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FULL PAPER

Synthesis and structures of Ti(III) and Ti(IV) complexes supported by a tridentate aryloxide ligand

Tsukasa Matsuo,[a] Hiroyuki Kawaguchi *[a] and Masahiro Sakai[b]

[a] *Coordination Chemistry Laboratories, Institute for Molecular Science and CREST, Japan Science and Technology Corporation (JST), Myodaiji, Okazaki, 444-8585, Japan. E-mail: hkawa@ims.ac.jp*

[b] *Research Center for Molecular Materials, Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan*

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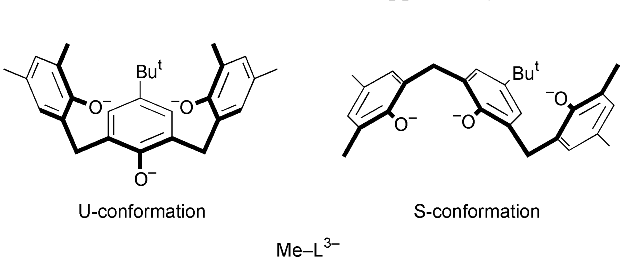
Titanium complexes of the tridentate aryloxide Me–L^{3-} [H$_3$(Me–L) = 2,6-bis(4,6-dimethylsalicyl)-4-*tert*-butylphenol] have been prepared. Reaction of TiCl$_4$ with 1 equivalent of H$_3$(Me–L) gave [Ti(Me–L)Cl]$_2$ **1**. Recrystallization of **1** from THF resulted in formation of the THF adduct Ti(Me–L)Cl(THF)$_2$ **2**. Treatment of **1** with [NEt$_4$]Cl in THF quantitatively gave [NEt$_4$][Ti$_2$(Me–L)$_2$Cl$_3$] **3**. Complex **1** was reduced with 2 equivalents of potassium to produce the Ti(III) complex [Ti(Me–L)(DME)]$_2$ **4**. Structures of **1**, **2**, **3** and **4** have been determined by X–ray analyses. For **1**, **2** and **4**, the Me–L ligand assumes a U-conformation. In the case of **3**, it is coordinated in an S-conformation.

Introduction

Development of ligands that play supporting roles in coordination chemistry has been the subject of intense interest for many years. In this connection, linked aryloxide ligands have been very attractive from the viewpoint of determination of the complex geometry and limited ligand disproportionation. For example, well characterized transition metal derivatives that utilized the [4]calixarene ligand were first reported in 1985 by Power,[1] and since then numerous research groups have been involved in the study of this class of compounds.[2] In this context, we are interested in acyclic aryloxide oligomers that are connected to each other at *ortho* positions through methylene linkers,[3,4] and our initial focus is on 2,6-bis(4,6-dimethylsalicyl)-4-*tert*-butylphenol [H$_3$(Me–L)].[5] One of the advantages of this system is the possible flexible coordination modes, and the Me–L^{3-} ligand can adopt either a U- or an S-conformation (Scheme 1). In addition, there is the opportunity for coordinative unsaturation as compared to the [4]calixarene system. However, transition metal complexes with linked aryloxide trimers are rare.[6]

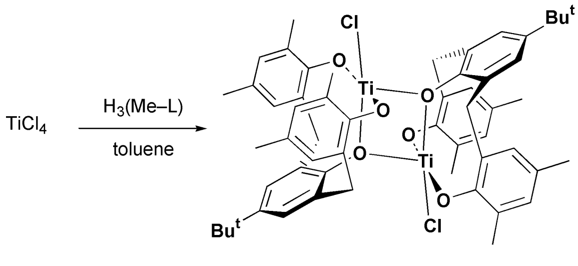


Scheme 1

Herein we present the coordination chemistry of the ligand Me–L^{3-} with tetravalent and trivalent titanium ions. Our study demonstrates that the coordination geometries of Me–L^{3-} are determined by a delicate balance of steric and/or electronic factors of the incoming ligands.

Results and discussion

Reaction of TiCl$_4$ with 1 equiv. of H$_3$(Me–L) in refluxing toluene followed by standard workup afforded [Ti(Me–L)Cl]$_2$ **1** as dark red crystals in 85% yield [eqn. (1)]. The ^{1}H NMR spectrum in CDCl$_3$ corresponds to a symmetrical conformation, and the methylene groups appear as one pair of doublets (δ 3.46 and 4.67) along with the singlets of one Bu^t (δ 1.17) and two Me groups (δ 2.24 and 2.38). The crystal structure of **1** was elucidated by X-ray analysis.



