

Complexes of tantalum with triaryloxides: Ligand and solvent effects on formation of hydride derivatives

Hiroyuki Kawaguchi *, Tsukasa Matsuo

Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444-8787, Japan

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Abstract

A family of tantalum compounds supported by the triaryloxide $[R-L]^{3-}$ ligands are reported [$H_3(R-L) = 2,6$ -bis(4-methyl-6-*R*-salicyl)-4-*tert*-butylphenol, where $R = Me$ or tBu]. The reaction of $H_3[Me-L]$ with $TaCl_5$ in toluene gave $[(Me-L)TaCl_2]_2$ (**1**). The [$tBu-L$] analogue $[(tBu-L)TaCl_2]_2$ (**2**) was synthesized via treatment of $TaCl_5$ with $Li_3[tBu-L]$. A THF solution of $LiBHET_3$ was added to **1** in toluene to provide $[(Me-L)TaCl(THF)]_2$ (**3**), while treatment of **2** with 2 equiv of $LiBHET_3$ or potassium in toluene followed by recrystallization from DME resulted in formation of $[M(DME)_3][\{(tBu-L)TaCl\}_2(\mu-Cl)]$ [$M = Li$ (**4a**), K (**4b**)]. When the amount of $MBHET_3$ ($M = Li, Na, K$) was increased to 5 equiv, the analogous reactions in toluene afforded $[\{(bit-tBu-L)Ta\}_2(\mu-H)_3M]$ [$M = Li(THF)_2$ (**5a**), $Na(DME)_2$ (**5b**), $K(DME)_2$ (**5c**)]. During the course of the reaction, the methylene CH activation of the ligand took place. Dissolution of **5a** in DME produced $[\{(bit-tBu-L)Ta\}_2(\mu-H)_3Li(DME)_2]$ (**6**), indicating that the coordinated THF molecules are labile. When the $2/LiBHET_3$ reaction was carried out in THF, the ring opening of THF occurred to yield $[(tBu-L)Ta(OBu^t)_2]_2$ (**7**) along with a trace amount of $[Li(THF)_4][\{(tBu-L)TaCl\}_2(\mu-OBu^t)]$ (**8**). Treatment of **2** with potassium hydride in DME yielded $[\{(tBu-L)TaCl_2K(DME)_2\}_2(\mu-OCH_2CH_2O)]$ (**9**), in which the ethane-1,2-diolate ligand arose from partial C–O bond rupture of DME. The X-ray crystal structures of **2**, **3**, **4**, **5a**, **6**, **7**, and **9** are described.

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Keywords: Tantalum; Aryloxide; Hydride; Multidentate ligand; C–O bond cleavage

1. Introduction

Multidentate ligands play an important role in organometallic and coordination chemistry, because of enhancing the stability of complexes and enforcing constrained coordination environments in comparison to their analogues containing monodentate ligands [1]. As part of an ongoing research project in metal complexes capable of activating small molecules, we have been exploring the chemistry of complexes supported by aryloxide-based multidentate ligands [2–5]. We are especially attracted by the tridentate, trianionic $[R-L]^{3-}$ triaryloxide ligands in which three aryloxide rings are

linearly joined in the *ortho* position by the methylene groups [$H_3(R-L) = 2,6$ -bis(4-methyl-6-*R*-salicyl)-4-*tert*-butylphenol, where $R = Me$ or tBu]. This ligand system is closely related to calixarene derivatives. Upon coordination to a metal center, the tridentate-ligand framework assumes a U-shaped conformation, which is reminiscent of the cone conformation of calix[4]arene. A significant advantage of the $[R-L]^{3-}$ ligand system is the ability to tailor steric properties to satisfy specific requirements via derivatization of the *ortho* substituents, enabling a degree of control to be gained over the chemistry that occurs at the metal center. Furthermore, there is the opportunity for coordinative unsaturation as compared to calix[4]arene. Recently, we [2–5] and other groups [6–9] demonstrated the synthesis of coordination compounds having these triaryloxide ligands.

* Corresponding author. Tel.: +81 564 595 587; fax: +81 564 595 589.
E-mail address: hkawa@ims.ac.jp (H. Kawaguchi).

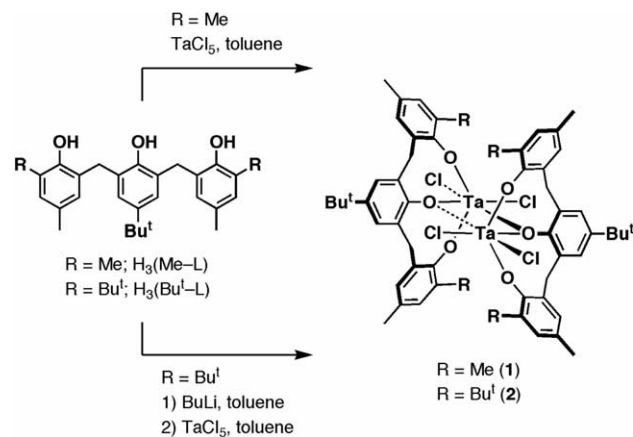
We previously reported that the [^tBu–L] ligand allowed for isolation of hydride-bridged dinuclear complexes of titanium(III) and zirconium(IV) [3], and these complexes are rare examples of non-metallocene group 4 metal hydrides [10]. Attempts to prepare the niobium analogue by the reaction of [(^tBu–L)NbCl₂]₂ with LiBHET₃ under dinitrogen resulted in formation of the nitride-bridged Nb(V) dinuclear complex [4]. This reaction presumably proceeds via a niobium hydride intermediate, which could cleave the N≡N bond along with the reductive elimination of H₂. Therefore we have extended the use of the [R–L] ligand to tantalum complexes and set out to investigate whether hydride complexes supported by the [R–L] auxiliary could be isolated. In this paper we describe the synthesis and structural properties of tantalum complexes based on the triaryloxy ligand. Portions of this work were communicated in the preliminary report [5].

2. Results and discussion

2.1. Synthesis of [(R–L)TaCl₂]₂ [R = Me (1), ^tBu (2)]

Our objective was to obtain well-characterized tantalum hydride complexes supported by aryloxy auxiliaries. The strategy was to use chloride derivatives bearing the [R–L] ligands (R = Me, ^tBu) as a substrate and triethylborohydrides MBHET₃ (M = Li, Na, K) as a hydride source. We thought it would be advantageous to use a linked-aryloxy [R–L] ligand, which would leave little possibility of reorganizing the molecule and leading to insoluble aryloxy-hydride polymeric products. As a hydride reagent, a stock THF solution of MBHET₃ (Aldrich) was used without further purification.

To prepare the substrates [(R–L)TaCl₂]₂ for the present investigation, the reactions of 1 equiv of H₃[Me–L] with TaCl₅ were examined in refluxing toluene. When the ligand precursor H₃[Me–L] was used, [(Me–L)TaCl₂]₂ (1) was obtained as an orange crystalline precipitate with evolution of HCl (Scheme 1). For the *tert*-butyl-substituted ligand precursor H₃[^tBu–L], the analogous reaction led to ligand degradation associated with loss of one of *tert*-butyl groups of [^tBu–L]^{3–}. The de-*tert*-butylation of the [^tBu–L] ligand during the reaction is not entirely unexpected given the fact that ligand degradation has already been observed in the reaction of NbCl₅ with H₃[^tBu–L] [2c]. In this case, the tantalum complex is a strong enough Lewis acid to effect a similar type of reaction chemistry. The synthesis of the niobium chloride derivative having the [^tBu–L] ligand was previously achieved from the reaction of NbCl₅ and the solvent-free trilithium salt Li₃[^tBu–L]. The similar route has been employed in the present work starting from TaCl₅ and Li₃[^tBu–L] in refluxing toluene.



Scheme 1. Synthesis of **1** and **2**.

The desired complex [(^tBu–L)TaCl₂]₂ (**2**) was isolated as a yellow solid, which was crystallized from a warm toluene solution. Upon isolation, these chloride derivatives are moderately soluble in CH₂Cl₂ and THF, sparingly soluble in toluene, and insoluble in hydrocarbons. Although **2** could be obtained in moderate yield, the low solubility in non-polar solvents renders isolation of LiCl-free **2** difficult. Combustion analyses and ¹H NMR data of **1** and **2** are in good agreement with their formulations. The ¹H NMR spectrum of each compound is indicative of a highly symmetric species in solution. The bridging methylene protons of the triaryloxy ligands appear as a pair of doublets.

