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Remarkable thermodynamic stability toward hydrolysis of tripodal titanium alkoxides†

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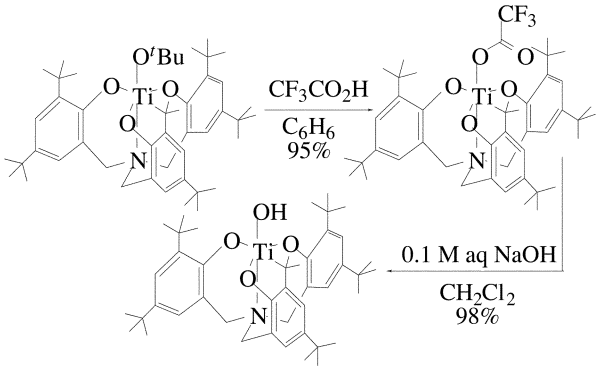
The monomeric titanium(IV) hydroxide complex, LTi(OH) (LH_3 = tris(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine), which is sterically inhibited from condensation to a μ-oxo dimer, cannot be prepared by hydrolysis of the alkoxide, with K_{eq} = 0.012 for hydrolysis of the titanium methoxide in THF.

The hydrolysis of metal alkoxides is a ubiquitous reaction of these complexes and forms the basis for the sol–gel route of metal oxide synthesis.[1] In general, this process is believed to involve initial hydrolysis of the metal alkoxide to form an intermediate metal hydroxide [eqn. (1)] which subsequently condenses with further metal alkoxide (or hydroxide) to build up μ-oxo bridges [eqn. (2)]. While discrete, well-defined terminal metal hydroxide complexes are not common, a number have been studied with respect to their formation by hydrolysis of metal alkoxides. In all cases thus far described, the hydrolysis equilibrium of eqn. (1) is either thermoneutral[2] or favorable.[3] Here we describe the preparation of an aminetris(phenoxide)–titanium(IV) hydroxide complex, LTi(OH) (LH_3 = tris(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine[4]). This hydroxide complex defies the expectations for eqns. (1)–(2), with both hydrolysis of the alkoxide and further condensation to the μ-oxo complex proving to be substantially uphill thermodynamically.

$$M\text{–}OR + H_2O \rightleftharpoons M\text{–}OH + ROH \quad (1)$$

$$M\text{–}OH + M\text{–}OR \rightleftharpoons M\text{–}O\text{–}M + ROH \quad (2)$$

The titanium *tert*-butoxide complex LTi(O^{t}Bu) is readily available in 96% yield as a bright yellow solid from condensation of the ligand with titanium *tert*-butoxide, analogous to the method used earlier to prepare the isopropoxide complex.[4] This alkoxide readily undergoes apical group exchange with more acidic reagents. For example, it reacts with trifluoroacetic acid to form the trifluoroacetate LTi(OCOCF$_3$), which appears to be η^1 by IR spectroscopy (ν_{CO} = 1719 cm^{-1}). The trifluoroacetate complex can be converted to the terminal hydroxide complex in excellent yield by treatment of the complex in organic solvents with aqueous sodium hydroxide [eqn. (3)]. The titanium hydroxide LTiOH has



(3)

been characterized spectroscopically† (*e.g.*, ν_{OH} = 3684 cm^{-1}) and by X-ray analysis of a crystal grown from tetrahydrofuran–water (Fig. 1).‡ The crystal structure shows that the trigonal bipyramidal complex is monomeric and contains a terminal hydroxide group that forms a short hydrogen bond to a lattice THF ($d_{O\cdots O7}$ = 2.727(3) Å). Terminal hydroxo complexes of titanium are rare, with only a few crystallographically characterized examples, all bearing bulky cyclopentadienyl groups as ancillary ligands.[5]

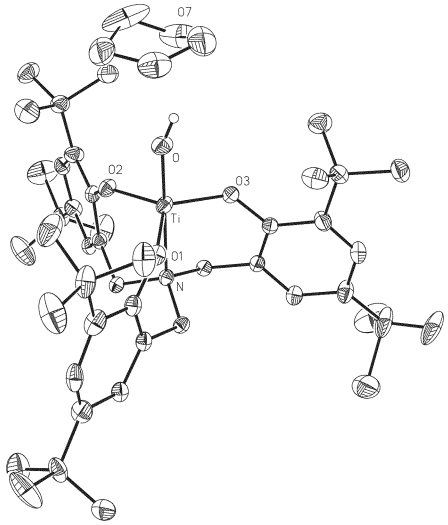


Fig. 1 Thermal ellipsoid plot of LTi(OH)·1.33 THF·0.5 C_6H_6, showing the metal complex and hydrogen-bonded THF.