(1)

1, 85% yield

According to X-ray analysis, an asymmetric unit consists of two crystallographically independent dimers. In addition, the lattice contains three toluene molecules per two molecules of the dimer. Because the two molecules (called molecule A and B) are structurally very similar, only molecule A is presented in Fig. 1. Selected bond distances and angles are listed in Table 1. Complex **1** is dimeric with two inversion-related Ti(Me–L)Cl units bridged by the central aryloxides of the Me–L ligands. Each titanium center has a distorted trigonal bipyramidal geometry. The equatorial plane is bound by two outer aryloxides of the ligand [O(1), O(3)] and one central aryloxide of another ligand [O(2A)], while one chlorine atom and one central phenoxide [O(2)] are on the axis with a Cl(1)–Ti(1)–O(2) angle of 159.9(1)°. The Ti atom is situated 0.20 Å above the plane defined by the equatorial donors, and is oriented toward the axial chloride ligand. The Me–L ligands in **1** assume a

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Table 1 Selected bond lengths (Å) and angles (°) for compound **1**[a]

Molecule A			
Ti(1)–O(1)	1.754(3)	Ti(1)–O(2)	2.046(2)
Ti(1)–O(3)	1.751(3)	Ti(1)–O(2A)	1.985(2)
Ti(1)–Cl(1)	2.278(1)	Ti(1)–Ti(1A)	3.294(1)
O(1)–Ti(1)–O(3)	114.3(2)	O(2)–Ti(1)–Cl(1)	159.9(1)
O(2)–Ti(1)–O(2A)	70.4(1)	Ti(1)–O(2)–Ti(1A)	109.6(1)
Ti(1)–O(1)–C(1)	165.5(3)	Ti(1)–O(2)–C(8)	120.2(2)
Ti(1)–O(3)–C(15)	164.7(3)	Ti(1A)–O(2)–C(8)	130.1(2)
Molecule B			
Ti(2)–O(4)	1.762(3)	Ti(2)–O(5)	2.053(2)
Ti(2)–O(6)	1.750(3)	Ti(2)–O(5A)	1.975(2)
Ti(2)–Cl(1)	2.275(1)	Ti(2)–Ti(2A)	3.300(1)
O(4)–Ti(2)–O(6)	113.9(1)	O(5)–Ti(2)–Cl(2)	159.19(8)
O(5)–Ti(2)–O(5A)	70.00(11)	Ti(2)–O(5)–Ti(2A)	110.00(11)
Ti(2)–O(4)–C(29)	162.5(3)	Ti(2)–O(5)–C(36)	117.9(2)
Ti(2)–O(6)–C(43)	173.6(3)	Ti(2A)–O(5)–C(36)	132.1(2)

[a] Atoms carrying the suffix A are related to their counterpart by the symmetry operator [$1 - x, 1 - y, -z$] and [$-x, 2 - y, 1 - z$] in molecule A and B, respectively.

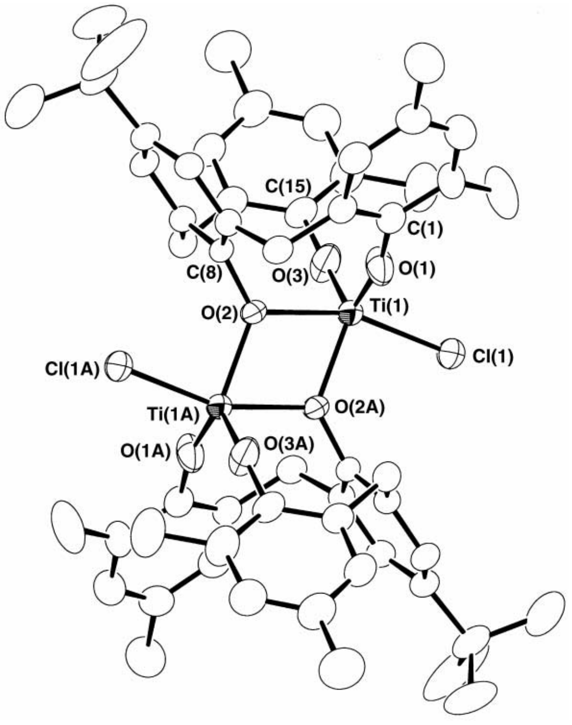


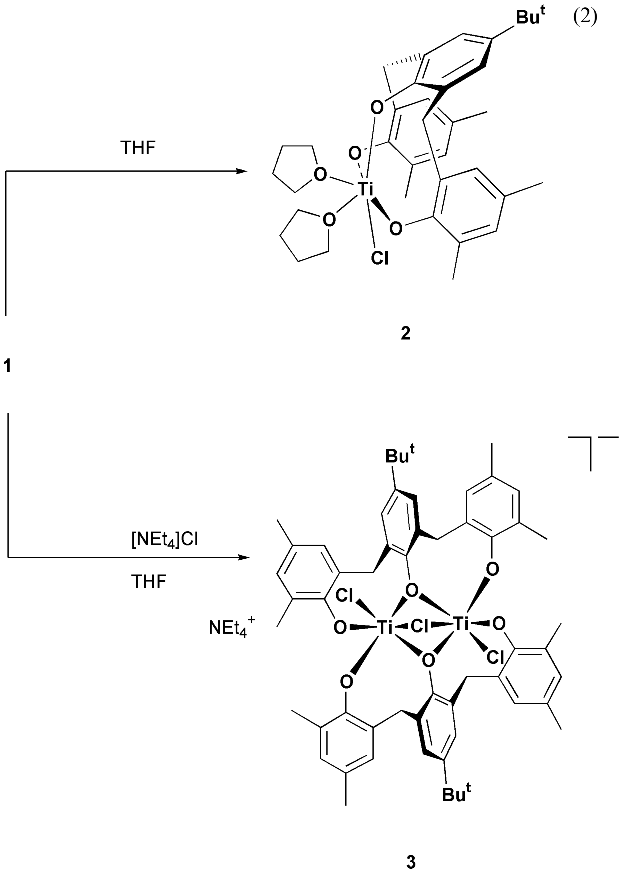
Fig. 1 Structure of molecule A in complex **1**.