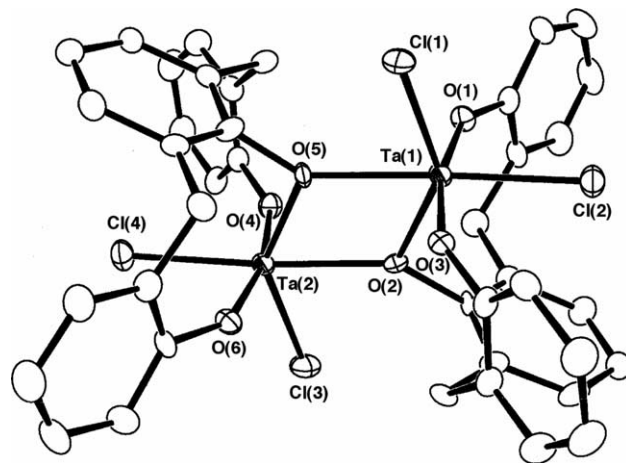


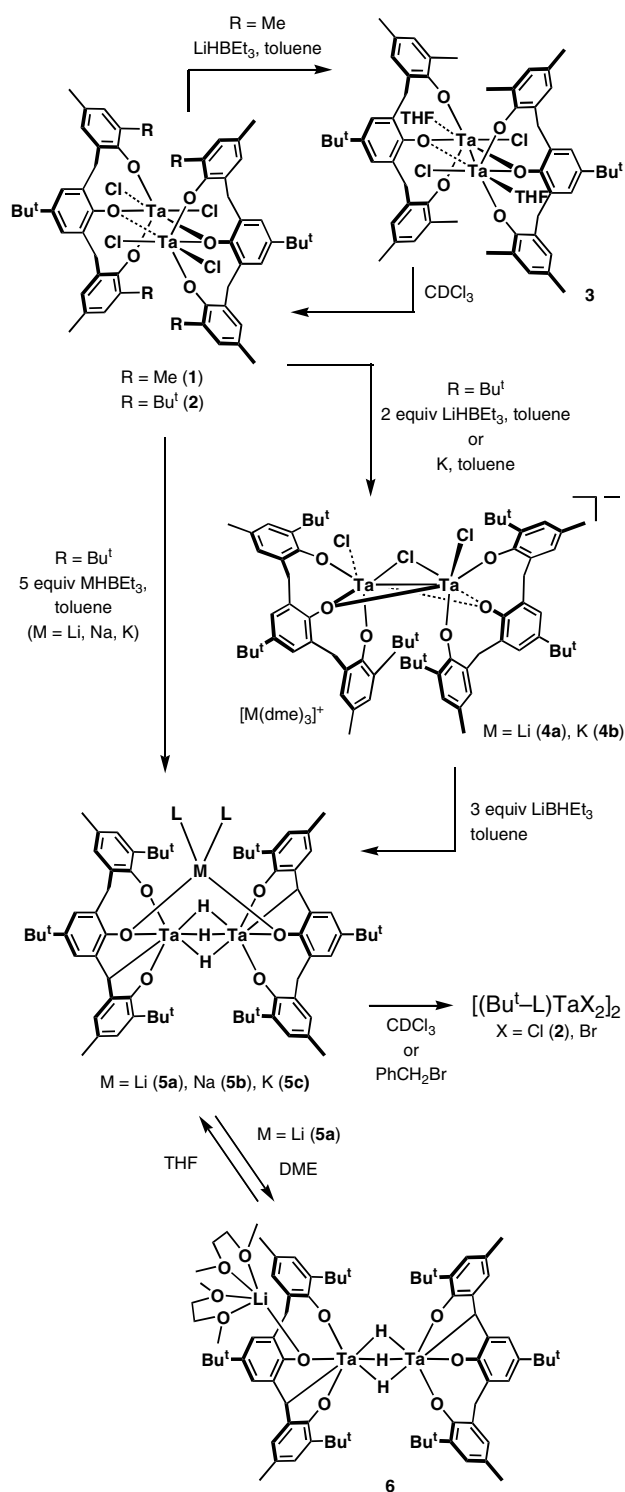
Fig. 1. Structure of [(^tBu–L)TaCl₂]₂ (**2**). Methyl and *tert*-butyl groups have been omitted for clarity. Selected bond distances (Å) and angles (°): Ta(1)–O(1) 1.905(4), Ta(1)–O(2) 2.066(3), Ta(1)–O(3) 1.905(4), Ta(1)–O(5) 2.197(4), Ta(2)–O(2) 2.190(4), Ta(2)–O(4) 1.904(4), Ta(2)–O(5) 2.062(4), Ta(2)–O(6) 1.891(4), Ta(1)–Cl(1) 2.319(1), Ta(1)–Cl(2) 2.350(2), Ta(2)–Cl(3) 2.320(1), Ta(2)–Cl(4) 2.352(2), Ta(1)–Ta(2) 3.6098(4), O(1)–Ta(1)–O(3) 168.1(2), O(4)–Ta(2)–O(6) 166.9(2), O(2)–Ta(1)–O(5) 63.9(1), O(2)–Ta(2)–O(5) 64.1(1), Ta(1)–O(2)–Ta(2) 116.0(1), Ta(1)–O(5)–Ta(2) 115.9(1), Cl(1)–Ta(1)–Cl(2) 104.79(5), Cl(3)–Ta(2)–Cl(4) 105.57(6).

The solid-state structure of **2** was confirmed by a single-crystal X-ray diffraction study (Fig. 1). The molecule of **2** is a dimer, which derives from the sharing of a central aryloxy group of the [^tBu–L] ligand to yield a planar Ta₂(μ-O)₂ ring. The bridging Ta–O distances reflect a dissymmetry in the Ta₂O₂ ring with two longer [2.197(4), 2.190(4) Å] and two shorter distances [2.066(3), 2.062(4) Å]. This distortion is probably attributed to steric crowding about the metal centers and geometrical constraint imposed by the tridentate ligand framework. The terminal Ta–O distances (average 1.901 Å) are longer than the bridging ones (average 2.129 Å) as expected. Each ^tBu–L ligand meridionally chelates a tantalum metal in a U-shaped conformation. The coordination sphere of each octahedral tantalum is completed by two mutually *cis* chloride ligands, with the Cl–Ta–Cl angles of 104.79(5)° and 105.57(6)°. The Ta–Cl distances (average 2.335 Å) are typical for Ta(V) complexes [11].

2.2. Reaction of [(Me–L)TaCl₂]₂ (**1**) with LiBHET₃

Addition of 2 equiv of LiBHET₃ in THF to a toluene suspension of **1** gave a brown precipitate of a mixture of LiCl and [(Me–L)TaCl(THF)]₂ (**3**) with the concomitant reduction of the metal center from Ta(V) to Ta(IV), in which LiBHET₃ functions as a reductant (Scheme 2). Analytically pure **3** was isolated in 67% yield after recrystallization from a warm toluene. The analogous reaction with excess LiBHET₃ did not proceed further than the Ta(IV) complex **3**. This is presumably due to the very low solubility of **3** in the reaction media (toluene/THF). Complex **3** is diamagnetic, and the ¹H NMR spectrum revealed the presence of coordinated THF as two broad signals. In addition, the resonance pattern due to the Me–L ligand are entirely analogous to that of **1**. The complex **3** is readily oxidized. When **3** was dissolved in CDCl₃, formation of the Ta(V) chloride dimer **1** was noticed according to its ¹H NMR spectrum.

The X-ray crystal structure of **3** confirms the dinuclear character of the compound in the solid state (Fig. 2). A crystallographically imposed center of inversion is located at the center of the Ta₂O₂ ring. The geometry at tantalum is distorted octahedral, with a chloride, a THF molecule, a tridentate [Me–L] ligand, and a central aryloxy of another [Me–L] ligand. Similar to **2**, the [Me–L] ligand is coordinated in a meridional manner and assumes a U-conformation. The coordinated THF molecule is inside the cavity of the U-shaped triaryloxy ligand and is bound *trans* to the bridging aryloxy [O(2*)] of another triaryloxy ligand. The terminal Ta–O(aryloxy) (average 1.923 Å) and the Ta–Cl distances (2.4368(9) Å) are increased from those found in the Ta(V) complex **2**, inferring a diminished donation of electron density from aryloxy



Scheme 2. Synthesis of **3**, **4**, **5**, and **6**.

and chloride groups by the Ta(IV) center in **3** relative to related Ta(V) species. In the planar Ta₂O₂ dimer ring the angles at O [85.35(7)°] are smaller than those at Ta [94.65(7)°], and the bridging Ta–O(2*) distance of 2.027(2) Å is significantly shortened as compared to the corresponding distances of **2** (average 2.194 Å). This observation is in keeping with the presence of a Ta–Ta

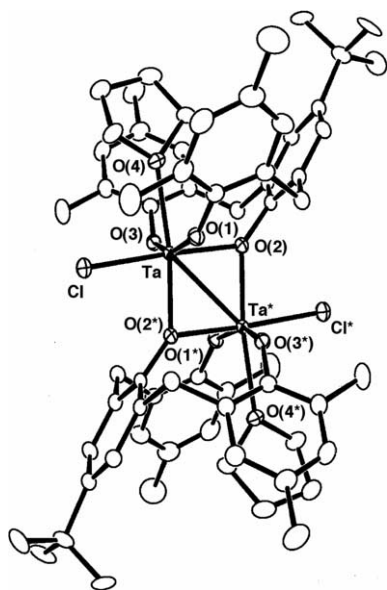


Fig. 2. Structure of $[(\text{Me-L})\text{TaCl}(\text{THF})_2]_2$ (**3**). One set of disordered *tert*-butyl groups have been omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Ta–O(1) 1.924(2), Ta–O(2) 2.105(2), Ta–O(3) 1.922(2), Ta–O(4) 2.293(2), Ta–O(2*) 2.027(2), Ta–Cl 2.4368(9), Ta–Ta* 2.8015(2), O(1)–Ta–O(3) 158.40(8), O(2)–Ta–Cl 177.05(5), O(4)–Ta–Cl 89.35(6), O(2)–Ta–O(2*) 94.65(7), Ta–O(2)–Ta* 85.35(7).

single bond of 2.8015(2) Å, which rationalizes its diamagnetism [12].

