand bound to one tantalum center. The two other hydrides remain intact and bridge the Ta–Ta unit. This conversion indicates that the counter cations play an important role in stabilizing the ditantalum hydride species, **23** and **26**.

Uranium Complexes

The reactions shown in Schemes 12 and 13 were employed in the preparation of uranyl and uranium(IV) complexes with linear-linked phenol trimers. In **28**, the phenol trimer acts as a bidentate diphenoxide-monophenol ligand, and one outer phenol group is not deprotonated. On the other hand, the structure of **29** shows that the trimer is facially coordinated to the uranium center in a U-conformation.



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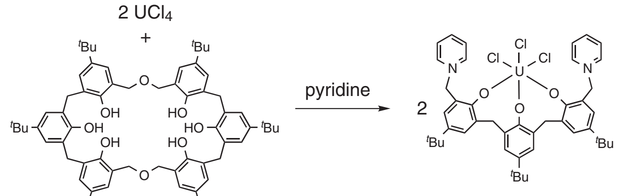
Scheme 12.



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Scheme 13.

Summary and Outlook

This short review has shown the ability of the linearly linked aryloxide trimer moiety to support novel coordination and organometallic chemistry with early transition metals. The flexible nature of the R–L ligand is revealed by the formation of U- and S-shaped compounds. The coordination mode of aryloxide tridentate ligands is determined by steric repulsion between the R–L core and incoming ligands as well as electronic interactions of both via the metal center. The exploration of the reactivity of many of complexes synthesized so far was started only recently. Extending this work to lanthanides and late transition metals may lead to some interesting new chemistry.

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