U-conformation, which is reminiscent of the cone conformation of calix[4]arene. The Ti(1)–O(2)–Ti(1A) bridge is asymmetric, and the bridging Ti(1)–O(2) and Ti(1)–O(2A) distances are 2.046(2) and 1.985(2) Å, respectively. The terminal and bridging Ti–O distances average 1.753 Å and 2.016 Å, respectively, and they are comparable to those found in the known titanium(IV) aryloxides.[4,7] The Ti–Ti separation of 3.294(1) Å is rather long.

Complex **1** readily adds external ligands due to the Lewis acidity of the titanium center. For example, dissolution of **1** in THF resulted in dissociation of the dimer **1** and formation of Ti(Me–L)Cl(THF)$_2$ **2** [eqn. (2)]. The ^{1}H NMR spectrum of **2** shows a pattern similar to that of **1**. Although crystals of the THF adduct **2** are solvated by THF, one set of resonances for the THF protons is observed. This indicates a rapid exchange between free THF and THF coordinated to the Ti center in **2** on the NMR time scale.

Table 2 Selected bond lengths (Å) and angles (°) for compound **2**

Ti–O(1)	1.796(2)	Ti–O(2)	1.889(2)
Ti–O(3)	1.796(2)	Ti–O(4)	2.200(2)
Ti–O(5)	2.217(2)	Ti–Cl(1)	2.394(1)
O(1)–Ti–O(3)	100.2(1)	O(1)–Ti–O(4)	171.1(1)
O(3)–Ti–O(5)	171.8(1)	O(2)–Ti–Cl(1)	163.6(1)
Ti–O(1)–C(1)	164.0(2)	Ti–O(2)–C(8)	119.7(2)
Ti–O(3)–C(15)	166.2(2)		



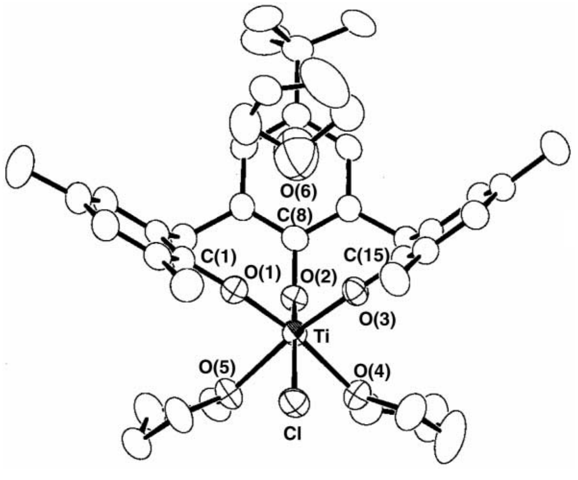


Fig. 2 Structure of **2**·THF.

The structure was determined by X-ray diffraction analysis (Fig. 2), and selected bond distances and angles are listed in Table 2. Complex **2** crystallizes with three THF molecules, from which one is incorporated in the Me–L ligand cavity. Complex **2** consists of discrete monomeric units where one Me–L ligand facially coordinates to titanium in the U-conformation. Octahedral coordination is completed by one chlorine atom and two mutually *cis* THF molecules. The central aryloxide ring of the Me–L ligand is arranged in a *trans*-position to the chlorine atom. The Ti–O(2) distance of the central aryloxide is 1.889(2) Å, while the Ti–O distances of the outer aryloxides [O(1) and

Table 3 Selected bond lengths (Å) and angles (°) for compound **3**

Ti(1)–O(1)	1.798(3)	Ti(1)–O(2)	2.064(3)
Ti(1)–O(4)	1.791(3)	Ti(1)–O(5)	2.028(3)
Ti(1)–Cl(1)	2.332(1)	Ti(1)–Cl(2)	2.635(1)
Ti(2)–O(2)	2.011(3)	Ti(2)–O(3)	1.802(3)
Ti(2)–O(5)	2.065(3)	Ti(2)–O(6)	1.785(3)
Ti(2)–Cl(2)	2.678(1)	Ti(2)–Cl(3)	2.318(1)
Ti(1)–Ti(2)	3.104(1)		
O(1)–Ti(1)–Cl(2)	165.3(1)	O(2)–Ti(1)–O(4)	162.3(1)
O(5)–Ti(1)–Cl(1)	160.8(1)	Cl(1)–Ti(1)–Cl(2)	88.6(1)
O(2)–Ti(2)–Cl(3)	159.5(1)	O(3)–Ti(2)–O(5)	161.7(1)
O(6)–Ti(2)–Cl(2)	165.6(1)	Cl(2)–Ti(2)–Cl(3)	89.6(1)
Ti(1)–Cl(2)–Ti(2)	71.51(3)	Ti(1)–O(2)–Ti(2)	99.3(1)
Ti(1)–O(5)–Ti(2)	98.6(1)	Ti(1)–O(1)–C(1)	147.3(3)
Ti(1)–O(2)–C(8)	139.0(2)	Ti(1)–O(4)–C(29)	167.3(3)
Ti(1)–O(5)–C(36)	132.8(2)	Ti(2)–O(2)–C(8)	121.8(2)
Ti(2)–O(3)–C(15)	154.3(3)	Ti(2)–O(5)–C(36)	128.3(2)
Ti(2)–O(6)–C(43)	162.6(3)		