2.3. Reactions of $[(^t\text{Bu-L})\text{TaCl}_2]_2$ (**2**) with MBHET_3 ($M = \text{Li, Na, K}$) and KH

In order to investigate the effect of an increase in steric bulk upon the reaction course, a slurry of the [$^t\text{Bu-L}$] complex **2** in toluene was treated with 2 equiv of LiBHET_3 in THF to give a green–brown solution. Upon removal of the solvent a brown solid was obtained that was recrystallized from DME/hexane to produce diamagnetic blue crystals of $[\text{Li}(\text{DME})_3][\{(^t\text{Bu-L})\text{TaCl}_2(\mu\text{-Cl})\}]$ (**4a**) in 28%. The metal center is reduced from Ta(V) to Ta(IV). Alternatively, reduction of **2** with a potassium film in DME resulted in formation of the potassium analogue $[\text{K}(\text{DME})_3][\{(^t\text{Bu-L})\text{TaCl}_2(\mu\text{-Cl})\}]$ (**4b**) in 70%, which was isolated from DME/hexane as blue crystals suitable for X-ray crystallography (vide infra). The use of excess potassium failed to further reduce the complex. The ^1H NMR spectra of **4a** and **4b** in THF-d_8 are very alike, and the methylene protons of the [$^t\text{Bu-L}$] ligands appear as two pairs of mutually coupled doublets. Additionally, there are three *tert*-butyl and two methyl singlets. These features indicate that the dimeric structure observed in the solid state is retained in solution.

The structure of the anion part of **4b** is shown in Fig. 3. There is no direct connection with the potassium

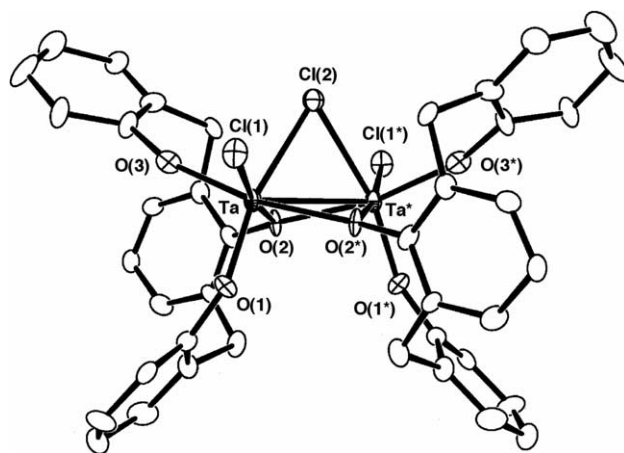


Fig. 3. Structure of the anion in $[\text{K}(\text{DME})_3][\{(^t\text{Bu-L})\text{TaCl}_2(\mu\text{-Cl})\}]_2$ (**4b**). Methyl and *tert*-butyl groups have been omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Ta–O(1) 1.910(6), Ta–O(2) 2.070(6), Ta–O(3) 1.953(7), Ta–O(2*) 2.109(6), Ta–Cl(1) 2.410(2), Ta–Cl(2) 2.552(3), Ta–Ta* 2.7105(4), O(1)–Ta–O(2) 89.8(3), O(1)–Ta–O(3) 103.5(3), O(2)–Ta–O(3) 86.6(3), Cl(1)–Ta–Cl(2) 88.49(6), Cl(1)–Ta–O(2) 169.9(2), Cl(2)–Ta–O(1) 166.1(2), Ta–O(2)–Ta* 80.9(2), Ta–Cl(2)–Ta* 64.17(8), Cl(1)–Ta–Ta*–Cl(1*) 63.43(7), O(2)–Ta–Ta*–O(2*) 146.0(4).

counterion, which is solvated by three DME molecules and well separated from its ionic counterpart. The anion has a crystallographically imposed C_2 symmetry, the 2-fold axis running through the Cl(2) atom and bisecting the Ta–Ta bond. In contrast to the meridional structures found in **2** and **3**, the flexible [$^t\text{Bu-L}$] ligand facially caps the tantalum atom in a U-shaped arrangement. The steric influence of the [$^t\text{Bu-L}$] ligand is demonstrated by a comparison between the Ta(IV) complexes, **3** and **4b**. The [Me-L] ligand in **3** assumes a conformation allowing the inclusion of a THF molecule that enters its cavity and is bound to the metal, whereas the bulky *tert*-butyl groups of the [$^t\text{Bu-L}$] ligand may prevent formation of the [$^t\text{Bu-L}$] complex analogous to **3** due to the increased congestions of the metal site. Instead, one chloride anion is incorporated into the dimer frame to generate an anionic $[\{(^t\text{Bu-L})\text{TaCl}_2(\mu\text{-Cl})\}]$ unit. Thus the dimer structure of the anion in **4** is formed by two octahedral tantalum atoms bridged by one chloride atom and two central aryloxy groups of the [$^t\text{Bu-L}$] ligands. The Ta–O distances [average 1.932 Å (terminal), 2.090 Å (bridging)] are similar to those of the Ta(IV) complex **3**, while the shortening of the triply bridged Ta–Ta distance [2.7105(4) Å] reflects the acute Ta–Cl(2)–Ta [64.17(8) $^\circ$] and Ta–O(2)–Ta angles [80.9(2) $^\circ$]. The terminal Ta–Cl(1) distance of 2.410(2) Å is longer than the bridging Ta–Cl(2) distance of 2.552(3) Å, and it is comparable to that of the related Ta(IV) complex **3** [2.4368(9) Å].

When the amount of LiBHET_3 was increased, $[\{(\text{bit-}^t\text{Bu-L})\text{Ta}_2(\mu\text{-H})_3\text{Li}(\text{THF})_2\}]$ (**5a**) was obtained as yellow crystals along with **4a**. Intramolecular metalation

of the methylene linkers in the $[(^t\text{Bu-L})\text{Ta}]$ complex took place to provide a new $[\text{bit-}^t\text{Bu-L}]^{4-}$ ligand. After experimenting with various amounts of LiBHET_3 , we found that optimum yields (62% isolated) could be obtained by reaction of **1** with 5 equiv of LiBHET_3 followed by filtration and concentration of the solution. The analogous reactions of **2** with NaBHET_3 and KBHET_3 gave $[(\text{bit-}^t\text{Bu-L})\text{Ta}]_2(\mu\text{-H})_3\text{M}(\text{THF})_2$ [$\text{M} = \text{Na}$ (**5b**), K (**5c**)] in moderate yields, after recrystallization from DME/hexane. This suggests that formation of the $\{[(\text{bit-}^t\text{Bu-L})\text{Ta}]_2(\mu\text{-H})_3\}^-$ dimeric core (vide infra) is independent of the nature of the counterion.

The molecular structures of **5a**, **5b**, and **5c** were established by X-ray analysis. Since their structures and geometrical parameters are very similar, those of the lithium adduct **5a** are described here (Fig. 4). The molecular structure of **5a** shows the dimer to be bridged by three hydrides, which were located and refined isotropically (Ta-H , 1.80–1.90 Å). The metalacyclic $\text{Ta-C}(7)$ and $\text{-C}(21)$ distances of 2.267(4) and 2.264(3) Å are normal for Ta(V) -alkyl compounds [11a,13]. Each C_{ispo} carbon of the central aryloxide of the $[\text{bit-}^t\text{Bu-L}]$ ligand forms close contact with the metal center [2.420(4) and 2.426(3) Å]. This is a consequence of the conformational constraint imposed by the $[\text{bit-}^t\text{Bu-L}]$ framework in **5a**. One lithium cation, solvated by two THF molecules, is connected to two central aryloxides [O(2), O(5)] of the $\text{bit-}^t\text{Bu-L}$ ligands. This requires the two $[(\text{bit-}^t\text{Bu-}$

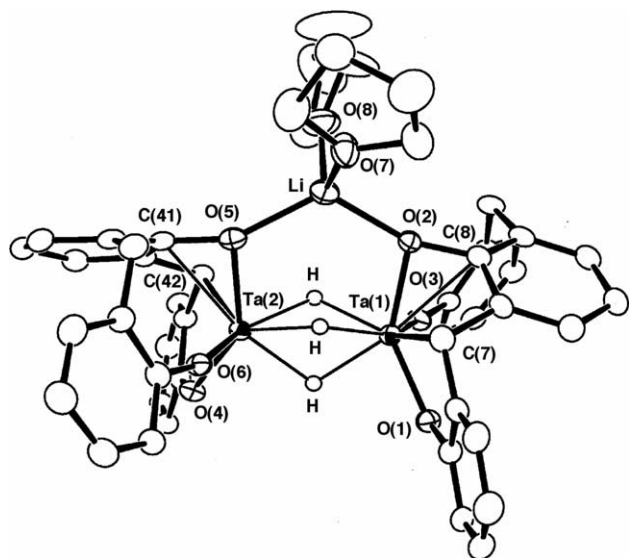
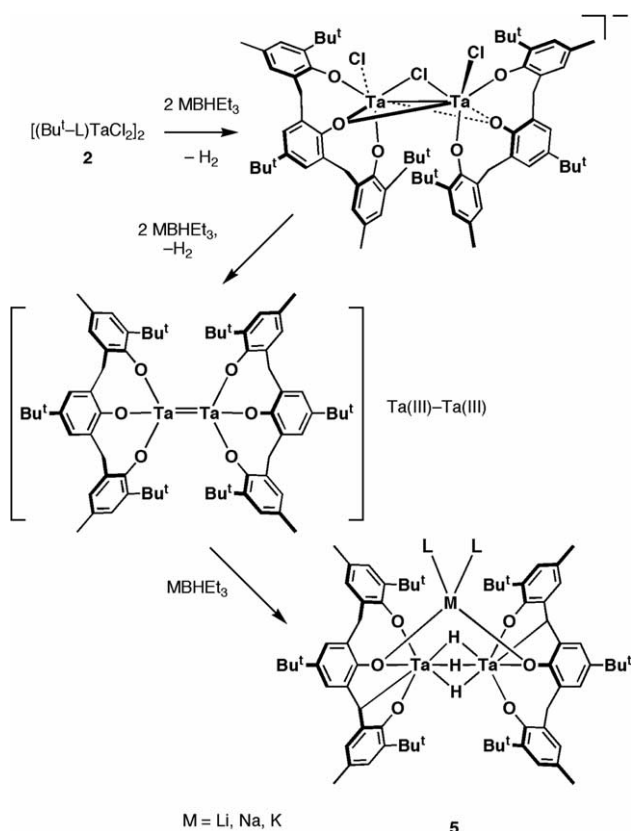