Remarkably, LTi(OH) cannot be isolated by direct hydrolysis of LTi(O^{t}Bu), which is moisture-stable as a solid or in solution in organic solvents. It is actually the reverse reaction that takes place readily, with the titanium hydroxide complex LTi(OH) suffering quantitative alcoholysis in the presence of even small amounts of simple alcohols such as methanol or *tert*-butanol. In solvents such as tetrahydrofuran or pyridine, detectable amounts of the hydroxide can be observed in equilibrium with the alkoxide only in the presence of large amounts of added water. Quantitative measurements by ^{1}H NMR of the hydrolysis of the titanium methoxide complex LTi(OMe) in these solvents indicate that the hydrolysis equilibrium is substantially unfavorable, with $K_{eq} \approx 10^{-2}$ in both cases [eqn. (4)]. Note that in donor solvents such as THF and pyridine, titanium binds a solvent molecule and is six-coordinate.

$$LTi(OCH_3)(solv) + H_2O \rightleftharpoons LTi(OH)(solv) + CH_3OH \quad (4)$$

solv = THF-d_8, K_{eq} = 0.0123 ± 0.0022
solv = C_5D_5N, K_{eq} = 0.024 ± 0.003

One reason for the paucity of terminal titanium hydroxides is the facility with which they usually condense to form μ-oxo complexes. LTiOH undergoes such condensation if its solutions are evaporated, where the process is driven by the low solubility of the μ-oxo complex LTi–O–TiL. The complex is stable in anhydrous solution, but the oxo bridge is cleaved quantitatively in the presence of even traces of water, reforming the terminal hydroxide. The crystal structure (Fig. 2)‡ shows a bent μ-oxo bridge (Ti1–O–Ti2 = 155.53(10)°) whose titanium–oxo distances of 1.825 Å are on the

† Electronic supplementary information (ESI) available: syntheses and spectroscopic characterization of new compounds. See http://www.rsc.org/suppdata/cc/b3/b315092e/

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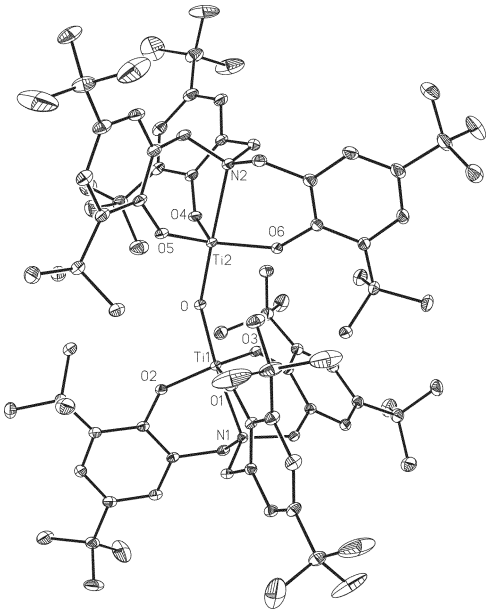

Fig. 2 Thermal ellipsoid plot of LTi–O–TiL·4 C_6H_6, with hydrogen atoms and solvent molecules omitted. Selected bond distances [Å] and angle [°]: Ti1–O, 1.8251(15); Ti2–O, 1.8256(15); Ti1–O–Ti2, 155.53(10).

long end of the range observed in non-metallocene complexes (1.77–1.84 Å); other structures with Ti–O distances over 1.82 Å also have substantially bent bridges.[6] Both the slight elongation of the titanium–oxygen bond and the low hydrolytic stability of LTi–O–TiL are undoubtedly of steric origin, as the *tert*-butyl groups on the trisphenoxide ligands are forced into close contact in the dimer, with eight inter-titanium methyl–methyl contacts with C–C distances shorter than the 4.0 Å sum of the van der Waals radii. This explanation is in accord with earlier observations of Kol and coworkers, who found that the titanium isopropoxide complex of the di-*tert*-butylphenoxide tripod, LTi(O*i*Pr), was stable to moisture in the solid state, while the analogous compound with dimethylphenoxides reacted with moist air to give a product tentatively identified as the μ-oxo complex.[4]

The reasons for the unprecedented *instability* of the terminal hydroxide with respect to alcoholysis are less apparent. The majority of well-characterized terminal metal hydroxides rely to some extent for their stability on steric bulk at the metal center, and this undoubtedly contributes to a preference for binding the small hydroxide ligand in complexes such as [$Tp^{Bu^t,Me}$]ZnX, where hydrolysis of the methoxide is extremely favorable (K_{eq} = 710).[3b] In the aminetris(phenoxide) complexes studied here, however, the steric bulk is placed on the periphery of the complex, where it inhibits aggregation without strongly impinging on the metal center. This makes the LTi complexes rather insensitive to such steric effects, with little discrimination for example between methoxide and *tert*-butoxide (K_{eq} for displacement of OCH_3 by ^{t}BuOH ≈ 1.4 in C_6D_6).