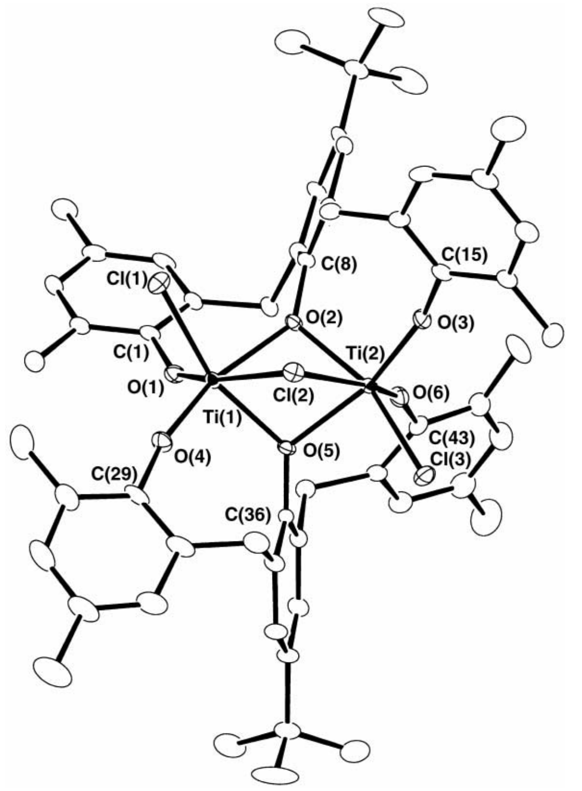


Fig. 3 Structure of the anion in **3**.

O(2)] are 1.796(2) Å. They are similar to terminal aryloxide ligands of known Ti(IV) complexes[4,7–9] but clearly distinct from each other. The shorter Ti–O bonds involving the outer aryloxides [O(1), O(3)] are coupled with the wider Ti–O–C bond angles at O(1) [164.0(2)°] and O(3) [166.2(2)°], indicative of a greater Ti–O π bonding interaction as compared to the central aryloxide [O(2), 119.7(2)°]. The O(1)–Ti–O(3) angle of 100.2(1)° is smaller than that in the parent dimer **1** (av. 114°). It is quite obvious that the Me–L ligand has to undergo significant distortion in order to accommodate two THF ligands, showing the flexibility of this ligand.

On the other hand, **1** was found to react cleanly with $[NEt_4]Cl$ in THF generating $[NEt_4][Ti_2(Me–L)_2Cl_3]$ **3**. The X-ray structure of **3** shows a dimer with two distorted octahedral metal centers connected through facial bridging (Fig. 3). The two Me–L ligands span both metals in an S-conformation. The central aryloxides of the two Me–L ligands and one chlorine atom serve as the bridges. Each metal coordination sphere is completed by one terminal chlorine atom. Selected bond distances and angles are listed in Table 3. The average terminal and bridging Ti–O distances of 1.794 and 2.042 Å are slightly longer than the corresponding values of **1**, reflecting an increase in coordination number of the metal center. As expected, the Ti–Ti distance of 3.104(1) Å is shortened relative to that of **1**.

Table 4 Selected bond lengths (Å) and angles (°) for compound **4**[a]

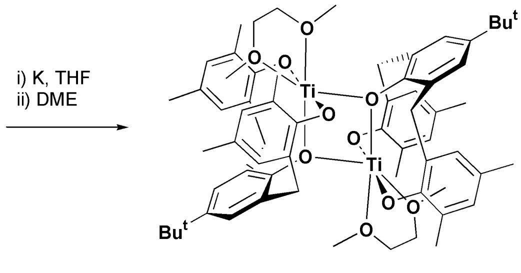
Ti–O(1)	1.912(2)	Ti–O(2)	2.073(2)
Ti–O(2A)	2.022(2)	Ti–O(3)	1.902(2)
Ti–O(4)	2.323(2)	Ti–O(5)	2.187(2)
Ti–Ti(A)	3.113(1)		
O(1)–Ti–O(3)	167.3(1)	O(2)–Ti–O(5)	178.2(1)
O(4)–Ti–O(2A)	171.1(1)	Ti–O(2)–Ti(A)	99.0(1)
Ti–O(1)–C(1)	149.1(2)	Ti–O(2)–C(8)	115.5(1)
Ti–O(3)–C(15)	151.8(2)		

[a] Atoms carrying the suffix A are related to their counterpart by the symmetry operator [1/2 − *x*, 1/2 − *y*, −*z*].