Fig. 4. Structure of $\{[(^t\text{Bu-L})\text{Ta}]_2(\text{H})_3\text{Li}(\text{THF})_2\}$ (**5a**). Methyl and *tert*-butyl groups have been omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): $\text{Ta}(1)\text{-O}(1)$ 1.958(2), $\text{Ta}(1)\text{-O}(2)$ 2.038(3), $\text{Ta}(1)\text{-O}(3)$ 1.946(2), $\text{Ta}(2)\text{-O}(4)$ 1.974(3), $\text{Ta}(2)\text{-O}(5)$ 2.028(3), $\text{Ta}(2)\text{-O}(6)$ 1.947(2), $\text{Ta}(1)\text{-C}(7)$ 2.267(4), $\text{Ta}(1)\text{-C}(8)$ 2.420(4), $\text{Ta}(2)\text{-C}(41)$ 2.264(3), $\text{Ta}(2)\text{-C}(42)$ 2.426(3), $\text{Ta}(1)\text{-Ta}(2)$ 2.9313(4), $\text{Li-O}(2)$ 1.946(8), $\text{Li-O}(5)$ 1.959(7), $\text{Ta}(1)\text{-H}$ 1.80–1.85, $\text{Ta}(2)\text{-H}$ 1.81–1.90, $\text{O}(1)\text{-Ta}(1)\text{-O}(2)$ 142.8(1), $\text{O}(1)\text{-Ta}(1)\text{-O}(3)$ 96.25(10), $\text{O}(2)\text{-Ta}(1)\text{-O}(3)$ 89.61(10), $\text{O}(4)\text{-Ta}(2)\text{-O}(5)$ 141.97(10), $\text{O}(4)\text{-Ta}(2)\text{-O}(6)$ 93.8(1), $\text{O}(5)\text{-Ta}(2)\text{-O}(6)$ 90.48(10), $\text{O}(2)\text{-Li-O}(5)$ 119.3(4), $\text{Ta}(1)\text{-H-Ta}(2)$ 102.9–108.5, $\text{O}(2)\text{-Ta-Ta-O}(5)$ 6.47(10).

$\text{L})\text{Ta}]$ ends of the molecule to be eclipsed. The short Ta-Ta distance of 2.9313(4) Å relative to that of **2** [3.6098(4) Å] is imposed by the three hydride bridges and not indicative of any metal-metal interaction because two metal centers are Ta(V) in this formalism. However, the metal-metal distance bridged by three hydrides in **5a** is substantially longer than the Ta(IV)-Ta(IV) single bonds found in **3** and **4**.

The hydride complexes **5a-c** show similar patterns in the ^1H NMR spectra, which are consistent with their solid-state structures. The metal-bound methine group appears as a singlet, and the remaining methylene protons of the ligand are observed a pair of doublets. In addition, the bridging hydrides appear equivalent at ca. 11 ppm, the downfield shift being characteristic of hydride ligands on a highly electrophilic metal center surrounded by hard donor groups [14] (cf. $[(\text{Me}_3\text{SiCH}_2)_2(\text{ArN}=\text{O})\text{Ta}(\mu\text{-H})(\mu\text{-}\eta^1\text{-Pr}_2\text{-tacn})\text{Li}]$, 11.03 ppm [15]). These features are essentially invariant over the temperature range from -80 to 20 $^\circ\text{C}$. On warming up to 60 $^\circ\text{C}$, these signals of methine, methylene, and hydride protons are observed to coalesce along with the partial decomposition of the hydride complexes due to their thermal instability [5,16]. This indicates that the methylene CH activation process is reversible. Thus the cyclometalated-hydride complex **5** could provide a masked-form of low-valent tantalum dimer.

The role of MBHET_3 ($\text{M} = \text{Li}, \text{Na}, \text{K}$) in the reaction with **2** is not only as a reducing agent but also as a hydride source. During the course of the reaction, 4 equiv of MBHET_3 is consumed with the reductive loss of H_2 . Subsequently, intramolecular addition of a methylene CH bond to a Ta(III)-Ta(III) intermediate may take place. The remaining triethylborohydride reactant appears to be incorporated as a hydride ligand in the final product. The proposal that the Ta(IV) dimer **4a** is an intermediate in the reaction can be confirmed by the preparation of **5a** from **4a** by addition of LiBHET_3 in toluene. It is noted that **4a** is not found to undergo intramolecular CH activation across a Ta(IV)-Ta(IV) bond, while there are precedents for oxidative addition of a CH bond to Ta(III) [17]. It was also reported that attempt to prepare the $d^2\text{-d}^2$ ditantalum(III) allene complex by reduction with sodium amalgam resulted in formation of the propynylidene-dihydride-bridging complex along with a double CH activation of the allene ligand [17d]. Therefore we prefer the mechanism via a Ta(III)-Ta(III) intermediate which undergoes CH activation of the ligand (Scheme 3). This mechanism is also in accordance with the observation that no elimination of HD and H_2 occurred in the reaction mixture of **2** and LiBDEt_3 . However, in the **2/LiBDEt}_3 reaction, it is not clear into which position of the final product the deuteride reagent is incorporated due to the reversible CH metalation process.**

Scheme 3. Proposed mechanism for the formation of **5**.

A comparison of niobium and tantalum complexes in the reactions with LiBHET₃ merits comment. The analogous reaction of [(^tBu-L)NbCl₂]₂ with LiBHET₃ may proceed via the Nb(II) species of the type [(^tBu-L)NbLi]_n, along with reductive elimination of hydrides, which subsequently binds, reduces, and cleaves dinitrogen to produce the Nb(V) nitride complex [4]. Since tantalum is known to stabilize higher oxidation states better than niobium, it is expected that the metal center is hardly reduced to Ta(II) in the **2**/triethylborohydride reaction system. When the metal center is reduced to Ta(III), the tantalum complex is prone to undergo intramolecular CH activation, resulting in formation of the Ta(V) hydride complex. On the other hand, the preliminary result shows that the tantalum complexes **5a–c** are inert toward dinitrogen (1 atm).

When **5a** was dissolved in CDCl₃, ¹H NMR assays revealed near quantitative conversion to **2** and the signal assigned to the hydride protons immediately disappeared. During the course of the reaction, the hydride ligand has migrated back to the methine carbon of the *bit*-^tBu-L ligand, restoring the tridentate ^tBu-L ligand. This reaction could be used in preparing a Ta(V) halide starting material. For example, treatment of **5a** with PhCH₂Br in toluene gave the bromide analogue [(^tBu-L)TaBr₂]₂. On the other hand, these hydride complexes did not react with D₂ gas. The mixture of **5a** and

LiBDEt₃ did not show any sign of the H/D exchange. Attempts to prepare the deuterated analogues such as [(*bit*-^tBu-L)Ta]₂(μ-D)₃Li(THF)₂ have been unsuccessful.

The THF molecules coordinated at lithium in **5a** can be readily replaced by DME. Treatment of **5a** in DME and subsequent addition of hexane produced yellow crystals formulated as [(*bit*-^tBu-L)Ta]₂(μ-H)₃Li(DME)₂ (**6**), which was identified by X-ray crystallography (Fig. 5). It is obvious that the molecule contains a [(*bit*-^tBu-L)Ta]₂(μ-H)₃ dimeric unit, like the structure of **5a**. The local geometry of the monomeric [(*bit*-^tBu-L)Ta] units is similar to that found in **5a**, and the Ta–O distances of **6** [Ta–O(central), average 2.024 Å; Ta–O(outer), 1.963 Å] resemble those of **5a** [2.033 and 1.956 Å, respectively]. However, the dimeric unit has to rearrange its conformation to accommodate a large [Li(DME)₂]⁺ unit. The unique feature of **6** is that as the lithium atom is coordinated by chelating DME instead of THF, one of the Li–O(aryloxy) bridging bonds is missing [Li–O(5) 5.052(7) Å] due to the increasing coordination number and steric crowding about small Li. One notable difference can be seen in the O(2)–Ta(1)–Ta(2)–O(5) torsion angle. While the opposing [*bit*-^tBu-L] ligands on Ta(1) and Ta(2) in **5a**

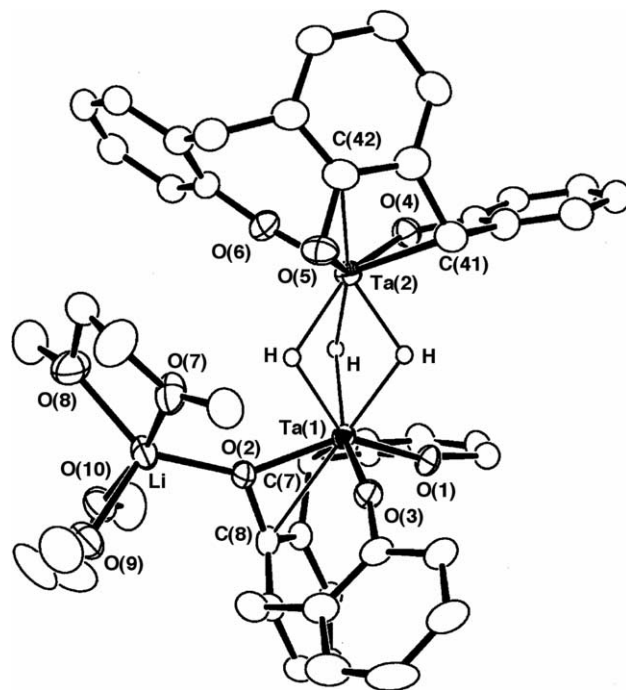


Fig. 5. Structure of [(^tBu-L)Ta]₂(H)₃Li(DME)₂ (**6**). Methyl and *tert*-butyl groups have been omitted for clarity. Selected bond distances (Å) and angles (°): Ta(1)–O(1) 1.973(3), Ta(1)–O(2) 2.049(2), Ta(1)–O(3) 1.954(2), Ta(2)–O(4) 1.968(3), Ta(2)–O(5) 2.002(3), Ta(2)–O(6) 1.956(3), Ta(1)–C(7) 2.254(4), Ta(1)–C(8) 2.411(4), Ta(2)–C(41) 2.276(4), Ta(2)–C(42) 2.416(4), Ta(1)–Ta(2) 2.9458(3), Li–O(2) 2.004(7), Ta(1)–H 1.80–1.85, Ta(2)–H 1.81–1.90, O(1)–Ta(1)–O(2) 139.2(1), O(1)–Ta(1)–O(3) 95.7(1), O(2)–Ta(1)–O(3) 89.1(1), O(4)–Ta(2)–O(5) 139.0(1), O(4)–Ta(2)–O(6) 94.9(1), O(5)–Ta(2)–O(6) 90.0(1), Ta(1)–H–Ta(2) 96.3–101.7, O(2)–Ta–Ta–O(5) 65.89(8).

