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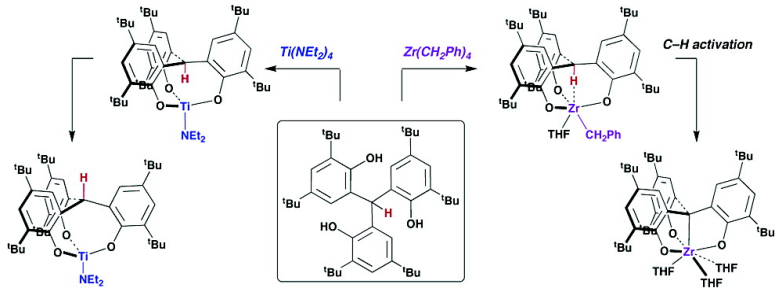

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Titanium and Zirconium Complexes of Preorganized Tripodal Triaryloxide Ligands

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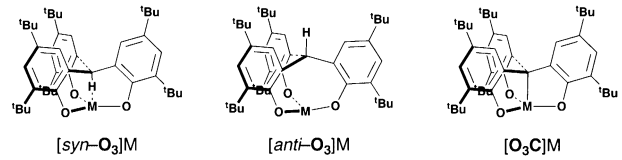
Multidentate ligands play an important role in coordination chemistry and catalyst design. An attractive multidentate ligand is a trianionic tetradentate ligand of the tripodal [X_3E] type (X = N, O, S; E = N, P), which had led to atrane molecules with unique structures and patterns of reactivity.[1] The degree of interaction between the metal center and the neutral E atom can exert a profound influence on the reactivity of the resulting complexes. In this context, a tri(2-oxyphenyl)methane-derived system appears practically attractive ($[O_3]^{3-}$ = tri(2-oxy-3,5-di-*tert*-butylphenyl)-methane). This ligand can coordinate to a metal in two forms, which differ mainly as a result of the relative stereochemistry at the methine carbon (*syn* and *anti* forms, Scheme 1). Furthermore, intramolecular metalation of the somewhat acidic methine linkage in the [O_3] complexes is expected to occur quite readily, resulting in formation of 5-carbametalatranes[2] ([O_3C] complexes). However, metal complexes with [O_3]-derived ligands are rare, and their coordination chemistry is largely unexplored.[3]

Following our interest in the chemistry of linearly linked triaryloxide tridentate ligands,[4] we set out to investigate the use of $[O_3]^{3-}$ as an auxiliary ligand. Here we report the synthesis of Ti and Zr complexes supported by the [O_3] ligand and the rearrangement of *syn*- to *anti*-complexes. In addition, formation of the [O_3C] complex via C−H activation of the [*syn*-O_3] ligand is described.

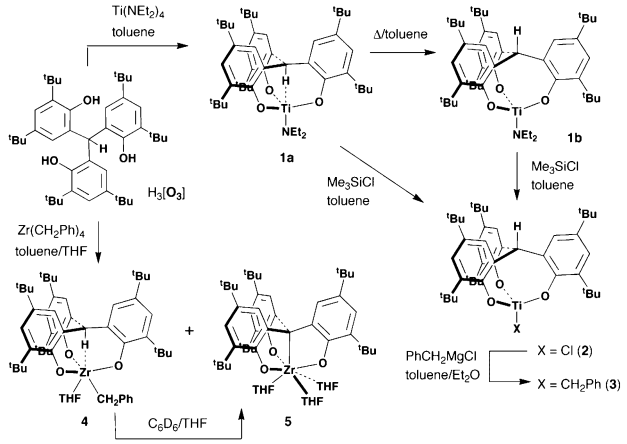
Amine elimination of $Ti(NEt_2)_4$ with $H_3[O_3]$ in toluene proceeded smoothly at room temperature to afford orange [*syn*-O_3]$Ti(NEt_2)$ (**1a**) in 76% isolated yield (Scheme 2). NMR data are useful indicators of complex formation. The ^{1}H and ^{13}C NMR spectra of **1a** indicate a molecule with 3-fold symmetry. An important feature of the ^{1}H NMR spectrum is the high-field shift of the proton attached to the methine carbon giving rise to a singlet at δ 4.96 (free $H_3[O_3]$, δ 5.94 in C_6D_6). In the ^{13}C NMR spectrum, the methine atom exhibits a signal at δ 45.88, which is comparable to that of $H_3[O_3]$ (δ 43.04). However, the small value of the $^1J_{CH}$ coupling constant of 91.1 Hz (126.8 Hz for $H_3[O_3]$) suggests some of agostic interaction between the metal and this proton (vide infra).