The solid-state structure of **3** is reflected in solution at room temperature by ^1H NMR spectroscopy. The methyl and *tert*-butyl protons of $Me–L^{3-}$ appear as four singlets (δ 2.38, 2.27, 2.19, 2.15) and one singlet (δ 1.11), respectively. The methylene protons of $Me–L^{3-}$ are observed as four doublets (δ 6.08, 5.43, 3.24, 2.99), in which one overlaps at δ 2.99 with the resonances due to the CH_2 protons of the NEt_4^+ cation. Isolation of **3** from the THF solution implies that this dimeric form is stable compared to **1**.

To examine the robustness of the Ti(Me–L) moiety towards reduction chemistry, **1** was treated with 2 equivalents of potassium in THF. The reaction proceeded smoothly to give a dark green solution. After removal of an insoluble material and replacement of the solvent with DME, $[Ti(Me–L)(DME)]_2$ **4** was isolated as apple-green crystals in 76% [eqn. (3)]. The ^1H NMR spectrum of **4** in THF-d_8 was not informative due to the paramagnetic nature of the Ti(III) compound. The solid state magnetic moment is 0.90 μ_B (per Ti atom) at room temperature, which is comparable to those of aryloxide-bridged Ti(III) dimers.[9–11] Upon adding CH_2Cl_2 to the solution of **4** in THF-d_8, we noticed the formation of the Ti(IV) complex **2** according to the ^1H NMR spectra. The formulation of **4** was eventually confirmed by X-ray analysis.

1



(3)

4, 76% yield

The structure of **4** is illustrated in Fig. 4, and selected bond distances and angles are listed in Table 4. The molecule adopts a dimeric structure in the solid, the dimer possessing a center of inversion about a central Ti_2O_2 square core. The geometry about titanium is best described as distorted octahedral, with a chelate DME ligand, a tridentate Me–L ligand, and a central aryloxide of another Me–L ligand. The central aryloxides of the Me–L ligand asymmetrically bridge two Ti metals [Ti–O(2), 2.073(2) Å; Ti–O(2A), 2.022(2) Å]. The average Ti–O distances of 1.907 Å (terminal) and 2.048 Å (bridging) are in the expected range for the corresponding distances of Ti(III) aryloxide.[9,10,12] The Me–L ligand is coordinated in a meridional manner and assumes a U-conformation. The Ti–O distances involving the chelate DME ligand [Ti–O(4), 2.323(2) Å; Ti–O(5), 2.187(2) Å] are noticeably different, because the methyl group attached to the O(4) atom experiences some steric repulsion within

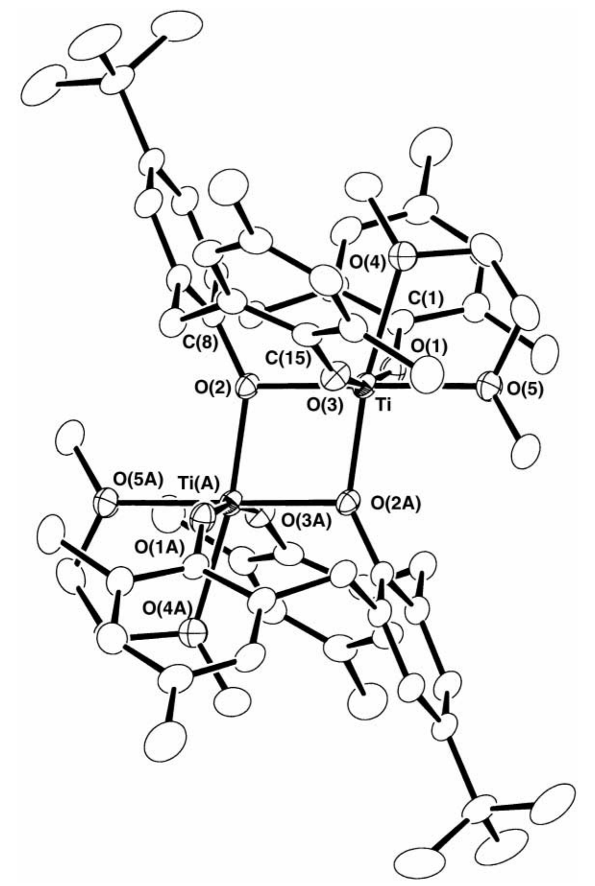


Fig. 4 Structure of **4**.

the cavity of the Me–L ligand. This may also be explained by electronic factors, and the long Ti–O(4) bond is *trans* to the short bridging Ti–O(2A) bond. Owing to steric congestion between the Me–L ligand and DME, the O(1)–Ti–O(3) angle of 167.3(1)° is opened up relative to those of **1** (av. 114.1°) and **2** (100.2(1)°). This again indicates the flexibility of this ligand. 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 **4**.

Conclusions

In this study, the coordination chemistry of the tridentate aryloxide Me–L^{3-} has been examined with titanium. The use of linked aryloxide ligands for synthesis of transition metal complexes is not a new approach to ligand design. Indeed, there are many examples of those in the literature.[1–4,8,9,13–15] What is significant about this work is that the examples of tetravalent and trivalent titanium complexes having a $Ti(OR)_3$ unit have been prepared in high yields. Other complexes with linked aryloxide dimers and calixarenes are known. However, our approach of using the acyclic aryloxide trimer Me–L^{3-} is unique to our knowledge. It can also be emphasized that coordination of Me–L^{3-} is flexible. Depending on the nature of incoming ligands, the Me–L^{3-} ligand can adopt either a U- or an S-conformation. Further studies into Me–L^{3-} and related linked aryloxides are in progress.