are eclipsed with a negligible O(2)–Ta(1)–Ta(2)–O(5) torsion angle of $6.47(10)^\circ$, the structure of **6** is assumed to have the two [(*bit*-^tBu–L)Ta] ends staggered with respect to each other [$65.89(8)^\circ$]. This structural feature contrasts with the eclipsed geometries found in **5b** and **5c**, where larger sodium and potassium solvated by two DME molecules can bridge the central aryloxides of the ligands. The Ta–Ta separation of $2.9458(3) \text{ \AA}$ is slightly elongated relative to that of **5a**.

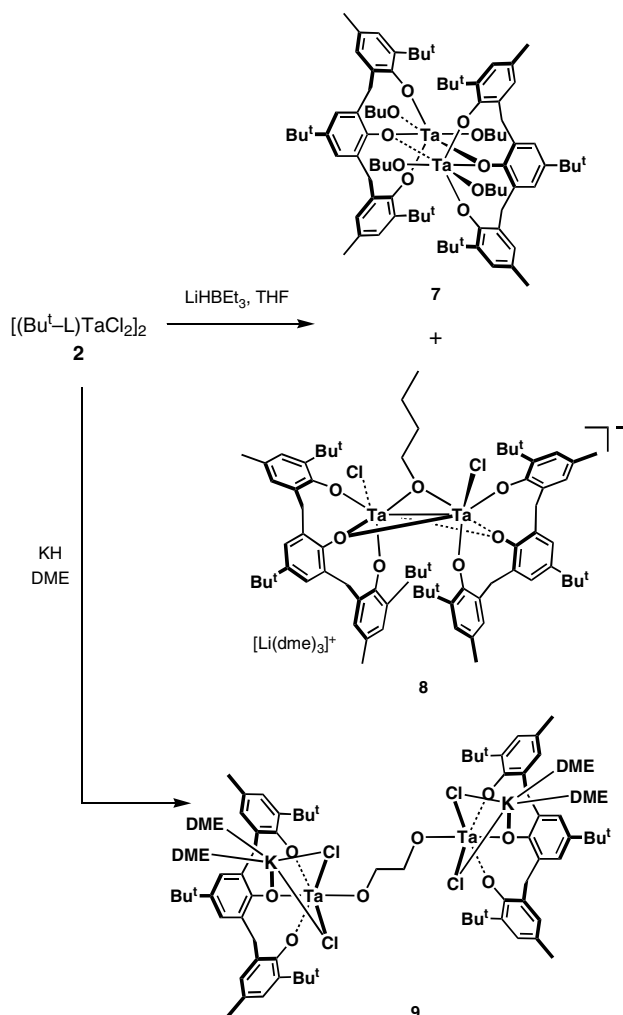
The ^1H NMR spectrum of **6** in THF- d_8 indicates that **5a** is regenerated along with free DME, because the Li-bound ligands are labile. However, we have not been successful in preparing their ion-separated salts and replacing the alkali cations by organic cations. The counter cations appear to be bound strongly to aryloxide oxygen atoms. Additionally, the counter ions might play an important role in stabilizing this dimeric structure. For example, addition of 18-crown-6 to a THF solution of **5c** was found to lead to facile C–O bond cleavage of the triaryloxide ligand [5].

2.4. C–O bond cleavage reactions of THF and DME

The choice of solvent and hydride reagent is crucial to the successful synthesis of the Ta(V) hydride complexes **5a–c**. For instance, the reaction of **2** with 4 equiv of LiBHET_3 was carried out in THF to produce a mixture of colorless **7** (major) and blue **8** (Scheme 4). Compounds **7** and **8** could not be isolated by fractional crystallization due to their similar solubility in toluene and THF, but large colorless crystals of **7** were manually separated from blue needle crystals of **8** with the aid of a microscope. Coupled with crystallographic data (vide infra), the ^1H NMR spectrum confirmed the formulation of **7** as $[(^t\text{Bu-L})\text{Ta}(\text{OBu}^n)_2]_2$. The ^1H NMR spectrum of **7** features two sets of resonances assigned to inequivalent *n*-butoxide ligands which arise from ring opening of THF, and this NMR data is consistent with the solid-state structure. Analytically pure **7** was independently prepared in 77% yield by treatment of **2** with 4 equiv of sodium butoxide in toluene.

The solid-state structure of **7** was determined by a single-crystal X-ray diffraction study (Fig. 6). The molecular structure reveals the dimeric nature of **7** with the halves related by a crystallographic center of symmetry. This dimeric species **7** has an overall geometry similar to the chloride derivatives **2**, with *n*-butoxide groups in place of chloride ligands. The bond distances and angles for **7** all fall within the typical ranges for triaryloxide ligands found in Ta(V) complexes. The Ta–O(*n*-butoxide) distances of average 1.860 \AA are shorter than the Ta–O(aryloxide) distances.

The minor component **8** was invariably contaminated by **7**, whose presence precluded NMR and elemental analyses of **8**. The crystals of **8** that were obtained after manual separation did not diffract well, preventing the



Scheme 4. Synthesis of **7**, **8**, and **9**.

acquisition of a high quality X-ray structure of this species. A low-resolution was obtained which at least confirmed connectivity (Scheme 4) [18]. The blue complex **8** is formulated as $[\text{Li}(\text{THF})_4][\{(^t\text{Bu-L})\text{TaCl}\}_2(\mu\text{-OBu}^n)]$. The structure of the anion part shows a dimer, which is closely related to that found in the chloride-bridging Ta(IV) dimer **4**. In **8**, the tantalum centers are bridged by one *n*-butoxide ligand and two central aryloxides of the ^tBu–L ligands. During the formation of **8**, reduction from Ta(V) to Ta(IV) took place along with the ring-opening reaction of THF. The reaction of **7** with LiBHET_3 in THF provided a mixture of unidentified products, and the conversion of **7–8** has been unsuccessful. This implies that formation of the *n*-butoxide Ta(V) complex **7** does not proceed via the Ta(IV) complex **8**.

The reaction of **2** with KH in DME was of interest in that **5c** could be regarded as the adduct of $[\{(^t\text{Bu-L})\text{Ta}\}_2(\mu\text{-H})_2]$ with a neutral KH reagent. Although **5c** did not form, a remarkable reaction occurred nonetheless. The ethane-1,2-diolate bridging complex $[\{(^t\text{Bu-L})\text{TaCl}_2\text{K}(\text{DME})_2\}_2(\mu\text{-OCH}_2\text{CH}_2\text{O})]$ (**9**), is obtained

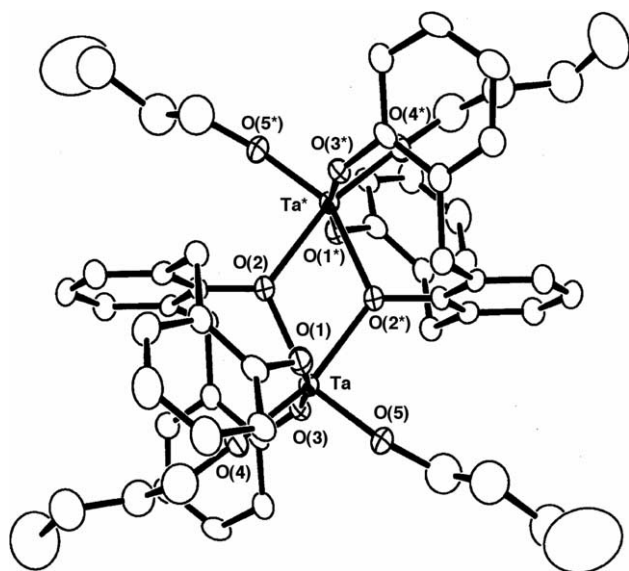


Fig. 6. Structure of $[(t\text{Bu-L})\text{Ta}(\text{OBu}^n)_2]_2$ (7). Methyl and *tert*-butyl groups, and one set of disordered *n*-butyl groups have been omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Ta–O(1) 1.968(4), Ta–O(2) 2.104(5), Ta–O(3) 1.964(4), Ta–O(4) 1.857(4), Ta–O(5) 1.862(4), Ta–O(2*) 2.167(4), Ta–Ta* 3.5905(4), O(1)–Ta–O(3) 169.7(1), O(4)–Ta–O(5) 109.0(2), O(2*)–Ta–O(4) 165.2(2), O(2)–Ta–O(5) 151.3(2), O(2)–Ta–O(2*) 65.6(1), Ta–O(2)–Ta* 114.4(2).

as light blue crystals in 54% yield. The presence of the ethane-1,2-diolate ligand is confirmed by the ^1H NMR spectrum, which exhibits a sharp singlet at 3.46 ppm with the appropriate intensity ratio. The ethane-1,2-diolate ligand in **9** is likely formed by C–O bond cleavage of a DME molecule of the solvent.