A single-crystal X-ray diffraction analysis of **1a** shows that the [O_3] ligand adopts a *syn*-conformation with approximate C_{3v} symmetry to give a distorted trigonal-bipyramid complex (Figure 1a).[5] The three aryloxide functions occupy the equatorial sites (av Ti−O = 1.852 Å; O−Ti−O = 108°), while the methine H(1) proton as well as the amide N atom [Ti−N = 1.864(2) Å] form the axial set [N−Ti−H(1) = 172.5(9) Å]. The Ti−H(1) distance of 1.66(2) Å [Ti−H(1)−C(1) = 168(2)°; C(1)−H(1) = 1.19(2) Å] is significantly shorter than those observed for common agostic Ti···H−C interactions[6] and is comparable to those of titanium hydride complexes.[7] Thus, the H(1) atom strongly interacts with the metal, which is evident from the ^{1}H NMR spectrum. We also note the short O···H(1) distances ranging from 1.86 to 2.05 Å. This structural feature may be ascribed to the conformationally constrained cage provided by the [*syn*-O_3] ligand. The potential strain of such an arrangement is alleviated by a flattening of the methine

Scheme 1



Scheme 2



C(1) atom, as evidenced by the sum of the C−C(1)−C angles of 352.7° (342.1° for $H_3[O_3]$). The structural motif of **1a** is similar to that found in $[(syn\text{-}O_3)TaCl_3]^-$.[3d]

Although **1a** is stable in the solid-state, heating the *syn*-complex in toluene resulted in the clean conversion to the *anti*-complex **1b** according to NMR spectroscopy. This suggests that **1a** is thermodynamically unstable with respect to **1b**, and the *syn*-isomer is a kinetically stabilized intermediate in the $Ti(NEt_2)_4/H_3[O_3]$ reaction. The transformation of **1a** to **1b** in C_7D_8 was determined to be first order in titanium according to ^{1}H NMR spectroscopy. Temperature dependence studies from 64 to 100 °C for this transformation allowed for extraction of the activation parameters $\Delta S^{\ddagger} = -35(1)$ cal/(mol K), $\Delta H^{\ddagger} = 16.3(4)$ kcal/mol from the Arrhenius plot. The negative entropy, indicative of ordering in the transition state, might be due to ring strain and/or solvation effects.[8]

The chloride derivative [*anti*-O_3]TiCl (**2**) was readily synthesized by reactions of **1a** and **1b** with Me_3SiCl in C_6D_6 according to NMR spectroscopy. Since the [O_3] ligand underwent facile rearrangement during the **1a**/Me_3SiCl reaction, attempts to prepare the *syn*-isomer of **2** have met with failure. Alkylation of **2** with $PhCH_2MgCl$ proceeded with retention of the *anti*-conformation to afford [*anti*-O_3]$Ti(CH_2Ph)$ (**3**) in 74% yield.

The NMR spectra are consistent with **1b**, **2**, and **3** having three-fold symmetry. The ^{1}H and ^{13}C NMR signals attributed to the methine linkage of the ligand appear to be sensitive criteria for distinguishing between the *syn*- and *anti*-forms. The methine proton resonances in the *anti*-complexes (**1b**, δ 6.04; **2**, δ 5.94; **3**, δ 5.89)

10.1021/ja053740m CCC: $30.25

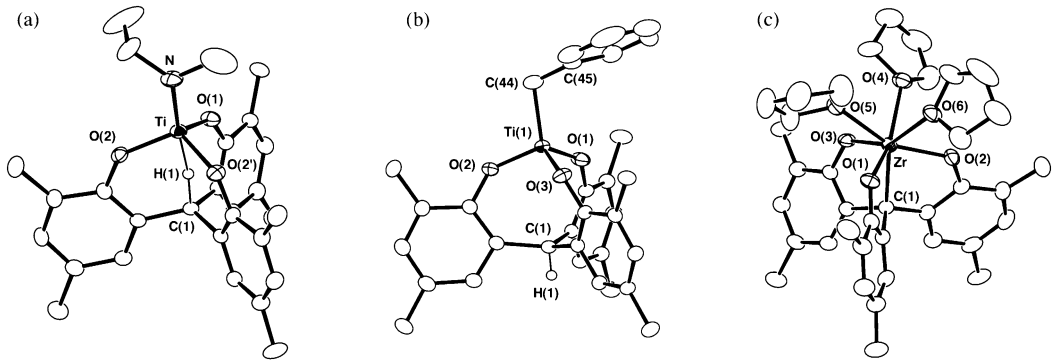


Figure 1. Molecular structures of (a) **1a**, (b) **3**, and (c) **5**. Methyl groups of the *tert*-butyl substituents have been omitted for clarity. Complex **1a** has crystallographic C_s symmetry about a plane including the O(1) aryloxide ring. The asymmetric unit of **3** contains two crystallographically independent molecules, and a view of one of them is given here.