Experimental

General

All manipulations of air and/or moisture sensitive materials were performed under an inert atmosphere of argon using standard Schlenk line techniques. All dried solvents and chemicals commercially available were used as received without further purification. Deuterated chloroform ($CDCl_3$) was distilled from calcium hydride prior to use. Deuterated tetrahydrofuran (THF-d_8) was dried and degassed over a potassium mirror *in vacuo* prior to use.

Elemental analyses (C, H and N) were carried out on a YANACO CHN Corder MT-6 element analyser. ^1H NMR (500 MHz) spectra were recorded at room temperature using a JEOL LA-500 spectrometer. Chemical shifts (in ppm) for ^1H NMR spectra were referenced to residual protic solvents peaks. Magnetic susceptibility was measured on a Quantum Design MPMS-7 SQUID susceptometer. Corrections were applied for diamagnetism calculated from Pascal constants.

Preparations

2,6-Bis(4,6-dimethylsalicyl)-4-*tert*-butylphenol [H_3(Me–L)]. The ligand [H_3(Me–L)] was prepared according to the reported method.[5,6] A mixture of 2,6-dihydroxymethyl-4-*tert*-butylphenol (20.0 g, 0.095 mol), 2,4-dimethylphenol (70.0 g, 0.57 mol), and conc. HCl (*ca.* 2 mL) in hexane (100 mL) was refluxed for 2 h. After the solvent was evaporated, excess 2,4-dimethylphenol was removed by distillation under reduced pressure. The residual solid was dissolved into dichloromethane–hexane (200 mL/100 mL), and then the solution was reduced to half its original volume. Colorless crystals of 2,6-bis(4,6-dimethylsalicyl)-4-*tert*-butylphenol [H_3(Me–L)] was obtained from this concentrated solution at −20 °C. More crystalline material could be obtained from the mother liquor. Yield 21.9 g, 55%. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.14 (s, 2H, Ph), 6.92 (s, 2H, Ph), 6.76 (s, 2H, Ph), 3.84 (s, 4H, CH_2), 2.20 (s, 6H, Me), 2.17 (s, 6H, Me), 1.27 (s, 9H, Bu^t).

[Ti(Me–L)Cl]$_2$ 1. Addition of $TiCl_4$ (0.99 g, 5.22 mmol) to a toluene (50 mL) solution of H_3(L–Me) (2.09 g, 5.00 mmol) immediately gave a red solution. The reaction mixture was stirred for 1 h in refluxing toluene. The solvent was removed *in vacuo*, and then the residue was washed with Et_2O to afford **1** as dark red crystals (85% yield). Elemental analysis (%) found C, 67.69; H, 6.25. $C_{56}H_{62}O_6Cl_2Ti_2$ requires C, 67.41; H 6.26. ^1H NMR ($CDCl_3$, 500 MHz): δ 6.98 (s, 4H, Ph), 6.88 (s, 4H, Ph), 6.76 (s, 4H, Ph), 4.67 (d, *J* 13.2, 4H, CH_2), 3.46 (d, *J* 13.2, 4H, CH_2), 2.38 (s, 12H, Me), 2.24 (s, 12H, Me), 1.17 (s, 18H, Bu^t).

Ti(Me–L)Cl(THF)$_2$ 2. Complex **1** was dissolved into THF and then removal of the solvent *in vacuo* quantitatively gave **2** as red microcrystals. This compound crystallized with THF molecules contained in the unit cell. Hence accurate microanalytical data was difficult to obtain due to partial loss of solvate during analysis. ^1H NMR ($CDCl_3$, 500 MHz): δ 6.97 (s, 2H, Ph), 6.87 (s, 2H, Ph), 6.75 (s, 2H, Ph), 4.67 (d, *J* 13.6, 2 H, CH_2), 3.76 (br s, THF), 3.46 (d, *J* 13.6 Hz, 2H, CH_2), 2.37 (s, 6H, Me), 2.24 (s, 6H, CH_3), 1.84 (br s, THF), 1.17 (s, 9H, Bu^t)

[NEt$_4$][Ti$_2$(Me–L)$_2$Cl$_3$] 3. A mixture of **1** (1.13 g, 1.14 mmol) and NEt_4Cl (96 mg, 0.58 mmol) in THF (20 mL) was stirred at room temperature for 22 h. After the solvent was removed *in vacuo*, **3** was quantitatively obtained as red crystals. Elemental analysis (%) found C, 64.29; H, 6.99; N, 1.20. $C_{64}H_{82}N_1O_6Cl_3Ti_2\cdot0.5CH_2Cl_2$ requires C, 64.24; H 6.94; N, 1.16. ^1H NMR ($CDCl_3$, 500 MHz): δ 6.62–6.81 (m, 12H, Ph), 6.08 (d, *J* 13.5, 2H, CH_2), 5.43 (d, *J* 13.5, 2H, CH_2), 3.24 (d, *J* 13.5, 2H, CH_2), 2.99 (d + q, 10H, linker CH_2 overlapping with CH_2 of the NEt_4^+ cation), 2.38 (s, 6H, Me), 2.27 (s, 6H, Me), 2.19 (s, 6H, Me), 2.15 (s, 6H, Me), 1.11 (s, 18H, Bu^t), 1.06 (t, *J* 7.2 Hz, 12H, NEt_4).