The molecular structure of **9** is shown in Fig. 7. The C(1)–C(1*) bond of the ethane-1,2-diolate linker lies on a crystallographic inversion center so that the halves of the molecule are identical. It is obvious that the compound contains a pair of the $[(t\text{Bu-L})\text{Ta}]^{2+}$ units, in which the U-shaped $[(t\text{Bu-L})]$ ligand bind to the metal center facially. The octahedral coordination sphere of tantalum is completed by two chlorides and one oxygen atom of the ethane-1,2-diolate linker. The potassium cation, solvated by two DME molecules, caps the triangle face defined by two chloride [Cl(1), Cl(2)] and one central aryloxide [O(2)] of the $[(t\text{Bu-L})]$ ligand. Thus the formulation assigns a formal 5+ oxidation state to the tantalum atom. The Ta–O and Ta–Cl bond distances are similar to the corresponding distances found in the Ta(V) complexes [11].

The nature of the byproducts of these reactions shown in Scheme 4 is not yet definitely established and requires further study. However, degradation of ethereal solvents such as THF and DME is often found in the synthesis of early transition metal and f-element complexes [19–24]. Ring-opening reaction of THF is well known to form *n*-butoxide compounds [19]. The C–O bond cleavage of DME to produce oxo, methoxide,

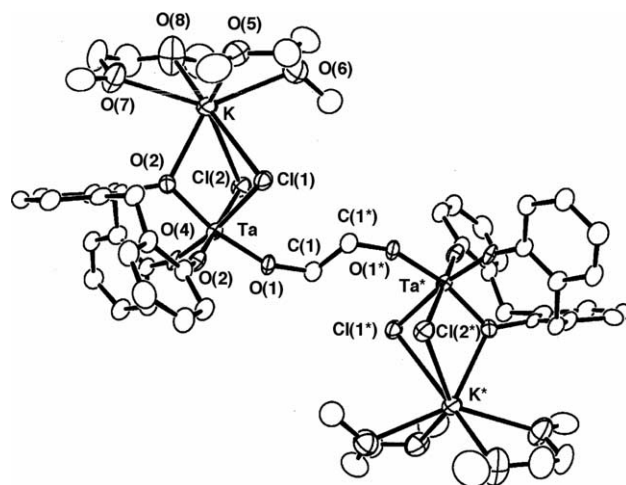


Fig. 7. Structure of the anion in $[(t\text{Bu-L})\text{TaCl}_2\text{K}(\text{DME})_2]_2(\mu\text{-OCH}_2\text{CH}_2\text{O})$ (**9**). Methyl and *tert*-butyl groups have been omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Ta–O(1) 1.870(6), Ta–O(2) 1.904(5), Ta–O(3) 1.984(6), Ta–O(4) 1.912(5), Ta–Cl(1) 2.484(2), Ta–Cl(2) 2.484(2), K–Cl(1) 3.166(3), K–Cl(2) 3.196(3), K–O(3) 2.678(5), K–O(4) 2.711(7), K–O(5) 2.770(8), K–O(6) 2.78(1), K–O(7) 2.675(9), C(1)–C(1*) 1.48(1), O(1)–Ta–O(2) 95.2(2), O(2)–Ta–O(3) 92.7(2), O(2)–Ta–O(4) 98.3(2), O(3)–Ta–O(4) 91.0(2), Cl(1)–Ta–Cl(2) 85.00(6), Cl(1)–K–Cl(2) 63.69(6), Ta–O(3)–K 110.4(2), Ta–Cl(1)–K 84.95(7), Ta–Cl(2)–K 84.31(7).

and 2-methoxy-ethoxide ligands has also precedent [22,23], whereas the generation of the ethane-1,2-diolate ligand via fragmentation of DME is less common. It is likely that the formation of *n*-butoxide and ethane-1,2-diolate complexes includes formation of an oxonium ion by coordination of THF and DME to the Lewis acidic Ta(V) center in **2**, which is opened and cleaved by nucleophilic attack by LiBHET_3 and KH , respectively. This first step is supported by the observation that the chloride complex **2** forms the labile solvent adducts with THF and DME according to ^1H NMR analysis. Although metal hydrides and low-valent metal complexes occasionally undergo C–O bond cleavage of ethereal molecules in mild conditions [19d,20,22], the Ta(IV) complexes (**3** and **4**) and the hydride complexes (**5a–c**) proved inert to C–O bond cleavage of THF and DME.

3. Conclusions

Tantalum complexes supported by triaryloxide ligands have been synthesized and structurally characterized. The $[\text{R-L}]$ ligands allow for isolation of Ta(V) and Ta(IV) chloride complexes, Ta(V) alkoxide complexes, and Ta(V) hydride complexes. The C–O bond rupture of THF and DME shows that the Ta(V) center having the $[(t\text{Bu-L})]$ ligand is highly Lewis acidic. Although this fragmentation of ethereal solvent proved troublesome, the hydride complexes **5a–c** could be prepared in moderate yields by the reactions of **2** with triethylborohydrides

in toluene. Once isolated, these hydride complexes are found to be inert towards THF and DME but thermally unstable. Complexes **5a–c** undergo reversible intramolecular CH activation of the methylene groups of the [^tBu–L] ligand, which suggests that they function as a masked low-valent dinuclear complex of tantalum. In this context, we expect these complexes to demonstrate a rich and varied chemistry.

4. Experimental

4.1. General methods

All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of argon or of dinitrogen using conventional Schlenk techniques and an MBraun dry-box (<1 ppm H₂O/O₂). The ligand precursors H₃(R–L) (R = Me, ^tBu) was prepared according to the reported method [2a,6,25]. All dried solvents and chemicals commercially available were used as received without further purification. Deuterated solvents were dried over appropriate drying reagents and then distilled trap-to-trap in vacuo. NMR spectra were recorded on JEOL Lambda-500 and JEOL JNM-GX500 spectrometers, and referenced internally to residual solvent resonances. Elemental analyses were measured using LECO–CHNS and Yanaco MT-6 and MSU-32 microanalyzers.

4.2. Syntheses

4.2.1. [(Me–L)TaCl₂]₂ (**1**)

Toluene (15 ml) was added to a mixture of H₃[Me–L] (0.28 g, 0.67 mmol) and TaCl₅ (0.24 g, 0.67 mmol). The resulting orange solution was refluxed for 3 h to drive off HCl gas and then allowed to cool, affording a orange crystalline solid. The solvent was decanted away from this solid, which was subsequently washed with hexane two times and dried under vacuum affording an orange solid of **1** (0.43 g, 96%). Complex **1** is slightly soluble in THF, DME, toluene, and chlorinated solvents.

Elemental analysis. Found: C, 50.22; H, 4.63%. Calc. for [C₅₆H₆₂O₆Cl₄Ta₂]: C, 50.39; H, 4.68. ¹H NMR (CDCl₃): δ 1.19 (s, 18H, ^tBu), 2.37 (s, 12H, Me), 2.41 (s, 12H, Me), 3.45 (d, *J* = 13.4 Hz, 4H, CH₂), 4.97 (d, *J* = 13.4 Hz, 4H, CH₂), 6.89 (s, 4H, Ar), 7.02 (s, 4H, Ar), 7.18 (s, 4H, Ar).

4.2.2. [(^tBu–L)TaCl₂]₂ (**2**)

A solution of butyllithium (1.60 M in hexane; 4.10 ml, 6.56 mmol) was added dropwise to H₃[^tBu–L] (1.10 g, 2.19 mmol) in toluene (20 ml) at 0 °C. The solution was warmed to room temperature and stirred for 1 h giving a white suspension of Li₃[^tBu–

L]. Solid TaCl₅ (0.78 g, 2.18 mmol) was added to the resulting mixture, and the solution immediately turned brown. The mixture was stirred for 4 h at reflux, during which time a yellow crystalline powder was formed. After standing at room temperature overnight, the yellow precipitate was isolated by filtration. Recrystallization from hot toluene gave **2**·(toluene)₂ as yellow blocks in 47% yield (0.86 g). The product is slightly soluble in THF, DME, toluene, and chlorinated solvents.

Elemental analysis. Found: C, 57.90; H, 5.87%. Calc. for [C₈₂H₁₀₂O₆Cl₄Ta₂]: C, 58.37; H, 6.09. ¹H NMR (CDCl₃): δ 1.21 (s, 18H, ^tBu), 1.42 (s, 36H, ^tBu), 2.35 (s, 12H, Me), 2.39 (s, 6H, toluene), 3.36 (d, *J* = 13.6 Hz, 4H, CH₂), 5.03 (d, *J* = 13.6 Hz, 4H, CH₂), 7.0–7.3 (m, 22H, Ar–H + toluene).

4.2.3. [(Me–L)TaCl(THF)]₂ (**3**)

A slurry of **1** (0.25 g, 0.19 mmol) in toluene (10 ml) was cooled to –78 °C, and 2 equiv of LiBHET₃ (1.0 M solution in THF; 0.38 mL) was added. The mixture was allowed to warm to room temperature and stirred for 10 h, during which time formation of a brown solid was observed. Filtration and drying under vacuum afforded 0.20 g of **3**·(toluene)₂ as a brown microcrystalline solid (67%). Analytically pure samples were obtained from slow cooling of a warm (60 °C) saturated toluene/THF solution to room temperature.