One possible explanation for the relative instability of the hydroxide is that there might be some problem in solvating LTiOH, perhaps because the *tert*-butyl groups impede access of the solvent to the OH group. However, this seems unlikely, given the observation of a rather short hydrogen bond between the Ti–OH group and THF in the solid state, and the small change in the hydrolysis equilibrium constant on changing the solvent from THF to pyridine. A second explanation is that the metal–oxygen bonding in the metal hydroxide is simply not as strong as in the alkoxides. Indeed, the observed Ti–O distance in LTi(OH) (1.810(2) Å) is longer than the Ti–O bonds in the alkoxides LTi(O*i*Pr) (1.778(4) Å)[4] and LTi(OCH_3) (1.7880(13) Å),‡ although the difference is small. The latter explanation is supported by the observation that the hydrolysis equilibria are entirely controlled by enthalpic factors (for hydrolysis of LTi(OMe) in THF, $\Delta H°$ = +2.1(6) kcal mol^{-1}, $\Delta S°$ = −1.8(19) cal mol^{-1} K^{-1}; in pyridine, $\Delta H°$ = +2.18(22) kcal mol^{-1}, $\Delta S°$ = +0.2(7) cal mol^{-1} K^{-1}). If solvation were critical, a significant entropic contribution would have been expected.

For titanium at least, the driving force for metal alkoxide hydrolysis in sterically unhindered systems is apparently not the initial formation of metal hydroxide, but rather the subsequent condensation to form Ti–O–Ti bridges. Furthermore, if the preference for alkoxide over hydroxide ligation is general in other metal alkoxides where the effects of steric bulk close to the metal center are minimized, it has potentially important implications in bioinorganic chemistry. Enzyme active sites use well-defined, partially desolvated pockets, rather than bulky ancillary ligands, to prevent oligomerization and otherwise control the coordination environment of metal centers. The zinc enzyme liver alcohol dehydrogenase is believed to involve formation of a metal alkoxide as an essential step in catalysis,[7] and similar coordination of an aldehyde hydrate may take place in the molybdoenzyme aldehyde oxidase.[8] The present work raises the intriguing possibility that such enzymes may use the electronics of the metal–oxygen bond, or possibly solvation effects, as a strategy to enhance the thermodynamics of forming metal alkoxides in dilute aqueous solution.

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Notes and references

‡ *Crystal data for* LTi(OH)·1.33 THF·0.5 C_6H_6: $C_{53.33}H_{80.67}NO_{5.33}Ti$, M = 869.09, hexagonal, $a = b$ = 27.7755(7) Å, c = 35.2084(13) Å, $\alpha = \beta$ = 90°, γ = 120°, T = 100 K, space group $R\bar{3}$, Z = 18, μ = 0.208 mm^{-1}, 13022 indep. refls. (9863 obsd), R_{int} = 0.0421, R (obsd. refls.) = 0.0760.

LTi–O–TiL·4 C_6H_6: $C_{114}H_{156}N_2O_7Ti_2$, M = 1762.21, triclinic, a = 15.7339(7) Å, b = 16.6517(8) Å, c = 20.8769(10), α = 78.5890(10)°, β = 88.7830(10)°, γ = 76.1170(10)°, T = 100 K, space group $P\bar{1}$, Z = 2, μ = 0.207 mm^{-1}, 25768 indep. refls. (20329 obsd), R_{int} = 0.0374, R (obsd. refls.) = 0.0713.

LTi(OCH_3): $C_{46}H_{69}NO_4Ti$, M = 747.92, monoclinic, a = 13.7727(7) Å, b = 11.7884(6) Å, c = 26.8649(13) Å, $\alpha = \gamma$ = 90°, β = 93.7760(10), T = 100 K, space group $P2_1/n$, Z = 4, μ = 0.237 mm^{-1}, 10792 indep. refls. (10214 obsd), R_{int} = 0.0318, R (obsd. refls.) = 0.0604. CCDC 225000–225002. See http://www.rsc.org/suppdata/cc/b3/b315092e/ for crystallographic data in .cif or other electronic format.

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