

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

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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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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.

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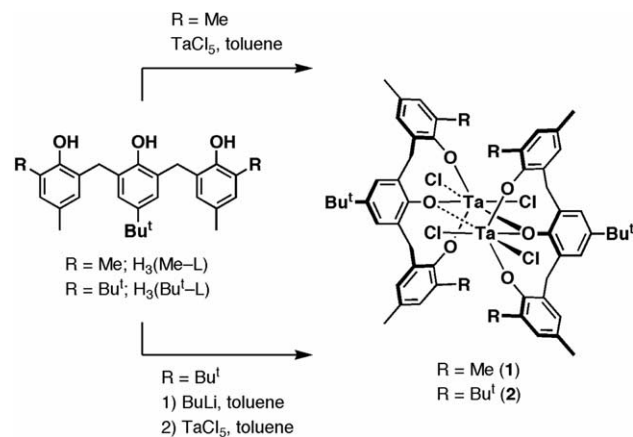
We previously reported that the [t Bu-L] ligand allowed for isolation of hydride-bridged dinuclear complexes of titanium(III) and zirconium(IV) [3], and these complexes are rare examples of non-metallocene group 4 metal hydrides [10]. Attempts to prepare the niobium analogue by the reaction of [t Bu-L]NbCl₂ 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), t Bu (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, t Bu) 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[t Bu-L], the analogous reaction led to ligand degradation associated with loss of one of *tert*-butyl groups of [t Bu-L]³⁻. The de-*tert*-butylation of the [t Bu-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[t Bu-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 [t Bu-L] ligand was previously achieved from the reaction of NbCl₅ and the solvent-free trilithium salt Li₃[t Bu-L]. The similar route has been employed in the present work starting from TaCl₅ and Li₃[t Bu-L] in refluxing toluene.



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

The desired complex [(t Bu-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.

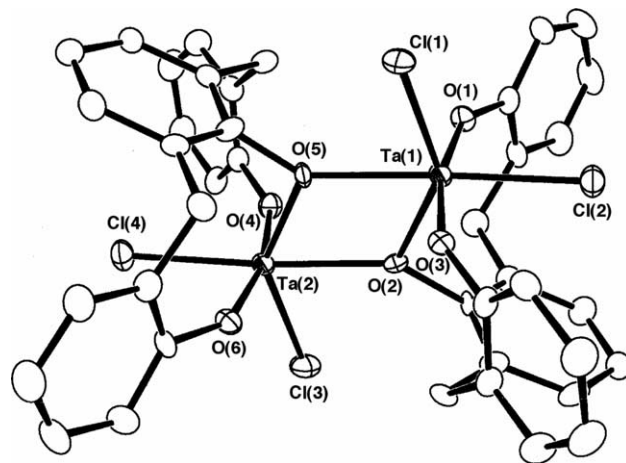


Fig. 1. Structure of [(t Bu-L)TaCl₂]₂ (**2**). Methyl and *tert*-butyl groups have been omitted for clarity. Selected bond distances (Å) and angles (°): Ta(1)–O(1) 1.905(4), Ta(1)–O(2) 2.066(3), Ta(1)–O(3) 1.905(4), Ta(1)–O(5) 2.197(4), Ta(2)–O(2) 2.190(4), Ta(2)–O(4) 1.904(4), Ta(2)–O(5) 2.062(4), Ta(2)–O(6) 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).

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