Elemental analysis. Found: C, 58.41; H, 5.72%. Calc. for [C₇₈H₉₄O₈Cl₂Ta₂]: C, 58.83; H, 5.95. ¹H NMR (THF-*d*₈): δ 0.64 (br, 8H, THF), 1.35 (s, 18H, ^tBu), 2.05 (s, 12H, Me), 2.15 (s, 6H, toluene), 2.63 (s, 12H, Me), 3.29 (br, 8H, THF), 3.66 (d, *J* = 13.3 Hz, 4H, CH₂), 5.29 (d, *J* = 13.3 Hz, 4H, CH₂), 7.0–7.3 (m, 22H, Ar–H + toluene).

4.2.4. [Li(DME)₃][{(^tBu–L)TaCl}₂(μ-Cl)] (**4a**)

A slurry of **2** (0.54 g, 0.32 mmol) in toluene (10 ml) was cooled to –78 °C, and 2 equiv of LiBHET₃ (1.0 M solution in THF; 0.64 mL) was added. The mixture was allowed to warm to room temperature and stirred for 20 h, during which time a color changed from yellow to brown. Removal of the volatiles and extraction with DME afforded a brown solution, from which 0.16 g of **3** precipitated as blue needles (28% yield).

Elemental analysis. Found: C, 54.41; H, 6.52%. Calc. for [C₈₀H₁₁₆O₁₂Cl₃LiTa₂]: C, 55.06; H, 6.70. ¹H NMR (THF-*d*₈): δ 1.15 (s, 18H, ^tBu), 1.17 (s, 18H, ^tBu), 1.18 (s, 18H, ^tBu), 2.11 (s, 6H, Me), 2.17 (s, 6H, Me), 2.92 (d, *J* = 13.5 Hz, 2H, CH₂), 3.23 (s, 18H, DME), 3.31 (d, *J* = 13.8 Hz, 2H, CH₂), 3.38 (s, 12H, DME), 5.13 (d, *J* = 13.5 Hz, 2H, CH₂), 5.64 (d, *J* = 13.8 Hz, 2H, CH₂), 6.75 (d, *J* = 1.9 Hz, 2H, Ar), 6.80 (s, 2H, Ar), 6.81 (s, 2H, Ar), 6.93 (d, *J* = 1.9 Hz, 2H, Ar), 7.03 (d, *J* = 2.1 Hz, 2H, Ar), 7.06 (d, *J* = 2.1 Hz, 2H, Ar).

4.2.5. $[K(DME)_3][\{(^tBu-L)TaCl\}_2(\mu-Cl)]$ (**4b**)

A slurry of **2** (0.44 g, 0.26 mmol) in toluene (40 ml) was added to a vessel containing an excess of potassium mirror. The mixture was stirred vigorously for 24 h. After centrifugation, the brown solution was evaporated to dryness. The residue was dissolved in DME and cooled to -30°C to give **4b** as blue crystals (0.32 g, 70%).

Elemental analysis. Found: C, 53.77; H, 6.39%. Calc. for $[C_{80}H_{116}O_{12}Cl_3KTa_2]$: C, 54.07; H, 6.58. $^1\text{H NMR}$ (THF- d_8): δ 1.15 (s, 18H, ^tBu), 1.17 (s, 18H, ^tBu), 1.18 (s, 18H, ^tBu), 2.12 (s, 6H, Me), 2.18 (s, 6H, Me), 2.93 (d, $J = 13.3$ Hz, 2H, CH_2), 3.23 (s, 18H, DME), 3.31 (d, $J = 13.9$ Hz, 2H, CH_2), 3.40 (s, 12H, DME), 5.13 (d, $J = 13.3$ Hz, 2H, CH_2), 5.66 (d, $J = 13.9$ Hz, 2H, CH_2), 6.76 (d, $J = 1.9$ Hz, 2H, Ar), 6.80 (s, 2H, Ar), 6.81 (s, 2H, Ar), 6.93 (d, $J = 1.9$ Hz, 2H, Ar), 7.04 (d, $J = 2.2$ Hz, 2H, Ar), 7.07 (d, $J = 2.2$ Hz, 2H, Ar).

4.2.6. $[\{(bit-^tBu-L)Ta\}_2(\mu-H)_3Li(THF)_2]$ (**5a**)

A THF solution of LiHBET_3 (1 M; 2.7 ml, 2.7 mmol) was added dropwise to a suspension of **2** (0.89 g, 0.52 mmol) in toluene (40 ml) that had been precooled to -78°C . The mixture was allowed to warm up to room temperature and stirred for 8 h. The resulting dark yellow solution was concentrated to ca. 5 mL and centrifuged to remove an insoluble material. The supernatant was layered with hexane to afford **5a** as yellow crystals (0.52 g, 62%).

Elemental analysis. Found: C, 61.89; H, 7.11%. Calc. for $[C_{83}H_{111}O_8LiTa_2]$: C, 62.09; H, 6.97. $^1\text{H NMR}$ (THF- d_8): δ 0.84 (s, 18H, ^tBu), 0.98 (s, 18H, ^tBu), 1.31 (s, 18H, ^tBu), 1.77 (m, THF), 2.18 (s, 6H, Me), 2.19 (s, 6H, Me), 3.34 (d, $J = 13.0$ Hz, 2H, CH_2), 3.62 (m, THF), 3.76 (s, 2H, CH), 4.64 (d, $J = 13.0$ Hz, 2H, CH_2), 6.30 (s, 2H, Ar), 6.51 (s, 2H, Ar), 6.65 (s, 2H, Ar), 6.77 (s, 2H, Ar), 6.80 (s, 2H, Ar), 6.91 (s, 2H, Ar), 10.7 (s, 3H, Ta-H).

4.2.7. $[\{(bit-^tBu-L)Ta\}_2(\mu-H)_3Na(DME)_2]$ (**5b**)

A THF solution of NaHBET_3 (1 M; 1.6 ml, 1.6 mmol) was added dropwise to a suspension of **2** (0.55 g, 0.33 mmol) in toluene (40 ml) that had been precooled to -78°C . The mixture was allowed to warm up to room temperature and stirred for 8 h. The resulting dark yellow solution was centrifuged to remove an insoluble material. The supernatant was evaporated to dryness. The brown residue was recrystallized from DME/hexane to yield **5b** as yellow crystals (0.24 g, 47%).

Elemental analysis. Found: C, 57.96; H, 6.67%. Calc. for $[C_{76}H_{107}O_{10}NaTa_2]$: C, 58.31; H, 6.89. $^1\text{H NMR}$ (THF- d_8): δ 1.06 (s, 18H, ^tBu), 1.10 (s, 18H, ^tBu), 1.22 (s, 18H, ^tBu), 2.29 (s, 6H, Me), 2.32 (s, 6H, Me), 3.38 (s, 12H, DME), 3.52 (d, $J = 13.6$ Hz, 2H; CH_2), 3.55 (s, 8H, DME), 4.11 (s, 2H, CH), 4.71 (d, $J = 13.6$ Hz, 2H, CH_2), 6.44 (s, 2H, Ar), 6.73 (s, 2H, Ar), 6.75 (s,

2H, Ar), 6.85 (s, 2H, Ar), 6.87 (s, 2H, Ar), 7.07 (s, 2H, Ar), 10.9 (s, 3H, Ta-H).

4.2.8. $[\{(bit-^tBu-L)Ta\}_2(\mu-H)_3K(DME)_2]$ (**5c**)

A 100 mL flask was charged with **2** (0.41 g, 0.24 mmol), KHBET_3 (1 M in THF; 1.2 ml, 1.2 mmol), and toluene (60 ml) at -78°C . Upon stirring the mixture at room temperature for 12 h, a dark yellow solution was obtained. After centrifugation to remove an insoluble solid, the supernatant was evaporated to dryness. The residue was extracted with DME. Addition of hexane resulted in the precipitation of **5c** as yellow crystals (0.21 g, 54%).

Elemental analysis. Found: C, 57.46; H, 6.62%. Calc. for $[C_{76}H_{107}O_{10}KTa_2]$: C, 57.71; H, 6.82. $^1\text{H NMR}$ (THF- d_8): δ 1.06 (s, 18H; ^tBu), 1.11 (s, 18H, ^tBu), 1.20 (s, 18H, ^tBu), 2.28 (s, 6H; Me), 2.32 (s, 6H; Me), 3.40 (s, 12H, DME), 3.50 (d, $J = 13.5$ Hz, 2H, CH_2), 3.56 (s, 8H, DME), 4.09 (s, 2H; CH), 4.73 (d, $J = 13.5$ Hz, 2H, CH_2), 6.46 (s, 2H, Ar), 6.74 (s, 2H, Ar), 6.76 (s, 2H, Ar), 6.86 (s, 2H, Ar), 6.87 (s, 2H, Ar), 7.07 (s, 2H, Ar), 10.8 (s, 3H, Ta-H).

4.2.9. $[\{(bit-^tBu-L)Ta\}_2(\mu-H)_3Li(DME)_2]$ (**6**)

After **5a** (0.21 g, 0.13 mmol) was dissolved in DME (20 ml), the solution was concentrated to 3 ml and layered with hexane to afford yellow crystals of **6** ($\text{DME}_{0.5}$) (0.17 g, 82%).

Elemental analysis. Found: C, 58.19; H, 7.15%. Calc. for $[C_{78}H_{112}O_{11}LiTa_2]$: C, 58.75; H, 7.08. The $^1\text{H NMR}$ spectrum of **6** in THF- d_8 exhibited a pattern identical to that of **5a** along with resonances ascribed to DME.