are shifted to lower fields than that of the *syn*-complex **1a**. In the ^{13}C NMR spectra, the methine carbon exhibits a signal at δ 64.14 for **1b**, δ 62.89 for **2**, and δ 64.0 for **3**, which represents a large downfield shift. Noteworthy, the $^1J_{CH}$ coupling constants (**1b**, 122.3 Hz; **2**, 122.6 Hz; **3**, 121.1 Hz) are larger than that observed in **1a** and is similar to that of $H_3[O_3]$.

To establish the *anti*-structure, an X-ray diffraction study was carried out on a single crystal of **3** (Figure 1b).[5] The complex exhibits approximate tetrahedral geometry about the Ti center (av Ti−O = 1.852 Å; O−Ti−O = 104.9°). In contrast to the *syn*-complex **1a** with C_{3v} symmetry, the [*anti*-O_3] ligand in **3** displays a propeller-like conformation [av O−Ti−C(1)−C torsion angles: 1.3° for **1a** and 16.4 for **3**], thereby relieving the strain in the eight-membered [TiO_2C_5] chelate ring. The [*anti*-O_3] ligand has a flattened methine carbon (ΣC−C(1)−C = 353°) similar to that found in **1a**. The benzyl ligand adopts an η^1-coordination.

When $Zr(CH_2Ph)_4$ was used instead of $Ti(NEt_2)_4$, the reaction with $H_3[O_3]$ in toluene/THF gave a mixture of [*syn*-O_3]Zr(CH_2-Ph)(THF) (**4**) and [O_3C]Zr(THF)$_3$ (**5**). In contrast to the stability of the *anti* complex **3**, the *syn* complex **4** underwent facile C−H activation of the ligand to generate **5** concomitant with elimination of toluene according to NMR spectra of the mixture. Intramolecular metalation in **4** appears to be facilitated by the preorganization of the ligand and the close proximity of the methine proton to the metal center having the benzyl group in the *syn*-conformation. While isolation in pure form was hampered by its instability, the identity of **4** is strongly supported by NMR data. The [O_3] ligand in **4** adopts a *syn*-conformation, as shown by the upfield ^1H NMR shift of the methine proton (δ 5.79) and the small $^1J_{CH}$ value of 96.8 Hz for the methine carbon (δ 40.5).

The formulation of **5** was inferred by a combination of ^1H and ^{13}C NMR spectra in addition to single-crystal X-ray diffraction data (Figure 1c). Most impressively, intramolecular C−H activation took place at the methine carbon of the ligand to form a 5-carbametalatrane structure. The Zr center is best described as capped octahedral, with the C(1) atom capping the aryloxide O_3 face [Zr−C(1) = 2.309(3) Å; average Zr−O_{Ar} = 2.043 Å, O_{Ar}−Zr−O_{Ar} = 113.5°]. Compound **5** is a rare example of an η^1-trityl complex.[9] Compared to that in **1a** and **3**, the C(1) atom assumes a normal sp^3 carbon geometry [av C−C(1)−C angle = 111.4°]. To accommodate adjacent tetrahedral [C(1)] and capped octahedral [Zr] geometries, the phenyl rings in **5** adopt the propeller geometry with av O−Zr−C(1)−C of 15.9°. The NMR spectra of **5** are consistent with the solid structure, and the signal of the C(1) atom appears as a singlet at δ 83.8 in the ^{13}C NMR spectrum.

In conclusion, the use of the [O_3] ligand turns out to be a convenient entry into intriguing metalatranes, which include an agostic M···H−C interaction and a M−C bond as a transannular interaction. While the Ti *syn*-complex **1a** underwent facile transformation to the *anti*-complexes **1b** and **2**, the Zr complex with the *syn*-structure **4** was easily converted into the 5-carbametalatrane **5** via intramolecular C−H activation. Reactivity studies with these group 4 metal complexes are ongoing.

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Supporting Information Available: Experimental procedures and CIF files for **1a**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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