[Ti(Me–L)(DME)]$_2$ 4. A 100 mL flask was charged with **1** (0.95 g, 0.95 mmol), potassium metal (85 mg, 2.17 mmol), and THF (50 mL). Upon stirring at room temperature for 20 h, the solution changed from red to dark green. After being

Table 5 Crystallographic data

Compound	**1**·1.5C$_7$H$_8$	**2**·3THF	**3**·3CH$_2$Cl$_2$	**4**
Formula	$C_{66.5}H_{74}O_6Cl_2Ti_2$	$C_{48}H_{71}O_8ClTi$	$C_{67}H_{88}NO_6Cl_9Ti_2$	$C_{64}H_{82}O_{10}Ti_2$
M	1136.02	859.44	1418.31	1107.15
T/K	193	193	173	173
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)
a/Å	11.8839(5)	12.901(1)	13.448(4)	23.319(9)
b/Å	16.0695(6)	20.966(1)	15.768(5)	15.250(6)
c/Å	17.2465(9)	17.2189(3)	19.078(5)	16.708(7)
α/°	88.638(3)		65.464(7)	
β/°	71.058(1)	90.9616(5)	76.20(1)	95.167(6)
γ/°	76.614(1)		88.95(1)	
V/Å	3025.8(2)	4656.7(4)	3559.0(2)	5917.3(4)
Z	2	4	2	4
D_c/g cm^{-3}	1.247	1.226	1.323	1.228
μ(Mo-Kα)/cm^{-1}	4.019	2.915	6.099	3.267
Measured reflections	28599	43651	27952	23265
Unique	13466	10635	15559	6744
GOF	1.011	1.029	1.014	1.031
$R1$ [$I > 2\sigma(I)$]	0.067	0.071	0.083	0.051
w$R2$ (all data)	0.178	0.191	0.253	0.138

centrifuged to remove an insoluble solid, the solvent was evaporated to dryness. The residue was recrystallized from DME (50 mL) to afford **4** as apple-green crystals in 76% yield. Elemental analysis (%) found C, 67.96; H, 7.26. $C_{64}H_{82}O_{10}Ti_2 \cdot C_4H_{10}O_2$ requires C, 68.22; H 7.75. $\mu_{eff} = 0.90\ \mu_B$.

Crystal structure determination

Crystallographic data for **1**, **2**, **3** and **4** are summarized in Table 5. Crystals of these complexes were mounted by nylon loops, which were set on a Rigaku Mercury CCD system with graphite monochromated Mo-Kα radiation (λ = 0.71070 Å) under a cold nitrogen stream. All structures were solved by direct methods and refined on F^2 by the full-matrix least-squares method using the Crystal Structure software package.[16,17] Anisotropic refinement was applied to all non-hydrogen atoms except for the distorted atoms, and all the hydrogen atoms were put at calculated positions.

Single crystals of **1** were obtained by crystallization from toluene. Two crystallographically independent dimers are present. The *tert*-butyl group belonging to one half of the molecule is disordered over two positions with occupancy factors of 50 : 50. The unit cell contains three toluene molecules as crystal solvents, and one of them was located on the inversion center. Single crystals of **2** were obtained by crystallization from THF, and the *tert*-butyl group is disordered over two positions with occupancy factors of 50 : 50. Single crystals of **3** and **4** were obtained by crystallization from CH$_2$Cl$_2$ and DME, respectively. Crystals of **3** were solvated by CH$_2$Cl$_2$.

CCDC reference numbers 172983–172985 and 176066.

See http://www.rsc.org/suppdata/dt/b1/b111362c/ for crystallographic data in CIF or other electronic format.

References

1 M. M. Olmstead, G. Sigel, H. Hope, X. Xu and P. P. Power, *J. Am. Chem. Soc.*, 1985, **107**, 8087.

2 Z. Asfari, V. Böhmer, J. Harrowfield and J. Vicens, *Calixarenes 2001*, Kluwer, Dordrecht, 2001; G. Guillemot, E. Solari, C. Floriani and C. Rizzoli, *Organometallics*, 2001, **20**, 607; A. Caselli, E. Solari, R. Scopelliti, C. Floriani, N. Re, C. Rizzoli and A. Chiesi-Villa, *J. Am. Chem. Soc.*, 2000, **122**, 3652; A. Caselli, E. Solari, R. Scopelliti and C. Floriani, *J. Am. Chem. Soc.*, 1999, **121**, 8296; C. Floriani, *Chem. Eur. J.*, 1999, **5**, 19; L. Giannini, A. Caselli, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, N. Re and A. Sgamellotti, *J. Am. Chem. Soc.*, 1997, **119**, 9198; C. Wieser, C. B. Dieleman and D. Matt, *Coord. Chem. Rev.*, 1997, **165**, 93; V. G. Gibson, C. Redshaw, W. Clegg and M. R. J. Elsegood, *J. Chem. Soc., Chem. Commun.*, 1995, 2371; V. Böhmer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 713; O. V. Ozerov, N. P. Rath and F. T. Ladipo, *J. Organomet. Chem.*, 1999, **586**, 223; O. V. Ozerov, B. O. Patrick and F. T. Ladipo, *J. Am. Chem. Soc.*, 2000, **122**, 6423; J. A. Acho, L. H. Doerrer and S. T. Lippard, *Inorg. Chem.*, 1995, **34**, 2542; M. H. Chisholm, K. Folting, W. E. Streib and D.-D. Wu, *Chem. Commun.*, 1998, 379.