4.2.10. Reaction of **2** with LiBHET_3 in THF

To a slurry of **2** (1.81 g, 1.07 mmol) in THF (40 ml) at -78°C was added 6 equiv of LiBHET_3 (1.0 M solution in THF; 6.4 ml). The mixture was allowed to warm up to room temperature, and the yellow color discharged to give a colorless homogeneous solution. After stirring for 4 h, the volatile components were removed in vacuo. The gray residue was extracted with toluene and centrifuged to remove an insoluble material. The toluene supernatant was concentrated and cooled to -30°C , yielding colorless blocks of $[(^t\text{Bu-L})\text{Ta}(\text{O}Bu^i)_2]_2$ (**7**) along with a trace amount of pale blue needles of $[\text{Li}(\text{THF})_4][\{(^t\text{Bu-L})\text{TaCl}\}_2(\mu-\text{O}Bu^i)]$ (**8**).

4.2.11. $[(^t\text{Bu-L})\text{Ta}(\text{O}Bu^i)_2]_2$ (**7**)

A mixture of 1-butanol (0.27 mL, 2.95 mmol) and NaH (70 mg, 2.9 mmol) in THF (30 ml) was stirred for 1 h and then the solvent was removed in vacuo. A suspension of **2** (1.25 g, 0.74 mmol) in toluene (60 ml) was added to the residue. The mixture was stirred at 80°C for 3 h, during which time the yellow color discharged to give a colorless solution and NaCl precipitated. The solution was centrifuged to remove an insoluble

Table 1
Experimental data for the X-ray diffraction of **2**, **3**, **4**, **5a**, **6**, **7**, and **9**

| | 2 | 3 | 4 | 5a | 6 | 7 | 9 |
|---|---|--|---|---|--|--|---|
| Formula | C ₈₂ H ₁₀₂ O ₆ Cl ₄ Ta ₂ | C ₇₈ H ₉₄ O ₈ Cl ₂ Ta ₂ | C ₈₀ H ₁₁₆ O ₁₂ Cl ₃ KTa ₂ | C ₈₃ H ₁₁₁ O ₈ LiTa ₂ | C ₈₀ H ₁₁₇ O ₁₂ LiTa ₂ | C ₈₄ H ₁₂₂ O ₁₀ Ta ₂ | C ₉₀ H ₁₄₀ O ₁₈ Cl ₄ K ₂ Ta ₂ |
| <i>M</i> | 1687.41 | 1592.40 | 1777.14 | 1605.62 | 1639.63 | 1653.78 | 2091.99 |
| Space group | <i>P</i> 1(bar) (no. 2) | <i>P</i> 2 ₁ / <i>c</i> (no. 14) | <i>C</i> 2/ <i>c</i> (no. 15) | <i>P</i> 1(bar) (no. 2) | <i>P</i> 2 ₁ / <i>n</i> (no. 14) | <i>P</i> 2 ₁ / <i>n</i> (no. 14) | <i>P</i> 1(bar) (no. 2) |
| <i>a</i> (Å) | 13.529(5) | 11.336(3) | 29.924(10) | 12.481(3) | 17.687(3) | 13.309(5) | 12.103(5) |
| <i>b</i> (Å) | 14.237(4) | 18.802(5) | 16.009(5) | 12.884(3) | 18.452(3) | 18.628(7) | 12.866(5) |
| <i>c</i> (Å) | 21.365(8) | 16.537(5) | 17.555(6) | 24.519(6) | 24.435(4) | 17.471(7) | 16.699(6) |
| α (°) | 73.911(9) | | | 81.175(5) | | | 79.544(13) |
| β (°) | 90.036(10) | 97.061(3) | 106.025(4) | 82.109(6) | 93.231(3) | 113.600(4) | 78.68(2) |
| γ (°) | 72.469(9) | | | 86.360(5) | | | 82.13(2) |
| <i>V</i> (Å ³) | 3754.4(22) | 3497.8(17) | 8083.1(46) | 3855(1) | 7961.7(25) | 3969.0(27) | 2493.6(17) |
| <i>Z</i> | 2 | 2 | 4 | 2 | 4 | 2 | 1 |
| <i>D</i> _c (g cm ⁻³) | 1.493 | 1.512 | 1.460 | 1.383 | 1.368 | 1.384 | 1.393 |
| μ (Mo K α) (cm ⁻¹) | 31.02 | 32.53 | 29.09 | 28.84 | 27.99 | 28.06 | 24.40 |
| Collected reflections | 29,255 | 27,109 | 65,070 | 30,172 | 60,921 | 31,926 | 38,508 |
| Unique reflections | 16,408 | 7985 | 9578 | 16,787 | 17,884 | 8854 | 10,637 |
| Parameters | 968 | 471 | 501 | 917 | 982 | 460 | 593 |
| <i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] | 0.045 | 0.025 | 0.077 | 0.032 | 0.031 | 0.043 | 0.071 |
| <i>wR</i> ₂ (all) | 0.088 | 0.058 | 0.209 | 0.075 | 0.072 | 0.116 | 0.201 |
| Goodness-of-fit | 1.066 | 1.053 | 1.000 | 1.058 | 1.055 | 1.025 | 1.002 |
| Largest residual peak and hole (e Å ⁻³) | 3.98 and -3.63 | 1.30 and -1.10 | 7.05 and -3.63 | 1.78 and -0.97 | 1.93 and -1.31 | 3.02 and -3.74 | 4.54 and -2.45 |

material. Concentration of the supernatant and cooling to $-30\text{ }^{\circ}\text{C}$ provided **7** as colorless crystals (0.94 g, 77% yield).

Data for **7**: Elemental analysis. Found: C, 59.52; H, 7.20%. Calc. for $[\text{C}_{84}\text{H}_{122}\text{O}_{10}\text{Ta}_2]$: C, 61.01; H, 7.44. ^1H NMR (CDCl_3): δ -0.35 (t, $J = 7.8$ Hz, 6H, $\text{O}(\text{CH}_2)_3\text{CH}_3$), -0.11 (m, 4H, CH_2), 0.04 (t, $J = 7.3$ Hz, 6H, $\text{O}(\text{CH}_2)\text{CH}_3$), 0.61 (m, 4H, CH_2), 0.75 (m, 4H, CH_2), 1.14 (s + m, 22H, overlapping CH_2 and ^tBu), 1.25 (s, 36H, ^tBu), 2.13 (s, 12H, Me), 2.43 (t, $J = 6.8$ Hz, 4H, OCH_2), 3.15 (d, $J = 12.9$ Hz, 4H, CH_2), 3.75 (m, 4H, OCH_2), 5.46 (d, $J = 12.9$ Hz, 4H, CH_2), 6.76 (s, 4H, Ar), 6.91 (s, 4H, Ar), 7.22 (s, 4H, Ar).

4.2.12. $[\{(^t\text{Bu}-L)\text{TaCl}_2\text{K}(\text{DME})_2\}_2(\text{OCH}_2\text{CH}_2\text{O})]$ (**9**)

A slurry of **2** (0.39 g, 0.23 mmol) in DME (30 ml) was added to a vessel containing potassium hydride (58 mg, 1.5 mmol) at $-78\text{ }^{\circ}\text{C}$. The mixture was allowed to warm up to room temperature and was stirred vigorously for 2 days. After centrifugation, the greenish brown solution was concentrated to 5 ml and layered with hexane to give **9**·(DME) as light blue crystals (0.26 g, 54%).

Elemental analysis. Found: C, 51.48; H, 6.74%. Calc. for $[\text{C}_{90}\text{H}_{140}\text{O}_{18}\text{Cl}_4\text{K}_2\text{Ta}_2]$: C, 51.67; H, 6.75. ^1H NMR ($\text{THF}-d_8$): δ 1.16 (s, 18H, ^tBu), 1.35 (s, 36H, ^tBu), 2.33 (s, 12H, Me), 3.22 (s, 30H, DME), 3.32 (d, $J = 13.5$ Hz, 4H, CH_2), 3.42 (s, 20H, DME), 3.46 (s, 4H, $\text{OCH}_2\text{CH}_2\text{O}$), 5.05 (d, $J = 13.5$ Hz, 4H, CH_2), 6.78 (s, 4H, Ar), 7.03 (s, 4H, Ar), 7.18 (s, 4H, Ar).

4.3. Crystallography

Crystallographic data are summarized in Table 1. X-ray quality single crystals were obtained from toluene/hexane [for **2** (yellow crystals), **3** (brown crystals), **5a** (yellow crystals), and **7** (colorless crystals)] and DME/hexane [**4** (blue crystals), **5b** (yellow crystals), **5c** (yellow crystals), **6** (yellow crystals), and **9** (light blue crystals)]. Crystals were covered in oil, and suitable single crystals were selected under a microscope and mounted on a Rigaku Mercury CCD (for **2**, **3**, **4b**, **5a**, **5c**, and **7**) or Saturn CCD (**5b**, **6**, and **9**) diffractometer equipped with a Rigaku GNNP low-temperature device. Data were collected at $-100\text{ }^{\circ}\text{C}$ under a cold nitrogen stream using graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71070\text{ \AA}$). The intensity images were obtained with ω scans of 0.5° interval per frame. The frame data were processed using the CrystalClear (Rigaku) program, and the reflection data were corrected for absorption with a REQAB program. All structures except for **3** were solved by Patterson methods, and the structure of **3** was solved by direct methods. These structures were refined on F^2 by the full-matrix least-squares method using CrystalStructure (Rigaku) software package. The metal hydride atoms for **5a**, **5b**, **5c** and **6** were located

and refined isotropically. Anisotropic refinement was applied to all non-hydrogen atoms except for disordered atoms, and hydrogen atoms were put at calculated positions with C–H distances of 0.97 \AA .

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 261910–261916 for compounds **2**, **3**, **4b**, **5b**, **6**, **7**, and **9**, and CCDC nos. 225528 and 225530 for **5a** and **5c**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CN2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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