3 L. Higham, M. Thornton-Pett and M. Bochman, *Polyhedron*, 1998, **17**, 3047; P. J. Toscano, E. J. Schermerhorn, C. Dettelbacher, D. Macherone and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1991, 933; S. W. Schweiger, D. L. Tillison, M. G. Thorn, P. E. Fanwick and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, 2001, 2401; M. H. Chisholm, J.-H. Huang, J. C. Huffman and I. P. Parkin, *Inorg. Chem.*, 1997, **36**, 1642; M. H. Chisholm, J.-H. Huang and J. C. Huffman, *J. Organomet. Chem.*, 1997, **528**, 221.

4 C. Floriani, F. Corazza, W. Lesureur, A. Chiesi-Villa and C. Guastini, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 66; M. H. Chisholm, J.-H. Huang, J. C. Huffman, W. E. Streib and D. Tiedtke, *Polyhedron*, 1997, **16**, 2941; J. Okuda, S. Fokken, H.-C. Kang and W. Massa, *Chem. Ber.*, 1995, **128**, 221; D. R. Mulford, P. E. Fanwick and I. P. Rothwell, *Polyhedron*, 2000, **19**, 35; P. V. Rao, C. P. Rao, E. K. Wegelius, E. Kolemainen and K. Rissanen, *J. Chem. Soc., Dalton Trans.*, 1999, 4469.

5 T. Sone, Y. Ohba and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 1111; B. Dhawan and C. D. Gutsche, *J. Org. Chem.*, 1983, **48**, 1536; V. Boehmer, D. Rathay and H. Kaemmerer, *Org. Prep. Proced. Int.*, 1978, **10**, 113.

6 Alkali metal clusters with linked aryloxide ligands, see: B. W. F. Gordon and M. J. Scott, *Inorg. Chim. Acta*, 2000, **297**, 206.

7 L. R. Chamberlain, L. D. Durfee, P. E. Fanwick, L. M. Kobriger, L. M. Latesky, A. K. Mcmullen, B. D. Steffey, I. P. Rothwell, K. Folting and J. C. Huffman, *J. Am. Chem. Soc.*, 1987, **109**, 6068; T. J. Boyle, N. W. Eilerts, J. A. Heppert and F. Takusagawa, *Organometallics*, 1994, **13**, 2118; H. Yasuda, Y. Nakayama, K. Takei, A. Nakamura, Y. Kai and N. Kasai, *J. Organomet. Chem.*, 1994, **473**, 105; P. E. Collier, A. J. Blake and P. Mountford, *J. Chem. Soc., Dalton. Trans.*, 1997, 2911; W. Clegg, M. R. J. Elsegood, S. J. Teat, C. Redshaw and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1998, 3037; J. M. Tanski, T. P. Valid, E. B. Lobkovsky and P. T. Wolczanski, *Inorg. Chem.*, 2000, **39**, 4756.

8 A. Kayal, A. F. Ducruet and S. C. Lee, *Inorg. Chem.*, 2000, **39**, 3696.

9 A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, N. Re, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chim. Acta*, 1998, **270**, 298.

10 R. Minhas, R. Duchateau, S. Gambarotta and C. Bensimon, *Inorg. Chem.*, 1992, **31**, 4933.

11 M. F. Lappert and A. R. Sanger, *J. Chem. Soc. A*, 1971, 1314.

12 M. Mazzanti, C. Floriani, C. Guastini and A. Chiesi-Villa, *J. Chem. Soc., Dalton. Trans.*, 1989, 1793; B. Cetinkaya, P. B. Hitchcock, M. F. Lappert, S. Torroni, J. L. Atwood, W. E. Hunter and M. J. Zaworotko, *J. Organomet. Chem.*, 1980, **188**, C31.

13 Y. Takashima, Y. Nakayama and A. Harada, *Chem. Lett.*, 2001, 488; Y. Nakayama, K. Watanabe, N. Ueyama, A. Nakamura, A. Harada and J. Okuda, *Organometallics*, 2000, **19**, 2498; E. Y. Tshuva, I. Goldberg, M. Kol and Z. Goldschmidt, *Organometallics*, 2001, **20**, 3017; P. L. Arnold, L. S. Natrajan, J. J. Hall, S. J. Bird and C. Wilson, *J. Organomet. Chem.*, 2002, **647**, 205.

14 A. Kayal and S. C. Lee, *Inorg. Chem.*, 2002, **41**, 321.

15 M. B. Dinger and M. J. Scott, *Inorg. Chem.*, 2001, **40**, 1029.

16 Crystal Structure Analysis Package, Rigaku and MSC, 2001.

17 D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, Chemical Crystallography Laboratory, Oxford, UK.